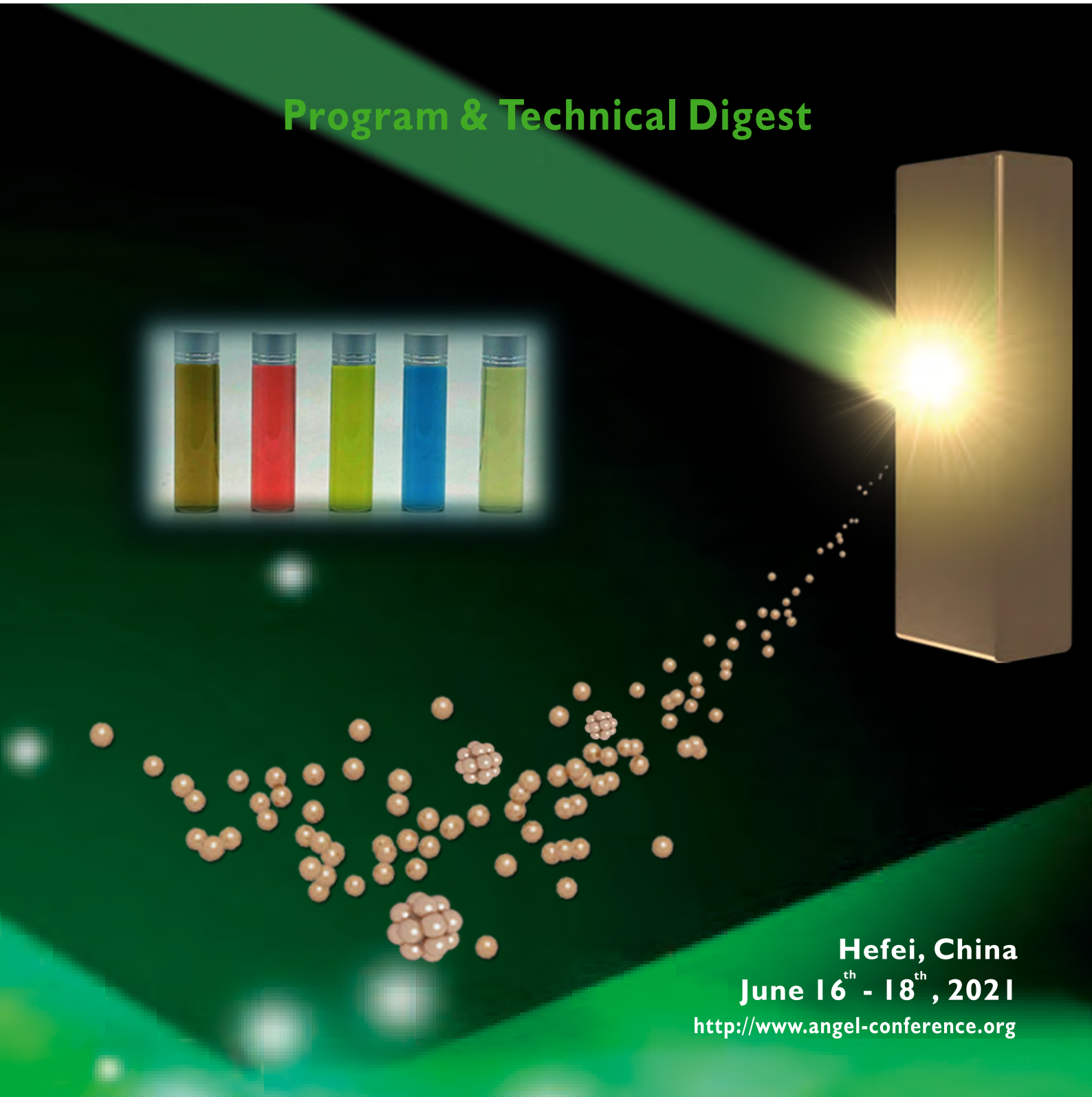
6th International Conference on Advanced Nanoparticle Generation & Excitation by Lasers in Liquids (ANGEL2021)

ANGEL
CONFERENCE

Organizer: Hefei Institutes of Physical Science, Chinese Academy of Sciences (CAS)

Program & Technical Digest



Hefei, China
June 16th - 18th, 2021
http://www.angel-conference.org

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Welcome to ANGEL2021

On behalf of the organizing committee, it is my great honor to welcome you to The 6th International Conference on Advanced Nanoparticle Generation & Excitation by Laser in Liquids (ANGEL2021), to be held from June 16-18, 2021 in Hefei, China.

ANGEL conference is the most important international events on laser technique involved in liquids. Since Anton Fojtik and Armin Henglein started to introduce the laser ablation in liquids, the content of this techinique has been greatly enriched. Researchers gradually summarized different interactions between laser and matter, including Laser Abaltion in Liquid (LAL), Laser Melting in Liquid (LML), Laser Fragmentation in Liquid (LFL), and Laser Defect-engineering in Liquid (LDL). On the basis of these processings, more and more functional nanomaterials and applications have been developed. The previous ANGEL conferences have greatly promoted the exchanges between researchers, and especially stimulated the research enthusiasm of young researchers.

ANGEL2021 continues the tradition inherited from past conferences and covers wide areas of laser processing in liquids, including modelling, in-situ characterization, nanomaterials fabrication, application, scale-up. ANGEL2021 also continues the international award called Fojtik Henglein Prize for the outstanding, recent scientific breakthrough in the field of laser synthesis and processing of colloids in liquids nanotechnology research, and help Programmee Committee (PC) and International Advisory Board (IAB) to promote ANGEL Decennial Awards. We believe that ANGEL2021 will provide a forum to stimulate fruitful international exchanges of knowledge.

The conference site, Hefei, as the capital of Anhui province, is an ancient city with more than 2000 years of history. Hefei is also the first pilot science and technology innovation city in China, a pilot innovation city of national significance and a member city of WTA (World Technopolis Association). We believe our city will support the best services for you on the basis of modern facilities and international management philosophies. We also believe the traditional culture of China will enrich new feelings and strengthen the impression about China for you.

In closing, I would like to express my sincere thanks to all of you. I also extend my best wishes for all of you.

Changhao Liang
ANGEL2021 conference chair

Notes

ANGEL2021 Conference

Venue: Swan Lake Hotel, Huaihe Hall

On-site registration: 15 June and morning 16 June, 2021

Conference date: June 16th-18th, 2021

Social program: Hefei Science-island Tour

Date: Morning of 2021.6.16

Travel: bus (arrive and depart)

Welcoming banquet

Date: 2021.6.16 evening

Location: Swan Lake Hotel

Accomodation

Hotel: Swan Lake Hotel

Committees

Programme Committee

Vincenzo Amendola (University of Padova/IT)
Tsuyoshi Asahi (Ehime University/JP)
Stephan Barcikowski (University of Duisburg-Essen/DE)
Giuseppe Compagnini (University of Catania/IT)
Naoto Koshizaki (Hokkaido University/JP)
Fumitaka Mafune (University of Tokyo/JP)
Georgy A. Shafeev (Russian Academy of Science/RU)
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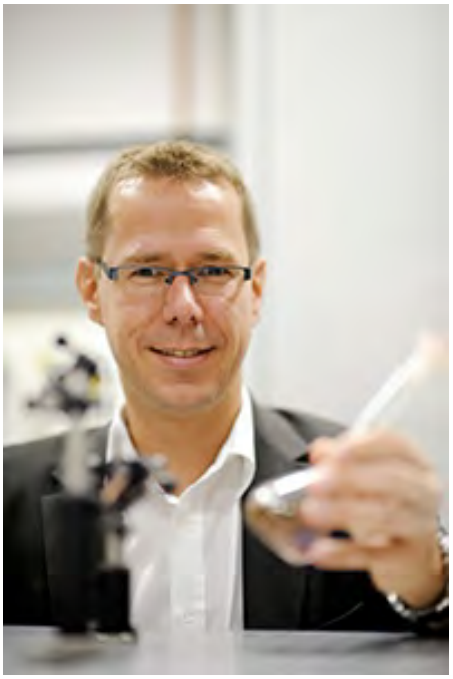

It was back in early spring 2009, when I first met one of the laser synthesis pioneers, Fumitaka Mafuné, in Japan. In Japanese (and also in European) tradition, you go to a bar to find out if you are likely to become friends in future. So we went to a nice place, and I have enjoyed some beer and edamame, while chatting about the growing community of this emerging field, we started putting down a list of pioneers and researchers we want to meet and talk to in future. (I still have this sheet of paper where all begun, but I cannot read my own handwriting of that evening anymore). We discussed back and forth about organizing a session on a larger conference, but as we do not like huge conferences with multiple parallel sessions ourselves, we agreed that we should give it a try to organize a free-standing conference without parallel session, purely on laser synthesis and processing of colloids. As he was the pioneer, older and much higher reputed, it was of course me who had to take over the work. First thing was finding a crispy acronym, and my PhD student Anna Neumeister who was our talented “acronym-machine” at these days created it: ANGEL. My former boss said “you will not have more than 20 attendees” and it was not so easy to find a good place. Silke Kramprich from the European Optical Society helped me a lot and we found “Engelberg” as a picturesque place. I thought that must be a good circumstance as “ENGEL” in German means “ANGEL”. Sasha Ediger created a nice logo, and everything went step-by step, now handed over to international chairs, trying to find beautiful places to meet, with exciting social program and even more exciting science.

Prof. habil. Dr.-Ing. Stephan Barcikowski

Organizer

Hefei Institutes of Physical Science, Chinese Academy of Sciences (CAS)

The Hefei Institutes of Physical Science，Chinese Academy of Sciences (HFIPS) is located on a beautiful peninsula near Shushan Lake in the western suburbs of Hefei, capital of Anhui Province, China. It was founded in 2003 by integrating five CAS institutes that had been established there before.

With twenty years of hard work by more than two thousand and seven hundred HFIPSers, HFIPS has grown at a very fast speed into one of the largest CAS institutes. It has constructed and operates two mega science facilities, the Experimental Advanced Superconducting Tokamak (EAST) and the Steady High Magnetic Field Facility (SHMFF) to enable cutting-edge research with a wide range from nuclear fusion of sun power to what will happen in matter when exposed to extreme conditions.

HFIPS integrates multidisciplinary expertise of its seven research units and world-class facilities to seek science solutions to challenges of world's scientific and technical frontiers. For almost twenty years since its establishment, HFIPS has been focusing on addressing national demands through the study of magnetic confinement fusion to explore strategic energy; environmental monitoring and pollution control technology for environment challenges; high magnetic field science and technology research to gain deeper understanding of matters and life; and cutting-edge interdisciplinary research to solve the challenges in materials, intelligence, health, modern agriculture and advanced manufacture.

Changhao Liang
Conference Chair

Changhao Liang (http://www.laser-nano.com)
Professor (chliang@issp.ac.cn)
Key Laboratory of Materials Physics and Anhui Key Laboratory of Nanomaterials and Nanotechnology, Institute of Solid State Physics, Hefei Institutes of Physical Science, Chinese Academy of Sciences.
Shushanhu Road 350, Hefei 230031, Anhui, P. R. China

Changhao LIANG joined in Lab of Nanostructured Materials, Institute of Solid State Physics (ISSP), as a Professor in 2008. He received his PhD from institute of Solid State Physics, Chinese Academy of Sciences in 2001. From 2001 to 2008, He did research in MPI for Metal Research in Germany, National Institute of Advanced Industrial Science and Technology (AIST), National Institute for Materials Science (NIMS) in Japan. Prof. Liang's research interests lie in Laser-Materials Interactions in Liquids and Gases, Nanostructured Materials for Energy & Bio-Applications. He has published more than 120 scientific papers in international journals with over 6000 total citations. Liang's research was mainly supported by project of National Science foundation of China, National Basic Research Program of China (973) and others.

Local organization committee

Yunyu Cai (Institute of Solid State Physics)
Jun Liu (Institute of Solid State Physics)
Hui Liu (Tianjin University)
Pu Liu (Sun Yat-Sen University)
Pengfei Li (Institute of Solid State Physics)
Shouliang Wu (Institute of Solid State Physics)
Lingli Wu (Institute of Solid State Physics)
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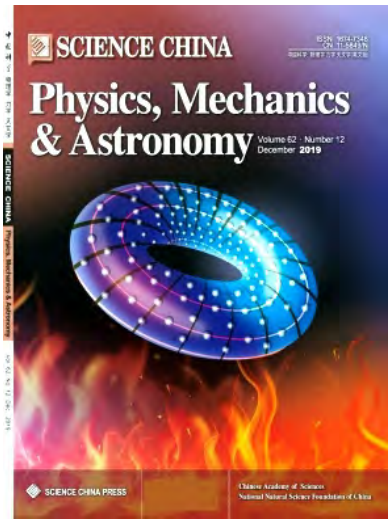
Accomodation

Heifei Xinqiao Internationl Airport	Airport bus (line 3)	~80min	RMB25 Yuan
	Taxi	~50min	RMB100 Yuan
	ANGEL Conference shuttle	~50min	Free
Hefeinan Railway Stationt	Bus(line156/108/104)	~60min	RMB2 Yuan
	Taxi	~15min	RMB20 Yuan
	ANGEL Conference shuttle	~15min	Free

Swan Lake Hotel, centered in Hefei Municipal & Cultural District and next to Swan Lake. It has won the honor of five-star hotel in 2009 and became one of the key buildings in Hefei. The grand hotel with comprehensive facilities for business conferences is co-funded by Anhui Publishing Group, Anhui Daily Press Group, Anhui TV Station and five other units. It covering 58600 square meters has total investment of 630 million RMB. On the second floor, the Multi-Functional Conference Center with a capacity of 2000 people is the largest one of this kind in Anhui Province. The hotel has about 260 guestrooms including deluxe VIP suites, comfortable single and twin rooms, equipped with modern amenities (TV, computer, free wifi etc.). It also provides fitness room and chatting room for guests.

Address: No. 888, Dongliu Road, Municipal & Cultural District, Hefei, Anhui Province, P. R. China

Call for papers



1. Science China Physics, Mechanics & Astronomy (Impact Factor: 4.226)

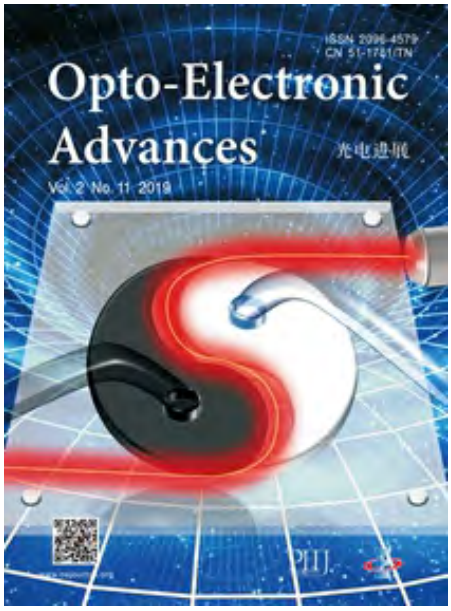
As an academic journal, it is co-sponsored by the Chinese Academy of Sciences and the National Natural Science Foundation of China, and published by Science China Press, is committed to publishing high-quality, original results in both basic and applied research. Reviews summarize representative results and achievements in a particular topic or an area, comment on the current state of research, and advise on the research directions. The author's own opinion and related discussion is solicited. Research papers report on important original results in all areas of physics, mechanics and astronomy. Brief reports present short reports in a timely manner of the latest important results.

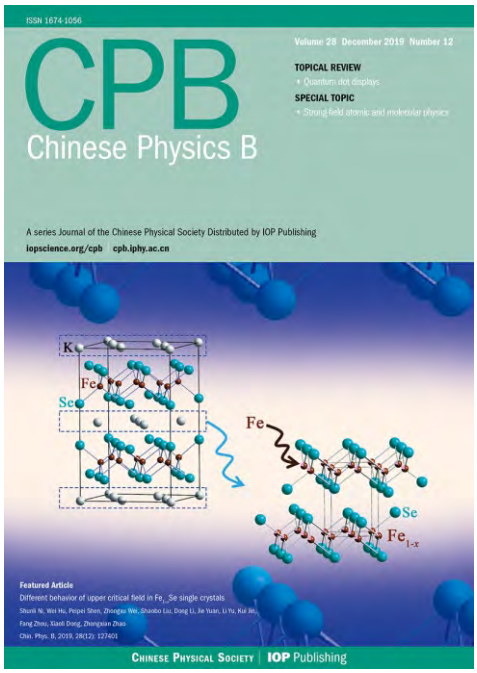
2. Opto-Electronic Advances (OEA, ISSN: 2096-4579)

It launched in March 2018, is a monthly international, peer-reviewed and free online English journal. OEA publishes top-quality original articles, letters and reviews covering all significant research activities in the broad area of optics, photonics and optoelectronics.

Main topics include:

- Light sources and sensors
- Optoelectronics
- Nanophotonics
- Plasmonics and metamaterials
- Optical imaging
- Biophotonics and biomedical optics
- Nonlinear optics and ultrafast photonics
- Optical communications
- Photovoltaics





3. Chinese Physics B (CPB, formerly Chinese Physics, Impact Factor: 1.223)

It is sponsored by Institute of Optics and Electronics, Chinese Academy of Sciences, China.It is sponsored by Chinese Physical Society and Institute of Physics, Chinese Academy of Sciences, is one of the most prestigious periodicals published in China, and ranks the top in Chinese physics journals. It publishes "original research papers", "rapid communications", and "reviews" on the latest developments and achievements in all branches of physics worldwide except nuclear physics and physics of elementary particles and fields.

Subject coverage includes:

- condensed matter and materials physics
- atomic, molecular, and optical physics
- statistical, nonlinear, and soft matter physics
- plasma physics
- interdisciplinary physics

Social programme: Science Island Tour

Date: June 16, 2021 (08:30-11:30; UTC+8)

Hefei Institutes of Physical Science is located on an island, so it is also called as Science Island and is one of China's top ten science tourism destinations.

1. EAST- Experimental Advanced Superconducting Tokamak

EAST is called as "Chinese Artificial Sun". Scientists in Hefei Institutes of Physical Science have set a new world record of achieving a plasma temperature of 120 million degrees Celsius for 101 seconds in the latest experiment in this May, a key step toward the test running of a fusion reactor. The ultimate goal of EAST, located at ASIPP in Hefei, is to create nuclear fusion like the Sun, using deuterium abound in the sea to provide a steady stream of clean energy.

EAST is designed on the basis of the latest tokamak achievements of the last century, aiming at the world fusion research forefront. Its mission is to conduct fundamental physics and engineering researches on advanced tokamak fusion reactors with a steady, safe and high performance, to provide a scientific base for experimental reactor design and construction, and to promote the development of plasma physics and related disciplines and technologies. EAST device has three distinct features: non-circular cross-section, fully superconducting magnets and fully actively water cooled plasma facing components (PFCs) which will be beneficial to explore the advanced steady-state plasma operation modes. EAST construction and physics research will provide direct experience for the construction of International Thermonuclear Experimental Reactor project (ITER), and play a leading role in high-performance steady-state plasma physics research in the world, and ultimately contribute to the development of ITER and the fusion energy. Compared with ITER, although smaller, EAST is similar to ITER in shape and equilibrium, yet more flexible. During the 10 years for ITER construction, EAST will be one of a few international devices that can be an important experimental test bench for conducting ITER related steady-state advanced plasma science and technology research.

Social programme: Science Island Tour

Date: June 16, 2021 (08:30-11:30; UTC+8)

2. SHMFF-Steady High Magnetic Field Facility

The Steady High Magnetic Field Facilities (hereinafter referred to as SHMFF), have been put into trial operation and commissioned for user service, since it started construction on May 18, 2008. SHMFF offers scientific researchers access to unique equipments housed in state-of-the-art facilities, and onsite experts to help visiting researchers take advantage of and make best use of the capabilities. Researchers also have the opportunity to collaborate with our experienced scientists and engineers who could be help in advance your scientific research.

SHMFF is a wide range of user facilities and services for multi-disciplinary and cross-disciplinary researches under steady high magnetic field, that span condensed matter, electron strong correlation, topological insulator, nano-material fabrication, chemical reaction, neurosciences, biochemistry, pharmacology, biomedical sciences and more. It's open to all qualified domestic and international users and therefore you are welcome to visit us and join us with your creative scientific proposal. Your valuable comments or suggestions are greatly appreciated.

Three water-cooled magnets have been finished and put into service: a 10 MW magnet producing 27.5 T in a 32 mm bore, a 24 MW magnet with 35 T in a 50 mm bore, and a 25.2 MW magnet producing 38.5 T in a 32 mm bore. The following instruments are available for users: an 18.8 T, 54 mm bore superconducting magnet with a 950 MHz spectrometer for high-resolution NMR; a 9.4 T, 400 mm bore, high field MRI scanner, an 18 T, 52 mm cold bore magnet with installed instrumentation for scanning tunneling microscopy, magnetic microscopy, and atomic force microscopy (SMA). Instruments not linked to particular magnets include cryostats and probes for transport and magnetic measurements; a fast-pulse optical measurement system; a Fourier transform infrared spectrometry system; and a high pressure measurement system.

Social programme: Science Island Tour

Date: June 16, 2021 (08:30-11:30; UTC+8)

3. ISSP-Institute of Solid State Physics, Chinese Academy of Sciences (CAS)

The Institute of Solid State Physics (ISSP), Chinese Academy of Sciences (CAS), was founded by Prof. T. S. Kê, a worldwide well-known solid-state physicist and metallurgist, in March 1982. ISSP is a support unit to the Anhui Provincial Key Laboratory of Materials Physics, Anhui Provincial Key Laboratory of Nanometer Materials and Technology, Anhui Provincial Engineering Technology Center of Nanomaterials and Applications and the Center for Computational Science.The founder of this Institute is the professor Ting-sui GE (T.S. Kê), a worldwide well-known solid-state physicist and metallurgist. T.S. Kê is the inventor of the Kê-type torsion pendulum (i.e. low-frequency torsion pendulum bears his name) and discoverer of the Kê grain-boundary internal friction peak in metals and metallic alloys. He also proposed the Kê grain-boundary model of disordered atomic groups. Meanwhile, he initially promote nanomateriabs fabrication in ISSP. Presently, research directions for ISSP cover Nano materials technology, new functional materials, computational physics, internal friction and defects of solids, materials physics under extreme environments, environmental and energy nanomaterials, nuclear engineering materials and special metallic materials.

official programme

Morning, June 16th, 2021 (UTC+8)			
Science Island Tour 08:30-11:30	1. EAST- Experimental Advanced Superconducting Tokamak 2. SHMFF-Steady High Magnetic Field Facility 3. ISSP-Institute of Solid State Physics, Chinese Academy of Sciences (CAS)		
12:00-13:00	Lunch Break		
Afternoon, June 16th, 2021 (UTC+8)			
Opening 14:30-14:50	Changhao Liang	Welcome speech	14:30-14:40
	Stephan Barcikowski	Opening remark	14:40-14:50
Topic: laser processing in liquids **Chairman: Prof. Georgy Shafeev**			
Memory talk 14:50-15:20	Anton Fojtik Czech Republic	Laser for NANO: Pioneering pulsed laser synthesis of colloids	
15:20-15:40	Sergey I. Kudryashov Russia	Novel criterion of laser-ablative nanoparticle yield in liquids: a route to quantitative technology	
15:40-16:00	Nikolai Tarasenko Belarus	Laser processing of colloids: application for compound nanoparticles fabrication and doping	
16:00-16:20	Spellauge Maximilian Germany	Early stage ablation dynamics of gold in air and water monitored by ultrafast pump-probe microscopy	
16:20-16:40	David Amans France	Surface chemistry of colloidal gold nanoparticles generated by laser ablation	
16:40-16:55	**Coffee Break**		
Topic: laser induced advanced nanostructures in liquids-I **Chairman: Prof. Tsuyoshi Asahi**			
Invited 16:55-17:20	Alina Manshina Russia	Low intense laser irradiation of substrate/solution interface as a single step synthesis of hybrid metal/carbon nanostructures	
17:20-17:40	Hongqiang Wang China	Laser-Generated Nano-Colloids for High Performance Perovskite Solar Cells	
17:40-18:00	Rafael O. T. Mendieta Czech Republic	Laser-mediated Ag nanoparticle decoration of PVDF nanofibrous membranes for an efficient oil/water separation	
18:00-18:20	Vincenzo Amendola Italy	Synthesis by laser ablation in liquid of alloy nanoparticles: controlling the structure and the composition for specific applications	
18:20-18:40	Alena Nastulyavichus Russia Student	Fighting pathogenic bacterial biofilms by bactericidal nanoparticles	
18:40-19:00	Andrei Kabashin France	Recent advances in laser synthesis of novel functional nanomaterials and their biomedical applications	
19:00-21:00	**Welcome Banquet**		
20:00-21:00	**PC&IAB Meeting**		

official programme

Morning, June 17th, 2021 (UTC+8)

Topic: Laser processing involved dynamics
Chairman: Prof. Hongqiang Wang

08:30-08:50	Leonid V. Zhigilei America	The effect of pulse duration on nanoparticle generation in pulsed laser ablation in liquids: Molecular dynamics study.
08:50-09:10	Alejandro Morales Betancourt America Student	Formation of $MoSe_2$ Nanosheets and Nanoscrolls obtained from Pulsed Laser Ablation in Deep Eutectic Solvent (PLADES)
09:10-09:30	Chaobo Chen America Student	Structure of Fe-Ni nanoparticles produced by laser ablation in water
Invited 09:30-09:55	Hui Liu China	preparation of metastable metal catalysts with high performance through laser ablation in liquid method
09:55-10:15	Yichun Wang China Student	Experimental study of femtosecond laser cavitation on gas productivity and composition
Journals Publicity 10:15-10:30	1. Wei Wang--Science China Physics, Mechanics & Astronomy 2. Jiali Xu--Opto-Electronic Advances 3. Jiuli Wang--Chinese Physics B	
10:30-10:45	**Coffee Break**	

Topic: Laser induced advanced semiconductors
Chairman: Prof. Bingqiang Cao

Invited 10:45-11:10	Dezhi Tan China	Highly defective nanocrystals as ultrafast optical switches: femtosecond laser processing in solution and efficient nonlinear optical response
11:10-11:30	Takamasa Ishigaki Japan	Influence of Hydrogen Peroxide Addition on Phase formation in Mn-doped TiO_2 Nanoparticles Prepared by Laser Ablation in Aqueous Solutions
11:30-11:50	Changhao Liang China	Construction of Metal-oxides Interfaces Assisted by Laser irradiation for enhanced electrochemical performance
11:50-12:10	Pu Liu China	LAL produced GQD-decorated ultrathin-Bi_2WO_6 nanosheet hydrogel composite with excellent synergistic effect of piezo-photocatalytic degradation
12:10-12:30	Mehdi Ranjbar Iran	Decorated WOx nanoparticles by laser assisted reduction in solutions for optical gas sensing
Flash Talk 1 12:30-12:45	1. Yan Zhao (China)--Laser-Assisted Synthesis of Pd Aerogel with Compressive Strain for Boosting Formate and Ethanol Electrooxidation 2. Zhe Li (China)--Stable Rhodium (IV) Oxide for Alkaline Hydrogen Evolution Reaction 3. Le Zhou (China)--Onion-structured Spherical MoS_2 Nanoparticles Induced by Laser Ablation in Water and Liquid Droplets' Radial Solidification/Oriented Growth Mechanism 4. Sihan Ji (China)--Laser assisted synthesis of porous Mn_3O_4/PtO_x nanocomposite for MRI and CT bimodal imaging 5. Yi Feng (China)--Electroreduction of Carbon Dioxide in Metallic Nanopores	
12:45-13:45	**Lunch Break**	

official programme

Afternoon, June 17th, 2021 (UTC+8)		
Topic: laser induced advanced nanostructures in liquids-II **Chairman: Prof. Vincenzo Amendola**		
Invited 14:30-14:55	Heinz P. Huber Germany	Ultrafast time-resolved studies on laser ablation of metals in air and liquid
14:55-15:15	Georgy Shafeev Russia	Generation of nanoparticles of phtalocyanines and their nanocomposites with gold nanoparticles by laser fragmentation in liquids
15:15-15:35	Takeshi Tsuji Japan	Preparation of gel-like structures, nanocomposites using laser ablation for CaO in alcohols
15:35-15:55	Natalie Tarasenka Belarus	Laser Assisted Synthesis of Cobalt-Doped Zinc Oxide Nanostructures
15:55-16:15	Vittorio Scardaci Italy	Monochromatic Light Driven Synthesis and Growth of Flat Silver Nanoparticles
16:15-16:35	Vladimir Shur Russia	Shape control of metal oxide nanoparticles produced by laser ablation in liquid
16:35-16:50	**Coffee Break**	
Topic: Modulation of laser processing in liquids **Chairman: Prof. David Amans**		
Invited 16:50-17:15	Nail Inogamov Russia	Laser ablation of gold in water by short and long pulses
17:15-17:35	Bilal Gökce Germany	Ablation target effects on nanoparticle productivity during laser ablation in liquids
17:35-17:55	Alexander Bulgakov Czech Republic	Laser-induced damage effects in opaque solids: Comparison of air and water environments
17:55-18:15	Matej Senegacnik Slovenia student	Cavitation bubble dynamics following laser-induced breakdown near a sharp-edge geometry
18:15-18:35	Carlos Doñate-Buendía Germany	Laser synthesis of colloidal nanoparticles and their adsorption on polymer microparticles for laser powder bed fusion.
Flash Talk 2 18:35-18:50	1. Marcello Condorelli (Italy)--Oxidation dynamics of copper nanoparticles under laser irradiation in the colloidal phase 2. Zhanna Fedorovich (Russia)--Study of Highly Defective Titanium Dioxide Prepared via Pulsed Laser Ablation 3. Anna Ziefuss (Germany)--Impact of electrolytes on particle size distributions of gold nanoclusters fabricated by nanosecond-pulsed laser fragmentation in liquids. 4. Oliwia Polit (Poland)--Physico-chemical processes in laser synthesis of composite particles based on iron (Fe) 5. Zaneta Swiatkowska-Warkocka (Polish)--Role of solvent and size of raw nanoparticles in composite particles formation during pulsed laser irradiation process	
18:50-20:00	**Dinner**	

official programme

Morning, June 18th, 2021 (UTC+8)

Topic: Application of laser generated nanoparticles/nanostructures in liquids-I
Chairman: Prof. Takeshi Tsuji

Invited 08:30-08:55	Wei Qian America	Plasmonic Metal Nanoparticles Generated by Femtosecond Pulsed Laser Ablation for Biomedical Optical and Photoacoustic Imaging
08:55-09:15	Sadasivan Shaji Mexico	Synthesis and properties of nanocomposite thin films of Sb_2S_3 with Si nanoparticles
09:15-09:35	Dongling Ma Canada	The application of laser-fabricated nanoparticles in photocatalysis
09:35-09:55	Tsuyoshi Asahi Japan	Fabrication of Porphyrin Nanoparticles and Their Phototoxicity to Rat Pheochromocytoma PC12 Cells
09:55-10:15	Miao Zhong China	Nanoporous Cu-Al catalyst for efficient electrochemical reduction of CO_2 to ethylene
Flash Talk 3 10:15-10:25	1. Ashish Nag (America)--One Step Bottom-Up Synthesis of Carbon-Supported Ultrasmall Metastable Ni Nanoparticles 2. Laysa Frias Batista (America)--Synthesis of Catalytically Active Naked Palladium Nanoparticles Via Laser Plasma 3. Rajesh Rawat (India)--Synthesis of Cu/CuO Nanoparticles using Laser Ablation: Effect of Fluence and Solvents	
10:25-10:40	**Coffee Break**	

Topic: laser induced advanced nanostructures in liquids-III
Chairman: Prof. Changhao Liang

Invited 10:40-11:05	Dongshi Zhang China	What did we neglect to study on particle generation during laser ablation in liquids?
11:05-11:25	Bingqiang Cao China	Metal Nanospheres Grown by Laser Irradiation with Enhanced Tribology Properties
11:25-11:45	Songyuan Ding China	Pulsed-heating method for synthesizing monodispersed and ultrasmall nanoparticles
11:45-12:05	Haoming Bao China	Ultrathin oxide layer wrapped plasmonic metal nanoparticles prepared by laser ablation in solution for ultrasensitive gas detection
12:05-12:25	Ameneh Farnoud Iran Student	Au@Pd colloidal nanoparticles by laser ablation in liquid for LSPR hydrogen sensing
12:25-13:25	**Lunch Break**	

official programme

Afternoon, June 18th, 2021 (UTC+8)

Topic: Advanced characterization for laser processing in liquids
Chairman: Prof. Nikolai Tarasenko

Invited 14:30-14:55	Norbert Linz Germany	Design and development of time-resolved photography for the investigation of primary processes in gold nanoparticle generation
14:55-15:15	Arsène Chemin France Student	Shock-Waves Generated by Laser ablation in Liquids
15:15-15:35	Morihisa Saeki Japan	In Situ Time-Resolved XAFS Study on Laser-Induced Particle Formation of Pd(II) Ion in a Solution
15:35-15:55	Anton Plech Germany	In situ mass evaluation and speciation in laser ablation of Zn in water
15:55-16:15	Hao Huang America Student On-site	Molecular dynamics simulation study of laser fragmentation in liquid
Flash Talk 4 16:15-16:27	1. Reza Poursalehi (Iran)--Optical and Structural Properties of Bi/Bi2O3 Nanoparticles Prepared via Pulsed Laser Ablation in Different Liquids 2. Vito Coviello (Italy)--Study of the relationship between the plasmonic properties and the electronic properties in Au-Co nanoalloys obtained by laser ablation in liquid 3. Vaijayanthi Ramesh (Germany)--Electrophoretic deposition of laser-generated Platinum Nanoparticles on neural prostheses 4. Carlos Doñate-Buendía (Germany)--Femtosecond pulsed laser ablation in liquids nanoparticle production increase by simultaneous spatial and temporal focusing	
16:27-16:40	**Coffee Break**	

Topic: Application of laser generated nanoparticles/nanostructures in liquids-II
Chairman: Prof. Giuseppe Compagnini

Invited 16:40-17:05	Takahiro Nakamura Japan	Solid-solution alloy nanoparticles fabricated by laser-induced nucleation method
17:00-17:25	Luisa D'Urso Germany	Photo-efficiency of TiO_2-Metal nanocatalysts prepared by pulsed laser ablation for oxidation of industrial water pollutants
17:25-17:45	Elena Fakhrutdinova Russia	PLA Synthesis and Photocatalytic Properties of Bismuth Silicates
17:45-18:05	Sven Reichenberger Germany	Pulsed laser defect engineering in liquid (PuDEL) of transition metal oxides for gradual heterogenous catalysis studies
18:05-18:25	Margarita Zhilnikova Russia Student	Generation of metallic nanoparticles by laser ablation in molten salts
18:25-18:45	Irina N. Saraeva Russia	You shall not pass: titanium nanospikes-based flow-through filter for liquid sterilization
Closing 18:45-19:15	Decennial Awards & Fojtik-Henglein Prize	
	Next ANGEL Information & Call for paper	
	Closing remark	

Awards

1. Fojtik Henglein Prize

- The Fojtik Henglein Prize rewards a significant scientific breakthrough, or a pioneering research result, within the framework of ANGEL conference series, then an uncommonly contribution to laser synthesis of colloids in liquids.
- The Fojtik Henglein Prize is awarded biannually, during the Angel conference, and rewards published research in last 2 to 3 years.
- It is mandatory for the prize winner to attend the ANGEL conference.
- A pre-selection is performed by a jury on the basis of the accepted abstracts for an oral contribution to the ANGEL conference. The jury members are the chair(s), the programme committee members, and the international advisory board members.
- The Fojtik Henglein Prize is delivered by the chair on behalf of the programme committee members, and the international advisory board members of the ANGEL conference series.

2. ANGEL Decennial Awards

On the occasion of the 10th anniversary, the ANGEL conference Program Committee and International Advisory Board present the “ANGEL Decennial Award” selection to celebrate all those people who contributed to the success of the field of Advanced Nanoparticle Generation and Excitation by Lasers in Liquids.

There are three award categories:

- ANGEL Decennial Award for Best Image - The best image related to ANGEL research.

The image can be an artwork, an experimental image, a combination of the two or any other image related to the field of laser synthesis and processing of colloids.

- ANGEL Decennial Publication Award - Innovative research article related to ANGEL topic.

Nominate a research article that inspired your research activity, or you consider exceptionally valuable for the field.

- ANGEL Decennial Big Challenge Award - The next biggest challenge or imagined advance in the field of ANGEL research or application

To explain (in less than 100 words) what is, according to your personal opinion, the next biggest scientific challenge that should be addressed by the ANGEL community, in order to progress the field and further increase the interest in this field.

Abstracts Printed

invited abstracts
oral abstracts
flash talk abstrcats
poster abstracts

Low intense laser irradiation of substrate/solution interface as a single step synthesis of hybrid metal/carbon nanostructures

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Heterogenic systems (substrate-solution interfaces) are extremely curious targets for the laser irradiation because of a wide diversity of processes that can be initiated as a result of laser effect as compared with homogeneous systems (solutions or solids). Another peculiarity of this system is the possibility of the initiation of not only physical process (evaporation, fragmentation, etc.) but also chemical process that results in generation materials with diverse chemical compositions. Moreover one can provide the tuning of the system's chemical activity by selecting either photochemical or thermochemical mode of laser exposure. Well and widely known approach using the highly intense laser irradiation of the interface between solid substrate and liquid phase results in many effects connected with laser ablation in liquids and the subsequent nanostructures formation. The low intense laser irradiation of substrate-solution interfaces is uncommon approach; however as we found, it opens novel way of multiphase nanostructures synthesis in a single step process. Here we present a particularly simple and efficient synthesis of hybrid nanostructures that are bimetal (Au-Ag, Cu-Ag or Pt-Ag) nanoclusters incorporated into carbonaceous matrix. This matrix can be amorphous or crystalline, and the details of the compositional outcome and the morphology (nanoparticles, nanoflakes and nanoflowers) can be controlled and steered by the laser deposition parameters.

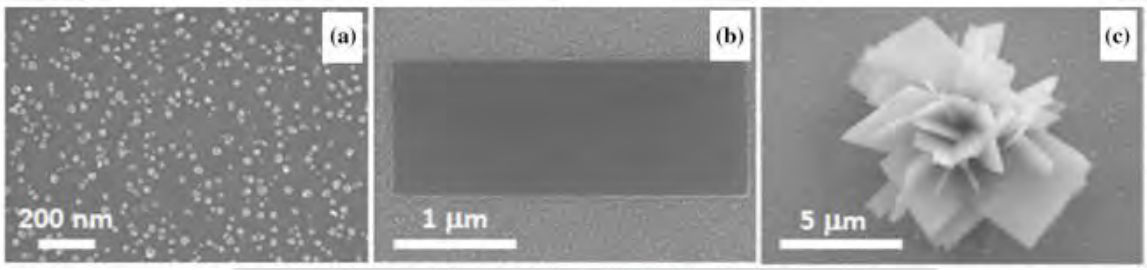

Figure 1 SEM images of typical nanostructures: (a) nanoparticles, (b) a nanoflake, and (c) a nanoflower obtained at the surface of ITO covered glass as a result of laser-induced deposition from solutions of supramolecular complexes [1].

The nanostructures (Fig. 1) are prepared in a single step as a result of laser-induced transformation of supramolecular complexes providing the building blocks for the formation of these nanoobjects. The deposited nanostructures offer a specific functionality as is exemplified by the surface enhanced Raman spectroscopy, and by the electrocatalytical performance [2,3,4]. Another unique peculiarity of the approach is the targeted decoration with hybrid metal/carbon nanostructures of different substrates (transparent and non-transparent) which may have any 2D or 3D topology [5].

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Laser for NANO.
Pioneering pulsed laser synthesis of colloids

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During the past several decades, "small-particle" research has become quite popular in various fields of physics and chemistry. By "small particles" are meant clusters of atoms or molecules of metals, semiconductors and others materials, ranging in size between single atoms or molecules and bulk materials.

In the year 1991 it has been assumed, that all substantial facts and technologies regarding nanoparticles were already known.
We have been using methods: Pulls radiolysis, Stop flow techniques, and chemical synthesis in liquid system, in solutions, chemical dissolution of big particles to small nanostructures.
What more was left besides tuning of existing manufacturing technologies and developing clever applications?

Could lasers be put to a good use?
Attempts were made, but without any particular breakthrough...
At that time, we aimed to new type of nanostructures and we really had not expected that usage of lasers could bring us something revolutionary.

But there was a surprize waiting around the corner...
We hoped that by an absorption of intense laser beam by a solid state material, producing temperature of plasma of many thousands kelvins (similar like in sonochemistry, where several thousand kelvins are reached in oscillating gas bubbles in a liquids [1]), similar effects could be reached. Nothing more, nothing less.

Initiating plasma by a focused laser beam (694nm Ruby laser flash) to thin film of solid state material thus creates conditions similar to a plasma discharge and cause ablation condition. When some liquid surrounds „hot plasma spot", evaporated products are very quickly cooled down and very small nanoparticles can be produced. We hoped that maybe under these conditions new colloidal particles and clusters could be produced. Perhaps, even some new form of nanostructures ?
First attempt was realised in a small 1 cm quartz cuvette. Filled by water, inside with a strip of metal.
Cuvette was placed into the laser beam focused on the metal foil.
All was working.
After several pulses…. show through potholes to the cuvette.
Very small, microscopic leak…..But was there.
In order to exclude this undesirable effect from happening, it was necessary to use a very short focal lens.
Reason: to avoid thermal destruction of cuvette walls.
What we had learnt from this experiment? We concluded that smaller particles are formed with increasing laser energy.
Smaller particles reacted more quickly with each other (case of silver oligomers) and some small metallic particles reacted with water and oxidized (in the case of Si nanoparticles).
Relatively broad size distribution was found in all experiments at laser synthesis of colloids.
(At that time we did not expect that this idea would have such an enthusiastic following)

Presently, situation for such a field of research, i.e., „Nanoparticle Generation by Lasers in Liquids", is becoming a much hotter topic due to availability of picosecond and femtosecond lasers. Shorter time for energy deposition causes less problems with high temperature, narrowing the size distribution, with possible applications in biological systems.

Where are we now and what's next?
Open the research mainly for biomedical and biomedicine applications.
For example, only this way can be prepare Fe /Ag magnetic nanoparticles, with high purity, which are at top interest for research against HIV virus and strategically defence against gram-positive batteries like anthrax (our attempt).
See the lecture….

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Highly defective nanocrystals as ultrafast optical switches: femtosecond laser processing in solution and efficient nonlinear optical response

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Exploring novel photonic materials with efficient nonlinear optical response is of great significance for ultrafast photonics. The effective defect control approach is a promising technique for the development of ultrafast optical devices because the optical properties and electronic structure of materials depend to a large extent on their defect structure. Here, we demonstrate a universal nonequilibrium strategy of femtosecond laser processing to synthesize a broad range of colloidal nanocrystals with simultaneous generation of abundant defects at room temperature.[1,2] The defect states endow the nanocrystals with broadband absorption and enhanced nonlinear optical response in the near-infrared region. The highly defective nanocrystals exhibit an ultrafast optical response of about 160 fs and are used to drive an ultrafast optical switch for generation of passively Q-switched laser pulses with a pulse duration of 910 ns at 1.0 μm. The nonequilibrium synthetic strategy offers a scalable and versatile technique for the exploration of defect mediated physical chemistry and high-performance nonlinear optical devices.

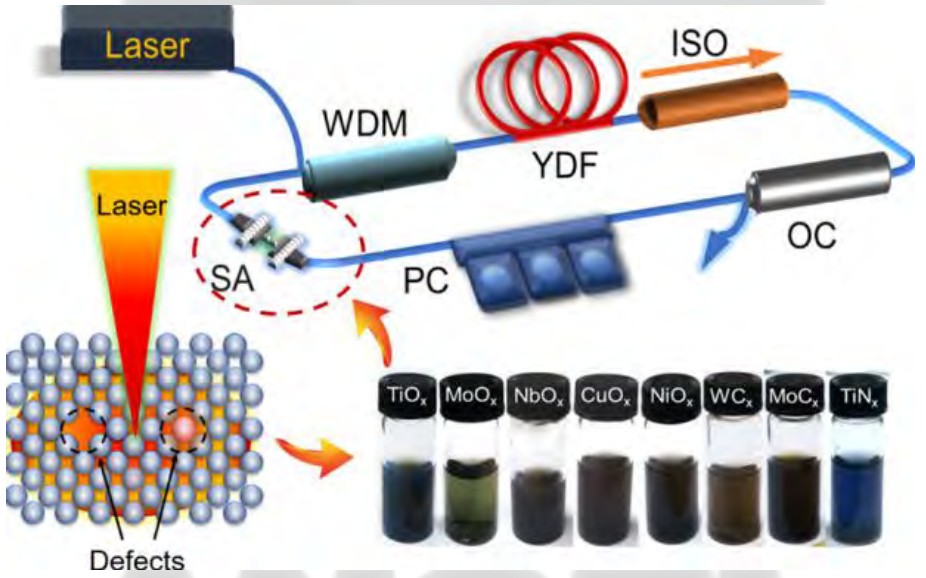

Figure 1 A universal nonequilibrium approach for the fabrication of plasmonic NCs along with simultaneous defect generation by fs laser processing in solution.

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What did we neglect to study on particle generation during laser ablation in liquids?

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The technique of laser ablation in liquids is now advancing very fast, as witnessed by increasing groups all over the world being dedicated to the fundamental and application aspects of this methodology. In the comprehensive review pushed in 2017 [1], Zhang et al. summarized a series of processes for laser ablation in liquids including the plasma phase, bubble gas phase, and liquid phase, as shown in Figure 1. Every factor in each phase definitely influences the chemical and physical properties of the synthesized nanomaterials. One may wonder whether it is the whole panorama of the ablation and whether some factors were neglected? Will these neglected factors play an important role in the particle formation and to what extent will they determine the properties of the nanomaterials?

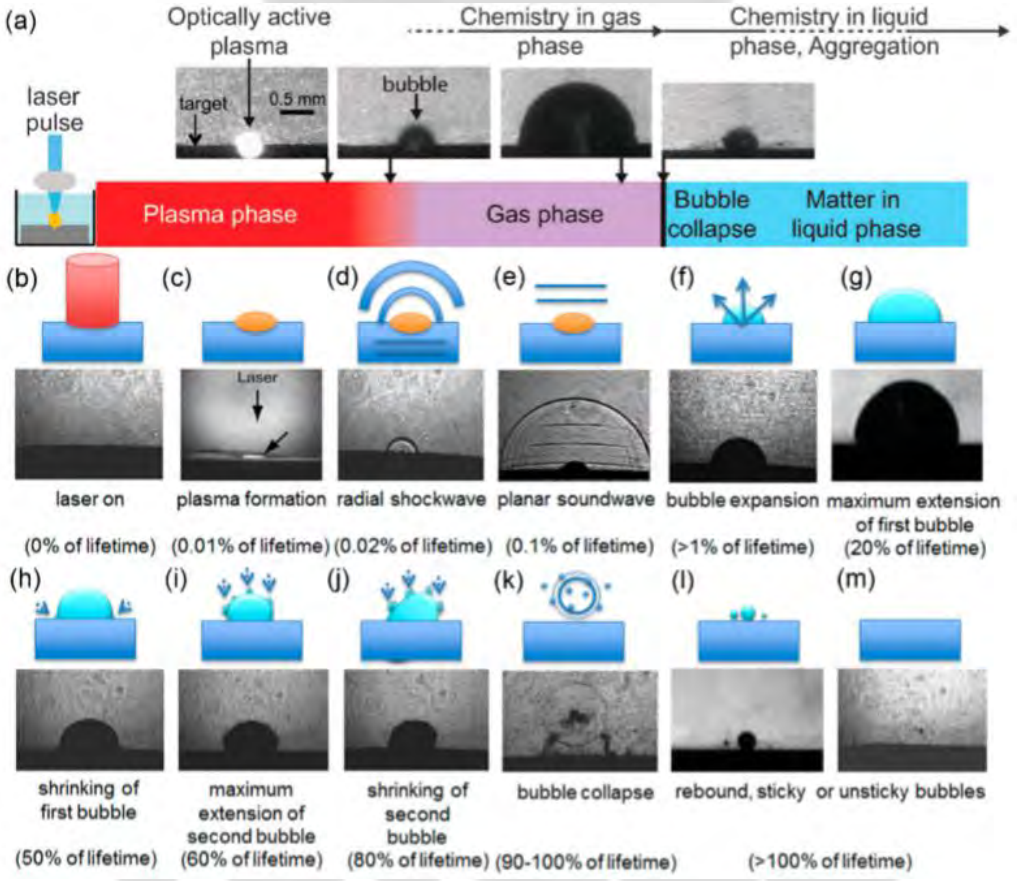

Figure 1 The whole panorama of laser ablation in liquids [1].

In this work, we will present some factors that have been neglected in previous studies but definitely influence the sizes and morphologies of as-prepared nanomaterials based on the data [2] we have obtained recently, in order to better understand the mechanisms that are responsible for the particle generation [3].

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Ultrafast time-resolved studies on laser ablation of metals

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Ultrashort-pulsed lasers have gained widespread use for both scientific and industrial applications due to high available peak intensities as well as their highly efficient and precise material ablation properties. A surface, irradiated with an ultrashort-pulse passes through a sequence of physical processes that occur over a wide temporal range, from femtoseconds to microseconds.

Open questions to date are why the pulse duration and why the temporal separation of pulse sequences influence the energy specific ablation volume.

Pump-probe ellipsometry (PPE) [1] reveals changes of the complex refractive index for the first tens of picoseconds, while pump-probe microscopy (PPM) [2] gives access to changes of the relative reflectivity from the initial femtosecond pulse impact to the final state at 10 µs. Figure 1 displays PPM experiments on Cu, Al and AISI304 in air, showing the transient evolution of the relative reflectivity change $\Delta R/R$ for probe-pulse delay times ranging between -12.5 ps and 10 µs. The samples were excited with a 680 fs laser pulse exhibiting a wavelength of 1056 nm at a fluence of $2.5\times\Phi_{th}$, where Φ_{th} denotes the respective ablation threshold fluence.

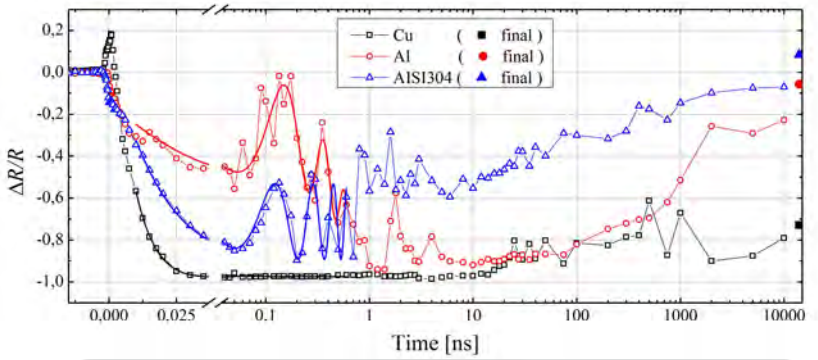

Figure 1 Relative reflectivity change $\Delta R/R$ of Cu (black open squares), Al (red open circles) and AISI304 (blue open triangles) for probe-pulse delays ranging between -12.5 ps and 10 µs. Each sample was excited by a fluence of $2.5\times\Phi_{th}$, where Φ_{th} denotes the ablation threshold fluence. Final state values of $\Delta R/R$, measured several seconds after pump-pulse impact are shown in the figure by solid symbols with respective shape and color.

The experiments indicate an ultrafast density decrease at the surface of 30% within the first 5 ps, a surface mechanical motion [3], separation and propagation of a spallation layer from about 100 ps to 5 ns, followed by spallation layer disintegration and generation of particles in the time range from 5 ns to 100 ns. The observed ablation dynamics help to explain pulse duration and separation trends on energy specific ablation volume.

Our measurements and simulations support the conclusion that the ablation process should be initiated by pulse durations shorter than the mechanical relaxation time of 5 ps and left un-interrupted until the final state is reached after about 1 µs.

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Preparation of metastable metal catalysts with high performance through laser ablation in liquid method

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Electrochemical water splitting has been known as an efficient strategy for the storage of intermittent electrical energy and obtaining clean fuel, via hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). The main concern for this technology is to design efficient and stable HER and OER electrocatalysts. Pulsed laser ablation in liquid (PLAL) method is usually adopted to prepare nanomaterials with unique physical and chemical structures, which are the very characteristics for electrocatalysts with high performance.

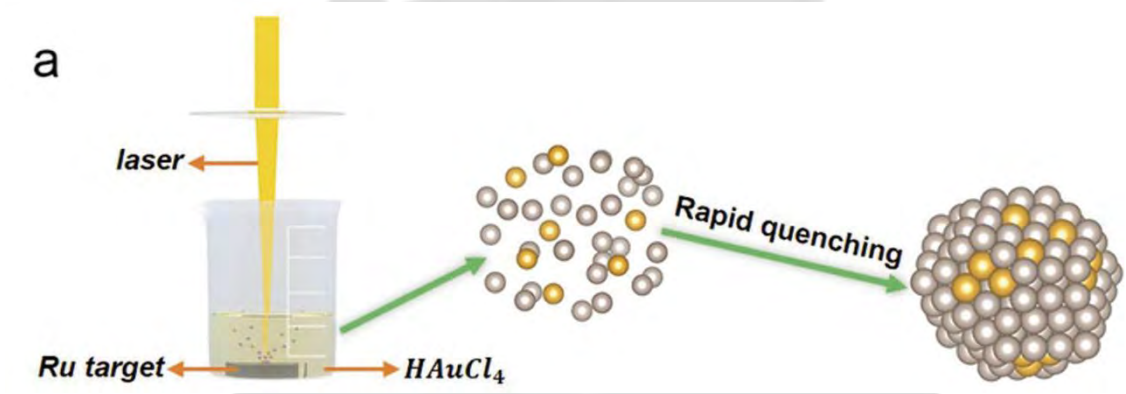

Figure 1 Schematic diagram of the synthetic process for single-atom catalysts.

In recent few years, we have reported a series of single-atom catalysts (SACs) with high HER or OER performance through the PLAL method. Figure 1a shows a typical schematic diagram of the synthetic process. Using this process, we realized the alloying of immiscible metals, and obtained RuAu[1], RuNi[2], IrAg[3] SACs by controlling the concentration of metal salts in the liquid phase. These catalysts exhibit unique electronic and geometric structures and thus possessing superior catalytic performance to commercial electrocatalysts such as Pt/C and Ir black. For example, RuAu SAA exhibits a high stability and a low overpotential, 24 mV@10 mA cm^{-2}, which is much lower than that of a Pt/C catalyst (46 mV) in alkaline media. Moreover, the turnover frequency of RuAu SAA is three times that of Pt/C catalyst. Density functional theory computation indicates the excellent catalytic activity of RuAu SAAs originates from the relay catalysis of Ru and Au active sites. These work opens a new avenue toward high-performance SACs via fast quenching of immiscible metals.

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Laser ablation of gold in water by short and long pulses

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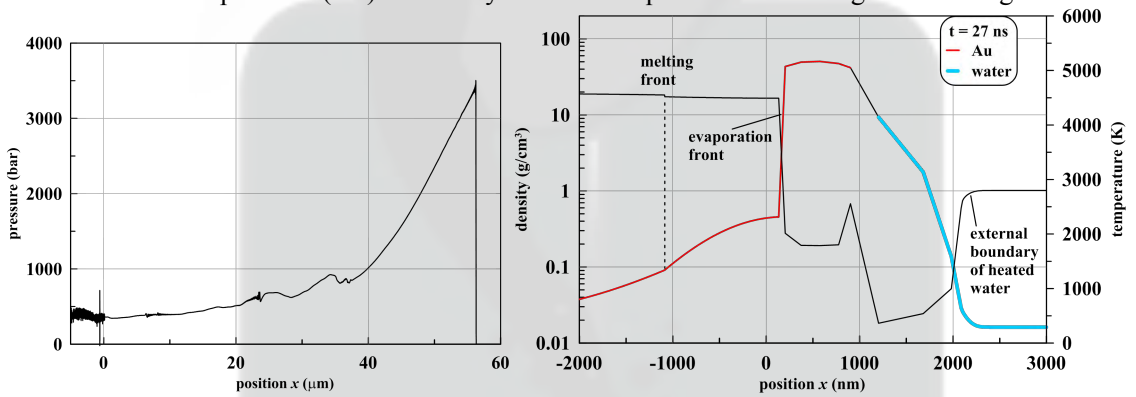
Laser ablation through liquid is an important process that have to be studied for numerous important applications which use laser ablation in liquid (LAL) [1-10] and laser shock peening (LSP) [6,7,11,12]. LAL is employed for production of suspensions of nanoparticles, while LSP is applied to increase hardness and fatique/corrosion resistance properties of a surface layer. A bubble appears in liquid around the laser spot focused at a target surface after strong enough laser pulse. In the paper we connect the early quasi-plane heated layer created by a pulse in liquid and the bubble forming at much later stages. In the previous works these early stage from one side and the late stage from another side existed mainly as independent entities. At least, quantitative links between them were unknown. We consider how the quasi-plane heated layer of liquid forms thank to thermal conduction, how gradually conduction becomes weaker, and how the heated layer of liquid nearly adiabatically expands to few orders of magnitude in volume during the drop of pressure. Our molecular dynamics simulations show that the heated layer is filled by the diffusive atomic metal-liquid mixture. Metal atoms began to condense into nanoparticles (NP) when they meet cold liquid outside the edge of a mixing zone.



These Figures are Figs 2 and 4 from [1], see also [2-10]. They show the LAL flow generated by 1 ns (full width e-folding time) duration, 0.9 J/cm^2 absorbed energy pulse at time 27 ns. The left panel presents distribution of pressure in global sense. We see shock in water. Gold-water contact is near x=0. Fine structure of the near contact zone is shown in the right panel. From left to right it consists from: solid gold (Au), liquid Au (a layer approx. 1 um thick), vaporized hot (T=5 kK) Au, hot (T=3-4 kK) very rarified (density 30 times less than 1 g/cm^3) water, and cold dense ("usual") water compressed to 400 bar, see the left panel.

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Design and development of time-resolved photography for the investigation of primary processes in gold nanoparticle generation

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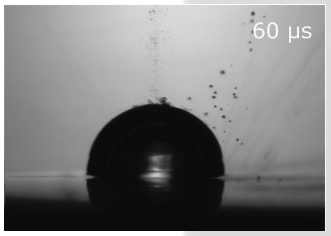
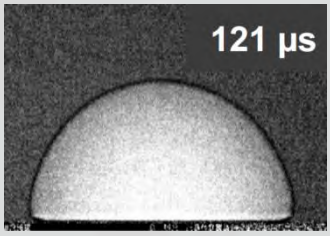
Pulsed laser ablation in liquids (LAL) is a growing field of research for the generation of nanoparticles with unique properties. Today, up to grams of nanoparticles can be produced per hour, but a comprehensive picture of the fundamental mechanisms in LAL nanoparticle generation is still missing. The ablation process is always associated with cavitation, because the high target temperature and ejection of ablated material cause a phase transition in the adjacent liquid that produces a rapidly expanding bubble filled with ablation products. After maximum bubble expansion, the bubble collapses again at the surface of the ablation target. Thus, first during ablation and initial bubble expansion and later during bubble collapse extremely high temperatures and pressures are reached, which result in specific features of material synthesis and modifications [1].

To investigate the underlying mechanisms during LAL nanoparticle generation, researchers tried to visualize the process by looking into the cavitation bubble. Unfortunately, neither shadowgraph flash imaging [2], nor x-ray flash radiography [3] achieved the required temporal and spatial resolution to image the initial material ejection and the subsequent nanoparticle formation process inside the cavitation bubble (Figs. 1 (a) and (b)).

(a) 

(b) 

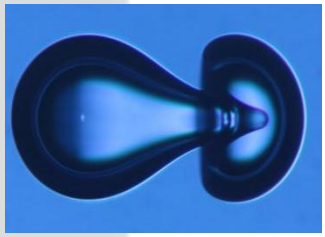
(c) 

Figure 1 : Imaging of mm sized cavitation bubbles during laser ablation in liquids: (a) Shadowgraph image [2], (b) x-ray flash radiography [3]. Both imaging techniques are not well suited for investigating material synthesis inside the bubble. In contrast, flash photography and Köhler illumination allows for a good view inside cavitation bubbles (c).

We developed a novel concept for the investigation of primary processes in gold nanoparticle generation with unprecedented temporal and spatial resolution. High temporal resolution is achieved by pumping a dye cell (LDS 698) with a SBS compressed Q-switched laser pulse (125 mJ, 532 nm, 100 ps). Sufficient dye concentration and a large laser spot provide a flat, extended incoherent light source that is well suited for Köhler illumination in flash photography which enables a view into the bubble (Fig. 1 (c)). High spatial resolution is achieved by photography of the LAL cavitation bubble through a water immersion microscope objective at large numerical aperture (NA = 0.8).

This experimental approach enables the investigation of LAL in a large range of laser parameters, using pulse durations from femtoseconds to nanoseconds at different radiant exposures. Experimental investigations can cover a larger parameter space and longer time span than molecular dynamics (MD) simulations that provide very detailed information on the early phase (few nanoseconds) of LAL with ultrashort laser pulses [4]. Comparison of experimental results and MD simulations will finally lead to a better understanding of the mechanisms of nanoparticle generation, and allow for an optimization of the process.

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Solid-solution alloy nanoparticles fabricated by laser-induced nucleation method

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A tightly focused femtosecond laser can produce high-energetic field at the focus. When the high-energetic field was formed in water, optical breakdown of water molecules occurred through multiphoton absorption process. Then reactive species (i.e., $H_2O \rightarrow e_{aq}^-$, $H^\cdot$, $OH^\cdot$, etc.) were generated. We reported formation of metal[1] and solid-solution alloy nanoparticles (NPs) with tunable compositions[2-8] by high intensity laser irradiation of mixed metallic salt solutions. The formation of those NPs in the absence of any reducing agents can be attributed to the reactive species generated by high-intensity laser irradiation of the solution. We named this noble physicochemical method for formation of NPs as laser-induced nucleation method.

Figure 1 shows XRD profiles of NPs fabricated by laser irradiation of mixed solution of rhodium (Rh) and platinum (Pt) ions with different mixing ratios. In the in the XRD profiles, single diffraction peaks were observed for all cases. In addition, XRD peaks were in between that of pure metals and shifted proportionally to the Pt molar fraction in the solution. Lattice parameters estimated from diffraction techniques were well agreed with the theoretical values obtained by Vegard's law. High-angle annular dark field (HAADF) and STEM-EDS mappings for RhPt binary alloy NPs were shown in Fig. 2. The EDS elemental mappings indicate a uniform elemental distribution of Rh and Pt in alloy NPs. It is also observed in the reconstructed image that no core–shell or phase segregated structures existed in the alloy NPs. Compositions of fabricated RhPd and RhPt alloy NPs in the solution with a mixing ratio of Rh : Pt = 1 : 1 were Rh53.1Pt46.9. These results strongly indicate that formation of all proportional solid-solution binary alloy NPs with fully tunable compositions irrespective to the immiscible nature of elements.

This talk will provide an outline of formation of metal and solid-solution alloy NPs by laser-induced nucleation method. Detailed structure and property of fabricated NPs will be also demonstrated.

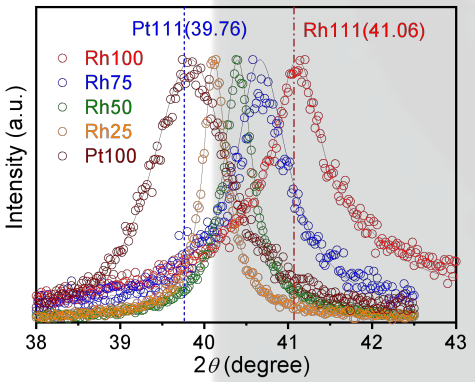

Figure 1 XRD profiles of NPs fabricated in RhPt mixed solutions.

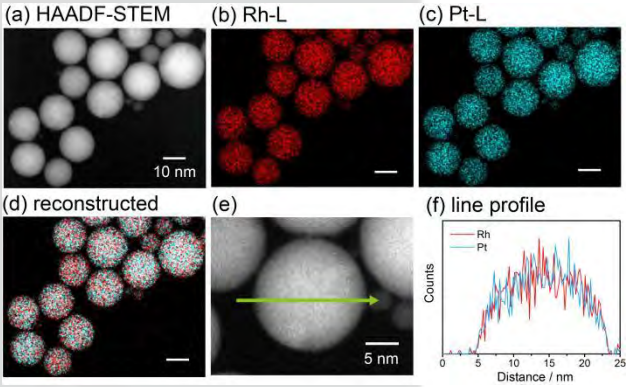

Figure 2 STEM-EDS mapping for the NPs fabricated in RhPt solution. (a) HAADF-STEM image, (b) Rh-L and (c) Pt-L STEM-EDS mappings, (d) reconstructed image, (e) magnified HAADF-STEM image of a particle in (a), and (f) line profile of Rh and Pt along the arrow in (e).

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Plasmonic Metal Nanoparticles Generated by Femtosecond Pulsed Laser Ablation for Biomedical Optical and Photoacoustic Imaging

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Plasmonic metal nanoparticles have emerged as particularly attractive exogenous contrast agents for a wide variety of biomedical imaging techniques, largely due to their excellent biocompatibility, low toxicity, and intense light absorption/scattering induced by the localized surface plasmon resonance tunable from ultraviolet to near-infrared holding great potential to improve these imaging techniques for detecting early-stage diseases with high sensitivity and specificity.

In this presentation, the application of gold (Au) and gold-silver (AuAg) alloy nanoparticles (NPs) for both dark-field light scattering imaging of live human cancer cells and enhanced photoacoustic microscopy (PAM) imaging of retinal blood vessels in vivo will be discussed. The Au and AuAg alloy NPs used in the present study were physically prepared via an approach of femtosecond laser ablation of bulk target in ultrapure water, allowing the fabrication of NPs with unique properties of capping agent-free surface and high purity. These unique properties enable us to functionalize NPs via the method of sequential conjugation as reported in our previous publication [1], which offers the capability of precisely tuning the number of different kinds of ligands bound onto NPs, thereby optimizing targeting ability, biocompatibility, and colloidal stability of the obtained nanoconjugates [2-4].

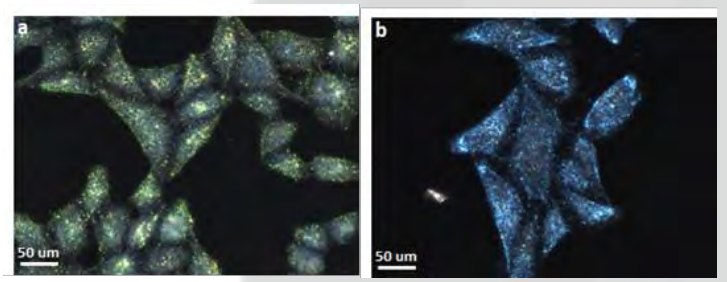
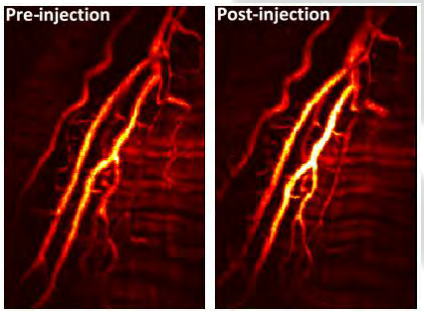


Figure 1. Dual-color dark-field light scattering imaging of live human cancer cells (HeLa cells). (a) Cells stained with spherical Au NPs (30 nm diameter) having LSPR peak around 520 nm appear green in colour. (b) Cells stained with spherical AuAg alloy NPs (30 nm diameter) having LSPR peak around 450 nm are seen blue in colour.

By using the method of sequential conjugation, Au and AuAg alloy NPs were conjugated with both thiol-functionalized methoxy polyethylene glycol (mPEG-SH) and RGD peptide, serving as stabilizers and targeting molecules for binding to cancer cells or specific biological sites of interest in vivo, respectively. After the fabrication of these nanoconjugates, they were incubated with HeLa cells and their application in dual-color (green and blue) dark-field light scattering imaging of live human cancer cells was demonstrated as shown in the figure 1.



Moreover, the 20 nm PEGylated Au NPs were intravenously injected into living rabbits for enhancing in-vivo imaging of retinal blood vessels. As it could be seen from PAM images in figure 2, there is a higher than 50% increase in PAM signal after intravenous administration of PEGylated Au NPs.

Figure 2. In-vivo PAM imaging of retinal blood vessels in living rabbit at the excitation wavelength of 532 nm before and after injection of PEGylated Au NPs. The PAM signal from retinal shown a higher than 50% increase after intravenous administration of Au NPs.

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see if papers later

Formation of MoSe2 Nanosheets and Nanoscrolls obtained from Pulsed Laser Ablation in Deep Eutectic Solvent (PLADES)

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Interest in the production of 2-dimentional (2-D) transition metal dichalcogenides (TDMCs), such as MoX_2, were X is a chalcogen atom such as S, Se or Te, continues to be of great interest due to their optical and electronic properties [1]. Once fabricated into atomically thin layer structure, these materials have a direct bandgap, strong spin–orbit coupling and favourable electronic and mechanical strain dependent properties which are attractive for electronics. Synthesis efforts of TMDCs have focused on methods such as chemical vapour deposition which results in small quantity yields, slow growth rates, toxic by-products and have high cost of production [2]. As an alternative, pulsed laser ablation in liquid (PLAL) is a promising economic, green alternative for synthesis of TMDCs. However, there are some barriers with the technique that limits synthesis of TMDCs and their subsequent application. Specifically, it has been shown that in the case of MoX_2 (X=S, Se, Te) the chemical processes during the plasma phase of the ablation can yield formation of variants including MoO_3 quantum dots when oxygen containing solvents are used [3].

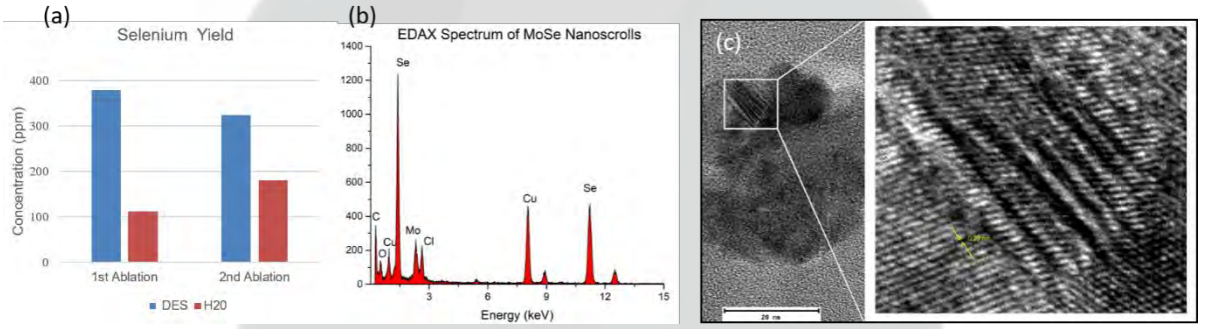

Figure 1. (a) Difference of the yield concentration in ppm of selenium present in $MoSe_2$ nanosheets synthesized in deep eutectic solvent (DES) and H_2O. (b) EDS analysis of $MoSe_2$ nanosheets synthesized in DES showing a low oxygen existence, compared to the selenium peaks. (c) TEM image of $MoSe_2$.Insert shows fringes indicating crystallinity.

To overcome this problem, in this work we produced $MoSe_2$ nanostructures via pulsed laser ablation in deep eutectic solvents (PLADES). We demonstrate that the introduction of an ionic liquid-like solvent which has low vapour pressure and low oxygen content is a viable alternative to obtain high yield of crystalline structures, compared with other solvents like water. The resulting crystalline structures and composition are confirmed by transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS). Our results show that in the presence of DES solvent forms nanosheets and nanoscrolls of $MoSe_2$ with minimum side product of MoO_3 which is influenced by the gradient of the viscosity, temperature and chemical composition of the solvent during the ablation process. Results of this work support the development of stable colloids of TMDCs in scalable quantities which can be readily integrated into future applications including biosensors and flexible electronics.

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Fighting pathogenic bacterial biofilms by bactericidal nanoparticles

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It has been established that organized communities of pathogenic bacteria having a complex structure can form on almost any surface and are the cause of many problems, including medical ones [1-3]. The growing resistance of bacteria to existing drugs and the lack of structures that could potentially form the basis of new antibiotics have put on the agenda the search for alternative ways to combat pathogenic microorganisms.

In this work, Ag, Cu, Au, nanoparticles produced by a method of laser ablation with the use of an Yb^{3+} doped fiber laser HTF Mark, Bulat (central wavelength λ = 1064 nm, pulsewidth FWHM τ = 120 ns), equipped with a galvanometric scanner and an f-theta objective (focal length F = 160 mm) were tested on antibacterial activity regarding Staphylococcus Aureus and Pseudomonas Aeruginosa. The resulting ablation products were deposited on the bare silica glass for nanoparticles investigation by methods of scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) (Fig.1). For research, the standard microbiological method for determining CFU (colony forming unit) was used. Experimental studies have shown that the use of the method of application laser transfer of silver and copper nanoparticles is an effective method in the fight against biofilms formed on a solid substrate.

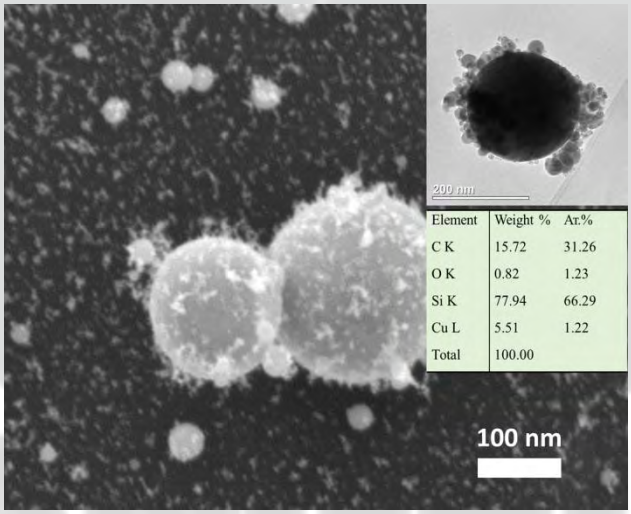

Figure 1 SEM image of Cu nanoparticles; insets: TEM image and EDX analysis

This work was supported by Russian Science Foundation (grant #18-15-00220)

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Laser-induced damage effects in opaque solids: Comparison of air and water environments

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Pulsed laser ablation in liquids (PLAL) is an efficient and flexible technique for nanoparticle production and surface nanostructuring. Although PLAL is simple in realization, the process itself is very complicated and still poorly understood. The complexity of the PLAL process can be illustrated by the example of the laser-induced damage threshold (DT), a well-defined parameter which can serve as a reference for modelling of the PLAL process. Available data on DTs in liquids are rather contradictory, provide threshold fluences higher, equal to, or lower than the corresponding values in air, and various mechanisms are invoked to explain the difference [1-3]. In this work, we have systematically investigated the DTs of a number of metals (Au, Ag, Au-Ag alloys, Sn, Ti) and semiconductors (Si, Ge) irradiated by IR laser pulses in water and air. The experiments were carried out with nano-, pico- and femtosecond pulses in single-shot and multi-short irradiation regimes. The experimental results are analyzed theoretically by solving the heat flow equation for the samples irradiated in air and in water. We demonstrate that ns-laser induced DTs of fairly refractory metals in water are considerably higher than the air values due to scattering of the incident laser light by the vapor-liquid interface. In contrast, for low-melt materials, when the melting point is below the water critical temperature, the DTs in air and water are virtually identical (Fig. 1). The scattering effects do not play any role for ultrashort laser pulses but then other processes come into play. The influences of the pulse duration, focusing conditions, water superheating and nucleation, accumulation effects and non-linear effects during laser pulse propagation in water are discussed. The effects of peculiarities of melting and ablation of different materials in liquids on nanoparticle formation under PLAL are also discussed.

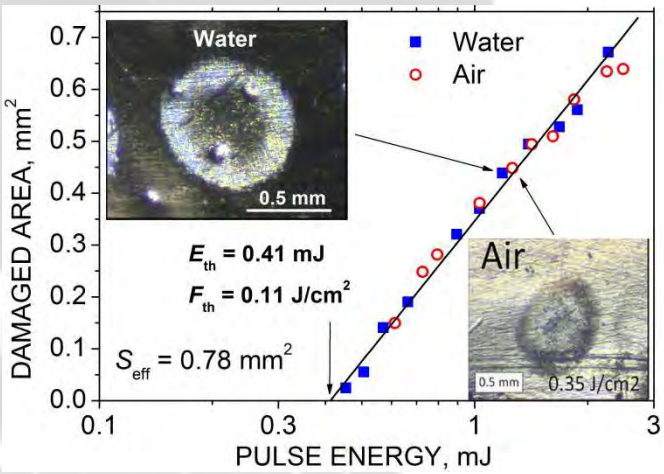

Figure 1 The area of the damage spots produced on the Sn surfaces in air and water as a function of laser pulse energy. The measured threshold energy, fluence and efficient spot area are indicated. The insets show optical microscope image of typical spots.

The work was supported by the RFBR (project 18-08-01383).

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Au@Pd colloidal nanoparticles by laser ablation in liquid for LSPR hydrogen sensing

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Gold nanoparticles (GNPs) were fabricated by pulsed laser ablation method (PLA) in DI water. $PdCl_2$ solution with different concentration was added to the obtained GNPs colloidal solutions. X-ray diffraction (XRD) confirmed the formation of metallic gold and presence of $PdCl_2$ phases. Transmission electron microscope (TEM) images along with X-ray photoelectron spectroscopy (XPS) revealed formation of the core-shell-like structures of $PdCl_2$/Au NPs. Au@Pd colloidal nanoparticles were prepared by simple mixing of $PdCl_2$ and colloidal gold nanoparticles (Au_1Pd_2 sample with molar ratio Au:Pd (1:2)). The gold LSPR peak first exhibits a red-shift due to accumulation of Pd^{2+} around the spherical gold nanoparticle and then undergoes a blue-shift by reduction of Pd^{2+} to metallic Pd due to hydrogen exposure.

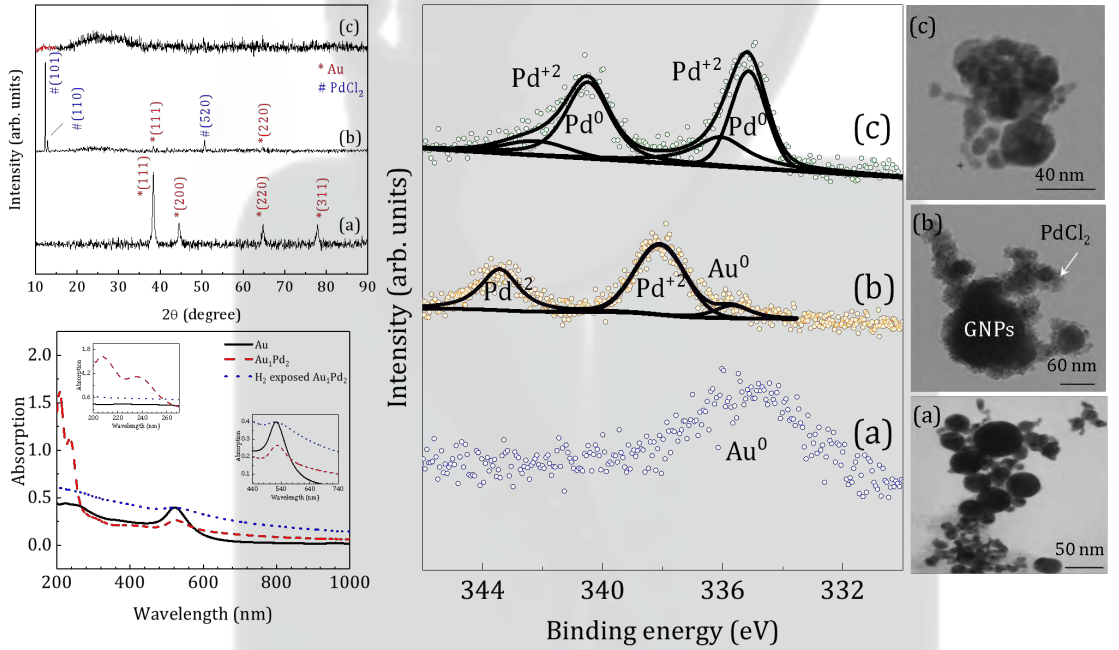

Figure 1 Left panel up: XRD, Left panel down: Absorption spectra of GNPs,Au_1Pd_2 sample before and after hydrogen exposure, middle panel: XPS and right panel: TEM images of (a) GNPs, (b) Au_1Pd_2 sample before and (c) after 10% H_2 exposure.

A strong correlation between gold LSPR spectral shift, $PdCl_2$ concentration (from beer lambert law) and hydrogen percent were observed [1]. The mechanism of LSPR gas sensing is, after adding $PdCl_2$ solution (in which Pd^{2+} cations exist), the surface negative charges of GNPs absorb palladium ions by the coulomb attraction force. Then a layer of Pd^{2+} is formed around the GNPs (see the TEM images). The accumulation of these particles causes the change in the dielectric properties of GNPs adjacent and leads to a red-shift in LSPR peak [2][3]. In the next step, with the injection of hydrogen gas, this Pd^{2+} layer reduces to metallic Pd NPs and as a result, the coulomb attraction force is eliminated. This causes the newly-formed Pd NPs to be separated from the GNPs and bare GNPs are obtained again. As a result, the LSPR absorption peak undergoes a blue-shift. As our data showed, these spectral shifts were correlated with the ratio of palladium to gold, and in particular the concentration of hydrogen gas. This could be a good candidate for the LSPR-based hydrogen gas sensor.

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Recent advances in laser synthesis of novel functional nanomaterials and their biomedical applications

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The presentation will overview our on-going activities on laser ablative synthesis of novel biocompatible colloidal nanomaterials and their testing in biomedical tasks. Our original approach is based on ultra-short (fs) laser ablation from a solid target or already formed water-suspended colloids to fabricate "bare" (ligand-free) nanoparticles (NPs) with well-controlled size characteristics [1,2], as well as coating of nanomaterials by functional molecules (dextran, PEG etc.) during the ablation process or afterwards [3,4]. The presentation will describe different approaches to achieve appropriate characteristics of plasmonic (Au, TiN), semiconductor (Si-based structures) and polymer dye nanomaterials and overview their biomedical applications. In particular, by performing *in vitro* and *in vivo* tests using small animal model we concluded on safety of Au [4,5], TiN [6] and Si [7,8] nanoparticles. We also found that bare laser-synthesized Au NPs can provide unique opportunities as SERS probes for identification of biological species such as yeast [9] and bacteria [10] cultures, as well as serve as electro-catalysts of glucose oxidation in biofuel cells for alimentation of bioimplantable devices such as pacemakers [11]. We also revealed a strong photothermal effect under the use semiconductor (Si) and plasmonic (TiN) nanoparticles and applied this effect in tasks of cancer hyperthermia [6]. We finally overview applications of Si NPs, which exhibit a unique combination of biocompatibility and biodegradability options [12,13]. In particular, we show that laser-synthesized NPs can be used as efficient markers in tasks of linear and non-linear optical Bioimaging [14]. In addition, these nanoparticles can be used in mild cancer therapies, e.g. as sensitizers of radiofrequency radiation-based hyperthermia [15] and safe carriers of therapeutic radionuclides in nuclear nanomedicine tasks [16].

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Pulsed-heating method for synthesizing monodispersed and ultrasmall nanoparticles

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The structure of a material depends on either thermodynamics or kinetics of the synthesitic reactions. While thermodynamics defines the most stable structures, kinetics controls the path and time scale in reaching the thermodynamic or metastable states. Steady-state energy supply may trigger near-equilibrium synthetic reactions, localized and transient injection of external energy and cooling down can create a non-equilibrium extreme environment, which is of great help in designing and synthesizing novel materials with metastable structures that are typically inaccessible from the conventional synthetic routes. In this presentation, we will firstly introduce our newly-developed GO-mediated pulsed laser heating method with heating rate larger than 1.0×10^9 °C/s, and its application in synthesizing sub-1 nm metal clusters with high loading amount of metal. Then, we will briefly introduce the synthesis of ultrasmall transition metal Oxides via coordination-directed laser irradiation in liquids, as well as its application in electroreduction of CO_2. These studies for materials synthesize under laser triggered pulsed high-power field, presenting a primary introduction toward the synthetic methodology under extreme environment, we hope this methodology to open up new horizons for designing material synthesis reactions with high efficiency.

Figure 1. The strategy for constructing extreme environment for material synthesis.

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In situ mass evaluation and speciation in laser ablation of Zn in water

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Speciation in pulsed laser ablation in liquids (PLAL) can be defined as the evolution of structures following the expulsion process, including nature of species, particle size evolution or chemical valency. While much is known for the final state, i. e. the post-mortem structures, it is still difficult to obtain such information in situ despite recent time-resolved structural studies [1, 2, 3] or luminescent probes [4,5].

The ablation from a metallic zinc target can be considered as a model system to investigate the reactions during the process. We have studied the nanosecond ablation of a zinc wire, which yields ZnO nanoparticles as final state [6, 7]. In addition to our established methods, such as time-resolved small angle X-ray scattering [8] or multicontrast imaging [2,9] we explored time-resolved X-ray absorption spectroscopy (XAFS) to reveal the valency as well as the absolute mass yield within the bubble [10] lifetime.

We found proof that (i) within a sub-millisecond time scale the ablated mass is entirely metallic and oxidation would only start on a later time and (ii) in nanosecond ablation the ablated mass is initially not only solid, but contains a considerable amount of cluster species. The derived absolute mass yield will be put in perspective to the energy deposition during the laser pulse.

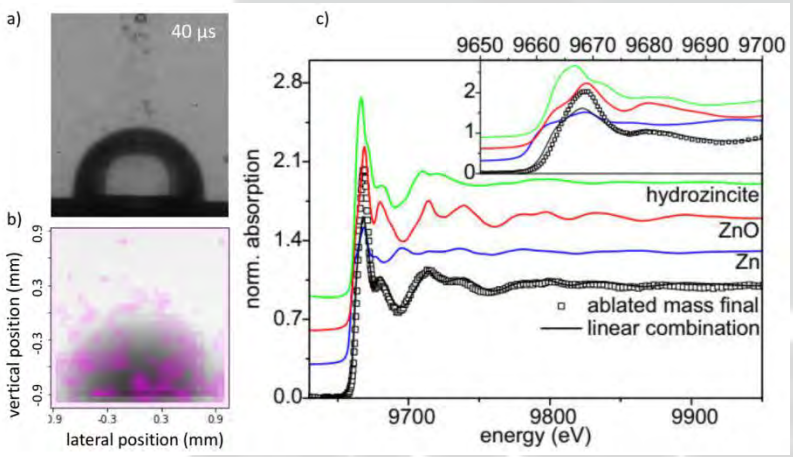

Figure 1: (a) Visible snapshot of the PLAL bubble at maximum extension at 40 µs compared to (b) radiographic image overlaid with dark-field signal (pink). (c) XAFS spectrum of the final state of the zinc suspension after ablation compared to model functions of different chemical products [7].

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Shock-Waves Generated by Laser ablation in Liquids

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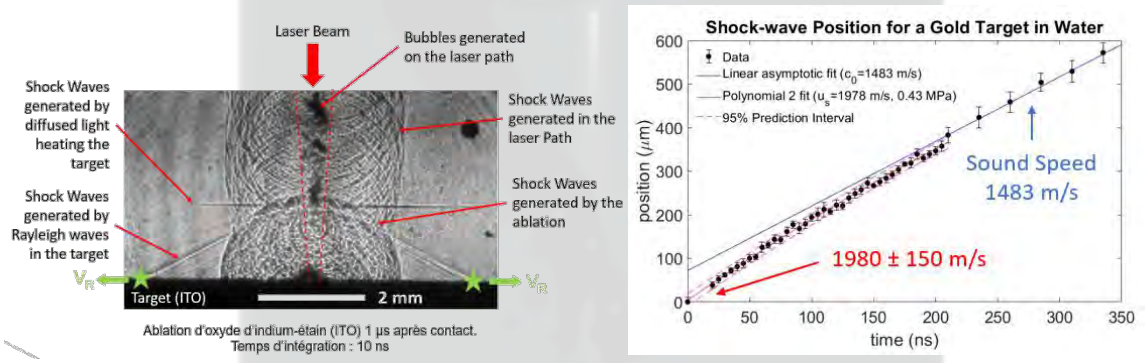
Laser ablation in liquids is now commonly used to generate colloidal solution of nanoparticles. At the very beginning of the ablation process, several shock-waves are released [1]. Understanding the origin and the behaviour of each of these features is of first interest. Indeed, shock-waves dynamics could provide information on pressure at the ablation point [2]. Furthermore, shock-waves in the target can damage the sample which is an important issue in LIBS measurement especially on organic materials [3]. The shock-waves can also induced phase transition in the target [4]. However, laser-generated shock-waves dynamics has not been fully addressed yet at a solid/liquid interface. Such measurements require imaging with a time resolution of a few nanoseconds and could be combined with local time-resolved pressure probe. Thus, we used Shadowgraph measurement with a time triggered iCCD in order to observe the phenomena. Thereby, we were able to measure the deceleration of the shock and we can deduce very high pressure at the ablation point (~ 1 GPa). Using a large set of target materials, we confirmed that the oblique shock waves (Mach cone) are due to the propagation of a Rayleigh surface wave. These two results open a new way to measure ablation point pressure and enable the characterisation of the surface waves on the target which is of first interest in surface characterisation and LIBS measurements. The subsequent better control of the ablation could also help to prevent target crushing during PLAL whish require post-processing to remove large particles from the as-produced colloids.



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Ablation target effects on nanoparticle productivity during laser ablation in liquids

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Laser ablation in liquids (LAL) has matured to an economically feasible method with applications in many areas [1]. While in many LAL-related studies the focus is placed on the effect of the surrounding liquid, the laser parameters or the material properties of the ablation target, the surface structure of the target which apparently changes during laser ablation is generally ignored. However, for nanoparticle productivity [2] the surface structure needs to be considered, since the ablation rate is strongly dependent on the optical properties of the target. If a surface structure such as laser-induced surface structures (LIPSS) are formed on the target (Fig. 1), laser-matter-interaction will change and possibly influence nanoparticle formation. One of the most important laser parameters in the context of LIPSS formation is the applied laser fluence, it has an immense impact on whether LIPSS is formed or not. Typically, a laser fluence close to the ablation threshold leads to distinct LIPSS features while in a high fluence regime LIPSS are often not formed anymore [3]. In contrast to LIPSS formation, LAL-nanoparticle productivity increases with higher fluence [2]. Hence, typically the highest possible fluence for a given LAL-setup is utilized for maximum nanoparticle productivity [2]. To understand the interplay between LIPSS and LAL, LIPSS formation on several metal targets are studied in this study [4]. Due to their relevance in plasmonics, biomedicine and catalysis the alloy systems of iron-gold and gold-silver as well as their constituent metals are studied in detail for different fluences and compositions and eventually correlated to nanoparticle productivity.

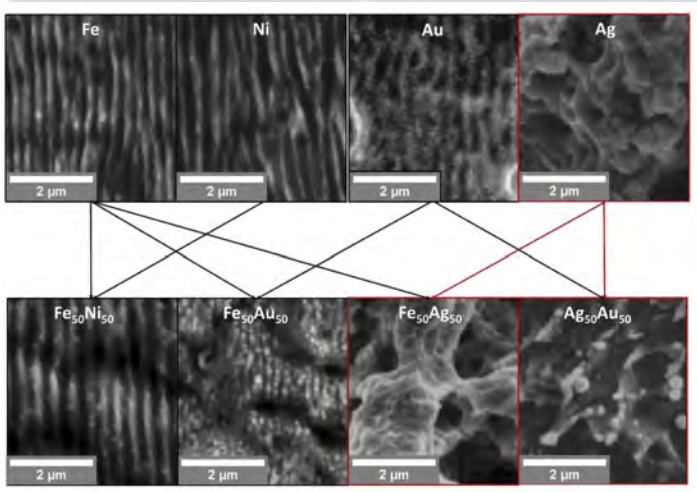

Figure 1 Scanning electron microscopy images of laser-ablated elemental metals and their alloys (50:50 composition) in water. Red frames mark metals that didn't form LIPSS while black frames mark the materials that formed LIPSS at the fixed laser parameters.

We find that the nanoparticles productivity linearly depends on the laser fluence when LIPSS is not formed, while a logarithmic trend and a decrease in productivity is evident when LIPSS is formed. To cancel LIPSS formation and recover from this decrease, a change to circularly polarized light is performed and an increase in nanoparticle productivity of more than 30% is observed.

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Metal Nanospheres Grown by Laser Irradiation with Enhanced Tribology Properties

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Laser irradiation is a new area in the field of material growth at the nanometer or submicron scale, where extreme non-equilibrium conditions, such as ultra-high temperature (~104 K) and ultra-high pressure (~106 Pa), may occur. [1] The instantaneous plasma caused by pulsed laser irradiation can be quenched in the surrounding liquid environment, resulting in remodeling and phase transformation of materials. [2, 3] Herein, we chose the metal nanoparticles (e.g. Cu, Ag) in a liquid as targets. The surfaces of metal particles melted and changed gradually to nanospheres under the alternate selective nanosecond laser heating and peripheral solution cooling. [4] Furthermore, the metal nanospheres by laser irradiation as lubricating additives exhibited excellent friction reduction and wear-resistant properties, which benefit from their spherical morphology and good solubility in different commercial lubricants. The spherical shape makes sliding friction transform into rolling friction easily under low load. Besides, the metal particles can be deposited and accumulated into the concave part of uneven friction surface to fill and repair the worn parts. Therefore, using this strategy, metal nanospheres particles as lubricating additives are of great significance for reducing mechanical friction and wear and improving the energy utilization efficiency.

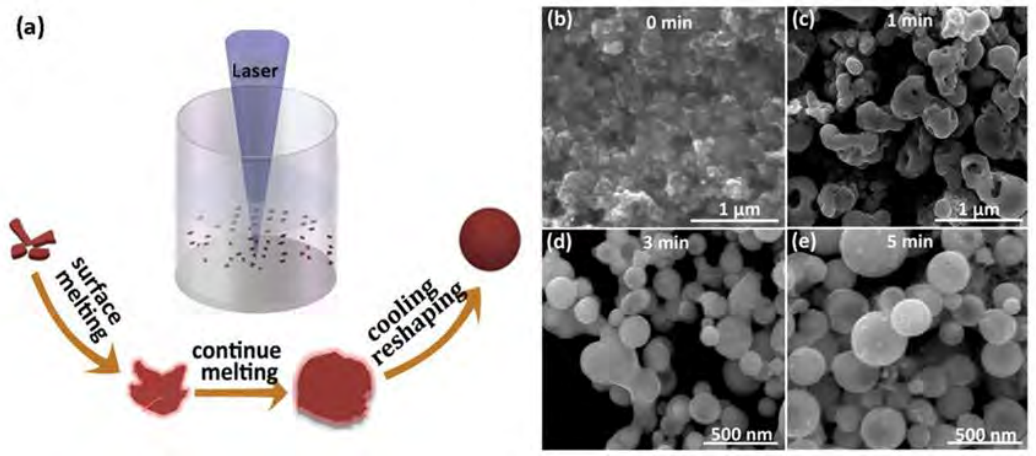

Figure 1 (a) Schematic illustration for the formation of the Cu nanospheres by laser irradiation. (b-e) The SEM images of the Cu nanoparticles with different laser irradiating time.

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Laser synthesis of colloidal nanoparticles and their adsorption on polymer microparticles for laser powder bed fusion

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Additive manufacturing by laser powder bed fusion (PBF-LB) of polymers is of great interest for prototyping and small-scale production. Since polymer powders have material-related limitations regarding their processability, they have become a decisive factor for PBF-LB. Nano-additives captures high interest to overcome these limitations and for expanding the material variety. However, to use nano-additives, a deep understanding of the interplay of the PBF-LB process with small mass fractions of nanoparticulate additives is required. Conventional additivation methods such as ball milling typically come with the disadvantage of agglomeration of the nanomaterial, which makes high filling rates necessary to achieve a sufficient surface dose. As an alternative, clean and surfactant-free nanoparticles can be generated using laser ablation and laser irradiation in liquids [1]. Thereafter, these colloidal nanoparticles are deposited on polymer micropowder supports to create and qualify new nanoparticle-composite powders for PBF-LB [2].

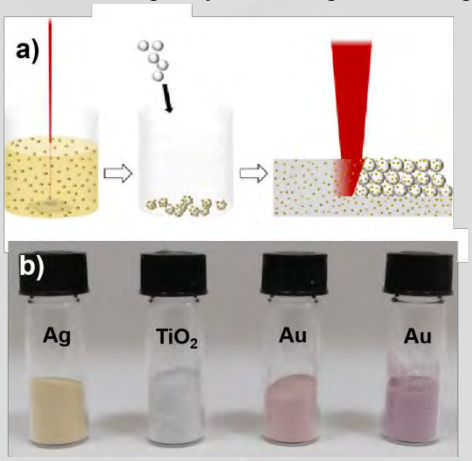

Figure 1. a) Scheme of the proposed methodology for laser generated nanoparticles supporting on polymer powders and the subsequent PBF-LB processing. b) Examples of a polymer powder after supporting of different laser generated nanoparticles.

Based on this approach polyamide 12 and thermoplastic polyurethane microparticles are decorated with a variety of different nanoparticles (e.g. silver, iron oxide, carbon) and processed via PBF-LB. To fully exploit the potential of this novel approach, an understanding of the electrostatic interaction between polymer and nanoparticles as well as the overall colloidal stability is important [3]. They govern the deposition process (support kinetics) and the dispersion quality. The nanoparticle material type, their degree of dispersion on the polymer microparticle surface, and their surface-specific loading density can alter the PBF-LB processability and enable introducing new functionalities to final parts.

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Construction of Metal-oxides Interfaces Assisted by Laser irradiation for enhanced electrochemical performance

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Regulation the metal–oxide interface is a crucial and feasible way to solve dynamic issues during the electrochemical reaction process, to improve the catalytic activity, particularly, as result of the strong interfacial confinement effects between metals and metal oxides.[1] Laser fabrication in liquids (LFL) is a convenient, effective and unique technique for designing and building metal-oxide interfaces such as Pd/TiO_2, Pd-PdO. The constructed Pd/TiO_2 can enable abundant protons and electrons to participate in the electrochemical N_2 reduction process to realize high selectivity and achieve a considerable NH_3 yield rate simultaneously.[2] Here, we present the design of heterogeneous catalysts to balance the relationship between hydrogen evolution and N_2 reduction reaction. Laser irradiation in liquids was first used to achieve reduction of PdO in aqueous medium resulting from the photothermal effect of laser.[3] The reduction degree of PdO and amount of PdO–Pd interfaces are intentionally controlled by adjusting the irradiation time, as shown in Fig. 1. The composite of PdO/Pd/CNTs, after 10 min irradiation with an optimal mass ratio of Pd (18%) to PdO (82%), presents the lowest overpotential and the highest NH_3 production rate of 18.2 μg $mg_{cat.}^{-1}$ h^{-1}, their faradaic efficiency reached 11.5% at 0.1 V vs RHE. Compared with Pd/C and PdO/CNTs, the abundant PdO–Pd interface on PdO/Pd/CNTs can act as the active site for N_2 dynamic activation and proton transitions, where the synergistic effect between Pd and PdO contributed to shorten the transmission route of protons and reduce the overpotential of the chemical reaction. In summary, this effort provides applicable strategy to design N_2-to-NH_3 transformation catalysts with controllable surface states and defects.

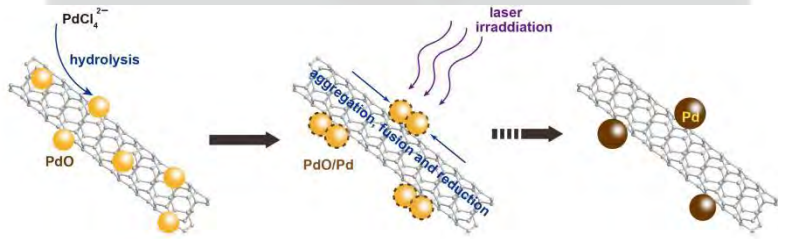

Fig. 1 Schematic illustration of the reduction of PdO to form Pd-PdO interface by laser irradiation.

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Structure of Fe-Ni nanoparticles produced by laser ablation in water

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Synthesis of FeNi nanoparticles by pulse laser ablation in liquids (LAL) is a topic of significant practical interest due to the potential application of magnetic nanoparticles in biomedicine and catalysis [1,2]. While the magnetic properties of nanoparticles are highly sensitive to the size, structure, and chemical ordering, the complete understanding of the size-dependent equilibrium structures of the FeNi nanoparticles is still lacking [3]. Moreover, the far-from-equilibrium conditions of nanoparticle synthesis in LAL further complicate the problem of predicting the structure of nanoparticles and, at the same time, provide an additional opportunity to control the structure through LAL synthesis parameters.

In this study, we combine computational and experimental study of nanoparticle generation in LAL of FeNi targets, with the goal of obtaining a complete understanding of both the size dependence of the equilibrium structure of nanoparticles and the effect of the highly nonequilibrium synthesis conditions realized in LAL. In particular, the equilibrium structure and compositional ordering in nanoparticles of different sizes are analyzed in a series of Metropolis Monte Carlo simulations. The formation of FeNi nanoparticles in LAL is investigated in simulations performed with a combined atomistic-continuum model developed for simulation of LAL [4] and parametrized for FeNi system [5]. Several large-scale (~122 million particles) simulations are performed in the phase explosion regime (see Figure 1a). Computational predictions of the nanoparticle size distribution, structure, and chemical ordering are related to the results of LAL experiments performed for similar conditions. In particular, high-resolution TEM images of individual nanoparticles have revealed the presence of high density of defects in nanoparticles synthesized by LAL, while the selected area diffraction measurements (see Figure 1b) suggest a possible existence of $L1_0$ (chemically ordered) phase.

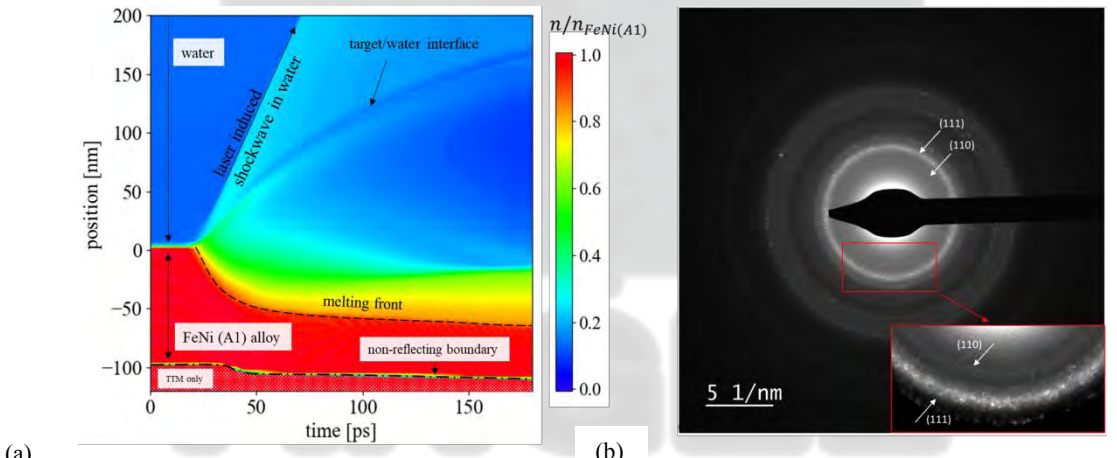

Fig. 1. (a) Contour plot illustrating the density evolution at the ir ge of laser ablation of a FeNi target irradiated by a 10 ps laser pulse, as predicted in a large-scale atomistic-continuum simulation. (b) TEM/SAD diffraction pattern of FeNi nanoparticle, where the diffraction ring of plane (110) indicates the appearing of the superlattice structure.

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Surface chemistry of colloidal gold nanoparticles generated by laser ablation

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Pulsed Laser Ablation in Liquids (PLAL) of a solid target results in the formation of ligand-free NPs which can be produced in organic or non-organic solvents. These systems are well-suited for the development of different technological applications [1]. Their surface chemical composition is expected to take part in the colloidal stability of the PLAL products. The resulting surface charge could be responsible of the electrostatic repulsion impeding their aggregation. However, no consensus [2-6] has been drawn so far on these questions and a precise knowledge of their surface properties and composition is mandatory. An experimental investigation of the surface chemistry occurring at the PLAL NP surface will be presented based on experiments conducted at SOLEIL synchrotron facility on the PLEIADES beamline. X-ray photoelectron spectroscopy measurements performed on free-standing [7,8] gold NPs will be reported addressing the question of (i) their surface oxidation state [9] and (ii) the chemical composition of their first's surface atomic layers. Signatures of halide-ions and possible gold oxidized atoms on the NPs surface have been evidenced, demonstrating that this technique provides a promising new way to study bare gold surfaces and a complementary insight to their colloidal stability.

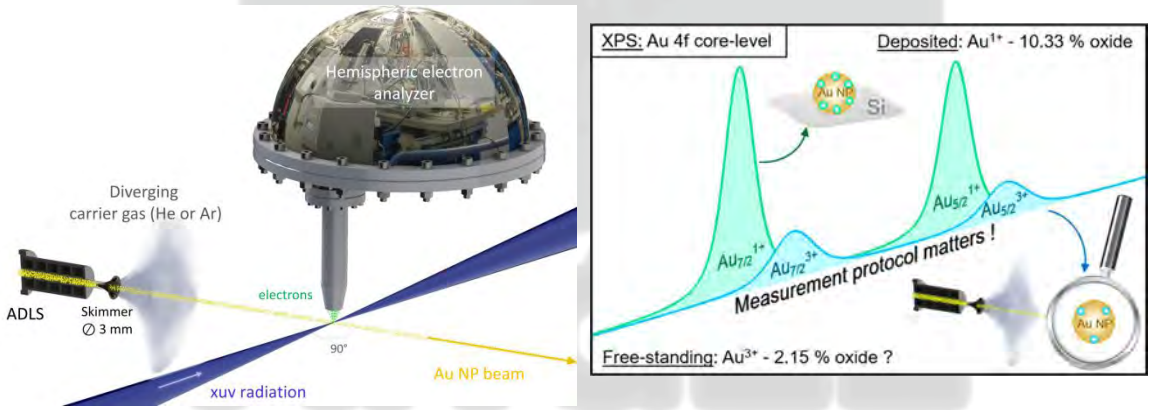

Figure 1 : (Left panel) Experimental setup of the XPS measurement of the Au NPs beam generated by means of the aerodynamics lens. (Right panel) Surface oxidation states of the Au NPs as a function of the measurement protocol.

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No papers yet but want to see if it comes out in something other than a conference proceedings.

PLA Synthesis and Photocatalytic Properties of Bismuth Silicates

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Bismuth silicates (BSO) are of great interest for application in photocatalysis due to the low recombination rate and high mobility of the photogenerated charge carriers [1]. BSO is prepared by solid-state reactions, mechanical activation, or the hydrothermal method. As a result of these synthetic approaches, micron and submicron particles are usually obtained. In this work, bismuth silicates were obtained by pulsed laser ablation in a liquid (PLA).

Pulse laser ablation was performed using a Q-switch Nd:YAG laser with the following parameters: 1064 nm, 7ns, 20 Hz, 160 mJ/pulse [2]. Separate colloids were preliminarily obtained by PLA of bulk targets of crystalline silicon and metallic bismuth in water. Then, the colloids were mixed in an atomic ratio for Bi:Si of 2:1, and additional irradiation with focused laser radiation for 2–3 hours was carried out [3]. As a result, bismuth silicate composite particles were formed. Colloids were dried in air at 60 °C for further research. The obtained powders were also annealed at the temperatures up to 600°C.

Figure 1a shows the UV-Vis spectra of BSO powders, showing the formation of an exciton absorption band already in the initial powder. This band becomes more intense upon annealing. The initial and annealed at 400 °C powders are amorphous for X-ray radiation and, presumably, may consist of various types of bismuth silicates. After annealing at 600 °C, the powder shows a well-pronounced crystalline structure of bismuth metasilicate Bi_2SiO_5. The initial BSO particles have a nearly spherical shape with an average diameter of about 20 nm (Figure 1b), which increases upon annealing: ~ 40 nm at 400 °C and ~ 500 nm at 600 °C.

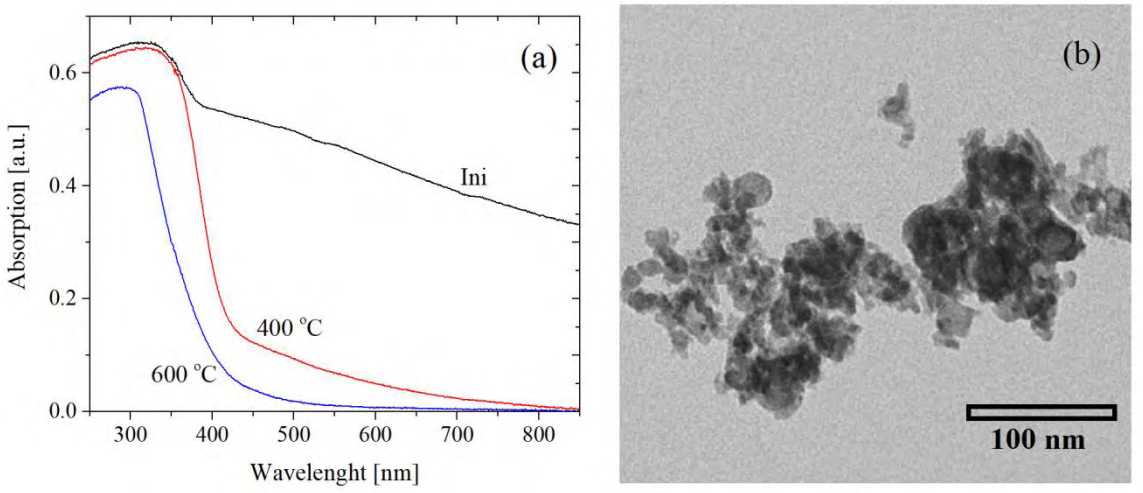

Figure 1 UV-Vis absorption (a) and TEM images of nanopowders BSO.

The photocatalytic properties of BSO powders in the decomposition of the rhodamine B dye under irradiation with an LED source (λ=378 nm) were investigated. The best photocatalytic activity was demonstrated by X-ray amorphous BSO samples having a large specific surface area.

This work was supported by the Russian Science Foundation, project No. 19-73-30026.

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Generation of nanoparticles of phtalocyanines and their nanocomposites with gold nanoparticles by laser fragmentation in liquids

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Phtalocyanines may find high range of applications as stable and luminescent dyes [1,2]. In this work, optical properties and morphology of laser generated Aluminum and Copper phthalocyanine nanoparticles (nAlPc and nCuPc) in water and acetone are experimentally studied [3]. Near infrared ytterbium laser of nanosecond pulse duration was used for Pc micro-powder fragmentation suspended in H_2O. Extinction spectra of Pc NPs colloidal solutions in MQ water were acquired by means of optical spectroscopy in the visible and near-IR range. The optical density the colloidal solutions of both nCuPc and nAlPc increase with laser fragmentation time. Transmission electron microscopy shows that nCuPc are made of short (100 nm) rectangular bars interconnected at various angles with other bars (Fig. 1). Similar morphology is observed for nAlPc. Laser exposure of the mixture of either nCuPc or nAlPc with Au NPs leads to aggregation of Au NPs and formation of core-shell nanocomposites.

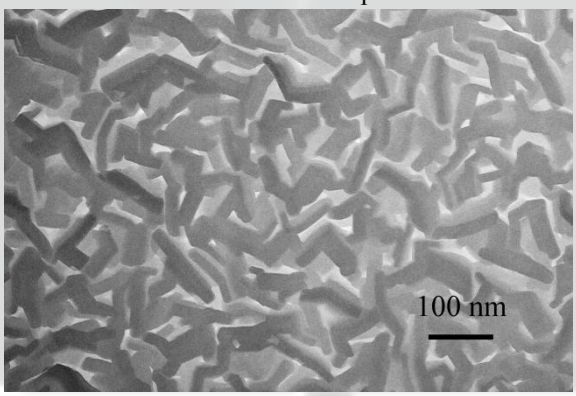

Fig. 1. NPs of Cu Pc at various stages of laser fragmentation after 10 min of fragmentation. Scale bar denotes 100 nm.

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Ultrathin oxide layer wrapped plasmonic metal nanoparticles prepared by laser ablation in solution for ultrasensitive gas detection

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The ultrathin and uniform oxide layer (<10 nm)-wrapped plasmonic metal (PM, such as Au, Ag and Cu, *etc.*) nanoparticles (NP) can greatly ensure the short-range surface plasmon resonance (SPR) properties of the inner core and the properties of the ultrathin shell synchronously, and thus have great potential in the fields of analysis, catalysis, and energy. However, the facile synthesis of these NPs is always a challenge for conventional physical or chemical methods. [1-2]

Here, we present a facile and one-step fabrication of such NPs through laser ablation of PM target in the aqueous solution of hydrolyzed metal ions. Firstly, the cations in the solution are hydrolyzed to form hydroxide [$M(OH)_x$] clusters with several nanometer sizes. Then the laser ablation of the metal target generates plasma, and further forms metal NPs with cooling. According to the double layer theory, these $M(OH)_x$ clusters and metal NPs carry opposite charges due to different species adsorbed on their surfaces. Through the coulomb interaction, these small $M(OH)_x$ clusters will be attracted to the larger sized metal NPs evenly, thereby forming $M(OH)_x$-wrapped metal NPs. With the subsequent thermal effect of the laser, these $M(OH)_x$ eventually convert the oxide layer. Such a formation is shown in Figure 1a. Technique analyses show that the shells and the PM cores are of several and tens nanometer, respectively (Figure 1b).

Because of ultrathin nature of the shells and sensitization of the metal core, such NPs show good conductometric response to trace gases. Taking Au@SnO_2 NPs response to H_2S gas as an example, the rapid detection can be realized with a detection limit at ppb level, as shown in Figure 1c. Additionally, the SPR-based short-range (restricted within 10 nm near the metal surface) [3] surface-enhanced Raman spectroscopy (SERS) effect enables efficient detection of the gaseous molecules via the chemical reaction between the target molecule and the oxide shells. Taking the detection of H_2S gas with Au@CuO NPs as an example, the ppb-level H_2S can be rapidly detected with the SERS identification of CuS, which is rapidly produced via the chemical reaction between the CuO layer and H_2S gas, as shown in Figure 1d.

This work provides a flexible and universal route to the ultrathin and uniform oxide layer-wrapped PM metal NPs, which can realize ultrasensitive gas detection via conductometric response and SERS.

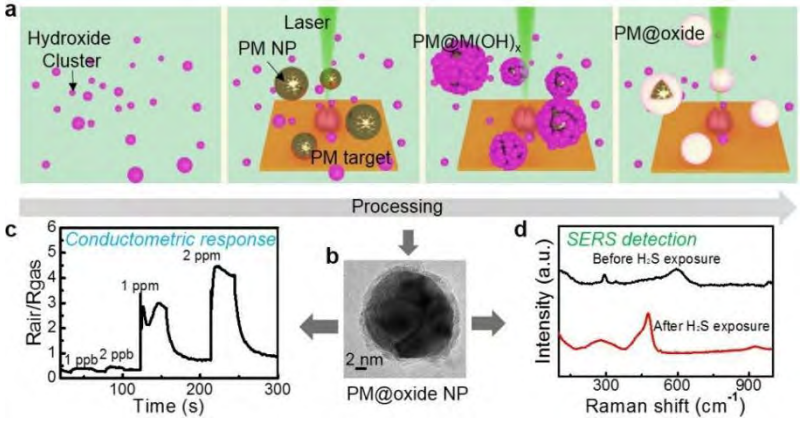

Figure 1 (a) The formation of the PM@oxide NPs, (b) a transmission electron microscopy image of a typical PM@oxide NP, (c) conductometric response of Au@SnO_2 NPs to H_2S gas, and (d) SERS-based detection of H_2S with Au@CuO NPs.

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Laser-Generated Nano-Colloids for High Performance Perovskite Solar Cells

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Planar optoelectronics have achieved tremendous success in fields including photovoltaics, light-emitting diodes, photodetectors, however, interface loss therein always acts as the dominate factor for the limitation of device performance. We herein demonstrate the technological superiority of laser processing of colloids on generating various nanocrystals in different solvents to address the interfacial loss of the optoelectronic films[1-5]. Exemplified by the hybrid perovskite solar cells, we show that the unique application of the laser processing of colloids on improving the extraction of the photogenerated charge carriers at grain boundaries of perovskite active layer and decreasing the energy barrier at interfaces between perovskite and charge transporting layer. In a simple device with regular planar configuration, formamidinium lead iodide based perovskite solar cells achieve maximum efficiencies over 24%. In addition, the PSCs based on the mixed-cation perovskite deliver more than one year of moisture stability as well as 1000 hours of thermal stability. We thus believe that the interfacial embedding of laser generated colloids will have important applications in optoelctronic applications.

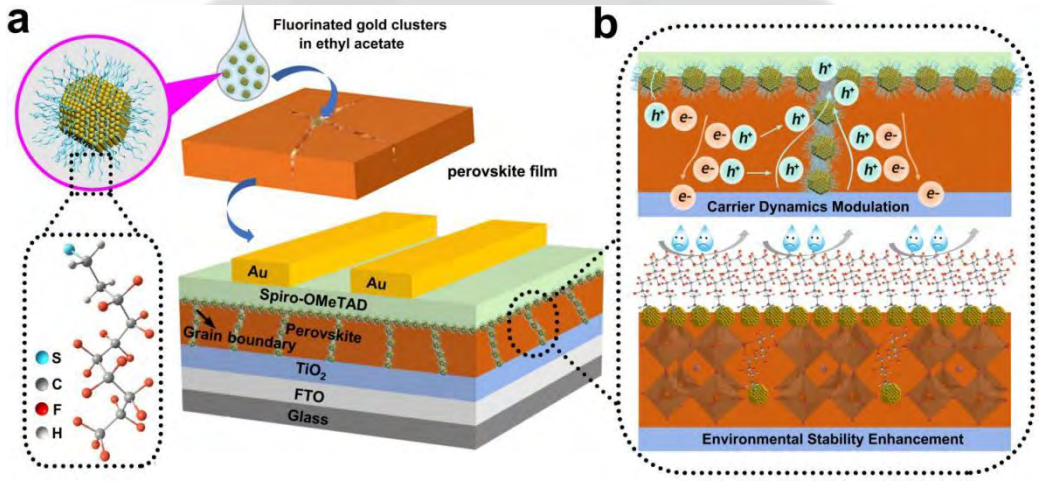

Figure 1 Laser manufactured hydrophobic Nano-Colloids as bifunctional interfacial mediator. a) Schematic illustration of interfacial embedding Nano-Colloids in the layer of perovskite. b) Schematic illustration of the function of Nano-Colloids for carrier dynamics modulation and improving environmental stability.

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You shall not pass: titanium nanospikes-based flow-through filter for liquid sterilization

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The cause of the majority of diseases, acquired by humanity, is the activity of pathogenic microorganisms. The constant use of antibiotics has led to the mutation of bacterial strains and their acquired resistivity [1, 2], which makes their use futile. Such "lion in the way" of human well-being is nowadays bypassed with the use of micro- and nanostructures with a wide specter of functionality. One of the most eligible methods of such structure manufacturing is laser ablation in liquid, which allows fabrication of nano- and microstructures with pre-designed morphology [3].

In this work, several Ti nanosctructures were tested as potential elements for liquid sterilization filter. We implemented the morphology (Fig. 1a) and tested their antibacterial properties with standard live-dead viability kit, (Fig. 1b). The most efficient type of nanostructures were found to be Ti nanospikes, fabricated with the use of ytterbium-doped fiber laser *Satsuma* (Amplitude Systems) (energy 7 μJ, repetition rate 100 kHz, scanning speed 50 mm/s). Nanostructured Ti was used afterwards for the construction of flow-through filter, providing the optimal contact of the bacteria in liquid with functional surfaces (Fig. 1c, d). Such filter allowed reducing the bacterial population from 10^6 to 10^4. Antibacterial properties were suggested to originate from the combined chemical toxicity of nanoparticles and the mechanical damage, caused by sharp nanoscale relief on Ti.

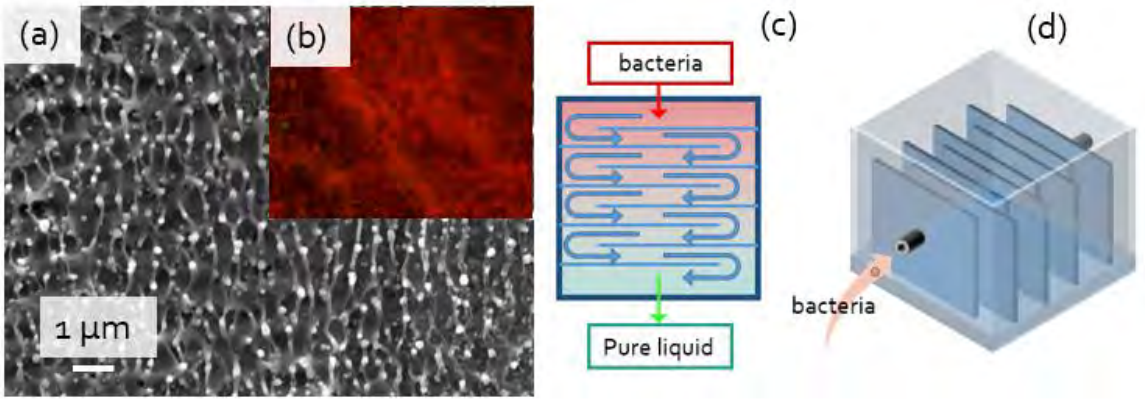

Figure 1. (a) SEM image of nanostructured Ti surface; (b) fluorescent photograph of the bacterial strains; (c) the upper view of flow-through filter and (d) its 3D model.

This work was supported by the Russian Science Foundation (project no. 18-15-00220).

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The effect of pulse duration on nanoparticle generation in pulsed laser ablation in liquids: Molecular dynamics study

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The generation of chemically clean and environmentally friendly nanoparticles (NPs) through pulsed laser ablation in liquids (PLAL) has a number of advantages over conventional chemical synthesis methods and has evolved into a thriving research field attracting laboratory and industrial applications. The practical importance of PLAL has stimulated computational efforts aimed at reveling the mechanisms of PLAL [1-4]. In particular, the results of recent large-scale atomistic modeling [2-4] suggest the existence of two distinct mechanisms of the NP formation, the rapid nucleation and growth of small NPs in the metal-water mixing region and the breakup of the hot metal layer into larger droplets due to the hydrodynamic instabilities. This computational prediction provides a plausible explanation for experimental observations of bimodal nanoparticle size distributions in femtosecond and picosecond PLAL experiments [4,5]. Moreover, the injection of large nanoparticles into water beyond the cavitation bubble boundary predicted in the simulations is confirmed in recent double-pulse cavitation bubble imaging experiments [4] as well as in time-resolved X-ray probing of the size and crystallinity of NPs present in the expanding cavitation bubble [6].

In the present study, we extend the atomistic simulations to longer (sub-nanosecond and nanosecond) laser pulses and focus our attention on the mechanisms responsible for the generation of nanoparticles at the initial dynamic stage of laser ablation. By relating results of these simulations to the physical picture established in earlier studies performed for shorter (up to tens of picoseconds) laser pulses, the dependence of the nanoparticle size distribution on laser pulse duration is discussed.

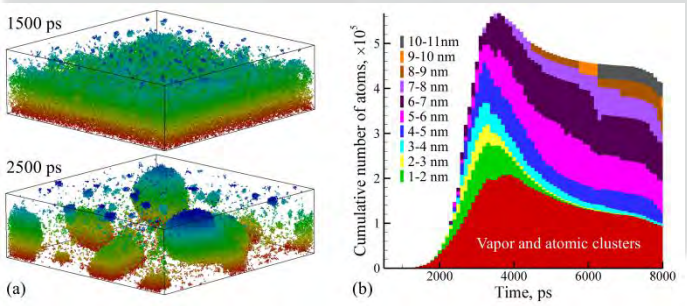

Figure 1. (a) Snapshots of an interfacial layer formed between the ablation plume and water environment in the simulation of a bulk Ag target irradiated in water by a 400 ps laser pulse. Water molecules are blanked, and the coloring is based on the vertical coordinate of Ag atoms. (b) The cumulative numbers individual Ag atoms and atomic clusters with diameters less than 1 nm (red color), and nanoparticles of different sizes (color coding defined in the legend) identified at different times during the simulation.

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Photo-efficiency of TiO_2-Metal nanocatalysts prepared by pulsed laser ablation for oxidation of industrial water pollutants

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The industrial waters contain different toxic volatile organic pollutants, among them, benzene, toluene, xylenes (BTX) and sulfolane are the most common and dangerous in petroleum refining operations and liquid-liquid extraction processes.

TiO_2 based nanoparticles have been largely employed in photocatalysis for their non-toxicity, good stability and low cost [1]. However, TiO_2 presents a wide band gap (3.2-3.0 eV) that restricts the use under UV irradiation. In order to enhance the TiO_2 photoefficiency under visible/solar light irradiation many efforts have been made from researchers in the last years. In particular, the self-doping of TiO_2 with Ti^{3+} atomic defects and the coupling with noble metal nanoparticles have attracted the attention of the scientific community. Here we discuss the possibility to remove BTX and sulfolane from contaminated industrial waters by using enhanced solar-light activated TiO_2 photocatalysts produced and modified by pulsed laser treatment (Figure **1a**), a greener, cheaper and easier approach than other conventional methods able to obtain highly photoactive TiO_2 species [2].

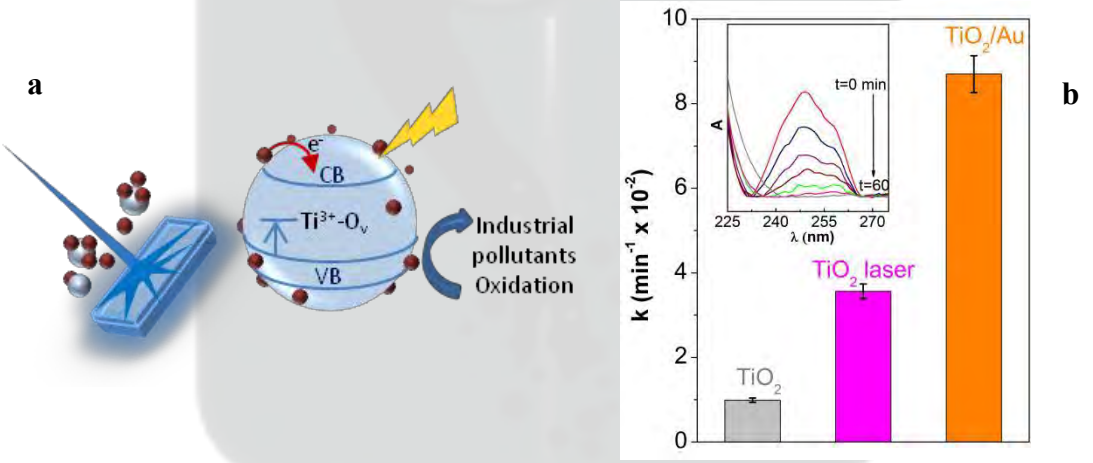

Figure 1 . a) Defects induced by laser irradiation on TiO_2; b) kinetic constants of the photodegradation of the BTX/sulfolane aqueous solution, inset: UV-VIS spectra of the solution in presence of TiO_2 laser treated catalyst.

Photocatalytic data (Figure **1b**) showed that the laser treatment of the TiO_2 led to a band-gap decrease which in turn resulted in an enhanced solar photoactivity of the laser-treated TiO_2 sample towards the degradation of organic pollutants in the analysed industrial waters. It was also found that the addition of gold nanoparticles to TiO_2 colloids further increased the photodegradation rate (Figure **1b**), due to the plasmon effect of the noble metal nanostructures [4].

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Generation of metallic nanoparticles by laser ablation in molten salts

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Laser ablation of metallic nanoparticles in various liquids is an active research topic [1-3]. Ambient media used for this purpose are typically liquid at room temperature. In this work, the generation of metal nanoparticles by ablation of solid targets in ionic liquids was studied. Sodium nitrate $NaNO_3$ and lithium nitrate $LiNO_3$ salts with a relatively low melting point were used as such liquids. An ytterbium fiber laser with pulse duration of 200 ns and energy of 1 mJ at repetition rate of 20 kHz was used as a laser radiation source. The salts were brought to the melting point from 300 to 320° C on a hotplate, then a solid target was placed in the resulting liquid. Laser ablation was then carried out at a constant temperature of 320° C. The spectrum of the resulting solid matrix after solidification (Figure 1) turned out to lack the usual plasmon resonance peak at the wavelength of about 520 nm. Instead, an increase in the absorption in the IR region (wavelengths from 750 to 1000 nm) was observed, which can be associated with the elongation of nanoparticles under the influence of surrounding matrices. A similar effect was reported earlier in [4] in case of polymer matrix.

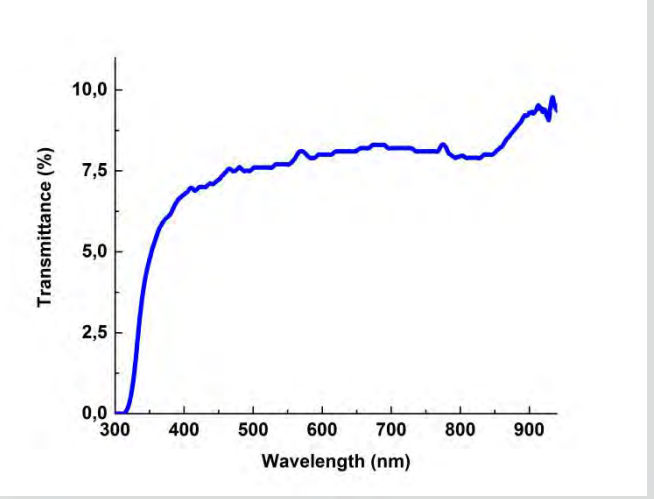

Figure 1 Transmittance of gold nanoparticles in solid sodium nitrate.

Specific morphology of gold target formed under laser ablation in the melts is discussed.

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Cavitation bubble dynamics following laser-induced breakdown near a sharp-edge geometry

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During the last decade, pulsed laser ablation in liquids (PLAL) received considerable attention when it comes to colloidal nanoparticles production [1]. Compared to the conventional methods such as mechanical milling, grinding, and wet chemical synthesis, it offers some appealing advantages [2] such as no contamination by abrasive tools and lack of dangerous chemical reactants in the production. Extensive research has already been devoted to this field, but the fundamentals of nanoparticles formation during PLAL are still not completely understood. One of the most important criterion in the use of PLAL as a tool for nanoparticle synthesis is the production rate. It has been shown [3] that productivity in the order of grams per hour can be achieved when optimal combination of laser parameters is used. Furthermore, using unconventional deformable geometry as the donor material can decrease the redeposition of nanoparticles, yielding higher production rates [4].

In this study, we investigate the development of cavitation bubbles and liquid dynamics on unconventional geometries [5]. Optical breakdown is thereby laser-induced in proximity to a sharp ("cliff-like" 90°) geometry of the solid submerged in water, ethanol, and polyethylene glycol 300 [Fig. 1(a)], while subsequent dynamics is studied by ultrafast shadowgraphy. Bubbles are induced by 1064-nm laser pulses with durations of 7-60 ns and energies of 10-55 mJ. Formation of a fixed-type secondary cavity is observed behind the edge where low-pressure area develops due to bubble-driven flow of the liquid [Fig. 1(b)]. This occurs when the velocity of liquid overflow exceeds ~20 m s^{-1}. A re-entrant liquid injection with up to ~40 m s^{-1} velocity may also occur inside the bubble as it overflows the edge of the sample [Fig. 1(c)]. Formation and characteristics of the injection evidently depend on the relation between the breakdown-edge offset and the bubble energy, as well as the properties of the surrounding liquid. Higher viscosity of the liquid prevents the generation of the jet.

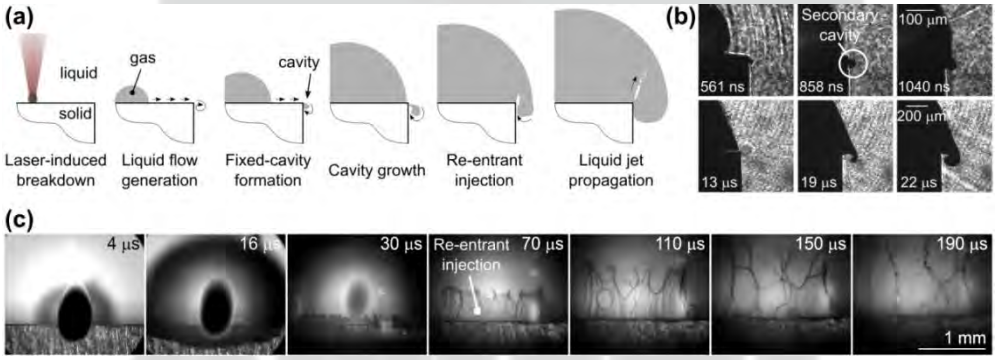

Figure 1. (a) Cavitation bubble development following laser-induced breakdown near a sharp geometry. (b) Formation of a fixed-type secondary cavity behind the edge. (c) Re-entrant liquid injection into the cavitation bubble.

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Early stage ablation dynamics of gold in air and water monitored by ultrafast pump-probe microscopy

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Despite the tremendous amount of research carried out in the field of pulsed laser ablation in liquids (PLAL) for colloid production, there are only a few works regarding the early stage dynamics of the involved processes. As pointed out by Kanitz et al. [1], a description of the ablation dynamics on a time scale ranging from femto- to microseconds would give valuable information about how to control the colloid production process and the chemical and physical properties of the laser generated nanoparticles. Pump-probe microscopy measurements, investigating the early time scales during ultrafast laser ablation of iron in different liquids show, that a hot dense metal layer is formed at the ablation plume-liquid interface [2], which was also predicted by molecular dynamics simulation [3].

In this work we report on pump-probe microscopy measurements [4] of a high purity bulk gold sample in air and water. Excitation of the sample was performed with a 3 ps pump-pulse, centred at 1056 nm. The transient relative reflectivity change $\Delta R/R$ of the sample surface is monitored by a 500 fs probe-pulse, centred at 528 nm. Figure 1 displays $\Delta R/R$ for probe pulse delay times Δt ranging between -15 ps and 4 ns. In each case the sample was excited by a fluence of $1.5\times\Phi_{th}$, where Φ_{th} denotes the ablation threshold fluence, which was measured to be 1.44 J/cm^2 and 2.35 J/cm^2 for air and water, respectively.

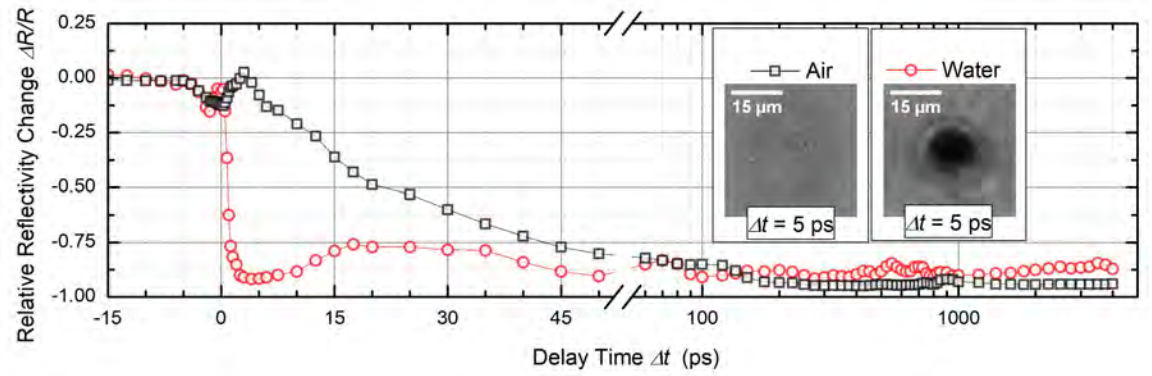

Figure 1: Relative reflectivity change $\Delta R/R$ of a laser irradiated gold sample for probe-pulse delay times Δt ranging between -15 ps and 4 ns. The transient reflectivity change is shown for the sample in air (black open squares) and water (red open circles). Image inlets show pump-probe microscopy images for laser ablation in air (left) and water (right) at Δt=5 ps. The transient $\Delta R/R$ values were obtained from the pump-probe microscopy images by averaging the relative reflectivity change over an area of 2.6 µm×2.6 µm, located in the centre of the images.

By comparing $\Delta R/R$ for laser ablation of gold immersed in air and water, quite different behaviours are observed. The decrease of the sample surface reflectivity to a minimum value of $\Delta R/R\approx0.9$ occurs much faster in water. In air the reflectivity minimum is reached at $\Delta t\approx100$ ps, while in water the reflectivity drops rapidly within the pump-pulse duration and reaches its minimum at $\Delta t\approx5$ ps.

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Decorated WO_x nanoparticles by laser assisted reduction in solutions for optical gas sensing

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The synthesis of transition metal oxide nanoparticles in the liquid media is of great importance for many applications such as chemical ad bio sensing [1]. These nanoparticles should also be activated for the desired analyte, so core-shell or binary structures consisting of two different phases, the catalyst and the active substance of the sensor, are required. In recent years, the optical sensing based on doped semiconductors having localized surface plasmon resonance (LSPR) properties has become very important. Pd or Pt are of most important hydrogen catalysts. Therefore, one of the interesting ways to synthesize these systems is laser ablation of the transition metal target followed by adding a noble metal salt solution (like $PdCl_2$). In this article we report our research on WO_x@Pd core-shell nanoparticles [2], [3]. Figure. 1 illustrates the laser ablation process, TEM image of core-shell NPs and the mechanism behind. It was found that the addition time of palladium salt is very effective on doing or not doing the formation of core-shell structures of WO_3@Pd so that at very short period of rests, a thin shell of palladium is formed on the tungsten oxide particles. In the presence of hydrogen, the system exhibits remarkable coloration and

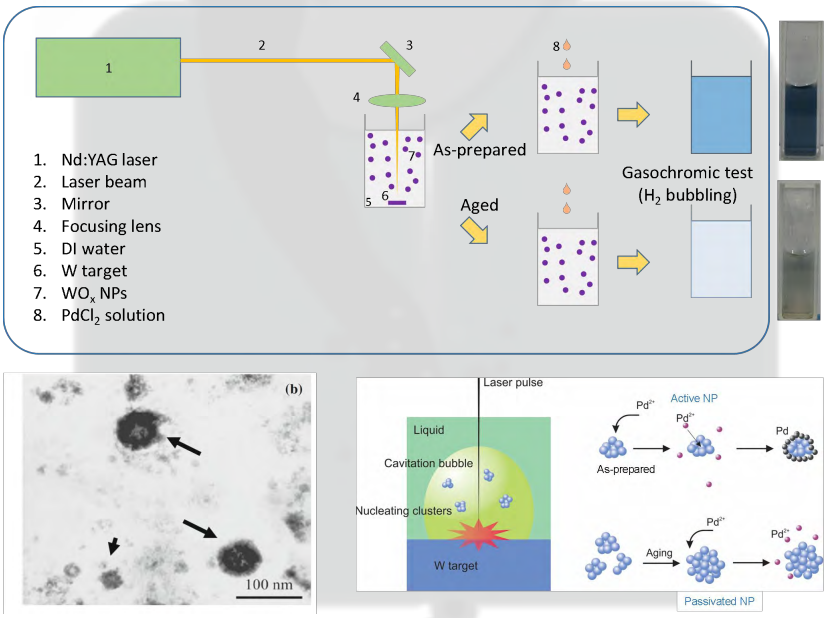

Figure 1 Laser assisted reduction process for synthesis of decorated LSPR materials WO_x). TEM images of WO_x@Pd (bottom left panel) core-shell structures. The other parts show the ability to detect hydrogen by these systems and the effect of resting time on core-shell structure formation.

appearance of localized surface plasmon resonance (LSPR) absorption band due to reduction of WO_x nanoparticles via hydrogen spill-over mechanism at the Pd shell. This phenomenon can be used as a visual or LSPR sensor for hydrogen. If the ablated species experience prolonged rest, no such effect can be observed. Overall, the process of laser ablation in the presence of reactive solutions is very extensive and requires further study.

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Nanoporous Cu-Al catalyst for efficient electrochemical reduction of CO_2 to ethylene

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Electrochemical reduction of carbon dioxide (CO_2) to valuable chemicals offers a promising means to large-scale storage of abundant and renewable solar and wind electricity while simultaneously decreasing worldwide carbon footprints. Until now, copper has been the predominant electrocatalyst for the production of multi-carbon products. Here we present the accelerated discovery of catalysts using a combined Density Functional Theory (DFT) and active machine learning (ML): we screen electrocatalytic materials *ab initio* over 16,000 DFT simulations. The results suggest that copper-rich Cu-Al alloys provide multiple sites and surface orientations that exhibit optimal CO adsorption energies near the top of the activity volcano plot for CO_2 reduction[1]. Experimentally, we develop a simple and scalable physical vapour deposition and chemical etching process to fabricate nanoporous Cu-Al catalysts that electrochemically reduced CO_2 to ethylene (C_2H_4) with a record Faradaic efficiency of 80% at a current density of 600 mA cm^{-2} (-1.8 to -2.1 V vs. RHE) in 1 M KOH electrolyte in a flow cell system. In situ X-ray absorption reveals how Cu and Al enable a favourable Cu coordination environment that enhances C-C dimerization[1]. The findings suggest new avenues by which multi-metallic systems can be devised that go beyond the limitations of conventional single-metal electrocatalysts.

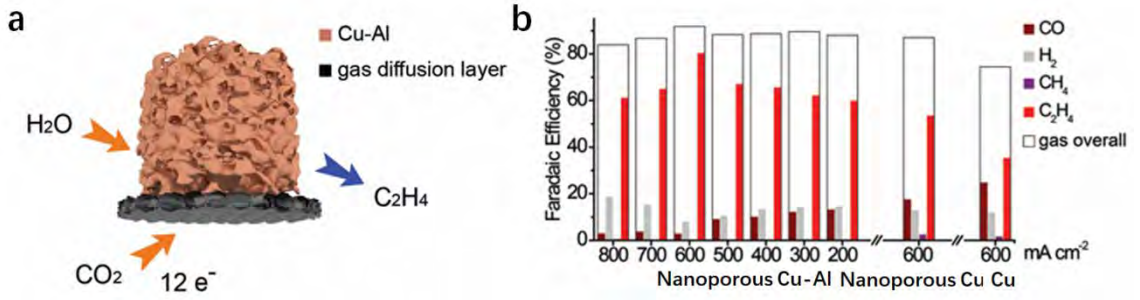

Figure 1. a. Schematic of electrochemical reduction of CO_2 to C_2H_4 using the nanoporous Cu-Al catalyst on a gas diffusion electrode. (b) Electrochemical performance of CO_2 to C_2H_4 with Cu-Al and Cu under different testing conditions.

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In Situ Time-Resolved XAFS Study on Laser-Induced Particle Formation of Pd(II) Ion in a Solution

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Irradiation of UV light into a H_2O/EtOH solution of palladium ion, Pd(II), excites charge-transfer band of the Pd(II) complex via one-photon absorption. Reaction of the excited Pd(II) complex with the EtOH results in reduction from Pd(II) to Pd(0), which is followed by spontaneous formation of $(Pd(0))_k$ nuclei,

$$Pd^{2+} + CH_3CH_2OH + h\nu \xrightarrow{k_1} \frac{1}{k}(Pd)_k + CH_3CHO + 2H^+ . \quad (1)$$

When the $(Pd)_k$ nuclei grow up to the $(Pd)_m$ particle with a give size, the $(Pd)_m$ behaves itself as a reduction catalyst and promotes the particle growth (autocatalytic growth) [1]. The process is described as

$$(Pd)_m + Pd^{2+} + CH_3CH_2OH \xrightarrow{k_2} (Pd)_{m+1} + CH_3CHO + 2H^+ . \quad (2)$$

A series of reaction are called photo-induced particle formation and are used for recovery of Pd metal from chemical waste solutions [2]. Previously, we showed that the irradiation of a nanosecond pulsed UV laser with high pulse energy into the Pd(II) solution forms the Pd particle with submicron size (100–500 nm), which has not been generated in the photo-induced particle formation using a UV lamp [3]. It indicates that the laser irradiation with high pulse energy promotes the Pd particle growth, the mechanism of which is unclear. In this work, we studied the particle formation in the Pd(II) solution in the laser irradiation with high pulse energy using time-resolved X-ray absorption fine structure (XAFS) spectroscopy.

Experimental details are described in ref [4]. The Pd particle formation was induced by irradiation of the pulsed 266-nm laser (10 Hz, pulse duration 8 ns) into the H_2O/EtOH solution of the $PdCl_4^{2-}$ complex. Figure 1 is a typical change of X-ray absorption near edge structure (XANES) in Pd K-edge, which gives change of the electronic structure of the Pd(II) and the Pd(0), during laser irradiation. The time-resolved XANES shows broadening of the edge width concomitantly with increasing the laser irradiation time.

Analysis of the XANES edge width gives us an information on the Pd(II) concentration [4]. Figure 2 is temporal changes of the Pd(II) concentration in the laser irradiation with a fluence of 19.9–59.7 mJ/cm^2. We analyzed the temporal changes of the Pd(II) concentration using the kinetic model based on the reactions 1 and 2, and shows that the fitting curves reproduce the experimental results. We further investigated dependence of the reaction rate coefficients, k_1 and k_2, on the laser fluences. The dependence elucidates that the photons contribute to reduction of the Pd(II) by the one-photon process and to the autocatalytic growth of Pd particles by the multiphoton process.

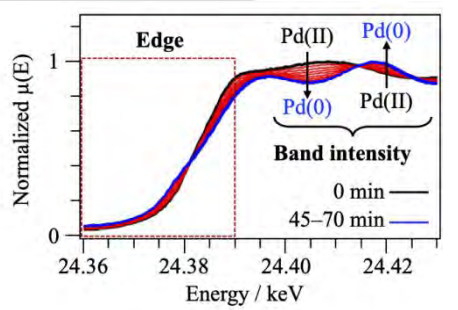

Figure 1 Time-resolved XANES spectra during laser irradiation with an interval of 5 min.

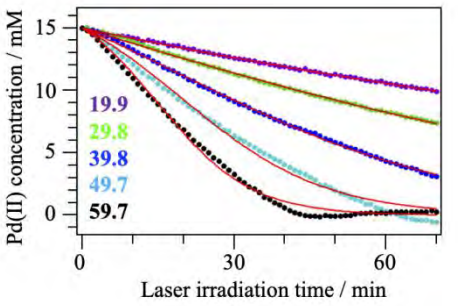

Figure 2 Temporal changes of the Pd(II) concentration in various laser fluences. Red lines are fitting curves of the kinetic model.

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Laser Assisted Synthesis of Cobalt-Doped Zinc Oxide Nanostructures

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Among the different doped ZnO structures, cobalt-doped ZnO films have attracted much attention because of their potential applications in magneto-electrical and magneto-optical devices, spintronics, and as passive Q-switchers (saturable absorbers) for near- and mid-infrared lasers [1,2]. In this work, we present the pulsed laser assisted fabrication of Co-doped ZnO nanocrystals in liquid with their further deposition into thin films on a glass substrate. The technique is based on sequential laser ablation of Zn and Co targets in distilled water. Nd:YAG laser (LOTIS TII, LS2134D), operating at 1064 nm (energy 80 mJ/pulse, repetition rate 10 Hz, pulse duration 10 ns) was used for ablation of the relevant targets [3]. The prepared colloidal solution was additionally subjected to irradiation with the unfocused beam of the second harmonic (wavelength 532 nm) of the same Nd:YAG laser. The purpose was to achieve the substitutional incorporation of Co^{2+} ions on the Zn site through the fast laser induced heating, subsequent co-melting, and re-solidification process at extremely high cooling rate. Figure 1 illustrates the scheme of the experimental procedure.

Figure 1 Schematic illustration of the experimental procedure used for preparation of cobalt-doped zinc oxide nanostructures

The morphology, structure and optical characteristics of the synthesized nanocrystals were analyzed using HRTEM, SAED, XPS, Raman and FTIR to find the optimal conditions for the formation of doped samples. The doping was proved by XPS, XRD, Raman and optical absorption measurements. The XRD and SAED patterns revealed lattice distortion of the nanoparticles prepared by sequential laser ablation. The average size of the particles prepared was less than 15 nm. Laser irradiation of the formed colloid resulted in co-melting of the nanoparticles with elongated structures formation.

The study of the phase composition of the ZnO:Co sample prepared by deposition of colloidal particles on the surface of the substrate under the conditions of additional exposure to laser radiation proved ZnO formation having wurtzite-type structure. After laser irradiation the reflections were weakened and broadened indicative of lattice distortion. Raman spectroscopy revealed disorder induced due to Co incorporation in the ZnO lattice and presence of defects. $E_2^{(high)}$ mode at 437 cm^{-1} of ZnO was broadened and weakened while the intensity of the LO band at 580 cm^{-1} related to the defects was increasing. The XPS analysis showed the formation of ZnO:Co films with a dopant concentration of about 6%.

The work was partially financed by the National Academy of Sciences of Belarus under project Convergence 2.4.06.

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Laser Processing of Colloids: Application for Compound Nanoparticles Fabrication and Doping

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Laser irradiation of colloids can induce targeted changes in the structural and physical properties of nanoparticles (NPs), that makes laser-induced modification (LIM) of NPs) in liquids a relevant topic in the last decades [1,2]. By varying laser pulse duration, wavelength and fluence a control of NPs inner structure and composition can be achieved. Among the novel applications of LIM, fabrication of multielement NPs are of special interest. This work is focused on application of laser-induced processes in fields of alloyed particles formation upon laser irradiation of the mixture of colloids (for synthesis of Ag-Cu, Ge-Sn, Zn-Cu NPs), doping of oxide nanocrystals (for example, ZnO:Co and ZnO:N:Ag NPs formation) and laser-induced chemistry in a mixture of NPs in solution (synthesis of SiC as well as binary and ternary Gd compounds).

The initial colloids were prepared by laser ablation in liquid technique. Nd:YAG laser (LOTIS TII, LS2134D), operating at 1064 nm (energy 80 mJ/pulse, repetition rate 10 Hz, pulse duration 10 ns) was used for ablation of the relevant targets [3]. For laser-induced modification, the unfocused beam of the second harmonic (wavelength 532 nm) of the same Nd:YAG laser was used. The phase composition, morphology, structure and optical properties of the synthesized NPs were investigated. Laser induced rapid heating, subsequent co-melting, and re-solidification processes at high cooling rates are considered to be experimentally achieved at the optimized laser processing parameters. As the result of laser modification of NPs is mostly determined by the temperature that is reached during the irradiation, a radiation emitted from the hot NPs was detected and analyzed using the blackbody-like approximation. Figure 1 demonstrates a principal scheme of laser assisted synthesis and modification experiments and as an example results of characterization of the Gd-Si NPs synthesized by laser irradiation of Gd and Si colloidal solutions mixture.

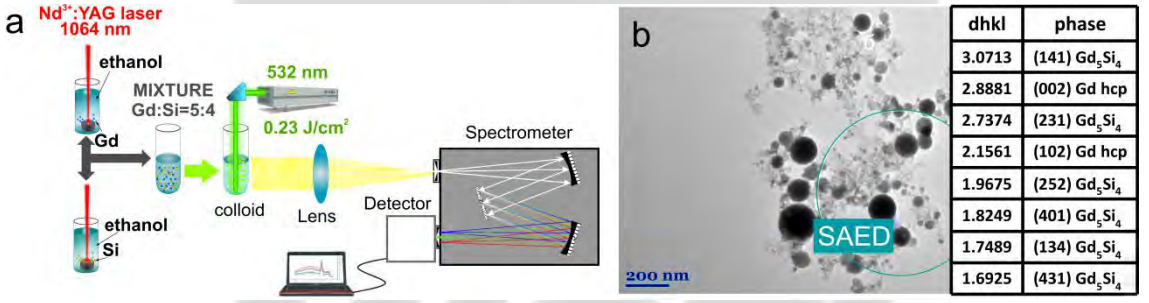

Figure 1 Schematic diagram of the experimental set-up (a) and results of characterization of the synthesized particles (b).

To explain a mechanism and to predict the result of LIM of NPs in solution, a theoretical model based on the balance between laser energy absorbed by the NP and the dissipation due to heat losses was proposed. The obtained results demonstrated that laser irradiation of colloidal NPs could provide unique possibilities not only for a change of the NPs size through the fragmentation and aggregation processes but also for the synthesis of compound and alloyed NPs with a control over their composition.

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LAL produced GQD-decorated ultrathin-Bi_2WO_6 nanosheet hydrogel composite with excellent synergistic effect of piezo-photocatalytic degradation

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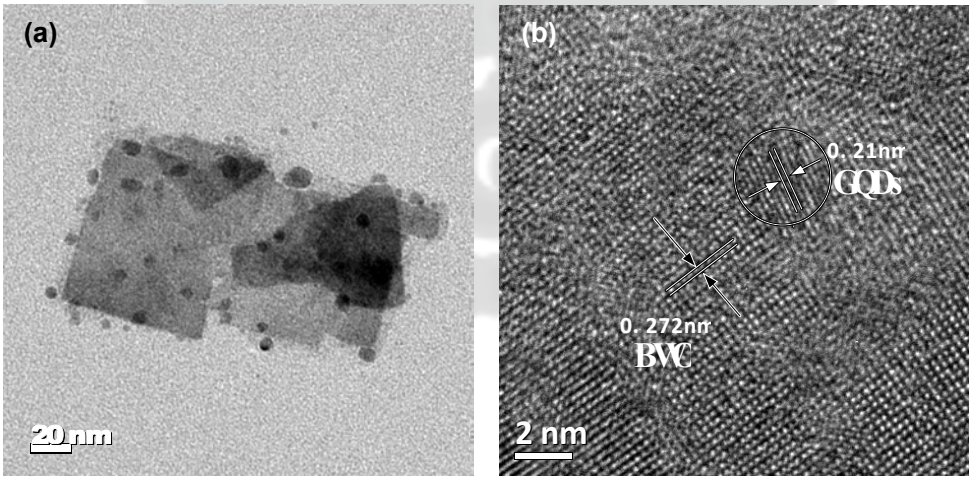
The emerging ultrathin materials with suitable energy band structure have been regarded as a robust type of photocatalyst. Among them, ultrathin Bi_2WO_6 nanostructure display intriguing piezo-photocatalytic performance due to its unique structural, electronic properties, strong light response and appealing energy band structure. On the other side, surface functional modification in materials usually play pivotal roles in photocatalytic processes as they can provide extra active sites and tune the band structure of semiconductors. Researchers have paid much attention on quantum-dots-modification in catalysts, however, few work has been reported on the role of graphene quantum dots (GQD) modification on ultrathin materials in the field of piezo-photocatalysis. In this study, the novel ultrathin GQD-modified Bi_2WO_6 nanosheets hydrogel (GQD-BWO hydrogel) with excellent usability and synergistic effect of piezo-photocatalysis has been successfully synthesized utilizing a facile two-step laser ablation in liquid (LAL) method and is applied in environment remediation. Specifically, in the porous hydrogel the ultrathin GQD-BWO nanosheets as the efficient piezo-photocatalyst were homogenously distributed, make the composite not only exhibits the great absorption toward the organic pollution, but also provides multidimensional quality and piezo-photocatalytic channels. The 2D structure of GQD-BWO nanosheets and its combination with porous hydrogel were beneficial to light absorption, which highly improves the utilization rate of light. The synergistic effect of the GQD-BWO composite greatly enhanced the removal rates of organic pollutants and made itself ease to separate and recycle in water purification. When the visible-light irradiation time lasted for 74 h, the removal rate of MB is nearly unchanged, indicating that the 2D GQD-BWO ultrathin nanosheets composite have a high stability. The construction of GQD-BWO composite hydrogel resolved the reclamation problem of catalyst and improved the piezo-photocatalytic activity of GQD-BWO nanosheets, thus greatly improved the removal rate of water pollutants and the related commercial applicability. This study will open up a new route to design advanced materials with GQD-modification vacancies for piezo-photocatalytic applications.



TEM images of ultrathin GQD-BWO nanosheets: (a) ultrathin GQD-modified Bi_2WO_6 nanosheets (b) corresponding HRTEM detection of the GQD-modified Bi_2WO_6 crystallographic plane.

Laser-mediated Ag nanoparticle decoration of PVDF nanofibrous membranes for an efficient oil/water separation

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Every year thousands of oil tons are leaked and spilled into the oceans worldwide during the extraction and transportation of oil, making it one of the principal sources of water pollution. Among the various explored solutions against such an alarming problem, the recovery of clean water from oily-emulsions by its effective filtration through nanofibrous membranes decorated with nanoparticles (NPs) is having a significant impact on the field. The nanofibrous membranes by themselves prevent the passage of oil droplets, enabling its separation from water. However, the efficiency and reusability of such materials are often deteriorated by their fouling, i.e., accumulation of emulsified oils, macromolecules, or some other foulants like organic matter over their surface [1]. Recently, the fouling problem has been partially alleviated by the incorporation of NPs over the membrane's surface, where the most explored NPs are those that provide hydrophilicity, surface charge change, and antibacterial properties [2]. In the current contribution, we explore the laser-mediated photoreduction of silver nitrate dissolved in water, which was previously reported by J. P. Abid et. al. [3], to synthesize ligand-free Ag NPs with an average particle diameter of 35 ± 10 nm in the presence of a dehydrofluorinated polyvinylidene-fluoride (PVDF) nanofibrous membrane. As no reducing or stabilizing agents are used at any stage of the process, the surface of the nanofibrous membrane, which has OH- functionalities acts as a capping agent for the recently created NPs, reaching in this way the NPs synthesis and surface decoration of the membrane in a single stage. As displayed in Fig. 1 a), the NPs decorate the surface of the membrane uniformly.

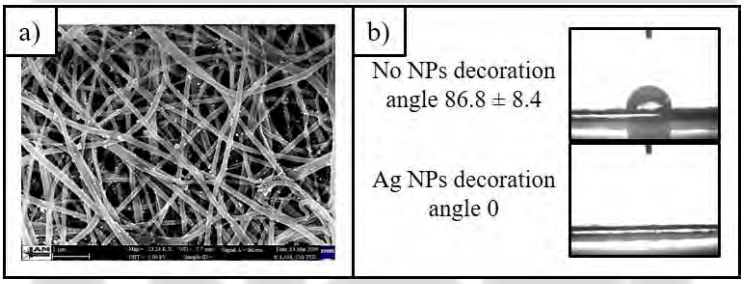

Figure 1 a) micrograph of the membrane decorated with the Ag NPs and b) contact angle test of the sample before and after the nanoparticle decoration, displaying that after the decoration, the membrane becomes hydrophilic.

The decoration provides hydrophilicity to the membranes (Fig. 1 b)) and a 3.8-fold improvement in the oil/water separation efficiency compared to the non-modified membranes. Overall, the methodology enables the production of an efficient membrane to separate water from oily emulsions, while the chemical waste production, often related to the NPs synthesis, is minimized.

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Synthesis and properties of nanocomposite thin films of Sb_2S_3 with Si nanoparticles

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Advantages of pulsed laser ablation in liquid (PLAL) for the synthesis of nanoparticles are the simple experimental setup, environmentally friendly process, high purity of the products and the formation of stable nanocolloids with limited use of chemical reactants [1]. Antimony sulfide (Sb_2S_3 stibnite) is an important environmentally benign material which finds applications in optical, optoelectronic and solar cells [2] etc. Mostly the deposition of Sb_2S_3 thin films was done by chemical methods (CBD) [3]. Silicon (Si) is well known as a semiconductor for commercial solar cells with high efficiency and long-term stability. PLAL was successfully used for obtaining nanoparticles of Si [4] and Sb_2S_3. Nanocomposite thin film fabrication from laser ablated nanocolloids by spray pyrolysis [5,6] and spin coating was already known. In this work, we used PLAL technique to synthesize nanoparticles of Sb_2S_3 and Si in different organic solvents using a nanosecond pulsed Nd:YAG laser.

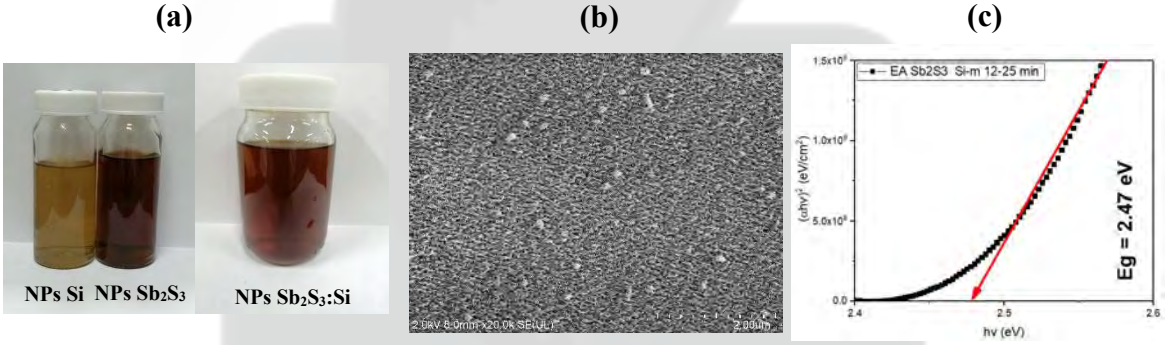

Figure 1 (a) Nanocolloids of Sb_2S_3 and mono-Si by PLAL and their mix (b) Micrography of Sb_2S_3 with mono-Si (c) Band gap Sb_2S_3 with m-Si.

Here we obtained nanocomposite thin films of Sb_2S_3:Si by spin coating/spray deposition of a mixed colloid containing Sb_2S_3 and Si nanoparticles. The nanoparticles as well as their composite thin films are characterized by various techniques to study their morphology (TEM/SEM), structure (XRD/Raman), composition and chemical states (XPS) and optical properties (UV-Vis-NIR spectroscopy). Further details of the results of these analysis and properties will be presented in this work.

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Novel criterion of laser-ablative nanoparticle yield in liquids: a route to quantitative technology

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Laser generation of colloidal nanoparticles (NPs) in liquids has matured as an eco-friendly and high-throughput top-down nanotechnology method, successfully developing in respect of material assortment, up-scaling and cost efficiency. In this talk, we demonstrate a breakthrough in *in-vitro* quantization of short (ns) and ultrashort (fs-ps) laser-induced colloidal NP yield in liquids, calibrated by the target mass-loss measurements and enabling comparative evaluation of NP yield in terms of absolute and relative values irrespective of the used experimental conditions [1]. The proposed output quantity could be further normalized to laser/electric power to represent cost-efficient NP yield.

First, this quantization was applied to our results on short-pulse (nanosecond) laser generation, demonstrating, how subcritical ablative plasma can manage phase-explosion mass-injection into a vapor bubble and drive its versus pressure and energy input (Figure 1) [2-6]. Our proposed quantitative parameter characterized *in vitro* mass yield and nanoparticle transformations during the multi-shot scans.

Laser energy coupling to plasma (fraction)

$$\eta = 1.7 \times 10^{-6} \frac{\Psi^{9/8} I^{1/2} \tau^{3/4}}{A^{1/4} \mu \lambda^{1/2}} \quad (1)$$

plasma pressure and surface pressurization, mechanical coupling efficiency,

$$P_a = 0.6 \frac{\Psi^{9/16} I^{3/4}}{A^{1/8} \lambda^{1/4} \tau^{1/8}} \quad (2)$$

$$C_m = \frac{P_a}{I} = 0.6 \frac{\Psi^{9/16}}{A^{1/8} \lambda^{1/4} \tau^{1/8}} \frac{1}{I^{1/4}} \quad (3)$$

and ablation rate regulated by screening plasma

$$\dot{M} = 2.66 \times 10^{-6} \frac{\Psi^{9/8} I^{1/2}}{A^{1/4} \lambda^{1/2} \tau^{1/4}}. \quad (4)$$

Figure 1 Universal scaling relationships, connecting energy input (1), plasma pressure (2) and momentum coupling (3), mass ablation rate (4) versus intensity I, pulse width τ, wavelength λ, atomic mass A and average charge Z (Ψ - product of A,Z), justified for liquid ambients in [2-6].

Similarly, the same quantitative parameter was employed to envision *in vitro* ultrashort-pulse (0.3-10 ps) laser ablation and NP generation in water, exhibiting the distinct correlation of common mass loss [1,7] and NP yields, as well as the NP formation paths.

Overall, the proposed novel quantitative NP yield criterion lays a ground for up-scaling and cost-efficient ablative short- and ultrashort-pulse laser fabrication of colloidal nanoparticles.

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Pulsed laser defect engineering in liquid (PuDEL) of transition metal oxides for gradual heterogenous catalysis studies

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Identifying and understanding structure-activity correlations in real-structure catalysts is essential for tailored catalyst design[1] but catalyst materials with gradually tuned properties are needed. Pulsed Laser Defect Engineering in Liquid (PuDEL) has shown to be a promising tool to gradually tune materials properties (e.g. band gap, crystal phase or photo-luminescence of TiO_2) and consequently catalytic activities.[2-6] This is achieved by carefully controlling the number of laser pulses per particle (see Fig. 1). Additional preabsorbed surfactant-free, laser-generated co-catalysts (e.g. Au NP) can further act as nanoantenna's especially efficient in case of low laser absorptivity e.g. when performing "on-resonant" PuDEL of Au NP@TiO2 with 532 nm laser pulses[6] The latter enables further systematic catalytic studies of potential active surface sites forming around the perimeter of co-catalyst and support during on-resonant PuDEL. With the main driving force of laser-induced structural transformation being the applied laser energy density, fluence gradients due to laser focussing by refraction at the cylindrically shaped liquid jet in state of the art setups needs to be avoided.[4]

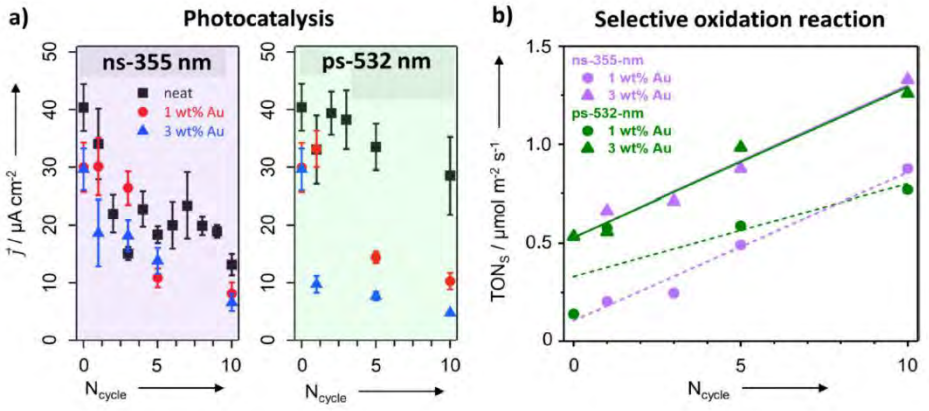

Figure 1: Effect of PuDEL of P25-TiO_2 (without and loaded with 1 wt% and 3 wt% of laser-generated Au NPs) on the catalytic activity shown for a): Photocurrent density *j* in photocatalysis[2,6] and b): Turn-over number (TON_S) of ethanol to acetic acid during selective oxidation reaction[2]. Data are shown with respect to the number (N_{cycle}) of laser irradiation cycles (~number of laser pulses) applied. Figure was taken from Ref. [2].

Within this presentation, first, an introduction to previous studies on PuDEL will be given. Subsequently, a new flat-jet setup, minimizing the effects of fluence gradients will be presented and evaluated regarding the homogeneity of the laser post-treatment at the example of well-established laser fragmentation of Au NP. Next, new results on PuDEL performed with spinel-based cobalt oxide nanoparticles in a flat jet setup leading to an alteration of the cobalt oxidation state and cation location in the lattice as well as improved electrocatalytic activity will be presented and discussed.

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Influence of H_2O_2 Addition on Phase Formation in Mn-doped TiO_2 Nanoparticles Prepared by Laser Ablation in Aqueous Solutions

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Titanium dioxide (TiO_2) appears typically in three phases, with the most common being the thermodynamically stable rutile and metastable anatase. Rutile powders have been widely used in many applications such as cosmetic and paint for high rate of visible light transmission and ultraviolet light shielding. Anatase powders are applied to deodorization, antifouling and purification of water or atmosphere exploiting its high photocatalystic characteristics. In the present work, we aim to synthesize Mn-doped TiO_2 nanoparticles by laser ablation in pure water and aqueous hydrogen peroxide solutions to control phase formation, dispersivity and size of nanoparticles.

Targets of pure and 0.5 mol.% Mn-doped rutile TiO_2 were prepared by sintering at 1,500°C in air to get relative density of about 97 %. Target sintered bodies were immersed in pure water and aqueous H_2O_2 solutions of 0-10 wt.%. Laser irradiation was carried out with a Q-switched Nd:YAG pulse laser source (wavelength 1064 nm, pulse width: 6 nsec, repetition frequency: 10 Hz) [1,2].

Figures 1(a) and (b) shows TEM images of non-doped TiO_2 nanoparticles synthesized by laser ablation in pure water and H_2O_2 aqueous solutions. Particles prepared in pure water are spherical, but not well dispersed. Mixing of H_2O_2 into water led to the decrease of particle size and the improvement of dispersivity. The changes would be due to electrostatic repulsion among formed clusters or grown particles, which was confirmed by the increased negative zeta-potential value of particles prepared in H_2O_2 aqueous solutions. Mn-doping gave a substantial change as shown in Figs. 1(c) and (d). Particles prepared in pure water consisted of coarse submicron-size particles and agglomerated nano-size particles, while those prepared in H_2O_2 aqueous solutions were composed of nano-size particles, which aggregated to form cancellous structure.

More interestingly, H_2O_2 addition in water gave rise to the change of phase formation. Particles prepared in pure water consisted of pure anatase phase irrespective of whether Mn is doped or not. Oxygen particle pressure in generated plume by laser irradiation, where nucleation takes place from a vapour phase, is quite low via a reaction equilibrium, $H_2O \leftrightarrow H_2 + ½\ O_2$. Formation of oxide ion vacancies in TiO_2 induced by the low oxygen partial pressure promotes the preferable formation of rutile nanoparticles [3,4]. H_2O_2 addition gave the change of phase formation. Mixing of ≥ 5 and ≥ 10 wt.% H_2O_2 to water led to the formation of anatase phase in synthesized non-doped and Mn-doped TiO_2 particles, respectively. Anatase phase content increased with the increase of H_2O_2 content in water. Oxygen is formed via a chemical reaction, $H_2O_2 \rightarrow H_2O + ½\ O_2$, and the increased oxygen partial pressure in plasma plume decreased the concentration of oxide ion vacancies in oxide particles [2]. Anatase TiO_2 particles were thus formed in synthesized powders.

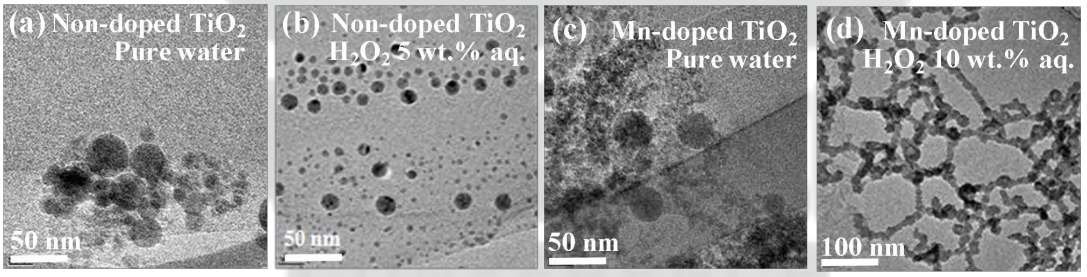

Figure 1 TEM images of TiO_2 nanoparticles synthesized by laser ablation in pure water and H_2O_2 aqueous solutions: (a), (b) non-doped TiO_2, (c), (d) 0.1 mol% Mn-doped TiO_2 .

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Preparation of gel-like structures, nanocomposites using laser ablation for CaO in alcohols.

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Nanoparticles (NPs) generated by laser ablation in liquids (LAL) can adsorb substances contained in the solvent efficiently onto their clean surface. This feature is useful when we consider functinalizing NPs. For example, NPs prepared in some organic solvents such as ethanol and acetone are negatively charged because the NPs adsorb the solvent molecules (in the ion form) during LAL. By using the electric charge, we can deposit the NPs on a plate using an electrophoresis method and prepare an electrode for lithium secondary battery [1], and a substrate for surface-assisted laser desorption ionization mass spectrometry [2]. In this paper, we report that such surface modification during LAL shows another interesting phenomenon that can be used to prepare functional materials, when we carried out LAL for CaO powder in alcohol [3].

0 min 30 min 60 min 90 min 120 min 180 min

Figure.1 Temporal appearance change of CaO powder dispersed in ethanol during laser ablation.

In the experiment, CaO powder was dispersed in alcohols (methanol, ethanol, and propanol). LAL for the CaO powder was carried out using focused 266 nm laser beam of a nanosecond pulse Nd:YAG laser.
Figure 1 shows photographs of CaO colloids during LAL. In 30 min, the colloidal solution became opaque slightly, indicating that fragmentation of the powders progressed. At ca. 60 min, the appearance of the colloidal solution changed drastically. The opacity of the colloidal solution decreases, but gel-like structures floating in the solution can be observed. When the colloidal solution in this state was dried, the volume of the dried powders were larger than that of the source CaO powder, implying that the density of the gel-like structures was lower than the original CaO powder. The gel-like structures disappeared after LAL for more than 120 min. It was remarkable that gel-like structures were formed during LAL, because we usually expect that only fragmentation can be induced by such strong laser irradiation. As the result of further experiments, it has been suggested that i) the gel-like structures are formed via the CaO NPs agglomeration, ii) the CaO NPs agglomeration is induced by partial neutralization of positively charged CaO NPs by ethanol that can provide negative charge when they are adsorbed onto the CaO NP surface.
In addition, we found that the gel-like structures are still positively charged. Therefore, when the gel-like structures were mixed with negatively charged gold or platinum NPs prepared by LAL in alcohol, metal-CaO nanocomposites were formed (Figure 2).

Figure.2 (a) CaO gel-AuNPs, and (b) CaO gel-PtNPs composite obtained by mixing a CaO gel colloid and a AuNP or PtNP colloid prepared by laser ablation in ethanol.

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Fabrication of Porphyrin Nanoparticles and Their Phototoxicity to Rat Pheochromocytoma PC12 Cells

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Nanoparticles having strong absorption in the visible to near-infrared region have attracted considerable interest in the research fields of photoacoustic imaging and phototherapy. [1] Important issues of nanoparticle colloids for bio and medical applications are low toxicity. Laser fragmentation in water as a nanoparticle preparation method has some advantages because an aqueous nanoparticle colloid can be obtained directory from a water suspension of the target compound powder without using any organic solvents.[2] Herein, we demonstrate the fabrication of porphyrin nanoparticle colloids and some results of the studies on their toxicity to rat pheochromocytoma (PC12) Cells.

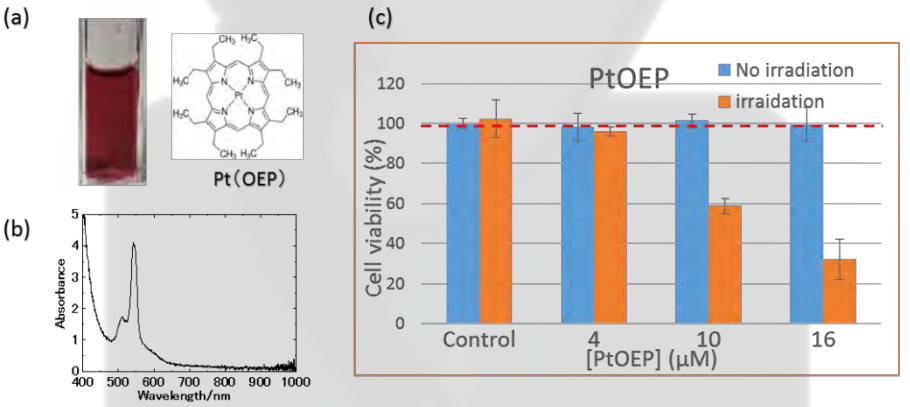

Figure 1 (a) photograph of the prepared Pt(OEP) nanoparrticle colloid and (b) its absorption spectrum. (c) Toxocity of Pt(OEP) nanoaprticles to rat PC12 cells, which were incubated in a culture medium containing the nanoparticles for 1 day, before(blue bars) and after (red bars) visible light (500-650 nm) irradiation.

Aqueous colloids of Pt octaethylporphyrin, Pt(OEP) were synthesized by nanosecond pulse laser (532-nm wavelength, 6-ns FWHM, 10-Hz repetition rate) irradiation to the suspension of Pt(OEP) powder (20 mwt%) in Pluronic® F127 aqueous solution (0.1 wt%). Figure 1(a), (b) show the photograph and the absorption spectrum of the prepared nanoparticle colloid. The Pt(OEP) nanoparticles dispersed in a phosphate buffered saline (PBS) solution and a cell culture medium stably for longer than 1 month. Figure 2 shows the result the toxicity to rat PC12 cells. The cell viability examined by the MTT assay did not changed by adding of the nanoparticles under a dark condition. On the other hand, the cell viability decreased drastically by visible light irradiation (20 mW/cm^2, 10 min) to the cells after 1 day incubation in a culture medium containing the nanoparticles. The results demonstrate clearly that the Pt(OEP) nanoparticles work as an effective photodynamic therapy reagent. The mechanism could be explained by singlet oxygen generation photosensitized by the nanoparticles because we confirmed efficient photosensitized generation of singlet oxygen in a solution by using 1,3-diphenylisobenzofuran as a Reagent for determination of singlet oxygen.

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Synthesis by laser ablation in liquid of alloy nanoparticles: controlling the structure and the composition for specific applications

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Laser ablation in liquid (LAL) allows the production of nanoparticles (NPs) with peculiar surface chemistry and a large variety of compositions, included metastable phases and nanocomposites, all by the same self standing and simple set up.[1-4] Currently, several efforts are undergoing to improve the control on laser generated nanomaterials and to precisely understand the formation mechanism of NPs.[5,6] In this context, nanoalloys of noble metals and transition metals are a useful case-study, because of the different chemical transformations observed in different elements subjected to the same laser ablation process.[7-9] On the other hand, these noble metal nanoalloys consist of metastable phases hardly achievable by other synthetic approaches, and have multiple functions appealing for a wide range of applications from catalysis[10] to photonics[11,12] and nanomedicine[13]. The results obtained so far with non-equilibrium nanoalloys, that are of interest for the general understanding of the processes behind the LAL technique and for improving the control on product structure, will be discussed. Then, it will be shown how these results allowed to extend the range of applications by accessing to a library of multifunctional nanomaterials.

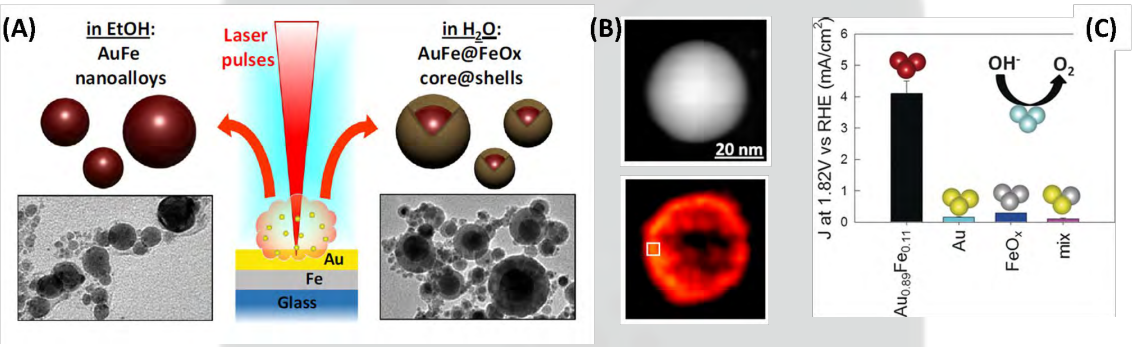

Figure 1. (A) Iron-rich Au-Fe nanoalloys are obtained in ethanol by nanosecond laser ablation of a bilayer Au/Fe film (left). When the same film is ablated in water, core-shell NPs of iron oxide-AuFe metal alloy (iron poor) are achieved.[8,9] These NPs possess interesting properties for photonics (B), exhibiting localized surface plasmons,[11] and for catalysis (C), with enhanced activity compared to single element analouges[10].

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Monochromatic Light Driven Synthesis and Growth of Flat Silver Nanoparticles

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Size and shape of metal nanoparticles play a key role in most of their technological applications because they determine their optical properties in the UV-Vis-NIR range [1,2]. Here, we demonstrate the "in liquid" formation of flat silver nanoparticles' colloids by pulsed laser beams and monochromatic LEDs, along with tri-sodium citrate (TSC) and H_2O_2 addition. Spherical Ag nanoparticles are initially obtained by pulsed laser ablation in water and citrate. In a second step, such spherical particles are transformed into flat nanoplates by adding H_2O_2 under monochromatic light irradiation at different wavelengths (405 nm, 515 nm and 730 nm) [3]. The obtained particles are characterized by UV-Vis spectrophotometry for plasmon resonance, Scanning Electron Microscopy for size and shape, and Atomic Force Microscopy (AFM) for thickness. The process yields nanoplates that show regular triangular shape and their size is dictated by citrate concentration and irradiation wavelength. Indeed higher citrate concentration (10mM) tend to limit the growth and to smaller and thinner nanoplates that show plasmon resonances in the Visible range, while lower citrate concentration (1mM) allow the growth of larger and thicker nanoplates, with plasmon resonances in the near IR (Fig. 1) [3]. Irradiation wavelength also plays an important role as longer wavelengths produce larger nanoplates [3], especially at higher citrate concentration.

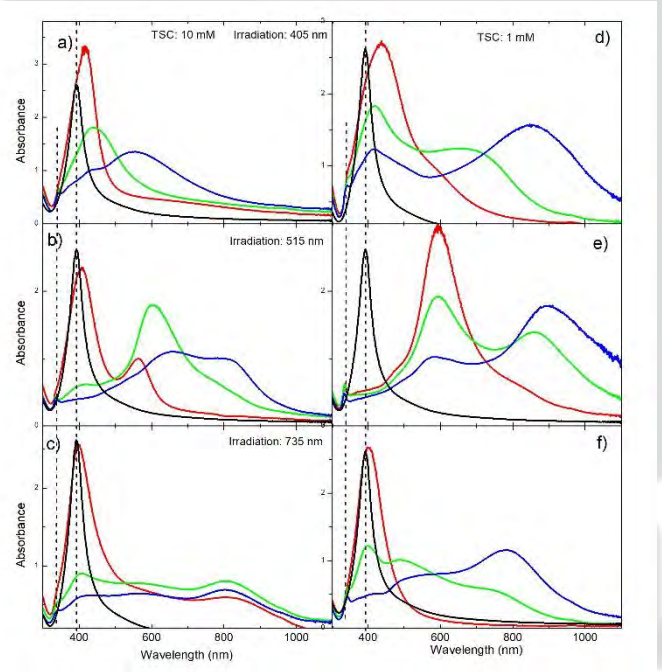

Figure 1. Absorption spectra from Ag nanoplates, at early (red lines), intermediate (green lines) and final (blue lines) growth stage at TSC 10 mM (left column) and 1 mM (right column) and at 405 nm (top line), 515 nm (middle line) and 730 nm (bottom line) irradiation wavelength, and initial spherical nanoparticles (black lines). Vertical dashed lines correspond to the plasmon resonance of sherical nanoparticles at 393 nm and to the transverse quadrupole resonance of flat nanoplates at 330-345 nm.

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Shape control of metal oxide nanoparticles produced by laser ablation in liquid

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The formation of the non-spherical metal oxide nanoparticles (MONPs) by laser ablation in liquids (water and isopropyl alcohol) has been studied using Pb, Cu and Zn metals. The variety of the non-spherical MONPs shapes, including circular and hexagonal sheets, octahedra, spindles, rods and fibers have been produced by variation of the ablation parameters, treatment of the target surface, PH and subsequent heating in water. The influence of unavoidable hot water treatment during laser ablation as an important mechanism leading to formation of the non-spherical MONPs has been demonstrated [1].

The Yb fiber laser with 1062 nm wavelength and 100 ns pulse duration has been used. The laser beam has been focused on the target surface (fluence 80 J/cm^2, spot diameter 40 μm). The NPs synthesis was performed in several stages: target surface treatment, laser ablation liquid, additional fragmentation and heating of the suspension for formation of proper shapes [2,3].

The Pb, Cu and Zn targets (99.99% purity) were used for laser ablation in deionized water and in isopropyl alcohol (IPA). The targets have been covered by oxide layer prepared by controlled oxidation procedure. It was demonstrated that only stable spherical metal nanoparticles with diameter below 30 nm have been produced by laser ablation in IPA. Thus, the key role of the water for MONPs creation was demonstrated.

The unavoidable hot water treatment during laser ablation in water plays a significant role in the formation of non-spherical nano-particles. It was found that the octahedra and rods appeared at the target surfaces even without laser ablation after water treatment at 75 ºC during about two minutes. (a)

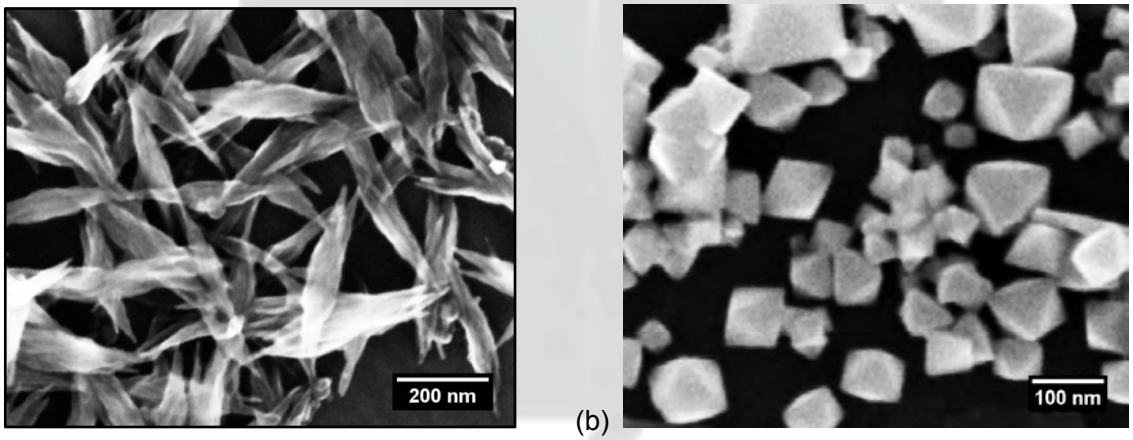

Figure 1 Single crystalline non-spherical metal oxide nanoparticles: (a) CuO nano-spindles, (b) PbO nano-octahedrons.

The obtained formation of non-spherical particles was explained in terms of metal oxidation and oriented growth processes. The PbO nanoparticles produced by laser ablation played the role of nuclei which phase depends on the target preparation procedure. The elevated water temperature during laser ablation accelerated the growth of nanocrystals.

The equipment of the Ural Center for Shared Use “Modern nanotechnology” UrFU was used. The work was supported by Government of the Russian Federation (Act 211, Agreement 02.A03.21.0006).

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Experimental study of femtosecond laser cavitation on gas productivity and composition

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At present, nanosecond laser ablation of biological tissues are used in coronary angioplasty[1,2]. However, the complex lesions such as heavy thrombus, calcified plaque or long term atheroma are still challenging. Ultrafast laser is a potential therapeutic for complex lesions due to its high peak intensity, non-selectivity of target and small heat affected zone. When an ultrafast laser pulse is shot in biomedical liquid environment, bubbles form as a result of cavitation[3].The mechanism of femtosecond laser cavitation in physiological liquid has not been fully studied, which will provide a strong theoretical basis for the next generation of laser coronary angioplasty.

In this paper, we study the cavitation of normal saline by femtosecond laser pulse from gas composition and productivity. The productivity of the cavitation gas is quantitatively detected by a home-made setup. The cavitation gas was collected and its composition was analyzed using GC2020 gas chromatograph. We found an original method for measuring gas productivity, and discussed the relationship between cavitation gas productivity and laser pulse energy with this method. The cavitation breakdown threshold of femtosecond laser was $1.4971*10^{17}W/cm^2$ by fitting the figure line. Through comparative experiments, it is proved that each laser pulse independently generates cavitation gas when the repetition frequency is less than 1000Hz. At the same time, we proved the main cavitation mechanism of femtosecond laser is the chemical decomposition of water by analyzing the gas composition. Figure 1 shows the relationship between gas productivity and average power as well as the gas chromatogram involved in this paper.

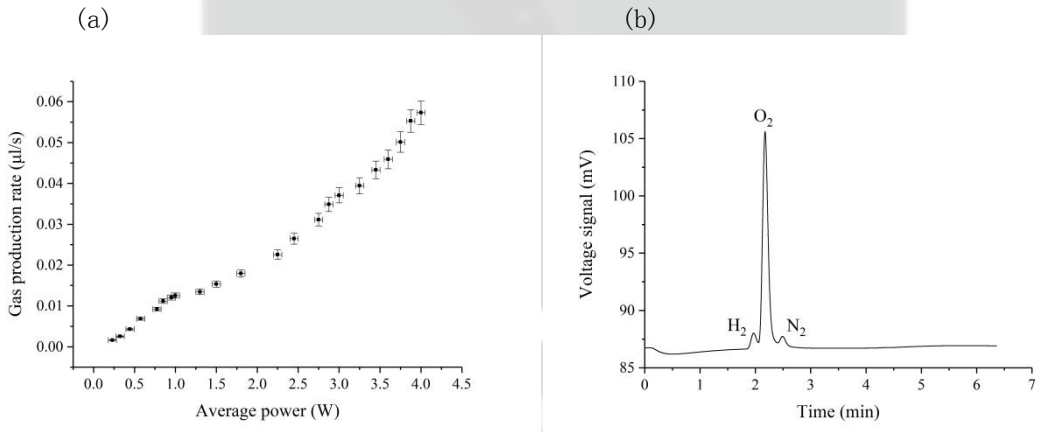

Figure 1 the relationship between gas productivity and average power as well as the gas chromatogram involved in this paper. (a) The relationship between gas productivity and average power. The laser amplifier used in the experiment is SOL ACE35F1KHp. The wavelength of the pulse laser is 800nm, the pulse width of the pulse laser is 35fs, the repetition frequency of the pulse laser is 1000Hz. (b) Gas chromatogram of cavitation gas. The peaks in the chromatogram correspond to hydrogen, oxygen, and nitrogen, from left to right, due to the dilution of air during collection.

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Impact of electrolytes on particle size distributions of gold nanoclusters fabricated by nanosecond-pulsed laser fragmentation in liquids

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Pulsed laser fragmentation in liquids (LFL) is a useful tool to tune the particle size distribution of laser-fabricated gold nanoparticles (NP), [1] yielding ligand-free ultra-small gold nanoclusters (AuNCs) with mean diameters < 3 nm highly relevant for applications in biology and catalysis. Herein, the particle formation process of AuNC is based on the re-crystallization of evaporated particles [2], which is naturally strongly affected by the surrounding medium and potential stabilizing additives. Therefore, in this experimental study, we investigated the extent to which the ionic strength and the pH-value during LFL influences the surface chemistry, the electrostatic stabilization, and, as a consequence, the particle size distributions and the yield of produced AuNCs [3].

To this end we utilized high-intensity nanosecond pulse laser sources and conducted all experiments in a liquid flow passage reactor, which allows a precise control of the energy input per volume. According to [1] LFL is a one-pulse and one-step event, yielding monomodal AuNCs in case a pulse peak power of 1.62 x 10^{12} W/m^2 is exceeded and the resulting particles possess a suitable electrostatic stabilization. Our findings highlight the reduction of the mean particle diameters and an increasing yield of particles < 3 nm in the presence of halide anions and at alkaline pH. Interestingly, the highest yield of AuNC is obtained when anions are applied at an alkaline pH, which indicates a synergistic influence of the ionic strength (at micromolar concentrations) and the pH value (at pH = 10). We further show that this effect is anion specific for a series of homologous halides. Here a direct Hofmeister´s series (HS) of anions is observed at neutral pH and reversal is found in the alkaline regime. In consecutive experiments, we examined the evolution of the particle size after LFL for samples in ultra-pure water and in salt at basic pH at ultra-short time scales using time-resolved X-ray scattering. We found clear evidence of limited growth on a microsecond time scale for samples in salt at pH 10 compared to water, leading to a final particle size of 3-4 nm.

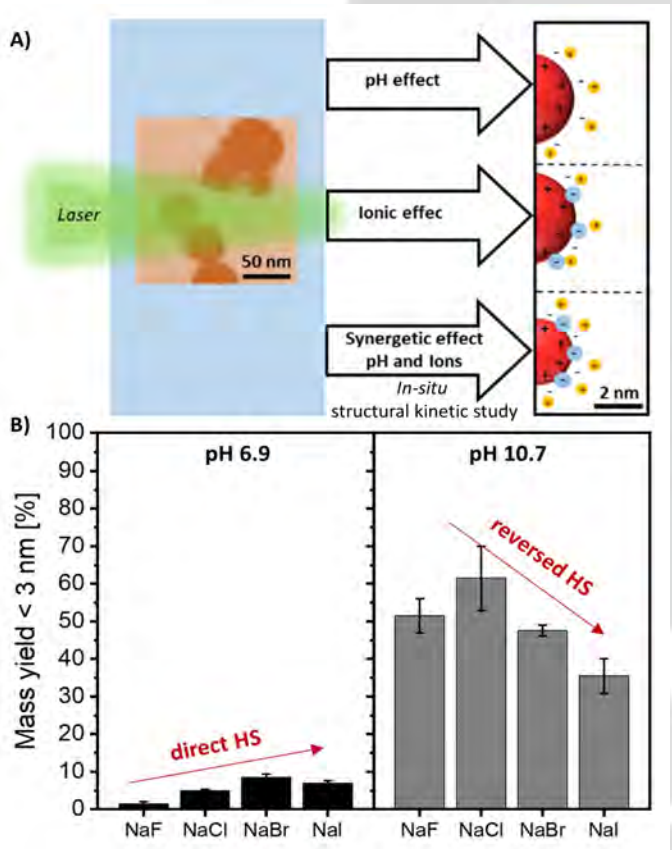

Figure 1 : A) Illustration of the fragmentation process, including visualisation of studied chemical influence factores [3]. B) Mass yield of particles after LFL using a 9 ns laser (532 nm, 0.1 kHz, 1.6 J/cm^2) [3].

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One Step Bottom-Up Synthesis of Carbon-Supported Ultrasmall Metastable Ni Nanoparticles

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The growing field of laser ablation in liquid (LAL) has emerged as a robust non-equilibrium synthesis route of various materials. A multitude of reported syntheses have been accumulated in reviews over the last decade [1, 2]. Most of these syntheses involve the 'top-down' approach of ablating a solid metal target or metal powder immersed in a liquid. However, most top-down methods result in particle sizes >5 nm with broad size distributions. Recently, sub-2 nm nanoparticles have been synthesized by employing 'bottom-up' approach of using molecular precursors instead of solid metal targets [3].

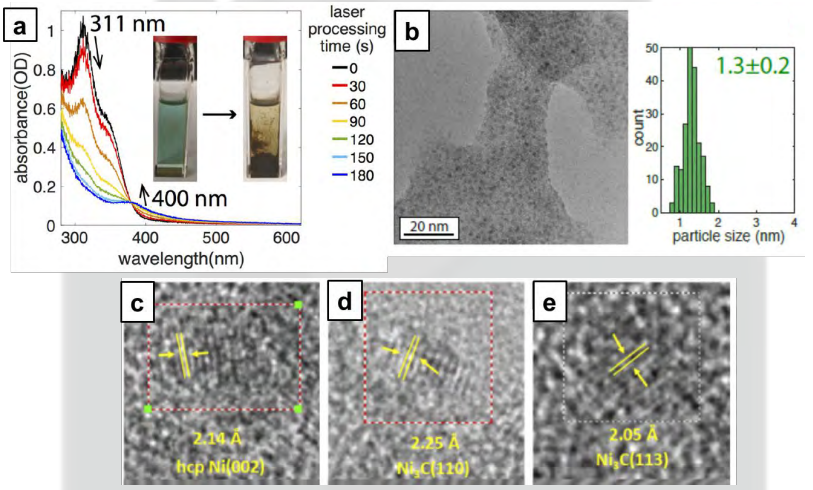

Figure 1 (a) Spectra of nickelocene during laser processing with photograph inset. (b) TEM image and size distributions of particles. (d, e, f) HRTEM images with lattice spacings of different particles observed in the same sample.

We have synthesized ultrasmall (~1.3 nm) Ni nanoparticles supported on carbon from nickelocene precursor in organic solvents using 800 nm, 30 fs laser pulses. Lattice fringe analysis of HRTEM images identified only metastable phases of Ni, *viz*. hcp-Ni and hcp-Ni_3C. No lattice fringes corresponding to the thermodynamically stable phases (fcc-Ni or NiO) were identified. Deconvoluted high-resolution XPS spectra of C1s and Ni2p contained peaks corresponding to Ni-C bonding. The reaction was monitored through *in-situ* UV-vis absorbance spectroscopy and first order kinetics were observed. Further studies on the reaction mechanism are currently underway. Preliminary studies indicate that the Ni-carbon materials exhibit electrocatalytic activity towards oxygen reduction reaction (ORR). Optimization of ORR experiments is also currently underway.

In summary, we have synthesized ultra-small, metastable and electrochemically active Ni nanoparticles on carbon support through a simple bottom-up one-step protocol.

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Femtosecond pulsed laser ablation in liquids nanoparticle production increase by simultaneous spatial and temporal focusing

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In the present work, a simultaneous spatial and temporal focusing (SSTF) setup is proposed for improving nanoparticle productivity of the method of femtosecond pulsed laser ablation in liquids (PLAL). The main drawback of employing femtosecond lasers in PLAL is that pulses experience energy losses in the liquid environment where the target is submerged [1]. This is due to the extreme power and intensity that cause nonlinear effects such as filamentation or optical breakdown that dramatically reduce the ablation efficiency. However, the SSTF setup is a breakthrough technology that allows to overcome these limitations by strongly confining the intensity distribution only to the focal volume, where the shortest femtosecond pulse duration is achieved, increasing pulse duration out of focus and reducing nonlinear energy losses, leading to an improved energy delivery to the target.

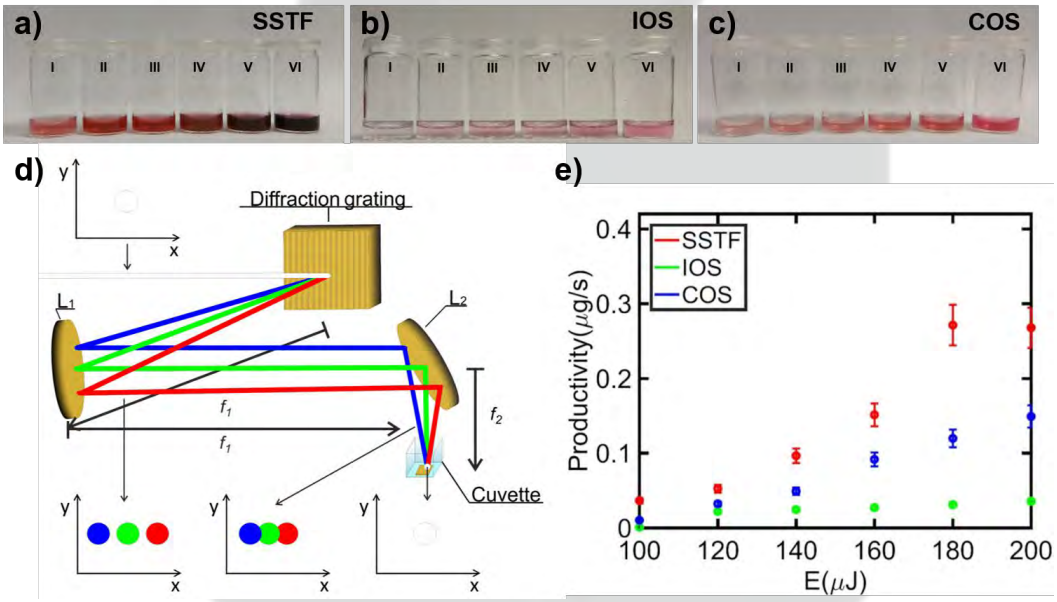

Figure 1. Image of the generated colloids as a function of the pulse energy I=100 μJ, II=120 μJ, III=140 μJ, IV=160 μJ, V=180 μJ, VI=200 μJ, for (a) SSTF, (b) IOS and (c) COS systems. (d) Implemented experimental setup of the SSTF technique for femtosecond laser ablation in liquid. (e) Productivity values obtained from the (a), (b) and (c) colloids proving the enhanced SSTF production.

The proposed SSTF system is compared against an analogous image system (IOS) without temporal focusing effect and the conventional PLAL setup (COS). A complete spatial, temporal and spectral characterization of each system is performed. Energy losses are evaluated through different water layers obtaining a maximum energy loss of 5% for the SSTF setup, 40% for the IOS system and 70% for the COS. This variation influences gold nanoparticle productivity leading to a maximum productivity increase of a factor ≈10 compared to the IOS system and ≈2 compared to the COS even when the experimental parameter are favourable for the compared systems. Hereby, the enhanced productivity is demonstrated [2, 3].

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Synthesis of Catalytically Active Naked Palladium Nanoparticles Via Laser Plasma

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Palladium nanoparticles (PdNPs) catalyze cross-coupling reactions that are of great importance in the assembly of highly functionalized organic molecules [1]. Femtosecond laser irradiation of aqueous media generates plasmas with high concentrations of reactive species such as hydrated electrons, hydrogen atoms, and hydroxyl radicals [2]. This plasma environment can reduce Pd^{2+} salt precursors to form PdNPs at room temperature without toxic solvents, capping agents, or surfactants, making it a "green" synthetic approach. This work focuses on optimizing the properties of "naked" PdNPs via femtosecond laser irradiation in aqueous solution. By varying the metal precursor, it is possible to tune the size and stability of PdNPs [3]. For particles synthesized from K_2PdCl_4, ~100 nm nanoflowers make up most of the population (Fig. 1a). Adding acid (HCl) stabilizes the small nanospheres that otherwise assemble the nanoflower structures (Fig. 1b). Using $Pd(NO_3)_2$ as a precursor produced new smaller nanopopcorn structures, and addition of acid (HNO_3) yields smaller particle sizes and longer lasting colloids (Fig. 1c-d).

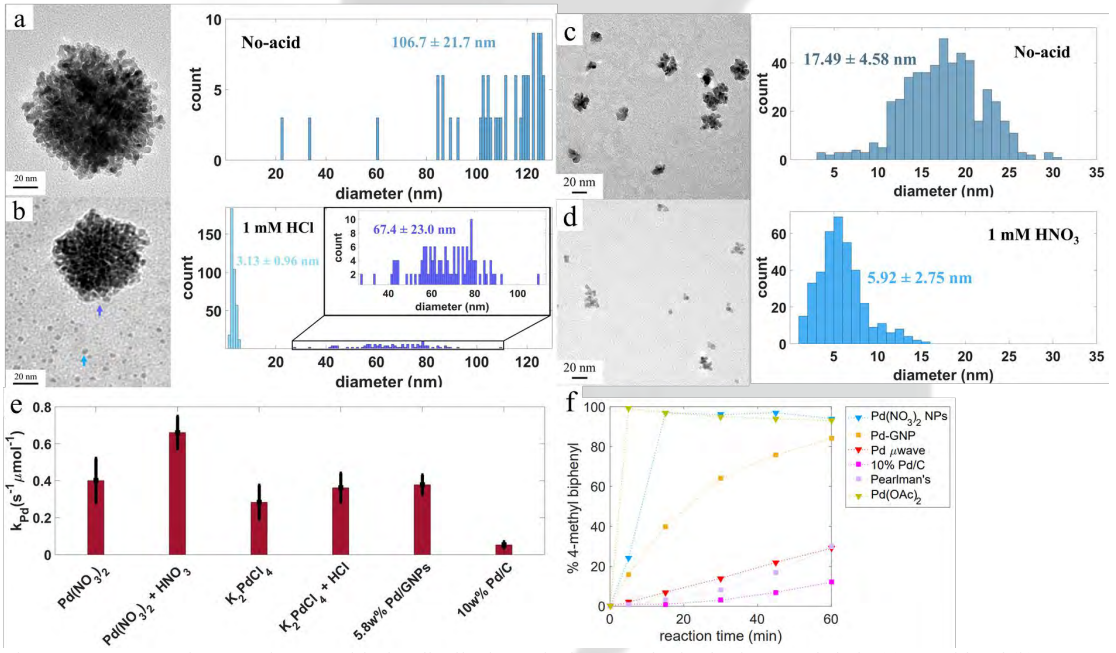

Figure 1. Representative TEM images with size distributions of PdNPs synthesized using K2PdCl4 in (a) no acid and (b)1 mM HCl, and Pd(NO3)2 in (c) no acid and (d) 1 mM HNO3. (e) kPd values for laser−PdNPs and other Pd-based catalysts. (f) 4-methyl biphenyl formation over time in the presence of Pd catalysts.

The samples were catalytically active toward the model para-nitrophenol reduction reaction and Suzuki cross coupling reactions, showing significantly higher catalytic activity than the readily available commercial Pd catalysts (Fig. 1e-f). k_{Pd} is the rate constant for PNP reaction normalized to the moles of Pd nanocatalyst added to the reaction. It is evident that PdNPs synthesized with $Pd(NO_3)_2$ and 1 mM HNO_3 are the most efficient catalysts (Fig. 1e) and also outperforms other palladium based catalysts in the suzuki cross coupling reaction, as seen in Fig. 1f where there is a higher rate for 4-methyl biphenyl formation over time.

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Onion-structured Spherical MoS_2 Nanoparticles Induced by Laser Ablation in Water and Liquid Droplets' Radial Solidification/Oriented Growth Mechanism

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Laser ablation in liquid is one of the few ways to synthesize spherical molybdenum sulfide (MoS_2, typically showing laminated structure) with smooth surface and exhibiting so-called fullerene-like structure.[1-3] However, as for formation mechanism of such fullerene-structured spherical MoS_2, it is still unclear and to be addressed.

Here, we have also used laser to ablate MoS_2 target in water and obtained mostly nearly perfectly spherical MoS_2 nanoparticles (NPs) in shape with smooth surface, and tens to hundreds of nanometers in diameters (Fig. 1i). Further microstructural examination (Fig. 1ii) has reveals that such spherical MoS_2 NPs are built by concentrically curved {002} planes and show onion-like structure. Besides, there exist shrinkage cavities (or voids) in central part of the MoS_2 NPs or small pores dispersed in the particles and a few tadpole-like long-tailed NPs in the products. All these indicate the marks of melting and molten liquid droplets' solidification during laser ablation, since the spherical and tadpole-like particles could originate from the solidification of the molten liquid droplets, and voids or porosities come from solidification-induced volume contraction.

Thus, a growth model (Fig. 1iii) for such onion-structured spherical MoS_2 NPs is presented. Briefly, the formation of such MoS_2 NPs may go through several main stages including laser-induced generation of molten MoS_2 liquid droplets, inward {002}-oriented growth by radial solidification of the liquid droplets, and voids left inside due to the density difference between solid and liquid phase of MoS_2. Based on our model, we think it has clarified the formation process of the spherical MoS_2 NPs with onion-like structure. Details can be available from Ref. 4.

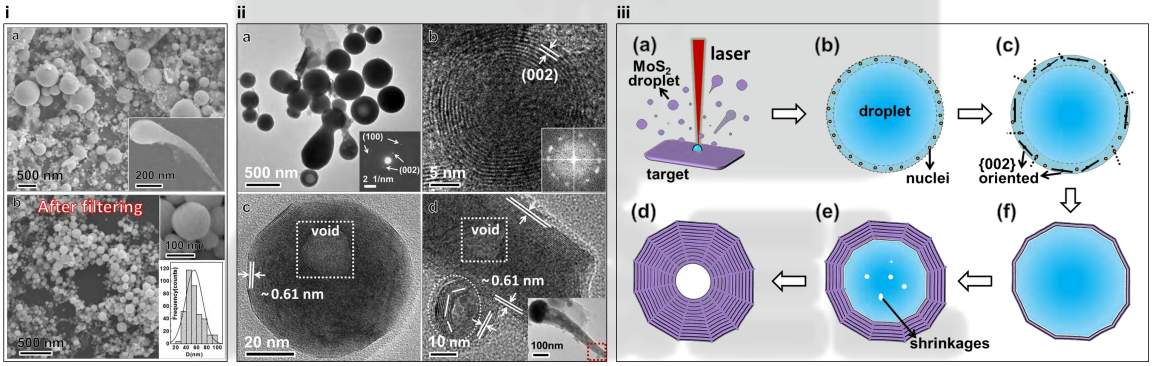

Figure 1 (i) Morphology, (ii) microstructure and (iii) growth mechanism of as-prepared MoS_2.

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Oxidation dynamics of copper nanoparticles under laser irradiation in the colloidal phase

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The irradiation of previously synthesized nanoparticles is one of the most important laser processes of nanomaterials in the colloidal form. Other than laser ablation, it has many advantages, including the ability to tailor the final product by adjustment of the irradiation conditions, to handle large amount of material and to use low cost and practical procedures [1]. In this way, irradiations can be used to change particles' shape (fragmentation), to induce phase changes and thermal effects (melting), and to drive a chemical interaction between the irradiated particles and the surroundings [2].
In this work, the evolution of colloidal copper nanoparticles under pulsed laser irradiation has been studies spectroscopically. Metallic Cu particles have been prepared tailoring a sol-gel based route (known as urea-glass-route), previously set up for the preparation of metal and metal nitride based nanoparticles[3]. The as-prepared Cu nanoparticles were then dispersed into water and alcohol media to form a colloid that was in a second step irradiated with nanosecond pulsed lasers under different conditions. A series of spectroscopic observations have been made. Plasmon resonance position (see fig.1) as well as Raman scattering features have been used to investigate the oxidation state of the particles, while electron microscopy is used to evaluate size and shape. The deep modifications of the plasmon resonance position can be attributed to the transformation of the nanoparticles into copper oxide (or copper core/copper oxide shell) structures. We have also considered Mie scattering solutions for metal core–oxide shell spherical particles in order to interpret the evolution of the optical response during irradiation. Interestingly, the transformation seems to be reversible under appropriate irradiation conditions.

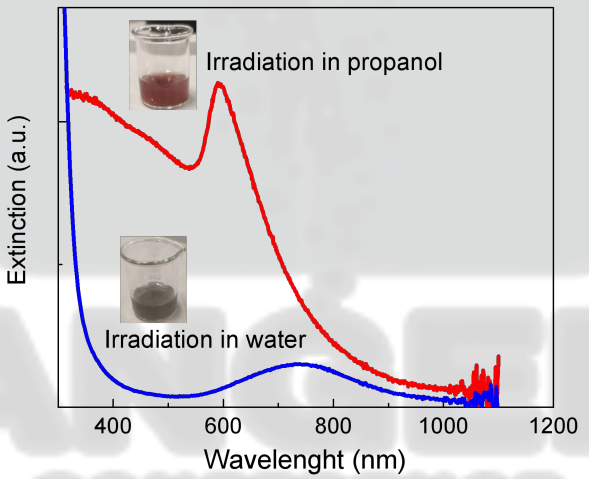

Figure 1 Typical plasmon resonances after the irradiation of colloidal copper nanoparticles in different liquid environments

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Physico-chemical processes in laser synthesis of composite particles based on iron (Fe).

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In the last decades, laser processing has become an important route for producing nanoparticles [1-2]. Pulsed laser ablation method uses a focusing laser beam which can bring high energy density on small areas on target what leads to explosive particles formation. Using an unfocused laser beam for irradiation nanoparticles dispersed in liquid results in a completely different formation of particles. These irradiated particles were melt, merged resulting in a submicrometer spherical particles formation [3-5].

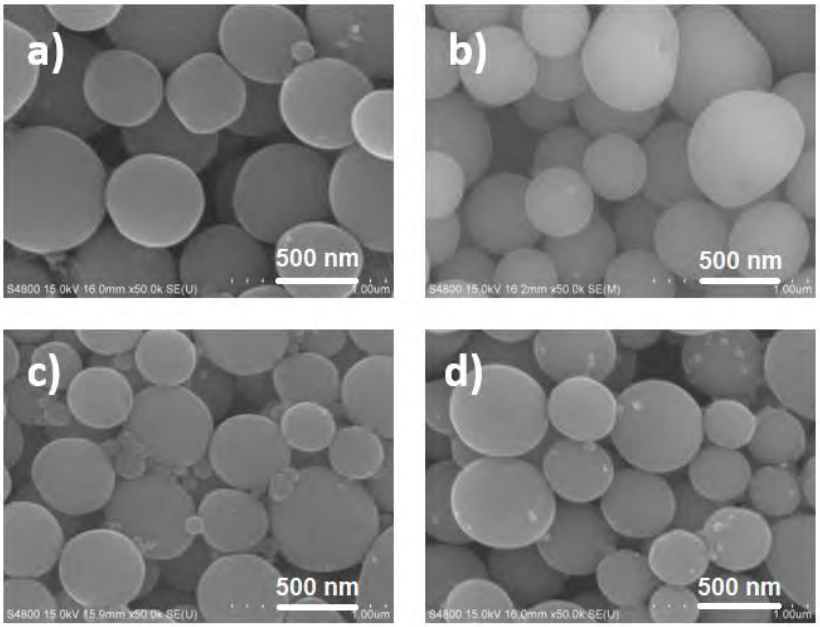

Figure 1 Images of nanoparticles and nanocomposites obtained by pulsed laser irradiation of α-Fe2O3 nanoparticles dispersed in different organic solvents: (a) toluene, (b) ethyl acetate, (c) acetone and (d) ethanol.

In this work taking iron oxides (α-Fe2O3, Fe3O4, FeO) particles as examples, we investigate and discuss the physical and chemical processes involved in particles formation by laser irradiation of nanoparticles dispersed in liquids. We will show the role of the solvent, and interaction not only between particles but also between particles and solvent molecules. The detailed discussion will be reported at the conference. We believe, that exploring the interactions between irradiated material and solvent molecules, and investigating the thermodynamic behavior of particles in various circumstances are needed to produce materials with specific structures and unique physical properties.

This work was supported by the Polish National Science Centre Program No. 2018/31/B/ST8/03043.

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Synthesis of Cu/CuO Nanoparticles using Laser Ablation: Effect of Fluence and Solvents

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Copper (Cu) being cheaper and had a vast potential in the field of medical and optical applications [1, 2]. In the present work, Cu/CuO nanoparticles (NPs) were synthesized by ablating Cu target using nanosecond pulsed laser operating at 1064 nm with 8 ns pulse duration in three different solvents viz: ethylene-glycol (EG), deionized water (DI) and ethanol (Eth). The effects of these solvents at a high laser fluence of 40 J/cm^2 was investigated to study the stability and morphological transformation of NPs using microscopic and spectroscopic techniques. We found that the morphology of these NPs is dependent on the physical properties of solvents (like viscosity, conductivity, polarity, and enthalpy) used in laser ablation (LA).

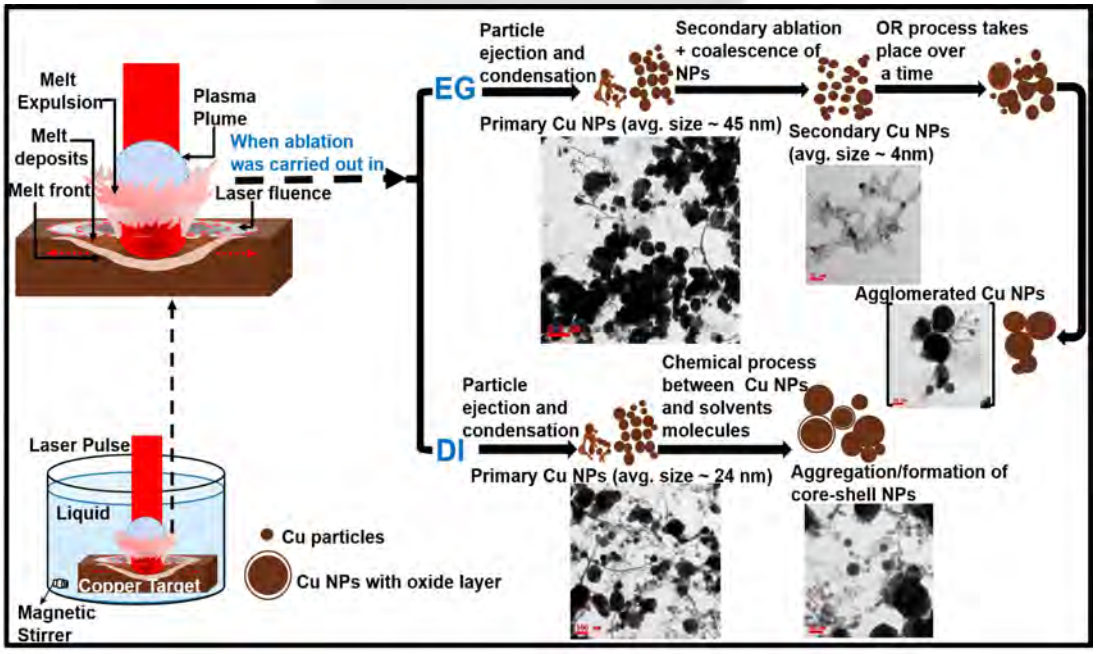

Figure 1 Schematic growth kinematics of Cu target ablated in EG and DI at a high laser fluence of 40 J/cm^2.

In EG and DI, we have observed droplets like features (like a tadpole and necklace-like structure) of NPs (as shown in figure 1) whereas in Eth hollow structure NPs were observed [3]. The growth mechanism of these morphologies during LA will be discussed elaborately, which is the main highlight of the present work. In addition, on monitoring the sample for a long time we have seen the effect of polarity and dielectric constant of the solvent on the stability of Cu NPs. This systematic study is expected to find application in the synthesis of nanostructures by tuning laser and liquid parameters.

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Electrophoretic deposition of laser-generated Platinum Nanoparticles on neural prostheses

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Later stages of Parkinson's disease in aged patients are a serious issue as the disease is to-date incurable and only symptom-relieving treatments are possible to improve their quality of life. For this purpose, deep brain stimulations (DBS) is commonly performed, where an electrode is implanted into deep brain regions and electrically stimulated to modulate neuronal activity and improve motor functions [1]. Due to the body's inflammatory response, scar tissue formation around the electrode results in an increased interface impedance by increasing the distance between implant and the brain tissue [2]. Even though various nano-structuring on electrode surfaces are being researched, landing on an ideal electrode with high performance has not yet been achieved [3].

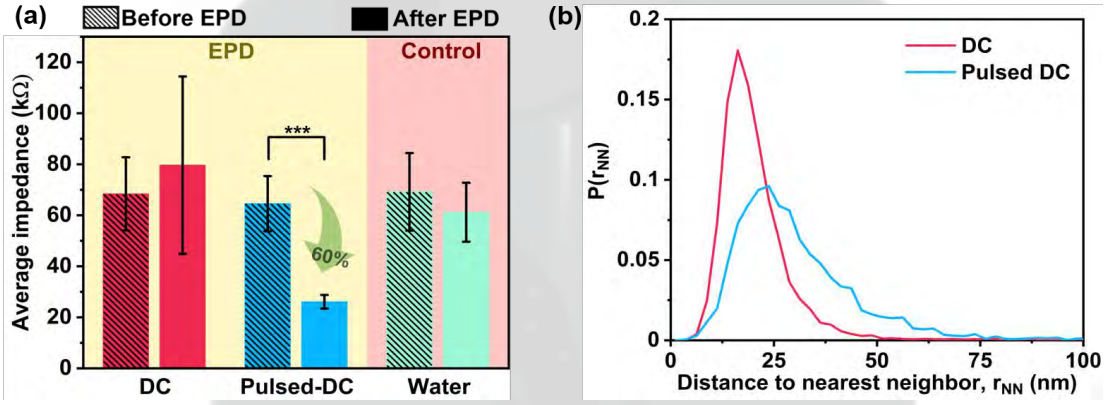

Figure 1 (a) In vitro impedance of DC and pulsed DC coated samples showing 60% reduction after pulsed DC coating. (b) Peak positions of probability histograms showing nearest neighbor distances after DC and pulsed DC EPD.

Therefore, in our study, we performed nano-structuring of Pt-Ir neural electrode surfaces using pulsed laser generated platinum nanoparticles (PtNPs) in water via electrophoretic deposition (EPD) technique to test the electrode performance. We employed laser generated nanoparticles as they are ligand-free, possess high surface charges for electrophoretic mobility and can be tailor-made based on the electrode material. We performed direct current (DC) and pulsed DC EPD using laser fragmented 10 nm sized particles in water and show that the depositions using pulsed DC fields decreased the impedance of neural electrodes significantly *in vitro* (Figure 1a). We also observed that the depositions in DC fields were highly clustered compared to their pulsed DC counterparts. This observation was quantitatively confirmed through a semi-automated image analysis (Figure 1b), where we computed probability histograms of nearest neighbor distances. DC histogram revealed a closely spaced deposition compared to a broadly spaced distribution of pulsed DC.
In the future, the coated samples will undergo long-term *in vivo* stimulation in rat models and their functionality will be evaluated.

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Optical and Structural Properties of Bi/Bi_2O_3 Nanoparticles Prepared via Pulsed Laser Ablation in Different Liquids

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Bismuth is low melting point semimetal that attracted attention as a new plasmonic material. In addition to optical applications, bismuth nanoparticles are promising alternative for lead-free solder and nanoparticle based computed tomography contrast agent [1]. Bi_2O_3 nanoparticles as a high refractive index wide band gap semiconductor have been attracted as a photocatalyst and optical coatings. Pulsed laser ablation in different liquids including water and organic carrier media is an efficient technique for preparation of both bismuth and Bi_2O_3 nanoparticles [2,3]. In this research bismuth based nanoparticles were prepared via pulsed Nd:YAG laser ablation of 99% bismuth target in 40 cc of water, ethanol, methanol, butanone and low molecular weight polyethylene glycol. The laser was irradiated at wavelength of 1064 nm, duration of 12 ns, repetition rate of 10 Hz and energy of 118 mJ/pulse. Figure 1a. Shows the XRD pattern of Bi based nanoparticles in water immediately and a week after preparation. The results shows that early time after ablation the nanoparticles mainly composed of bismuth phase with small amounts of Bi_2O_3 and due to the oxidation the nanoparticles changed to bismuth oxide gradually. Therefore, as demonstrated in Figure 1b. controlling the oxidation rate of the particles and tuning the optical properties collude be carried out in water to obtain the gray oxide nanoparticles with lower band gap. The average size of the particles in water is about 27 nm.

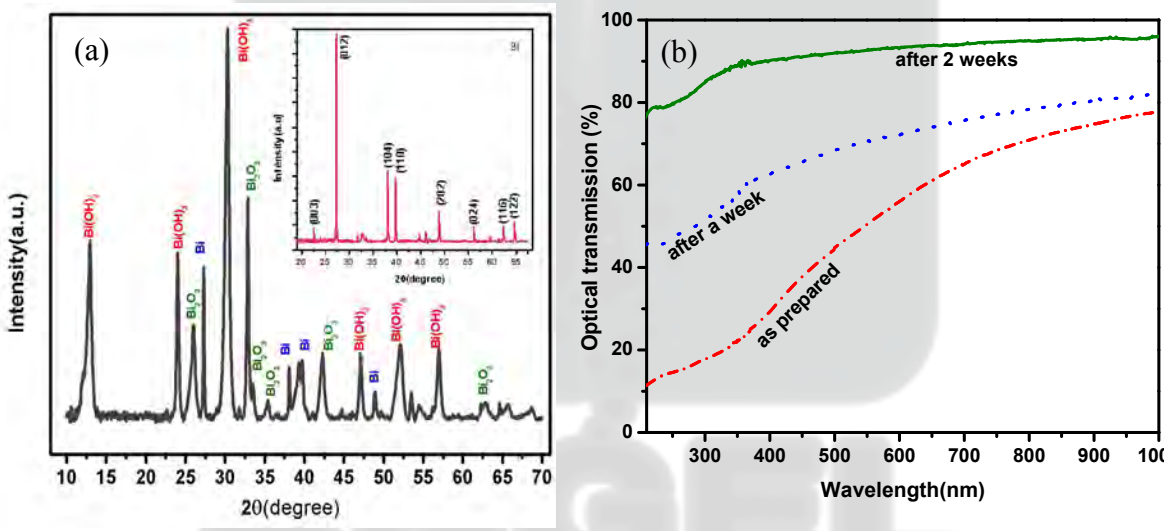

Figure 1 (a) XRD pattern of aged bismuth based nanoparticles that synthesized in water. Inset: XRD pattern of as-prepared nanoparticles in water (b) Optical transmission spectra of the bismuth based colloidal solution in water at different times

In organic liquids, the prepared samples are pure bismuth nanoparticles with different size between 30 and 55 nm which can be attributed to the nature of the laser ablation media including dipole moment and the size of the molecules of the liquids or the steric stabilisation of the particles by polyethylene glycol.

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Laser assisted synthesis of porous Mn_3O_4/PtO_2 nanocomposite for MRI and CT bimodal imaging

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It has always been a great challenge for large size Mn_3O_4 nanoparticles to be a T_1 magnetic resonance imaging (MRI) contrast agent (CA) with a higher longitudinal mole relaxation rates (R_1) than the Magnevist used in clinic.[1,2] Herein, we first presented a composited nanostructure of porous Mn_3O_4 decorated with tiny PtO_2 nanoparticles (Mn_3O_4/PtO_2), which had the R_1 value of 20.48 $mM^{-1}\cdot s^{-1}$ much higher than that of Magnevist （5.18 $mM^{-1}\cdot s^{-1}$), and which also had excellent computed tomography (CT) imaging contrast performance. Combining laser ablation of a manganese bulk in water with further laser irradiation of above ablation generated MnO_x nanoparticles, polycrystalline Mn_3O_4 nanoparticles had been produced, and further etched by $[PtCl_4]^{2-}$ to form the porous structure and decorated with PtO_2 nanoparticles simultaneously.[3] With growingly drastic etch, the proportion of sacrificed Mn_3O_4 and loaded PtO_2 changed with inverse trends. When the molar ratio of Pt to Mn of the final porous Mn_3O_4/PtO_2 nanocomposite reached 3.230, it showed excellent T_1 contrast performance in experiments implemented both in vitro and in vivo. We assumed that the synergetic effect between porous Mn_3O_4 nanostructure and tightly accumulated PtO_2 nanoparticles induced such great enhancement of R_1, which had been demonstrated to be correlated with the number of water molecules coordinated in the inner shell and the tumbling time (τR) of CA.[4,5] Initial cytotoxicity and hemolysis assays both indicated the negligible toxicity of porous Mn_3O_4/PtO_2 nanoparticles in cells. Pharmacokinetics assays further confirms that porous Mn_3O_4/PtO_2 nanoparticles had be almost excreted out in 24 hours after tail vein injection and no evident organ damage has been found. On the other hand, in CT imaging tests, the Hounsfield unit (HU) value of porous Mn_3O_4/PtO_2 nanoparticles reaches 24.4 HU·L per g and showed good contrast capability in in vivo experiments. These findings showcases new insights for improving and broadening contrast capabilities of Mn_3O_4 nanoparticles, and also pave the way for their practical potential in clinic.

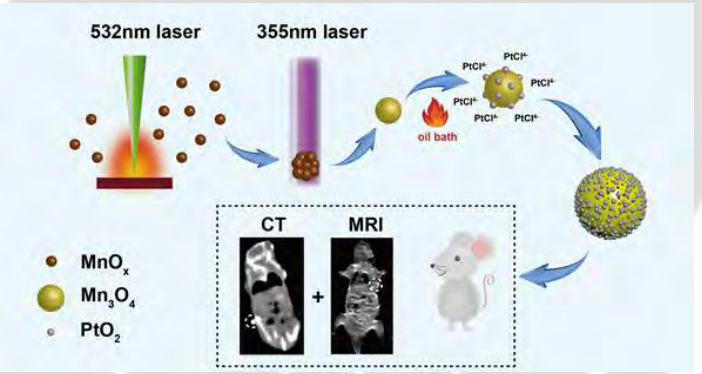

Figure 1. Schematic of formation of Mn_3O_4/PtO_2 nanocomposite and its application.

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Study of the relationship between the plasmonic properties and the electronic properties in Au-Co nanoalloys obtained by laser ablation in liquid

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In the last few years, the nano-world has become more and more attractive due to the large variety of applications of nanoparticles (NPs). To date, the research in multifunctional and multi-metallic nanomaterials (NMs) is very interesting. The combination of noble metals like gold and other metals like cobalt, in example, leads to new nanomaterials in which both metals' peculiar properties are mixed into a new unexplored alloy.[1,2] Alloying two or more plasmonic, magnetic and catalytic metals makes wider their fields of application. However, the common metastable nature of these alloys makes difficult their synthesis.[3] Due to its synthetic conditions, Laser Ablation in Liquid (LAL) synthesis results as one of the best routes to obtain these NPs.[4] Despite the lack in the control of the NPs size, post synthesis treatment as the Sedimentation Based Separation (SBS) allow the size control.[5]
Plasmonic properties are easy to study by UV-Vis spectroscopy,[6] TEM and XRD analysis are sufficient to obtain information about the size, the crystal structure and the composition of the NPs. By a fusion of these experimental data with Density Functional Theory (DFT) calculations, is possible to find information about the relation between of electronic and crystal structure and plasmonic properties of these systems.

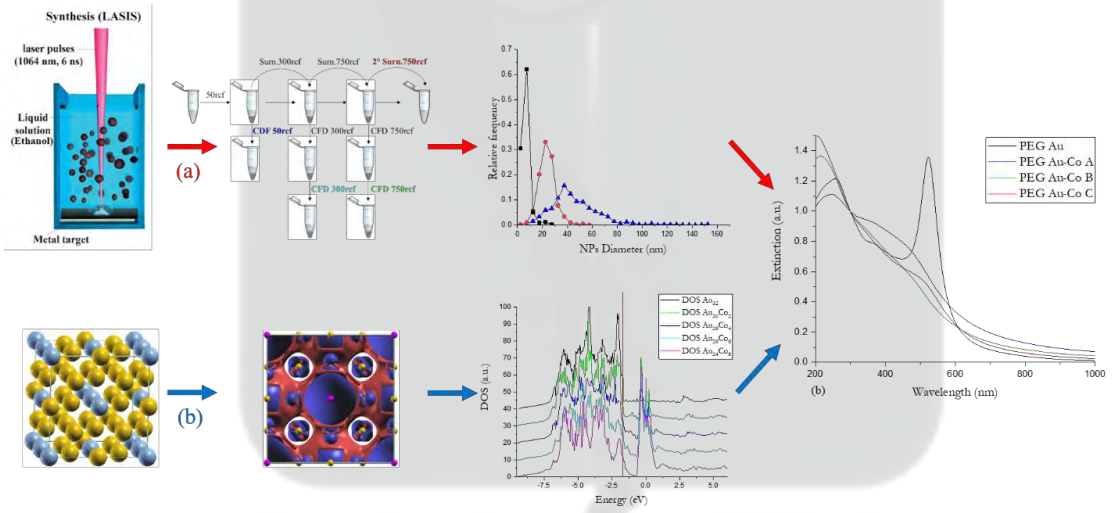

Figure 1. (a) Experimental path: the synthesis followed by the SBS procedure, allow the obtainment of different size alloys' NPs. TEM and XRD analysis are sufficient for the knowledge of composition and size of NPs. (b) Theoretical path: starting from crystal supercell model systems electronic structure are obtained. The study of the Density of States (DOS) makes clear the electronic contribution of the single metal in the alloy. Both the paths are needed to have a full understanding of how LSPR changes.

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Electroreduction of Carbon Dioxide in Metallic Nanopores

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Metallic catalysts with nanopores are advantageous on improving both activity and selectivity, while the reason behind that remains unclear all along.[1-3] In this work, porous Zn nanoparticles (P-Zn) were adopted as a model catalyst to investigate the catalytic behavior of metallic nanopores. In-situ X-ray absorption spectroscopy, in-situ Fourier transform infrared spectroscopy and density functional theory (DFT) analyses reveal that the concave surface of nanopores works like a pincer to capture and clamp CO_2 and H_2O precursors simultaneously, thus lowering the energy barriers of CO_2 electroreduction. Resultantly, the pincer mechanism endows P-Zn with a high Faradic efficiency (98.1%) towards CO production at the potential of -0.95 V *vs.* RHE. Moreover, DFT calculation demonstrates that Co and Cu nanopores exhibit the pincer behavior as well, suggesting that the pincer mechanism is universal for metallic nanopores.

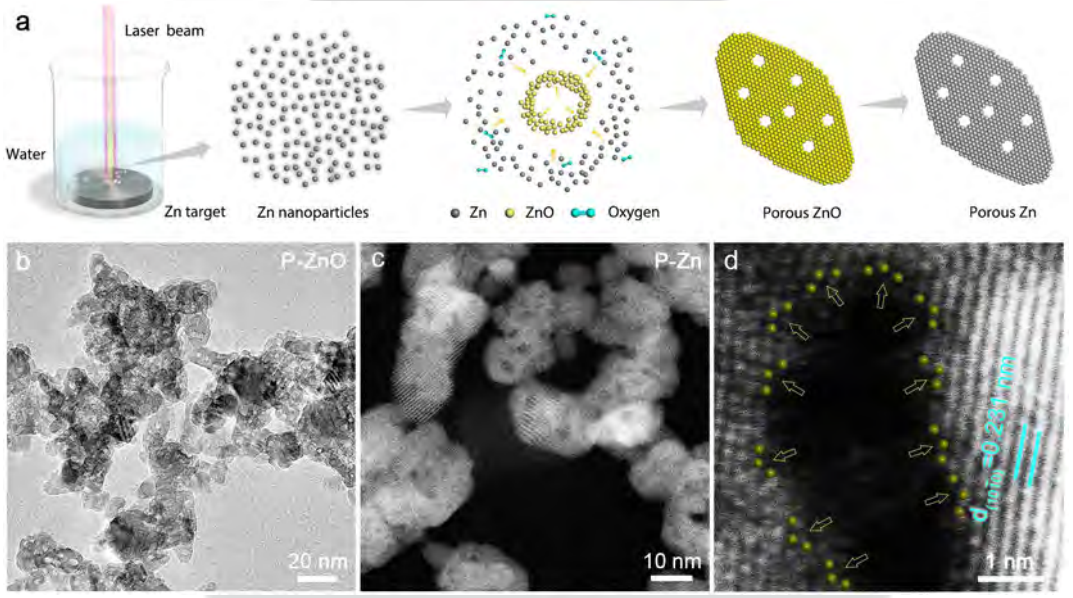

Figure 1. The preparation of P-Zn via PLAL. (a) Schematic illustration of the synthesis of P-Zn by laser ablation in O_2-saturated water and the subsequent electroreduction. (b) TEM image of P-ZnO. (c) HAADF-STEM and (d) high-resolution HAADF-STEM images of P-Zn, the yellow dots mark the atoms around corners.

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Role of solvent and size of raw nanoparticles in composite particles formation during pulsed laser irradiation process

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In the last decades, laser processing has become an important route for producing nanoparticles. Pulsed laser ablation method uses a focusing laser beam which can bring high energy density on small areas on target what leads to explosive particles formation. Using an unfocused laser beam for irradiation nanoparticles dispersed in liquid results in a completely different formation of particles. These irradiated particles were melt, merged resulting in a submicrometer spherical particles formation [1-3].

Hybrid particles (nanocomposites and nanoalloys) are one of the most exciting research objects in materials science because their optical, catalytic, and magnetic properties, different from their bulk values, may have numerous immediate technological applications. The inner structure is an essential parameter referring to these properties. Many possible structures can be encountered ranging from the formation of alloys to the coexistence of segregated phases (core−shell, onion-like, or Janus particles). Their occurrence depends on the physicochemical properties of both metals but also on the nanoparticle size, composition, environment, and method of synthesis. Pulsed laser irradiation method give possibility for synthesis and control a variety of composite particles with various morphology (core-shell, alloy) and compositions which are not only metals or oxides but also non-equilibrium bimetallic alloys (Fig.1) [1-4].

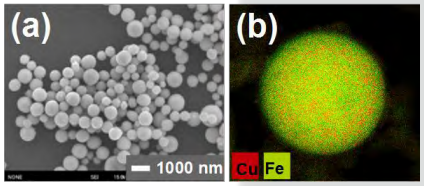

Figure 1 SEM image (a) and EDS elemental mappings (b) of CuFe particles obtained by pulse laser irradiation of Cu and Fe_3O_4 nanoparticles dispersed in ethanol. Conditions of laser irradiation 532nm, 170 mJ/impuls·cm^2, 1h.

Here, taking metal (Au, Ag) and metal oxides (α-Fe_2O_3, Fe_3O_4, CoO, NiO, CuO) particles as examples, we focus our attention at the better understanding physical and chemical processes involved in particles formation by laser irradiation of nanoparticles dispersed in liquids. We will show the role of solvent, and interaction not only between particles but also between particles and solvent molecules. Additionally we will discuss how the internal structure of hybrid particles generated by laser irradiation are ruled by solvent and size of raw nanoparticles in colloidal solution (Figs. 2) [1,4]. The detailed discussion will be reported at the conference. We believe, that exploring the interactions between irradiated material and solvent molecules, and investigating the thermodynamic behavior of particles in various circumstances are needed to produce materials with specific structures and unique physical properties.

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Study of Highly Defective Titanium Dioxide Prepared via Pulsed Laser Ablation

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Nowadays nanodispersed titanium dioxide is widely used in photovoltaic devices, in the "green technologies" of solar energy, as well as in the production of bactericidal materials and sunscreens [1, 2]. Currently, new technologies are developed to obtain titania-based materials, which absorb light in the visible region and exhibit high photocatalytic activity. We obtained superfine dark blue titanium dioxide with intense absorption in the visible spectral range using pulsed laser ablation (PLA) method [3]. TiO_2 powder was synthesized in the following way. At first, a colloidal solution of Ti in distilled water was obtained by PLA using Nd:YAG laser (wavelength of 1064 nm, frequency of 20 Hz, pulse duration of 7 ns). Then the colloidal solution was dried at 60 °C. After that, the powder was annealed at different temperatures.

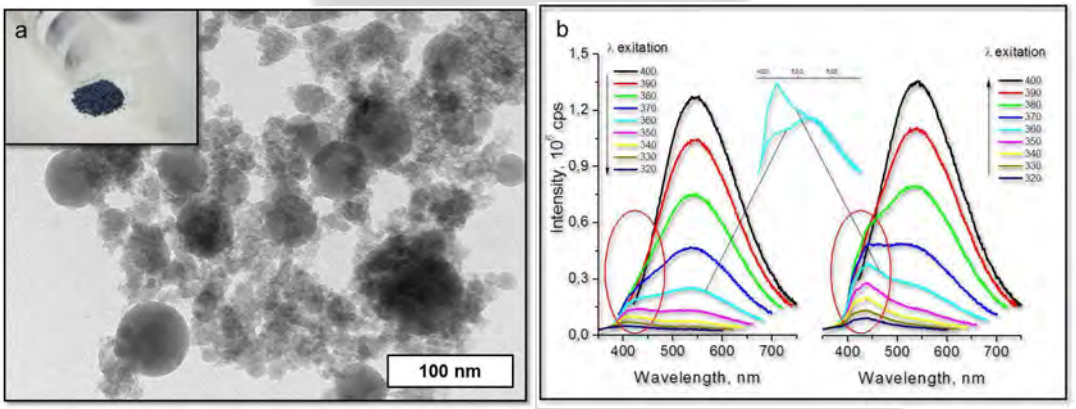

Figure 1 TEM image (a) and photoluminescence spectra (b) of TiO_2 powder.

The initial TiO_2 is a dark blue powder (figure 1a) having spesific surface area of 227 m^2/g. It consists of the spherical particles with an average size of 5-10 nm, and an insignificant number of large particles with a size up to 80 nm. The initial material is X-ray amorphous, and only after annealing at 400 °C the phases of anatase 67 % and rutile 33 % are formed. Also, after annealing the sample color changes to light grey at 400 °C and becomes white at 600 °C. It was found, that TiO_2 DRS spectra showed an intense additional absorption in visible region. This is due to the presence of defects of various nature in the structure of TiO_2. The fluorescence bands (figure 1b) in the 380-800 nm region belong to different types of oxygen vacancies (F, F^+ and F^{2+}centers) and self-trapped exiton states (STE). It was found that the emission spectrum varies its profile depending on the increase (from 320 to 400 nm) or decrease (from 400 to 320 nm) of the excitation wavelength. This change in the spectrum is associated with a relatively long lifetime of STE states.

This work was supported by the Russian Science Foundation, project No. 19-73-30026.

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Stable Rhodium (IV) Oxide for Alkaline Hydrogen Evolution Reaction

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Water electrolysis in alkaline electrolyte is an attractive way towards clean hydrogen energy via hydrogen evolution reaction (HER), whereas the sluggish water dissociation impedes the following hydrogen evolution [1-3]. Noble metal oxides possess promising capability on catalyzing water dissociation and hydrogen evolution [4,5]; however, they have never been utilized for HER due to the instability under the reductive potential. Here we show that the compressive strain can stabilize RhO_2 clusters and promote their catalytic activity. To this end, we engineer a strawberry-like structure with RhO_2 clusters embedded in the surface layer of Rh nanoparticle, in which the incompatibility between oxide cluster and metal substrate causes intensive compressive strain. As such, RhO_2 clusters remain stable at a reduction potential up to -0.3 V vs. RHE, and present an alkaline HER activity superior to commercial Pt/C.

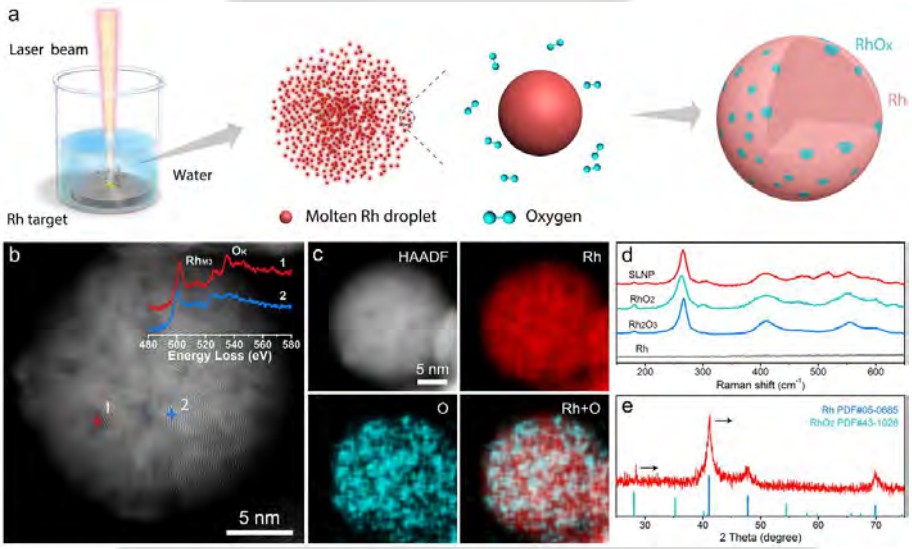

Figure 2. Preparation and Characterizations of SLNP catalyst. a) Schematic illustration on the PLAL synthesis and structure of SLNP catalyst. b) HAADF-STEM image of SLNP. The inset is the Rh M_3-edge and O K-edge EELS spectra collected at point 1 and 2, respectively. c) EDS-mapping images of SLNP. d) Raman spectra of SLNP and RhO_2, Rh_2O_3 Rh references. e), XRD pattern of SLNP catalyst.

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Laser generation of sulfur-doped silicon nanoparticles

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Silicon is important material, which is used for many applications, including microelectronics, nanobiotechnology, photonics etc. [1]. In addition, silicon is applied in commercial solar cells [2] and it is important to increase their efficiency.

In this work, composite amorphous/nanocrystalline Si nanoparticles functionalized by laser-mediated hyperdoping with donor sulphur atoms and small clusters were produced. This can provide both sulfur-donor free-carrier electrical conductivity, and engineered mid-IR free-carrier and impurity-based interband absorption for wide range of biomedical and photonic applications [3]. The produced colloidal solutions were dry-deposited onto the fluorite (CaF_2) substrates for the IR spectral characterization (Fig 1a). Remarkably, the 200-nm thick layer of the dry-deposited hyperdoped Si NPs on the 2-mm thick, double-side polished fluorite substrate exhibits near−mid-IR (spectral range – 1-25 μm) transmittance considerably lower, comparing to not only the substrate, but also to the 0.38-mm thick double-side polished Si wafer precursor (Fig 1a). The colloidal nanoparticles were also characterized in terms of their typical dimensions and crystalline structure by transmission electron microscopy (TEM) (Fig.1b).

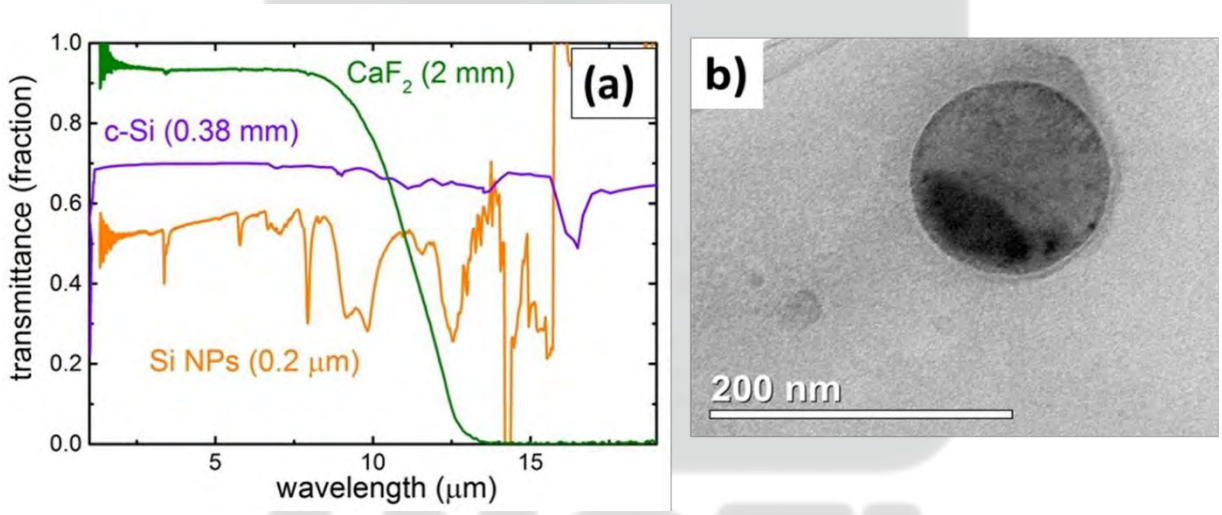

Figure 1 Near-mid IR optical properties of hyperdoped NPs: (a) transmittance spectra of fluorite substrate, c-Si wafer and S-hyperdoped Si-NP layer; (b) TEM image of silicon nanoparticles doped carbon and sulfur

TEM visualization exhibits co-existing ordered crystalline and amorphous inclusions in the hybrid nanoparticles.

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Upscaling of laser-ablative nanoparticle production in liquids

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Due to unique physical, chemical and optic properties, nanoparticles are used in various fields of science and technology, including such as medicine, nanophotonics and nanoplasmonics [1-2]. Method of laser ablation allows to obtain nanoparticles with high purity [3]. But for industrial production it is important to enhance the nanoparticles productivity.

For the efficient generation of nanoparticles of various materials by laser ablation, it is necessary to develop an optimal mode of action on the target, which, in turn, requires an understanding of the basic processes that occur during the interaction of high-power laser radiation with matter.

The ablation efficiency and the yield of nanoparticles can be estimated by the loss of mass of the substance, as well as by the diagnosis of the spectra of the extinction coefficient of colloidal nanoparticles. So, using the example of gold nanoparticles, the values of the extinction coefficient for various spectral ranges are determined. Values at 420 nm correspond to the region of interband transitions in bulk gold, and therefore the dynamics of the coefficient change in this region allows to estimate the direct yield of nanoparticles due to laser ablation, since their contribution to the absorption does not depend on the size of the nanoparticles (Fig.1).

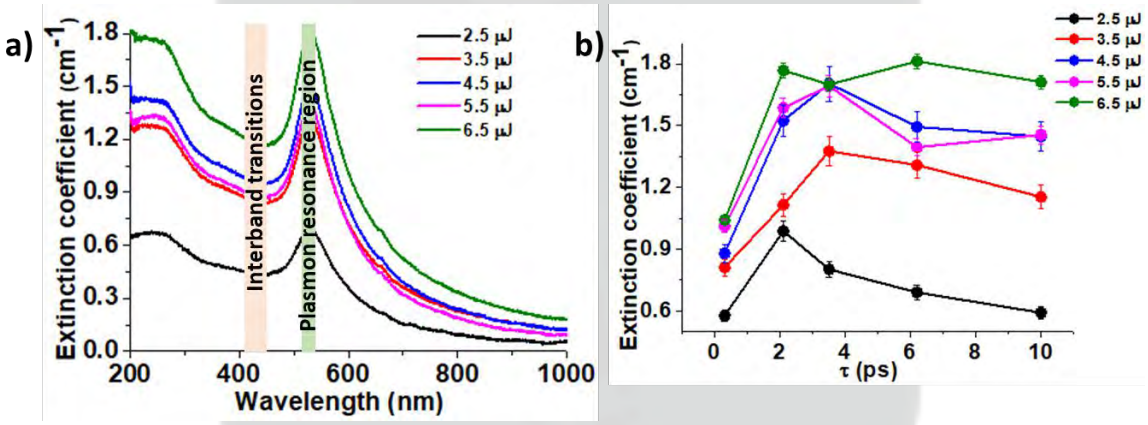

Figure 1 (a) Extinction coefficient for gold colloid nanoparticles produced by method of laser ablation at different pulse energy (pulse duration: 6.2 ps) (b) dependence extinction coefficient on pulse duration (at the peak of plasmon resonance-530 nm)

This work was supported by Russian Science Foundation (grant #18-15-00220)

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Rapid Synthesis of Ultrasmall Non-noble Metal Nanoparticles

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Transition metal nanoparticles (NPs) with diameter less than 5 nm, possess unique and intriguing physicochemical properties, has a significant potential foreground in emerging energy conversion or chemical production related heterogeneous catalytic reactions. However, due to the size-dependent thermodynamic instability and the fairly quick coarsening kinetics of ultrasmall NPs, controlled synthesis of ultrasmall non-noble metal NPs remains a great challenge. Here, we provide a pulsed high-temperature pyrolysis strategy to modulate the nucleation and growth of metal-organic framework (MOF) derived transition metal NPs. We employed electricity-triggered or nanosecond laser-triggered pulsed high temperature to controllably synthesis MOF-derived sub-5 nm metal NPs and even sub-1 nm metal clusters with high loading amount of metal, respectively. We substantiated that by regulating the heating rate and pyrolysis temperature, one can kinetically restrain the thermally activated atom diffusion as well as the crystallite migration and coalescence, and then modulate the nucleation and growth of MOF-derived metal NPs. This work not only provides a general method for fabricating abundant MOF-derived ultrasmall NPs, but also be helpful in guiding other pulsed heating methods for synthesizing thermodynamically metastable size materials by virtue of the fast kinetics of pulsed high temperature.

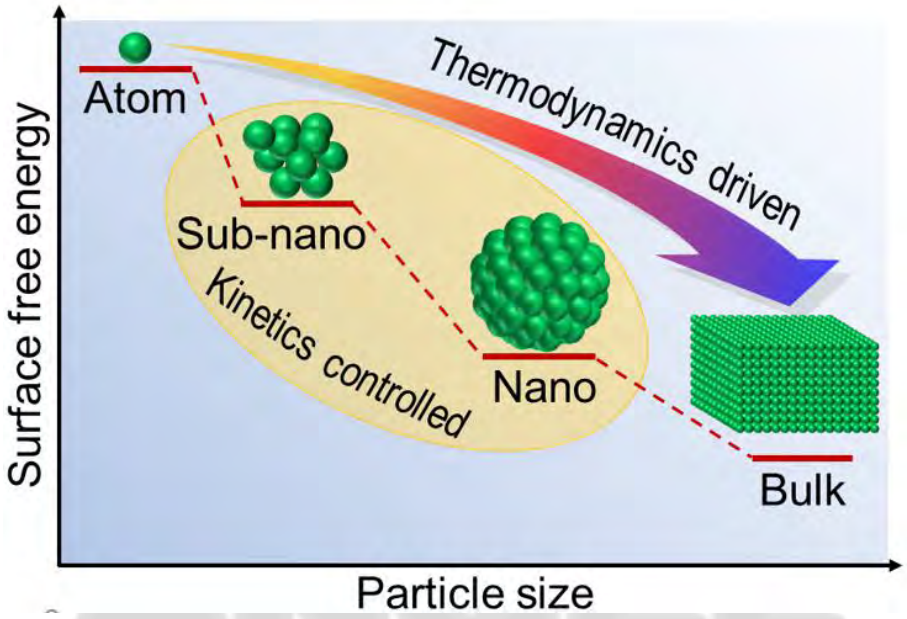

Figure 1. Kinetics dominated evolution of metal particles under pulsed high-temperature.

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Mechanistic study of picosecond laser fragmentation by *in-situ* X-ray scattering

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Laser fragmentation (LFL) is a useful tool to tailor particle sizes of laser-fabricated nanoparticles (NP) under high purity conditions yielding ultra-small NP with a mean diameter < 3nm e.g. for biological applications including sensing and in-vivo/in-vitro targeting. Tuning particle size and surface properties in general, requires an adequate and generalized process control strategy and in turn demanding for a comprehensive insight into underlying fragmentation and ripening mechanisms. Yet, in case of the fragmentation with high intensity pulsed lasers, the individual mechanistic differentiation between effects from energy deposition kinetics (pulse duration) and driving force for fragmentation (laser intensity) are still challenging [1]. The nanoscale confinement significantly influences particle growth [2] already on ultra-short time scales and hence requires attention. This has not been investigated on ps- to ns-scale in depth.

In this work we systematically examined the LFL of AuNP (Figure 1A) using wide (WAXS) and small angle (SAXS) time-resolved X-ray scattering to differentiate effects resulting from laser irradiation itself and the chemical nature of the surrounding medium [3]. Laser-material interaction leads to a temperature rise within the particles and subsequently the medium, causing phase transitions such as particle melting, bubble growth in aqueous solution seen in WAXS or particle decomposition and the formation of new product particles seen in SAXS. For instance, an increase of the SAXS signal after vanishing of the vapor bubble (> 10-20 ns) correlates with the formation of new particles whose signal we were able to monitor up to a delay of 10 µs (Figure 1B). We found indications of a quenched growth and higher diffusion-limitation after 1 µs for samples in salt compared to water, leading to a final particle size of 3-4 nm. Interestingly, we found clusters of a finite initial size after a few ps, which excludes a pure evaporation and condensation process and can be explained by the occurrence of spinodal decomposition also known as phase explosion.

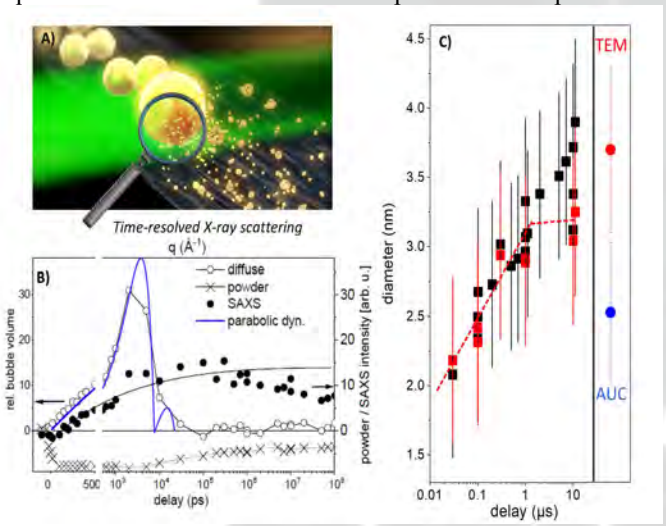

Figure 1 : A) Illustration of the LFL process. B) Time-dependent transient changes of the diffuse and powder scattering caused by laser irradiation. SAXS signal contains particle melting and recrystallization. C) Evolution of the particle size as function of delay for the dominant size fraction. Black squares represent fragmentation in pure water and red

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Time Resolved LIBS-LIF measurements on Laser-Generated Plasma

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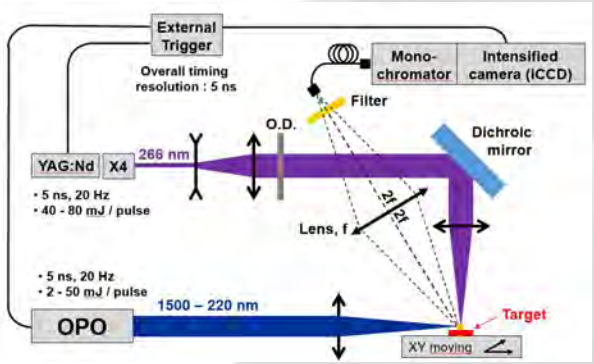
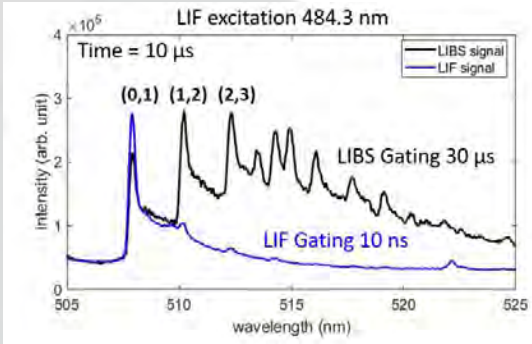
Nucleation processes occurring during laser ablation in liquids remains an open question [1]. In order to control the production of nanoparticles, it is necessary to understand and measure their growth, when and where it occurs. However, no direct measurement of the nucleation phenomena exists. Indeed, one needs *in situ*, time-resolved measurement of the molecules forming in the plasma when in cools down. Emission spectroscopy is limited to early times, when the plasma is hot enough to emit light and only atomic and diatomic molecules have been observed [2]. Using pulsed laser induced fluorescence [3] of the molecules inside the plasma and time-resolved iCCD acquisition, we show that it is possible to probe the composition of the plasma on a longer time scale and observe, for the first time, the appearance of triatomic molecules. Time resolved LIBS-LIF is a promising technique to characterize the composition of laser generated plasma in time and nucleation phenomena.





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Solvents-dependent selective fabrication of fcc and hcp structured ruthenium nanoparticles during liquid-phase laser ablation

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Ruthenium nanoparticles (Ru NPs) with face-centered cubic (*fcc*) structure exhibit more excellent catalytic activity than that with hexagonal close-packed (*hcp*) structure. However, the formation of *fcc* Ru needs high temperature at least 1800 K, which is a metastable phase and hard to prepare. In this study, we present a tunable fabrication of *fcc* and *hcp* Ru NPs by laser ablation of Ru target in designated solvents. In several organic solvents, including methanol, ethanol and acetone, mixture of *fcc* and *hcp* Ru NPs are obtained, on which encase by graphite carbon layers, while in deionized water only hcp Ru NPs formed. We speculate that the laser-target interaction generated plasma and subsequent quenching process provide an extreme condition (4000~5000 K, 10~15 GPa) for the formation of fcc structure. Importantly, the graphite carbon layers sourced from the thermal decomposition of solvent molecules prevent the further evolution of metastable *fcc* structure into stable *hcp* structure. Clarification of the solvents effects promise the tunable fabrication of metal nanoparticles with desired crystallographic structure during laser ablation in liquids.

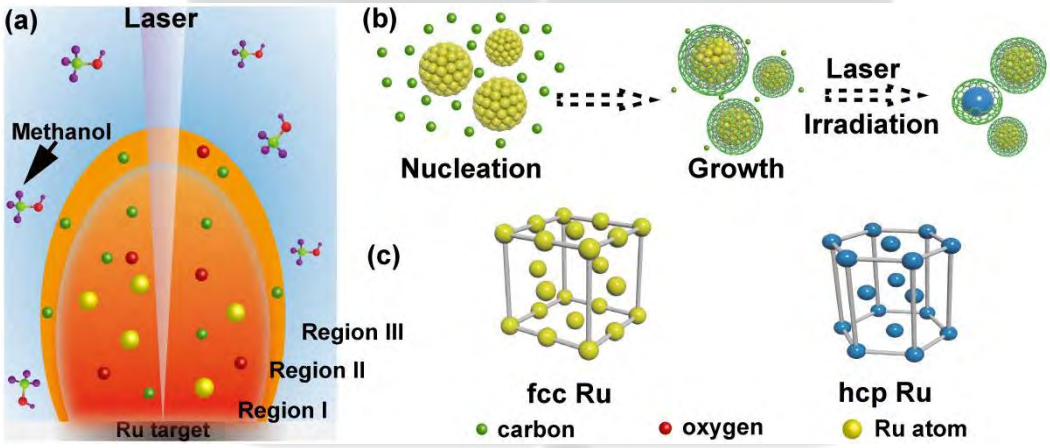

Figure 1 Illustration of the Formation of the Final Products in Methanol. (a) The state of the plasma plume in solution. (b) Nucleation and growth of crystals in Region II. (c) The crystal structure of Ru NPs.

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Laser irradiation synthesized carbon encapsulating ultrafine transition metal nanoparticles for highly efficient oxygen evolution

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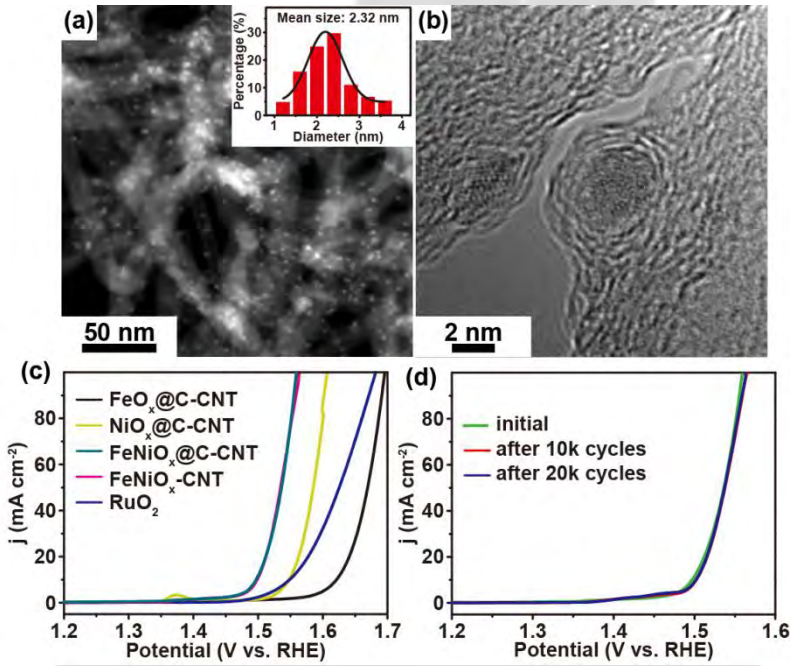

Figure1. (a) HAADF-STEM image and (b) HRTEM image of FeNiO$_x$@C-CNT, (c) the LSV curves of corrsponding catalysts with iR-compensation measured in 1 M KOH at a scan rate of 5 mV s^{-1}, (d) LSV curves of FeNiO$_x$@C-CNT before and after stability test.

Developing efficient electrocatalysts with high activity and stability for oxygen evolution reaction (OER) is of crucial importance [1-3]. Herein, carbon shell encapsulating ultrafine FeNiO$_x$ NPs with an average size of 2.32 nm uniformly disperse on CNT (denoted as FeNiO$_x$@C-CNT) was synthesized via a simple laser irradiation technique. Benefit from the small size and high dispersion of FeNiO$_x$ NPs, the as-prepared FeNiO$_x$@C-CNT composites present excellent electrocatalytic OER activity. As evidenced by the electrochemical results, the composites show a low overpotential of 267 mV at 10 mA cm^{-2} as well as a small tafel slope of 46.29 mV dec^{-1}. Additionally, encapsulation by the carbon shell effectively preserve the FeNiO$_x$ NPs from degrading by the harsh external condition, showing almost unfading electrocatalytic activity after 20000 potential cycles. Importantly, this strategy is universal and could be extended to synthesis other type of carbon shell encapsulating metal-based material (e.g. FeO$_x$@C-CNT, CoO$_x$@C-CNT, NiO$_x$@C-CNT and MnO$_x$@C-CNT), which might provide a new way to construct high-efficiency electrocatalysts.

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Hybrid Hydrodynamic and Molecular Dynamics Model for Simulation of Laser Ablation in Liquids

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Recent development of a computational model combining two temperature model (TTM) for the description of laser excitation and subsequent relaxation of conduction-band electrons, atomistic molecular dynamics (MD) method for modeling of laser-induced phase transformations in a metal target, coarse-grained (CG) representation of the liquid environment, and non-reflecting boundary (NRB) conditions designed to mimic the propagation of the laser-induced pressure waves through the boundaries of the computational domain has enabled detailed exploration of the mechanisms of laser ablation in liquids (LAL) [1-3]. One limitation of the TTM-MD-CG-NRB model, however, is that it does not allow one to study the long-term evolution of laser-induced shock waves in the liquid environment [4] and relies on NRB conditions to represent the effect of the pressure evolution outside the TTM-MD-CG computational cell. In order to address this shortcoming and enable large-scale modeling of laser-induced shock waves, we incorporated a compressible hydrodynamic (HD) model into the general framework of the TTM-MD-CG model. In addition to tracking the shock wave propagation in liquid, the HD model provides a more reliable representation of the feedback of the surrounding liquid region to the behavior of the expanding cavitation bubble modeled with atomistic and coarse-grained MD.

The implementation of the HD part of the model is based on one-dimensional Euler equation [5] solved with the Lax-Wendroff scheme. The boundary cells of the HD spatial discretization overlap with the MD region, and the values of velocity, density and energy predicted by MD are averaged with the ones predicted by the HD model. A plane is set as the boundary for MD, and the pressure and velocity at this plane is controlled by forces acting from both the MD and HD parts of the model. The equation of state for the HD model is fitted to the one predicted in MD simulations to get a consistent representation of properties of liquid environment by the CG MD and HD parts of the model. The results of test simulations illustrated in Figure 1a demonstrate a good agreement between the shockwave propagation predicted in an MD simulation performed with computational cell extended up to 1.25 μm into liquid and the hybrid MD-HD approach performed with a much smaller (and computationally cheaper) MD part of the model.

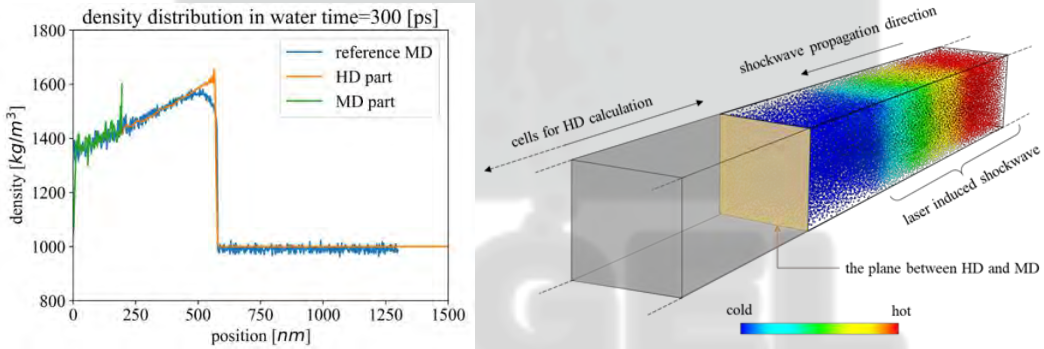

Figure 1. (a) Density distribution predicted for 300 ps after laser irradiation of a Ag target by a 10 ps laser pule by a hybrid MD-HD simulation (orange and green curves) and a pure MD simulation with longer computational cell (blue curve). (b) Snapshot of an interfacial region between MD and HD parts of the model shown for a time before the shock wave reached the interface. The atoms in the MD region are colored by temperature and the orange plane is the boundary of MD domain.

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Electric Field-Assisted Pulsed Laser Ablation Synthesis of MoS_2 nanoparticles for overall water splitting

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Developing and constructing low-cost, high-performance electrocatalysts is vital for overall water splitting. Transition metal chalcogenides shows considerable promise as electrocatalysts for this reaction. However, a large-scale hydrogen production through electrochemical water splitting depends on the availability of earth-abundant electrocatalysts and a suitable electrolyte medium. In this work, we demonstrate the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) performance of electrocatalytic materials can be controlled by their surface functionalization. Herein, we report synthesis of multi-layered MoS_2 nanoparticles (NPs) on Ni-Foam by using electric field assisted pulse laser ablation (EF-PLAL) [1-3]. For HER and OER measurement different samples are synthesised by varying the electric field using in-situ setup. Significantly, as-prepared electrocatalyst synthesized at higher electric field shows the excellent activity for HER and electrocatalyst synthesized at lower electric field for OER activity, affording overpotential of 339mV and 348mV @50mAcm-^{2} current density respectively. Also these electrocatalysts treated for overall water splitting using two electrode setup with cell voltage 1.78V to achieve current density of 10mAcm^{-2}.This study provides favourable electrocatalyst for developing high-performance non-Pt or RuO_2-based clean and environmental friendly energy in alkaline solution.

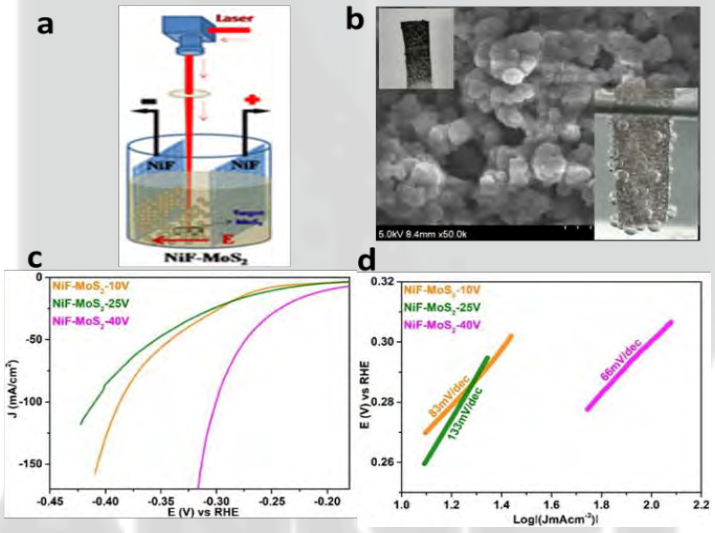

Figure 1. (a) Schematic illustration for the synthesis of NMs by EF-LAL, (b) SEM image (inset. Synthesized NPs on NiF and bubble formation during HER measurement, (c) HER polarization curve and (d) Tafel slope of synthesised NPs.

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Generation of nanoparticles of $BaTiO_3$ by laser ablation in liquids

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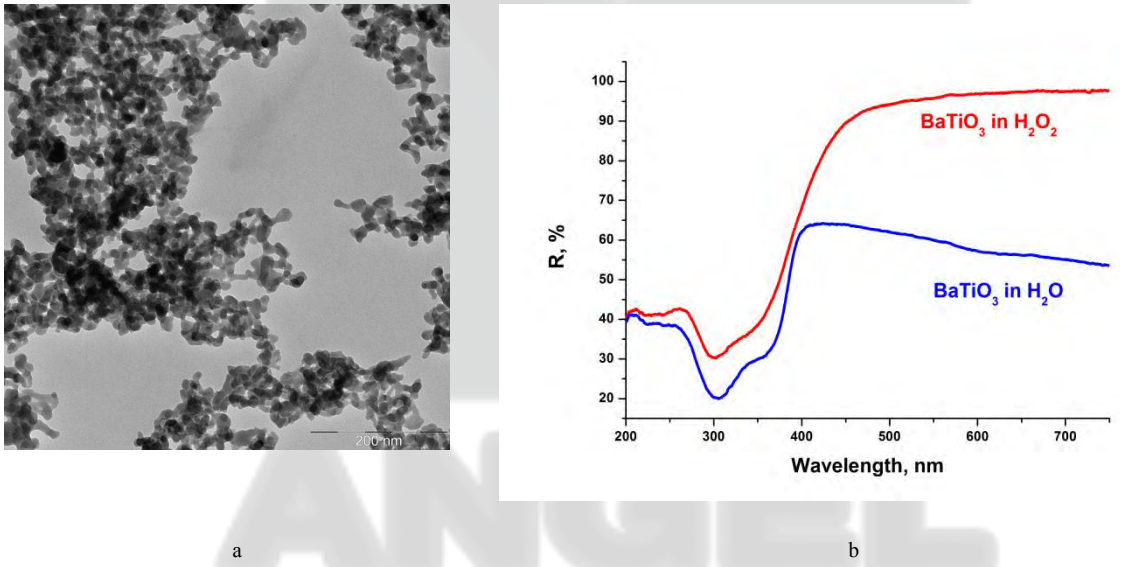
$BaTiO_3$ is ferroelectric with a Curie temperature of 120 °C. Above 120 °C, it is paraelectric with a cubic perovskite-type structure, while from 120 to 5 °C it has a tetragonal phase [1]. In recent years, semiconductor photocatalysts have been attracting increasing attentions in anticipation of employing them as a green and sustainable technology to solve the energy and environmental issues such as the generation of hydrogen and photocatalytic water splitting [2].The technique of laser ablation in liquids was applied for generation of nanoparticles of perovskite $BaTiO_3$ (BTO). Two near-IR laser sources were used, either an Yb: KGW laser operating either at 170 fs pulse duration or 1 ps pulse duration at laser wavelength of 1030 nm and repetition rate of 1 kHz or a fiber Yb laser operating at 1060-1070 nm wavelength range at pulse duration of 200 ns and repetition rate of 20 kHz. Sintered pellet made of $BaTiO_3$ powder was used as the ablation target. Laser ablation was performed in two liquids: in H_2O (MQ grade) and in 30% H_2O_2. BTO nanoparticles were characterized by Raman spectroscopy, X-ray diffraction, and Transmission Electron Microscopy. The morphology of nanoparticles obtained by laser ablation of BTO target in H_2O_2 is presented in Figure 1.



a b

Figure 1. TEM view of NPs of BTO generated by ablation in H_2O_2 at pulse duration of 200 ns. Scale bar denotes 200 nm (a). Reflectivity of BTO nanoparticles generated by laser ablation in H_2O and H_2O_2 (b) with respect to Al_2O_3 ceramics.

Reflection spectra of BTO nanoparticles show that some oxygen is lost under ablation in H_2O similarly to ablation of other oxides [3,4]. The ablation in H_2O_2 results in the reflection spectrum of initial BTO.

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Polarization-sensitive surface-enhanced in situ luminescence spectroscopy of individual *S. aureus* bacteria on gold nanospikes

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Sharp-edged nano- and microstructures exhibit prominent antibacterial properties due to mechanical rupture of the cell membrane [1 – 3]. In our work, nanospikes, fabricated on a 1-μm thick gold (Au) film by laser ablation with the use of 1030-nm femtosecond laser system, were tested as potential elements for antibacterial surfaces and plasmonic luminescence sensors. *Staphylococcus aureus* bacteria were stained by live/dead viability kit, the dead ones getting the red colour, caused by the penetration of luminescent dye propidium iodide through the damaged cell membrane. Photoluminescence was pumped by 515-nm femtosecond laser pulses with linear (Gaussian beam), circular, azimuthal and radial (Laguerre-Gaussian beam) polarizations, exciting the transverse plasmon resonance of the nanospikes and their apex lightning-rod near-field. According to the numerical electrodynamic modeling, the observed strong increase in photolumonescence yield for radial polarization, while slightly lower - for circular and azimuthal polarizations, comparing to low luminescence intensities for the linear laser polarization, was related to their different laser-nanospike coupling efficiencies, enabling time-resolved observation of the bactericidal dynamics of the individual bacteria.

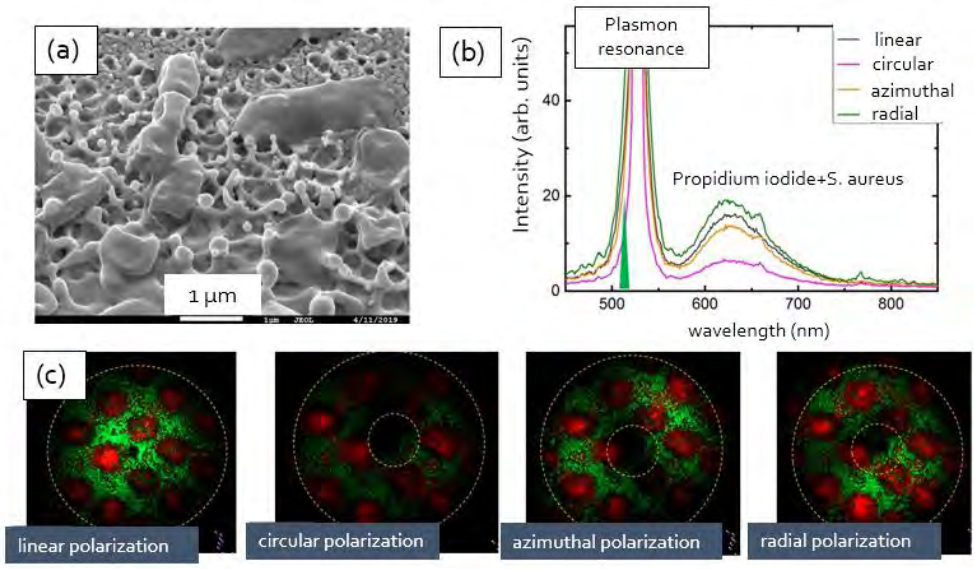

Figure 1. (a) SEM image of laser-fabricated nanospikes on a 1-μm thick gold film; (b) photoluminescence spectra of bacteria on Au nanospikes, acquired at different polarization; (c) microphotographs of the dead (red) bacteria, illuminated with 515-nm laser radiation with the corresponding polarization.

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Effect of liquid environment on single-pulse ablative generation of laser induced periodic surface structures and nanoparticles

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The effect of a liquid environment on the fundamental mechanisms of laser-assisted surface nanostructuring and generation of nanoparticles by laser ablation is investigated in a closely integrated computational and experimental study. A large-scale molecular dynamics simulation of spatially-modulated ablation of Cr in water are performed with a model recently developed for simulation of laser ablation in liquids [1,2]. The simulation reveals a complex picture of dynamic interaction between the ablation plume and water, which involves rapid deceleration of the ablation plume by water environment, formation and prompt disintegration of a hot metal layer at the interface between the ablation plume and water, lateral redistribution and redeposition of a major fraction of the ablation plume, and eventual formation of smooth frozen surface features. A good agreement between the shapes of the surface features predicted in the simulation and the ones generated in single pulse laser ablation experiments performed for Cr in water supports the mechanistic insights revealed in the simulations. Comparison of the results with earlier experimental and modeling studies of ablative surface nanostructuring in air and vacuum [3,4] suggests that the presence of liquid environment can eliminate the sharp features of surface morphology, reduce the amount of material removed from the target by more than an order of magnitude, and narrow down the nanoparticle size distribution. Moreover, the computational predictions of the effective incorporation of molecules constituting the liquid environment into the surface region of the irradiated target and the generation of strong vacancy supersaturation suggest a potential for hyperdoping of laser-generated surfaces by solutes present in the liquid environment.

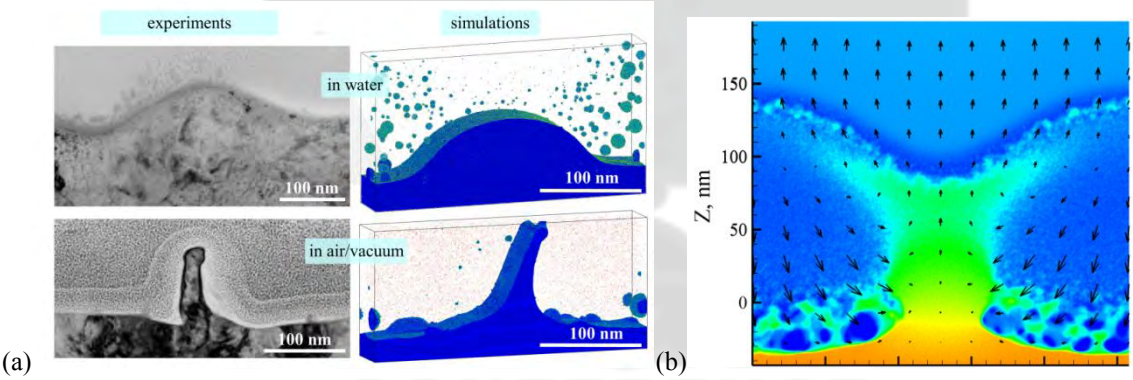

Figure 1. Results of experimental and computational study of the generation of surface morphology on a Cr (001) target irradiated by a single 200 fs pulse in water and vacuum/air: (a) The shapes of the surface protrusions observed in TEM images of cross-sectional slices extracted from irradiated spots and predicted in large-scale atomistic simulations; (b) Contour plot of density distribution predicted in the simulation for a time of 200 ps after the laser pulse.

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Third-order nonlinearity of laser synthesized Ag nanoplates

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Noble metal anisotropic nanoparticles, differently from spherical shaped nanoparticles, exhibit multiple surface plasmon resonances due to their size and shape, moreover, the presence of shaped tips can enhance the electric field by lightning rods effects, resulting in a very high enhancement of metal optical properties. The most common way to synthesized Ag anisotropic nanoparticles is by wet chemical synthesis, but the presence of byproducts, due to the synthesis process, influences the properties of the obtained colloids. Thanks to the combination of laser ablation in liquids and photochemical reactions, it is possible to obtain high purity Ag triangular-shaped nanoparticles with enhanced optical properties[1].

Ag nanoplates were prepared by a two-step method: first, spherical Ag nanoparticles were obtained by laser ablation (Nd: YAG 1064 nm) in water in presence of citrate, then the spherical particles were converted to triangular nanoplates by H_2O_2 under light irradiation. The nature of the nonlinear effect was investigated by the Z-scan technique, using an Nd: YAG laser at 532 nm and laser fluences of 1 J/cm^2 [2].

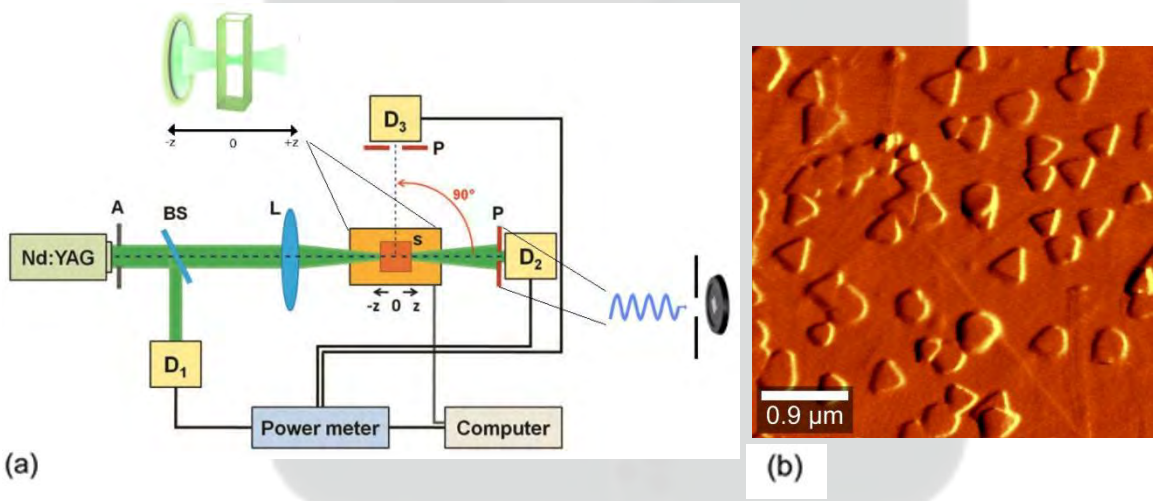

Figure 1 (a) Experimental setup of the Z-scan measurements, (b) AFM image of the Ag nanoplates obtained by chemical-free synthesis.

We determined both the nonlinear absorption coefficient β, the 90° scattering signal S and the refraction one n_2. A high second-order hyperpolarizability c value of 1.1* 10^{-30} esu, essentially attributed to a plasmonic effect, has been measured [3]. Moreover, the good optical transparency in the visible region and a relatively good photo-stability make these colloids comparable with other metal-based materials and interesting for potential applications as saturable absorbers in photonic devices operating from the visible to the IR.

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Solvents dominated phase transition of LAL induced Se colloids probed by in-situ Raman spectroscopy

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The solid-liquid interfacial interactions between nanoparticles and solvent molecules play an important role in the growth and phase transition of nanoparticles in colloidal solution. Though we have studied the spontaneous growth and phase transition process of uncapped Ge and Te NPs by utilizing ex-situ strategies[1-2], we are still trying to find a more precise method to monitor these processes. Herein, we successfully monitor the phase transition process of LAL induced Se colloids using liquid phase in-situ Raman spectroscopy (LPRS). Se colloids with amorphous structure are initially synthesized by laser ablation of Se target in deionized water, which are subsequently treated by centrifugation and redispersion into three typical polar aprotic solvents, including dimethyl formamide, acetone and ethyl acetate. LPRS is used to monitor the phase transition of Se colloids in various polar aprotic solvents under room temperature and pressure. The results reveal a power function relationship between the evolution of amorphous Se to trigonal Se and aging time, further indicate that Se colloids display the fastest rate of phase transition in dimethyl formamide, then followed by acetone and ethyl acetate in turn. Interestingly, the variation tendency in the rate of phase transition is same with the change of viscosity, but inverse with the variation of polarity of three kinds of solvent molecules.

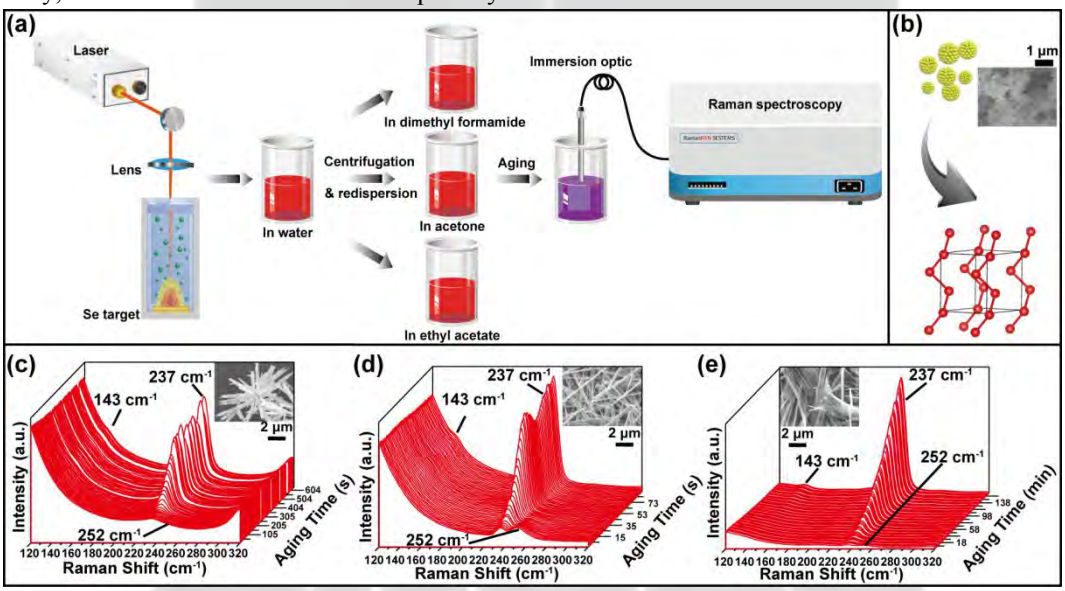

Figure 1. (a) Schematic of the formation and in-situ monitoring the Se colloids in various solvents. (b) phase transition of Se colloids. The in-situ monitoring results of Se colloids phase transition: (c) In dimethyl formamide, (d) In acetone, (e) In ethyl acetate.

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Hybrid nanostructured material of ZnO-Au-rGO using Pulsed Laser Ablation in Liquid for Photocatalytic Degradation of Hazardous Pollutant

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Herein, Solar light active ZnO/Au/RGO ternary nanocomposites were successfully synthesized by the advanced Pulsed Laser Ablation (PLA) technique in liquid medium. The photocatalytic activity of as synthesized ternary nanocomposites was evaluated for the degradation of Methylene Blue(MB) under solar light irradiation. The optimal ZnO/Au-15%/rGO-5% wt. showed the higher degradation efficiency than bare ZnO. The density of the plasmonic Au nanoparticle and carbonaceous Nano matrix of RGO on ZnO could be altered by changing the concentration of gold (5% 10%, 15%,20%wt.) and RGO as (2.5%,5%,7.5%wt.) using by pulsed laser irradiation(PLI) and ultrasonic exfoliation- dispersion method. The synthesized materials were characterized using X-ray diffraction **(**XRD), RAMAN spectroscopy, Field emission scanning electron microscopy(FESEM), High resolution transmission electron microscopy**(**HRTEM), UV-visible spectroscopy, Photoluminescence spectroscopy. The enhanced photocatalytic activity is attributed to the efficient separation and transfer of photo induced electron-hole pairs in ZnO/Au(15%wt.)/RGO(5%wt.) ternary nanocomposites. The photocatalytic material shows high percentage of degradation even after four consecutive cycles. The radical –scavenging test revealed that hydroxyl radicals are the prominent species in the degradation of methylene Blue up to 95%. The superior photocatalytic activity revealed that the ZnO/Au(15%wt.)/RGO(5%wt.) ternary nanocomposites could be a promising material for wastewater treatment and other environmental remediation applications.

Ultrafine Cu nanoparticles anchored on reduced graphene oxide present excellent catalytic performance toward 4-nitrophenol reduction

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Owing to abundant unsaturated metal atoms on their surfaces, ultrafine metal nanoparticles (NPs) have higher densities of catalytic active sites than their bulk counterparts, consequently presenting higher atomic efficiencies and degrees of catalytic activity[1−4].Downsizing copper nanoparticles (Cu NPs) can effectively improve their catalytic activity, but simultaneously ensuring structural stability is always a challenge. In this study, by laser ablating a Cu target in a graphene oxide (GO) solution and reduction treatment, pure Cu NPs (2.0 ± 0.4 nm) are evenly scattered on reduced graphene oxide (rGO). The morphological characterization are shown in Figure. As-prepared Cu/rGO nanocomposites (NCs) are applied as catalysts for 4-nitrophenol (4-NP) reduction. The NCs display higher mass-normalized rate constants and turnover frequencies than most reported Cu catalysts. Owing to the stable conjugation between ultrafine Cu NPs and rGO, the Cu/rGO catalysts have good catalytic stability, that is, the conversion efficiency of 4-NP is still over 92.0% even after 10 successive cycles.

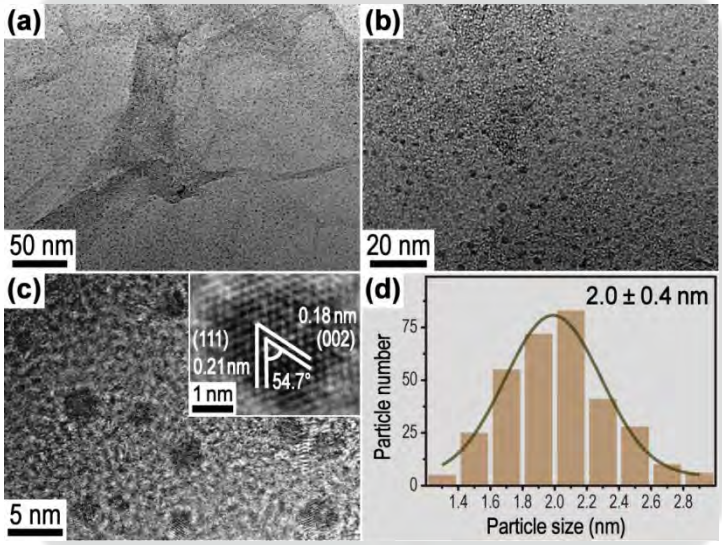

Figure. (a, b, c) TEM images of Cu/rGO NCs. (d) size distribution histogram of Cu NPs.

References:

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Laser ablation in liquids for the assembly of Se@Au chain-oligomers with long-term stability for photothermal inhibition of tumor cells

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For the potential use of Au nanoparticles (NPs) in photothermal therapy, it is important and effective to achieve the uniaxial assembly of Au NPs to allow enhanced absorption in the near infrared (NIR) region [1-3]. Herein, we first presented the construction of amorphous selenium encapsulated gold (Se@Au) chain-oligomers by successive laser ablation of Au and Se targets in sodium chloride solution without other toxic precursors, stabilizers, or templating molecules. Se@Au chain-oligomers showed evidently enhanced NIR absorption and excellent photothermal transduction efficiency (η), which was higher than 47% at 808 nm. After being stored for 1 year, the Se@Au colloids still exhibited outstanding photothermal performance. The cytotoxicity assay demonstrated that there is negligible toxicity of Se@Au chain-oligomers in cells, but cell viability declined to only 1% in phototherapeutic experiments that were implemented in vitro. In intracellular Reactive Oxygen Species (ROS) generation measurements, Se@Au chain-oligomers could trigger a 35.9% increment of ROS upon laser irradiation. The possible synergetic effects between the anticancer function of Se and photothermal behaviors of Se@Au oligomers were intended to increase ROS level in cells. Therefore, such designed Se@Au chain-oligomers of high stability exhibit promising potential for their use as in vivo photothermal therapeutic agents.

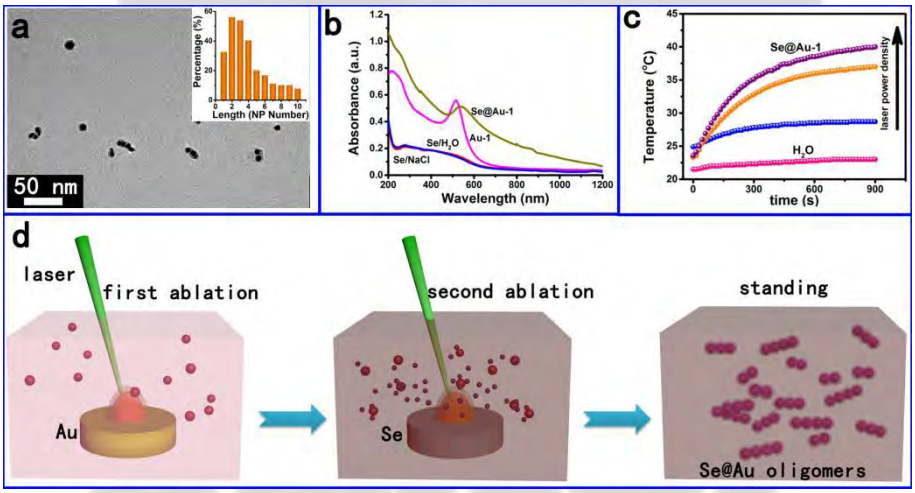

Figure 1 a. TEM images of Se@Au chain-oligomers colloid (Se@Au-1) and the bar graph of percent distributions of various oligomers. b. Optical absorption spectra of pure Se colloids that were ablated in water and aqueous NaCl solution, pure Au colloids (Au-1), and Se@Au-1. c. Temperature elevation of water and Se@Au-1 with increased power densities. d. A schematic of the formation processes of Se@Au chain-oligomers from the first ablation of the Au bulk, second ablation of the Se bulk, to final standing for 48 hours.

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Laser ablation in liquid synthesis and optical temperature sensing of $YGdO_3:Er^{3+}$ nanoparticles

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$YGdO_3:Er^{3+}$ nanoparticles were successfully synthesized by pulsed laser ablation in liquid method [1,2]. The structural and morphological properties of the product are investigated by X-Ray diffraction and transmission electron microscopy. The upconversion photoluminescence properties were investigated in detail. Obvious stark splitting phenomena were observed in the green and red emission bands. The decay behaviors of three emission bands were studied. Based on thermal coupled energy level related upconversion fluorescence intensity ratio, the temperature sensing properties of product were studied. Linear function has been used to reveal the relationship between fluorescence intensity ratio and temperature [3]. Using stark sublevels related emission bands, sensitivity of the temperature sensor was successfully enhanced. These results suggest the $YGdO_3:Er^{3+}$ nanoparticles prepared via pulsed laser ablation in liquid are promising luminescent materials for optical thermometry.

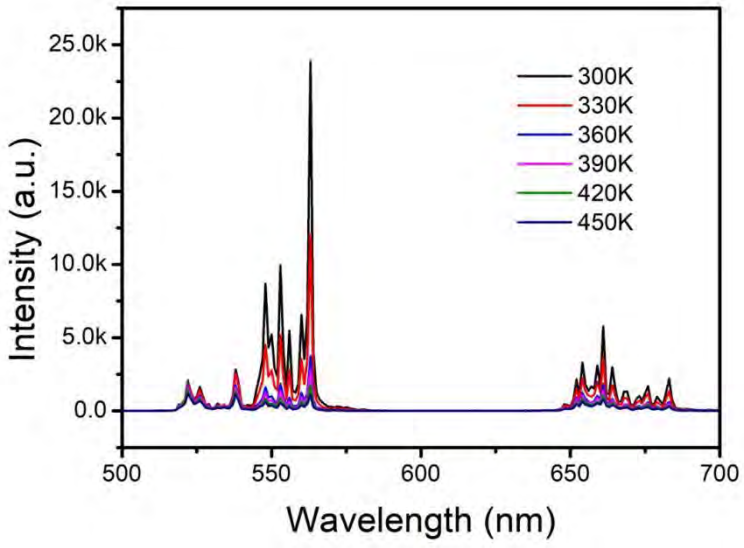

Figure 1 Upconversion photoluminescence spectra of products as a function of temperature

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Effects of laser-generated surfactant-free Ag nanoparticles on soil enzyme activities, bacterial community structure and function

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More attentions should be paid to the effects of AgNPs exposure in soil environments. Crucially, there is still largely unknown of which particular bacterial taxa respond to AgNPs and the changes in soil bacterial community composition after contamination[1]. And, it is of great significance to investigate the effect of AgNPs on soil bacteria-related function[2,3].

Nevertheless, to our knowledge, this is the first report on the effects of surfactant-free AgNPs prepared by laser ablation in liquids (LAL) on soil enzyme activities and bacterial community structure. The purpose of this study is to expound the following questions: (1) Whether there are correlation between soluble and bio-available Ag and enzyme activity and bacterial community; (2) Whether and to what extent soil bacteria respond to AgNPs depends on the dose and exposure time at community level; (3) Whether exposure to AgNPs causes differences in soil function. To this end, the content of $Ca(NO_3)_2$-extractable Ag and DTPA-extractable Ag, and the activities of four types of soil enzymes were measured in soil treated with AgNPs at 2,10, 20 mg/kg after 7, 14 and 30 d of exposure. In addition, the changes of soil bacterial community structure, composition and functional profile were analyzed by high-throughput sequencing to determine the response of soil bacterial community to surfactant-free AgNPs.

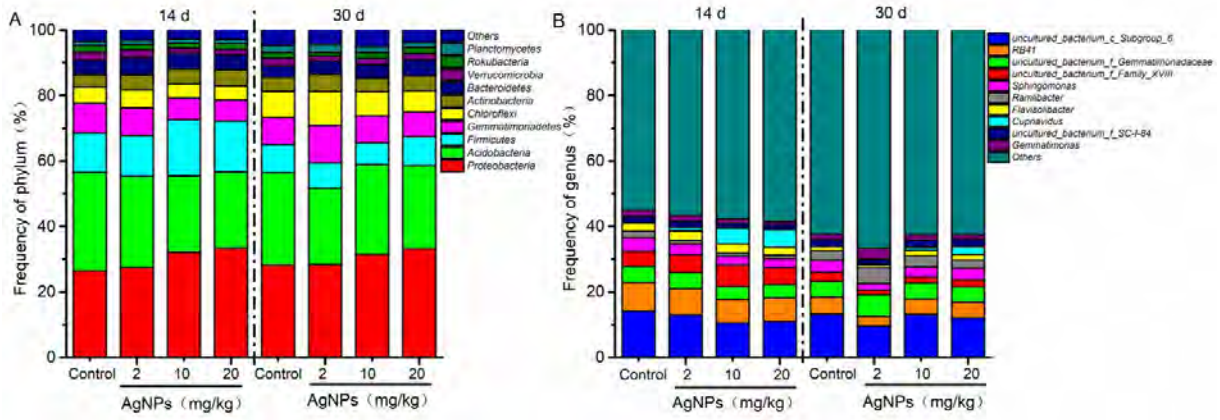

Figure 1. Bacterial community structure at the phylum (A) and genus (B) levels. The soil samples at 14 and 30 days of incubation with 0, 2,10 and 20 mg/kg AgNPs, respectively.

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Rapid Synthesis of PtAg nanoalloys for Oxygen Reduction Reaction

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It is urgently needed to develop efficient and stable electrocatalysts for oxygen reduction reaction (ORR) [1, 2]. Currently, ORR catalysts used commercially are based on Pt nanoparticles with a size of 3-5 nm. Such a small size not only impairs the stability and durability of the catalyst, but it is basically impossible to improve the specific activity by designing the surface structure. Given the low abundance, increasing cost and sustainability issues associated with precious metals such as Pt, it is not difficult to understand why there is an urgent need to reduce the use of Pt. Gradually, alloy strategy was widely adopted, because it can not only reduce the Pt loading but also optimize the geometric and electronic structure of Pt [3]. Herein, we synthesize the PtAg nanoalloys with the nanochain structure by laser irradiation in a few minutes. The PtAg nanoalloys with the nanochain structure have obtained good performance and durability. Importantly, this strategy can be extended to synthesize other Pt-based nanoalloy materials, which may provide a new efficient method for constructing efficient and durable electrocatalysts.

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Laser-Assisted Synthesis of Pd Aerogel with Compressive Strain for Boosting Formate and Ethanol Electrooxidation

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Laser ablating technology is beneficial for producing defect-rich ultra-small nanoparticles, which often need to be loaded on carbon-containing materials to avoid agglomeration. To prevent carbon corrosion of carbon materials, noble metal porous materials are widely used in electrocatalysis due to their high specific surface area and electrical conductivity [1]. In our work, the laser-induced palladium nanoparticles (L-Pd NPs) were assembled anisotropically to generate defect-rich Pd aerogels (L-Pd aerogel) with a three-dimensional porous structure (figure 1). We found that Pd nanoparticles prepared by laser (L-Pd NPs) have dislocations, but no strain. Pd aerogels prepared by hydrothermal method (S-Pd aerogel) have obvious grain boundaries and twins structure, but no dislocation and strain. Commercial Pd/C does not exhibit the above-mentioned defects and strains. L-Pd aerogel has strains and a large amount of dislocations retained with the help of grain boundaries and twins (figure 2). We think that the grain boundaries and twins of the aerogel avoid the diffusion of dislocations in the particles [2-3]. The compressive strain downshifting the d-band center of Pd, caused by the defective structure, thereby weakening the adsorption of the two toxic intermediates H* and CO*. The electrochemical results show that the mass and specific activities of the obtained Pd aerogel for the formate oxidation reaction are 2.26 and 1.99 times higher than those of the commercial Pd/C. The excellent activity of the Pd aerogel for ethanol oxidation reaction has also been observed. After adjusting the gel structure, the mass activity can reach 3.83 A mg^{-1}, which is 2.8 times that of the commercially available Pd/C [4].

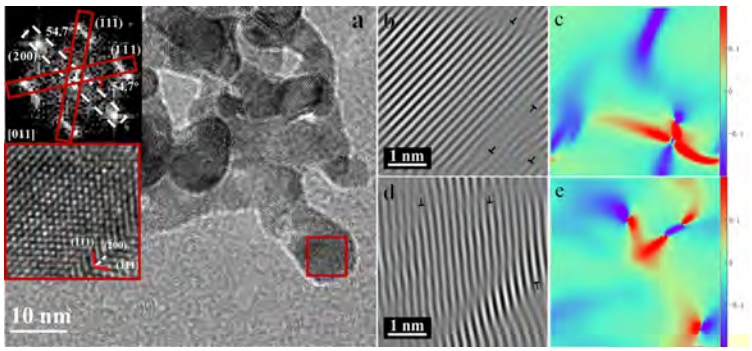

Figure 2. The defect and strain characterizations of the L-Pd aerogel. (a) HRTEM image of the L-Pd aerogel. The insets are the enlarged image and Fourier transform image of the red frame area in (a). (b,d) IFFT patterns of $(\bar{2}00)$ and $(1\bar{1}1)$ planes, respectively. (c,e) Strain distributions of the $(\bar{2}00)$ and $(1\bar{1}1)$ planes, respectively. (The positive and negative values on the scale bar represent tensile and compressive strain)

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