4TH CONFERENCE ON ADVANCED NANOPARTICLE GENERATION AND EXCITATION BY LASERS IN LIQUIDS (ANGEL)

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09–12 MAY 2016

ATLANTIC Hotel
Essen I Germany

PROGRAM

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Venue
ATLANTIC Congress Hotel Essen
Norbertstraße 2a • 45131 Essen/DE

Date
09–12 May 2016

Conference website
www.angel-conference.org

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Dear colleagues,

After decades of intensive nanoresearch, nanoparticles are widely implemented as functional elements on surfaces, into volumes and as nanohybrids, with a wide spectrum of applications such as optics, biomedicine and catalysis or energy science. However, integration of the “nanofunction” into products is still limited due to drawbacks of gas phase and chemical synthesis methods regarding particle aggregation and material variety.

As an alternative synthesis route, nanoparticle generation by lasers in liquids has proven its capability to generate and conjugate totally ligand-free colloidal nanoparticle building blocks. Recent studies highlight unique properties of laser-generated nanoparticles potentially harvested in real-world applications. At the same time, the community discovered novel process routes and describe unique material properties yielded by this exceptional, scalable synthesis method.

ANGEL is the international scientific conference series on Advanced Nanoparticle Generation and Excitation by Lasers in Liquids. The ANGEL Conference series brings the international community together to discuss scientific issues in this context.

After the successful first conference of ANGEL 2010 in Engelberg/CH, ANGEL 2012 took place in Taormina/IT, and ANGEL 2014 was organised in Matsuyama/JP, now ANGEL 2016 will occur in Essen/DE. Following the tradition, we will have no parallel sessions, assembling altogether in one room at the relaxing Atlantic hotel. A bunch of breaks and the poster sessions will further stimulate scientific discussion. Encouraging participation of young researchers, a number of grants and a preconference tutorial is accessible exclusively for students.

Moreover, we intensified the social event program, including a rooftop welcome reception, dinner at a local brewery, a charming theatre evening and the excursion to the UNESCO world cultural heritage “Zollverein”.

Dear young researchers, dear colleagues, it would be a pleasure to welcome you at ANGEL 2016!

Vincenzo Amendola
Conference chair

Stephan Barcikowski
Conference chair

The venue city: Essen

It's perfectly possible, even literally. Describe Essen? Now that's a completely different thing, because this city has not only one face but many aspects. Where should the focus be? Which profile? Which image? The image of coal, steel and soot-blackened sky has been history for a long time – partly due to the City of Culture title in the year 2010. But how can one describe a city for which the words "Industrial Culture" and "Industrial Nature" were practically invented, whose UNESCO World Heritage Site, the Zollverein, represents the figurehead for an entire region? Essen, Centre of Industrial Culture, has had more visitors than ever before in recent years. That's one thing. And there's more:

There is the cathedral of Essen build 1250 a. d. right in the city centre, 10 minutes by public transport from the conference venue. It is open to the public and one of its treasures is the candelabrum dated 1000 a. d. and the Golden Madonna, the oldest fully sculptured figure of Mary in the world. In the south part of the city there is the Baldeney Lake, on which you will have great view from "Villa Hügel". It belonged to the Krupp family of industrialists and was built by Alfred Krupp in 1873 as a residence, now open to the public.

Essen has a lively city centre, with the "Limbecker Platz", "Limbecker Strasse" and "Viehofer Strasse to Kettwiger Strasse" being famous for shopping. A varied gastronomy scene ranging from Michelin star cuisine to the legendary "Currywurst". And – Essen is one of the greenest cities in Germany – an aspect that anyone who has experienced Essen at first hand will admit. The conference hotel is just at the entrance of the large Gruga Park. Enjoy the spring flowers.

We invite you to explore this fascinating city in the context of our extensive social program. It includes a guided tour through (yes, through!) the huge coke oven of the "Zeche Zollverein", hearty dinner at typical German brewery and a visit of the charming show of the GOP Varieté Theatre. But before the conference starts, we will welcome you at the roof of the Venue Hotel, located right in south city district "Ruettenscheid", popular for cafés, dining and pups.

Want more? Another UNESCO World Heritage is also not too far. Only 50 minutes by bullet train (ICE) from Essen you reach the Cologne Cathedral directly in front of Cologne main station. It is Germany's most visited landmark, attracting an average of 20,000 people a day.

Travel

By car, parking

If you use a navigation system, please enter the destination address “Grugaplatz, 45131 Essen”. ATLANTIS hotel offers parking space in its basement garage for guests.

Arrival by plane

The closest airport to the Atlantic Hotel is located in Duesseldorf (see step-by-step directions at www.angel-conference.org). Skytrain brings you to station where three trains “RE” leave hourly. Overall trip from airport customs to hotel lobby takes 40 minutes, you pay 11.50 EUR one way. If you go by taxi you will arrive the hotel within 30 minutes (ca. 65 EUR).
The distance from other international airports like Frankfurt/Main, Amsterdam or Berlin is ca. 3 hours by bullet train (ICE). Therefore, it is recommended to arrive at Duesseldorf airport.

Pick-up service

We will arrange pick-up for participants arriving on Sunday before welcome reception. For this, please send an email to angel@conventus.de (flight number, arrival time).

Public transportation to the venue

For an environmentally friendly arrival, we recommend the utilization of the Deutsche Bahn AG. At Essen Central Station, there are daily more than 120 ICE-, InterCity-, EuroCity- and InterRegio-connections in all directions. From Essen Central Station, you can take a subway (U11) which directly runs you to our hotel in only 5 minutes/4 stations. Exit at station “Messe Ost/Gruga”. The hotel is located directly at the opposite of the subway station. At the conference website, you can find a step-by-step guide from airport to the ATLANTIC hotel.

Costs

Inside Essen, passengers can travel up to three stops on a short-distance ticket which costs 1.50 EUR, or throughout the entire city area on a Fare Class A ticket, which costs 2.50 EUR. Within the VRR area, the same ticket is valid for all buses, trams and light rail services, and for the rapid transit and regional trains of Deutsche Bahn. Other offers include the 4-journey ticket (“Vierer-Karte”), which costs 9.00 EUR for Fare Class A, or the day ticket (Fare Class A for 5.50 EUR). The 4-journey ticket can either be used for four journeys by one person, or one journey by four persons. The day ticket is valid one day long for up to five persons.
Tram tickets can only be bought from the ticket vending machines, which are located at every stop, or from the customer service centres, but not from the driver.

Accommodation at the venue hotel

The Atlantic Congress Hotel Essen is a superior business hotel in Essen's "Ruettenscheid" district, known for restaurants, local-style bars, and small shops. Düsseldorf International Airport is only a 30 minutes' drive or 40 minutes' transport away. From the subway station directly outside the hotel, guests can access the rest of Essen, the 2010 European Capital of Culture. The 248 stylish rooms are luxuriously fitted with multi-head showers, a selection of pillows.

Price: 1 Single room 169 EUR (breakfast included)
1 Double room 189 EUR (breakfast included)


Please quote the special conference booking code "ANGEL 16" when booking to benefit from the special conference rates. Conventus acts as an intermediary for hotel reservations and therefore assumes no liability for reservations. Changes and cancellations have to be addressed to the according hotels directly. The cancellation terms of the individual hotels apply.

Alternative hotels in Essen

Hotel Lorenz***
RüttenscheiderStraße187•45131Essen/DE

Phone: +49 201 799 46
E-mail: info@lorenz-essen.de
Distance: 400m to the conference venue

Rüttenscheider Stern***
Alma Straße 7-9 • 45130 Essen/DE
Phone: +49 201 777729
Distance: 1.1 km to the conference venue

Im Girardet Haus***
Girardetstraße 2-38 • 45131 Essen/DE
Phone: +49 201 87238-16
E-mail: info@das-girardet-haus.de
Distance: 500 m to the conference venue

Motel One***
Kennedyplatz 3 • 45127 Essen/DE
Phone: +49 201 4375370
E-mail: essen@motel-one.com
Distance: 2.8 km to the conference venue

General terms and conditions

Please find our general terms and conditions at www.angel-conference.org.

Did you Know?

Conventus is the professional Congress Organiser of the ANGEL Conference*

*ADVANCED NANOPARTICLE GENERATION AND EXCITATION BY LASERS IN LIQUIDS

conventus
CONGRESSMANAGEMENT

Information for authors and attendees

Oral presentation

Time slots
Keynote talk: 45 minutes
Invited talk: 30 minutes including 5 minutes for discussion
Oral contribution: 20 minutes including 5 minutes for discussion
Please prepare your presentation for the allotted amount of time. Chairs and moderators may interrupt should you overrun your time limit.

Presentation upload: Speakers are requested to upload their presentation to the computer in the lecture hall (room 1). Professional staff and equipment will be available for you to arrange and preview your presentation.

Presentation format: Please bring your presentation on a USB mass storage, CD-ROM or DVD and include all video files. File formats: ppt, pptx and pdf. A Windows-based presentation computer will be provided. To guarantee a smooth running program please upload your presentation in due time – at least 2 hours before your presentation is due to start.

For Mac users: To make sure your presentation is displayed correctly, please:
• bring your presentation as pdf-file with fonts embedded or
• restrict yourself to Arial/Times New Roman (not Times)/Courier New (not Courier)/Symbol/Wingdings when creating your ppt- or pptx-file.

Technical equipment: All technical equipment (presentation computer, video projector, sound system, laser pointer) will be available on-site. It is not possible to use your personal laptop.

Poster presentation

Poster authors are requested to be present at their posters during the official poster session. Please prepare and print your poster in advance to the conference.

The posters should have a size of DIN A0 (84,1 cm x 118,9 cm) preferably in a portrait format (not landscape format). Please do not use any other type of pins than those provided. All poster boards will be labelled with a poster number. You can find your poster number in the program book. The size of the poster boards is 110 cm (width) x 150 cm (height). All posters have to be mounted until 10:00 AM on Monday, 09 May 2016. Posters have to be removed until 10:00 AM on Thursday, 12 May 2016 at the latest. Any posters left on the boards at the close of the poster session will be discarded.

There is both a dedicated poster session **(official poster session will be held on Monday, 09 May 2016, 17:00–19:00)** and multiple breaks in the poster hall (room 2/3 – next door to the lecture hall).

Registration

Registration desk

The registration desk is located in the lobby of the ATLANTIC Hotel Essen.

On-site registration hours

Sunday	08 May	17:00–20:00
Monday	09 May	08:00–18:00
Tuesday	10 May	08:30–13:30
Wednesday	11 May	08:00–17:30
Thursday	12 May	08:00–12:00

Information/Receipts/Confirmation of attendance/Cash payment

Attendees requiring a payment receipt or confirmation of attendance may obtain these documents on-site at the registration desk. Attendees paying by cash are requested to have the exact change ready in Euro.

Registration and fees

At least one author of an accepted oral or poster presentation is requested to register properly in advance to the conference. The full-time-registration includes admission to the conference, coffee breaks, lunches, snacks & drinks during the poster session as well as a main program. The abstractbook (with the complete volume of accepted abstracts) can be downloaded at the conference website www.angel-conference.org.

Fee

Student/Regular	240 EUR/480 EUR

Social program

Welcome Reception (08 May 2016)	free of charge
Social Evening in the restaurant “Dampfe” (09 May 2016)	35 EUR
Excursion (half-day) (10 May 2016)	40 EUR
Gala Dinner in the GOP Varieté (11 May 2016)	40/80 EUR (Student/Regular)

Internet corner and WIFI access

WIFI is available for free throughout the whole conference area. Please ask at the registration desk for the login data.

Special issue

The most significant contributions from ANGEL 2016 will be published in a special issue of a renowed journal (details will be provided by the chairs during the conference).

Best presentation award

The best student oral contribution will be awarded with 100 EUR. The best three student poster presentations will be awarded with 300 EUR, 200 EUR, 100 EUR. All student oral and poster contributions are eligible to the prize. The criteria for the award are relevance, originality, scientific merit and clarity and will be evaluated by the program committee.

Social program

Welcome reception • Sunday, 08 May 2016
We would like to invite you to join the welcome reception at the roof deck of the ATLANTIC Hotel Essen. Have a nice evening with your conference colleagues and exhibitors in a relaxed atmosphere, enjoying drinks and snacks from the buffet and listen to the black & white saxophone quartett.

Date	Sunday, 08 May 2016
Time	from 19:30
Location	ATLANTIC Hotel Essen (roof-deck)
Costs	This event is free of charge (registration requested)
Dress Code	Casual


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© Atlantic Hotel

Social evening in the restaurant "Dampfe" • Monday, 09 May 2016
The next social evening will take place in the restaurant "Dampfe". Tonight is your chance: to warm up with friends and colleagues and have an enjoyable evening in a typical German brewery.

Date	Monday, 09 May 2016
Time	from 20:00
Location	Restaurant Dampfe, Heinrich-Brauns-Strasse 9–15, 45355 Essen/DE
Costs	35 EUR (Buffet, Beverages incl.)
Dress Code	Leisure look
Transfer	Taxi shuttle service (approx. 8 km)


© www.dampfe.de

Excursion • Tuesday, 10 May 2016
We invite you to explore the fascinating city of Essen in the context of our excursion to the most impressive sights. It includes a visit of the "Villa Hügel", a guided tour through (yes, through!) the huge coke oven of the "Zollverein Coal Mine Industrial Complex" and finally we will visit the Essen cathedral treasury.
In the evening either you have a shopping tour through the inner city of Essen or go back to the Atlantic Hotel. The AB/PC Committee is invited to the restaurant "Ruettenscheider Hausbrauerei".

Date	Tuesday, 10 May 2016
Duration	5 h
Costs	40 EUR (fully booked)
Program	13:30 Bus shuttle from ATLANTIC HOTEL
	14:15 Guided tour "Villa Hügel"
	14:45 Group photo
	15:30 Guided tour Zeche Zollverein
	17:30 Guided tour Cathedral-Treasury
	18:15 Hotel transfer or city shopping on your own
	18:30 AB/PC evening in the restaurant "Rüttenscheider Hausbrauerei"

Gala dinner in the GOP Varieté • Wednesday, 11 May 2016
The gala dinner will take place on Wednesday, 11 May from 18:00–22:00 in the GOP Varieté. The registration fee includes a 3 course menu and an spectacular artistic show.

Date	Wednesday, 11 May 2016
Time	18:00–20:00 3 course menu
	20:00–22:00 "Wet the Show" (varieté show)
Location	GOP Varieté, Rottstraße 30, 45127 Essen/DE
Costs	40 EUR Student/80 EUR Regular
Dress Code:	Gala dress
Transfer	Taxi shuttle service (17:45 from ATLANTIC Hotel)


sponsored by Evonik

Sunday, 8 May 2016	Monday, 9 May 2016	Tuesday, 10 May 2016	Wednesday, 11 May 2016	Thursday, 12 May 2016
From 08:00	**07:45–08:45**	**08:00–09:00**	**08:00 09:00**	**08:00–09:00**
	Registration	Poster Coffee	Poster Coffee	**Progr. Comm. Meeting** (Room 7)
	08:45–09:30	**09:00–10:20/Session 4**	**09:00–10:30/Session 6**	**09:00–10:00**
	Musical Intermezzo / Opening	T:10 Shuichi Hashimoto (Tokushima/JP) T11: Tsuyoshi Asahi (Matusyama/JP) T12: Sandra Jendrzej (Essen/DE) T13: Maria E. Shcherbina (Dolgoprudny/RU) P. 22	**INV5: Changhao Liang (Anhui/CN)** T18: Alexander Kanitz (Bochum/DE) T19: Gilles Ledoux (Villeurbanne/FR) **INV6: Wolfgang Kautek (Vienna/AT)** P. 26	Poster Coffee
	09:30–10:15/Keynote Talk			**10:00–11:50/Session 10**
	KN1: Naoto Koshizaki (Hokkaido/JP) P. 16	**10:20–10:50**	**10:30–11:00**	**INV10: Ken-ichi Saitow (Hiroshima/JP)** T29: Jiahao Yan (Guangzhou/CN) T30: Shota Sakaki (Sapporo, Hokkaido/JP) T31: Yoshie Ishikawa (Tsukuba/JP) T32: Marcus Lau (Essen/DE) P. 33
	10:15–10:45	Coffee Break at Posters	Coffee Break at Posters	
	Coffee Break at Posters	**10:50–12:40/ Session 5**	**11:00–12:30/Session 7**	**11:50–12:15**
	10:45–12:35/Session 1	T:14 Vincenzo Amendola (Padova/IT) T15: Georgy Shafeev (Moscow/RU) T16: Dongling Ma (Varennes/CA) T17: Galina Marzun (Duisburg/DE) **FCI Pioneer Lect.: A. Fojtik (Kladno/CZ)** P. 24	**INV7: Hiroyuki Wada (Tokyo/JP)** T20: Weiping Cai (Hefei/CN) T21: R. O. Torres-Mendieta (Castellón/ES) T22: Haohao Wang (Yokohama/JP) P. 27	Closing Remarks & Student Awards Ceremony P. 35
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Welcome Reception Roof deck of the Atlantic Hotel P. 12	Taxi shuttle service **From 20:00** **Social Evening** Dinner in the restaurant "DAMPFE" P. 12	Free Evening	**Gala Dinner: GOP Varieté** 18.00-20.00: 3 course menu 20.00-22.00: varieté show EVONIK INDUSTRIES P. 13	

08:00–20:00 Pick up service
DUS airport international arrival hall

15:00–19:00 Tutorial with practical course
University Duisburg-Essen (building S7, Universitätsstraße 2, 45141 Essen/DE)

16:30–18:30 Program committee meeting
Atlantic Hotel (room 7)

17:00–20:00 On-site registration
Atlantic Hotel (lobby)

From 19:30 Welcome reception
Atlantic Hotel (roof-deck)

07:45–08:45 On-site registration

08:45-09:00 Musical intermezzo (string quartet)

09:00–09:30 Opening of the conference
S. Barcikowski (Essen/DE), V. Amendola (Padova/IT)

09:30–10:15 Keynote talk
Chairs S. Barcikowski (Essen/DE), V. Amendola (Padova/IT)

KN1 Pulsed laser melting in liquid for submicrometer spherical particles – formation mechanism and applications
N. Koshizaki (Hokkaido/JP)

Pulsed laser melting in liquid is a novel technique to produce submicrometer spherical particles of various materials. Raw nanoparticles dispersed in liquid are irradiated by a pulsed laser with moderate fluence (50–200 mJ pulse-1 cm-2), resulting in melting of irradiated particles and subsequent submicrometer spherical particle formation. To understand the formation mechanism, particle heating-melting-evaporation model is often used to explain fluence-size dependence, assuming no heat dissipation. Here we calculated typical temperature time profile of submicrometer spherical particle in water by pulsed laser irradiation by FEM, considering the heat dissipation to water. Promptly after laser pulse ends, temperature decrease starts and proceeds rapidly in several tens of nanoseconds. This result suggests that the energy in the particle is dissipated even during the pulsed laser heating using longer pulse width, resulting in lower attained temperature and high threshold for spherical particle formation. This prediction is experimentally confirmed. Another interesting feature of the product is spherical but single-crystalline. Internal structure of spherical particles is important to understand the formation and crystallization mechanism. Cross-sectional TEM image indicated they are almost perfect single crystal, dominant for smaller particles than 500 nm, and formed in the initial stage of laser irradiation.

10:45–12:35 **Session 1 • Fundamentals of laser ablation in liquids – modelling and spectroscopic studies**
Chairs D. Amans (Villeurbanne/FR), N. Koshizaki (Hokkaido/JP)

10:45 Spectroscopic studies of laser ablation dynamics in liquid phase
INV1 S. M. Park (Seoul/KR)

Laser ablation dynamics of a silver target in aqueous phase was investigated to examine the effects of the ablation laser power, electrolytes in the solution, and magnetic field applied to the plume on the formation and expansion of laser induced plasma plume, bubbles, and silver nanoparticles. The lifetime of the plasma emission increased with magnetic field and electrolytes, but they had no influence on the conversion of laser energy to the energy of laser-induced bubbles formed thereafter. And it turned out that the laser power was the key parameter in determining the size of the bubbles. Besides, we have explored the effects of solvents with different viscosities on the expansion dynamics of the plume and the cavitation bubbles together with the size and shape of nanoparticles.

11:15 Reactions of atomic species in laser ablation plasma in water studied by time dependent atomic spectroscopy
T1
FCI Lecture
T. Sakka, A. Kawasaki, A. Matsumoto, T. Honda, K.-I. Amano
N. Nishi (Kyoto/JP)

We try to clarify the mechanism of nanoparticle generation by liquid phase laser ablation. We have investigated the oxidation of Ti nanoparticles generated by the laser ablation of Ti metal plate in water. When the target was placed in HAuCl4 aqueous solution, we obtained amorphous TiO2 particles, while crystalline TiO2 was obtained in pure water. This suggests that the oxidation occurs after metal nanoparticles are ejected into the liquid phase. However, such evidence is rather indirect. To obtain more direct information we have preformed nanosecond time-resolved atomic absorption spectroscopy. We were successful in obtaining absorption spectra by transmitting the light through the bubble as small as 0.2 mm. From the spectra we obtained absolute amount of the atoms in the ground state, which is the majority among all the atomic energy states. In the experiment the atoms in the bubble ablated from the target and those originating in the solution were detected as a function of delay time. Although there is a difference between the decay times depending on the species, atoms disappear in $\sim$10 μs. This is extremely short compared with the duration of the cavitation bubble ($\sim$200 μs). We believe that nucleation of the nanoparticles occurs only in the early stage in the bubble expansion, and the growth of particles is due to the coalescence of the clusters formed in the early stage.

11:35 Atomistic simulations of laser ablation of metals in water environment
T2
C.-Y. Shih, C. Wu, M. Shugaev, L. Zhigilei (Charlottesville, VA/US)

We report the results of the first atomistic simulations of laser ablation of metal targets in liquid environment. A model combining a coarse-grained representation of liquid (parameterized for water), a fully atomistic description of laser interactions with metal targets, and acoustic impedance matching boundary conditions is developed for the simulations. The model is implemented in a computationally-efficient parallel code, which is used to perform a series of large-scale simulations of laser ablation of thin silver films deposited on a silica substrate, bulk silver and bulk aluminum targets.
In contrast to the laser ablation via phase explosion in vacuum, the phase decomposition in the liquid environment is partially suppressed and the hot metal vapor/clusters ejected from the irradiated target are localized in a low-density mixing region where the liquid is brought to the supercritical state. The main nanoparticle formation mechanism is found to be the condensation of clusters from the metal vapor, followed by coalescence and coarsening within the supercritical water region (the cavitation bubble). The results of the simulations support the notion of the important role of the cavitation bubble in the process of nanoparticle formation, often suggested in interpretation of experimental observation. The simulations also provide interpretation of the formation of a bimodal nanoparticle size distribution commonly observed in experiments.

11:55 Hierarchical mapping of the pulsed-laser ablation dynamics in liquid
T3
A. Plech (Eggenstein-Leopoldshafen/DE)
S. Ibrahimkutty (Eggenstein-Leopoldshafen, Stuttgart/DE)
T. dos Santos Rolo, T. Baumbach (Eggenstein-Leopoldshafen/DE)
A. Menzel (Villingen/CH), P. Wagener, S. Barcikowski (Essen/DE)

Particle synthesis during pulsed-laser ablation in liquid is a multiscale process involving the occurrence of atoms, cluster and nanoparticles, their subsequent interaction and agglomeration, and finally their dynamic confinement within the fluid and vapor formation. In order to resolve these structural levels we combine time-resolved small-angle X-ray scattering (SAXS) with X-ray full-field imaging. The results emphasize the important influence on the confinement of ablated matter within the cavitation bubble on morphology and yield of the nanoparticles. Most

of the material is contained in the bubble and retracted upon bubble collapse. This is a major cause for particle agglomeration and final size distribution. Furthermore quantitative injection of material into the liquid is reserved to a jet-like emission of mass after collapse of a second bubble.

12:15 T4 **Laser interactions with colloidal nanoparticles – mechanisms and control possibilities**

T. E. Itina, A. Rudenko (St. Etienne/FR)

Colloidal nanoparticles have found many applications in various areas as bio-sensing, bio-medicine, catalysis, optics and photonics, new energy sources, cosmetics, etc. Laser systems provide unique possibilities not only for synthesis of these nanoparticles, but also for a control over their sizes. In fact, depending on the experimental conditions, laser interactions with colloidal nanoparticles can either promote nanoparticle growth or induce their fragmentation. Because of the complexity of the physical and chemical processes involved, many of these interesting effects are still unclear and require much more analysis. To better understand these processes, we numerically examine laser interactions with nanoparticles in the presence of a liquid environment. In particular, we focus attention on such effects as (i) laser field propagation, scattering and absorption; (ii) local field enhancement and liquid ionization; (iii) nanoparticle heating and fragmentation; (iv) final aggregation. The effects of laser wavelength and pulse duration, liquid environment, as well as of nanoparticle material, initial particle sizes and concentration are underlined based on the proposed combined modeling.

13:30–15:00 Session 2 • Fundamentals of laser ablation in liquids • Cavitation bubble dynamics

Chairs A. Kabashin (Marseille/FR), Y. Ito (Nagaoka, Niigata/JP)

13:30 INV2 **What can we learn from the bubble diagnoses?**

D. Amans (Villeurbanne/FR)

Pulsed laser ablation in liquids (PLAL) is a versatile technological approach to producing nanoparticle colloids with ligand-free or functionalized surfaces. Nowadays, this popular technique is increasingly employed, but the underlying mechanisms are not fully understood yet. Initially, a laser interacts with a bulk target, creating a hot and dense plasma. The energy exchange between the plasma and the liquid, and the rapid expansion, result in plasma quenching after few microseconds. Then, numerous authors reported the formation of a bubble from which nanoparticles are released. According to small angle x-ray scattering measurements, the bubble cavity should support nucleation and growth of nanoparticles. However, two fundamental features remain largely unknown: the chemical composition and the thermodynamic properties within the bubble. Using time-resolved plasma spectroscopy and ultrafast imaging, we address both issues. From a Rayleigh-Plesset based model, we demonstrated that (i) inertial forces drive the bubble dynamics, (ii) vapor evolution is adiabatic, (iii) the bubble is mainly composed of evaporated solvent and (iv) there is no significant mass exchange during the first bubble oscillation. Moreover we present a fully microscopic approach based on a first-principle study, and propose a scenario of composition gas evolution leading to the first seeds. This approach is illustrated in the framework of alumina.

14:00 T5
Cavitation bubble dynamics and nanoparticle size distributions in laser ablation in liquids
D. M. Bubb (Camden, NJ/US)

Recent work has shown the importance of the cavitation bubble on both the size and distribution of nanoparticles produced by laser ablation in liquids. When the height of the liquid column over the target is varied between 2–15 mm, the mean particle diameter is strongly influenced. In the present work, a 25 ps 1064 nm laser operating at a fluence of 20 J/cm2 is used to create colloidal Au particles suspended in DDI water, and the particle diameter and distribution width becomes larger as the liquid column above the target grows. Likewise, when the pressure is changed from 17–187 kPa, the particle diameter us strongly influenced. In both cases, the size distribution is strongly correlated with the maximum cavitation bubble radius. Shadowgraph images were collected of the cavitation bubble and the radius as a function of time was fit to the Rayleigh-Plesset equation in order to obtain the temperature and pressure during the bubble collapse. The bubble dynamics during collapse determine whether a re-entrant jet forms which appears to influence the size distribution of nanoparticles. The time required for bubble collapse also appears to strongly influence the particle size and we hypothesize that a heuristic model based upon La Mer's diagram might be used to help target desired nanoparticle properties during LAL.

14:20 T6
Effects of multiple irradiations on laser-induced bubbles in laser ablation in liquid observed through high-speed laser stroboscopic videography
Y. Ito, R. Tanabe, S. Kurata, S. Sumiya (Nagaoka, Niigata/JP)

There are many to be clarified in nanoparticle production processes in LAL. We have developed a high-speed laser stroboscopic videography system which enables visual observations at intervals of as short as 1 μs. Using this imaging system, we investigated the dynamics of nanoparticle formation by LAL. In our previous study, we have reported the dynamics of cavitation bubbles induced by LAL and found reduction of bubble size and jet-like shadows in water after multiple-pulse irradiation. Further investigations on the effects of number of irradiated pulses are reported. The cavitation bubble's radius induced by LAL becomes smaller with increasing number of irradiated laser pulses. Jet-like shadow is observed immediately after the laser irradiation along the laser path during LAL in water after multiple-pulse irradiation and rather quickly disappears. The jet-like shadow becomes more evident with increasing number of laser pulses. But it was not observed in freshly filled water that had not yet been irradiated. These shadows disappeared within a few μs and are considered to be microbubbles induced by interactions between nanoparticles in the water and the incident laser. These results clearly indicate that the cavitation bubble's radius becomes small due to attenuation of incident laser pulse energy by interaction with nanoparticles suspending in water.

14:40 T7
Electrical discharge in a laser ablation-induced cavitation bubble
K. Sasaki, Y. Takahashi (Sapporo/JP)

In this work, we tried to produce an electrical discharge inside a laser ablation-induced cavitation bubble. We induced a relatively large cavitation bubble with the maximum radius of approximately 3 mm by ablating a titanium target installed in water. A needle electrode, which was connected to a high-voltage power supply (dc or pulsed), was placed at a distance of 0.5 mm from the gas/liquid boundary of the cavitation bubble at the maximum size, and the titanium target was electrically grounded. At a delay time after applying a pulsed high voltage to the needle electrode, we observed the formation of a swelling from the cavitation bubble. The swelling was lengthened toward the needle electrode. We observed an electrical discharge between the needle electrode and the target when they are connected by the cavitation bubble and its swelling. After the discharge, the swelling became another cavitation bubble with the dynamics of the expansion, the shrinkage, and the collapse. It is noted that both the directions of the swelling lengthening and the discharge channel are perpendicular to the gas/liquid boundary of the cavitation bubble. This experimental result suggests that the electric field is perpendicular to the gas/liquid boundary because of the existence of movable electrical charges in (or on the surface of) the cavitation bubble.

15:30–16:40 **Session 3 • Nanoparticle scale-up and methodological improvements**
Chairs S. Hashimoto (Tokushima/JP), S. M. Park (Seoul/KR)

15:30
INV3

Strategies for the scale-up of laser ablation synthesis of colloids

B. Goekce, R. Streubel, S. Barcikowski (Essen/DE)

Pulsed Laser Ablation in Liquids is an innovative method which is used to obtain colloidal solutions of nanoparticles that show unique properties and are not achievable by conventional synthesis methods. However, this method lacks of key parameters and scaling factors as well as a correlation between these factors and the occurring operating costs. During the laser driven synthesis cavitation bubbles filled with nanoparticles are formed. These cavitation bubbles along with already dispersed nanoparticles in the solution are the two major factors that limit the energy that can be coupled into the target material by shielding subsequent laser pulses. While the latter shielding effect can be avoided by suitable fluid handling avoiding the former is more difficult due to the lifetime ($\sim$100μs) and the size ($\sim$100μm) of cavitation bubbles which depend on the laser energy and pulse duration. In this work we present strategies to scale up the process by enhancing the productivity of the synthesis. One approach utilizes a high-repetition rate laser system consisting of a 500W ps-laser source and a laser scanner that reaches a scanning speed of up to 500m/s. This unique system enables spatial bypassing the cavitation bubble and thereby applying most of the laser energy to the target. The cavitation bubbles are laterally separated by varying the scanning speed in order to obtain the best scanning parameters. A further approach includes a multi-beam scanner that is capable of splitting up the laser beam into up to 144 separate beams. Thus, higher energies can be applied to the target without forming too large cavitation bubbles. These strategies are discussed and productivities of up to 5 gram per hour are demonstrated in a continuous process.

16:00
T8

Controlling mass transport during pulsed-laser ablation in liquids using a high-speed rotating target

N. Chaoui, A. Resano Garcia, Y. Battie, A. Koch
A. En Naciri (Metz, Forbach/FR)

In its principle, Pulsed-Laser Ablation in Liquids (PLAL) appears as simple and versatile method to produce nanoparticles. However, due to its numerous processing parameters and their complex interdependence, this method has the main disadvantages of i) being hardly reproducible and ii) having a relatively weak productivity. The complexity of PLAL is well illustrated by the increase of the NPs concentration in the liquid as a function of irradiation time which may lead to an increasing absorption and/or scattering of the laser beam during the process. In a very recent paper, we showed that, even when using a laser wavelength which is far from the resonance band, the laser beam can be strongly attenuated due to the development and slow diffusion of a dense NPs layers in front of the target as the ablation proceeds. As a consequence, the ablation yield during the process can be considerably reduced. This raises the question of mass transport in PLAL that has been rarely considered in the literature up to now. In order to address this issue, we propose a novel design of PLAL setup, based on the irradiation of a high-speed rotating target. We show how the control of the nanoparticles mass transport allows us to considerably improve both repeatability and productivity of the process. Furthermore, the configuration of the proposed system enables the quantification and monitoring of both attenuation factor of the laser beam and ablation yield as a function of exposure time. Finally, the links between the laser energy attenuation, the ablation yield and repeatability of the colloids properties are revealed and discussed in terms of mass transport.

16:20 T9 **Pulsed laser ablation in high pressure liquid during noble metal nanoparticles production**

M. Dell'Aglio, G. Valenza, R. Gaudiuso (Bari/IT)
M. Lopez-Claros (Malaga/ES), A. Santagata (Potenza/IT)
A. De Giacomo (Bari/IT)

In this work the effect of liquid pressure on Pulsed Laser Ablation in Liquids (PLAL) for the production of noble metal Nanoparticles (NPs) in water was investigated by Optical Emission Spectroscopy (OES), imaging and shadowgraph experiments, in a range of pressure between 1 to 120 Bar. In this frame the study of how the plasma features and the consequent cavitation effects depend on the external pressure were correlated to the NP size and stability, which were investigated by means of Surface Plasmon Resonance spectroscopy, Z-potential and microscopy techniques. Finally, fundamental aspects of high-pressure PLAL are discussed in terms of plasma processes, NP production yield and NP size.

16:40–17:00 **Group photo**
Meeting Point: Lobby ATLANTIC Hotel

17:00–19:00 **Poster session** (see page 36)
Poster authors are requested to be present at their posters during the official poster session.

From 20:00 **Dinner at restaurant "Dampfe"** (see page 12)

08:00–09:00 Poster coffee (see page 36)

09:00–10:20 **Session 4 • Fundamentals of laser fragmentation in liquids**
Chairs V. Amendola (Padova/IT), T. Asahi (Matusyama/JP)

09:00
T10
FCI Lecture

Transient extinction spectroscopic study on laser-gold nanoparticle interaction

S. Hashimoto (Tokushima/JP)

The interaction of gold nanoparticles (AuNPs) with lasers have been a subject of intense research efforts for more than 15 years. Physics involved in the event is complicated. Our group has been involved in this problem for a couple of years[1]. Here we show our observation for a low irradiance regime where only photothermal mechanism prevails. We applied the transient extinction spectroscopy assisted by the transmission electron microscopy (TEM), revealing that the lase-NP interaction is described by particle heating-cooling, radial-dependent medium temperature or refractive index changes, and bubble nucleation, expansion and collapse. Simultaneously, postmortem TEM observation suggested the formation of small particles presumably due to particle size reduction. We show that the bubble dynamics and the particle size reduction are closely interconnected. We found that bubbles can be suppressed by applying high pressures exceeding the critical pressure (22.1 MPa for water) of the medium. Here we focus two fundamental points. Plech group[3] and Lapotko group[4] independently discovered that the bubble formation threshold decreased monotonously with increasing AuNP diameter […]

09:20
T11

Time-resolved fluorescence spectroscopic study on the mechanism of pulsed-laser ablation of organic microcrystals in water

T. Asahi, K. Shikama, T. Ishikawa, Y. Ishibashi (Matusyama/JP)

We demonstrate the time-resolved fluorescence spectroscopic study on ns-laser induced heating of organic microcrystals dispersed in water. Aqueous colloids of perylene microcrystals having a sub-mm particle size prepared by a re-precipitation method were used as a sample. The time-resolved fluorescence of the sample irradiated by a single-shot nanosecond laser pulse was measured with a gated-image intensifier CCD spectrometer, and the laser-intensity dependent fluorescence spectra was analyzed in comparing with the temperature change of the fluorescence spectra under a very weak excitation condition. We succeeded in direct measurements of the temperature of microcrystal during and after intense nanosecond pulse excitation. The value of the temperature elevation was estimated about 100°C at the intensity of 10 mJ/cm2. On the other hand, at fluences above 50 mJ/cm2, a similar fluorescence to that of molten perylene was observed, which indicates that microcrystals undergoes to melting in a nanosecond time scale by intense ns-laser pulse excitation. We conducted also a numerical simulation of the laser heating dynamics of organic microcrystals in water by taking into accounts of relaxation processes of the excited states and cooling process by the surrounding water. The laser heating mechanism will be discussed in details based on both the experimental and simulation results.

Student presentation

09:40 T12

What causes the instability of ligand-free, laser-generated noble metal colloids? – A kinetic study

S. Jendrzej, B. Gökce (Essen/DE), V. Amendola (Padova/IT)
S. Barcikowski (Essen/DE)

Since pulsed laser ablation in liquids is a new technique for the synthesis of colloidal noble metal nanomaterials, most researches focus on the nanoparticle formation mechanism, productivity and the specific functionalization of nanoparticles in water. However, studies regarding the time-dependent nanoparticle stability are rarely performed, although the change of nanoparticle properties is related to almost every nanoparticle colloid and has a high impact on the reproducibility of the size quality. Besides common nanoparticle aging, which arises from the tendency to reduce the Gibbs energy under formation of coalesced nanoparticles, atom clusters generated during laser irradiation process have a high impact on the nanoparticle stability. UV/VIS spectroscopy reveals a significant change of the optical properties of laser-fragmented Pt nanoparticles at same mass concentration. The extinction increase and further analytical methods give strong indication for a growth mechanism of the post irradiated Pt colloid, where the maximum growth tendency is observed immediately after laser fragmentation, while a gradual growth even continues after a measurement period of 50 days. We assume a nanoparticle growth at the expense of atom clusters, whereby the atom cluster concentration decreases over time. The rapid growth (< 1 d) is kinetically modelled by barrierless growth, while the prolonged growth is described by a combination of coalescence and Ostwald ripening.

10:00 T13

Transfer equation for the description of the dynamics of Au and Ag Nanoparticle ensemble in liquid under pulsed laser irradiation

M. E. Shcherbina, N. A. Kirichenko, A. A. Serkov, I. I. Rakov (Moscow/RU)

Laser-assisted fragmentation of Au and Ag nanoparticles in liquid under nanosecond laser pulses is examined experimentally by measurement of the size distribution function of particles at several moments of time. Initial concentration of particles is about 1014 cm-3 with typical size of order 30 nm. Theoretical approach based on the transfer equation in phase space of particle sizes is proposed to describe the phenomena under consideration. Constructed mathematical model is implemented with parameters corresponding to the conditions of the experiments concerned. The results of mathematical simulation are in a good agreement with the experimental data. Suggested method allows to take into account factors, which can influence on the dynamics of the process, such as, for instance, external fields or spatial heterogeneity within an area of laser impact.

10:50–12:40 **Session 5 • Nano-alloys and core-shell particles – Synthesis and applications**

Chairs S. Barcikowski (Essen/DE), A. Müller (Pasadena, CA/US)

10:50 T14 FCI Lecture

Nanoalloys and laser ablation synthesis in solution – a joint venture with reciprocal advantages to the two fields

V. Amendola (Padova/IT)

Laser ablation of solid targets in liquid environment allows the production of nanoparticles (NPs) with peculiar surface chemistry and a large variety of compositions, included metastable phases and nanocomposites. Despite this technique is the subject of an increasing interest for its potential in the preparation of nanomaterials, and seminal investigations were performed in recent years to understand the physical and chemical processes involved, there are still several issues related to the control of products and to the complete understanding of NPs formation mechanism.
Bimetallic nanoalloys are a useful case-study for laser ablation, because one can exploit the different reactivity of the two elements composing the solid solution to obtain insights about the mechanism of NPs formation. In particular, by the morphological analysis of laser-generated Au-Fe and Ag-Fe NPs as a function of the reactive environment exploited for the synthesis, we were able to speculate about the role of solvent reactivity and cavitation bubble on the final products. On the other hand, these noble metal nanoalloys consist of metastable phases not achievable by competitor methods such as wet chemistry synthesis. Therefore laser ablation can play a relevant role in the expansion of the type of nanoalloys currently available. Interestingly, the multiple functions of these nanoalloys have been exploited for plasmonics, surface enhanced Raman scattering (SERS), photonics and nanomedicine.

11:10 T15

Laser alloying of Co nanorods and Al nanoparticles in liquid

G. Shafeev, E. Barmina, I. Sukhov, G. Viau (Moscow/RU)

Experimental results are presented on laser alloying of Co nanorods with Al spherical nanoparticles by laser exposure of their mixture in liquid ethanol. The nanoparticles are characterized by Transmission Electron Microscopy and Disk Measuring Centrifuge. It is demonstrated that the initial morphology of nanoparticles is modified with time of laser exposure. Co nanorods are transformed into Co nanospheres eventually covered by a layer of Al. The evolution of the size distribution function is studied with the time of laser exposure. The size of nanoparticles takes a stationary level, which remains stable upon the time of laser exposure. The results are discussed from the view point of interaction of molten nanoparticles inside the cavitation bubble filled with liquid vapor.

11:30 T16 FCI Lecture

Development of Au and AuPt alloy nanoparticles via pulsed laser ablation for catalytic applications

D. Ma (Varennes/CA)

Nanofabrication based on advanced laser techniques has become a popular top-down approach for preparing metal nanoparticles (NPs) in solution. In this presentation, I will introduce some of our work on the preparation and catalytic application of Au and AuPt alloy NPs. Basically, stable colloidal Au or AuPt NPs were fabricated via pulsed laser ablation in water, which leads to almost naked surface that is highly beneficial for catalytic applications. They were further combined with various supports for catalytic investigations. For instance, Au NPs decorated CeO2 nanotubes exhibit remarkably higher catalytic activity for nitrophenol reduction in comparison to similar catalysts composed of chemically prepared Au NPs. The important role of unique surface chemistry of laser fabricated Au NPs in catalysis was further demonstrated in CO oxidation reaction in gas phase. In addition to showing considerably enhanced catalytic activity, laser-Au NPs show quite strong surface plasmon resonance. Very recently, we used laser-Au NPs for plasmon enhanced photocatalysis. E.g., we synthesized a new class of materials: plasmonic Au NP decorated upconverting- NaYF4:Yb3+, Er3+, Tm3+ -core@porous-TiO2-shell

microspheres with uniform size distribution, high catalytic activity and excellent stability. The work represents the first demonstration of exploiting both plasmonic and upconversion concepts in photocatalysis towards generating a broadband photocatalyst.

Student presentation

11:50 T17 **Nickel-molybdenum nanoparticles for the substitution of platinum in electrocatalysis**

G. Marzun, P. Wagener, A. Levish, V. Mackert (Duisburg/DE)
S. Barcikowski (Essen/DE)

Studies to find a replacement of the scarce and expensive noble metal platinum for hydrogen evolution reaction were done. We synthesized nickel-molybdenum nanoparticles with different compositions by pulsed laser ablation in different solvents and studied their alloy formation. For this purpose, targets of desired composition were formed by pressing and subsequent sintering of mixed nickel and molybdenum micro powders. While mostly defined alloy nanoparticles were formed in acetone, according to TEM-EDX pulsed laser ablation in water resulted in a formation of nanoparticles with mixed composition. However, XRD analysis of nickel-molybdenum nanoparticles in water revealed a significant lattice strain for nickel in the molybdenum rich colloids and smaller crystallites. Electrocatalytic investigations indicated an enhanced activity for hydrogen evolution reaction. Thus laser-generated nickel-molybdenum represent a high potential of non-noble materials to substitute platinum for electrocatalytic applications.

12:10 INV4 FCI Lecture **Pioneering pulsed laser synthesis of colloids**

A. Fojtik (Kladno/CZ)

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 1992 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 […]

13:30–18:15 Excursion (see page 13)

From 18:30 PC/AB evening in the “Ruettenscheider Hausbrauerei” (Girardetstraße 2, 45131 Essen/DE)

08:00–09:00 Poster coffee (see page 36)

09:00–10:30 **Session 6 • Reactive laser ablation in liquids**
Chairs D. Amans (Villeurbanne/FR), C. Rehbock (Essen/DE)

09:00
INV5

Activity and reactivity of colloidal nanoparticles generated by pulsed laser ablation in liquids

C. Liang (Anhui/CN)

Liquid-confined plasma plume induced by laser-target interaction provided an extreme non-equilibrium condition for nanoparticles (NPs) growth. Those NPs with narrow size distribution, high reactivity, metastable structure and uncapped surfaces, are great benefit to explore the unusual physical and chemical properties of nanoparticles, especially those induced by the size/surface effects. In this talk, first we would like to show our efforts on the formation, structure and property investigation of elements such as Ge, Te, Se colloidal NPs. Secondly, we present great potentials of reactive LAL-generated colloidal NPs as unique precursors for semiconductor doping and assembly of new functional materials [1-5]. As example outlined as Figure 1, assisted by external experimental conditions such as light, high temperature, high magnetic field, the mixture of LAL-generated colloids A and B, can display unique growth process, as well as formation of designed materials and structures for energy and environmental applications.

Student presentation

09:30
T18

Ultrashort pulsed laser ablation of iron in different liquids – from the USP ablation law to the generated nanoparticles

A. Kanitz, J. S. Hoppius, A. Ostendorf, E. L. Gurevich (Bochum/DE)

For the generation of iron-based nanoparticles, pulsed laser ablation in liquids (PLAL) is a promising but challenging approach. Due to its versatility, PLAL yields the opportunity to generate different iron-based nanoparticles by simply changing the target, liquid or laser parameters. In our work, we used femtosecond-PLAL to generate iron-based nanoparticles from a pure iron target. The advantage of femtosecond laser ablation is that the energy deposition is mainly decoupled from the ablation mechanism. In order to understand the controllability of the nanoparticle generation process, the investigation covered two different aspects of the generation process: Firstly, the ablation process and ablation rate were systematically investigated by in-situ optical emission measurements and ex-situ microscopy techniques. It could be confirmed that the ablation law for ultrashort pulse ablation is also valid for metals within the same liquid. However, the total ablation rate significantly differs from one liquid to another. With respect to the broad range of possible parameters and since the ablation rate is of fundamental importance for further industrial application, we secondly choose to investigate the generated nanoparticles at the point of maximum ablation rate. They have been investigated by TEM, XPS, Raman and VSM. Finally, the obtained results will be compared to other experimental results of iron-based nanoparticles in order to understand the underlying mechanisms of the nanoparticle generation of reactive materials such as iron.

09:50
T19

Effect of the ligand-metal bindings on the luminescence of nano-ruby

G. Ledoux, J. Lam, A. Chemin, C. Martinet, A. Cornet, K. Lebbou
C. Dujardin (Villeurbanne/FR), F. Chaput (Lyon/France), B. Gökce
S. Barcikowski (Essen/DE), D. Amans (Villeurbanne/FR)

When doped with Cr3+ the corundum phase (α) of alumina (Al2O3) is called ruby. It shows interesting optical properties such as the pressure dependence of its R fluorescence lines which is commonly used as a continuous pressure sensor. In order to check the validity of Laplace-Young pressure conjecture on small particles ruby is a candidate of

choice. Synthesis of α-Al2O3 nanoparticles, with an average size larger than 30 nm, has been reported previously. But no evidence of α-Al2O3 nanoparticles with sizes smaller than 10 nm has been reported.
Using 2-[2-(2-methoxyethoxy) ethoxy] acetic acid, we have successfully synthesized highly reproducible monodisperse luminescent nano-ruby. The obtained size distribution shows little dependence on the laser source, with about 4 nm median size, and less than 1 nm standard deviation. In this work, we measure the pressure dependence of the Cr3+ luminescence and show that for pressures under 11 GPa, the shift of the R1 line in the nanoparticles is identical to the one observed in bulk ruby. The inner pressure of the nano-rubies is then directly measured from their own luminescence. If Laplace-Young conjecture was relevant for solid matter, we should measure a luminescence shift, compared to bulk rubies. However, this is not the case; the surface energies can drive the thermodynamic stable phase for nanoparticles, as depicted by Mc Hale et al., but this change definitively does not correspond to a pressure induced shift in the phase diagram.

10:10
INV6

Laser assisted synthesis of colloidal nanoparticles in various fluids

W. Kautek, N. Lasemi, O. Bomati-Miguel, U. Pacher
C. Rentenberger, K. Richter (Vienna/AT)
R. Lahoz (Zaragoza/ES)

Laser-assisted generation of metal nanoparticles (NPs) in liquids promises high purity which cannot be reached by conventional manufacturing routes since no chemical precursors are required [1]. The complex mechanism involves a series of steps extended over many orders of magnitude in time [2] involving e.g. ablation, plasma expansion inside a gas bubble, the penetration of condensed nano-sized phases into the liquid, but also secondary beam-colloid interaction (Fig.). An overview of recent investigations of the laser generation of pure colloidal aqueous and non-aqueous fluids is presented. Few attempts exist to quantify the influence of the target material conversion in air in a multi-pulse experiment [3]. Moreover, incubation investigations for solid-liquid interfaces practically are non-existent. Therefore, a systematic investigation of the behaviour of various fluids on this phenomenon have been undertaken in order to elucidate the influence of laser wavelength and pulse repetition rate on colloidal core-shell properties.

11:00–12:30 Session 7 • Inorganic nanoparticles and doped 2D structures

Chairs K. Saitow (Hiroshima/JP), T. Sakka (Kyoto/JP)

11:00
INV7

Inorganic nanoparticles prepared by laser process in liquid and their applications

H. Wada (Tokyo/JP)

We prepared inorganic nanoparticles by laser process in liquid which were summarized in this talk. (1) Upconversion nanoparticle Y2O3: Er, Yb: Prepared nanoparticles were highly crystalline and existence of dopants in a nanoparticle was verified by transmission electron microscopy-energy dispersive X-ray analysis (TEM-EDS). Less-invasive cancer care, photodynamic therapy (PDT), was improved by the combination of upconversion nanoparticles and photo sensitizer. In vitro experiment using cancer cells was performed to investigate this effect. (2) Afterglow nanoparticle Sr2MgSi2O7: Eu, Dy: Capping nanoparticle with polyethylene glycol (PEG) was investigated to improve afterglow properties. (3) Yellow phosphor YAG: Ce: The nanoparticles which were single phase of YAG without YAP and YAM were also obtained by this method. Photoluminescence properties were changed by nanosized structure. (4) Semiconductor nanoparticles Si, InP: Laser wavelength and fluence dependencies were investigated. One application of semiconductor nanoparticle is solar cell. Nozik et al. proposed quantum dot sensitized solar cell which had the potential of high conversion efficiency. To investigate the effect of Si nanoparticles, this solar cell was demonstrated. (5) Spherical nanoparticles of TiN (laser melting in liquid): Increase in fluence increased the diameter of spherical particle. The surface of the spherical nanoparticle was slightly oxidized.

11:30 Metal NPs-decorated FeOCl nanosheets induced by laser ablation in
T20 solutions and their Local reaction-driven planar growth
FCI Lecture W. Cai (Hefei/CN)

The nanoplate-like iron oxychloride (FeOCl) has important applications in such as low-dimensional conductors, secondary lithium batteries and Fenton-like catalyst, etc. [1-3] The FeOCl is usually prepared by the chemical vapor transport technique, which is time consuming and need high temperature. Controlled fabrication of FeOCl nanosheets and especially, metal nanoparticles (NPs)-decorated ones has been expected.
In present work, we present a general route to fabricate the metal NPs-decorated FeOCl nanosheets based on laser ablation of metal targets in FeCl3 solutions. Using this method, we could obtain a series of metal NPs-decorated FeOCl nanosheets, which depend on the used metal targets including Au, Pd, Pt, Fe, Cr, Ti, Al, etc. The FeOCl nanosheets possess (010) preferred orientations. It has been revealed that formation of the metal NPs-decorated FeOCl nanosheets is attributed to the plasma plume-induced local reaction, which drives the planar growth of FeOCl. These NPs-decorated FeOCl nanosheets have exhibited good thermal stability and abundant surface functional groups, which adsorbs abundant H2O molecular and oxygen species. Such materials have also important application potential in gas sensors. As an example, we will report the sensing properties to HCl gas at room temperature for the Au NPs-decorated FeOCl nanosheets, which have exhibited high sensitivity and selectivity to HCl.

Student presentation

11:50 Direct laser synthesis of gold nanoparticles and immobilization on
T21 graphene sheets
R. O. Torres-Mendieta, D. Ventura Espinosa, S. Sabater, J. Lancis, J. Mata
G. Minguez Vega (Castellón/ES)

Graphene decorated with metallic nanoparticles (MNPs) promise to be ideal hybrid systems that can be used in optoelectronic and electronic applications, since is expected the exploitation of a combination of electronic characteristics in graphene and optical characteristics in metallic nanostructures. The design of such graphene-metal assemblies is traditionally achieved by in-situ reducing of metal salts in the presence of graphene derivatives. However, this methodology does not avoid the production of chemical waste and the presence of co-ligands in the nanoparticles formed leading to cross-chemical undesired effects. In this work we propose the production of metal nanostructures and direct immobilization onto graphene sheets in a single reaction stage using a strategy that does not require reductor or stabilizer agent. Pulsed Laser Ablation in Liquids (PLAL), a top-down strategy where pulsed laser radiation is used to generate NPs from a high purity gold disc surrounded by a graphene-oxide suspension by means of ablation phenomena, the produced material then is naturally hooked to the graphene surface. In the other and, the interaction between the graphene-oxide sheets and the laser radiation promotes its reduction. The results reveal that the graphene-oxide sheets acts as a support of the NPs and has an influence on their size, and in the whole process there is no any chemical waste production. This work constitutes a clear improvement over the synthesis of graphene-metal assemblies and a practical methodology which may inspire future developments of efficient decoration of graphene and related materials.

12:10 Fabrication of YVO4:Eu3+Ovoid-like nanoparticles by laser ablation in liquid
T22 H. Wang, O. Odawara, H. Wada (Yokohama/JP)

During the past decade, dramatic efforts have been dedicated to exploring rare-earth doped nanoparticles, whose optical properties and low cytotoxicity are promising for biological application. YVO4:Eu3+ is an important red emitting phosphor while it was used widely in color television, high-pressure mercury lamp, et.al because of its suitable crystal structure and high chemical stability. In particular, YVO4:Eu3+ nanocrystal is promising material for biological applications. In this study, YVO4:Eu3+ colloidal nanoparticles are prepared by laser ablation in DI water which possesses the merits of high efficiency, low-cost and environment-friendly. Pellets for laser ablation were

prepared by pressing commercial YVO4:Eu3+ powders at 100MPa for 3min. The pellet was irradiated in DI water by a Q-switched Nd:YAG pulsed laser providing a 13ns pulse at 532nm wavelength with a repetition rate of 10Hz. The properties of phase, morphology and luminescence are characterized by X-ray diffractometer (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and photoluminescence spectrophotometry (PL). Elemental analysis of point-mode and area-mode are performed by energy-dispersive X-ray spectroscopy (EDS). Structure and crystallinity analysis of YVO4:Eu3+ were analyzed by XRD. All diffraction peaks for both target and nanoparticles can be indexed as tetragonal phase of YVO4 (JCPDS, No.17-0341), indicating that all the particles possess highly crystalline structures without any impurity phases. The nanocrystallite size estimated from the full width at half maximum (FWHM) of the (200) peak according to the Debye-Scherrer formula revealed that the average crystallite size of YVO4:Eu3+ were around 8nm in diameter. The ovoid-like nanoparticles have diameter of 70-110nm, which are composed of numerous nanocrystallites deduced from XRD result.

13:30–15:00 Session 8 • Energy application, catalysis of laser-synthesized particles

Chairs C. Liang (Anhui/CN), G. Marzun (Duisburg/DE)

13:30 INV8 FCI Lecture — Catalytic nanomaterials synthesized by pulsed laser ablation in liquids for sustainable energy applications

A. M. Müller (Pasadena, CA/US)

We employed pulsed laser ablation in liquids (PLAL) to synthesize nanomaterials with unique electronic and catalytic properties for clean energy applications. The need for innovative technologies that solve our energy and concomitant climate crisis has never been more urgent. Solar water splitting is an attractive, carbon-neutral approach to provide environmentally benign hydrogen fuel. The water oxidation half reaction requires four coupled electron and proton transfer steps, for which robust and efficient catalysts are needed. Global scalability demands that all materials consist of non-scarce elements. We synthesized novel, earth-abundant, surfactant-free materials for electrocatalytic water oxidation. Addition of metal ions into the aqueous ablation liquid allowed for the preparation of mixed-metal nanomaterials with tailored compositions. The resulting nanocatalysts were screened for water oxidation activity, rendering PLAL a rapid-throughput method for catalyst design. Our [NiFe]-layered double hydroxide nanosheets are the best earth-abundant catalysts developed to date, with 100% conversion of electricity to oxygen and highest catalytic activity. A series of PLAL-made Ni–Fe materials with systematically varied Fe content revealed that oxygen evolution activity in basic electrolyte increased as Fe content decreased to 22%. Addition of Ti4+ and La3+ ions further enhanced electrocatalysis, reaching 10 mA cm−2 at 260 mV overpotential.

14:00 T23 — A sacrificial reactive route toward noble metal nanoparticle-graphene based nanocomposites as electrochemical catalysts

Z. Tian, S. Wu, J. Liu, C. Liang (Hefei/CN)

An environmentally friendly route to prepare platinum/reduced graphene oxide (Pt/rGO) nanocomposites (NCs) with highly reactive MnOx colloids as reducing agents and sacrificial templates was presented. The colloids are obtained by laser ablation of a metallic Mn target in graphene oxide (GO)-containing solution. Structural and morphological investigations of the as-prepared NCs revealed that ultrafine Pt nanoparticles (NPs) with an average size of 1.8 (±0.6) nm are uniformly dispersed on the surfaces of rGO nanosheets. Compared with com mercial Pt/C catalysts, Pt/rGO NCs with highly electrochemically active surface areas show remarkably improved catalytic activity and durability toward methanol oxidation. All of these characteristics can be attributed to the small particle size and uniform distribution of Pt NPs, as well as the excellent electrical conductivity and stability of the rGO catalyst support.

Student presentation

14:20 T24 **'In liquid' laser modification and photocatalytic water splitting activity of TiO2 nanoparticles**

G. Compagnini, M. E. Fragalà, R. Fiorenza, S. Scirè, L. D'Urso, O. Puglisi
S. Scalese, S. Filice (Catania/IT), E. Fazio (Messina/IT)

This work demonstrates that laser irradiation of TiO2 colloidal suspensions in water produces deep modifications in the nanoparticle structure in such a way to enhance the photocatalytic water splitting efficiency under ultraviolet irradiation. If visible or UV laser radiation (532 or 355 nm) is used to irradiate a TiO2 colloid with fluences below 300 mJ/cm2, changes have been observed in the size, shape and crystalline phase of the NPs and this affects the photocatalytic mechanisms and evidences an increase in the H2 production yield up to a factor 3. All crystalline phases of titania have been investigated (namely brookite, anatase and rutile) evidencing similarities and differences. We consider these results forerunners to build up sensitized heterostructures using organic dyes, quantum dots or plasmonic nanoparticles in order to obtain water splitting under solar light.

14:40 T25 **PLAL produced transition metal chalcogenides as efficient electrocatalysts for hydrogen generation**

B. Mahler (Villeurbanne/FR), M. S. Prevot (Lausanne/FR), D. Amans
F. Boudjada, G. Ledoux, C. Dujardin (Villeurbanne/FR)
K. Sivula (Lausanne/FR)

Transition metal chalcogenides have emerged over the past few years as highly efficient photocatalysts and electro-catalysts for water splitting and especially hydrogen evolution reaction (HER). They appear as low cost alternatives compared to the traditional efficient noble metal HER catalysts such as platinum. Among these materials, molybdenum chalcogenides are of particular interest due to their low cost and high activity. The Molybdenum/Sulfur system for example, can take numerous crystal structures with different stoichiometries, all of them been efficient HER catalysts. Pulsed laser ablation in liquids (PLAL) could be a useful way to synthesize ligands-free nanoscale molybdenum sulfide compounds for water splitting. We explored in details the formation of MoS2 nanostructures by PLAL and correlate the electrocatalytic activity of the obtained nanoparticules to their structure. The PLAL synthesis is surprisingly efficient to produce MoSx HER electrocatalysts exhibiting characteristics close to the best Mo-based HER electrocatalysts reported so far. The synthesized nanoparticles exhibit low overpotential onset as well as high current density. This study demonstrates the potential of PLAL synthetic routes for the formation of highly efficient cata lysts for the hydrogen evolution reaction and this approach can be further extended to a broad range of other transition metal chalcogenides.

15:30–17:00 **Session 9 • Biomedical applications and conjugation with biomolecules**
Chairs G. Compagnini (Catania/IT), G. Shafeev (Moscow/RU)

15:30 INV9 **Laser-ablative synthesis of functional nanomaterials for cancer theranostics**

A. Kabashin (Marseille/FR)

The presentation will overview our on-going activities on laser ablative synthesis of some biocompatible colloidal nanomaterials (Au, Si etc) and their testing in biomedical tasks. Our approach is based on ultra-short (fs) laser ablation from a solid target [1] or already formed water-suspended colloids [2] to achieve an efficient control of size characteristics of "bare" ligand-free nanomaterials, or fabricate nanomaterials coated by functional biopolymers

(dextran, PEG) to minimize immune response of biological systems. Our experiments in vitro demonstrate an excellent cell uptake of both bare and functional nanomaterials, while the composition of protein corona covering nanoparticles complexes in biological environment promises a good transport of nanomaterials in vivo [3]. We also found that a systemic administration of such nanomaterials in small animal model is not accompanied by any toxicity effects, while Si nanoparticles are rapidly sequestered by the liver and spleen, then further biodegraded and directly eliminated with the urine. Laser-synthesized nanomaterials are now actively tested in cancer diagnostics and therapy (theranostics) tasks. In particular, our experiments showed that laser-synthesized nanomaterials can provide a much better efficiency compared to chemically synthesized counterparts in a newly introduced method of mild cancer therapy using Si nanoparticles as sensitizers of radiofrequency radiation-based hyperthermia [4]. Finally, we showed that bare metal nanoparticles synthesized by laser ablation can provide an order of magnitude better response in glucose oxidation tasks, which promises their use as elecrocatalysts in bioimplantable therapeutic devices [5].

16:00 T26

Laser Ablated gold and iron oxide nanoparticles arranged in a core-shell-satellite architecture for efficient immunomagnetic sorting, SERS detection and photothermal treatment of cancer cells

F. Bertorelle (Padova/IT), M. Pinto (Verona/IT), R. Pilot, L. Litti, S. Fiameni V. Amendola, G. Conti (Padova/IT), G. Toffoli (Aviano/IT), M. Colombatti G. Fracasso (Verona/IT), M. Meneghetti (Padova/IT)

An advantage in using Laser Ablation technique for nanoparticles fabrication instead of a chemical reduction synthesis is that one obtains stable nanoparticles with a surface free of ligands, so functionalization can occur directly after nanoparticles synthesis and less purification passages are needed since no ligand-exchange reaction are involved. Obviously this is important in particular when nanoparticles have to be applied in the field of nanomedicine or biology. With Laser Ablation we obtain both gold nanoparticles (AuNPs) and iron oxide nanoparticles (FeOxNPs) in water starting from pure gold and iron bulk targets. Gold nanoparticles are achieving increasing interest in nanomedicine because of their biocompatibility, easy functionalization and optical properties which make them a powerful cells detection tool using, for example, SERS spectroscopy. Iron oxide nanoparticles, in particular those made of magnetite, can be used for cell sorting exploiting their magnetic properties. We show the synthesis of core-shell-satellite nanosystems (CSS NS) made of an iron oxide NPs core, dye-doped silica shell and AuNPs as satellite decoration. These nanosystems shows high SERS activity and they are functionalized with an antibody specific for PSMA antigen overexpressed by prostatic cancer cells. CSS NS can be efficiently used in the selective immunomagnetic sorting of prostatic cancer cells and, coupling immunomagnetic sorting with single-cell SERS analysis, a reduction of false positive arising from immunomagnetic sorting procedure is obtained. We also show application of CSS NS in photothermal treatment of prostatic cancer cells using 647 nm laser wavelengths.

Student presentation

16:20 T27

In vivo applications of neural electrodes structured with laser-generated platinum nanoparticles

C. Rehbock, S. Koenen, J. Jakobi (Essen/DE), S. Angelov, H. Heissler K. Schwabe, J. Krauss (Hannover/DE), S. Barcikowski (Essen/DE)

Neuronal PtIr electrodes for the treatment of Parkinson´s disease via Deep Brain Stimulation (DBS) were nanostructured with laser-generated Pt nanoparticles (NP). The aim of this study was a reduction in the electrode´s impedance to increase the efficiency of DBS. Naostructuring was realized using electrophoretic deposition (EPD) carried out with a two electrode system where the neural electrode served as a working electrode. Here, particles obtained by pulsed laser ablation in liquid (PLAL) are particularly beneficial as they are completely ligand-free, carry a high surface charge and can be made of the same material as the electrode, which makes them ideal candidates

for efficient deposition. A systematic study in the presence of different ligands could clearly show that the rate of electrophoretic deposition of ligand-free nanoparticles was higher than in the presence of ligands. Exemplary SEM images clearly verify, that an EPD process, optimized concerning voltage, deposition time and particle concentration yields homogeneously distributed surface coatings on the electrode surface. In consecutive experiments, coated electrodes were employed in in vivo trials with rats where DBS was conducted for a period of 3 weeks and impedance was monitored. These findings clearly revealed that impedance in case of NP coated electrodes was more stable over time and a significant reduction in impedance in comparison to uncoated control electrodes was found after 3 weeks of DBS.

16:40 T28 **Carbon nanotubes functionalized with laser-generated gold nanobioconjugates for application as hybrid nanosensors**

A. Barchanski, D. Funk, C. L. Sajti, B. Chichkov (Hannover/DE)

Fabrication of carbon nanotube-based sensor systems is not trivial, as the perfect graphitic structure of carbon nanotubes (CNTs) is destroyed by covalent surface functionalization, resulting in a modification of the physical properties. Here, the efficient, non-covalent functionalization of CNTs with laser-generated gold nanoparticles (AuNPs) and gold nanobioconjugates is presented in a single-step process. A CNT loading up to 45 % was reached with ligand-free AuNPs, indicating a high affinity of the partially oxidized gold surface towards the CNTs. Furthermore, biomolecules, such as single-stranded DNA (ssDNA) and bovine serum albumin (BSA) were applied for the direct attachment and CNT loadings of 2–20 % for ssDNA and between 1–9 % for BSA were determined. If the biomolecules were conjugated to laser-generated nanoparticles, tremendously increased CNT loadings of 9–45 % for AuNP-ssDNA nanobioconjugates and 8–41 % for AuNP-BSA nanobioconjugates were reached. Moreover, the resulting hybrids were pH- and ionic strength-independent, indicating weak physical interactions. In order to demonstrate exact orientation of biomolecules and thus functionality of hybrid nanosensors, biological immunoassays are performed. In summary, the non-covalent functionalization of CNTs with laser-generated gold nanoparticles and gold nanobiohybrids is a novel, promising route for hybrid nanosensor fabrication.

18:00–22:00 Gala Dinner at GOP Varieté (see page 13)

08:00–09:00 Program committee meeting
Atlantic Hotel (room 7)

09:00–10:00 Poster coffee (see page 36)
Atlantic Hotel (room 2/3)

10:00–11:50 **Session 10 • Optical properties and laser melting**
Chairs B. Goekce (Essen/DE), H. Wada (Tokyo/JP)

10:00
INV10 **Nanomaterial synthesis and the enhanced performances of optoelectrical devices**
K.-I. Saitow (Higashihiroshima/JP)

In our previous studies, we reported RGB or white-light-continuum photoluminescence of Si nanoparticle (NP), SERS-active gold nanomaterials, all of which were fabricated by the pulsed laser ablation (PLA) in supercritical fluid. Recently, we synthesized the colloidal Si quantum dots (QD) by the PLA in solution. Using the colloidal Si-QDs and conductive polymer solution, a hybrid light-emitting diode (LED) was developed by solution processes. The electroluminescence spectrum of Si-QDs was firstly observed in a blue wavelength region. Current density and optical power density of the hybrid LED were 280 times and 350 times higher than those of previously reported values, respectively. As another topic, Si-NPs were used as material of photovoltaic. By adding the Si-NPs into organic polymer (P3HT) solution, 50- and 12-fold enhancement of the hole mobility and hole density, respectively, was achieved in a Si-NC/P3HT hybrid film. Such a hybrid LED and/or hybrid photovoltaic has been expected as a next-generation optoelectrical device because of stability, flexible, and facile solution process. These noble hybrid devices are accomplished by the nanomaterials prepared by the PLA in solution.

Student presentation
10:30
T29 **Magnetically induced transparency at visible wavelengths in silicon nanosphere oligomers fabricated by fs-laser ablation**
J. Yan, P. Liu, Z. Lin, G. Yang (Guangzhou/CN)

Silicon nanospheres are excellent scatterers possessing directional scattering and low-loss properties in the visible region, making them superior to noble metals in optical applications. Electromagnetically induced transparency (EIT) is a quantum interference effect in three-level atomic systems that eliminates the absorption at the resonance frequency and gives rise to a narrow transparency window. Combining EIT with plasmonic structures, the destructive interference between overlapped narrow and broad plasmonic modes creates plasmon-induced transparency (PIT). However, the relative large ohmic loss in the metals confines the applications of PIT to the visible wavelengths. To overcome these issues, we report the first experimental demonstration of EIT-like phenomena in the visible region based upon arbitrarily aggregated silicon nanospheres with diameters from 100nm to 200nm fabricated by fs-LAL (femtosecond laser ablation in liquid). The formed electric gap mode hybridizing with the narrow magnetic resonances in the oligomers leads to transmission enhancement and antireflection. Therefore, we call this phenomenon magnetically induced transparency (MIT, see the schematic graph).
Unlike metal plasmonic oligomers, the characteristic spectra of silicon nanosphere oligomers are less dependent upon the number of particles, the states of aggregation and even the size of the distributions. Accordingly, EIT can be much more easily realized in all-dielectric nanospheres, which is significant for promising applications, such as a unit cell to build MIT-based epsilon-near-zero (ENZ) metamaterials.

Student presentation

10:50 T30

Pulse width effect on particle melting in liquid by nanosecond pulsed laser irradiation

S. Sakaki, N. Koshizaki (Sapporo, Hokkaido/JP), H. Ikenoue (Fukuoka/JP)
T. Tsuji (Matsue, Shimane/JP), Y. Ishikawa (Tsukuba, Ibaraki/JP)

Recently, synthesis of submicrometer spherical particles by irradiating with nanosecond pulsed laser to particles dispersed in liquid is reported. Raw particles absorbing laser energy are melted and fused, then cooled in spherical shape by surface tension of the droplet. This method can be applied to various kinds of materials, even most of metals or oxide semiconductors, for synthesis of crystalline spherical particles. Nanosecond pulse heating allows for particle melting in liquid because pulse duration time is shorter than the typical time for particle cooling. Zinc oxide and silver nanoparticles (Sigma-Aldrich, particle size < 100 nm) were dispersed in de-ionized water respectively with the concentration of 0.2 mg/ml. These nanoparticles in de-ionized water were irradiated with third harmonic of Nd: YAG laser (Continuum Inc., wavelength 355 nm, pulse width 7ns, pulse frequency 10 Hz) and KrF excimer laser (Gigaphoton Inc., wavelength 248 nm, pulse width 50 ns, pulse frequency 100 Hz).
SEM images of zinc oxide particles after laser irradiation. Zinc oxide show that submicrometer spherical particles were obtained at the laser fluence of 50 mJ pulse-1 cm-2 when irradiated with Nd: YAG laser and at 81 mJ pulse-1 cm-2 when irradiated with KrF excimer laser. Similarly, laser fluence threshold for submicrometer spherical particle formation of silver increased with pulse width. Absorption efficiency of the materials calculated using Mie theory at the wavelengths is not so different in submicrometer size range, and pulse interval is sufficiently long for particle cooling. Therefore, the difference in threshold is mainly caused by the difference in pulse width. By considering cooling effect from the surrounding of the particle under the simple model, the energy accumulated during laser heating of particle start to be lost at several tens of nanoseconds. These results suggest that heat energy is dissipated from particle to surrounding vaporized liquid during nanosecond pulse heating.

11:10 T31

Nano-sphere formation by pulsed laser melting in liquid

Y. Ishikawa (Tsukuba/JP), N. Koshizaki (Sapporo/JP)

We have reported that submicrometer spheres are obtained as a main product by laser irradiation on raw nanoparticles dispersed in liquid with weaker laser fluence than that in pulsed laser ablation in liquid (PLAL). We call this process “pulsed laser melting in liquid (PLML)”. In this study, we discuss an influence of laser fluence on size of obtained particles in case of TiO2 raw particles. Size distributions depended on irradiation fluence. Size distribution with range from 50 nm to 300 nm and peak at 200 nm was observed by particles obtained by irradiation at 66 mJ cm-2 pulse-1. Size distribution broadening and a main peak top shift to larger size were prominent with the increase in laser fluence, while the size distribution curve split into two curves with a dip at 200 nm. The formation of such bimodal size distribution of obtained particles is well explained based on the phase transition fluence curves deduced by Mie theory, which have minimum fluence at particle size of 200 nm. It means that a temperature of particle 200 nm in size is easily increased by laser heating due to the low laser energy absorption at smaller particle size and high heat capacity of a single particle at larger particle size. Therefore, absence of particles 200 nm in size was observed in particles obtained by higher laser fluence irradiation due to selectively evaporation of particles 200 nm in size, while several dozen nanometer particles and large submicrometer particles were obtained.

Student presentation

11:30 Identification of intermediates during laser melting of supported nanoparticles

T32 M. Lau, A. Ziefuss, T. Komossa, S. Barcikowski (Essen/DE)

Laser melting for fabrication of sub-micrometer spheres (SMS) is a method established by Koshizaki and co-workers. The laser melting process can transfer nanoparticle agglomerates or non-spherical mirco- and sub-microparticles into SMS. Beside melting and re-solidification as spherical particles chemical conversions are also possible. These fascinating observations motivated us to investigate what happens if supported nanoparticles on sub-micro- and microparticles are exposed to laser melting conditions. For this we used monodisperse gold nanoparticles supported on zinc oxide and performed laser melting in a continuous liquid flow known for precise fluence control. During the sequential irradiation of supported gold nanoparticles we could identify intermediates as shown in the Figure. These intermediates are transferred into SMS whereby the gold nanoparticles are included in their zinc oxide carrier particles. Characterization of SMS and gold nanoparticle sizes respectively shows that the gold nanoparticles melt on zinc oxides surface prior to a complete inclusion.

11:50–12:15 Closing remarks and student awards ceremony

16:40–18:30 Poster session (and throughout conference breaks)

Energy application, catalysis of laser-synthesized particles

P1 Influence of the characteristics of spherical metallic nanoparticles in water on effective absorption of radiation and nanoparticle heating
N. Tarasenko (Minsk/BY)

Absorption of laser and optical radiation in different spectral intervals by nanoparticles, a light-to-heat conversion, the heating of nanoparticles is used in nanoenergy, photonics, photocatalysis, etc. The efficiency of applications of metallic nanoparticles for photo-thermal nanotechnology depends on characteristics of nanoparticles, radiation and surrounding medium.
Optical properties of several metallic (zinc, nickel, titanium) nanoparticles are theoretically investigated in the spectral interval 300 - 2500 nm and the analysis of them has been carried out. The investigation of the influence of nanoparticle parameters (type of metal, their radii of 50, 75, 100 nm, concentration) on optical properties of nanoparticles has been conducted. The influence of nanoparticle concentration on optical properties of nanofluids, containing of nanoparticles, is established and carried out.

Student presentation

P2 Naodiamond-embedded cuprous oxide nanocrystals for broad-spectrum photocatalytic hydrogen evolution
Z. Lin, G. Yang, J. Xiao (Guangzhou/CN)

Nanodiamond that is achieved by laser irradiation of a suspension of graphite powder in ethanol is used to improve the photocatalytic hydrogen evolution reaction (HER) of Cu2O for the first time. Generally, Cu2O is considered as an attractive photocatalyst for HER. However, it shows poor photocatalytic performance and photostability due to its short electron diffusion length and low hole mobility. Nondiamond carbon dots (CDs), which are primarily made up of sp2 hybridized C atoms, have been used to improve the photocatalytic HER of various semiconductors recently. Another fascinating carbon nanomaterials is nanodiamond (ND), which is primarily made up of sp3 hybridized C atoms and has scarcely been used in photocatalytic HER. In this contribution, we report that the ND-embedded Cu2O nanocrystals (NEC) exhibit a tremendous improvement in HER performance, compared with pure Cu2O. It is also established that the broad spectral response and electron injection from ND to Cu2O play a dominant role. Overall, these findings suggest that ND is an important metal-free optoelectronic material that is a promising component for high-efficiency photocatalysts. And laser ablation/irradiation in liquid is a powerful method to prepare novel nanomaterials.

P3 Broad spectrum-driven efficient water splitting using reduced TiO2-graphene oxide heterostructure via photon and electron pathways
L. lihua, Y. Guowei, Y. Lili, L. Zhaoyong, X. Jun (Guangzhou/CN)

The practical application of pure titanium dioxide (TiO2) in water splitting is still hampered by its low solar-to-hydrogen conversion efficiency and quantum efficiency. Here,we demonstrate that the broad spectrum-driven efficient water splitting using the heterostructure between reduced TiO2 nanoparticle and reduced graphene oxide (RGO) via the photon and electron pathways.Reduced TiO2 (TiO2-x) for extending the optical response from ultraviolet to visible and RGO for both luminiferous and promoting charge conducting were realized by a one-step surfactant-free upon a unique process of laser irradiation in liquid.In the case of water splitting using the TiO2-x-graphene oxide heterostructure as a photocatalyst, a maximum hydrogen production rate of 16 mmol/h/g was obtained under simulated sunlight irradiation,with quantum efficiencies of 5.15% at $\lambda = 365 \pm 10$ nm and 1.84% at $\lambda = 405 \pm 10$ nm, and an overall solar energy conversion efficiency of 7.15%.Such efficient photocatalysis was achieved through photon and electron pathways.

Student presentation

P4 Tuning of the oxygen-functionalities on graphene oxide and graphene oxide-TiO2 by pulsed lased irradiation for dye degradation

S. Filice, D. D'Angelo, G. Compagnini, M. Sinatra, E. Fazio, V. Privitera
S. Scalese (Catania/IT)

Pulsed laser with visible wavelength (532 nm) is suitable to finely tune the quantity and type of oxygen functionalization on graphene oxide (GO) layers, tailoring both the hydrophilicity and the spectroscopic features of the final GO suspension. A concentrated solution of GO prepared by the modified Hummers method was irradiated for different times by pulsed laser (RGO). In addition, a pulsed laser irradiation process of mixed solution of GO and RGO with P25 titania for 15 minutes is also used for producing nanocomposite materials. SEM analysis showed that RGO layers appear to be smaller and more irregular than the GO ones; TiO2 particles are distributed homogeneously on the surface of both GO and RGO, without the formation of big aggregates. C1s XPS spectra indicate a reduction in the oxygen content in RGO, as expected. The comparison between GO, RGO and the same materials mixed with P25 suggests that reduction of GO can be accelerated by adding TiO2 and irradiating for 15 min the solution. We have studied the efficiency of GO and RGO in the methylene blue (MB) removal in water: an excellent adsorption capacity is observed for both GO and RGO, in particular MB absorption and aggregation depend on the GO concentration and irradiation time. Composites showed an increase of MB degradation under Uv-Vis light irradiation compared to the mere adsorption. In particular, it's evident that GO increases the MB degradation ability of P25 respect to its photocatalytic activity alone.

Student presentation

P5 Structural evolution of electrospun TiO2 nanofibers driven by pulse laser irradiation in liquid toward enhanced photocatalytic activity

H. J. Jung (Jinju/KR), Y. L. Kim (Seoul/KR), Y. Seong (Jinju/KR)
M. H. Kim (Seoul/KR), M. Y. Choi (Jinju/KR)

We introduce a facile crystalline phase control of electrospun TiO2 nanofibers as well as their enhanced photochemical responses via the combination of electrospinning and pulse laser irradiation (PLI) in liquid. We have successfully performed the transformation of the anatase phase into the rutile phase for electrospun TiO2 nanofibers driven by PLI process. Additionally, the mixed phase of TiO2 nanofibers showed the enhanced photocatalytic activity for decomposing methylene blue, compared with pure anatase and rutile TiO2 nanofibers.

P6 Solar nanofluid fabricated by a femtosecond laser-assisted technique

O. Torres-Mendieta, R. Mondragon (Castellón de la Plana/ES)
V. Puerto-Belda (Burjassot/ES), O. Mendoza-Yero (Castellón de la Plana/ES)
P. Andrés (Burjassot/ES), J. Lancis, E. Juliá,
G. Mínguez-Vega (Castellón de la Plana/ES)

Solar nanofluids are an innovative type of fluids that are able to direct harvest solar radiation. The basic idea of a solar nanofluid is to use heat transfer fluids, which usually have low absorption in the visible and near infrared range, in combination with nanoparticles. Then, a volumetric absorption within the fluid itself is promoted, which increases the photothermal efficiency. In this contribution, we present the fabrication of a solar nanofluid of tin nanoparticles synthesized in ethylene glycol by femtosecond pulsed laser ablation in liquids (PLAL). During the synthesis, the tin nanoparticles are quickly oxidize by the air oxygen diluted in the ethylene glycol. This nanoparticles are collected as colloids in the fluid creating the nanofluid with its characteristic black color. For comparison, we also made a solar nanofluid with commercial tin nanoparticles by mixing the nanoparticles with ethylene glycol at the same concentration. To quantitatively evaluate the sunlight absorption capability of the nanofluid we characterize the transmission spectra of both samples through the time. In comparison with the solar nanofluid made with commercial nanoparticles, the solar nanofluid made with

PLAL shows a higher stability and a low transmission spectrum for the visible wavelengths. Consequently, the nanofluid produced by PLAL presents a higher absorption efficiency. In fact, after ten days, the improved ration is of a factor of 3.

P7 Single-step fabrication of ultra-small nanoparticles by laser ablation in liquid

H. Deng, J. Liu, A. Wei, D. Chen (Guangzhou/CN)

Since photo-electrochemical splitting water on electrodes was reported in 1972, photocatalytic splitting water into over semiconductor photocatalysts using solar irradiation has attracted a lot of attentions. Metal doped lanthanide titanite is a promising photocatalyst for photocatalytic production, because it can narrow the band gap of to use visible light. Various of methods have been investigated to synthesize previously, but simple method with potential low cost of operation is of particular interest. Here, we synthesize the ultra-small pyrochlore-type nano particles by laser ablation in liquid (LAL) which is a facile and environmentally friendly top-down technique, has attracted increasing attention in preparation of ultra-small nanoparticles. The size of photocatalysis is important for photo-catalytic efficiency. A decrease in particle size could be expected to lead to a higher efficiency in photocatalysis. The TEM result shows that the nanoparticles we synthesized are less than 30 nanometer. The structure was characterizated by XRD. Our research shows that the LAL technique is promising for fabricating ultra-small doped nanoparticles which is a potential good photocatalyst for photocatalytic production.

P54 Catalytic reduction of p-nitrophenol by using naked gold nanoparticle decorated TiO2 nanofibers

M. S. Yavuz (Kayseri/TK)

Gold nanoparticles (AuNPs) supported on metal oxides has attracted much attention due to remarkably active catalysts especially for CO oxidation [1]. Au catalysts have been used in many inorganic and organic reactions such as reduction of organic compounds including selective oxidation of H2 to H2O2[2]. p-nitrophenol, also known as 4-nitrophenol, is among the most common organic water pollutants found in industrial and agricultural industry. The release of nitrophenols into the environment gives rise to destructive influences to biological ecosystems. Up to now, various techniques have been developed to overcome this problem, including photocatalytic degradation, adsorption, microbial degradation and catalytic reduction [3]. Herein, we focus on a new and novel technique to obtain AuNP decorated TiO2 nanofibers (Au@TiO2) through pulsed laser ablation technique in liquids. We present the reduction of a nitro group of p-nitrophenol using NaBH4 as the reducing agent in the presence of Au@TiO2 catalyst which showed relatively high catalytic activity. The catalytic reduction of 4-nitrophenol to 4-aminophenol was clearly analyzed by using UV-Vis spectroscopy analysis, even using a relatively small amount of Au@TiO2 catalyst. These metal oxides supported Au catalysts exist a significant potential as catalyst for various reactions.

Laser nanoparticle heating/phototherapy

P8 Formation of oxide shell on spherical metallic nanoparticles under laser radiation action and its influence on nanoparticle optical properties

N. Tarasenko (Minsk/BY)

Efficiency of applications of metallic nanoparticles for laser and optical nanotechnology strongly depends on plasmonic and optical properties of nanoparticles. The action of intense laser radiation on metallic nanoparticles leads to possible oxidation of surface layer of nanoparticles and the formation of oxide shell on them. Plasmonic and optical properties of several metallic (titanium, zinc, nickel) nanoparticles with and without oxide shells are theoretically investigated and analysis of them is carried out. The formation of oxide shell leads to significant changes in the factors of absorption, scattering and extinction of optical (laser) radiation by nanoparticles in wide spectral radiation intervals.

P9 Structural kinetics of the pulsed-laser irradiation of gold nanorod suspensions

A. Plech (Eggenstein-Leopoldshafen/DE), S. Ibrahimkutty (Stuttgart/DE)
D. Issenmann (Eggenstein-Leopoldshafen/DE), G. Newby (Grenoble/FR)

Gold nanoparticles figure good absorbers for photothermal applications from photoacoustic imaging to tissue treatment. The associated effects include heat release in a nanoscale environment, vapor bubble formation and particle explosion. Spherical particles (gold, silver) are widely accessible, easy to fabricate and manipulate, but show high absorption cross section only in the visible to UV. In contrast, gold nanorods have a tunable plasmon resonance in the near-IR, which can be matched to the near-IR window of biological tissue. We have investigated the ultrafast kinetics of particle excitation and bubble formation via time-resolved X-ray scattering with a 100 ps time resolution. The results show that vapor bubble formation is indeed easily provoked, but it is also clear that particles are very sensitive to non-reversible structural modification, such as shape transformation.

Laser-generated nanoparticle polymer composites

Student presentation

P10 High aspect ratio FeNi nanostrand-polymer composites with controllable length and thickness

E. Maurer, B. Gökce, S. Barcikowski (Essen/DE)

For a variety of applications the availability of optically transparent and electrically conductive materials is important. Without these materials today's smartphones would not work. A possible alternative for the frequently used but scarce ITO (indium doped tin oxide) is the application of polymer-nanoparticle composites with tailored properties. To obtain conductive paths within the polymer-nanoparticle-composites magnetic nanoparticles can be aligned in chains during their embedding process. In previous work our group showed that magnetic alloy nanoparticles can be synthesized by pulsed laser ablation in liquid (PLAL) and embedded into a photoresist. The application of PLAL is particularly advantageous since the magnetic alloy nanoparticles are free of ligands allowing the best particle-matrix coupling and no additional influence on the conductivity of the aligned chains.
In this work we present an approach to tailor high aspect ratio FeNi nanostrand-PMMA-composites. This approach exploits the bimodal volume distribution of picosecond-laser-generated nanoparticles which are embedded into a solidifying polymer solution. We show the synthesis of FeNi-nanostrands with a controllable length and thickness, thus overcoming the limited strand-length in previous literature by a factor of 40 while maintaining a transparency of >75%.

Modelling and fundamentals of laser ablation and particle fragmentation in liquids

P11 Kinetic model of noble metal nanoparticle growth in laser-induced plasma expansion in liquid

F. Taccogna, G. Valenza, A. De Giacomo, M. Dell'Aglio,
R. Gaudiuso (Bari/IT)

Modeling the growth of noble metal nanoparticles in liquid-phase laser ablation is very important to optimize and control the size and the structure of nanoparticles. However, the detailed formation process of nanoparticles after laser ablation is still unclear. In the present study, we have investigated for the first time the kinetic growth of nanoparticles synthesized by laser ablation in water, emphisizing the leading role of plasma medium and in particular the

electrostatic agglomeration due to the charging of the nanoparticle in plasma plume. In this work a fully kinetic Particle-in-Cell / Monte Carlo Collision (PIC-MCC) model is used to describe the plasma system around the nanoparticle embryos; the model allows knowing self-consistently (the electrostatic field around the nanoparticle is solved) the electron and ion current collected on the surface which drives the nanoparticle charging and growing (Fig. 1) and the exact ion energy distribution function of the ions impinging the nanoparticle surface (Fig. 2). Finally, a molecular dynamics model of the atomic evaporation from the nanoparticle surface is coupled to the plasma and nanoparticle charging models. The obtained results have been then coupled with plasma optical emission investigation and shodowgraph experiments in order to find out the main connections between the plasma processes and the nanoparticle characteristics in terms of size and stability.

P12 Laser induced plasma and bubble dynamics during the PLAL on wire-shaped target inside water jet flow and their role on nanoparticles production

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The nanoparticles (NPs) features produced by Pulsed Laser Ablation in Liquid (PLAL) can be varied changing some experimental parameters. NPs productivity as well as NPs shape and dimension can be influenced by using a wire shaped target immersed in water, by varying the liquid thickness and by using a liquid flow. In this work PLAL was performed on a wire-shaped target immersed in a water flow to investigate the laser induced plasma and bubble dynamics occurring during the NPs production. For studying how plasma parameters evolve in a water jet, Optical Emission Spectroscopy has been employed whereas for the study of bubble dynamics, high temporal resolved shadowgraphic images have been used. It has been consequently possible to retrieve details about possible relationships occurring among the plasma, bubble dynamics and the produced NPs features.

P13 Copper colloids by pulsed laser irradiation of suspended powders: fragmentation or reductive ablation mechanism

C. Schaumberg, M. Wollgarten, K. Rademann (Berlin/DE)

The synthesis of colloidal nanoparticles can be achieved by pulsed laser irradiation of suspended powders. Compared to the irradiation of bulk targets this approach leads to a higher productivity and may even give access to new materials. Unfortunately, not much is known on the mechanism of the size reduction of the micrometer sized precursor powder to the nanometer sized colloidal product. The laser irradiation of copper compounds is used as a model system to discuss two distinct mechanisms of nanoparticle formation. Copper precursor powders are suspended in water or an organic liquid and irradiated with a nanosecond pulsed laser. The use of copper compounds like CuO and Cu3N lead to the formation of metallic copper colloids. Inside the generated plasma copper atoms nucleate and form small primary particles, which later coalesce to larger secondary nanoparticles. Thus this mechanism can be described as a reductive ablation. In contrast, the laser irradiation of e. g. CuI suspensions follows a direct fragmentation mechanism. In this case the chemical composition of the material is preserved and the particle size distribution shifts to smaller particle diameters under ongoing laser irradiation. In principle, both processes may occur at the same time. Yet, in most cases only the one or the other mechanism is observed. As this has an tremendous effect on the properties of the resulting nanomaterials, it becomes vital to understand which parameters trigger the dominating mechanism.

P14 Non-monotonous yield of Ag and Au nanoparticles during femtosecond/picosecond laser ablation in water

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The ablative synthesis of metal nanoparticles was carried out using an Yb-ion doped fiber laser (the central wavelength $\lambda = 1030$ nm, FWHM pulsewidth $\tau = 0.3$ ps, repetition rate f = 500 kHz, average energy $\sim 10\ \mu$J in the TEM00 mode). The laser beam was focused via focusing objective (focal length 10 cm) of galvanoscanner ATEKO to a spot with radius $\sigma 1/e \approx 15\ \mu$m (peak laser fluence on the surface F0 $\approx$ 2,1 J/cm2) and raster-scanned across 2x2 mm2 regions of an optically-polished Ag or Au samples (99.99%) under a layer of deionized water ($\sim$ 2 mm) at the constant scanning velocity of 6 mm/s with laser pulsewidth varied from 0.3 to 9.9 ps by a built-in grating pulse compressor. The ablation of the Ag and Au targets with laser shots of different pulsewidths resulted in a non-monotonous NP yield, illustrated by the colloids' absorption spectra. The increase of pulsewidth results in local reduction of colloidal absorbance, defined by NPs yield intensity, with minimum corresponding to 4 ps for Ag and 3 ps for Au colloid, which could be caused by transient picosecond-scale nucleation of vapor nanobubbles in the water layer, boiling at the target interface, distorting the liquid medium and shifting the laser beam focus.

P15 Ablative plume lifetimes during high-repetition rate femtosecond laser generation of nanoparticles in air and liquid media measured by optical emission spectroscopy

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Laser ablation of Au (1 mm-thick), Ag (3 mm-thick), Ti (0.1 mm-thick) and Si (0.5 mm-thick) samples was carried out using fiber laser Satsuma, delivering IR (central wavelength $\lambda = 1030$ nm), 300-fs pulses with energy $\sim$10 μJ at repetition rate 0-2 MHz. Time-resolved characterization of ablative plumes, emerged from the constantly moved targets without/with a layer of water or isopropyl alcohol, was performed by studying their optical emission in the spectral range 195-800 nm at the peak fluence F0 $\approx$ 7 J/cm2 using spectrometer Spectro-Physics 74050 with an intensified charge-coupled camera device Andor iStar. The intensity of Ti ionic (Ti II) lines at 399-405 nm decreases in water by 150 times, while in IPA – by 70 times; Ag atomic lines intensities (Ag I 328.07 and 338.29 nm) in IPA drops by 400 times; Si I line intensity at 288 nm decreases in water and IPA by 20 and 17 times, respectively. Though ablative plumes of the different materials exhibit diverse emission times in air - $\approx$ 20 ns (Ti), 7-8 ns (Si), 10 ns (Ag), their spectral emission times in liquids are almost unchanged (overall $\sim$ 2 ns), indicating much shorter lifetimes and spatial extension of ablative plumes in liquids, unlike air, and limiting NP condensation in plumes during their expansion.

P16 Coffee rings effect during drying of colloid drop produced by laser ablation in liquid – experiment and computer simulation

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Formation of the ring-like patterns of silver nanoparticles (NPs) during drying of colloid drop caused by coffee ring effect has been studied experimentally and by computer simulation. The drop shape evolution during jump-like motion of its contact line was in situ observed. Two interleaved stages of the drop shape evolution were separated for computer simulation.
The stable colloid of Ag NPs has been produced by laser ablation in liquid. The metal target (polished 3-mm-thick plate of pure Ag) covered by layer of pure deionized water has been ablated by focused beam of the Yb fiber infrared laser (wavelength 1064 nm, pulse duration 100 ns, pulse energy 1 mJ, frequency 21 kHz). The charged spherically shaped Ag NPs with averaged size about 50 nm appeared in the water as a result of condensation [1]. The spatial distribution of the nanoparticles on the substrate was measured by scanning electron microscope Cross-Beam Workstation Auriga, Carl Zeiss. The formation of the nested rings was obtained for NPs concentration about 0.5 g/l, whereas the uniform distribution of NPs appeared for concentration about 0.1 g/l. For ring formation the odd stages represents decreasing of the drop height and the even stages - the fast shift of the contact line [2,3]. The first and all subsequent odd stages corresponded to slow drop volume reduction at constant base radius. The second and all subsequent even stages represented the jump-like shift of the contact line at constant drop volume. The transitions from odd stages to the even ones were obtained, when the drop shape parameter achieved the critical value. The sequence of odd and even stages led to jerky motion of the contact line characterized by series of the base radii. The proposed model allowed extracting the important parameters characterizing the formation of the NPs pattern during drying of colloid drop. The proposed experimental results and the model of ring structure formation were used for realization of the effect of Surface Enhanced Raman Spectroscopy based on the giant increase of the Raman signal which is very important for biomedical sensors.

Nano-alloys, core-shell particle

P17 TiC and TiC@C nanoparticles obtained by laser ablation in liquid

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R. Teghil (Potenza/IT)

While the synthesis of nanosized oxide materials by laser ablation in liquid has been widely reported, nonoxide ceramics nanoparticles are usually obtained by mechano-chemical synthesis, using severe experimental conditions. Titanium carbide (TiC) particles have been the subject of significant interest as they are excellent ceramic reinforcements for various metallic materials. In fact, TiC have high melting point, high hardness, low friction coefficient, and good corrosion resistance. In particular, nanosized TiC particles are considered as a promising microstructural modifier and mechanical strengthener for particle-dispersed composite alloys. TiC has been successfully integrated into structural components, including magnetic recording heads, transparent optical materials, and composite biocompatible materials. The incapsulation of TiC nanoparticles in carbon can improve their surface hardness and corrosion and thermal shock resistance. In this context, we have carried out a study to obtain nanosized titanium carbide particles and core-shell structures by laser ablation of titanium carbide or titanium target in different organic solvents characterized by different C/H ratio. The mechanisms of solid ablation in liquid by nanosecond and femtosecond laser sources (Nd: YAG, 532nm, 7nm, 10Hz and Nd: glass, 527nm, 250fs, 10Hz) have been compared by using fast imaging techniques. Nanomaterials obtained have been characterized by TEM, XRD and micro-Raman spectroscopy.

P18 Liquid assisted pulsed laser ablation for synthesis of composite nanostructures

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M. Nedelko (Minsk/BY)

In this report several approaches of pulsed laser ablation technique in liquids (PLAL), for example based on the sequential ablation of different targets in the same solution, simultaneous ablation of combined targets, post irradiation as well as a combination of different approaches will be discussed for preparing nanometer sized multimetallic and composites nanoparticles (NPs). Capabilities of the PLAL technique for synthesis of zinc based alloy (Ag-ZnO, Zn-Al-Cu), ceramic (PZN, PZT, BiFeO3) and magnetic nanoparticles on a base of compounds and alloys of gadolinium were studied. By controlling laser irradiation time, laser fluence and liquid composition, different structures like core-shell and hollow particles were synthesized. Laser treatment of the synthesized structures by the second harmonic of the Nd:YAG laser (wavelength 532 nm, pulse duration 10 ns) was shown to result in their morphological and structural modifications through the laser-induced fragmentation and fusion processes.

P19 Experimental study of Ti and Al alloy nanoparticle formation induced by laser irradiation of their mixture colloidal solution

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Ablation of a composite Ti-Al target in liquid isopropanol saturated with molecular hydrogen using picosecond laser pulses is known to lead to core-shell Al@Ti nanoparticles generation. Aim of present experiment was to obtain and characterize the composite nanoparticles in case of laser exposure of nanoparticles mixture colloidal solution. Pure metallic Ti (98%) and Al (99%) nanoparticles obtained via electric explosion were used for the initial samples preparation. Laser irradiation of nanoparticles mixture was shown to result in composite nanoparticles formation. Fragmentation and agglomeration processes during the laser exposure of colloidal solutions were also studied. Transmission electron microscopy and disc measuring centrifuge were used for nanoparticle size and morphology analysis. Extinction spectra of colloidal solutions were studied by means of optical spectroscopy. XRD studies of generated nanoparticles were used for crystal structure characterization of obtained nanoparticles. The described technique may serve as a promising method of high amounts of pure composite metallic nanoparticles generation.

P20 Synthesis of Cu-Ag alloy nanoparticles by pulsed Nd:YAG laser ablation of bulk alloyed target in different liquid environments

R. Poursalehi, S. Dadashi (Tehran/IR)

Alloy nanoparticle have recently become the focus of research because of their tunable physical properties. Although many studies were investigated the synthesis of Au-Ag and Au-Cu nanostructures a few methods have been reported on synthesis of Cu-Ag alloy nanoparticles. The focus of this work is on synthesis of alloy Cu-Ag nanoparticles by laser ablation in liquid. In this study Cu-Ag alloy nanoparticles with different mole fractions were prepared by pulsed laser ablation of corresponding per-alloyed targets in acetone and water. The targets with different Cu: Ag molar ratio were cleaned and placed on the bottom of a glass vial filled with ablation environments. A pulsed Nd: YAG laser was used for the ablation. Crystal structure, size and optical properties of the targets and alloy nanoparticles were characterized by X-ray diffraction (XRD), scanning electron microscopy and UV–visible spectroscopy respectively. Preparation of alloyed target and nanoparticles reveals by XRD patterns and spectral shift of surface plasmon resonance peaks of colloidal alloy nanoparticles individually. This study could provide a method for the synthesis of stable colloidal Cu-Ag alloy nanoparticles with an arbitrary composition in liquid.

Student presentation

P21 Core-shell iron-tungsten nanoparticles by laser-assisted synthesis in liquid Contact

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Laser ablation in liquid ambient is a potential technique to produce biocompatible nanoparticles for a variety of medical applications. Tungsten-iron core-shell nanoparticle colloids may play a role as an absorbing medium for magnetic resonance imaging accompanied by high x-ray absorptivity. In the present work, tungsten-iron core-shell nanoparticles were generated by nanosecond laser ablation (532 nm, 20 Hz, 5 ns) of iron-tungsten ceramics in ethanol and water. The modified laser parameters such as pulse accumulation (200 and 1000) and energies of (48 and 28 mJ) were chosen after studying the threshold fluences of ceramics at applied various numbers of pulses (50, 100, 200, 500 and 1000) and various energies (48, 38 and 28 mJ) in water and ethanol, Additionally; the incubation behaviour of these ceramics in air, water and ethanol were considered and discussed. Several multiple-core/shell and hollow-core/shell (quantum bubbles) nanoparticles were observed. The size distribution, chemical composition, and crystallinity of these nanoparticles were identified by TEM, EDX, and selected area electron diffraction (SAED).

P22 Interference lithography method for periodical arrangement of nanoparticle clusters synthesized by laser ablation in liquid

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Nanoparticles (NPs) that self-assemble into ordered nanostructures present unusual structural and opto-electric characteristics. Especially, the creation of a large area array of nanoparticle clusters (NPCs) is one of the most important interdisciplinary topics in current materials science and optoelectronics for the manipulation of tuneable photonic devices. To date, many assembling methods have been tried to control the ordering and orientation of NPCs. However, achieving a well ordered array of NPCs is still a complex and expensive process. Herein, we demonstrate the combined fabrication method of a periodic array of NPCs over a large area using the drop-casting and laser interference lithography. Au NPs generated by using the laser ablation in liquid technique were used in the formation process of periodic array of NPCs.

Nano-hybrids, conjugation with organics and biomolecules

P23 Noble metal nanoparticles produced by pulsed laser ablation in liquid and their interaction with proteins

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In this work noble metal nanoparticles (Ag, Au and Pt) in water were produced by Pulsed Laser Ablation in Liquid (PLAL) and allowed to react with Ubiquitin (Ub), Human Serum Albumin (HSA) (or Bovine Serum Albumin (BSA)) and Human Serum (HS), since it is known that the interaction of NPs with proteins can be a key issue in addressing the problem of nanotoxicity for biological and medical applications. In particular a different behavior of bared NPs and citrate-coated NPs interacting with Ub has been explored as well as the competition for the absorption on NPs surface between different proteins (Ub and HSA) has been observed. To study this last dynamic equilibrium, the system AgNPs + Ub was incubated with HSA and HS respectively, in order to understand if and how the exchange between Ub and other proteins occur. The surface plasmon resonance (SPR) absorption spectroscopy has been employed to monitor the fast changes occurring in the NP colloidal solutions upon interaction with proteins and TEM analysis have been then performed to confirm results.

Student presentation

P24 Functional laser-generated gold-nano-conjugates for in vitro bioapplications

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S. Barcikowski (Essen/DE)

This work focuses on the design and laser synthesis of bioconjugates with decisive biological functionality applying different biomolecules. Therefore, 5 nm gold nanoparticles (AuNPs) were prepared by laser ablation in micromolar saline solution. Laser synthesis was followed by ex situ bioconjugation. Conjugates were assessed according to their surface coverage, aggregation tendencies, size and charge. The specific functionality and applicability of these constructs is demonstrated in two separate relevant bioapplications. In a first approach, AuNPs were conjugated with ligands specifically targeting Aβ known to be involved in neurodegenerative disorders like Alzheimer´s disease. We demonstrate a reduction of cellularly produced neurotoxic Aβ-species in presence of functional nanobioconjugates, while the effects were significantly stronger compared to free ligands deployed in equimolar dose, probably due to high local ligand concentrations and multivalent effects of ligands immobilized on the AuNPs surface. In a second approach, bivalent laser-generated conjugates carrying cell penetrating peptides and oligonucleotides were used for cell penetration and transfection experiments. TEM and confocal microscopy studies show that the conjugates were transported into the cytoplasm of regulatory T cells. Cellular uptake went along with translocation of dissolved siRNA across the cell membrane into the nucleus verified by downregulation of GFP expression in the corresponding cells.

P25 Laser ablated gold nanoparticles decorated with a new Gd-loaded polymer for SERS-MRI multimodal imaging

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P. Marzola, M. Colombatti (Verona/IT), M. Meneghetti (Padova/IT)

The advent of multimodal contrast agents (MCAs) offers new interesting diagnostic possibilities, converging the benefits of multiple and complementary imaging techniques. 1 Magnetic resonance imaging uses safe radiations and allows total body screening, but suffers on low spatial resolution if compared to optical contrast agents, that is characterized, however, by low tissue penetration depths. Surface Enhanced Raman Spectroscopy (SERS) is a vibrational technique amplified by a plasmonic substrates, namely noble metal nanoparticles. SERS allows imaging at sub-micrometer resolution with intensities comparable to fluorescence. 2 If dyes are used as SERS labels, multicomponent analysis can take place using the same laser excitation, namely one obtains an easy multiplexing analysis.3 Into this context we designed the synthesis of SuperDOTA, a new polyethylene glycol based polymer characterized by high Gd3+ loadings. SuperDOTA consists by three main fractions. The first is a cysteine amino acid, containing a thiol group for a stable linking to AuNPs surfaces. The second moiety is a repetition of a short PEG spacer and a DOTA based branch for the Gd3+ chelation. The third is a long-chain PEG, to enhance the biocompatibility and the immune-stealth properties of the nanosystems. Gold nanoparticles were obtained by laser ablation synthesis in solvent (LASiS) and are organized as an high efficient substrate for enhanced Raman scattering substrates. Silicon Naphthalocyanine, used as SERS label, was functionalized with mercaptoethanol on both the apical sites to improve the optimal situation in which the dye molecule stays between two plasmonic particles, ea. in an hot spot. The new nanostructure is used for multicontrast imaging using both T1-MRI and SERS also for in-vivo measurements.

P26 Selenium nanoparticles synthesized in the presence of chitosan by nanosecond pulsed laser ablation

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X. Peralta (San Antonio, TX/US)

The ability to produce functionalized nanoparticles by a one-step synthesis method is very challenging particularly for biomedical applications. Among nanoparticle archetypes, selenium has been found to have potential towards therapeutic medical applications such as antimicrobial and antioxidant activity due to its wide presence in biological systems in the form of selenium containing proteins. The goal of this study is to synthesize selenium nanoparticles from a bulk selenium pellet using Chitosan, a biological derived polymer, for templating and to demonstrate that this is an attractive approach toward facile, scalable, and biocompatible nanoparticles with excellent stability in aqueous environments. Chitosan is a linear amino- polysaccharide consisting of glucosamine and N-acetylglucosamine units. Abundantly found in nature, it is derived from the deacetylation of chitin which extracted from the exoskeleton of crustaceans such as shrimps and crabs, as well from the cell walls of some fungi. Selenium pellets were irradiated by a nanosecond Nd: YAG laser operating at 1064 nm and 20Hz in the presence of either the chitosan biopolymer or deionized water as a control. During the experiment selenium spherical nanoparticles produced using chitosan were sub-50 nm and formed a highly stable nanoparticle suspension. After removal of excess chitosan, the biopolymer is found to cap the nanoparticles through surface adsorption, which renders them water soluble and biocompatible, and provides functional groups such as hydroxyl and amino groups for further attachment of biomolecules. The nanoparticles remain stable in aqueous solutions with pH ranging from 4 to 7.4. The chitosan coated selenium nanoparticles show a highly potent antifungal activity by inhibiting the growth of Candida albicans preformed biofilms. Compared with pure chitosan, known for its antimicrobial activity, and the uncoated selenium nanoparticles, chitosan coated selenium nanoparticles appear to work additively, resulting in the increased antifungal activity observed.

Nanoparticle productivity/scale-up

P27 High production rate using low cost laser source

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G. Ledoux, D. Amans (Villeurbanne/FR)

The production rate of PLAL depends on many parameters; the wavelength, the pulse duration, the fluence, the pulse overlaps between successive pulses and the height of the applied
liquid layer. However, the main scale-up criteria remains the pulse repetition rate of the laser source. Since the ablation processes require high fluence, most setups use lasers with low pulse repetition rate (10 Hz). Combining kHz pulse repetition rates with high peak powers leads to expensive laser sources. A cheap solution to achieve high power in a short pulse is the Master Oscillator Power Amplifier (MOPA) architecture. We have built a continuous flow setup using a laser source based on a single-crystal fiber amplifier, with 1 kHz repetition rate, 1064 nm wavelength, 2 mJ/pulse and 800 ps pulse duration. With this configuration, we reach for gold nanoparticles a production rate of 0.2 g/h and a mass concentration up to 0.5 g/L. The ablation is performed in an aqueous solution of NaBr which ensures the colloidal stability of the produced nanoparticles. In addition, the continuous flow avoids post-irradiation of the produced nanoparticles, which can lead to fragmentation, evaporation and aggregation processes. We then produced highly concentrated colloidal solutions of ligand-free gold nanoparticles with 9.1 nm median size, and 3 nm standard deviation.

P28 Silver films obtained by laser ablation in liquids and electrophoretic deposition

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Nanoparticles and films of Ag have aroused intense research interest in nanotechnology due to their well known properties, such as good conductivity, localized surface plasmon resonances, antibacterial and catalytic effects, etc. The films based on noble metals are objective of intense investigation due to the optical properties introduced by the characteristic localized surface plasmon resonances, leading to an optical local field enhancement. In this work we report the results of combination the laser ablation in liquids technique and electrophoretic deposition to obtain films of Ag. The laser source used consisted of a pulsed diode-pumped Nd: YVO4 laser. It provides laser pulses at 532 nm with pulse duration of 50 ns, a repetition rate of 20 kHz and an average output power of 6 W. The Ag has been ablated in water while an electric field of 30 V was applied between the electrodes. The obtained particles and films were characterized by means of transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM) and UV/VIS absorption spectroscopy.

P55 Laser assisted synthesis of carbon nanostructures with controlled viscosity for printing and biological sensing applications

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New carbon based materials with unique properties have triggered a lot of scientific interest, especially for a variety of bio-sensing applications [1]. Recently, our group reported the generation of various forms of carbon nanostructures (crystalline carbon nanoparticles and carbon nanotubes) by Pulsed Laser Ablation in Liquid (PLAL) via high-frequency Nd:YAG laser ablation, and established a phase control mechanism dependent on the laser pulse energy. Carbon nanostructures in the size range (50–100nm) could be of significant interest in the development of ultrasensitive substrates for sensing applications as they provide both mechanical support and a conducting path for electrochemical detection.

Here, we report on the production of high quality carbon nanostructures via Pulsed Laser Ablation in Liquid (PLAL) in de-ionised water. Systematic studies were performed to control the morphology of structures by tuning ablation parameters such as laser fluence, energy and the irradiation time. Homogeneous and stable nanoparticle suspensions with viscosities ranging from 0.89 to 12 mPa.s were obtained by suspending the nanoparticles in different solvent mixtures such as glycerol–water and isopropanol–water [2]. These results present an exciting alternative method to engineer carbon nanoparticles and their potential use as a ligand-free nano-ink for ink jet printing (jetting) applications. Raman spectroscopy confirmed graphitic-like structure of nanoparticles and the surface chemistry was revealed by Fourier transform infrared (FTIR) spectroscopy demonstrate sufficient electrostatic stabilization to avoid particle coagulation or flocculation.

Subsequently, the obtained colloidal solution was deposited onto laser-textured polymer surfaces as promising substrates for potential applications in biochemical separations. Direct-write laser processing was employed to create microchannels on a 188 μm thin cyclic olefin polymer (COP) substrates - altering physical and chemical properties of surfaces allowing changes in wettability and optical transmission [3]. Uniformity and repeatability of substrates post-coating was examined using Scanning Electron Microscopy (SEM). Changes in composition and optical properties as a result of both the laser-texturing and carbon nanoparticle coating was investigated using FTIR spectroscopy, UV-Vis and florescence spectroscopy . The results are discussed in the context of achieving surfaces optimised for microfluidic applications.

Pulsed laser optoporation with nanoparticles

P29 Influence of laser ablated gold nanoparticles on the nonlinear absorption of rhodamine B solution with different concentrations

F. Hajiesmaeilbaigi, Y. Golian, A. Motamedi, E. Bostandoustnik (Tehran/IR)

In recent years, nonlinear optical responses of materials such as colloidal nanoparticles (NPs) and organic molecules have been investigated [1].Dye molecules are used as a gain media in tunable laser, two-photon microscopy, optical limiting and so on. NPs have variety of unique spectroscopic, electronic and chemical properties. Metal NPs exhibit rich plasmonic resonance properties due to collective oscillations of electrons in visible range. Mixture of dye solution and metal NPs can be used as laser medium, so absorption enhancement of dye in due to surface plasmon can significantly improve the laser performances.In this study, Au colloidal NPs were prepared by the laser ablation method of metal target in DI water [2]. The target was irradiated by active Q-Switched Nd:YAG laser with 20 ns pulse width operated at 10 Hz repetition rate for Au colloidal nanoparticles formation. Absorption studies were carried out using UV-Visible spectrometer for the laser dye Rhodamine B dissolved in doubled distilled DI water with the presence of Au NPs. Also, the morphology of the Au NPs was investigated by TEM Image. Here, we report our results on the measurement of nonlinear absorption in Au/Rhodamine B solution in different concentrations of Rhodamine B using the standard z-scan technique [3]. The excitation source was 150 mW CW laser at 532 nm. The input beam was focused with 19.5 cm lens and the corresponding peak intensity was estimated to be 3.98×103 W/cm2. We observed the reversed saturable absorption behavior at the order of 10-3cm/W which can be probably due to either two photons or excited state absorption. There is decreasing trend for value of nonlinear absorption coefficient as the concentration decreases. This may be attributed to the fact that decreasing the concentration causes less particles to be thermally excited, so the reduce effect can be expected.

Reactive laser ablation of liquids for particle synthesis

P30 Synthesis of cadmium sulfide nanomaterials by pulsed laser ablation in liquid environmental technique

A. Darwish, W. Eisa, A. Shabaka, H. Talaat (Giza/EG)

Pulsed laser ablation in a liquid medium is a promising technique as compared to the other synthetic methods to synthesize different materials in nanoscale form. The laser parameters (e.g.; wavelength, pulse width, fluence, and repetition frequency) and using an appropriate liquid medium (e.g.; aqueous/nonaqueous liquid or solution with surfactant) were tightly controlled during and after the ablation process. By optimizing these parameters, the particle size and distribution of materials (e.g.; cadmium Sulfide) can be adjusted. The UV-visible absorption spectra and weight changes of targets were used for the characterization and comparison of products.

P31 Carbyne with finite length – the one-dimensional sp-carbon

J. Xiao, G. Yang, J. Li, B. Pan, P. Liu (Guangzhou/CN)

Carbyne is the one-dimensional allotrope of carbon composed of sp-hybridized carbon atoms. Definitive evidence for carbyne has remained elusive, in spite of its synthesis or preparation described in the laboratory. Given the remarkably technological breakthroughs offered by other allotropes of carbon, including diamond, graphite, fullerenes, carbon nanotubes and graphene, interest in carbyne and its unusual potential properties remains intense. Here, we report the first synthesis of the carbyne with finite length clearly composed of alternating single and triple bonds using a novel process involving laser ablation in liquid. Spectroscopic analyses confirm that the product is the structure of the sp hybridization with the alternating carbon–carbon single and triple bonds. We observe purple–blue fluorescence emissions from the gap between the carbyne highest occupied and lowest unoccupied

molecular orbitals. Condensed-phase carbyne crystals have a hexagonal lattice, and resemble the white crystalline powder produced by drying a carbyne solution. We also establish that the combination of gold and alcohol seems crucial in the carbyne formation, because carbon-hydrogen bonds can be cleaved with the help of gold catalyst under the favorable thermodynamic environment provided by laser ablation in liquid. This laboratory synthesis of carbyne will enable exploration of its properties and applications.

P32 Understanding the spontaneous growth of LAL induced uncapped tellurium nanoparticles in solvents

J. Liu, X. Zhu, Y. Lin, C. Liang (Hefei/CN)

Understanding the thermodynamic behavior and growth kinetics of colloidal nanoparticles is indispensable guide to synthesize materials with desired structures and properties. Here, we present the specific uncapped tellurium (Te) colloidal nanoparticles obtained by laser ablation in various protic or aprotic solvents, such as water, methanol, ethanol acetone and dichloromethane. At ambient temperature and pressure, the uncapped Te nanoparticles in different solvents spontaneously experienced a similar “nanoparticles-nanochains-agglomerates-microspheres” evolution growth. The distinctive growth kinetics show strong dependence on the polarity and the spatial structure of solvent molecules. Furthermore, the obtained uncapped Te nanoparticles and Te nanochains displayed a prominent size-dependent and structure-inherited chemical reductive ability. These findings give additional insights regarding the growth of active uncapped colloidal nanoparticles, supply an alternative route to design novel nanostructures of alloys, telluride and functional composites by using Te as reactive precursor.

Student presentation

P33 Generation of Fluorinated Hydrophilic Carbon Nanoparticles from Water/Hexafluorobenzene Bilayer Solution by Femtosecond Laser Pulses

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We reported the production of hydrophilic carbon nanoparticles (CNPs) from benzene/water bilayer solution by femtosecond irradiation. This method allows us to use a variety of organic molecules as a carbon source. We could control the elemental composition of CNPs surface by selecting suitable organic molecules. In this study, we synthesized fluorinated hydrophilic CNPs from water/hexafluorobenzene bilayer (W/HFB) solution. The water layer of aerated W/HFB bilayer solution was exposed to the focused femtosecond laser pulses. The morphology of CNPs was observed by TEM. The properties of CNPs were analyzed by using IR and Raman spectroscopy. XPS and SEM-EDS measurements indicated that fluorine was successfully incorporated into hydrophilic CNPs surface. The primary reaction mechanism will be discussed.

P34 Facile Preparation of Cu2O and CuO Nanoparticles by Pulsed Laser Ablation in NaOH Solutions of Different Concentration

Y. Seong, H. J. Jung, M. Y. Choi (Jinju/KR)

Synthesis of metal oxides with low cost and well-defined morphology has attracted considerable attention because metal-oxide nanoparticles exhibit useful optical or electrical functions as well as catalytic actions for various applications. Cuprous oxide (Cu2O) and cupric oxide (CuO) are naturally abundant, nontoxic, low-cost, potential photovoltaic materials that have a wide range of potential applications in electronic and photonic devices, solar cells,1 thin-film transistors, and heterogeneous catalysts because of their low energy gap (2.17 and 1.2 eV, respectively) and high catalytic activity. Various synthetic methods, including electrodeposition, vacuum evaporation, and hydrothermal method, have been used to synthesize Cu2O and CuO. Among the various particle fabrication methods, pulsed laser ablation in liquid (PLAL) is currently attracting great interest for the synthesis of a variety of novel nanomaterials because of its simplicity and versatility. In this study, Cu-based nanoparticles, including Cu, Cu2O, and CuO, were prepared by PLA at different concentrations of NaOH.

Student presentation

P35 Plasmonic properties of indium and indium oxide nanoparticles grown in liquid medium

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Nobel metal nanoparticles act as efficient plasmonic nanoantennas having the remarkable ability to confine light in their near-field regime. Silver (Ag) and gold (Au) are the most extensively explored plasmonic materials that sustain strong localised surface plasmon resonance (LSPR) in the visible-infared region of the electromagnetic spectrum.Unfortunately, Ag and Au do not support strong LSPRs in the high frequency ultra-violet (UV) and deep UV region. Indium is a promising active plasmonic metal that supports SPR in the ultraviolet with low absorption loss. This extended accessibility makes Indium an attractive material for UV plasmonic, chemical sensing, catalysis and more recently in UV-SERS. In this paper, we report “green” synthesis of indium oxide nanoparticles (NPs) by pulsed laser ablation in liquid (PLAL) technique with the aim to study the influence of the laser fluence, liquid media and surfactant on the morphology and optical absorption of the NPs. Indium oxide (In2O3) is a versatile transparent conducting oxide material with high electrical conductivity offering diverse applications in the fields of electronic, sensing and photovoltaic.Indium oxide nanoparticles (NPs) have been produced by irradiating metallic indium (In) target immersed in ultra-pure water (DI),ethanol and tetrahydrofuran (THF) with a second harmonic (532 nm) Nd:YAG laser beam for 30 min. The optical absorption measurements reveal that the yield of NPs and plasmonic response varies with laser fluence. XPS analysis indicates the formation In3+ chemical state together with asymmetric and broaden In3d peaks for indium oxide formation. For the case of indium ablated in different concentration of CTAB (0.1, 0.5, 1, 5, 10 mM), ablation yield increased with increase in concentration of CTAB and an optimum yield is obtained at CMC (~1 mM). TEM micrograph shows the formation of chain-like nanoparticles with dimensions of about 10-20 nm. Finite difference time domain (FDTD) method is employed to calculate the localized surface plasmon resonance (LSPR) wavelength and the near-field generated by pure indium NPs in presence of DI, ethanol and THF.

P36 Silica aerogel obtained by femtosecond laser irradiation of TEOS

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A. Galasso, R. Teghil (Potenza/IT)

Laser ablation in liquid (LAL) is a recent technique widely used for the production of colloidal solution of nanomaterials. In this work, the LAL experiments have been realized by irradiating tetraethyl orthosilicate (TEOS), which is a liquid usually employed as reagent in the sol – gel technique with the purpose to produce silica gel
It has been shown that, by irradiating TEOS with an ultrashort fs laser, a solid foam is obtained. Information about the product morphology has been obtained by means of electronic microscopy techniques, the bonds structure has been studied through of IR and Raman measurements. The composition has been estimated employing EDX technique. This structure is made by network of micro – wires, which in turn seem to be made up of smaller structure having nanometric size. This highly porous sample, having a large surface, is characteristics of materials known as aerogels, which are the less dense kind of solid known. This material have peculiar properties which make it interesting in technological fields. Usually, aerogels are obtained trough sol – gel process characterized by hydrolysis and condensation reactions. In our case, a gas phase thermal decomposition mechanism has been proposed. A Pd doped aerogel has been obtained by ablating a Pd solid target immersed in TEOS. The obtained composite aerogel can be useful for applications in the field of catalysis.

Student presentation

P37 Pulsed laser synthesis of W-based particles in C-Si-O-H environment

L. Shih-Siang, S. Pouyan, C. Shuei-yuan (Kaohsiung City/TW)

Polycrystalline W plate in BCC structure was subjected to pulsed laser ablation (PLA, Nd-YAG laser using 1064 nm excitation under free run mode and 1000 mJ/pulse) in tetraethyl orthosilicate to fabricate W-based crystallites with specific size, composition and crystal structures. The W-based nanoparticles less than 20 nm in size thus formed are of predominant rocksalt-type (γ-WC) and minor β-type (A15 simple cubic structure, a typical occurrence in the presence of oxygen [1,2]), as indicated by X-ray diffraction (Fig. 1a) and bright field image (BFI) coupled with selected area electron diffraction (SAED) (Figs. 1b and 1c) taken by transmission electron microscopy (TEM, FEI Tecnai G2 F20 at 200 kV).By contrast, C-overdoped W particulates with ordered body-centered orthorhombic (OBCO) structure were ynthesized by inward diffusion of C from substrate upon pulsed laser heating in vacuum when PLA of W plate was conducted in vacuum using 1064 nm excitation under Q-switch mode and 600 mJ/pulse [3]. Under such a case, the OBCO particulate typically showed (hkl) facets edge on in the [010] zone axis against the C-doped BCC-W nanocondensates with decreasing size away from the particulate (cf. red arrow in Fig. 2) [3]. This knowledge is of concern to the kinetic phase selection of the W-based materials in the C-Si-O-H environment.

Semiconductor and dielectric nanoparticle

P38 Doping nanoparticles from ions dissolved in the liquid: the case of Gd2O3:Eu3+

G. Ledoux, A. Chemin, J. Lam, G. Ledoux, D. Amans (Villeurbanne/FR)

Doping nanocrystals allows modifying their optical or electrical properties. In the case of PLAL, the standard route is to prepare doped material as a pellet using solid state reaction. Such approach suffers from potential inhomogeneity and has to follow the thermodynamic law regarding distribution coefficient of dopants. In this contribution, we use salts in the solvent to dope the nanoparticles during the condensation of the plasma obtained by the ablation of undoped materials. This alternative route is of high interest to potentially obtain higher doping level or to incorporate unusual activators. It also demonstrates the deep interaction between the plasma and the solvent. For this purpose, we prepared Gd2O3:Eu3+ nanoparticle, a well-known red luminescent sesquioxides containing gadolinium which is also known as a contrast agent for nuclear magnetic resonance imaging. In addition, Eu3+ is a well know structural probe, since its optical response depends strongly on the crystal field symmetry at the point defect. It thus brings information about crystallinity, is sensitive to the crystallographic phase, the surface, and the defects of which the as-produced particles generally suffer. We performed the ablation of cubic phase Gd2O3 targets immersed in aqueous solutions of EuCl3. We show that the produced nanoparticles are doped in the core. We also determined the efficiency of the doping process as a function of the salt concentration. From the luminescence spectra showing a monoclinic crystallographic phase feature, it appears that the doping process favors the smallest nanoparticles.

P39 SnS thin films from nanocolloids prepared by pulsed laser ablation in liquid

J. Johny, S. Shaji, D. A. Avellaneda
B. Krishnan (San Nicolas de los Garza/MX)

Pulsed laser ablation in liquid (PLAL) is a one step method to produce pure nanoparticles. Tin sulfide (SnS) is a p-type semiconductor which finds applications in solar cells and photovoltaic devices due to its optimal band gap. Spray technique is an effective one to obtain nanostructured thin films. In this work, we report the fabrication and characterization of SnS nanocolloids by pulsed laser ablation and their thin films by spray technique. SnS NPs were produced using pulsed laser ablation of SnS target in N, N Dimethylformamide and acetone.

Thin films of SnS were successfully deposited on glass substrates by spraying the colloidal suspension obtained by laser ablation. The characterization of the nanoparticles and thin films were done by Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), X-ray Photoelectron Spectroscopy (XPS) and UV-Vis absorption spectroscopy. XPS analysis confirmed the elemental composition as well as the chemical state of these thin films. The study explores the application of PLAL to produce nanocolloids and their deposition as thin films for optoelectronics.

P40 Structure and properties of CdS nanoparticles obtained by pulsed laser ablation in liquid

S. Shaji, G. G. Guillen, B. Krishnan (San Nicolas de los Garza/MX)

Cadmium sulphide (CdS) is a significant II–VI compound semiconductor material with applications in optoelectronics and photonics. Pulsed Laser Ablation in Liquids (PLAL) has become an efficient physical method for fabrication of nanomaterials. Cadmium sulfide (CdS) nanoparticles were synthesized by pulsed laser ablation of a CdS target by the 532 and 1064 nm outputs from a pulsed (10 ns, 10 Hz) Nd: YAG laser in different liquid media. The morphology, crystalline structure, chemical state and elemental composition, optical absorption and luminescent properties were analyzed using Transmission Electron Microscopy (TEM), X-ray diffraction (XRD), X-Ray Photoelectron Spectroscopy (XPS), UV-Visible absorption spectroscopy and room temperature photoluminescence spectroscopy. TEM analysis demonstrated that the energy fluence and liquid medium resulted with different morphologies for CdS nanoparticles. XRD and XPS results confirmed the crystallinity and chemical states of these nanoparticles. The optical band gap energies for CdS nanocolloids were evaluated from their UV-Visible absorption spectra and they showed emissions in the green region.

P41 Enhanced optical response of noble metal-ZnO hybrid nanostructures prepared by pulsed laser ablation in polymeric water solutions

L. D'Urso (Catania/IT), E. Fazio (Messina/IT), G. Compagnini (Catania/IT)
F. Neri (Messina/IT)

Zinc oxide (ZnO) with direct wide band gap and high exciton binding energy is one of the most promising materials for ultraviolet light-emitting devices. Nanometer-sized ZnO particles exhibit a significant enhancement of the broad near-UV luminescence peak with respect to the bulk material. However, the strong visible emission associated with surface defects of nanoparticles, generally accompanies the enhancement of the excitonic transition in the UV. Recently, surface plasmon mediated emission was considered to further improve the quantum efficiency of light emitting materials [1]. Here we report on laser-generated metal (Me=Ag,Au)-semiconductor (ZnO) hybrid nanostructures in water or polymeric media, with tunable structural and optical properties. Morphology and composition of Me-ZnO heterostructures were investigated by X-ray diffraction, Scanning Transmission Electron microscopy, X-ray photoelectron and Raman spectroscopies, while for the optical properties, photoluminescence and UV-visible analysis were performed. Our results show a significant enhancement of the broad near-UV luminescence peak of ZnO and a substantial reduction of some selected visible emission features in presence of Me nanoparticles. This behavior can be explained in terms of near-field optical coupling between metal surface plasmons and ZnO excitons. It should be considered that Me nanoparticles are chemically reactive at the interface with ZnO and oxidation phenomena may occur, affecting the UV emission [2] We show that a change in the composition of the ablation medium (by introducing PVA chains) may influence surface oxidation, thus enhancing the UV light emission. Further, wide band gap materials have been recently considered for nonlinear optical (NLO) applications in integrated optics. In this contest, third-order optical nonlinearity was measured using the Z-scan technique at the wavelength of 532 nm with a 6 ns laser pulse. Our aqueous dispersions Me-ZnO show self-defocusing nonlinearity and good nonlinear absorption behavior. We outline that different NLO activation mechanisms can be induced in Me-ZnO hybrid nanostructures by varying the ablation medium. Scattering coefficient and nonlinear refractive index values decrease while nonlinear absorption one increases in the presence of silver nanoparticles, suggesting an enhancement of the exciton oscillator strength related to the high electric field values in proximity of the metal nanoparticles.

P42 Photoluminescent carbon nanoparticles generated by laser treatment of graphite powder under liquid layer

N. Tarasenka, A. Butsen, A. Stupak, N. Tarasenko (Minsk/BY)

We report the one-step synthesis approach for preparation of luminescent carbon NPs via laser irradiation of graphite powder under layer of the organic solvent (octane) or aqueous glucose solution. This is a simple approach for the fabrication of carbon dots with tunable photoluminescence (PL) that differs from the other preparation methods as no post-passivation step is required. The sizes of the prepared NPs were mainly distributed in the range of 2–5 nm with an average value of 3 nm. The photoluminescence spectra are dependent on the laser excitation wavelength; when the excitation wavelength changed from 290 nm to 450 nm, emission wavelength shifted from 330 to 515 nm, respectively. The excitation-dependent PL behavior of C-dots can be attributed to differences in sizes of NPs in the sample and/or different emissive sites on NPs surfaces. The highest intensities of emission bands were detected for excitation wavelength of 290 nm.

Size control during laser ablation, fragmentation and melting

Student presentation

P43 Real time diagnostic of the nanoparticle shape evolution during the fragmentation

A. Resano-Garcia, Y. Battie, A. En Naciri, N. Chaoui (Metz/FR)

Metal nanoparticles exhibit unique optical properties such as surface plasmon resonances (SPR) coming from the collective oscillations of their electrons. SPR are increasingly utilized in many fields of applied sciences. Frontier areas of research and development require the precise control of the nanoparticle size and shape during their synthesis. In this context, we have developed an optical characterization tool to estimate the nanoparticle shape distribution from their absorption spectra. These spectra are quantitatively analyzed by using a new effective medium theory. Contrary to common effective medium theory, our calculation takes into account the nanoparticle shape dispersion. The estimated distributions are in close agreement with the ones deduced from TEM. By applying our procedure to gold nanorods exposed to a pulsed laser beam, we demonstrate that this characterization tool enables a real time diagnostic of the evolution of the nanoparticle shape during their fragmentation.

Student presentation

P44 Laser-generated Pt nanoparticles as highly pure accumulation platform for medically relevant radioisotopes

S. Jendrzej, B. Gökce, S. Barcikowski (Essen/DE)

The radioisotope Iodine-123 is a widely used radioactive material in nuclear medicine imaging. For an efficient application of the radionuclide a high I-123-concentraion and purity is required. These properties are essential for adequate detection of emitted γ-rays and to prevent radiation exposure to patients by isotopes with longer half-lives. The production of I 123 in a cyclotron and subsequent accumulation of I-123 by ion exchange resins are limited in drug concentration. [1] A promising method to achieve high I-123 concentrations consists of adsorption of radioisotope to laser-generated nanoparticles in liquids. The nanoparticles are produced ligand free in water by picosecond pulsed laser ablation of a metal target corresponding to a reactive surface with a high affinity for negatively charged ligands, such as I-123. [2] Laser-fragmentation and centrifugation leads to monomodal and monodisperse platinum nanoparticles with a high surface area of 56 m2/g particles. In contrast, laser-generated nanoparticles without subsequent laser-fragmentation feature a 2.8 times lower surface area corresponding to a lower radionuclide density on nanoparticles. Based on this work platinum nanoparticles are supported to titanium dioxide microparticles in a filled column. Since the nanoparticles are immobilized, agglomeration is prevented. [3] Laser-generated nanoparticles are favored for this new and promising method of I-123 accumulation, since their pure surface do not contaminate the medically relevant I-123-eluate by ligands.

P45 Temporal and spectral characterization of breakdown plasma induced by laser radiation in nanoparticles colloidal solutions

A. Serkov, I. Rakov, P. Kuzmin, G. Shafeev (Moscrow/RU)

Temporal and spectral characteristics of laser breakdown plasma induced in nanoparticles colloidal solutions were experimentally studied. Near-infrared laser sources of nanosecond pulse duration were used. It was shown that under certain experimental conditions nanosized plasma around nanoparticles may change to laser-induced breakdown plasma in liquid. The dependencies of the plasma temporal and spectral characteristics on laser pulse duration as well as resulting nanoparticles properties were studied. Laser-induced breakdown plasma lifetime was shown to be comparable to laser pulse duration. The efficacy of the gold and silver nanoparticles fragmentation was shown to depend on laser pulse duration. Similar experiments were carried out under reduced external pressure. It turned out to affect plasma and nanoparticles properties. Transmission electron microscopy and disc measuring centrifuge were used for nanoparticle size and morphology analysis. Extinction spectra of colloidal solutions and emission spectra of plasma were studied by means of optical spectroscopy.

P46 Laser-assisted generation of Gd-containing nanoparticles in liquids

P. Kuzmin, M. Petrov, V. Voronov, G. Shafeev (Moscow/RU)

PLAL allows generation of large variety of nanoparticles even of those of chemically active materials. In this report the experimental results are presented on generation of Gd-containing nanoparticles via laser ablation of a bulk Gd and alloyed GdTi targets in various liquids (water, ethanol, n-propanol, DMSO, etc). Ablation of targets was carried out using a Nd: YAG laser with pulse duration of 200 ns and repetition rate of 20 kHz at 1064 nm output. Chemical composition of resulting nanoparticles determined with the help of X-ray diffraction is shown to depend on the nature of surrounding liquid. Ablation of Gd target in either water or ethanol results in the formation of Gd2O3 nanoparticles.
In this case the chemical composition of resulting nanoparticles is more complex. Nanoparticles obtained by ablation of a bulk Gd target in DMSO show their plasmon resonance in the visible and are therefore metallic. The generated nanoparticles are suitable to further biomedical applications.

P47 Nanoparticle colloids of one-dimensional assembly of perylenediimide prepared by laser ablation

S. Sasaki, S. Higuchi, T. Asahi (Matsuyama/JP)

Laser ablation in liquid has advantages for preparing organic nanoparticles because sample microcrystalline powder suspended in a poor solvent can be converted directory into stable nanoparticle colloids without any chemical additives. Here, we report nanoparticle colloids of fluorescent perylenediimide (PTCDI) prepared by nanosecond laser ablation, and compared them to those by a conventional reprecipitation method. Fluorescence nanoparticle colloids were obtained by nanosecond laser irradiation (532-nm wavelength and 8-ns pulse width) to PTCDI powder in acetonitrile. The nanoparticles had cubic or rod-like shapes with a mean size of 50 nm, and they dispersed stably for longer than 1 month in acetonitrile. On the other hand, the aggregates of fibers having several micrometers length and a few tens width were obtained by reprecipitation from a chloroform solution of PTCDI, and the fibers did not disperse in acetonitrile. The nanoparticles by laser ablation and the fibers by reprecipitation showed the absorption spectrum having a red-shifted peak wavelength (570 nm) from the absorption peak of a solution and fluorescence spectrum with broad peaks at 640 and 670 nm. In both nanostructure, PTCDI molecules are considered to form a J-aggregate-like stacking, although the morphology and the size differ from each other. We will present and discussed the fluorescence properties of the nanoparticles, comparing to those of nanofibers.

Student presentation

P48 Fabrication of nanofiber colloids of copper phthalocyanine nanoparticles by laser ablation in liquids

R. Kihara, S. Imada, T. Asahi (Matsuyama/JP)

Fabrication of colloidal nanofibers of copper phthalocyanine (CuPc) by nanosecond laser ablation of its micro-crystals in ethanol and acetonitrile was investigated. A mixture (5.0 x 10-3 wt%) of CuPc powder and ethanol or acetonitrile was exposed to nanosecond Nd3+: YAG laser pulses (532 nm, 8 ns FWHM, 10 Hz), and stable colloids of the nanoparticles were obtained at laser fluences above 35 mJ/cm2 in each solvent. The nanoparticles having rectangular shape (a mean size of 45 nm in width and 150 nm in length) was obtained at the fluence of 35 mJ/cm2, and the absorption showed the characteristic spectral shape of β-form crystal. On the other hand, at 140 mJ/cm2, spherical nanoparticles with a mean diameter of 25 nm was formed just after laser irradiation, and the nanoparticles grew up to fibers (a mean width of 30 nm, length of 200 nm) in a few weeks after preparation, accompanying with the absorption spectral change that could be ascribed to a crystalline phase transition from α- to β-form. It was also found that the size and shape of β-form nanoparticles of CuPc could be controlled by tuning the laser fluence and the temperature; i.e. nanofibers or nano-rods having larger aspect ratios were obtained when the nanoparticles were prepared at higher laser fluences or when they stood at higher temperatures.

P49 NAYF4 nanoparticles generation by pulsed laser ablation in water

L. Gemini, M.- C. Hernandez, R. Kling (Talence/FR)

Abstract has been withdrawn.

Student presentation

P50 Influence of laser wavelength on formation of boron nitride nanoparticles in liquid medium

M. Meixus, M. Boutinguiza, A. Chantada, A. Riveiro, J. del Val Garcia
R. Comesaña, F. Lusquiños, J. Pou (Vigo/ES)

Boron nitride nanomaterials have been attaining special interest due to their unique properties, such as chemical inertness, thermal stability and mechanical strength. Moreover, likewise graphene, boron nitride has several crystalline varieties each one with its own individualities. In this work, we have studied the synthesis of boron nitride nanoparticles by pulsed laser ablation in different solvents. Therefore, a solid BN target was accommodated in a glass vessel filled with liquid up to 1 mm over the upper surface of the BN sheet. Various laser sources working at different wavelengths and different irradiation parameters were used to carry out the experiments. The crystalline phases and morphology of the obtained nanoparticles were characterized by means of scanning electron microscopy (SEM), transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM). In this study, the effect of laser wavelength on the fabrication of Boron Nitride nanoparticles was investigated.

P51 Selenium nanoparticles synthesized by femtosecond laser ablation in DI water

G. Guisbiers, G. Naranjo, E. Hernandez, H. H. Lara, K. L. Nash
X. G. Peralta (San Antonio/US)

Selenium (Se) is a trace element that is essential for life (adult dietary requirement ~40 µg Se/day) while at the same time being toxic at high levels (>3200-6700 µg Se/day). Selenium enters the food chain through the plants consumed by humans and animals. The plants absorb the selenium directly from the soil therefore selenium intake among human populations is highly dependent on the geographical area. In human beings, selenium is incorporated into at least 25 selenoproteins that have a wide range of effects e.g. antioxidant activity, chemopreventive, anti-inflammatory and antiviral properties. Selenium prevents also the growth and proliferation of E. coli and S. aureus, the two bacteria that are mainly responsible of nosocomial diseases. Therefore, there is a growing interest in synthesizing selenium nanoparticles for nanomedical applications. The goal of this investigation is to report on the first synthesis of selenium nanoparticles by pulsed laser ablation in liquids using a femtosecond laser. With this laser, two different mechanisms of nanoparticle production are involved: melting and photo-fragmentation. Nanoparticles produced by melting were crystalline with a size ~ 25 nm while the ones produced by photo-fragmentation were amorphous with sizes ~ 100 nm. In addition, the irradiation is accompanied by a laser induced bubbles "boiling bubble" reaching a macroscopic size of several millimeters after several minutes of irradiation and preventing the bulk selenium pellet of further ablation. Finally, those nanoparticles were used to inhibit the growth of Candida albicans.

P52 Inner structural analysis of silver submicron spherical particles fabricated by pulsed laser melting in liquid

T. Nakamura (Sendai, Sapporo/JP), H. Magara (Sendai/JP), S. Sakaki
N. Koshizaki (Sapporo/JP), S. Sato (Sendai/JP)

Submicron spherical particles (SSPs) of metals, alloys, oxides and semiconductors have been successfully fabricated by pulsed laser melting (PLM) in liquid medium. The fabricated particles have unique structural features of spherical shape, uniform size distribution and crystalline structure. In the present study, inner structure of metal SSPs was analyzed by electron backscattering diffraction (EBSD) to understand the formation mechanism. Raw particles of silver with the diameter of smaller than 100 nm were dispersed into ultrapure water with the concentration of 200 ppm. The second harmonics of a Nd: YAG pulsed laser (wavelength: 532 nm, repetition rate: 30 Hz, pulse width: 8 ns, beam diameter: 8 mm) was employed for PLM without focusing. Laser fluence condition on the surface of the colloidal solution was set at 50 mJ/cm2. A magnetic stirrer was used to prevent gravitational settling of the suspension. Silver SSPs with the average diameter of about 200 nm were obtained through selective heating of source particles by PLM in the colloidal solution after 180 min irradiation. Fabricated particles were separated by centrifugation with 2000 rpm for 30 min. For EBSD analysis, Ag SSPs were fixed on a copper-based bulk metallic glass plate (ϕ=12 mm, Cu36Zr48Ag8Al, BMG Inc.) as a substrate to keep conductivity and suppress EBSD from it for microscopic analysis. Focused Ga+ ion beam was used to obtain cross-sectional surface of the Ag SSPs. Many hemispherical particles having defects inside it were clearly seen without charging during SEM observation. The hemispherical particles were identified as Ag without any impurities by energy-dispersive X-ray spectroscopy (EDS). One can see in the EBSD mapping of the hemispherical particles that fabricated SSPs are mixture of poly-crystal and single crystal particles composed of multi- and single-colored area, respectively. According to the result, these SSPs with crystalline nature are formed through a repetitive multi-step process such as agglomeration of primary particles, melting, solidification and agglomeration of relatively larger particles. It seems that crystal growth of Ag SSPs did not occur in melting process of relatively larger particles.

P53 Synthesis of stable colloids of metal and metal oxide nanoparticles for nanotoxicological research

V. Y. Shur, A. Tyurnina, D. Kuznetsov, E. Linker
G. Burban (Ekaterinburg/RU)

Currently, the expansion of the study of nanoparticle toxicity (nanotoxicology) needs production of the stable colloids of high concentration with model pure nanoparticles of given composition, sizes and shapes [1]. The laser ablation in water gives the unique ability to produce the colloids of pure metals and metal oxides with required parameters. The stable colloids of Au, Ag, CuO, NiO, Fe2O3, and Mn3O4 nanoparticles with narrow distribution functions and concentration up to 0.5 g/l have been produced to study the impact of the nanoparticles on the biological cells [2]. 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/cm2, spot diameter 40 μm). The NPs synthesis was performed in several stages: surface treatment by focused laser beam scanning, ablation the target, separated additional fragmentation, drying to increase the concentration of the solution up to 0.5 g/l and heating for nanoparticle self-organization and reshape [3]. It was revealed that the treatment representing the number of the scanning cycles for removing the surface nanocrystalline layer of the target allows to decrease the NPs sizes and to increase the reproducibility from cycle to cycle. The separated additional fragmentation process has been applied before and after suspension concentration to increase its stability and for further reduce of the particle sizes.Scanning electron microscope CrossBeam Workstation Auriga, Carl Zeiss scanning probe microscope Ntegra-Aura, NT-MDT and particle size analyzer Zetasizer Nano ZS, Malvern were used for analysis the target surface condition and parameters of nanoparticles (z - potential and sizes) after each step of the synthesis. The impact of nanoparticles on alveolar macrophageshas been in vivo studied by atomic force microscopy and by scanning electron microscopy. In was found that phagocytosis of nanoparticles leads to change of the cells surface morphology at the nano-scale. The pits were absent on the surface of reference cell. The sizes of nano-pits revealed by atomic force microscopy on the surface of the cells of rats administered by nanoparticles are close to the sizes of used nanoparticles. This fact confirms the absence of aggregation.

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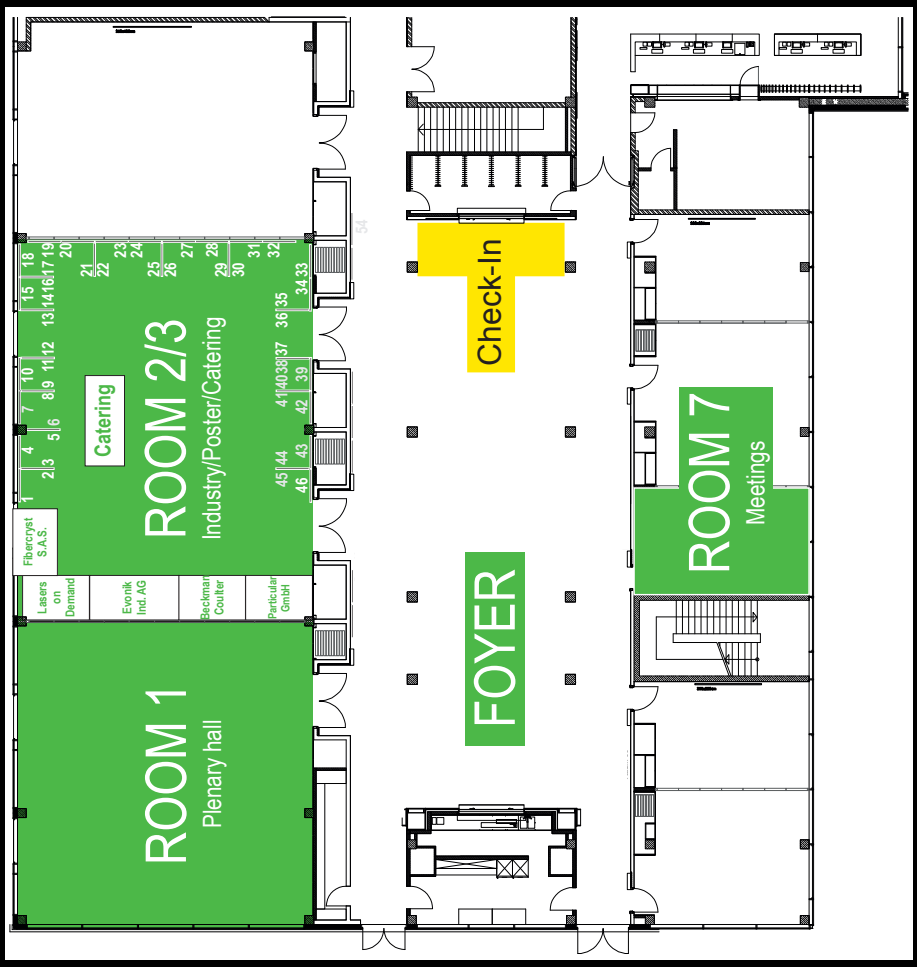
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