



# ANGEL2014

*May 19-21, 2014  
Matsuyama, Japan*



## 3<sup>rd</sup> Conference on Advanced Nanoparticle Generation and Excitation by Lasers in Liquids

### PROGRAM

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# **ANGEL2014**

## 3<sup>rd</sup> Conference on Advanced Nanoparticle Generation and Excitation by Lasers in Liquids

Matsuyama, Japan  
May 19-21, 2014

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# Organization

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ANGEL (Advanced Nanoparticle Generation and Excitation by Laser in Liquid) is a conference series that brings the international community together to discuss scientific issues in the context of laser-generated nanoparticles in liquids. Following the first conference in 2010 in Engelberg, Switzerland, and the second one in 2012 in Sicily, Italy, ANGEL2014 is held in Matsuyama, Japan.

### SCOPE

Today, nanoparticles are widely implemented as functional elements on surfaces, into volumes and as nanohybrids, resulting for example in bioactive composites and nanobiomarkers. Nowadays, however, only a limited variety of materials that may be integrated into advanced functional materials are available. Laser ablation and nanoparticle generation in liquids has been proposed as an alternative synthesis method of advanced nanomaterials, addressing some of these drawbacks of the current fabrication methods.

In the last decade, laser ablation in liquid has proven to be a unique and efficient technique to generate, excite, fragment, and conjugate elemental, nanoalloy, semiconductor, ceramic, and organic nanoparticles. This exciting method bears strong advantages:

- (i) Chemical precursors are not required and thus a pure colloid is obtained by a simple, one step process.
- (ii) Laser-generated nanoparticles have a high surface activity - the surface is not blocked by ligands.
- (iii) This method can be applied universally with an almost unlimited variety of materials and solvents.

It has recently been shown that these advantages are of value in comparison to conventional synthesis, in particular in the applications to the fields of biomedicine and catalyst. Pulse laser excitation induces not only ablation of solids but also fragmentation, melting, and annealing, which results in the unique properties of the generated nanomaterials, such as submicrometer spheres, metastable phases, and organic-inorganic nano-composites. The recent advancements and critical aspects in the fields of pulse laser-based nanomaterial generation in liquids will be discussed at ANGEL 2014.

### TOPICS

Modeling and fundamentals of pulse laser-based nanomaterial generation

Metal, carbon, semiconductor, and organic nanoparticles

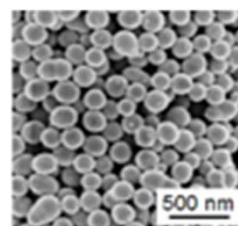
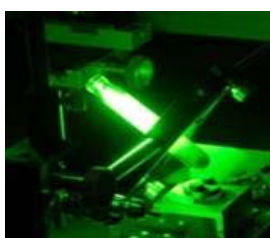
Nano-alloys, core-shell particle, nano-composites

Nano-hybrids, conjugation with organic molecules and biomolecules

Submicrometer spheres

Applications to biomedicine, catalyst, photonics, sensor, and more

Nanoparticle productivity / scale-up



## INFORMATION FOR AUTHORS AND ATTENDEES

### VENUE

Oral presentation: Room Duemila, 3F Hotel JAL City Matsuyama

Poster presentation: Room Festa, 2F Hotel JAL City Matsuyama

### ORAL PRESENTATIONS

Time slots	Keynote talk	45 min including 5-min discussion
	Invited talks	30 min including 5-min discussion
	Oral contributed talks	20 min including 5-min discussion

Oral presentations will be given by using an electronic projector and Microsoft PowerPoint software.

Please connect your own PC with an electronic projector prior to your presentation.

Ensure that your computer is equipped with the proper monitor connector (mini D-sub 15 pin) . If your computer does not have this connection, please bring an appropriate converter with you.

### POSTER PRESENTATIONS

Poster set-up and removal is in the responsibility of the authors. Pins for display will be available in the poster room.

The poster session room will open at 15:00 Monday, 19 May. Any posters left on the boards at the close of the poster session will be discarded.

Poster numbers will be displayed on the poster boards to show authors.

The size of the poster boards is 90 cm (width) x 200 cm (height).

### WIFI ACCESS

Free WIFI access will be available at the conference location (1F Lobby, 3F Lobby).

### BEST STUDENT PRESENTATION AWARD

The best student contribution and the best poster presentation of ANGEL 2014 will be awarded. All student oral and all poster contributions are eligible to the prize. The criteria for the award are relevance, originality, scientific merit and clarity.

### CONFERENCE BANQUET

The conference banquet will be taking place on Tuesday, 20 May from 19:00 - 21:00 in the venue hotel (Room Duemila). The banquet fee includes an buffet with cold & warm food as well as beverages and drinks (beer, wine, etc.)

Where: Room Duemila, 3F Hotel JAL City Matsuyama

When: Tuesday, 20 May; 19:00 - 21:00

Costs per person: 10,000 JPY ( including TAX)

### SOCIAL PROGRAMME

The social programme on Monday, 19 May from 14:30 - 17:00 will include a tram to the city centre of Matsuyama, a cable car to Matsuyama Castle and guided walking tour through the historic castle.

Meeting-place: 1F Lobby, Hotel JAL City Matsuyama

Meeting time: 14:30, Tuesday, 20 May

**Please Note:** The participation in the banquet and in the social programme is optional and required separate registration

### INTERNAL MEETINGS

Programme Committee Breakfast: Wednesday, 21 May, 2014

Location: La Terrazza, 1F Hotel JAL City Matsuyama. Time: 08:00-09:00

## Sunday, 18 May

16:00-18:00 Pre-Registration

## Monday, 19 May

09:00-09:15 *Opening*

09:15-10:00 Keynote talk *chaired by Fumitake Mafuné; The University of Tokyo*

Strategies to harvest the unique properties of PLAL-generated nanomaterials in biomedical and energy applications

Stephan Barcikowski; *University of Duisburg-Essen (GERMANY)*

10:00-11:00 Session 1: Application 1 *chaired by Giuseppe Compagnini ; University of Catania*

11:00-11:20 *Coffee break*

11:20-12:20 Session 2: Application 1 (continued) *chaired by Georgy A. Shafeev; Russian Academy of Sciences*

12:20-13:40 *Lunch*

13:40-15:30 Session 3: Mechanism *chaired by Stephan Barcikowski; University of Duisburg-Essen*

INVITED 1: Generation processes of nanoparticles in liquid-phase laser ablation: Insights obtained by in-situ diagnostics

Koichi Sasaki; *Hokkaido University (JAPAN)*

15:30-16:00 *Coffee break*

16:00-17:30 Session 4: Methodology *chaired by Tsuyoshi Asahi; Ehime University*

INVITED 2: Nanoparticle synthesis by picosecond laser ablation of thin-films in liquids

Sean M. O'Malley; *Rutgers University - Camden (USA)*

17:50-19:30 Poster session

## Tuesday, 20 May

09:00-10:40 Session 5: Sub-micrometer sphere *chaired by Dongsik Kim; POSTECH*

10:40-11:00 *Coffee break*

11:00-12:50 Session 6: Material 1 *chaired by Alessandro De Giacomo; University of Bari*

INVITED 3: Controllable synthesis of functional nanostructures by long-pulse-width laser

Du Xi-Wen; *Tianjin University (CHINA)*

13:00-14:20 *Lunch*

14:30-17:00 *Excursion*

19:00-21:00 *Banquet*

## Wednesday, 21 May

09:00-10:50 Session 7: Material 2 *chaired by Koichi Sasaki; Hokkaido University*

INVITED 4: Double pulse laser ablation in liquid for the production of nano-structures: fundamental aspects and potential advantages

Alessandro. De Giacomo; *University of Bari (ITALY)*

10:50-11:10 *Coffee break*

11:10-12:50 Session 8: Material 2 (continued) *chaired by Sean M. O'Malley; Rutgers University - Camden*

12:50-14:10 *Lunch*

14:10-15:20 Session 9: Application 2 *chaired by Moreno Meneghetti; University of Padova*

INVITED 5: Laser treatment to modify thermal and colloidal properties of nanofluids

Dongsik Kim; *POSTECH (SOUTH KORIA)*

15:20-15:40 *Coffee break*

15:40-17:00 Session 10: Application 2 (continued) *chaired by Takeshi Tsuji; Shimane University*

17:00-17:15 *Closing Remarks & Student Award Ceremony*

09:00-09:15 OPENING BY THE CHAIRS

*Tsuyoshi Asahi ; Ehime University  
Fumitake Mafuné ; The University of Tokyo*

09:15-10:00 KEYNOTE TALK

*Chair: Fumitake Mafuné ; The University of Tokyo*

### **Strategies to harvest the unique properties of PLAL-generated nanomaterials in biomedical and energy applications**

*S. Barcikowski ; Technical Chemistry I and Center for Nanointegration Duisburg-Essen (CENIDE), University of Duisburg-Essen (GERMANY)*

In this contribution, examples of harvesting the unique properties of laser-fabricated nanoparticles in the field of biomedicine and catalysis are given, emphasising efforts to address the limits of the methods, particularly: i) achieving monodisperse nanoparticles using in-situ grafting on catalyst supports or trace amounts of salts without any surfactants or organic ligands, thus keeping the high purity of colloids made by laser ablation; ii) upscaling the productivity as non-cost-effectively as possible by optimizing the process, laser parameters, or target geometry; iii) strategies towards real-world applications with integrated laser-made nanomaterials, at the examples of surface coatings, polymer composites, and supported particles.

Session 1: APPLICATION 1

*Chair: Giuseppe Compagnini; University of Catania*

10:00-10:20 1O-01

### **Preparation and biomedical application of upconversion nanoparticles prepared by laser ablation in liquid**

*T. Ikehata, T. Nunokawa, O. Odawara, H. Wada ; Tokyo Institute of Technology (JAPAN)*

Y<sub>2</sub>O<sub>3</sub>:Er,Yb upconversion nanoparticles were prepared by laser ablation in liquid and the optical properties were investigated for PDT. Target of laser ablation in liquid was prepared by sol-gel method. The powder was sintered in an electric furnace. The target was irradiated with focused pulse laser beam. Prepared sample was identified by X-ray diffraction. Particle size was measured by scanning electric microscopy. Upconversion spectra were measured by fluorescence spectrometer. The possibility of PDT was investigated. Chlorin e6 was used as a photosensitizer. Singlet oxygen which was one of ROS was determined by the 1,3-diphenylisobenzofuran bleaching method.

10:20-10:40 1O-02

### **One-step synthesis of dual-modality nanoprobe for *in vivo* imaging**

*J. Xiao<sup>1,2</sup>, X. M. Tian<sup>3</sup>, C. Yang<sup>2</sup>, P. Liu<sup>1</sup>, N. Q. Luo<sup>1</sup>, Y. Liang<sup>1</sup>, H. B. Li<sup>1</sup>, D. H. Chen<sup>1</sup>, L. Li<sup>2</sup>, G. W. Yang<sup>1</sup>; <sup>1</sup> Institute of Optoelectronic and Functional Composite Materials, Nanotechnology Research Center, School of Physics & Engineering, Sun Yat-sen University; <sup>2</sup> Imaging Diagnosis and Interventional Center, Sun Yat-sen University Cancer Center; <sup>3</sup> Department of Biomedical Engineering, Guangzhou Medical University (CHINA)*

We synthesize these dual-modality nanoprobe by choosing Gd<sub>2</sub>O<sub>3</sub> as a solid target and various Ln<sup>3+</sup> ionic liquid as the solvent. Our measurements indicate that the water proton relaxivity is 12.27 mM<sup>-1</sup>s<sup>-1</sup> when adding these NPs. Besides, their red, green, blue fluorescence are observed with naked eyes. Cell fluorescence images also show these NPs to be good fluorescence imaging agent. We further demonstrate that these nanoprobe are safe and effective targeted probes for *in vivo* imaging based on the *in vitro* and *in vivo* assessments of biocompatibility. These findings provide useful information for the application of dual-modality nanoprobe in biomedical applications.

10:40-11:00 1O-03

### **SERS-active Ag-Au alloy nanoparticles obtained by laser ablation in liquids for sensing methylene blue**

*O. Olea-Mejía, M. Camacho-Lopez, G. Rodriguez-De La Concha, M. Fernandez-Mondragon, O. Olea-Cardoso; Autonomous University of the State of Mexico (MEXICO)*

We have prepared alloy nanoparticles of Ag and Au in water and ethanol for sensing methylene blue. The particles were obtained from targets with different compositions in water and ethanol as the liquid media. The spherical particles obtained are completely alloyed as shown by the UV-Vis spectra and the single-particle EDS analysis performed in a Scanning-TEM microscope. When no particles are used it is impossible to observe any Raman peak of the methylene blue, however when the particles are used several Raman peaks can be easily resolved. All samples showed SERS effect, however the highest intensities were recorded when pure Ag particles were employed. It was possible to observe the tallest Raman peak at concentrations as low as 1x10<sup>-10</sup> mole/L (5.2x10<sup>-5</sup> ppm) which is an extremely high sensitivity.

11:00-11:20 Coffee break



## Session 2: APPLICATION1 (continued)

Chair: *Georgy A. Shafeev; Russian Academy of Sciences*

11:20-11:40 1O-04

**Multifunctional nanostructures obtained by laser ablation synthesis in solution with plasmonic properties for SERS signals and magnetic properties for MRI and for magnetic selection.***M. Meneghetti<sup>1</sup>, V. Amendola<sup>1</sup>, F. Bertorelle<sup>1</sup>, S. Scaramuzza<sup>1</sup>, A. Scarsi<sup>1</sup>, L. Litti<sup>1</sup>, M. Gobbo<sup>1</sup>, M. Pinto<sup>2</sup>, G. Fracasso<sup>2</sup>, M. Colombatti<sup>2</sup>; <sup>1</sup> University of Padova, Dep. of Chemical Sciences; <sup>2</sup> University of Verona, Dept. of Pathology (ITALY)*

Laser Ablation in solution (LASiS) allows to synthesize nanomaterials with plasmonic and magnetic properties. We show these type of nanostructures can be obtained by LASiS of an Au-Fe alloy target or by assembling naked nanoparticles of gold and iron oxide obtained separately by LASiS. These nanostructures with multiple functionalities are interesting for the control of systems to which the nanostructures can be coupled. Functionalization of these nanostructure for example with antibodies allows to use the antibody-antigen interaction for magnetic selection and SERS identification of cells and in particular of tumour cells.

11:40-12:00 1O-05

*Student presentation***Pulsed laser ablation in aqueous polymer precursor solutions for embedding bioactive nanoparticles in situ into microgel fibres for the care of burn wounds***N. Million<sup>1</sup>, P. Nachev<sup>2</sup>, V. Coger<sup>3</sup>, A. Pich<sup>2</sup>, K. Reimers<sup>3</sup>, P. M. Vogt<sup>3</sup>, S. Barcikowski<sup>1</sup>; <sup>1</sup> Technical Chemistry I and Center for Nanointegration Duisburg-Essen, University of Duisburg-Essen; <sup>2</sup> Interactive Materials Research, Institute for Macromolecular and Technical Chemistry, RWTH Aachen University; <sup>3</sup> Department of Plastic, Hand- and Reconstructive Surgery, Hannover Medical School (GERMANY)*

The use of nanoparticle loaded microgels acting as carrier substance for drug delivery has reached a field of great interest in medicine. In this work it is shown that copolymer microgel fibers loaded with ZnO nanoparticles, which show a cell stimulating effect and support of wound healing, can be prepared in situ using laser ablation technique and processed to cover wounds for the application in treatment of burns. Aqueous media guarantees the absence of toxic substances and the thermal stability of the microgels enables sterilization processes. The successful embedding of ZnO nanoparticles offers possible usage of different bioactive metals.

12:00-12:20 1O-06

**Oocyte maturation as a highly sensitive model to explore toxicity of metal and metal alloy nanoparticles***D. Tiedemann<sup>1</sup>, U. Taylor<sup>1</sup>, C. Rehbock<sup>2</sup>, J. Jakobi<sup>2</sup>, S. Klein<sup>1</sup>, W.A. Kues<sup>1</sup>, S. Barcikowski<sup>2</sup>, D. Rath<sup>1</sup>; <sup>1</sup> Institute of Farm Animal Genetics, Friedrich-Loeffler-Institut, Federal Research Institute of Animal Health; <sup>2</sup> Technical Chemistry I and Center for Nanointegration Duisburg-Essen (CENIDE), University of Duisburg-Essen (GERMANY)*

The multitude of applications of nanoparticles does not correspond to current knowledge on the kind of toxicity these particles might unfold. Reprotoxicity in particular has hardly been investigated. The presented study aimed to develop a model for efficient reprotoxicological screening of nanoparticles. In vitro oocyte maturation is delicate and very susceptible to disturbances. It represents an excellent functional test for nanotoxicological examinations. Oocytes were exposed to either pure gold or silver nanoparticles, gold-silver alloy nanoparticles, nickel-titanium alloy nanoparticles or chromium-steel alloy nanoparticles. Silver nanoparticles and gold-silver alloy nanoparticles were detected to elicit a considerable reprotoxicity.

12:20-13:40 Lunch

## Session 3: MECHANISM

Chair: *Stephan Barcikowski; University of Duisburg-Essen*

13:40-14:10 INVITED TALK 1

**Generation processes of nanoparticles in liquid-phase laser ablation: Insights obtained by in-situ diagnostics***K. Sasaki; Hokkaido University (JAPAN)*

We have found that nanoparticles are produced inside the cavitation bubble in liquid-phase laser ablation. This has been confirmed by in-situ laser light scattering combined with shadowgraph imaging. In addition, it has also been found that nanoparticles are stored inside the cavitation bubble until the collapse. This means that nanoparticles are placed in the reaction field with a high pressure and a high temperature at the collapse of the cavitation bubble. The enhancement of the crystallinity of nanoparticles is obtained by pressurizing the ambient liquid, which is caused by the change in the dynamics of cavitation bubble.

14:10-14:30 1O-07

**Spectroscopy of molecular and atomic species during laser ablation in liquids: questions regarding chemistry and local thermodynamic equilibrium**

*D. Amans<sup>1</sup>, J. Lam<sup>1</sup>, F. Chaput<sup>2</sup>, M. Diouf<sup>1</sup>, G. Ledoux<sup>1</sup>, N. Mary<sup>3</sup>, K. Masenelli-Varlot<sup>3</sup>, V. Motto-Ros<sup>1</sup>, C. Dujardin<sup>1</sup>;*

*<sup>1</sup>UMR5306 CNRS, Institut Lumière Matière, University Lyon 1; <sup>2</sup>UMR5182 CNRS, Laboratoire de Chimie, ENS Lyon; <sup>3</sup>UMR5510 CNRS, MATEIS, INSA-Lyon (FRANCE).*

During PLAL, the nucleation of the nanoparticles in the gas phase and their growth is not clear, due to the difficulty of following the gas composition as well as the thermodynamic parameters. Using plasma spectroscopy during the synthesis of gamma-Al<sub>2</sub>O<sub>3</sub> nanoparticles, we measured the electron density, the density ratio between the Al atoms and AlO molecules, and the rotational and vibrational temperatures of the AlO molecules. However, the validity of our plasma analysis raised the question of the local thermodynamic equilibrium. We then tested the Drawin / MacWhirter criterion for a plasma containing molecules.

14:30-14:50 1O-08

*Student presentation*

**On the use of computational chemistry to understand the cluster generation processes**

*J. Lam, A. Alloïche, C. Dujardin, G. Ledoux, D. Amans; Institut Lumière Matière, University Lyon 1 (FRANCE)*

In the context of Pulse Laser Ablation in Liquid, it appears crucial to obtain the most complete understanding of the highly complex particle growth processes. Most of the time, the investigation techniques do not provide any information about the chemical composition for the gas phase system ( $T > 10$  microseconds). To this purpose, we developed different numerical tools used in computational chemistry. Density Functional Theory (DFT) calculation enabled to simulate the physical properties of the Al<sub>x</sub>O<sub>y</sub> molecules. In a second step, it also provides a solid framework to predict the chemical reactions and geometrical structures for the synthesized nanoparticles.

14:50-15:10 1O-09

*Student presentation*

**Effect of laser fluence on atomic density ratio in the plasma produced by ns laser ablation on a Cu-Zn alloy**

*A. Matsumoto<sup>1</sup>, A. Tamura<sup>1</sup>, K. Kubotsu<sup>1</sup>, A. Kawasaki<sup>1</sup>, K. Fukami<sup>2</sup>, B. Thornton<sup>3</sup>, N. Nishi<sup>1</sup>, T. Sakka<sup>1</sup>;* *<sup>1</sup>Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University; <sup>2</sup>Department of Material Science and Engineering, Graduate School of Engineering, Kyoto University; <sup>3</sup>Underwater Technology Research Center, Institute of Industrial Science, The University of Tokyo (JAPAN)*

For the production of alloy nanoparticles by laser ablation, it is important to investigate the plasma produced on an alloy target. We performed emission spectroscopy of ns laser ablation plasma produced on a Cu-Zn target (Zn/Cu = 0.54) in air with different laser fluences. Atomic density ratio in the plasma was evaluated from the emission spectrum. The values of Zn/Cu were 0.98 and 1.86 for laser fluences of 500 and 17 mJ/cm<sup>2</sup>, respectively. We consider that the composition of the plasma is attributed to the difference of thermal properties between constituent atoms and the heat propagation in the target surface.

15:10-15:30 1O-10

**Bubble dynamics in laser ablation in liquid studied through high-speed laser stroboscopic videography**

*R. Tanabe, K. Tamura, T. Nguyen, T. Sugiura, Y. Ito; Nagaoka University of Technology (JAPAN)*

Dynamics of laser ablation induced by a nanosecond laser pulse in pure water has been studied through high-speed laser stroboscopic videography method. A cavitation bubble was formed by the laser pulse and it oscillated several times in a few milliseconds. Any ejection of particles at the boundary of the first bubble is not observed in our images during its growth and shrink periods. As an attempt for observing inside the first bubble, a narrow, rectangular volume was defined in liquid by two glass plates and the laser ablation was induced in this volume. Images obtained, however, do not show any distinguishable structure in gas phase inside the bubble.

15:30-16:00 Coffee break

## Session 4: METHODOLOGY

Chair: *Tsuyoshi Asahi; Ehime University*

16:00-16:30 INVITED TALK 2

**Nanoparticle synthesis by picosecond laser ablation of thin-films in liquids***S. O'Malley, D. Bubb; Rutgers University - Camden (USA)*

Thin-films deposited on glass substrates are utilized as ablation targets for nanoparticle synthesis via the laser ablation in liquids methods. The average nanoparticle size was found to decrease with increasing film thickness. Results are discussed in terms of differences in thermal conductivity at the film-substrate interface and average temperature reached in the thin-film. Other considerations that may influence nanoparticle size such as influence of the liquid layer height above the target are investigated via shadowgraph imaging, TEM, and dynamic light scattering.

16:30-16:50 10-11

**Hydrophilic and hydrophobic carbon nanoparticle production from organic/water bilayer with laser plasma filament***T. Yatsuhashi; Graduate School of Science, Osaka City University (JAPAN)*

Hydrophilic and hydrophobic carbon nanoparticles were formed by femtosecond laser irradiation to the water layer of an aerated benzene/water bilayer solution. Focusing intense femtosecond laser pulses onto water creates a high density of reactive species in a well-confined volume; i.e., plasma filament. The properties of the particle surface were controlled simply by adjusting the laser focusing position, the duration between the sample preparation and the laser irradiation. Hydroxyl group is the origin of the hydrophilicity, and the particle had a graphitic and disordered structure. We discuss the subsequent reaction mechanism leading to nanoparticles of different surface characters.

16:50-17:10 10-12

*Student presentation***Synthesis of gold nanoparticles colloids by highly-intense laser irradiation of aqueous solution in a continuous flow***Muttaqin, T. Nakamura, S. Sato; IMRAM, Tohoku University (JAPAN)*

Metal nanoparticles (NPs) are getting more attention in modern advanced materials science because they have unique properties in physical, chemical and biological aspects, and have remarkable potentials in many applications, for example, in catalysts or in sensors. The control of purity and particle size of metal NPs are still an obstacle to be handled, therefore finding a novel technique is necessary to overcome aforementioned barrier. Femtosecond laser irradiation is one of novel techniques for generating metal NPs both in pure form and in alloys. This method can generate metal NPs directly using ultra-short laser irradiation on the metal salt solution.

17:10-17:30 10-13

*Student presentation***Laser fragmentation and mass-specific energy balancing in a free liquid jet for fragmentation threshold determination***M. Lau, S. Barcikowski; Technical Chemistry I and Center for Nanointegration Duisburg-Essen, University of Duisburg-Essen (GERMANY)*

Pulsed laser fragmentation in liquid (PLFL) is a versatile and 'green' technique to fabricate nanoparticles from micro- and sub-microparticles dispersed in a liquid phase. We investigated the influence of laser fluence on PLFL using zinc oxide in a free liquid jet, confining the particle suspension to the focal region and correlated the change in particle size to the mass-specific energy intake. For this the complete particle size distribution of the suspension was characterized. Further a process window for enhanced fragmentation is defined.

17:50-19:30 Poster session

Hotel JAL City Matsuyama, Festa

Session 5: SUB-MICROMETER SPHERES

Chair: Dongsik Kim; POSTECH

09:00-09:20 2O-14

**Reactive fabrication of MgTi<sub>2</sub>O<sub>5</sub> spherical particles by pulsed laser melting in liquid from raw particle mixture**

*Y. Ishikawa<sup>1</sup>, N. Koshizaki<sup>2</sup>; <sup>1</sup> National Institute of Advanced Industrial Science and Technology; <sup>2</sup> Hokkaido University (JAPAN)*

Our group has reported that submicrometer-sized spherical particles can be fabricated by pulsed laser melting in liquid in which raw nanoparticles dispersed in liquid are irradiated by a pulsed laser with adequate fluence. From single-component raw particles, spherical particles are formed without changing the material just by simple melting, or those of material different from the raw particles are formed reactively with surrounding liquid component. Recently two-component raw particle mixture cases were reported. In this study, we attempt to fabricate spherical complex oxide particles from raw particle mixture by mimicking conventional ceramic powder reaction technique.

09:20-09:40 2O-15

**Totally surfactant-free Au submicrometer spheres with variable surface textures fabricated by pulsed laser melting in liquid (PLML)**

*C. Rehbock, J. Zwartscholten, S. Barcikowski; Technical Chemistry I and Center for Nanointegration Duisburg-Essen, University of Duisburg-Essen (GERMANY)*

Gold Submicrometer Spheres (Au-SMS) are applicable in optics (SERS, bioimaging) and may be fabricated by PLML. State of the art synthesis, however, includes the use of ligands to control aggregation, which limits biological applications. To overcome these limitations we used NaCl to induce aggregation, while in a consecutive step we performed reirradiation with a ns-laser ( $\lambda=532$  nm). Via SEM we could confirm that particle size increases with the fluence while simultaneously the portion of wrinkled surface textures became more abundant. Additionally, we could proof that surface texture is influenced by the educt materials, larger educt nanoparticles preferably yielded smoother surfaces.

09:40-10:00 2O-16

**Fabrication of calcium phosphate submicrometer spheres by pulsed laser irradiation to calcium phosphate reaction mixture**

*M. Nakamura<sup>1</sup>, A. Oyane<sup>1</sup>, I. Sakamaki<sup>1</sup>, Y. Ishikawa<sup>1</sup>, Y. Shimizu<sup>1</sup>, K. Koga<sup>1</sup>, K. Kawaguchi<sup>1</sup>, N. Koshizaki<sup>1,2</sup>; <sup>1</sup> National Institute of Advanced Industrial Science and Technology; <sup>2</sup> Hokkaido University (JAPAN)*

Iron-containing calcium phosphate submicrometer spheres were successfully fabricated by pulsed laser irradiation to a reaction mixture of calcium, phosphate, and ferric ion solutions. Without ferric ions in the reaction mixture, no spheres were obtained even after the laser irradiation, indicating that ferric ions played a crucial role in the formation of spheres. Our process is simple and rapid, and would be useful in the fabrication of calcium phosphate-based spheres for drug and gene delivery.

10:00-10:20 2O-17

**Preparation of non-toxic gold submicron-sized particles using laser-induced melting in liquids**

*T. Tsuji<sup>1</sup>, Y. Higashi<sup>2</sup>, M. Tsuji<sup>2</sup>, Y. Ishikawa<sup>3</sup>, N. Koshizaki<sup>4</sup>; <sup>1</sup> Shimane University; <sup>2</sup> Kyushu University; <sup>3</sup> National Institute of Advanced Industrial Science and Technology; <sup>4</sup> Hokkaido University (JAPAN)*

Recently, the laser-induced melting in liquids method, in which colloidal nanoparticles (NPs) are irradiated by non-focused laser beam at moderate fluence, attracts much attention as a novel and conventional technique to prepare spherical submicron-sized particles (SSMPs). We revealed that the control of the agglomeration conditions of the source NPs is necessary to obtain SSMPs. In the previous study, tri-sodium citrate was used to control the agglomeration conditions of the source NPs. In the present work, NaCl is employed to control the agglomeration conditions of the source NPs and to prepare non-toxic gold SSMPs. Differing from citrate, NaCl is not decomposed by laser irradiation and form no unnecessary byproduct.

Hotel JAL City Matsuyama, Duemila

10:20-10:40 2O-18

**Synthesis of the non-equilibrium bimetallic nano-alloys by pulse laser melting in liquid**

*Z. Swiatkowska-Warkocka*<sup>1</sup>, *A. Pyatenko*<sup>2</sup>, *N. Koshizaki*<sup>3</sup>; <sup>1</sup> *Institute of Nuclear Physics (PL)*; <sup>2</sup> *National Institute of Advanced Industrial Science and Technology*; <sup>3</sup> *Hokkaido University (JAPAN)*

Nano-composites and nano-alloys are versatile materials for a manifold of applications in optics, magnetics, catalysis activity, corrosion resistance, electrochemistry, and biotechnology. Among them alloys of gold (Au) with the magnetic 3d elements iron (Fe), cobalt (Co), and nickel (Ni) are fascinating materials because they are immiscible under equilibrium conditions, but non-equilibrium phases are of interest for their potential multifunctional optical, catalytic, and magnetic properties. Here, we demonstrate our recent research on laser-based synthesis of nano-composites, in particular nano-alloys of Au with 3d transition metals.

10:40-11:00 Coffee break

**Session 6: MATERIAL 1***Chair: Alessandro De Giacomo: University of Bari*

11:00-11:30 INVITED TALK 3

**Controllable synthesis of functional nanostructures by long-pulse-width laser**

*D. Xi-wen*, *Y. Jing*, *N. Kai-Yang*; *School of Materials Science and Engineering, Tianjin University (CHINA)*

In this presentation, we show some advantages of millisecond laser on the controllable preparation of nanostructures. Firstly, millisecond laser can be employed to synthesize nanostructures with controllable morphologies, such as core-shell nanoparticles, nanocubes, nanowires, heterostructures, hollow nanoparticles and ordered arrays of nanoparticles. Secondly, millisecond laser can transform semiconductor powders into monodisperse quantum dots which exhibit controllable sizes and narrow dispersions (5.4% - 8.7%). Thirdly, millisecond laser can deaggregate the detonation nanodiamonds completely, and well-dispersed nanodiamonds can be obtained. Our works demonstrate that millisecond laser is a powerful tool for achieving high-quality nanomaterials.

11:30-11:50 2O-19

**Pulsed laser ablation of CuInGaSe<sub>2</sub> alloy in different liquid media**

*M. I. Mendivil*<sup>1</sup>, *L.V. García*<sup>1</sup>, *G.A. Castillo*<sup>1</sup>, *T.K. Das Roy*<sup>1</sup>, *D. Avellaneda*<sup>1</sup>, *B. Krishnan*<sup>1,2</sup>, *S. Shaji*<sup>1,2</sup>; <sup>1</sup> *Facultad de Ingeniería Mecánica y Eléctrica, Universidad Autónoma de Nuevo León*; <sup>2</sup> *CIIDIT- Universidad Autónoma de Nuevo León (MEXICO)*

Currently the nanofabrication of complex structures is a novel topic. Pulsed laser ablation in liquid medium (PLALM) is a useful technique to produce nanostructures with the direct ablation of the alloy material as target. CuInGaSe<sub>2</sub> (CIGS) is an alloy with applications in the photovoltaic industry. In this report, we used a Q-switched nanosecond pulsed Nd:YAG laser (532 nm, 10 ns, 10 Hz) for ablation of a CuInGaSe<sub>2</sub> (1:0.3:0.7:2 at%) alloy target in distilled water, acetone and ethanol. We studied the effects of laser energy fluence and liquid media on the properties of the ablated products. The nanoparticles obtained were analyzed by transmission electron microscopy (TEM), X-ray Energy Dispersion Spectroscopy (EDAX), selected area electron diffraction (SAED), X-ray photoelectron spectroscopy (XPS) and UV-Vis absorption spectroscopy. XPS results confirmed the chemical state and composition of the ablated products. TEM analysis showed that there were some differences in the morphologies of the nanomaterials obtained that were dependent on the liquid media. In distilled water and ethanol, the nanoparticles were spherical combined with other products whereas in acetone was predominantly spherical and smaller in size. The optical properties for these colloidal solution obtained by ablation process were analyzed using UV-visible absorption spectroscopy. The results demonstrated the use of PLALM as a useful technique for synthesis of nanomaterials of quaternary photovoltaic materials.

11:50-12:10 2O-20

**Pd-based alloy nanoparticles through femtosecond laser irradiation of aqueous solution supported on oxide**

*M. Sarker*, *T. Nakamura*, *S. Sato*; *IMRAM, Tohoku University (JAPAN)*

Metal and alloy NPs with the control of composition, size and shape are of special interests because of their essential role in the three-way catalysis. In this respect, Pd, Rh-Pd and Rh-Pd-Pt NPs fabricated by femtosecond laser with desirable compositions were supported on aluminum oxide (gamma-phase, 99.97 %, metal basis, Alfa Aesar) having the surface area of 80-120 m<sup>2</sup>/g. The sample was dried using a freeze dryer. Granules of 212-235 μm in diameter were formed from the obtained powder of supported material. Catalytic activities of unsupported and supported samples will be compared with respect to the conversion of CO.

12:10-12:30 2O-21

**Generation of core-shell nanoparticles Ti@Al by laser ablation in liquid for hydrogen storage**

*E. V. Barmina*<sup>1,2</sup>, *A. A. Serkov*<sup>1,2</sup>, *A. V. Simakin*<sup>1,2</sup>, *P. G. Kuzmin*<sup>1,2</sup>, *V. V. Voronov*<sup>3</sup>, *G. A. Shafeev*<sup>1,2</sup>; <sup>1</sup>Wave Research Center of A.M. Prokhorov General Physics Institute of the Russian Academy of Sciences; <sup>2</sup>Advanced Energy Technologies, Ltd.; <sup>3</sup>A.M. Prokhorov General Physics Institute of the Russian Academy of Sciences (RUSSIAN FEDERATION)

Core-shell nanoparticles Ti@Al are generated by ablation of a composite Ti-Al target in liquid isopropanol saturated with molecular hydrogen using a Nd:YAG laser with pulse duration of 10 ps and repetition rate of 200 kHz. Transmission Electron Microscopy analysis of generated NPs reveals their core-shell structure with Ti core and Al shell. Average size of NPs determined with the help of measuring disc centrifuge is around 100 nm. The dependence of hydrogen content in generated NPs is studied as the function of experimental parameters, such as fluence on the target, total exposure time, ratio of Ti/Al, etc.

12:30-12:50 2O-22

**Preparation of metal sulfide semiconductor nanoparticles by a solution-phase laser ablation method**

*R.-D. Sun*<sup>1</sup>, *T. Tsuji*<sup>2</sup>; <sup>1</sup>Sekisui Chemical Co., Ltd.; <sup>2</sup>Kyushu University (JAPAN)

Metal sulfide semiconductor nanoparticles were successfully prepared by using a liquid-phase laser ablation method, and their physical properties were investigated.

12:50-13:00 Group Photo

13:00-14:20 Lunch

14:30-17:00 Excursion

19:00-21:00 Banquet

## Session 7: MATERIAL 2

Chair: Koichi Sasaki; Hokkaido University

09:00-09:30 INVITED TALK 4

**Double pulse laser ablation in liquid for the production of nano-structures: fundamental aspects and potential advantages***A. De Giacomo*<sup>1,2</sup>, *M. Dell'Aglio*<sup>2</sup>, *R. ElRashedy*<sup>1</sup>, *R. Gaudio*<sup>2</sup>, *E. Bronzini*<sup>1</sup>, *O. De Pascale*<sup>2</sup>, *G. Palazzo*<sup>1</sup>; <sup>1</sup> University of Bari; <sup>2</sup> CNR-IMIP (ITALY)

Experiments of single and double pulse Laser Ablation in Liquids (LAL) were carried out for studying the production of nanoparticles (NPs) in water, which revealed the fundamental role of plasma evolution and cavitation bubble dynamics in the formation of nanostructure and in their corresponding properties. Different techniques were used for studying the phenomena occurring during LAL at different conditions. These include Optical Emission Spectroscopy, fast camera shadowgraph and laser scattering, and combination of spectroscopic and microscopic techniques. The obtained results were linked to obtain a comprehensive description of the main features of LAL process and consequent applications.

09:30-09:50 3O-23

Student presentation

**Laser ablation of copper precursors suspended in organic liquids***C. A. Schaumberg*<sup>1</sup>, *M. Wollgarten*<sup>2</sup>, *K. Rademann*<sup>1</sup>; <sup>1</sup> Department of Chemistry, Humboldt-Universität zu Berlin; <sup>2</sup> Helmholtz-Zentrum Berlin für Materialien und Energie (GERMANY)

A promising alternative to PLAL of solid targets is the usage of suspended powders. If non-metallic precursors are used changes in the chemical composition are observed. Our investigations focus on the PLAL of a variety of copper precursors suspended in organic liquids. The chemical composition of the resulting particles is revealed by EFTEM and EELS. We report the impact of the choice of the precursor on the production rate, the size distribution and the chemical composition of the synthesized nanoparticles. The profound knowledge of the involved reaction paths extends the synthetic possibilities of PLAL.

09:50-10:10 3O-24

**Surfactant-free small nanoparticles trapped on silica particles prepared by pulsed laser ablation in liquid***F. Mafuné*<sup>1</sup>, *T. Okamoto*<sup>2</sup>, *M. Ito*<sup>2</sup>; <sup>1</sup> The University of Tokyo; <sup>2</sup> DENSO Corporation (JAPAN)

Small Ni nanoparticles supported on silica particles were formed by pulsed laser ablation in liquid. Water dispersing surfactant-free silica particles was used here as a solvent, and a bulk Ni metal plate as a target. The nanoparticles formed by laser ablation in water were readily stabilized by the silica particles, whereas Ni nanoparticles prepared in water without silica were found to be precipitated a few hours after aggregation into 5-30 nm particles. The nanoparticles were characterized by TEM, dark-field STEM and optical absorption spectroscopy, which indicated that small 1-3 nm Ni nanoparticles were adsorbed on the surface of silica.

10:10-10:30 3O-25

**Self-assembly of nanoparticles into nanowires under laser exposure in liquids***A. Serkov*, *E. Barmina*, *P. Kuzmin*, *G. Shafeev*; Wave Research Center of A.M. Prokhorov General Physics Institute of the Russian Academy of Sciences (RUSSIAN FEDERATION)

Experimental results are presented on the process of self-assembly of nanoparticles under their exposure to picosecond laser radiation in water. Self-assembly of nanoparticles into nanowires occurs under laser ablation of cathodically biased target. Similar self-assembly is observed in excess of free electrons in the solution due to presence of beta-active ions, e.g., tritium or uranium ions. As the result, the position of the plasmon resonance of Au nanoparticles shifts from 530 nm to red or infrared region. Transmission Electron Microscopy confirms the formation of nanowires with high aspect ratio ranging from 3 to 10. Possible mechanisms of self-assembly are discussed.

10:30-10:50 3O-26

**Reactivity of colloidal nanoparticles generated by laser ablation in liquids***J. Liu*, *Z. Tian*, *C. Liang*; Institute of Solid State Physics, Chinese Academy of Sciences (CHINA)

Laser ablation in liquids (LAL) is a non-equilibrium process to synthesize nanoparticles (NPs) with unique characteristics that may not be available by normal chemical routes, such as ultra-small size distribution, high reactivity, metastable structure and uncapped surfaces. These characteristics are particularly useful for exploring the unusual properties and application of LAL-induced NPs.<sup>1-3</sup> In this presentation, we show our efforts on reactivity investigation of simple elements Ge, Si, Te and Se NPs. As showing in Figure 1, novel Te hydrosols can be fabricated by LAL technique without using of any chemical stable reagents. These pure Te colloidal NPs display highly reactive ability, which could react with H<sub>2</sub>O at a low heating temperature and disproportionate to H<sub>2</sub>Te and H<sub>2</sub>TeO<sub>3</sub>. Furthermore, through reaction between different metal ions and Te hydrosols, a series of telluride compounds can be fabricated such as well-dispersed Ag<sub>2</sub>Te nanospheres.

10:50-11:10 Coffee break

Session 8: MATERIAL 2 (continued)

Chair: Sean M. O'Malley; Rutgers University - Camden

11:10-11:30 3O-27

**Solvent-dependence of dispersion stability of organic semiconductor colloids prepared by laser ablation**

H.-G. Jeon<sup>1</sup>, S. Haramiishi<sup>1</sup>, J. Miyazawa<sup>2</sup>, M. Ichikawa<sup>2</sup>, N. Oguma<sup>3</sup>, T. Asahi<sup>1</sup>, H. Ihori<sup>1</sup>, M. Fujii<sup>1</sup>; <sup>1</sup> Ehime University; <sup>2</sup> Shinshu University; <sup>3</sup> Dainichiseika Color & Chemicals Mfg. Co. Ltd. (JAPAN)

Laser ablation of organic materials, especially organic semiconductors, in a poor solvent is a very useful and effective method for the preparation of its colloids. However, only a little was known about the dispersion stability of those colloids. In this paper, we report some results about the dispersion stability of PTCDI-C13 colloids prepared by laser ablation in various solvents. The dispersion stability of colloids evaluated by measuring the zeta-potential and the change of absorbance after laser ablation is affected strongly not by the dielectric constant nor the dipole moment but by the functional group of solvents.

11:30-11:50 3O-28

**Electron transfer of porphyrin-polypeptide composite particles produced by laser ablation**

K. Leonard, A. Kaminaga, J. Kurawaki; Kagoshima University (JAPAN)

In this work, we report on the formation of microcrystals of zinc tetraphenyl porphyrin (ZnTPP) / homopolypeptide consisting of L-histidine (poly(His)) composite materials produced by laser ablation in poor solvents. FT-IRAS, absorption and fluorescence spectroscopic techniques provide detailed information concerning both chemical structure and intermolecular interactions within the microstructured area.

11:50-12:10 3O-29

**Advances in porous graphene and graphene quantum dots synthesis by pulsed laser ablation in liquid environments**

G. Compagnini<sup>1</sup>, P. Russo<sup>1</sup>, A. Hu<sup>2</sup>, R. Li<sup>2</sup>; <sup>1</sup> University of Catania (ITALY); <sup>2</sup> University of Tennessee (USA)

We present some experiments for nanosecond and femtosecond laser synthesis of Graphene Related Materials (GRMs) in a liquid environment, evidencing differences in the obtained materials as a function of fluence and pulse duration. Basically we observed competitive processes involving the formation of graphene oxide, porous graphene and graphene quantum dots. The obtained GRMs lie either at the water-air interface or well stabilized into the liquid medium and this is correlated to the degree of hydrophobicity of the produced sheets (degree of oxidation). Hypotheses on the mechanism of formation will be given, considering combined water breakdown and coal gasification phenomena.

12:10-12:30 3O-30

**Bismuth-based nanostructures obtained by laser ablation in liquids**

O. Olea-Mejia<sup>1</sup>, L. Escobar-Alarcon<sup>2</sup>, E. Velarde-Granados<sup>1</sup>, R. Lopez-Castañares<sup>1</sup>, O. Olea-Cardoso<sup>1</sup>; <sup>1</sup> Universidad Autonoma del Estado de Mexico; <sup>2</sup> Insituto Nacional de Investigaciones Nucleares (MEXICO)

The aim of this study was the synthesis and characterization of bismuth based nanostructures, such as nanoparticles and nanotubes. The influence of the experimental parameters such as energy fluence and the type of solvent on the properties of the nanostructures was studied. The obtained nanostructures were characterized by SEM, TEM and UV-Vis Spectroscopy. Depending on the preparation conditions, nanoparticles (Bi and/or Bi<sub>2</sub>O<sub>3</sub>) or nanotubres (Bi<sub>2</sub>O<sub>3</sub>) can be obtained. The nanostructures are highly crystalline and their size varies from 2 to 30 nm depending on the experimental procedure. The UV-Vis measurements showed the typical absorption band around 270 nm, from nanometer sized Bi particles. Bi<sub>2</sub>O<sub>3</sub> nanotubes are obtained at intermediate fluences and they have a diameter of 50 nm with lengths up to 5 micrometers.

12:30-12:50 3O-31

**Laser-induced phase-structure changes in ZnO colloidal nanoparticles**

N. Tarasenko, A. Butsen, N. Tarasenka; Institute of Physics, National Academy of Sciences of Belarus (BELARUS)

The results of laser induced modification of zinc oxide nanoparticles produced by laser ablation in liquid have been presented.

12:50-14:10 Lunch



## Session 9: APPLICATION 2

Chair: *Moreno Meneghetti; University of Padova*

14:10-14:40 INVITED TALK 5

**Laser treatment to modify thermal and colloidal properties of nanofluids***D. Kim; POSTECH (SOUTH KOREA)*

In this talk, the effects of pulsed-laser treatment of nanofluids, i.e., colloidal suspensions of nanoparticles, on their colloidal properties are presented, with emphasis on thermal conductivity and colloidal stability. First, laser-based techniques to synthesize/modify nanofluids are introduced. Secondly, nanosecond laser treatment to modify the thermal/rheological properties of various nanofluids and the size of the contained particles are summarized. Finally, a novel femtosecond laser processing technique to increase the colloidal stability and thermal conductivity of nanofluids is reported. Substantial enhancement of colloidal stability and/or thermal conductivity was obtained by the laser treatment of alumina nanoparticles in water.

14:40-15:00 3O-32

*Student presentation***Si quantum dots synthesized by pulsed laser ablation and development of whitish blue LED***Y. Xin<sup>1</sup>, K. Nishio<sup>1</sup>, K. Saitow<sup>1,2</sup>; <sup>1</sup> Graduate School of Science, Hiroshima University; <sup>2</sup> N-BARD, Hiroshima University (JAPAN)*

Silicon (Si) nanomaterials have attracted much attention as a promising material in optoelectronic devices because of non-toxicity, cost-effective, and abundance on the earth. We demonstrate Si quantum dots (QDs) solution synthesized by PLA in organic solvent, showing whitish blue photoluminescence. Using the Si-QDs solution and conductive polymer, a hybrid light-emitting diode (LED) was developed by solution processes. As a result, the electroluminescence spectrum of Si-QDs was observed in blue wavelength region at lower applied voltage. Significant increases of current density and optical power density were also obtained, which are 280 times and 350 times higher than reported values, respectively.

15:00-15:20 3O-33

*Student presentation***Synthesis and nanomedicine application of nanoparticles prepared by laser ablation in liquid***H.-P. Chen<sup>1,2</sup>, J. Liu<sup>1</sup>, F. Chen<sup>1</sup>, A. Wei<sup>3</sup>, D. Chen<sup>1</sup>; <sup>1</sup> School of Physics & Engineering, Sun Yat-Sen University; <sup>2</sup> School of information engineering, Guangdong Medical College; <sup>3</sup> School of Material and Energy, Guangdong University of Technology (CHINA)*

We propose a general, facile and simple approach to preparing dualmodal contrast agents with high spatial resolution for magnetic resonance imaging and high sensitivity for fluorescence imaging by combining the LAL with solid state reaction techniques.

Tm<sup>3+</sup>, Tb<sup>3+</sup>, and Eu<sup>3+</sup> doped Gd<sub>2</sub>O<sub>3</sub> targets and the corresponding nanoparticles colloids are prepared, respectively. Meanwhile, their blue green and red visible fluorescence are observed and their emission spectra are studied. We take Gd<sub>2</sub>O<sub>3</sub>:Tb<sup>3+</sup> as an example to evaluate the potential of using these particles in MRI besides fluorescence imaging, showing that the particles prepared can be used as MRI and fluorescence imaging dualmodal contrast agents.

15:20-15:40 Coffee break

## Session 10: APPLICATIONS 2 (continued)

Chair: *Takeshi Tsuji; Shimane University*

15:40-16:00 3O-34

**Photoluminescent nanoparticles generated by high repetition rate femtosecond lasers***M. Hernandez<sup>1</sup>, M. Faucon<sup>1</sup>, A. Garcia<sup>2</sup>, R. Kling<sup>1</sup>; <sup>1</sup> ALPhANOV; <sup>2</sup> ICMCB (FRANCE)*

Unlike nanosecond lasers, femtosecond lasers allow non-thermal effects processes. In this paper, we use a new industrial femtosecond Yb doped fiber laser working with pulse duration below 350fs and average power up to 20W to demonstrate the efficiency of the photoluminescent nanoparticles generation. This laser permits to reach high repetition rate to realize ablation in liquid. By using high scan speeds during the ablation we are able to increase the particle generation rate. We study the influence of the fluence on nanoparticles size distribution from up-converting materials.

16:00-16:20 3O-35

**Influence of surface hydrogenation on the phase formation in  $Y_2O_3$  nanoparticles by the laser ablation in solutions**

*S. Al-Mamun<sup>1</sup>, T. Ishigaki<sup>1</sup>, T. Uchikoshi<sup>2</sup>, M. Sumiya<sup>2</sup>; <sup>1</sup> Hosei University; <sup>2</sup> National Institute for Materials Science (JAPAN)*  
 $Y_2O_3$  and  $Y_2O_3:Eu^{3+}$  nanoparticles were synthesized by the pulsed-laser ablation in aqueous solutions. The influence of surface hydrogenation on the phase formation was examined by changing the pH of aqueous solutions and adding  $H_2O_2$  into water. The decrease of solution pH and the addition of  $H_2O_2$  into water gave rise to the hydrogenation of particle surface. The surface hydrogenation led to not only the decrease of particle size, but also the change of phase selection, which could be explained by the relaxation of surface energy. The improvement of PL properties was shown through the suppression of monoclinic phase formation.

16:20-16:40 3O-36

**Laser treated graphene oxide for dye removal water treatments**

*P. Russo<sup>1</sup>, S. F. Spano<sup>1</sup>, A. Hu<sup>2</sup>, G. Compagnini<sup>1</sup>; <sup>1</sup> University of Catania (ITALY); <sup>2</sup> University of Tennessee (USA)*  
Water treatment for the elimination of contaminants usually involves photocatalytic degradation with  $TiO_2$  powder. One limitation of  $TiO_2$  is the weak degradation under visible light.  $TiO_2$  catalytic performance can be improved doping it with different elements. Recently, graphene and graphene oxide (GO) have been employed in this direction. Here, we investigated the properties of laser treated GO (LT-GO) suspensions for methylene blue (MB) degradation. GO sheets were irradiated with a nanosecond laser that ensures a strict control of the degree of reduction in a green way. MB degradation efficiency of LT-GO alone and with  $TiO_2$  nanoparticles ( $TiO_2@LT-GO$ ) was investigated.

16:40-17:00 3O-37

**Z-scan measurement of nonlinear refractive index of graphene based on laser ablation**

*S. Hesami Afshar, P. Parvin, T. Mohammadi, S. Mehdadi, A. Bavali, H. Habibiyani, R. Karimi; Department of Energy Engineering and Physics, AmirKabir University of Technology (IRAN)*  
Under strong laser illumination, few-layer graphene exhibits a nonlinear phase shift. Here, we distinguish this nonlinear optical effect which used to be named nonlinear refractive index. Using Z-scan measurement, we show that fabricated graphene based on Q-switched Nd:YAG laser ablation possesses a giant nonlinear refractive index in comparison with graphene powders fabricated by chemical method.

17:00-17:15 CLOSING REMARKS & STUDENT AWARD CEREMONY

P-01

**CW Laser-Induced morphological changes of single gold nanoparticles supported on a glass substrate**

*K. Setoura, Y. Okada, S. Hashimoto; The University of Tokushima (JAPAN)*

We investigate the continuous wave laser-induced morphological changes of gold nanoparticles at single particle levels. The method provides us with better control over the nanoparticle heating and the related morphological changes. Further, the single particle study of such heating phenomenon helps us to clarify the morphological changes of a given particle as a function of time under irradiation with specific laser intensity. It is assumed that the laser-induced size-reduction takes place without any surface evaporation at particle temperatures above the bp for nanosecond pulsed-laser illumination. The current work suggests that the evaporation of Au NPs can be well-controlled by controlling the duration of irradiation using CW laser, which permits us the size-controlled preparation of Au NPs.

P-02

**Observation of the plasmon absorption band shifts of the silver nanoparticles formed by the laser ablation in a solution**

*Y. Murakami<sup>1</sup>, C. Ming Jing<sup>2</sup>; <sup>1</sup>Hachinohe National College of Technology, <sup>2</sup>Nagaoka National College of Technology (JAPAN)*

Laser ablation of silver plate in a solution with various surfactants were performed and it was found that anionic surfactant gave shorter wavenelgth shifts, while cationic surfactants gave longer wavelength shifts. Laser ablations using amphoteric surfactants were also performed and it was observed that spectral peak shift was changed with pH. In fluence of the dissolved gas on the size distribution of silver nanopartilces formed by laser ablation was also performed and the increase of the size of silver nanoparticle was observed for the laser ablation in water under the high-pressure CO<sub>2</sub> compared to that in pure water.

P-03

**Laser ablation at air-suspension interface using Cu target for fabrication of monodisperse nanoparticles**

*T. Nishi, N. Takahashi, Y. Akimoto; TOYOTA CENTRAL R&D LABS., INC. (JAPAN)*

We demonstrated laser ablation at air-suspension interface for the generation of monodisperse nanoparticle stably dispersed in water. In this study, we prepared Cu series nanocolloid by laser ablation at air-suspension interface using Cu series nanocolloid. After laser ablation at air-suspension interface, monodisperse nanoparticles stably dispersed in pure water could be obtained form nanoparticles with broad size distribution unstably dispersed in pure water.

P-04

*Student presentation*

**Computational study on pulsed-laser-induced size reduction of gold nanoparticles in water at high pressure**

*M. Strasser, K. Setoura, U. Langbein, S. Hashimoto; The University of Tokushima (JAPAN)*

Laser-induced size reduction of Au nanoparticles (NPs) had been the subject of many experimental studies and was found to depend on three parameters: ambient pressure, laser intensity and excitation wavelength. High pressure experiment prohibits vapor bubble formation in ambient atmosphere, offering a convenient method to control the heat dissipation in the NP. We used a two-temperature model to calculate the NP temperature under ns-pulse laser irradiation. It was found that the shape transformation of Au NPs takes place at temperatures between the melting point and boiling poin of Au.

P-05

**Formation of wide bandgap cerium oxide nanoparticles by laser ablation in aqueous solution**

*Y. Takeda<sup>1</sup>, F. Mafune<sup>2</sup>; <sup>1</sup>Genesis Research Institute, Inc.(JAPAN); <sup>2</sup>The University of Tokyo (JAPAN)*

Cerium oxide nanoparticles were produced by laser ablation in an aqueous solution. Submicron-sized cerium oxide particles were size-reduced by pulsed-laser irradiation into those having diameters of 3.6 nm. It was found that the bandgap of the nanoparticle is larger and the concentration of Ce<sup>3+</sup> in it is higher than those prepared by other conventional methods. These characteristic structures are likely to originate from more defect sites in the nanoparticles produced by laser ablation, where an O<sup>2-</sup> ion is less coordinated by the Ce ions, resulting in removal of the O atom and reduction of Ce<sup>4+</sup> into Ce<sup>3+</sup>.

P-06

**Laser ablation of Titanium in liquid in external electric field**

*E. Barmina*<sup>1</sup>, *V. Prischepa*<sup>1</sup>, *A. Serkov*<sup>1</sup>, *G. Shafeev*<sup>1</sup>, *V. Voronov*<sup>2</sup>; <sup>1</sup>Wave Research Center of A.M. Prokhorov General Physics Institute of the Russian Academy of Sciences; <sup>2</sup>A.M. Prokhorov General Physics Institute of the Russian Academy of Sciences (RUSSIAN FEDERATION)

Ablation of a bulk Ti target by 10 picosecond laser pulses in water is experimentally studied in external DC electric field. It is demonstrated that both the lateral size of nanostructures on Ti surface and their density depend on the electric field applied to the target. X-ray diffraction of generated nanoparticles shows difference in the crystallographic structure of nanoparticles of non-stoichiometric Ti oxides generated with and without electric field. The results are interpreted on the basis of instability of the melt on Ti surface in the electric field and simultaneous reduction of hydrogen from water due to electrolysis.

P-07

**Stability of metal nanoparticles fabricated by high-intensity femtosecond laser irradiation of aqueous solution**

*T. Nakamura*<sup>1</sup>, *A. Pyatenko*<sup>2</sup>, *S. Sato*<sup>1</sup>; <sup>1</sup>Institute of Multidisciplinary Research for Advanced Materials, Tohoku University; <sup>2</sup>National Institute of Advanced Industrial Science and Technology (JAPAN)

We demonstrated the preparation of stable colloids of noble metal and alloy nanoparticles (NPs) by high-intensity femtosecond laser irradiation of metallic salt solution without any reducing agents and surfactants. Although the prepared colloid of Au and Au-Pt alloy NPs over 20 min irradiation was stable for a month, the platinum colloid was deposited on the bottom of the cuvette within a couple of days. The stability of the colloid may be attributed to the surface charging of the NPs through the fragmentation of gold by aftercoming pulses because of the low fragmentation threshold of gold compared to platinum.

P-08

*Student presentation***Specific solvents produce specific phase Ni nanoparticles via pulsed laser ablation in solvents**

*H. J. Jung*, *M. Choi*; Gyeongsang National University (SOUTH KOREA)

We report a simple and controllable preparation of face centered cubic (fcc) and hexagonal close-packed (hcp) Ni nanoparticles by a pulsed Nd-YAG laser ablation method in various solvents, such as deionized water, methanol, hexane, and acetonitrile. We generate Ni/NiO and fcc/hcp Ni nanoparticles by a laser ablation to a Ni plate submerged in various solvents, followed by a post-ablation to the colloidal solutions. Interestingly, the phases of Ni nanoparticles prepared via PLAL show a strong dependence on the solvents used in the ablation process. Ni/NiO, pure fcc, and mixture of fcc and hcp Ni nanoparticles were generated in DI water, methanol, and hexane or acetonitrile, respectively. After the post-ablation, however, pure fcc Ni nanoparticles were generated in methanol and hexane; while pure hcp Ni was formed in acetonitrile. We think that the solvent dependence on the phase of Ni nanocrystals is related to the specific heat of solvents that plays an important role kinetically and thermodynamically in the process of cooling the plasma plume where the nanoparticles nucleate and coalesce to a specific phase. Formation of graphite layers on Ni nanoparticles fabricated in hexane and acetonitrile is also discussed. The Ni nanoparticles prepared from PLAL were analyzed by X-ray diffraction (XRD) measurements, X-ray photoelectron spectroscopy (XPS), field emission scanning electron microscopy (FE-SEM), high resolution transmission electron microscopy (HRTEM), and fast Fourier transform (FFT) analysis.

P-09

*Student presentation***Direct observation of aluminium and zinc ions produced via pulsed laser ablation in liquid : a 'turn-on' and 'turn-off' fluorescence study**

*S. Lee*, *A. Ahn*, *M. Choi*; Gyeongsang National University (SOUTH KOREA)

Al and Zn metal plates were ablated by a pulsed Nd:YAG laser to produce nano-structured Al with gamma-Alumina and Zn with ZnO in deionized water without any surfactants or catalysts, respectively. In this study, direct evidence for the production of Al<sup>3+</sup> and Zn<sup>2+</sup> ions from the plasma plume is presented for the first time by characterizing the absorption and emission spectra of their [Al(salophen)] and [Zn(TPPS)] complex. Very interestingly, a remarkable increase in the fluorescence intensity was observed when the Al<sup>3+</sup> ions, produced via the pulsed laser ablation, complexed with the salophen ligand. On the other hand, a decrease in the fluorescence intensity was observed when the Zn<sup>2+</sup> ions, complexed with the TPPS ligand. The fluorescence 'turn-on' and 'turn-off' was investigated by DFT/TD-DFT calculations. Based on these results, mechanisms for the production of aluminium with alumina and zinc with zinc oxide nanoparticles in the pulsed laser ablation in liquid (PLAL) process are proposed.

P-10

Student presentation

**Synthesis of polyynes by liquid-phase laser ablation and preparation of polyyne-liquid crystal composite material**

*A. Shibata, R. Matsutani, K. Inoue, T. Sanada, K. Kojima; Ritsumeikan University (JAPAN)*

In order to prepare new composite materials, we prepared polyyne containing liquid crystal of 4'-pentyl-4-biphenylcarbonitrile (PCH5). The polyynes have been prepared by liquid-phase laser ablation using graphite targets and each organic solvent. A hexane solution of polyyne C<sub>10</sub>H<sub>2</sub>, C<sub>12</sub>H<sub>2</sub> or C<sub>14</sub>H<sub>2</sub> was mixed with a hexane solution of PCH5 with stirring, and the resulting solution was dried for 48 h to volatilize hexane. We detected Raman peaks of polyyne C<sub>10</sub>H<sub>2</sub> (2147 cm<sup>-1</sup>), C<sub>12</sub>H<sub>2</sub> (2128 cm<sup>-1</sup>) and C<sub>14</sub>H<sub>2</sub> (2084 cm<sup>-1</sup>). The above results indicate that we could prepare polyyne-liquid crystal composite materials of C<sub>10</sub>H<sub>2</sub>-PCH5, C<sub>12</sub>H<sub>2</sub>-PCH5 and C<sub>14</sub>H<sub>2</sub>-PCH5.

P-11

**Zinc oxide nanorods prepared via laser ablation in water**

*T. Hatta, K. Koizumi, S. A. Kulinich, S. Iwamori, S. Yamaguchi; Tokai University (JAPAN)*

The study presents ZnO nanorods prepared by means of millisecond laser. Zn plates were ablated in pure water without adding any surfactants or external heating.

P-12

Student presentation

**Detection of ground-state species in laser-induced cavitation bubbles by absorption spectroscopy**

*A. Kawasaki, A. Tamura, A. Matsumoto, K. Fukami, N. Nishi, T. Sakka; Kyoto University (JAPAN)*

Liquid-phase laser ablation generates plasma and a cavitation bubble at the irradiation spot. The process is applicable to nanoparticle production directly in liquids. We established a method to observe absorption spectra of the species in the bubble by using supercontinuum light as an incident light. Since the beam was directional and most of the beam could transmit through the bubble, we have successfully obtained absorption spectra of the species in the bubble. The present method provides useful insight for the clarification of the mechanism dominating the nanoparticle generation by liquid-phase laser ablation.

P-13

**Preparation of blue-emitting colloidal Si nanocrystals by laser ablation of porous silicon in liquid**

*T. Nakamura<sup>1</sup>, Z. Yuan<sup>1</sup>, S. Hashimoto<sup>2</sup>, S. Adachi<sup>1</sup>; <sup>1</sup> Gunma University; <sup>2</sup> The University of Tokushima (JAPAN)*

In this work, we propose a new method to prepare blue-emitting Si nanocrystals from porous silicon (PSi). By pulsed laser irradiation on PSi in liquid, blue-emitting colloidal Si nanocrystals were obtained. We investigated their luminescence properties by steady-state and time-transient photoluminescence (PL) measurements, and found that the linearly increased relation of PL intensity with etching time of PSi both for colloidal Si and PSi, indicating that the number of the colloidal Si depends on the surface porous layer volume.

P-14

Student presentation

**Nb-doped titanium oxide nanoparticles synthesized by laser ablation in liquid**

*A. Watanabe, R. Nakajima, T. Ishigaki; Department of Chemical Science and Technology, Hosei University (JAPAN)*

Dispersed non-doped and Nb-doped TiO<sub>2</sub> nanoparticles were synthesized by laser ablation in the aqueous solutions of various pH values. Particles synthesized in acid and neutral solutions were well dispersed, while those synthesized in basic solutions are agglomerated. Particles synthesized in neutral solution consisted of only rutile phase. However, those prepared in acid and basic solutions contained a small amount of impurity Ti<sub>4</sub>O<sub>7</sub> and Ti<sub>3</sub>O phases as well as rutile. Nb-doped TiO<sub>2</sub> nanoparticles synthesized in a water at pH of ~7 were mainly composed of rutile, and the high concentration of Nb doping was achieved.

P-15

Student presentation

**Target conditions affecting the productivity of Y<sub>2</sub>O<sub>3</sub> nanoparticles by laser ablation in water**

*M. Shida, S. Al Mamun, T. Ishigaki; Hosei University (JAPAN)*

The influence of target conditions, such as the induced surface roughness by irradiation and the thermal conductivity of target materials, was examined on the nanoparticles productivity in the synthesis of Y<sub>2</sub>O<sub>3</sub> nano-size powders by laser ablation in water. Sintered Y<sub>2</sub>O<sub>3</sub> was immersed in ultrapure water contained in a small 20 ml beaker which was mounted on a motor-driven rotator. The inner diameter of ablation trench circle was changed from 1 to 3.5 mm. The productivity of Y<sub>2</sub>O<sub>3</sub> nanoparticles was increased with the increase of the inner diameter of ablation trench and the porosity of sintered target compacts.

P-16

**Calcium phosphate deposition on a cobalt-chrome alloy by a laser-assisted biomimetic process**

A. Oyane<sup>1</sup>, M. Nakamura<sup>1</sup>, I. Sakamaki<sup>1</sup>, K. Koga<sup>1</sup>, Y. Ishikawa<sup>1</sup>, N. Koshizaki<sup>1,2</sup>; <sup>1</sup> National Institute of Advanced Industrial Science and Technology; <sup>2</sup> Hokkaido University (JAPAN)

Recently, we developed a laser-assisted biomimetic (LAB) process for calcium phosphate deposition on a polymer substrate utilizing low energy pulsed laser. In the present study, we aimed to apply the LAB process for calcium phosphate deposition on a substrate of cobalt-chrome alloy (CoCr) that is an important implant material used in dental and orthopaedic applications. The LAB process was found to be effective in area-specific calcium phosphate deposition on the CoCr substrate as well as that on the previously reported polymer substrate. The present calcium phosphate deposition technique would be useful for surface functionalization of CoCr-based implants.

P-17

Student presentation

**Charge and ligand effects on Au and Pt nanoparticle electrodeposition for medical application**

S. Koenen<sup>1</sup>, C. Streich<sup>1</sup>, J. Jakobi<sup>1</sup>, S. Angelov<sup>2</sup>, H. Heissler<sup>2</sup>, K. Schwabe<sup>2</sup>, J. Krauss<sup>2</sup>, S. Barcikowski<sup>1</sup>; <sup>1</sup> University of Duisburg-Essen and Center for Nanointegration Duisburg-Essen; <sup>2</sup> Hannover Medical School, Department of Neurosurgery (GERMANY)

Over the last decades nanoparticles gained an increased interest in different fields like catalysis and medicine. The generated nanoparticles for these applications are generally capped with ligands. However, ligands are often not desired for various applications. Therefore, bare, ligand-free nanoparticles created via laser ablation in liquids offer a great advantage over ligand-capped nanoparticles. One application in which bare nanoparticles offer an advantage is the electrophoretic deposition of nanoparticles on medical implants where ligands around the nanoparticles may have a negative effect on the deposition. In this study the usefulness of ligand-free nanoparticles in contrast to ligand-capped nanoparticles is shown.

P-18

Student presentation

**Synthesis and antibacterial assessment of zinc oxide nanoparticles**

M.-H. Chi<sup>1</sup>, H.-Y. Lin<sup>1</sup>, M.-H. Lee<sup>2</sup>; <sup>1</sup> Department of Chemical and Materials Engineering, National University of Kaohsiung; <sup>2</sup> Department of Materials Science and Engineering, I-Shou University (TAIWAN)

Zinc oxide nanoparticles were synthesized by a hydrothermal method using aqueous zinc nitrate and sodium hydroxide, and then characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), energy dispersive spectrometer (EDS) and fluorescence spectroscopy (PL). The morphologies and particle size of zinc oxide nanoparticles can be controlled by varying the concentrations of sodium hydroxide solution and mixing speed. The SEM images of spherical ZnO nanoparticles showing their size were from 50 nm to 100 nm in Figure 1. The emission peak of PL spectrum at 467 nm has been observed when the excitation spectrum was 210 nm. NPs are able to attach the membrane of bacteria by electrostatic interaction and disrupt the integrity of the bacterial membrane. The antibacterial activity of zinc oxide nanoparticles were investigated using Gram-negative bacteria Escherichia. Coli (E. Coli). ZnO NPs exhibited a preferential ability to suppress growth of E.coli. The cytotoxicity of ZnO nanoparticles on human embryonic kidney cells (HEK293) was also examined. The results indicated that no significant reduction on HEK293 cell growth (over 80% of viability at 1mg/c.c.). The results might provide ZnO NPs can be applied in the area of foods and medicine.

P-19

Student presentation

**Oxidative laser fragmentation for ligand-free non-plasmonic gold atom clusters and their deposition on graphene nanosheets**

I. Haxhija<sup>1</sup>, M. Lau<sup>1</sup>, R. Intartaglia<sup>2</sup>, F. Brandi<sup>2</sup>, J. Nakamura<sup>3</sup>, S. Barcikowski<sup>1</sup>; <sup>1</sup> Center for Nanointegration Duisburg-Essen, Nano Energy Technic Center (NETZ), University of Duisburg-Essen (GERMANY);

<sup>2</sup> Nanophysics, Istituto Italiano di Tecnologia (ITALY); <sup>3</sup> Faculty of Pure and Applied Sciences, University of Tsukuba (JAPAN)

The generation of nanoparticles via pulsed laser ablation in liquids is a "green" technique, which provides pure colloids and allows different target-solvent combinations. Disadvantageous is the broad particle size distribution, which can be avoided by further treatment with appropriate laser fluence. Amendola et al. reported on 4 nm small gold nanoparticles. We show that the oxidative laser fragmentation leads to the generation of non plasmon resonant gold clusters with a mean size of 2.5 nm using hydrogen peroxide as an oxidative agent. Due to the purity and ultra small particle size, these gold clusters are very interesting for heterogeneous catalysis.

P-20

**Precise and quantitative charge balancing for the preparation of nanoparticle-peptide conjugates with laser-generated gold nanoparticles as model system for in vitro bioapplications**

*L. Gamrad<sup>1</sup>, C. Rehbock<sup>1</sup>, J. Krawinkel<sup>2</sup>, B. Tumursukh<sup>2</sup>, A. Heisterkamp<sup>2</sup>, S. Barcikowski<sup>1</sup>; <sup>1</sup> Technical Chemistry I, University of Duisburg-Essen and Center for Nanointegration Duisburg-Essen; <sup>2</sup> Institute of Applied Optics, Abbe Center of Photonics, Friedrich-Schiller-University (GERMANY)*

This work focuses on charge effects between nanoparticles and opposite charged ligands. Creating a suitable model system, small monodisperse gold nanoparticles were generated by pulsed laser ablation in liquid providing a bare surface, free from any surfactants. Particles were ex situ conjugated with different types of cell penetrating peptides and subsequently investigated concerning their aggregation tendencies and long-term stabilities. For future bioapplications, the time and concentration dependent uptake of conjugates and the formation of endosomes in cell lines were characterized. This model system enables the determination and interpretation of effects like charge compensation depending on the peptide's charge and length.

P-21

**Laser-induced synthesis and decay of Tritium under exposure of solid targets in heavy water**

*E.V. Barmina<sup>1</sup>, S. F. Timashev<sup>2,3</sup>, G. A. Shafeev<sup>1</sup>; <sup>1</sup> Wave Research Center of A.M. Prokhorov General Physics Institute of the Russian Academy of Sciences; <sup>2</sup> L.Ya. Karpov Institute of Physical Chemistry; <sup>3</sup> National Research Nuclear University (RUSSIAN FEDERATION)*

The processes of laser-assisted synthesis of Tritium nuclei and their laser-induced decay in cold plasma in the vicinity of solid targets (Au, Ti, Se, etc.) immersed into heavy water are experimentally realized at peak laser intensity of  $10^{10}$ - $10^{13}$  W/cm<sup>2</sup>. Tritium is synthesized without any cathodic bias on the target though the application of this bias largely increases the rate of its synthesis. The competing process of laser-induced accelerated beta-decay of Tritium takes place in case of target exposure in D<sub>2</sub>O with initial Tritium content. Possible applications of the process of laser-induced accelerated decay of Tritium are discussed.

P-22

*Student presentation*

**Simultaneous observation of nascent bubble and plasma induced by laser ablation in water**

*A. Tamura, A. Matsumoto, K. Fukami, N. Nishi, T. Sakka; Kyoto University (JAPAN)*

To clarify the mechanism of liquid-phase laser ablation process, the spatial relationship between plasma evolution and formation of a cavitation bubble should be investigated. We compared the bubble image during laser irradiation with the plasma emission image observed simultaneously. The size of the emission region is close to the bubble size at the middle of the laser profile and the shape of the bubble surface seems to reflect the shape of the plasma periphery. This result indicates that the ablated species interact with surrounding water.

P-23

*Student presentation*

**Non-costeffective parameters of laser-assisted nanoparticle synthesis for scale-up**

*S. Kohsakowski<sup>1</sup>, S. Reichenberger<sup>1,2</sup>, S. Barcikowski<sup>1</sup>, P. Wagener<sup>1</sup>; <sup>1</sup> University of Duisburg-Essen, Technical Chemistry I and Center of Nanointegration Duisburg-Essen; <sup>2</sup> Hochschule Niederrhein-University of Applied Science, (GERMANY)*

Laser-generated nanoparticles are promising materials for numerous applications. For this, new ways are being sought to increase the nanoparticle productivity of laser-assisted synthesis. An increase in nanoparticle productivity can be achieved by increasing the laser power (costeffective), but also by various non-costeffective parameters. In this work, we present approaches to increase nanoparticle productivity by varying non-costeffective parameters: (i) Target shape: Higher productivities could be achieved recently by using a wire as a starting material in comparison to bulk metal. Therefore a target-wire is continuously fed in a small liquid filament and the wire shape results in an higher nanoparticle yield. (ii) Scan pattern: The nanoparticle productivity could be influenced by the scan pattern of the target, which allows a better utilization of the ablation target to reach a scale-up of the nanoparticle synthesis. (iii) Adjusting liquid flow: The use of a continuous flow allows a constant nanoparticle concentration and high productivities for long ablation times, in comparison with a saturation in a batch chamber which is the today's state of the art. Generally, it is possible to scale-up the nanoparticle synthesis by the optimization of non-costeffective parameters.

P-24

Student presentation

**Synthesis and characterization of palladium nanoparticles in distilled water, methanol, SDS and ethylene glycol***M. I. Mendivil Palma*<sup>1</sup>, *G. García*<sup>1</sup>, *G. A. Castillo*<sup>1</sup>, *T. K. Das Roy*<sup>1</sup>, *D. Avellaneda*<sup>1</sup>, *B. Krishnan*<sup>1,2</sup>, *S. Shaji*<sup>1,2</sup>;<sup>1</sup> *Facultad de Ingeniería Mecánica y Eléctrica, Universidad Autónoma de Nuevo León*; <sup>2</sup> *CIIDIT- Universidad Autónoma de Nuevo León (MEXICO)*

Pulsed laser ablation in liquid media as a prominent technique for nanofabrication was employed to synthesize palladium (Pd) nanoparticles in different liquids. The synthesis of Pd nanoparticles was developed using a pulsed Nd:YAG laser with its fundamental wavelength output (1064 nm) having an energy of 600 mJ/pulse (10 Hz, 10 ns). The energy fluencies were varied in order to study its effect on the ablation process and the properties of the final products. A vertical configuration was used for the pulsed laser ablation with a horizontal scan system to improve the ablation and to increase the efficiency of these experiments. Pure Pd metal target has been irradiated in distilled water, methanol, sodium dodecyl sulfate (SDS) and ethylene glycol (EG). The mean size, size distributions, shape, elemental composition and optical properties of nanoparticles synthesized at different irradiation configuration were examined. The nanoparticles were characterized by transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and UV-Vis absorption spectroscopy. The TEM characterizations showed smaller nanoparticles in distilled water in comparison with the other liquids. Spherical morphology was observed for Pd nanoparticles synthesized in distilled water and methanol. In the case of SDS and EG, spherical nanoparticles embedded on the surfactant were observed. Also there was an effect of laser fluencies on the optical properties of the Pd nanoparticles.

P-25

Student presentation

**Production of luminescent nanoparticles Mn<sup>2+</sup>:Zn<sub>2</sub>GeO<sub>4</sub> by pulsed laser ablation in aqueous solutions and organic solvents***T. Masuda*<sup>1</sup>, *K. Yamauchi*<sup>1</sup>, *T. Sanada*<sup>1</sup>, *N. Wada*<sup>2</sup>, *K. Kojima*<sup>1</sup>; <sup>1</sup> *Ritsumeikan University*; <sup>2</sup> *Suzuka National College of Technology (JAPAN)*

We synthesized 0.1MnO-1.5Eu<sub>2</sub>O<sub>3</sub>-25ZnO-75GeO<sub>2</sub> nanoparticles by sol-gel method and pulsed laser ablation in liquid phase, and investigated the influence of the kind of liquids on some properties of nanoparticles. XRD patterns of all samples showed trigonal Zn<sub>2</sub>GeO<sub>4</sub> and hexagonal GeO<sub>2</sub> crystals. In all samples particle size became smaller by PLA, especially in the samples produced in acid and basic aqueous solutions and in nonpolar solvents. In all samples, an excitation band was observed at 250 nm, which corresponds to absorption due to a Ge<sup>2+</sup> center. A luminescence band was observed at 535 nm, which is due to the transition from <sup>4</sup>T<sub>1</sub> to <sup>6</sup>A<sub>1</sub> of Mn<sup>2+</sup> ions in a tetrahedral site. Different values of luminescence quantum yield were obtained among the samples produced in the kinds of liquids.

P-26

**Laser-based synthesis and application of catalytic active nanoparticles***P. Wagener*<sup>1</sup>, *G. Marzun*<sup>1</sup>, *Y. Lu*<sup>2</sup>, *M. Ballauff*<sup>2</sup>, *S. Barcikowski*<sup>1</sup>; <sup>1</sup> *University of Duisburg-Essen, Technical Chemistry I and Center of Nanointegration Duisburg-Essen*; <sup>2</sup> *Helmholtz-Zentrum Berlin, Soft Matter and Functional Materials (GERMANY)*

We showed how to laser-fabricate heterogeneous catalysts by supporting metal nanoparticles which is strongly influenced by nanoparticle ligand surface coverage. Catalytic activity of laser-generated gold nanoparticles was tested by the reduction of 4-nitrophenol by sodium borohydride. Kinetic analysis shows that the Au-nanoparticles synthesized by laser ablation are among the most active catalyst for this reaction. Catalyst activation by surface restructuring of laser-generated nanoparticles is much faster than chemically-prepared ones, possible due to higher defect density and partial-oxidized nanoparticle surface proven by XPS.

P-27

**Preparation of titanium nitride spherical particles by laser melting in liquid***K. Kawasoe*<sup>1</sup>, *Y. Ishikawa*<sup>2</sup>, *N. Koshizaki*<sup>3</sup>, *O. Odawara*<sup>1</sup>, *H. Wada*<sup>1</sup>; <sup>1</sup> *Tokyo Institute of Technology*; <sup>2</sup> *National Institute of Advanced Industrial Science and Technology*; <sup>3</sup> *Hokkaido University (JAPAN)*

Titanium nitride spherical particles were prepared and investigated. Titanium nitride rectangular nanoparticles were purchased as raw material. The nanoparticles in DI water were irradiated with unfocused laser beam. The morphologies of samples were investigated by SEM, TEM and STEM. The spherical particles were obtained at the energy density more than 80 mJ/cm<sup>2</sup>, while laser ablation occurred at that more than 350 mJ/cm<sup>2</sup>. Main peaks of XRD were almost same as raw material TiN. Small peaks of TiO<sub>2</sub> (rutile) were observed at energy density of more than 77 mJ/cm<sup>2</sup> and those of TiO<sub>2</sub> (anatase) were observed at that of more than 107 mJ/cm<sup>2</sup>.



P-28

**Surface modification of gold nanoparticles prepared in organic solvent**

*M. Čížková<sup>1</sup>, O. Votava<sup>2</sup>, J. Michl<sup>1,3</sup>; <sup>1</sup> IOCB AS CR (CZECH REPUBLIC); <sup>2</sup> J. Heyrovsky Institute of Physical Chemistry AS CR (CZECH REPUBLIC); <sup>3</sup> University of Colorado Boulder (USA).*

The formation of unstabilized gold nanoparticles by laser ablation in organic solvents is examined. The surface of so prepared nanoparticles is modified either by exposition of nanoparticles to an organotin compound or by accomplishment of the laser ablation in the presence of the organostannane. Further, cubical gold nanoparticles are prepared by the photochemical reduction of HAuCl<sub>4</sub> in an organic solvent.

P-29

*Student presentation*

**Two photon photochemical synthesis of silver nanoparticles in aqueous solution of silver nitrate using UV pulsed laser irradiation; Concentration effect of SDS on the formation yield**

*U. Qazi, S. Kajimoto, H. Fukumura; Tohoku University (JAPAN)*

We describe the results for fabrication of nano-sized spherical silver nanoparticles (AgNPs) using ns laser irradiation in aqueous solutions of silver nitrate and surfactant. The concentration effect of sodium dodecyl sulfate (SDS) along with irradiation time on size distribution and production efficiency of AgNPs is investigated. The use of higher concentration of SDS facilitates the fabrication of stable nanoparticles with controlled size and shape distribution.

P-30

*Student presentation*

**Fabrication of ZnO spherical particles by pulsed laser melting in liquid using KrF excimer laser**

*S. Sakaki<sup>1</sup>, N. Koshizaki<sup>1</sup>, H. Ikenoue<sup>2</sup>, T. Tsuji<sup>3</sup>, Y. Ishikawa<sup>4</sup>; <sup>1</sup> Hokkaido University; <sup>2</sup> Kyusyu University; <sup>3</sup> Shimane University; <sup>4</sup> National Institute of Advanced Industrial Science and Technology (JAPAN)*

We previously reported a novel fabrication technique of ZnO submicrometer spherical particles by irradiating the third harmonic of a pulsed Nd:YAG laser (355 nm) to colloidal raw nanoparticles dispersed in liquid. Here we use a KrF excimer laser (248 nm) instead for ZnO spherical particle fabrication. Submicrometer spheres obtained by KrF laser irradiation had different particle size and threshold fluence for spherical particle formation from those obtained by Nd:YAG laser. This result is probably due to the difference in wavelength and pulse width of irradiating laser.

P-31

**Enhancement anticancer effect of Gemcitabine and Kaempferol using multifunctional nanostructured lipid carriers (NLCs) on A549 cell line**

*M.-J. Tsai<sup>1,2</sup>, C.-C. Lee<sup>3</sup>, P.-C. Wu<sup>3</sup>, Y.-H. Tsai<sup>3</sup>; <sup>1</sup> Department of Neurology, China Medical University Hospital; <sup>2</sup> School of Medicine, Medical College, China Medical University; <sup>3</sup> School of Pharmacy, Kaohsiung Medical University*

Gemcitabine HCl is a nucleoside analog that phosphorylated by deoxycytidine kinase to active form dFdCTP inhibiting cellular DNA synthesis. It's widely used to treat solid tumors including colon, lung, bladder and ovarian cancers. Kaempferol is an active constituent of Ginkgo Biloba L., and found induced apoptosis in human non-small lung carcinoma. In order to delivery gemcitabine and kaempferol simultaneously to cancer cell, we used NLCs as drug vehicle and added functional moieties to increase antitumor efficacy. The results showed the combination of gemcitabine and kaempferol enhanced antitumor efficacy in human lung cancer cell line, A549 cells and tracing nanoparticles distribution.

P-32

**Automated system to fabricate submicrometer spherical particles by pulsed laser melting in liquid**

*N. Koshizaki<sup>1</sup>, Y. Ishikawa<sup>2</sup>, K. Sue<sup>3</sup>; <sup>1</sup> Hokkaido University; <sup>2</sup> National Institute of Advanced Industrial Science and Technology (JAPAN)*

We previously reported a novel technique 'pulsed laser melting in liquid' for fabrication of various submicrometer spherical particles. In this process raw nanoparticles dispersed in liquid are irradiated by a pulsed laser at relatively low fluence using unfocused laser beam. Furthermore window-less open irradiation of laser is possible even onto organic solvent under appropriate conditions. Thus the apparatus design for mass production of spherical particles can be more flexible to the automated system. Here we present flow system and auto-batch system for continuous production of submicrometer spherical particles. The features of each system are discussed.

P-33

**Relationship between optical emission and ambient density on laser ablation process in supercritical CO<sub>2</sub>***N. Takada<sup>1</sup>, M. Mardis<sup>1</sup>, K. Sasaki<sup>2</sup>, M. Goto<sup>1</sup>; <sup>1</sup> Nagoya University; <sup>2</sup> Hokkaido University (JAPAN)*

Physical and thermal properties such as density, thermal conductivity, viscosity can be tuned from gas-like to liquid-like by changing the temperature and the pressure in supercritical fluid state. In this work, laser ablation of a Ni target was carried out in supercritical CO<sub>2</sub>. Analysis results to synthesized Ni nanoparticles and laser ablation phenomena will be discussed in comparison to those in the case of Au target.

P-34

**Molecular dots pattern synthesized by a laser induced molecular nanojet in water***M. Goto, A. Kasahara, M. Tosa; National Institute for Materials Science (JAPAN)*

Molecular dots pattern was synthesized by molecular nanojet in water, which was induced by a pulsed laser irradiation. In the technique, organic molecules photoexcited by a pulsed laser were transferred through liquids layer such as water and tightly fixed onto metal substrates over an area of several hundred nanometers. Also, we succeeded in observing the molecular nanojet directly in water by time-resolved shadowgraphy. This advanced technique is considered to be applicable to fabrication of functional molecular dots pattern in a designated region on hard materials for the purpose of production of molecular devices, molecular sensors and optoelectronics.

P-35

**Precise control of biomolecule coverage on the surface of gold nanoparticles generated by pulsed laser ablation and its application in cancer research***Y. Ichikawa<sup>1</sup>, W. Qian<sup>2</sup>, W. Guo<sup>2</sup>, R. Collison<sup>2</sup>, B. Liu<sup>2</sup>; <sup>1</sup> AISIN SEIKI Co., Ltd.(JAPAN); <sup>2</sup> IMRA America In. (USA)*

In this paper, we study the effect of biomolecule coverage on the colloid stability during conjugation, using gold nanoparticles (GNPs) produced by pulsed laser ablation in water. We first report two examples of stable partial conjugation of GNPs with polyethylene glycol (PEG) and bovine serum albumin (BSA). We next present an application of such partial conjugation in a cancer cell uptake study where GNPs are first conjugated with partial coverage of PEG and then loaded with cell penetration peptide RGD by simple physical adsorption.

P-36

*Student presentation***Preparation of flavonoids nanoparticle colloids by laser fragmentation in water and its toxicity to HeLa cell***S. Kamasoku, M. T. Y. Nguyen, Y. Yoshioka, M. Tamura, Asahi; Ehime University (JAPAN)*

Pure nanoparticle colloids of water-insoluble flavonoids, which are a class of plant secondary metabolites, were prepared by nanosecond pulsed laser irradiation to their microcrystalline powder dispersed in distilled water. We succeeded in preparing stable nanoparticle colloids having the particle size about 50 nm for isoflavone compounds. Results of toxicity assay for HeLa cells is demonstrated.

P-37

**Excited state relaxation process of fullerene C60 nanoparticles prepared by laser fragmentation in water***Y. Ishibashi, M. Arinishi, T. Asahi; Ehime University (JAPAN)*

Aqueous colloids of fullerene C60 nanoparticle with a mean size of 50 nm were prepared by ns pulse laser fragmentation of its microcrystal in distilled water, and their excited-state relaxation processes were measured by time-resolved spectroscopy. Ps time correlated single-photon counting measurement revealed that the fluorescence almost decayed with a time constant of ca. 30 ps, which was not observed for C60 bulk crystals. Furthermore, this rapid decay depended on the particle size and pH of water. These observations indicate that the rapid decay is due to the fluorescence quenching at the interface between the particle surface and water.

P-38

**Time-resolved fluorescence study on pulse laser fragmentation of perylene microcrystals in water**

*T. Ishikawa, K. Shikama, Y. Ishibashi, T. Asahi; Ehime University (JAPAN)*

To study the mechanism of pulsed laser fragmentation of organic microcrystals in water we measured nanosecond time-resolved fluorescence spectra of perylene microcrystalline powder dispersed in water upon pulse irradiation (355-nm wavelength, 8 ns FWHM pulse width). The fluorescence spectra depending on the laser fluence were able to be ascribed well to transient heating of the microcrystal due to intense pulse laser irradiation. The temperature elevation was estimated to be about 100°C at the fluence of 10 mJ/cm<sup>2</sup>. We also demonstrated heating of the microcrystal in 5 ns time followed by a cooling on the 50-ns time scale.

P-39

**SERS of graphene-Ag nanoparticle hybrid fabricated by laser ablation**

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Raman spectra of graphene samples with and without silver (Ag) nanoparticles (Ag NPs) were obtained to investigate the surface enhanced Raman scattering (SERS) substrates. More enhancements were observed in the hybrid graphene-Ag NPs in comparison with the SERS samples of graphene prepared by drop casting Ag NPs. Furthermore, the concentration of NPs is essential in SERS enhancement.

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**Magnetic properties of graphene generated by laser ablation**

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In this work, magnetic properties of new carbon-based material, graphene generated by laser ablation in Cryogenic Media was studied and improving its magnetic properties by hybridization with silver atoms was carried out. Results shows this graphene sample is low defect and strong diamagnetism and hybrid graphene has better magnetism in comparing with pristine sample.

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**Platinum nanoparticles synthesized via laser-induced photoreduction in dynamic phase separating media**

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Fluorescent platinum compounds were obtained as a result of photo-reduction of platinum-ions during laser-induced phase separation process in 2-butoxyethanol and water mixtures. Ultrafast phase separation was induced by irradiating a nanosecond IR laser pulse, which directly excites water molecules in aqueous solution and causes a rapid temperature rise. After a certain delay time, a UV laser pulse was introduced to induce photo-reduction of tetrachloroplatinum ions dissolved in the solution. With the delay time of 5 microseconds, UV fluorescent platinum compounds were synthesized, whereas red fluorescent products were obtained in 2-butoxyethanol-water mixture without IR pulse irradiation.

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**Challenges of plasma spectroscopy underwater: on the use of molecules and its consequences**

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Laser ablation underwater raises many interests in the fundamental point of view but also, in more applicative features. In this context, it seems crucial to be able to measure experimentally the thermodynamic properties of the plasma created underwater. Plasma Spectroscopy is a tool that enables such an achievement. However, due to various peculiar attributes, a different approach including the use of molecules must be carried out.