

Gold highlights at the 11th “Trends in Nanotechnology” International Conference (TNT 2010) in Braga, Portugal, September 6–10, 2010

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Published online: 1 March 2011

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Abstract A report on the gold highlights on the 11th “Trends in Nanotechnology” International Conference (TNT 2010) held in Braga, Portugal, on September 6–10, 2010 is presented. There were around 300 participants attending this meeting. Gold-related subjects had a strong presence by 2 invited lectures, 13 keynote lectures, 13 oral presentations, and 35 posters. Moreover, seven posters dealing with gold were awarded for poster prizes. Subjects covering a wide range, like self-assembly, colloids, nanobiotechnology, scanning probe methods, carbon nanotube-based materials, nanochemistry, low-dimension materials, nanostructured and nanoparticles-based materials, nano-optics and nano-photonics, were presented.

Introduction

There were around 300 participants attending this meeting. The majority came from Europe, however other countries like the USA, Canada, Brazil, Mexico, Japan, Korea, and Australia, were also represented. Most participants were from Universities and Research Institutes; but some representatives from industry were also present, working in several nanotechnology areas. The event took place in the recently built International Iberian Nanotechnology Laboratory in Braga.

Gold-related subjects had a strong presence by 2 invited lectures (out of a total of 4), 13 keynote lectures (out of 28), 13 oral presentations (out of 48), and 35 posters (out of

around 175). Moreover, 7 posters dealing with gold were awarded for poster prizes (out of the total 19 awards given at this conference for student presenters).

The conference started with an invited lecture of Uzi Landman (Georgia Institute of Technology in the USA), entitled “Small is different: physics and chemistry in the non-scalable nano regime”, who told the audience some delightful “golden stories”. The speaker remembered the unexpected results obtained by Haruta in the early 1980s with catalysis by gold and explained the gold's relativistic effects and the 15% relativistic correction (one of the largest existing) needed (as if this correction was not taken into account, gold should have the color of silver!). He also told about his recent results on methane activation reactions and production of ethylene [1].

Self-assembly

The second invited lecture, inserted in the *Self-Assembly* session (sponsored by CIC nanoGUNE Consolider, Spain), was given by Klaus Kern (Max-Planck Institute in Germany), on “Nanoscale electronic contacts”. Examples of graphene monolayers contacted by gold electrodes were given and it was explained that Au contacts result in p-type doping of graphene. Nanoscopic solar cells containing Au and Pd were also referred.

Two keynote lectures were given in the same session. The first, by Ehud Gazit (Tel Aviv University, Israel), explained the process of attachment of gold nanoparticles (NPs) to a peptide nanotube via a common molecular recognition element. A model for fabricating a coaxial nanowire (NW) was also presented [2].

The second keynote lecture by Magali Lingenfelder (Institute of Materials Science from Barcelona, Spain), dealt

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with “Chiral recognition on surfaces”. Examples of thiol self-assembled monolayers (SAMs) fabricated on gold-coated glass slides that lead to crystal growth of theophylline were given.

Colloids

In the *Colloids* session (sponsored by Frimat, Switzerland), Luis Liz-Marzán (University of Vigo, Spain) was the speaker of a keynote lecture on “Self-Assembly and Directed Assembly of Gold Nanoparticles”. 2D and 3D superlattices made of gold nanorods can be obtained through the use of dimeric surfactants as capping agents in aqueous solution. The synthesis and self-assembly of Au NWs at oleylamine was also referred.

Nanobiotechnology

The *Nanobiotechnology* session (sponsored by Institute for Bioengineering of Catalonia in Barcelona, Spain) had two keynote lectures dealing with gold. One was given by Janos Vörös (Swiss Federal Institute of Technology in Zurich, Switzerland). The speaker explained how the special optical properties of gold NPs can be used to design biosensors based on the localized surface plasmon resonance phenomena. Their plasmonic properties can be combined with electrochemistry or nanowire-based sensing.

The other keynote lecture was presented by Valentyn Novosad (Argonne National Laboratory in the USA), and showed that gold-coated lithographically defined vortex microdisks with an Fe-Ni magnetic core can be biofunctionalized with anti-human-IL13a2R antibody for specifically targeting human glioblastoma cells.

Also in this session, Ricardo Franco (New University of Lisbon in Portugal), shared the design of a gold NP-based rapid detection test using specific antibodies to detect the malaria parasite *Plasmodium falciparum* antigens in clinical samples using mercaptoundecanoic acid-capped Au NPs conjugated with 2E6 (monoclonal) antibodies. These antibodies specifically recognize the parasite's Heat Shock Protein 70, as confirmed by Western blot analysis. This work is of extreme importance since there is an urgent need to develop tests to be used in Malaria affected zones.

Other oral presentations dealing with the use of gold in *biotechnology*, included Eulália Pereira (from the same group) who spoke about the “Green Photocatalytic Synthesis of Au and Ag Nanoparticles”. The advantages of this synthesis include low energy consumption (room temperature), short reaction time (less than 4 min) and the use of non-toxic reagents (as toxic surfactants commonly used as capping agents are replaced by water soluble polymers like

starch, acacia gum, and cellulose). Au triangular nanoplates (Fig. 1; [3]) and nanocubes were obtained.

Teresa Neves Petersen (Aalborg University in Denmark) spoke about “Engineering biosensors and nanoparticle based drug carriers”. She explained about light-assisted molecular immobilization (LAMI), which is a novel technology through which, by the use of UV-light, a large variety of protein and other biomolecules can be covalently attached onto thiol reactive surfaces, like thiolated glass/quartz, gold, or silicon [4]. Insulin and bovine serum albumin were immobilized on Au and Fe₃O₄@Au NPs, which can have applications in nanomedicine.

In a parallel session on “NanoResearch in Portugal”, Gonçalo Doria (New University of Lisbon), talked about the use of noble metal NPs for multiplex cancer diagnostic. The synthesis and functionalization with thiol-ssDNA of pure gold and gold–silver alloy NPs was carried out, yielding different nanoplates, which were combined to allow for the simultaneous differential detection of different nucleic acids sequences related to cancer. This work was also presented in the senior poster session.

Some posters dealing with the applications of gold on nanobiotechnology were also presented. Juan Gallo (Center for Cooperative Research in Biomaterials, Spain), got one of the three Ipod Nanos awarded by the Phantoms Foundation for his work dealing with superparamagnetic glyconanoparticles designed to specifically label cells, tissues, or organs. Deposition of a gold shell occurred in non-polar solvents and a ligand exchange reaction with amphiphilic sugar conjugates and carboxylic linkers was performed to make these particles water soluble.

Other poster presentations made by students included the work of Bruno Veigas (New University of Lisbon) who presented a colorimetric method for the rapid detection of the *Mycobacterium tuberculosis* complex strains and for the simultaneous detection of mutations associated with rifampicin resistance, at room temperature, with remarkable sensitivity, in a few hours. This type of assay can be useful in the initial management of suspected tuberculosis cases, especially from areas with high rates of drug resistance.

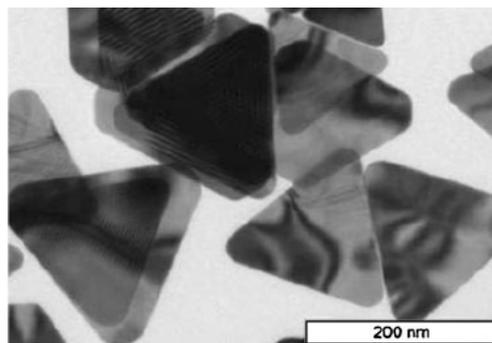


Fig. 1 Gold nanotriangles (adapted from [3])

Miguel Larginho (from the same University) reported on an inexpensive, fast, and simple methodology for nucleic acids extraction for improvement of the subsequent detection using a gold nanoprobe-based colorimetric assay. By using the sonoreactor for simultaneous cell bursting and DNA fragmentation, this protocol saves time and enhances the target availability for hybridisation with the nanoprobes.

Manuel Martins (University of Aveiro in Portugal) presented his investigation on synthetic optically active nanocomposites and magnetic latexes, such as magnetic and gold polymer nanostructures prepared by a miniemulsion polymerization technique.

Michael Bache (Technical University of Denmark) presented his work on pesticide detection. The 2,6 dichlorobenzamide residue assay was performed using a surface stress induced based detection system, consisting on four gold-coated cantilevers and piezo-resistive readout.

The senior poster session included the work of Inês Gomes (New University of Lisbon), on the development of a biosensor, based on bionanoconjugates of tyrosinase on gold NPs, taking advantage of the high surface areas of the latter, their unique electrochemical properties, and ideal protein conjugation chemistry afforded by suitable functionalization. The process is promising for the development of an enzymatic biosensor for phenolic compounds with high activity and specificity.

Pedro Baptista (from the same University) presented a simple approach to allow the enrichment of a nucleic acid mixture for a specific sequence/target of interest, taking advantage of the ease of functionalization provided by the Au-NPs surface via a thiol bond—capture nanoprobe.

Scanning probe methods

Laure Fabié (Center for Material Elaboration and Structural Studies in Toulouse, France) spoke about “Nanodroplet deposition and manipulation with an Atomic Force Microscopy (AFM) tip”. The process of fabrication of pyramidal and gold-coated AFM tips, including channel milling and surface functionalisation, was explained.

The student poster of Miroslav Valtr (Czech Metrology Institute in Brno, Czech Republic) dealt with “AFM characterization of nanoparticles on rough surfaces”. Examples for gold, palladium, and polystyrene NPs prepared using different methods were given.

Carbon nanotube (CNT)-based materials

On the *Nanotubes and Graphene* session (sponsored by GDRI, Synchrotron Soleil, France, and nanoICT Coordination Action), a keynote lecture from Stephen Hofmann

(University of Cambridge in the UK), dealt with the “Understanding of crystal growth on the nano-scale”. Ge/Au was used as a model system and the formation of a liquid Au-Ge layer on sub-30 nm Au catalyst crystals was shown.

Marion Cranney (Institute of Materials Sciences of Mulhouse, France) spoke about “Resonators created by intercalated gold nanoclusters under monolayer graphene on SiC”. She explained that p-doping of epitaxial graphene occurs by depositing Au atoms which intercalate between the buffer Layer and graphene monolayer. Intercalated quasi “free standing” gold monolayer and small Au clusters can be obtained.

Paolo Bondavalli (Thales Research and Technology in Grenoble, France) presented an oral dealing with “Gas sensor based on Carbon Nanotubes Field Effect transistors fabricated using an Original Dynamic Air-Brush technique (patented) for single walled CNTs deposition”. Examples junctions in vacuum (n-type) and in air (p-type) were given. Au/CNT Measurements before and after exposure to NH₃, NO₂, CO at concentrations of 50 ppm for Ti, Au, Pd, Pt electrodes permit to identify an electronic fingerprinting of each gas.

Chang-Soo Han (Korean Institute of Machinery and Materials) presented an oral on “Fast and wavelength selective photoresponse from quantum dot/CNT hybrid”. A Cr/Au electrode is part of the Filed Effect Transistor structure of hybrid material fabricated using dielectrophoresis.

A senior poster by Jan Prasek (Brno University of Technology in Czech Republic) dealt with the fabrication of a three-electrode electrochemical sensor for an easy and sensitive determination of heavy metal ions and phytochelatin. The CNT were deposited using plasma enhanced CVD direct grown on Au, Ag, and Pt electrodes at atmospheric pressure.

The work of Taechang An and WooSeok Choi (Pohang University of Science and Technology in Korea) dealt with “Fabrication of Functional Micro- and Nanoneedle electrodes”. Au was successfully coated on a CNT nanoneedle template.

A poster of Simon Altenburg (Christian-Albrechts-University in Kiel, Germany), dealing with “Scanning tunneling microscopic investigations into electron transport through graphene” had the prize GDR-I on Science and Applications of Nanotubes. For this work, a Au tip was used to contact graphene layers on Ru(111) surface.

Nanochemistry

Kohei Uosaki (International Center for Materials Nano-architectonics in Japan) presented a keynote lecture dealing

with “Formation, Characterization and Catalytic Properties of Metal Nanoclusters within Molecular Layers”. The electrochemical formation of metallic Au on top of hexanedithiol SAM-covered Au(111) surface was discussed. A decanethiol monolayer was constructed on a Au layer, which was formed by the reduction of preadsorbed AuCl_4^- ion on a hexanedithiol/Au(111) electrode.

Manuel Lopez Quintela (University of Santiago de Compostela in Spain), spoke about the catalytic properties of gold clusters, mainly focusing on their different electrocatalytic properties and also their ability to catalyze and direct the growth of anisotropic structures like rods and prisms.

The poster of Enrique Carbó-Argibay (University of Vigo), dealt with “Tuning the Gold Nanorods Morphology”. Three different growth processes were described where gold nanorods, single crystal, and pentatwinned, acted as seeds. The overgrowth of the single crystal gold nanorods lead to particles with octahedral geometry (Fig. 2), while the pentatwinned gold nanorods give rise to particles with quasi-decahedral geometry. This nice poster won the CIC nanoGUNE Consolider prize.

Another poster student was presented by Lenka Veverková (University of Prague in Czech Republic). The work dealt with the “Interactions of heparine with polymethinium salts capped gold nanoparticles in aqueous environment”. At basic pH, the NPs have negative charge on the surface due to carboxylate groups and this allowed immobilization of polymethinium salts which have posi-

tive charge due to quaternary nitrogen atoms by ionic bond. It is also possible to immobilize polymethinium salts by direct immobilization to non-modified gold NPs because of their negative surface charge.

Low-dimension materials

Afshin Dadvanda (University of Quebec, Canada) presented a poster dealing with the development of a simple method for the synthesis of nano-heterostructures consisting of lanthanide-doped NaYF_4 nanocrystals dendritically decorated with CdSe QDs. The two-contact devices were prepared by spin-coating of solution of studied NPs in toluene on Si/SiO₂ substrates pre-patterned with Au electrodes. This poster got one of the four Natural Sciences and Engineering Research Council of Canada awards.

Mariana Proença (University of Porto, Portugal) won a prize from the Portuguese Foundation of Science and Technology for her poster dealing with Ni nanowired inside nanoporous alumina templates fabrication. The electrochemical depositions were performed applying a constant potential using three electrodes, being one of them made of gold sputtered on one side of the porous membrane as working electrode. The uniformity of the Ni deposition was found to be dependent on the quality of the membranes and gold contact underneath.

Other posters presented by students included the work of Audra Lukman (University of Sydney, Australia), dealing with the simple greener economic process of “Synthesis of Ag and Au Nanoparticles in Aqueous Solutions Mediated by Naturally Occurring Compounds in Common Sprouting Seed Exudates”. Gold nanocrystals were fabricated by subjecting KAuCl_4 with green lentil (*Lens culinaris*) seed exudates and yielded an appreciable number of triangular shaped gold NPs. Various particle sizes and shapes could be obtained by simply modifying the reaction conditions.

Raphael Grütter (Laboratory of Biosensors and Bioelectronics in Zurich, Switzerland) presented his work dealing with “Deposition and Modification of Nanowires by FluidFM technology”, which is a combination of AFM with nanofluidics. An example of deposition (in air) of Au-colloids (5 nm) onto a polyethylenimine-coated Si-wafer was shown.

The senior poster session included the work of Maria Arroyo-Hernández (Institute of Microelectronics of Madrid, Spain) dealing with “Catalytic growth of ZnO nanowires by rf magnetron sputtering”. Gold thin films were grown by resistive thermal evaporation in a ultra-high vacuum chamber on both Si(100) and sapphire single crystalline substrates. It was shown that only a 4 nm thickness Au film promotes the vertical growth of ZnO nanowires.

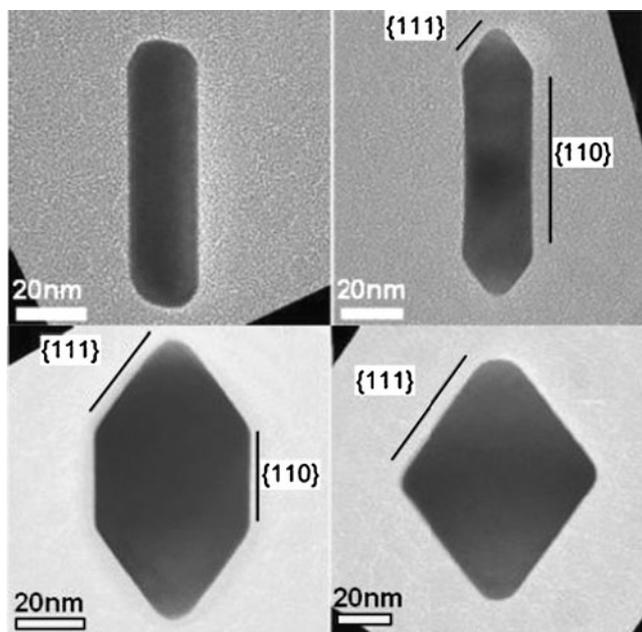


Fig. 2 Transmission electron microscopy (TEM) images of the overgrowth of single crystal gold nanorods from cylindrical shape to octahedral shape (adapted from the abstract)

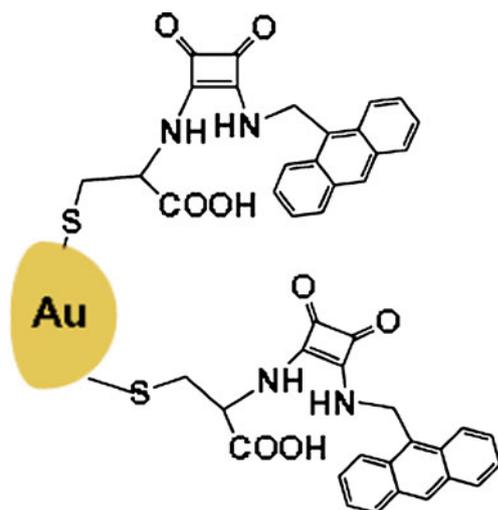


Fig. 3 Gold NPs with squaramide groups (adapted from the abstract)

Nanostructured and nanoparticles-based materials

The following posters were presented by students:

- Zakaria Abd El-Fattah (Center of Materials Physics in San Sebastián, Spain), presented results dealing with an Angle Resolved Photoemission Spectroscopy study of Au-doped 1 and 2 ML on Ag/Cu(111) systems.
- Belkacem Kadari (National Institute of Scientific Research of Canada), showed the results of photo- and electroluminescence studies of silicon nanocrystals embedded in SiO₂. The best results for electroluminescence have been obtained for electrical devices with top golden semitransparent contact and bottom silver contact.
- Radim Hrdy (Brno University of Technology in Czech Republic), presented a poster dealing with “Electrochemical Perforation of the Aluminum Oxide Barrier Layer in Thin Film Micro Sensors”. The microsystem used, a small comb-like electrochemical sensor, was prepared by deposition of gold microstructures on silicon, silicon oxide, and titanium multilayer.
- Pavel Žvátora (Institute of Chemical Technology in Prague, Czech Republic) demonstrated the possibility of preparing a surface-enhanced Raman scattering active substrate by sputtering deposition of gold layers on synthetic polymer foils of Polytetrafluorethylene that are cheap and easy to manipulate.
- Ondřej Černohorský (Czech Technical University in Prague) explained the preparation and study of interfaces with various metals (Au, Pd, Pt, and Ag) in NP form on InP substrates for hydrogen detection in air. The size of NPs was about 20 nm.

In the senior poster session, Katerina Piksová (from the same University) had a poster that showed nice SEM

images of Au nanolayers deposited by electrophoresis onto semiconductor wafers.

Jeróni Morey (University of Palma de Mallorca, Spain) presented a poster dealing with the synthesis of gold squaramide NPs (Fig.3). TEM analysis indicated an average core diameter of 15 nm.

Sónia Carabineiro (University of Porto, Portugal), presented her results on gold NPs supported on magnesium oxide for CO oxidation prepared by different methods. The best results were obtained by double impregnation of the support with HAuCl₄ and Na₂CO₃, yielding 2–12-nm gold NPs with an average size of 5.4 nm.

Nano-Optics and nano-photonics

Romain Quidant (Institute of Photonic Sciences in Barcelona, Spain), spoke in a keynote lecture about “Plasmon nano-optics for Biosciences: Sensing, Trapping and hyperthermia”. In his keynote lecture, a gold NP was the protagonist due to thermal and optical properties. The speaker also mentioned his recent work on tracking doping substances with colloid gold particles [5].

Another keynote lecture, given by Juan José Saenz (Universidad Autónoma de Madrid, Spain), dealt with “Nanoparticle Dynamics in Non-Conservative Optical Fields”. The diffusion of 50-nm gold NPs in water under the electromagnetic interactions produced by two crossed optical standing waves was studied using Langevin molecular dynamics calculations.

Francisco García-Vidal (from the same University) gave a keynote lecture about “Plasmonic waveguides”. The speaker described the theoretical study of electromagnetic fields with wedge plasmon polaritons. Gold was represented by a Drude-Lorentz type dielectric function.

Another keynote lecture was given by Yuji Kuwahara (Osaka University in Japan), who spoke about “Optical and transport properties in molecular nanosystems observed by STM-based techniques”. Results on plasmon-enhanced copper phthalocyanine (CuPc) fluorescence on an Au(111) substrate by STM-LE were reported. Au NPs effectively

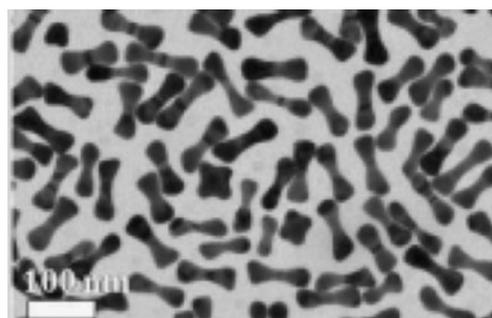


Fig. 4 TEM image of Au dumbbells (adapted from the abstract)

increase the internal quantum efficiency of an organic light emission diode owing to their strong coupling of excitons with localized surface plasmons.

Alexander Govorov (Ohio University in the USA) spoke in a keynote lecture and showed a peptide for gold reduction and synthesis, antibody recognition, and the antibody mediated assembly of gold/quantum dot nanostructures through a network of antibody-epitope and streptavidin/biotin interfaces. Optically, these structures exhibited increased quenching of fluorescence dependent on the number of attached gold particles [6]. The physical properties of excitons in hybrid complexes composed of semiconductor and metal nanoparticles (Au-NP-CdSe-NP complexes with a polyethyleneglycol linker) were also discussed.

Maria Ujué González (Microelectronics Institute of Madrid, Spain), spoke about “Increasing the modulation depth in Au/Co/Au magnetoplasmonic interferometers”. The speaker explained that hybrid magnetoplasmonic materials with ferromagnetic (such as Fe, Co, and Ni) and plasmonic (like Au and Ag) metals can be produced, which can have advantages in nanophotonic devices.

Diana Martín Becerra (from the same group) talked in the Ph.D. parallel sessions about “Wavelength dependence of the surface plasmons polaritons wavevector magnetic modulation in Au/Co/Au films”. This work was also presented in the student poster session and got the Keren Prize for the best poster.

Maria Cardinal from (University of Vigo), in the same session, talks about the formation of gold dumbbell-like NPs (Fig. 4) through seeded growth of preformed nanorods (average aspect ratio ~4), by reduction of HAuCl_4 with ascorbic acid. The as-prepared Au dumbbells were coated with silver in an aqueous solution containing CTAB, AgNO_3 , NaOH, and ascorbic acid. This work was also presented in the form of poster.

Marta Castro Lopez (Institute of Photonic Sciences in Spain), presented orally in the same session and in the form of poster, an experimental study of optical rod nanoantennas of three different metals: aluminum, silver, and gold. She said that gold is the most used material for photonics.

Aya Fujiki (Osaka University in Japan) showed her investigations on the emission properties of N,N'-diheptyl-3,4,9,10-perylenebiscarboximide thin films on the highly oriented pyrolytic graphite and the Au(111) surfaces using tunneling electrons from a scanning tunneling microscope (STM). This work was presented in the Ph.D. parallel session and as a student poster presentation.

The senior poster of Yusuke Miyake (from the same University) dealt with “Tunneling-current-induced light emission from chiral binaphthylene-perylenebiscarboxydiimide dimer” on similar graphite and Au(111) surfaces.

A NSERC-CRSNG (NanoIP) prize was awarded to Dominic Lepage (University of Sherbrooke in Canada) for

his poster on “Hyperspectral imaging of surface plasmon resonance effects induced by uncollimated semiconductor radiation”. A novel imaging technique, based on the hyperspectral photoluminescence mapping of surface plasmon resonance events was presented and nice images of a SiO_2 -Au-photoresist architecture were shown.

Aida Serrano (Universidad Complutense de Madrid), presented a student poster describing the depositing of Au films with different thicknesses onto sodalime glass substrates by thermal evaporation that were annealed in air up to 500°C , causing morphological modification that changed their optical properties.

In the senior poster of Antonio García-Martín (Institute of Microelectronics of Madrid) the magneto-optical response of a series of pure gold nanostructures was presented for the first time. The magneto-optical effects in pure plasmonic nanostructures may find important applications in plasmonic modulators or in the improvement of the biosensing performance of metal nanostructures. In another poster, the same author showed that by growing a monolayer of polystyrene spheres (diameter size similar to working wavelength) on a gold substrate it is possible to obtain hybrid photonic-plasmonic resonances coupling.

Acknowledgements I am grateful to Prof. Luis Liz-Marzán, Prof. Romain Quidant, Prof. Alexander Govorov and Dr. Eulália Pereira for providing the PowerPoint slides used for their talks and giving me further information about their work.

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