O 43: Plasmonics and Nanooptics IV

nau. Germany.

Time: Wednesday 10:30–13:15

O 43.1 Wed 10:30 H31

Repetitive hole-mask colloidal lithography for large-area multi-shape plasmonic nanostructures — \bullet Jun Zhao¹, Sarah JABER², PAUL MULVANEY², and HARALD GIESSEN¹ — ¹4th Physics Institute and Research Center SCoPE, University of Stuttgart, Germany — ²School of Chemistry and Bio21 Institute, University of Melbourne, Australia

We fabricate large-area (cm2 size) plasmonic nanostructures of multiple shapes, orientations, and sizes. We utilize repetitive hole-mask colloidal lithography with sparsely distributed polystyrene beads. Multiple lithography leads to neat structures with high area coverage and very little nanostructure touching or overlap. The optical spectra of our sample show well modulated resonances, which confirm the high quality of our fabrication method. Our method is useful to create polarization-independent split-ring arrays, broadband multi-peak infrared antennas for SEIRA enhancement[1], nanostructures with simultaneous SERS and SEIRA enhancement in the visible and IR, as well as chiral 3D plasmonic structures with C3 or C4 symmetry.

[1] S. Cataldo, J. Zhao, F. Neubrech, B. Frank, C. Zhang, P. V. Braun, H. Giessen, ACS Nano 2012, 6, 979.

O 43.2 Wed 10:45 H31 **Plasmonic Sensing using Hydrogen induced Phase Transi tions in Yttrium Nanoparticles** — •NIKOLAI STROHFELDT¹, AN-PREAS, THERE 1. ENANG. NUMBER OF A PARTY AND A PARTY A

DREAS TITTL¹, FRANK NEUBRECH¹, UWE KREIBIG², and HARALD GIESSEN¹ — ¹4th Physics Institute and Research Center Scope, University of Stuttgart, D-70550 Stuttgart, Germany — ²I. Physikalisches Institut 1A der RWTH Aachen, D-52056 Aachen, Germany

We utilize the subsequent hydration of Yttrium nanoparticles [1] to construct an extremely sensitive optical hydrogen detector. Upon the reaction pathway $Y \rightarrow YH_2 \rightarrow YH_3$ the material undergoes two phase transitions. The second transition from the metallic YH₂ to the dielectric YH₃ is reversible at room temperature and therefore highly interesting for hydrogen sensing applications. Our lithographically defined 50 nm thick and 200 nm diameter nanoparticles exhibit a strong and sharp particle plasmon resonance in the metallic YH₂ state. Upon exposure with 4% H₂ in N₂, within seconds the particle plasmon absorption vanishes completely as the particles undergoes a reversible metal-to-insulator phase transition to YH₃. This large relative change will enable the construction of novel, ultra-sensitive, optical, single-nanoparticle hydrogen sensors in the future.

[1] G. Bour, A. Reinholdt, A. Stepanov, C. Keutgen, and U. Kreibig, "Optical and electrical properties of hydrogenated yttrium nanoparticles," The European Physical Journal D **16**, 219-223 (2001).

O 43.3 Wed 11:00 H31

Detecting low concentrations of pollutant chemicals in water by SERS:Combining optimised nanoparticle ensembles and SERDS — \bullet ROBERT OSSIG¹, YONG-HYOK KWON², HEINZ-DETLEF KRONFELDT², and FRANK HUBENTHAL¹ — ¹Institut für Physik and CINSaT, Universität Kassel, Germany — ²Technische Universität Berlin, Institut für Optik und Atomare Physik, Germany

We present a sensor that is suitable to detect very low concentrations of pollutant chemicals, e.g. polycyclic aromatic hydrocarbons (PAHs). To meet the European Quality Standard (EQS) criteria for PAHs, which require limits of detection (LOD) in the sub $n\mathrm{Mol}/\mathrm{l}$ regime, we combined surface enhanced Raman spectroscopy (SERS) with shifted excitation Raman difference spectroscopy (SERDS) and used supported noble metal nanoparticles (NPs) as SERS substrates. The NPs were prepared by Volmer-Weber growth under ultra high vacuum conditions. To gain optimal SERS enhancement the NPs plasmon resonance positions were tuned to coincide with the excitation wavelengths for SERDS. We demonstrate that our sensor using bare NPs yield LODs between 2 and 4 nMol/l, sufficient to detect the maximum allowable concentration of PAHs in water, as determined by the EQS. Furthermore we can reliably detect these concentrations in about 10 minutes. However, the annual average concentration requires LODs below the nMol/l regime. To reliably detect such low concentrations the functionalization of the NPs is currently under investigation. The functionalization enhances the adsorption of probe molecules to the NPs, which leads to a further improvement of the LOD.

Location: H31

O 43.4 Wed 11:15 H31

Strong SERS Enhancement Based on Large Area Controllable Gold Nanoparticle Arrays with High Uniformity and Reproducibility — •YAN ZHENG, CHENGLIANG WANG, WENXIN WANG, FELIX STOSBERG, and YONG LEI — Fachgebiet 3D-Nanostrukturierung, Institut fuer Physik & IMN MacroNano, Technische Universitaet Ilmenau, Germany

Significant SERS (surface enhanced Raman Scattering) enhancement with uniformity and reproducibility are achieved based on controllable highly ordered gold nanoparticle arrays, which can be obtained in large area by using ultra-thin alumina membranes (UTAMs) as shadow masks[1-2]. By controlling the anodization process, the pore-widening period of UTAM masks and the thermal deposition of nanoparticles, ordered Au nanoparticle arrays with different diameter and different surface morphology were obtained[3]. The Raman spectra of the Au nanoparticle arrays suggest that rough surface morphology can facilitate the SERS effect and the optimum diameter of nanoparticles is about 55 nm. All the results indicate that the template-prepared highly ordered Au nanoparticles on Si wafers with reproducible homogeneous SERS signals are high performance SERS substrates, which shall have important applications for SERS-related devices.

Lei Y., Yang S.H., Wu M.H., Wilde G., Chemical Society Reviews, 40(3), 1247-1258, 2011.
 Yang S.K., Cai W.P., Kong L.C., Lei Y., Advanced Functional Materials. 20(15), 2527-2533, 2010.
 Wen L.Y., Wu M.H., Ostendorp S., Chen K., Wilde G., Lei Y., Small, 6(5), 695-699, 2010.

O 43.5 Wed 11:30 H31 Fabrication of plasmonic Ag/Au arrays used as sensitive platform for glucose assay — •WENXIN WANG, YAN ZHENG, AHMED SHUKUR HAMEED AL-HADDAD, YAN MI, HUAPING ZHAO, and YONG LEI — Fachgebiet 3D-Nanostrukturierung, Institut fuer Physik & IMN MacroNano (ZIK), Institute for Physics and IMN MacroNano (ZIK), Technische Universitaet Ilmenau, Prof. Schmidt Str. 26, 98693 Ilme-

A noble Ag/Au plasmonic array used for glucose detection based on enzyme-responsive was first obtained. Such kind of Ag arrays stands on the Au covered substrate which connected with glucose oxide (GOx) was prepared via mutil-steps physical vapor deposition combined with ultra-thin anodic alumina membranes. When the GOx from the substrate meeting with glucose, the produced H2O2 will etching origin Ag array into porous that will induce the variation of its optical property. Because plasmon resonance is sensitive to the structure, therefore with this new platform, even a little glucose can quickly detected from the shifting of extinction spectrum. We believe this king of glucose sensing platform has bright future in commercial application.

O 43.6 Wed 11:45 H31

Plasmonic Smart Dust for Probing Local Chemical Reactions — •ANDREAS TITTL¹, XINGHUI YIN¹, HARALD GIESSEN¹, XIANG-DONG TIAN², CHRISTIAN KREMERS³, DMITRY N. CHIGRIN³, ZHONG-Qun Tian², and Na Liu⁴ — ¹4th Physics Institute and Research Center Scope, University of Stuttgart — ²State Key Laboratory for Physical Chemistry of Solid Surfaces and Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University ³Institute of High-Frequency and Communication Technology, Faculty of Electrical, Information and Media Engineering, University of ${\rm Wuppertal} - {}^4{\rm Max} \; {\rm Planck} \; {\rm Institute} \; {\rm for} \; {\rm Intelligent} \; {\rm Systems}, \; {\rm Stuttgart}$ We demonstrate an all-optical probing technique based on plasmonic smart dust for monitoring local chemical reactions in real time. Our smart dust consists of silica shell-isolated gold nanoparticles which can work as strong light concentrators and optically report subtle changes at their pinning sites on the probed surface during reaction processes. In particular, we investigate the hydrogen dissociation and subsequent absorption in neighboring palladium films with both "dust-on-film" and "film-on-dust" platforms. Our single particle scattering measurements illustrate the ability of this technique to optically resolve chemical reactions while they occur on various surface morphologies. The presented technique offers a unique scheme for real-time, label-free, and highresolution probing of local reaction kinetics in a plethora of chemical reactions on surfaces.

O 43.7 Wed 12:00 H31

Label-free single-protein optical sensing and imaging — •MAREK PILIARIK and VAHID SANDOGHDAR — Max Planck Institute for the Science of Light Günther-Scharowsky-Str. 1, Building 24 91058 Erlangen, Germany

To date, the sensitivity of optical detection and imaging of individual molecules is strictly limited to species with strong fluorescence or absorption properties. We report on a new approach based on the direct detection of the light scattered by biomolecular species such as proteins without the need for any labels. The underlying mechanism of our detection method is the interference between the light coherently scattered by the analyte (e.g. a protein molecule adsorbed on the substrate) and the laser beam partially reflected at the substrate-water interface. By combining this method with microfluidics and surface functionalization of the substrate, we show that it is possible to detect and image a single protein in real time and distinguish it from a large background of other scatterers. We discuss the application of our approach for ultrasensitive label-free biosensing.

O 43.8 Wed 12:15 H31

Voltage clamped single gold nanoparticles as nanoscale pH-sensors — •CYNTHIA VIDAL¹, MARTIN DJIANGO¹, CALIN HRELESCU¹, THOMAS A. KLAR¹, ANDREI I. MARDARE², and ACHIM WALTER HASSEL² — ¹Institute of Applied Physics, — ²Institute for Chemical Technology of Inorganic Materials, Johannes Kepler University, 4040 Linz, Austria

The surface chemistry of gold nanoparticles plays a crucial role when used in biodiagnostics, in surface enhanced Raman scattering and catalysis. The processes of double layer charging, increased damping of the plasmons due to adsorbates, and oxidation of single gold nanorods were recently investigated by optical dark field spectroscopy of voltage-clamped single gold nanoparticles [1,2]. In this work, the pH-dependence of the reversible formation/reduction of hydrous gold oxide layers on a single nanoparticle was investigated by combining electrochemistry with monitoring the plasmon resonance of single gold nanorods in a dark field microscope. Changing from an acidic environment to a more basic one, a shift of the hydrous oxide reduction point to lower potentials is observed. In combination with cyclic voltammetry results, the spectral shifts of the nanoparticle plasmon resonance can be correlated with these phenomena. The presented combination of electrochemistry and optical spectroscopy at a single nanoparticle level allows for the use of single gold nanoparticles as nanoelectrodes, providing a novel tool for electrochemistry and electro catalysis on the nanoscale. [1] Nano Lett. 12, 1247 (2012) [2] Nanoscale 4, 2339 (2012)

O 43.9 Wed 12:30 H31

Broadband subwavelength imaging using a tunable grapheneens — •PEINING LI and THOMAS TAUBNER — RWTH Aachen University, Sommerfeldstraße 14, 52074 Aachen, Germany

Graphene as a one-atom-thick planar sheet can support surface plasmons at infrared (IR) and terahertz (THz) frequencies, opening up exciting possibilities for the emerging research field of graphene plasmonics. Here, we theoretically report that a layered graphene-lens (GL) enables the enhancement of evanescent waves for near-field subdiffractive imaging [1]. Compared to other resonant imaging devices like superlenses [2,3], the nonresonant operation of the GL provides the advantages of a broad intrinsic bandwidth and a low sensitivity to losses, while still maintaining a good subwavelength resolution of better than $\lambda/10$. Most importantly, thanks to the large tunability of the graphene, we show that our GL is a continuously frequency-tunable subwavelength-imaging device in the IR and THz regions, thus allowing for ultrabroadband spectral applications.

[1] P. Li, T. Taubner, ACS Nano, In press.

- [2] J. B. Pendry, Phys. Rev. Lett., 85, 3966-3969, (2000).
- [3] T. Taubner et. al., Science, 313, 1595-1595, (2006).

O 43.10 Wed 12:45 H31

Antenna-enhanced infrared near-field nanospectroscopy of a polymer — •Jón Mattis Hoffmann, Benedikt Hauer, and Thomas Taubner — I. Institute of Physics (IA), RWTH Aachen University, Sommerfeldstraße 14, 52074 Aachen, Germany

Infrared spectroscopy is a powerfull characterization tool which allows for the investigation of chemical properties of a sample by directly probing molecular vibrations. On nanometer scale this is enabled by scattering-type scanning near-field optical microscopy (s-SNOM). This technique provides information about topographical and chemical material properties with subwavelength resolution.[1]

In this work, we demonstrate that the sensitivity of s-SNOM can be improved by means of infrared resonant antennas. This is comparable to the application of resonant nanostructures in far-field surfaceenhanced infrared spectroscopy (SEIRS).[2] Here, antennas prepared with colloidal lithography are used to enhance the spectra of a polymer coverlayer. We find that the near-field amplitude spectra of the polymer obtained on resonant structures are increased in absolute value as well as in contrast over those obtained on non-resonant, highly reflective materials such as gold.[3]

[1] F. Keilmann et al. in Nano-Optics and Near-Field Optical Microscopy ed. by A. Zayats and D. Richards, 235 (ArtechHouse, 2009).

[2] F. Neubrech et. al., Physical Review Letters 105, 157403 (2008).
[3] J. M. Hoffmann et. al., Applied Physics Letters 101, 193105 (2012).

O 43.11 Wed 13:00 H31

Raman spectra of individual carbon nanotubes manipulated by surface plasmons — •NICOLA PARADISO, FATEMEH YAGHOBIAN, TOBIAS KORN, CHRISTIAN SCHÜLLER, and CHRISTOPH STRUNK — Institut für Experimentelle und Angewandte Physik, Universität Regensburg.

The Raman spectrum of individual carbon nanotubes (CNTs) can be enhanced by noble metal nanoparticles, due to surface-enhanced Raman scattering (SERS). In this work we exploit lithographically patterned nanoparticles to locally obtain SERS from the desired position along a CNT. Such structures consist of arrays of sharp triangular metal pads separated by a 20 nm-wide gap, which are fabricated via electron beam lithography. AFM scans allow us to align the lithography so that the CNT is lying within the gap between two nanostructures. When illuminated with the Raman source, surface-plasmons are generated at the surface of these gap sized engineered structures. This method allows us to separately characterize electromagnetic and the chemical contributions in SERS. In particular, we have analyzed how the presence of noble metal structures manipulates the radial breath mode in the spectrum, and how the G+/G- amplitude ratio is locally modified. Such an "on-chip" optical interface will make it possible to manipulate the optical features of the CNTs and allow to directly assigning the chirality of given individual CNTs.