

CPP 8: Nanoparticles I

Time: Monday 10:30–12:30

Location: ZEU 114

CPP 8.1 Mon 10:30 ZEU 114

Nanoscale pH-sensing with Polymer coated Gold Nanorods — ●IRENE AMENT, JAN BECKER, ANDREAS HENKEL, SEBASTIAN PIERRAT, LUIGI CARBONE, and CARSTEN SÖNNICHSEN — Institute for Physical Chemistry, University of Mainz, Germany

We report a reversible nanoscale pH-sensor consisting of a gold nanorod covered with the pH sensitive polymer Poly(acrylic acid). This polymer is covalently bound to the gold particle by cystein side groups and deprotonates under basic conditions. At high pH, the backbone is therefore stretched by the repelling forces of the negative charges and the packing becomes less dense, lowering the refractive index around the particle. This change in the refractive index induces a shift in the plasmon resonance, which we detect with single particle dark field spectroscopy. With such a reversible system we detect pH variations at the nanometer scale and could potentially map pH landscapes with high precision.

CPP 8.2 Mon 10:45 ZEU 114

Investigation of nucleation and growth processes of gold nanoparticles via coupled in situ SAXS/XANES — ●JÖRG POLTE¹, FRIEDMAR DELISSEN¹, TORSTEN T. AHNER², SERGEY SOKOLOV², RALPH KRAEHNERT², MARTIN RADTKE¹, UWE REINHOLZ¹, HEINRICH RIESEMEIER¹, FRANZISKA EMMERLING¹, and ANDREAS F. THÜNEMANN¹ — ¹BAM Federal Institute for Materials Research and Testing Richard-Willstätter-Str. 11, 12489 Berlin — ²LIKAT - Leibniz Institute for Catalysis, Richard-Willstätter-Str. 12, 12489 Berlin

Gold nanoparticles (AuNP) are among the most studied nanoscale material due to prospective applications in areas such as medicine, biotechnology and catalysis [1, 2]. To control the size and shape of metal nanoparticles, a detailed understanding of the mechanism and kinetics of precursor reduction and particle growth is essential. We report on a new method to determine in parallel the oxidation state of the reactants as well as the size, number and polydispersity of formed particles in-situ. The method relies on time-resolved XANES and SAXS measurements carried out on sample droplets exposed to synchrotron radiation. Supplemented by in-situ UV-Vis and SEM, the evolution of AuNP during reduction and particle formation was explored using different reducing agent. From the data, a mechanistic scheme is developed explaining the different phases of particle formation and growth, thus providing a basis for improved control over the synthesis process. [1] J. Park, J. Joo, S. G. Kwon, Y. Jang, T. Hyeon, *Angewandte Chemie-International Edition* 2007, 46, 4630. [2] M. C. Daniel, D. Astruc, *Chemical Reviews* 2004, 104, 293.

CPP 8.3 Mon 11:00 ZEU 114

Kinetic study of binding of multivalent ligands on size selected gold nanoparticles — ●SUGUNA PERUMAL, ANDREAS HOFMANN, CHRISTINA GRAF, and ECKART RÜHL — Physikalisches und Theoretische Chemie, Institut für Chemie und Biochemie, Freie Universität Berlin, Takustr. 3, 14195 Berlin

A kinetics study of binding of multivalent ligands on different kinds of nanoparticles is presented. The enhanced binding of multiple ligands in one entity to multiple receptors is known as the multivalency effect. Flexible thiol functionalized multivalent ligands are synthesized by using reported procedures. Pyrene bound nanoparticles are prepared by wet colloidal chemistry and characterized by transmission electron microscopy. The multivalency effects are investigated by exchanging pyrene bound to gold nanoparticles with multivalent ligands and studying this process via fluorescence spectroscopy. The fluorescence of the pyrene moiety is completely quenched when it is directly bound to gold nanoparticles. It recovers completely after desorption from nanoparticles after an exchange with mono- or multivalent ligands. The change of the fluorescence intensity of the pyrene moiety is measured as a function of time. Multivalency effects are observed by comparing the rate constants of monovalent and di- or trivalent thiol ligands. However, no enhancement effects are observed between trivalent and divalent thiol ligands on gold nanoparticles. Hence, we assume that only two thiol groups are binding in case of the trivalent ligands. Further, the influence of the particle size on the exchange kinetics is discussed.

CPP 8.4 Mon 11:15 ZEU 114

Nanoscale Characterization of Single Metal Nanoparticles by their Scattering Patterns — ●TINA ZÜCHNER¹, FRANK WACKENHUT¹, ANTONIO VIRGILIO FAILLA^{1,2}, and ALFRED J. MEIXNER¹ — ¹Eberhard-Karls-Universität Tübingen, Institute of Physical and Theoretical Chemistry, Tübingen, Germany — ²University of Cambridge, The Cancer Research UK, Cambridge, UK

We present a novel route to detect the environment of metal nanoparticles by means of confocal interference scattering microscopy in combination with higher order laser modes. Each scattering pattern results as the sum of the light reflected at the interface between two dielectric media and the light scattered by the particles. The images not only show directly the orientation of individual Au nanorods [1-3], but are also extremely sensitive on variations of the local environment [4]. In fact, changing the refractive index of the surrounding medium strongly influences e.g. the signal to noise ratio, the amplitude and the contrast sign which in addition reveals the nature of the interface between two dielectric media. A quantitative understanding of the refractive index's influence on the scattering pattern was achieved by comparing the experimental results and our theoretical calculations.

[1] A.V. Failla, H. Qian, H. Qian, A. Hartschuh and A.J. Meixner, *Nano Lett.* 6, 1374 (2006). [2] A.V. Failla, S. Jäger, T. Züchner, M. Steiner and A.J. Meixner, *Opt. Expr.* 15, 8532 (2007). [3] T. Züchner, A.V. Failla, A. Hartschuh and A.J. Meixner, *J. Microsc.* 229, 337 (2008). [4] T. Züchner, A.V. Failla, M. Steiner and A.J. Meixner, *Opt. Expr.* 16, 14635 (2008).

CPP 8.5 Mon 11:30 ZEU 114

Strukturelle und elektronische Eigenschaften von Biomolekülen auf isolierten Goldnanopartikeln — ●RENE LEWINSKI, CHRISTINA GRAF, BURKHARD LANGER, BERNHARD GRUNDKÖTTER, BERNHARD WASSERMANN and ECKART RÜHL — Institut für Chemie und Biochemie, Freie Universität Berlin, Takustr. 3, 14195 Berlin

Die Oberflächenmodifikation von Nanopartikeln (NP) mit einfachen Biomolekülen wie z.B. Aminosäuren ermöglicht neue Anwendungen als Sensoren und Diagnostika. Zur Optimierung dieser Systeme ist ein detailliertes Verständnis der Wechselwirkungen zwischen den Biomolekülen und den NP erforderlich. NEXAFS (Near Edge X-ray Absorption Fine Structure)-Spektroskopie ist eine empfindliche Methode zur Untersuchung der lokalen elektronischen Struktur sowohl organischer Moleküle als auch der NP. Ihr Einsatz führt aber durch die intensive Röntgenstrahlung oft zu Strahlenschäden. Wir haben deshalb NP in einem freien Partikelstrahl mittels NEXAFS untersucht. Die Lösungen wurden versprüht, getrocknet und mit einer aerodynamischen Linse in den Bereich der Synchrotronstrahlung überführt. Hierdurch werden sowohl der Kontakt zu einem Substrat als auch Strahlenschäden vermieden. Mit schwefelhaltigen Biomolekülen funktionalisierte Gold-NP wurden mit den Spektren der entsprechenden reinen Liganden verglichen, wobei signifikante spektrale Verschiebungen beobachtet wurden. Insbesondere konnte trotz der relativ stabilen S-Au Bindung, eine partielle Oxidation der Liganden nachgewiesen werden. Auch zwischen mono- und bivalent gebundenen Liganden kann ein signifikanter Unterschied in der lokalen elektronischen Struktur festgestellt werden.

CPP 8.6 Mon 11:45 ZEU 114

Size-controlled functionalized magnetite nanoparticles and their cellular uptake — ●SEBASTIAN WEIBELS¹, ANJA SOMMER¹, STEFANIE KLEIN¹, JESSICA PLOETTNER¹, KLAUS GIEB², KONSTANTIN PETUKHOV², and CAROLA KRYSCHI¹ — ¹Dept. Chemistry and Pharmacy, Physical Chemistry I, FAU, Egerlandstr. 3, 91058 Erlangen — ²Physical Institute III, FAU, Erwin-Rommel-Str. 1, 91058 Erlangen

Magnetite nanoparticles (MNP) were synthesized by coprecipitating Fe(II)/Fe(III)solutions with an ammonia solution, and their sizes were tuned between 4 and 15 nm by varying the concentrations of the reactants. Repulsive interactions between the MNP and their solubility in polar and unpolar solvents were obtained by functionalizing the MNP with suited organic acids. FTIR spectra of successfully functionalized MNP indicate covalent binding via the carboxylic group. The MNP sizes were determined under a high-resolution transmission electron microscope, while the magnetic properties in dependence on temperature were investigated using a SQUID magnetometer. The uptake of functionalized MNP by Caco-2 cells were imaged by transmission electron microscopy.

CPP 8.7 Mon 12:00 ZEU 114

Nass-chemisch hergestellte, dotierte Lithiumniobat-Nanopartikel* — ●BASTIAN KNABE, DANIEL SCHÜTZE und KARSTEN BUSE — Physikalisches Institut, Universität Bonn, Wegelerstr. 8, 53115 Bonn

Dotierte Lithiumniobat-Nanopartikel versprechen neue optische Eigenschaften, die der entsprechende Volumenkristall nicht aufweist. Wir demonstrieren einen nass-chemischen Ansatz zur Erzeugung dotierter Lithiumniobat-Nanopartikel aus Metallalkoholaten. Die angestrebte Größe liegt dabei unter 50 nm. Grad und Verteilung der Dotierung werden mit Hilfe energiegefilterter Transmissionselektronenmikroskopie und Elektronenenergieverlustspektroskopie nachgewiesen.

*Wir danken der DFG und der Deutschen Telekom AG für finanzielle Unterstützung.

CPP 8.8 Mon 12:15 ZEU 114

Influence of silicon dioxide nanoparticles on the isothermal cure of a silicone rubber. — ●BARTOSZ ZIELINSKI, ULRICH MÜLLER, MARTINE PHILIPP, JÖRG BALLER, ROLAND SANCTUARY, and JAN KRISTIAN KRÜGER — LPM, University of Luxembourg, Luxembourg

Incorporation of nanoparticles is nowadays widely used to improve physical and chemical properties of polymer materials. This is mainly caused by the fact that very often the polymer nanocomposites show physical properties not found in the corresponding microstructured material. The justifications for that behaviour are: size- and surface-induced properties of the nanoparticles themselves, topological constraints within the matrix material for high concentrations of nanoparticles and last but not least specific surface interactions between the nanoparticles and the polymer matrix. These chemical and/or physical interactions change the properties of the polymer nanocomposites and result in the creation of the so-called interphases.

Because there are already strong interactions between the single components of the silicone rubber and the nanoparticles which lead to the formation of new structures it will be shown how these interactions influence the curing process of the silicone rubber. We will discuss the influence of the nanoparticles on the optical and thermal properties for a two-component silicone rubber system filled with silicon nanoparticles. The results will be interpreted in terms of particles induced structure formation.

Refractometry and temperature modulated calorimetry have been used as experimental techniques.