

MO 71 Dynamics and Spectroscopy at Interfaces

Zeit: Freitag 10:40–12:25

Raum: H12

MO 71.1 Fr 10:40 H12

Ultrafast heterogeneous electron transfer: escape dynamics of injected electrons — ●LARS GUNDLACH, RALPH ERNSTORFER, JODI SZARKO, ANTJE NEUBAUER, LIANA SOCACIU-SIEBERT, and FRANK WILLIG — Hahn-Meitner-Institute, Department: Dynamics of Interfacial Reactions SE4, Glienickestrasse 100, 14109 Berlin, Germany

So far, most investigations of heterogeneous electron transfer focused on the time scale the electrons take to leave the molecules. Here, we report on the dynamics taking place after the electron has left the molecule. Ultrafast electron escape dynamics following excitation of the interfacial charge transfer complex of catechol prepared on the rutile TiO₂(110) surface was investigated with femtosecond two-photon photoemission. Photo-induced interfacial charge transfer was instantaneous. Thus, the rise of the signal was controlled by the crosscorrelation function. The energy distribution of the hot electrons generated at the surface was measured as 2PPE spectra. The decay of the 2PPE signal was non-exponential with time constants ranging from 10 fs to picoseconds. It was attributed to the release of the electrons from the surface and escape into the bulk of the semiconductor.

MO 71.2 Fr 10:55 H12

Structural influence of the dye on the dynamics of ultrafast heterogeneous electron transfer in a dye/semiconductor system

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The organic dye perylene attached via different anchor and spacer groups to TiO₂ surfaces were investigated in order to elucidate the influence of the molecular structure of the dye molecules on the dynamics of ultrafast heterogeneous electron transfer. For the electron transfer, the perylene functions as the electron donor in which the donor state lies above the edge of the conduction band minimum of the acceptor TiO₂. The electron transfer to TiO₂ surfaces has significant importance in the Graetzel cell, a dye-sensitized solar cell. The investigations were performed with two different time-resolved methods. Measurements with two photon photoemission (2PPE) spectroscopy were carried out on a rutile TiO₂ (110) single crystal surface and measurements with transient absorption were done on colloidal films of anatase TiO₂. Both techniques were employed under UHV conditions to avoid the photodecomposition of the perylene chromophore in the presence of water. The results of both methods on different perylene-derivatives at the TiO₂ surfaces will be shown and compared.

MO 71.3 Fr 11:10 H12

Observation of pH dependent back-electron transfer dynamics in Alizarin - TiO₂ adsorbates: Importance of trap states — ●MATYLITSKY VICTOR, LENZ MARTIN, and WACHTVEITL JOSEF — Goethe -University Frankfurt/Main, Institute of Physical and Theoretical Chemistry, Marie-Curie-Str. 11, D-60439 Frankfurt/Main, Germany

The dependence of the interfacial electron transfer in alizarin sensitized TiO₂ nanoparticles from sample pH has been examined via transient absorption spectroscopy in the visible spectral region. Excitation of the alizarin/TiO₂ system leads to a very fast electron injection (<100 fs) over a wide pH range. Back electron transfer shows a complicated multiphase kinetics and strongly depends on the acidity of the solution. The drastic changes in electron transfer dynamics upon varying the pH are explained by Nernstian-type change in the semiconductor band energy. Indeed, a change of sample pH values over seven units leads to a ~0.42 eV change of the conduction band edge position (i.e. the nominal free energy of the electron in the electrode). This change was sufficient to push the system to a condition, where direct electron injection to intraband gap surface states could be investigated. The existence of an electron transfer pathway via surface trap states is supported by the similarity of the observed back electron transfer kinetics of alizarin/TiO₂ at pH 9 and alizarin/ZrO₂ reported in earlier work (J. Phys. Chem. B 2000, 104, 8995), where the conduction band edge is approximately 1eV above the excited state of the dye. The influence of surface trap states on interfacial electron transfer and a detailed analysis of their population, depopulation and relaxation kinetics will be presented.

MO 71.4 Fr 11:25 H12

Influence of the Organic Cappings of CdSe Nanoparticles on the Charge Carrier Relaxation Dynamics — ●TOBIAS E. SCHRADER¹, BIRGIT VON HOLT¹, STEPHAN MALKMUS¹, THOMAS BRUST¹, WOLFGANG J. SCHREIER¹, FLORIAN O. KOLLER¹, STEFAN KUDERA², WOLFGANG PARAK², and MARKUS BRAUN¹ — ¹Ludwig-Maximilians-Universität, Lehrstuhl für BioMolekulare Optik, Oettingenstr. 67, 80538 München — ²Ludwig-Maximilians-Universität, Lehrstuhl für Angewandte Physik, Amalienstr. 54, 80799 München

CdSe nanoparticles (NPs) have attracted much scientific interest because of their potential applications in labelling proteins in living cells. Organic cappings of NPs serve two purposes: Firstly they determine the surface chemistry of the NPs and therefore are a key to biological applications. Secondly they improve the fluorescence quantum yield which is crucial for the application as protein markers. With time resolved visible pump, visible and infrared probe spectroscopy we have investigated the charge carrier dynamics in NPs. With the electron acceptor naphthoquinone as capping faster decay times (90 ps and 1.3 ns) of the 1 S_{3/2} to 1 S_e transition at 4.6 μm are observed as compared for the hole acceptor pyridine (120 ps and 4.1 ns). This can be interpreted by the fact that naphthoquinone provides efficient traps to the electron whose signal is observed in the IR transient.

MO 71.5 Fr 11:40 H12

Molecular view of hidden interfaces — ●SYLVIE ROKE — Max-Planck Institute for Metals Research, Heisenbergstr. 3, 70569 Stuttgart

Many important chemical, physical and biological phenomena occur at interfaces of small particles. Most of the tools presently available to study these interfaces use invasive techniques or model systems. Ideally, one would want a non-invasive technique that allows the study of interface structure and dynamics with molecular specificity.

By combining light scattering and femtosecond vibrational sum frequency generation (a technique that has been used to mostly study flat interfaces) we are able to study the interfaces of sub-micron particles in solution on a molecular level. Using a nonlinear Rayleigh Gans Debye model we can extract information about the order and orientation of interface molecules and simultaneously obtain the shape and size of the particles [1]. Two demonstrations of sum frequency scattering will be presented. The first will deal with colloidal dispersions of sterically stabilized silica particles that undergo a gelation transition [2].

Second, we will present valuable insights in the interface properties of lactate particles, which are being used as a new medicine against liver malignancies [3].

[1] S. Roke, et al. Phys. Rev. Lett., 91, 258302 (2003).

[2] S. Roke et al. to be published in J. Phys: Condens Matter., 17, S3467 (2005)

[3] J. F. W. Nijsen et al., Eur. J. Nucl. Med. B, 26, 699 (1999)

MO 71.6 Fr 11:55 H12

Surface Enhanced Raman Spectroscopy (SERS) with Nano-Structured Gold Surfaces — ●M. SACKMANN, T. BALSTER, and A. MATERNY — International University Bremen, Bremen

Raman spectroscopy is a common tool for qualitative and quantitative chemical analysis of molecules even in a mixture of different substances. Although, the unique identification of adenine molecules is possible via their vibrational lines, high concentrations (mmol/l) are needed for qualitative results due to the low scattering cross section for non-resonant excitation. The intensity of the Raman spectra is amplified by the use of the Surface Enhanced Raman Scattering (SERS) technique. While the use of silver sols only results in a limited reproducibility of the Raman line intensities, nano-structured gold surfaces, if used as SERS-active substrates, in principle should combine the high sensitivity with better reproducibility. For this purpose, we have produced gratings of gold dots on Si(001) surfaces by means of electron beam lithography. The distance between the gold nanostructures was varied between 350 to 370 nm and for the diameters of the gold dots values between 50 to 320 nm were chosen. The samples are characterized by reflection spectroscopy, to determine the resonance of the grating structure. Recent measurement results with Raman microscopy of adenine (ppm concentrations) on these structures will be presented.

MO 71.7 Fr 12:10 H12

Extreme Adsorption Capability of Nanodiamond and Detectability of Lysozyme Concentration by Fluorescence Method — •VICTOR WEI-KEH WU^{1,2,3} and KOWA CHEN¹ —
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UV-Absorbance has been applied usually, for resolution of Lysozyme (containing 4 tryptophanes) up to ca. 50-100 μM , via Sore band at 409 nm. The adsorption capability of Nanodiamond(ND) $\phi=100$ nm - nearly all kinds of proteins in a sol. can be completely adsorbed¹, and the detectability of extremely diluted lysozyme solution are demonstrated. Diff. conc. of lysozyme (M=14300 g/mole, Sigma Chemical) of chicken egg white betw. 1-500 nM were prepared in KPBS buffer sol. of 7 mM. Xenon Lamp (2500 W, L.P. Associates, Inc.) for 285 nm with 3 mm slit width was used. A quartz cuvette with 10x10 cross section was used. Sol. well stirred, fluorescence was collected perpendicularly with PMA-11 of Hamamatsu. The linearity of the detected fluorescence counts depend. upon the lysozyme conc. betw. 10-500 nM was well measurable. The ND used, was 5-20 μg . The lysozyme adsorption capability by ND can be distinguishably followed down to 10 nM. This is 10^4 as powerful as by UV-Absorbance, and can be a new method for doping control². *Wu is the correspondance author. **Ref. 1.** X.-L. Kong, et al., *AC*, **77**, 259 (2005), **2.** J. Wallrafen, *GIT*, **49**, 644 (2005).