

Tuesday Afternoon Poster Sessions

Biological, Organic, and Soft Materials Focus Topic

Room: Hall D - Session BO-TuP

Biological, Organic, and Soft Materials Focus Topic Poster Session

BO-TuP1 Photoluminescence Characterization of Highly-Functional Molecule Doped Polythiophene Films Modified by Donor and Acceptor Molecules. *H. Kato, S. Takemura, H. Kobe, Y. Mori, Y. Matsuoka, K. Shimada, T. Hiramatsu, N. Nanba, K. Matsui*, Kanto Gakuin University, Japan

Conducting polymer polythiophene (PT) films incorporated with highly-functional molecules such as copper phthalocyanine (CuPc), fullerene C60, and rhodamine B (RB) were synthesized and characterized by photoluminescence measurements in order to fabricate organic hybrid materials with optical emission properties. The changes in photoluminescent properties of the hybrid polymer materials were investigated in the presence of electric field during the synthesis. The affection to the photoluminescence properties by donor and acceptor molecules such as tetrathiafulvalene (TTF) and tetracyanoquinodimethane (TCNQ) were also investigated. The electrochemical polymerization was performed in acetonitrile containing thiophene monomer and (Et)4NBF4 as a supporting electrolyte and the polymerization on an indium tin oxide (ITO) was conducted by applying positive voltage to the anode. The molecule doping in the polymer film was performed by electrochemical and diffusion methods. Photoluminescence emission peak was observed at 594 nm in the case of PT doped sample with CuPc by diffusion method. The emission peak was observed at 540 nm shifted to the lower wavelength in the case of electrochemically positive voltage applied sample after CuPc was diffused into the PT. Adding C60 molecules to the CuPc diffused PT sample by the diffusion method made the emission peak shift to the higher wavelength at 730 nm suggesting the molecular interaction between CuPc and C60 in the photoluminescence emission process because double emission peaks were observed at 590 and 735 nm in the case of single doping of C60. In the case of single doping of C60, successive electrochemical process made the double emission peaks single peak at 580 nm. TTF and TCNQ adding to the hybrid polymer films caused peak shift, peak loss and enhancement. In the case of RB diffused PT sample, photoluminescence peak at 590 nm was observed. Electrochemical process made the photoluminescence peak shift which depended on the applied voltage. Adding TCNQ to the RB diffused PT caused the enhancement of the emission peak. The present work clarified that the photoluminescence emission peak position was varied and controlled by electrochemically applying voltage or adding donor and acceptor molecules. This work was supported by High-Tech Research Center Project aided by MEXT.

BO-TuP2 Structured Polyelectrolyte Surfaces: Tunable Surface Morphology and its Influence on Biofouling. *X. Cao, F. Wode, A. Rosenhahn, M. Grunze*, University of Heidelberg, Germany, *J. Fu, J. Ji, J. Shen*, Zhejiang University, P.R. China, *F. Leisten*, University of Hannover, Germany, *R. Mutton, C. Sheelagh, A. Clare*, University of Newcastle, UK, *M. Pettitt, M. Callow*, University of Birmingham, UK

In the search for new coatings to protect surfaces from biofouling in marine environments the surface morphology is one important variable. In order to study the influence of different structure sizes, bioinspired polyelectrolyte multilayer coatings were applied and their effect on the settlement of *Ulva* linza zoospores and Barnacle cyprids was studied. The multilayers were constructed by the deposition of oppositely charged polyelectrolytes through layer-by-layer deposition. Hierarchical surface structures with different texture sizes and roughnesses were obtained by adjusting the preparation conditions. Surface characterization was carried out by contact angle measurement, spectral ellipsometry, X-ray photoelectron spectroscopy, scanning electron microscopy, atomic force microscopy and confocal microscopy to quantify wetting properties, coverage, chemistry, lateral size and aspect ratio of the topographical features. We discuss how variation of the salt concentration changes resulting morphologies. Settlement of *Ulva* spores and Barnacle cyprids was significantly affected by texture size and roughness. We compare the effect of topography on biofouling with the surface properties and the contact area for the different organisms. Surface modifications with fluorinated silane and poly(ethylene glycol) (PEG) combine the effects of chemistry and topography. Fluorinated, hydrophobic multilayers exhibited higher settlement than the uncoated polyelectrolyte surfaces for *Ulva* and reduced settlement for barnacle cyprids, while for PEG coated hydrophilic surfaces the anti-fouling performance was drastically enhanced.

BO-TuP3 Characterization and 3D Numerical Modeling of a UV/Ozone Duplex Sterilizer. *J.E. Jee, W.K. Yang, J.H. Joo*, Kunsan National University, Korea

We investigated sterilization characteristics of UV lights by counting the number of bacteria units with varying sterilization time and distance from the light source. When we irradiated 253.7nm on pens, we used UV transparent quartz plate as a support and put a reflecting plate and UV effect is increased about twice. But even with an Al reflector, multi-layered pens could not be treated properly from UV irradiation only. So, we focused on an idea that UV light of 184.9nm could generate ozone and developed a new sterilizer. Ozone generating lamp could treat more uniformly multi-layered pens with a stirring fan by supplying ozone to shadowed surfaces and keep out the temperature rising. Distribution of UV irradiation intensity and ozone supply were analyzed by a 3D model with varying geometry, position of reflectors and fans and confirmed by a semiconductor UV sensor and ozone analyser. We tried to evaluate the enhancement of a TiO₂ photocatalytic surface by direct sampling with a differentially pumped QMS.

BO-TuP4 Angle Resolved XPS Studies of Plasma Treated Polymers. *P. Mack, T. Carney, R.G. White*, Thermo Fisher Scientific, UK

Plasma treated polymers are becoming more significant in materials applications. Angle resolved X-ray photoelectron spectroscopy (ARXPS) is a useful tool for the analysis of these types of materials, where the modification takes place at various depths in the surface. Advanced data collection protocols, which make use of the Thermo Scientific's unique parallel angle resolving capability, were employed to minimise sample damage whilst maintaining data quality. Additionally, state-of-the-art software was used to maximise the information extracted from the ARXPS data.

BO-TuP5 Time-of-Flight Secondary Ion Mass Spectrometric (ToF-SIMS) Analysis for the Study of the Tertiary Structure of Polysiloxanes in Monolayer Films, Blends and Copolymers. *H.K. Moon, J.A. Gardella*, University at Buffalo

Time of flight secondary ion mass spectrometry (ToF-SIMS) is a powerful technique that can be used to investigate the conformation at the surface of a polymer film. Since the late 1990's TOF-SIMS studies of polymer tertiary structure have been reported for only a few polymers.¹⁻⁴ In this study, poly(methylphenylsiloxane) (PMPHS) is studied as another candidate polymer. The films which have the different conformations were manufactured by using Langmuir technique and solution cast method. For these different films, the difference of the fragment ion clusters in the high mass range of TOF-SIMS spectrum was investigated and additionally, reflection-absorption Fourier transform infrared spectroscopy (RA-FTIR) was used to confirm the result of ToF-SIMS. However, previous ToF-SIMS studies of tertiary structures of the polymers at their surface have been limited to the fundamental Langmuir model system.¹⁻⁴ Thus, the tertiary structure of poly(dimethylsiloxane) (PDMS) in a more realistic model will be investigated by using ToF-SIMS. First, the tertiary conformations of PDMS monolayers on a polystyrene (PS) substrate, as determined from high mass fragment intensity ratios⁴ are determined. Then, the conformations of PDMS blocks, in a PS-PDMS-PS block copolymer, segregated at the surface of blends of PDMS-PS block copolymer and PS homopolymer are determined.⁵ Thus, the PDMS film on the PS substrate can be regarded to the intermediate model between PDMS in the fundamental Langmuir film and PDMS segregated at the surface of a PDMS/PS copolymer or blend film.

¹ Nowak, R. W.; Gardella, J. A., Jr.; Wood T. D.; Zimmerman P. A.; Hercules D. M. *Anal. Chem.* 2000, 72, 19, 4585.

² Yan W.-Y.; Gardella, J. A., Jr. *Secondary Ion Mass Spectrometry*; John Wiley and Sons: New York, 1998, 451.

³ Rey-Santos, R.; Piwowar, A. M.; Alvarado, L. Z.; Gardella, J. A., Jr. *Appl. Surf. Sci.* 2006, 252, 19, 6605.

⁴ Piwowar, A. M.; Gardella, J. A., Jr. *Anal. Chem.* 2007, 79, 4126.

⁵ Xian, C.; Gardella, J. A., Jr. *Macromolecules* 1994, 27, 3363.

BO-TuP6 Partitioning Fracture Energy of a Molecularly Tailored Interface: Bond Cleavage and Plasticity. *A. Jain, Y. Zhou, S. Nayak, P. Ganesan*, Rensselaer Polytechnic Institute, *M. Lane*, Emory and Henry College, *G. Ramanath*, Rensselaer Polytechnic Institute

Separating the work of adhesion and plastic energy contributions to fracture toughness is essential to understand the mechanisms of interface debonding in thin film stacks and tailoring thin interfaces with desired properties for many applications. Here, we quantitatively separate the two contributions for Cu-silica interfaces modified with a molecular nanolayer by four-point bend testing at controlled environments to reveal the controlling mechanisms of energy dissipation. Recent work has shown that annealing

Cu-silica interfaces treated with sub-nm-thick molecular nanolayers (MNLs) of a mercaptan-terminated organosilane MNL can yield manifold increase in toughness due to Cu-S bonding and thermally-activated siloxane (Si-O-Si) bridging. The increased fracture toughness, however, exceeds that of fused silica, indicating the importance of secondary absorbing processes in the Cu layer. Since Si-O-Si bridges are susceptible to hydrolysis, varying the water content provides a facile means for tuning the strength of the Si-O-Si bridges, and hence for isolating the contributions of the work of adhesion and the plastic energy. We measured interface toughness of Cu/MNL/SiO₂ structures by four-point-bend testing as a function of water partial pressure p_{H2O} under fixed displacement. In all cases, X-ray photoelectron spectroscopy measurements of the fracture surfaces indicated debonding due to siloxane bridge fission at the MNL-SiO₂ interface. The resultant plots of debond rate, V , vs. debond driving energy, G , show two distinct regimes. At p_{H2O} < 1100 Pa, the plasticity in the Cu layer is the dominant contributor to the fracture toughness, as indicated by a high $dG/d(\ln p_{H2O})$, which captures the relative extents of plastic energy dissipation and work of adhesion. At p_{H2O} > 1100 Pa, $dG/d(\ln p_{H2O})$ decreases by a factor of 3, due to the diminished role of large scale plasticity. Thus, our results indicate that interfacial strengthening has a multiplicative effect on the fracture toughness through a factorial contribution due to plastic energy. This result is supported quantitatively by density functional theory calculations of bond stretching in the MNL and siloxane bond breaking in the presence of water. Further, our calculations indicate water decreases the Si-O-Si bond energy by at least a third of its value in vacuum. Our results are of significance for many applications involving molecularly tailored interfaces exposed to environmental and mechanical stresses.

BO-TuP7 Tracking of Motile Organisms by Digital In-Line Holography. *S. Weisse, M. Heydt, A. Rosenhahn*, University of Heidelberg, Germany, *M. Pettitt, M. Callow, J. Callow*, The University of Birmingham, UK, *N. Heddergott, M. Engstler*, Technical University of Darmstadt, Germany, *M. Grunze*, University of Heidelberg, Germany

Digital in-line holography is based on the original idea of D. Gabor's "new microscopic principle". Using this technique an interference pattern of both the so-called "source wave" and the "object wave" is recorded which contains three dimensional information about the observation volume. Real space information about the objects can be retrieved from these holograms through application of a reconstruction algorithm. One great advantage of a holographic instrument is that focusing can be done subsequently on a computer and three dimensional information about the object of interest can be obtained. Micro-fluidic experiments and tracking algae and bacteria, have shown that moving objects can be followed in three dimensions with remarkable accuracy and high time resolution. We present two applications for this technique: understanding biofouling and following the locomotion of pathogens. The exploration behavior of zoospores of the green algae *Ulva* is monitored to develop a deeper insight on how biofouling occurs on surfaces. Three surfaces (glass, a fluorinated surface and a PEG2000 surface) with different antifouling performances were investigated. For these three samples full 3D motion patterns were analyzed. In the bulk water, far from the surface, spores exhibit the same motility regardless of the investigated surfaces. In close proximity to the surface motility is significantly different. The interpretation of the exploration data leads to the previously unknown conclusion that these three surfaces are colonized via a different mechanism by zoospores. A second application involves examination of the locomotion of the blood parasite *Trypanosoma brucei*, the causative agent of African Sleeping sickness. The self-propulsion of *Trypanosoma brucei* in the bloodstream of a mammalian host is an essential part of its ability to withstand the mammalian immune system. To gain deeper insights into the pathogenesis of this blood parasite, a thermo-controllable flow channel setup was developed to allow the measurement of trypanosome trajectories under physiological conditions. Measurements are carried out in a buffer solution with dextran added to mimic the viscosity of mammalian blood and with and without flow to fully characterize motility. The obtained trajectories at different ambient properties are correlated with known effects in pathogenesis.

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