

**CROWNE PLAZA HOTEL
TERRIGAL, NSW
AUSTRALIA**

NOVEMBER 27TH - 30TH 2005

PROGRAMME AND ABSTRACTS

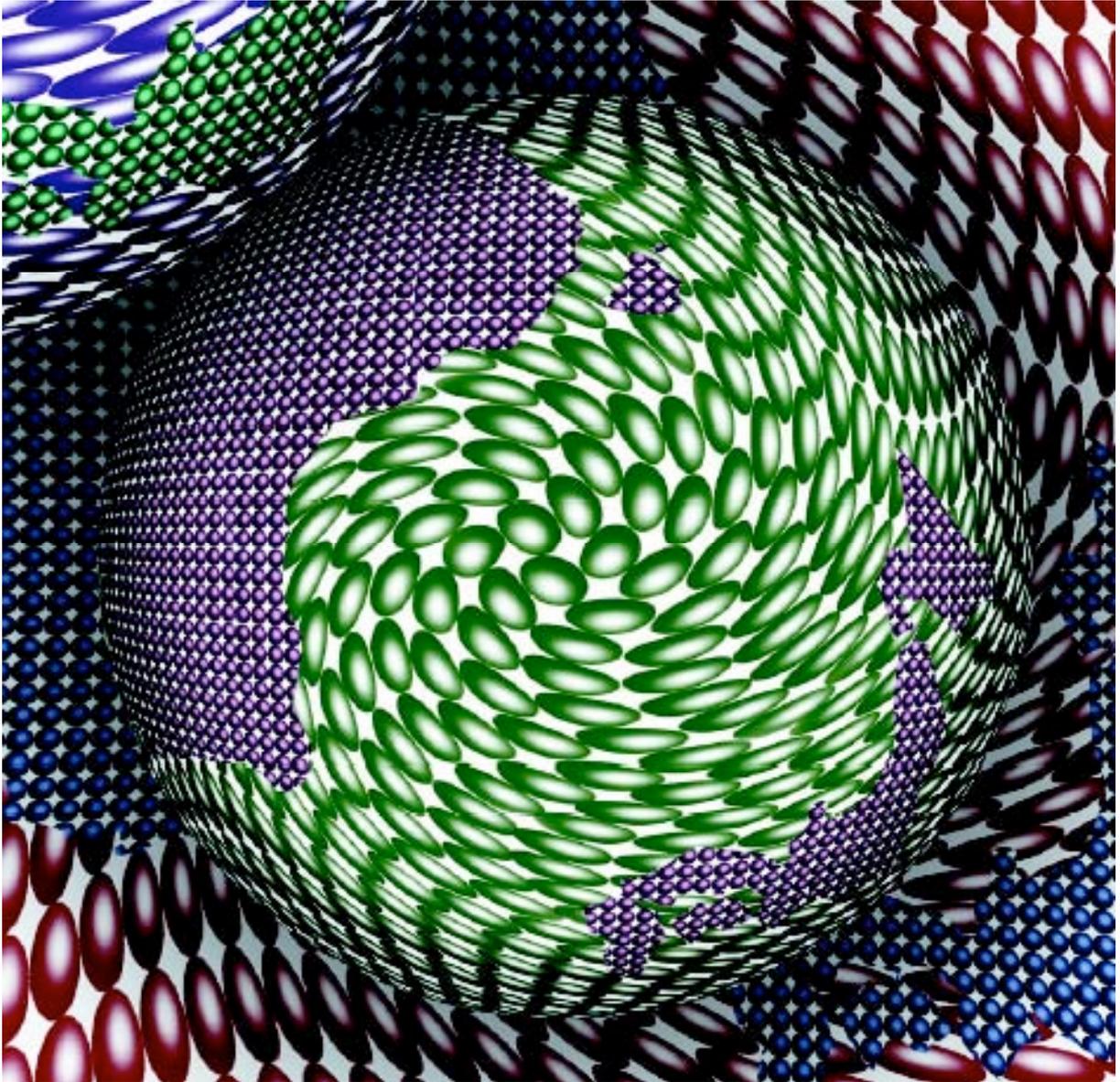


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Welcome Message

On behalf of the organizing committee welcome to Terrigal and to the 8th Japan-Australia Colloid and Interface Gakkai. These meetings have since 1992 provided an opportunity for Japanese and Australian colloid scientists to engage both intellectually and socially and have resulted in many successful collaborations over the years. It is my wish that this conference will continue to provide a mechanism for building collaborations, particularly for the emerging cohort of promising colloid and interface scientists. To encourage the next generation to follow the example of the eminent senior scientists at this meeting in building collaborations, early career researchers have been honoured with keynote presentations at this meeting. This was made possible by the Australian ARC Nanotechnology Network who provided the financial support that has enabled us to encourage the attendance of a number of early career scientists from both Japan and Australia.

This meeting would not have been possible without the strong organizational support of the Colloid and Interfaces Division of the RACI and the Japan Chemical Society.

We greatly appreciate the financial support provided by RMIT and the Particulate Fluids Processing Centre at the University of Melbourne. We also thank Sun Masamune, the Australian Sake producers, who have helped us with the "Kagami Biraki" or Sake Ceremony.

I am greatly indebted to the organizing committee, Erica, George, Gayle, Tom & Pat, for their great efforts. Thanks to them, I am confident that we will have a very successful meeting.

I would also like to thank you for your attendance. I am sure that you will find the science exciting and your participation in this meeting rewarding.

Vince Craig

A handwritten signature in black ink, appearing to read 'Vince Craig', with a stylized flourish at the end.

Chair, Gakkai 2005

Conferences in this Series

#	Year	Dates	Location	Delegates
1	1992	May	Kyushu University, Japan	60 Japanese 10 Australian
2	1992	December	Sorrento (near Melbourne), Australia	12 Japanese 40 Australian 8 Other
3	1994	October	Kyushu University, Japan	50 Japanese 20 Australian
4	1996	April	Sorrento (near Melbourne), Australia	Unknown
5	1998	13-15 July	Kyushu University, Japan	110 Japanese 22 Australian
6	2003	16-17 February	Coogee in Sydney, Australia	15 Japanese 75 Australian
7	2004	8-11 September	Ube, Japan	110 Japanese 15 Australian
8	2005	27-30 November	Terrigal, Australia	~ 30 Japanese ~ 35 Australian ~3 Other

Local Organising Committee

Chair & Technical Programme

Vince Craig

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Local Organiser

(Venue and Accommodation)

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Patrick Hartley

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Our Many Thanks To Japanese Liason

Kazue Kurihara

Webpage Design

Jamie Schulz

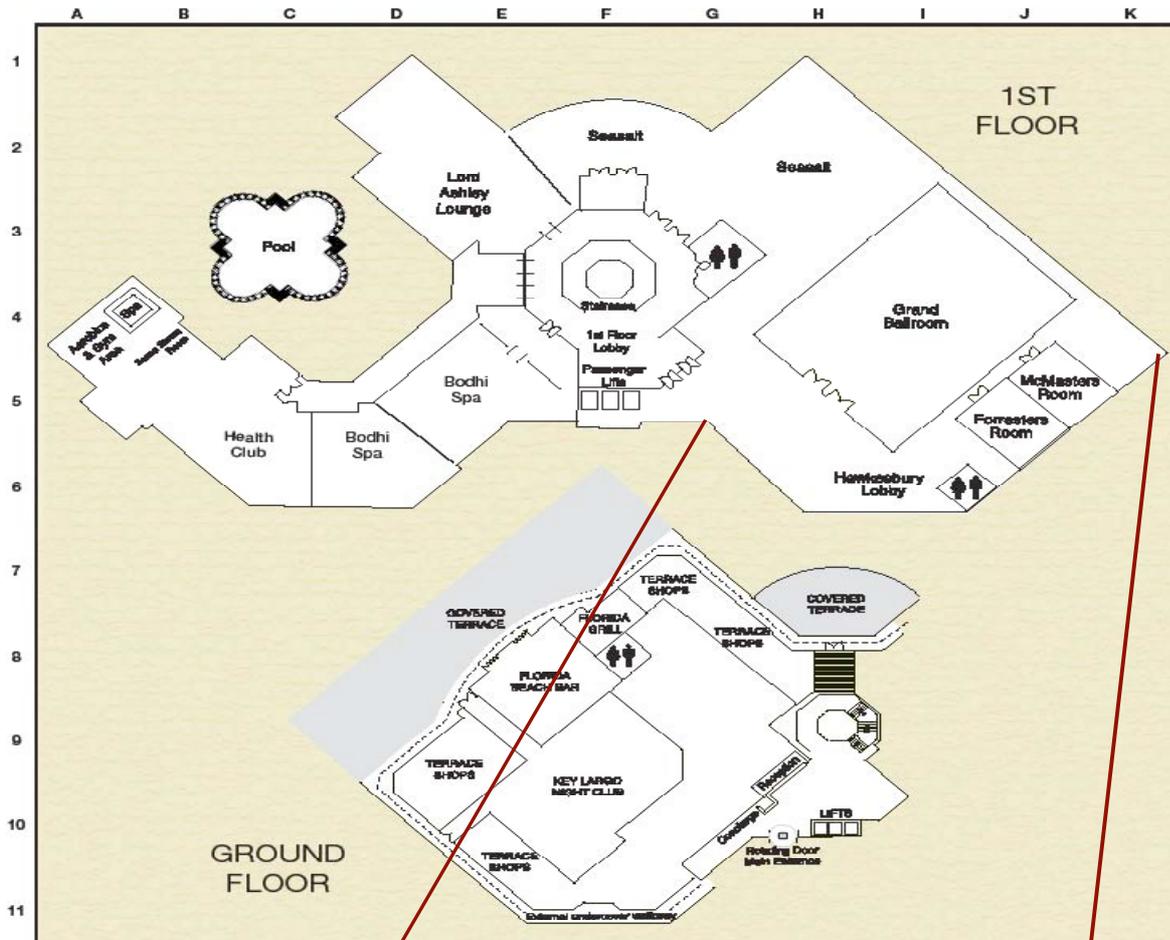
Artwork

Tim Wetherell

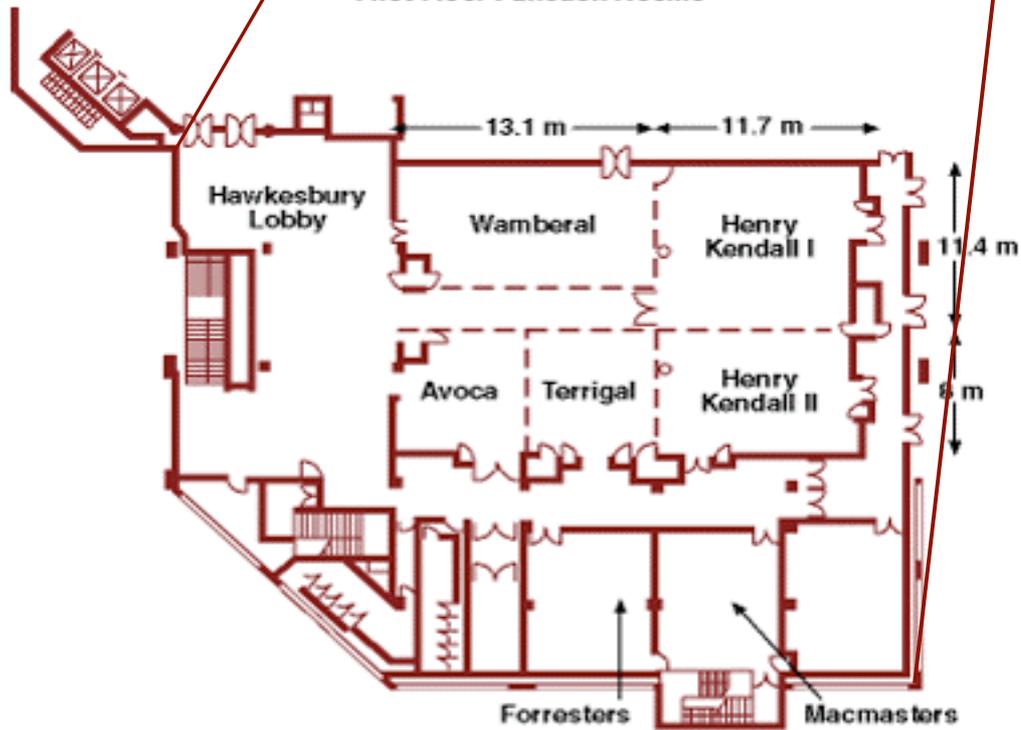
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Shaun Howard

Venue Map



First Floor Function Rooms



Locations

Conference

Registration	Hawkesbury Lobby
Talks	Henry Kendall Rooms 1 & 2
Posters	Hawkesbury Lobby

Provided Meals

<i>Sunday</i>	
<i>7pm Dinner</i>	<i>Lord Ashley Lounge – Seasalt Restaurant</i>
<i>Monday</i>	
<i>7am- 8:55am Breakfast</i>	<i>Seasalt Restaurant</i>
<i>12:55pm - 1:55pm Lunch</i>	<i>Seasalt Restaurant</i>
<i>Tuesday</i>	
<i>7am – 9am Breakfast</i>	<i>Seasalt Restaurant</i>
<i>12:40 pm – 1:40 pm Lunch</i>	<i>Covered Terrace Ground Floor</i>
<i>7:00 pm Dinner</i>	<i>Pacific Ballroom</i>
<i>Wednesday</i>	
<i>7am- 8:55am Breakfast</i>	<i>Seasalt Restaurant</i>
<i>12:45 pm – 1:45 pm Lunch</i>	<i>Seasalt Restaurant</i>

Programme

Sunday 27th November

5pm-6pm	Registration	Hawkesbury Lobby Crowne Plaza Hotel Terrigal
7pm	Welcome Dinner	Lower Seasalt Restaurant

Monday 28th of November 2005

8:55 am		Welcome
9:05 am	Yoshio Okahata	Detection of Conformation Changes of Liposomes and Proteins on a QCM
9:25 am	Calum Drummond	Effects of Degassing on the Long-Range Attractive Force between Hydrophobic Surfaces in Water
9:45 am	Koji Tsuchiya	Structural Change of DNA/Cationic Amphiphile Complexes
10:05 am	Max Lu	Composite membranes of polymer and inorganic colloidal particles with high proton conductivity and low methanol permeability
10:25 am	Teiji Kato	Study on the PFPE Monolayer Lubrication and Direct Observation of PEPE Lubricant Molecules by Cryo-AFM under Ultra-High Vacuum
10:45 am		Morning Tea
11:00 am	Keynote Taku Iiyama	The Direct Determination of Intermolecular Structure of Molecular Assemblies in a Nanospace Using in situ XRD and Reverse Monte Carlo Method
11:35 am	Greg Warr	Self-Assembly of Polymerizable Cationic Surfactants
11:55 am	Yoshinori Nagai	Geometrical and Topological Approach for Understanding Protein Structures
12:15 pm	Hiroyuki Mayama	Fractal Body Created with a Designed Template Method
12:35 pm	Masahiko Abe	Development of a Novel Preparation of Liposomes Using Supercritical Carbon Dioxide
12:55 pm		Lunch – Seasalt Restaurant
1:55 pm	Kazue Kurihara	Long Range Attraction between Hydrogen-Bonded Molecular Macroclusters Formed on Silica Surfaces
2:15 pm	Geoff Stevens	Effect of Surfactants on the Transfer of Metal Ions Across Liquid-Liquid Interfaces
2:35 pm	Mori Takamasa	Slurry Characterization by Hydrostatic Pressure Measurement -Analysis Based on Mass Flux Ratio-
2:55 pm	Ko Higashitani	Multivalent Cations Adsorption Effect on Friction between Silica Surfaces
3:15 pm		Afternoon Tea
3:30 pm	Keynote Hiroshi Sakuma	Shear Resonance Measurement on Liquids Confined between Non-transparent Substrates
4:05 pm	Cathy McNamee	Optimising the drug delivery system for malignant melanoma cells
4:25 pm	Tossy Nagamura	Ultrafast photoresponses and applications of polymer thin film containing gold nanorods
4:45 pm	Masatoshi Fujii	Surface Forces of Colloidal Polystyrene Particle in Aqueous Solutions of Ionic Amphipathic Molecules
5:05 pm	Close	

Tuesday 29th of November 2005

9:00am

Announcements

Nanoparticles Session

9:05 am	Kaoru Tamada	Application of Self-assembly and Metal Nanoparticles: High density SPR Bio-Sensor
9:25 am	Shigenori Fujikawa	Fabrication of Sub-30-nm Metal Oxide Nanoline Patterns by Size Reduction Lithography Combined with the Surface Sol-Gel Process
9:45 am	Takahiro Ohkubo	Nano-Restricted Hydration Structure of Metal Ions Revealed by EXAFS
10:05 am	Hu Yan	Synthesis and Functions of Poly(N-isopropylacrylamide) Gel Trapping Polymeric Micelles
10:25 am	Naoki Toshima	Spontaneous Formation of Core/Shell Bimetallic Nanoparticles by Mixing Metal Nanoparticles: Spectroscopic and Calorimetric Studies

10:45 am

Morning Tea

11:00 am	Paul Mulvaney	Luminescence from CdSe Quantum Dots
11:20 am	Masa-aki Haga	Fabrication of Layered Nanostructures Composed of Inorganic Exfoliated Nanosheets and Rod-shaped Metal Complexes Toward Photoelectronic Devices
11:40 am	Kizhanipuram Vinodgopal	Sonochemical Synthesis of Metal Nanocolloids for Fuel Cell Catalysts

Completion of Nanoparticles Session

12:00	Hideki Sakai	Control of Viscoelasticity using Photochemical Reaction
12:20 pm	Sumio Ozeki	Hydrogels Deformed by Steady Magnetic Fields

12:40 pm

Lunch- Covered Terrace Ground Floor

2:00 pm

Excursion and Afternoon tea
Australian Reptile Park

6:00pm

Poster Session
Hawkesbury Lobby

7:00pm

Conference Dinner
Pacific Ballroom Crowne Plaza Hotel, Terrigal

Wednesday 30th of November

8:55 am		Announcements
9:00 am	Masa Hara	STM studies of self Assembled Monolayers
9:20 am	Musa Baloch	Parameters for the measurement of oil/water emulsion quality
9:40 am	Laurence Meagher	Bridging Interactions between Silica and Grafted PEO Surfaces
10:00 am	Jim Beattie	The Intrinsic Charge at the Oil/Water Interface
10:20 am		Morning Tea
10:50 am	Keynote Syuji Fujii	Stimulus-responsive emulsifiers based on nanocomposite microgel particles
11:25 am	Keiko Gotoh	Surface modification of poly(ethylene terephthalate) by excimer ultraviolet light
11:45 am	Ray Dagastine	Measurements of Static and Hydrodynamic Interaction Forces between Pluronic Stabilized Oil Droplets
12:05 pm	Derek Chan	Interacting Deformable Drops: Complex Shapes – Simple Forces
12:25 pm	Roger Horn	Measurement of forces affecting the approach of an air bubble to a flat solid surface
12:45 pm		Lunch- Seasalt Restaurant
1:45 pm	Keynote Kenichi Sakai	Self-Assembly of pH-Responsive Diblock Copolymer Micelles at Solid/Aqueous Solution Interfaces
2:20 pm	Kazatumi Sakamoto	Synthesis of Ribbon Shaped Mesoporous Silica using Novel Silica Precursor templated from ribbon phase surfactant self organization.
2:40 pm	Peter Majewski	Silane-based Self-Assembled Monolayers for Water Treatment
3:00 pm	Patrick Hartley	Functional Mesophases for Bioseparations
3:20pm	Satomi Ohnishi	Influence of adsorbed/condensed cyclohexane between mica surfaces on stick-slip frictional behavior
3:40 pm	Hiroshi Naguchi	Clathrate-Formation Mediated Adsorption of Methane on Cu-Complex Crystals
4:05 pm	Tom Healy	Summary
4:15 pm		Afternoon Tea

Session Chairs

<i>Session</i>	<i>Time</i>	<i>Chair</i>
1	Mon 8:55 - 10:45	Russell Crawford
2	Mon 11:00 – 12:55	Shannon Notley
3	Mon 1:55 – 3:15	Paul Fitzgerald
4	Mon 3:30 - 5:05	Erica Wanless
5	Tues 9:00 - 10:45	Tom Healy
6	Tues 11:00 – 12:40	Gayle Morris
7	Wed 9:00 –10:20	Rob Atkin
8	Wed 10:50 - 12:25	Yang Gan
9	Wed 1:45- 4:15	George Franks

Abstracts

Detection of Conformation Changes of Liposomes and Proteins on a QCM

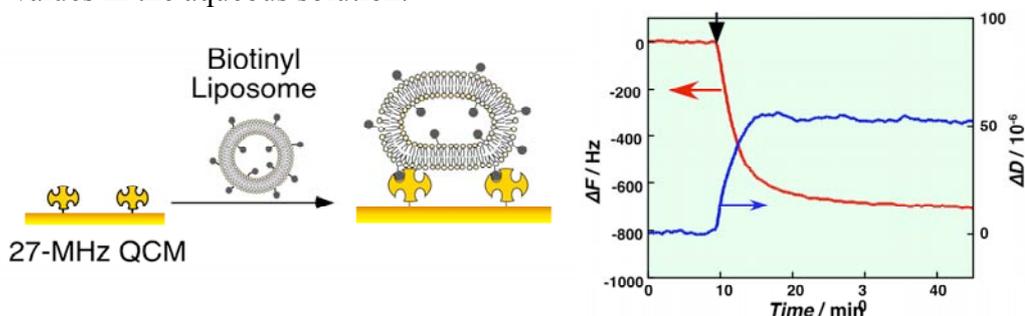
Yoshio Okahata, Yukari Ishizu, Tomomitsu Ozeki, and Hiroyuki Furusawa

Department of Biomolecular Engineering, Tokyo Institute of Technology, 4259 Nagatsuda, Midori-ku, Yokohama, Japan. 226- 8501

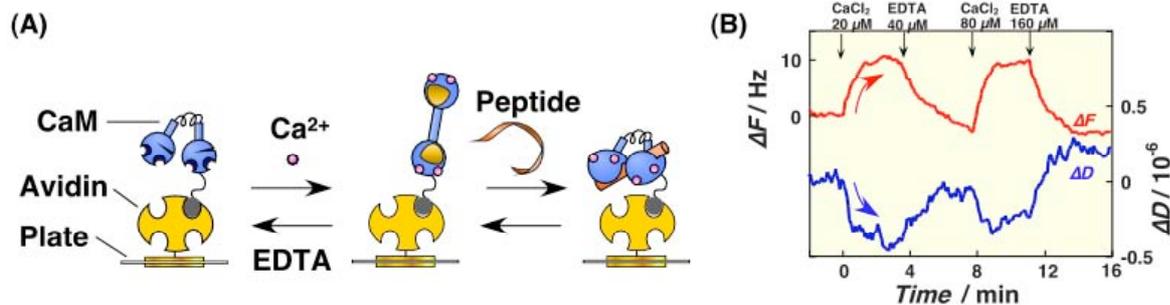
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A quartz-crystal microbalance (QCM) has been known as a simple microbalance when it vibrates with an oscillation circuit. In the case of a 27-MHz QCM, when the mass of 0.62 ng cm^{-2} was attached on the QCM surface, the frequency of 1 Hz was decreased in the air phase. When biomolecules such as DNAs, proteins and polysaccharides were immobilized on the QCM surface, it was difficult to discuss real mass changes on the QCM plate from simple resonance frequency changes (ΔF) in aqueous solution, because of effects of hydration and/or viscoelasticity of these molecules. By using a 27-MHz piezoelectric quartz oscillator connected with a vector network analyser, we have obtained both resonance frequency changes (ΔF) and energy dissipation changes (ΔD) during binding processes in the aqueous solution.

In this paper, we followed the binding process of liposomes by using a 27-MHz QCM with a vector network analyser and the viscoelasticity changes of liposomes such as phase transition from gel to liquid crystal or the shrinkage of the size were followed from both ΔF and ΔD values in the aqueous solution.



We also followed the conformation changes of proteins on the QCM plate. We immobilized Calmodulin (CaM), a calcium binding protein, on the QCM. When calcium ions were injected to the CaM-immobilized QCM, mass changes of calcium ions binding on CaM could not be detected, as they were too small. However, conformation changes of CaM depending on a calcium ion binding could be observed as ΔD values. Moreover, K_d values of CaM for calcium ions binding were obtained from ΔD values depending on calcium concentrations.



Effects of Degassing on the Long-Range Attractive Force between Hydrophobic Surfaces in Water

Hallam Stevens,[#] Robert F. Considine,[%] Calum J. Drummond,[§]
Robert A. Hayes,[†] and Phil Attard[‡]

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The long-ranged attractions between hydrophobic amorphous fluoropolymer surfaces are measured in water with and without dissolved air. An atomic force microscope is used to obtain more than 500 measured jump-in distances, which yields statistically reliable results. It is found that the range of the attraction and its variability is generally significantly decreased in deaerated water compared to normal, aerated water. However the range and strength of the attraction in deaerated water remain significantly greater than the van der Waals attraction for this system. The experimental observations are consistent with (1) nanobubbles being primarily responsible for the long-ranged attraction in normal water, (2) nanobubbles not being present in deaerated water when the surfaces are not in contact, and (3) the attraction in the absence of nanobubbles being most probably due to the approach to the separation-induced spinodal cavitation of the type identified by Bérard et al. [*J. Chem. Phys.* **1993** 98, 7236]. It is argued that the measurements in deaerated water reveal the bare or pristine hydrophobic attraction unobscured by nanobubbles.

Structural Change of DNA/Cationic Amphiphile Complexes

Koji Tsuchiya¹, Hisanori Nakanishi¹, Kazutoshi Sakamoto¹, Teisaku Nakamura¹,
Takahiro Ohkubo², Hideki Sakai^{1,2}, and Masahiko Abe^{1,2}

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Introduction

DNA/cationic amphiphile complexes are a promising vehicle for gene delivery. Meanwhile, DNA is known to form various self-assemblies such as coils, rods, and spheres depending on the polarity of solvent and temperature. However, in many cases of DNA application, the control of DNA structure is required at constant temperature and solvent. We report morphological change in DNA structure for aqueous DNA/cationic amphiphile solutions mainly obtained by cryogenic transmission microscopy (cryo-TEM).

Experimental Section

Cetyltrimethylammonium bromide (CTAB), a typical cationic surfactant, was added to DNA (molecular weight = 70,000, 75.7 bp) dispersions with various molar ratios. DNA/CTAB aggregates for these solutions were directly observed by cryo-TEM. First, a small amount (3-5 μ l) of sample solution was placed on a copper grid covered by a holey carbon film. The sample drop was blotted with a filter paper to form a thin liquid film on the grid (<300nm), and immediately plunged into liquid ethane cooled by liquid nitrogen (-175C). Specimens are kept at about -173C and imaged in a transmission electron microscope (H-7650, Hitachi Science Systems, Ltd.).

Results and Discussion

At CTAB concentrations above its critical micellar concentration (cmc), DNA/CTAB dispersions were separated into two-phases, and precipitate was observed in the solution. Cryo-TEM images revealed that various DNA/CTAB aggregates, such as spherical, doughnut-like (Figure 1), and rod-like structures, were formed in dilute DNA/CTAB solution depending on CTAB concentrations. This morphological change in DNA structure is attributable to the formation of DNA/CTAB complex due to the electrostatic attraction. Because the surface charge density of DNA is decreased with increasing CTAB concentrations, DNA molecules are more densely aggregated with CTAB concentrations. Now we are trying to observe the structure of DNA mixed with different cationic amphiphiles. These results will also be reported in this presentation.

Composite membranes of polymer and inorganic colloidal particles with high proton conductivity and low methanol permeability

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Commercially available proton exchange membranes such as Nafion do not meet the requirements for direct methanol fuel cells, partly due to their high methanol permeability. The aim of this work is to develop a new class of high-proton conductivity membranes, with thermal and mechanical stability similar to Nafion and reduced methanol permeability. Nanocomposite membranes were produced by the in-situ sol-gel synthesis of silicon dioxide particles in preformed Nafion membranes. Microstructural modification of Nafion membranes with silica nanoparticles was shown to reduce methanol crossover from $7.48 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for pure Nafion[®] to $2.86 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for nanocomposite nafion membranes (Methanol 50% (v/v) solution, 75°C). Best results were achieved with a silica composition of 2.6% (w/w). Colloidal silica particles formed in situ inhibit the transport of methanol through Nafion by blocking sites necessary for methanol diffusion through the polymer electrolyte membrane.

As an alternative system to Nafion, which is very expensive, we also used polyvinyl alcohol (PVA) as the polymer matrix, and dispersing phosphosilicate colloidal particles through a sol-gel process enhances the proton conductivity. Cast membranes with thickness of 80-200 μm are extremely flexible and suitable for application in direct methanol fuel cells. The synthesis process based on the colloidal suspension of POSi particle led to the homogenous dispersal of functional phosphosilicate particles in PVA matrix. A high proton conductivity of 0.02 Scm^{-1} at 70 °C and 90% relative humidity (RH) was obtained, and methanol permeability of the membrane is reduced by a factor of 5-10 compared with that of Nafion 117 measured under the same conditions.

Study on the PFPE Monolayer Lubrication and Direct Observation of PEPE Lubricant Molecules by Cryo-AFM under Ultra-High Vacuum

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Hard discs are the most important memory media for not only computer systems but also music recording media like i-Pod or for image storage media, etc.. Memory density of hard disc systems increases rapidly in recent years and with increasing density, the distance between disc surface and reading-writing head decreases rapidly. The distance becomes now less than 10 nm and the thickness of the surface lubricant layer is requested to be less than few nm. This thickness corresponds to almost a monomolecular layer of lubricant molecules. Almost all hard disc systems use a PFPE lubricant, Z-dol, of which molecules have two OH groups at both ends of PFPE chains. Therefore, this PFPE lubricant can form stable insoluble monolayers at the water surface by spreading from a volatile solvent solution, and the surface density of lubricant molecules can be controlled by compression of the monolayer with movable barriers. The monolayer can be transferred to a solid substrate surface by the Langmuir-Blodgett (LB) technique. In this paper, we report studies on the monolayer lubrication and direct observation of PFPE lubricant molecules by using cryo-AFM under ultra-high vacuum.

A monolayer of molecular weight fractionated Z-dol (M.W. 2000) is transferred to a surface of gold-sputtered mica. Non-contact AFM observation was done using JSPM-4500 at very low temperature under ultra-high vacuum. It was made clear that lowering of the sample temperature to below the glass transition temperature of PFPE is essential to observe PFPE lubricant molecules, and the ultra-high vacuum environment is also essential to prevent freezing of water on the sample at the low temperatures. With increasing sample temperature gradually from 90 K, we could observe molecular images of PFPE lubricant molecules up to 132 K. At or above 134 K, however, molecular images disappeared. This means that segmental motions of PFPE chains start above this temperature.

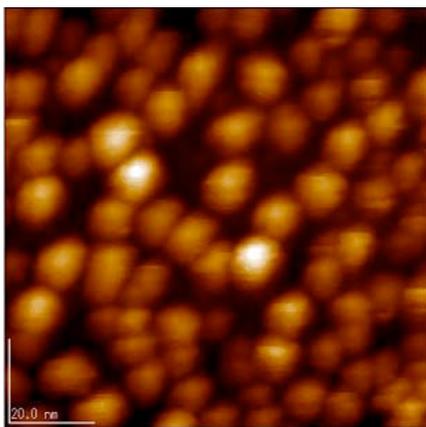


Figure 1, AFM image of Z-dol

Figure 1 shows a non-contact AFM image of Z-dol 2000 lubricant monolayer on the gold-sputtered mica surface. Image size is 100 x 100 nm². Individual PFPE lubricant molecule is observed as a random coil of PFPE chain. It is expected that lubricant molecules should be observed more densely from the π -A isotherm of the lubricant monolayer.

This might be due to the ineffective transfer process of the monolayer by hydrophobicity of the gold-sputtered mica surface. Study on the molecular weight dependency of the molecular images of the lubricant by cryo-AFM under ultra high vacuum is now in progress.

The Direct Determination of Intermolecular Structure of Molecular Assemblies in a Nanospace Using *in situ* XRD and Reverse Monte Carlo Method

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The behaviours of molecules confined in small space have attracted much attention. These molecules show the phenomena such as unique phase transition and ordered structure formation. One of the origins of these phenomena is the fact that the adsorbed phase is constituted by small number of molecules. The pore width of microporous materials such as the activated carbon and zeolite is about 1nm that corresponds to only about 4 layers for water and 1.5 layers for CHCl_3 .

The direct determination method for the intermolecular structure of molecular assemblies in the limited spaces has strongly desired from the view point of catalytic, biological and adsorption science. However, the analysis method for molecules in the micropore is limited in molecular level, because the microporous space is surrounded by the solid. X-ray can penetrate various materials, so we can detect directly the structural information on inner space itself with the X-ray techniques. The information of intermolecular structure among adsorbed molecules can be obtained by *in situ* X-ray diffraction (XRD) measurements. In previous studies, Iiyama et al. showed that water molecules formed a solid like structure in the carbon micropore even at room temperature from radial distribution function analysis of XRD results [1]. Furthermore, the evidence for the formation of organized molecular assembly of water in carbon micropore was shown by using *in situ* small angle X-ray scattering (SAXS) [2,3].

We will report an elaborate method to determine directly intermolecular structure of adsorbed phase using XRD measurements and their reverse Monte-Carlo (RMC) analyse [4]. This method gives a direct image of adsorbed phase in the micropore, even though it is

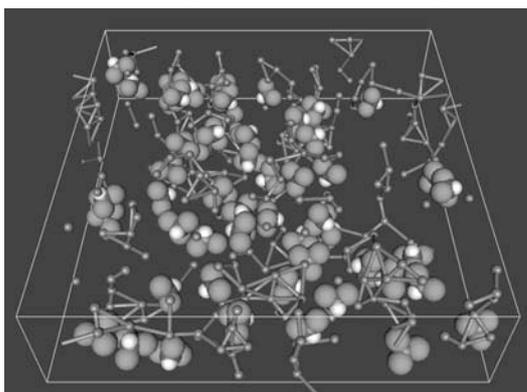


Fig. The snapshot of $\text{H}_2\text{O} / \text{CHCl}_3$ binary adsorption in the 1.63 nm carbon micropore by RMC simulation.

complicated adsorption system containing binary adsorbates. We tried to determine intermolecular structures of H_2O , CHCl_3 , $\text{C}_2\text{H}_5\text{OH}$ and these binary mixtures adsorbed on activated carbon fibers (ACFs) at room temperature. In $\text{H}_2\text{O}/\text{ACF}$ adsorption system, the H_2O cluster formation was confirmed. When CHCl_3 was added to the $\text{H}_2\text{O}/\text{ACF}$ system, both H_2O and CHCl_3 molecules were mixed well in the micropore, associating with destruction of water structure. We will discuss in detail about these systems with snap shots of molecular arrangements of adsorbed molecules in the carbon micropore.

- [1] T. Iiyama, K. Nishikawa, T. Otowa, K. Kaneko, *J. Phys. Chem.*, **99**, 10075-10076 (1995).
- [2] T. Iiyama, M. Ruike, K. Kaneko, *Chem. Phys. Lett.*, **331**, 359-364 (2000).
- [3] T. Iiyama, Y. Kobayashi, K. Kaneko, S. Ozeki, *J. Coll. Surf. A*, **241**, 207-213 (2004).
- [4] T. Iiyama, R. Aragaki, T. Urushibara, S. Ozeki, *Langmuir*, preparing to submit.

Monday 11:35 am

Self-Assembly of Polymerizable Cationic Surfactants

Gregory G. Warr, Kathryn Topp, Robert Chan, and Regina Schwering

School of Chemistry, The University of Sydney, NSW 2006

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Two classes of surfactants cations containing polymerizable groups are investigated; dodecyldimethylammonioethylmethacrylate and vinyl-N-dodecylpyridinium salts. We will describe studies of the bulk and interfacial assembly of these polymerizable surfmers employing a combination of optical and infrared microscopy, small-angle neutron scattering, neutron reflectometry and atomic force microscopy.

Their self-assembly into adsorbed aggregates, bulk micelles and liquid crystals, and their polymerization behaviour, depends critically on the counterion, an effect that seems to have been overlooked in earlier studies. By ion exchange and electrolyte addition we will show how aggregate morphology and phase behaviour changes for acetate, chloride, bromide, salicylate and trifluoromethanesulfonate salts, allowing under some circumstances preservation of morphology post-polymerization. The behaviour of mixtures with conventional (non-polymerizable) surfactants will also be described.

Geometrical and Topological Approach for Understanding Protein Structures

Yoshinori Nagai¹, Hiroshi Wako², and Stephen Hyde³

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We treat proteins as strings that are trained alpha carbons. A string folded forms a 3-D structure where some C_{α} s are close to each other and some C_{α} s are far away within the constraint that C_{α} s are keeping a string. As known well, proteins have the secondary structures such as helix or beta sheet (or beta strands). The secondary structure means that C_{α} s are located closely and regularly with randomly distributed small deviations.

The first our approach to the protein structure was to characterize local patches of a protein (see Fig. 1) by geometrical curvatures, namely, Gaussian and mean curvatures. Examples are shown in Fig.2 for an all alpha-helix protein (PDB code 1thb) and in Fig.3 for an all-beta protein (PDB code 8fab). As seen from figures, helices and beta sheets are recognizable in curvature values, but it is difficult to recognize whether a beta sheet patch is parallel or anti-parallel only using a patch shown in Fig.1. To separate the parallel and anti-parallel beta strand patches, the curvatures for another four sided surface formed by second nearest alpha carbons are required. Thus those become recognizable in 4-dimensional space.

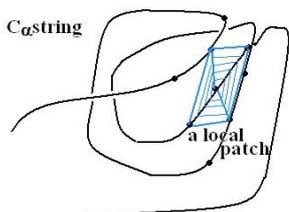


Fig.1 definition of a local patch

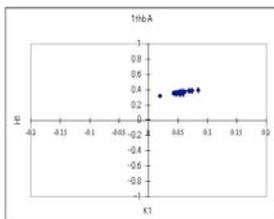


Fig.2 1thb Gaussian and mean curvatures (K,H)

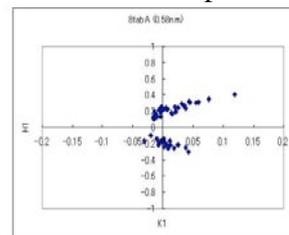


Fig.3 8fab Gaussian and mean curvatures (K,H)

Recently we have been interested in fractal dimensions of protein structure. The correlation integrals are used for the purpose. The correlation integral proposed by Grassberger and Procaccia is the integral of the distribution of two point distances in embedded space. We developed the concept to the topological distance of C_{α} s, where distances between alpha carbons are quantized to unity and count minimum path between C_{α} s that changes by contact of them. The results for proteins 1thb and 8fab are shown in Fig. 4.

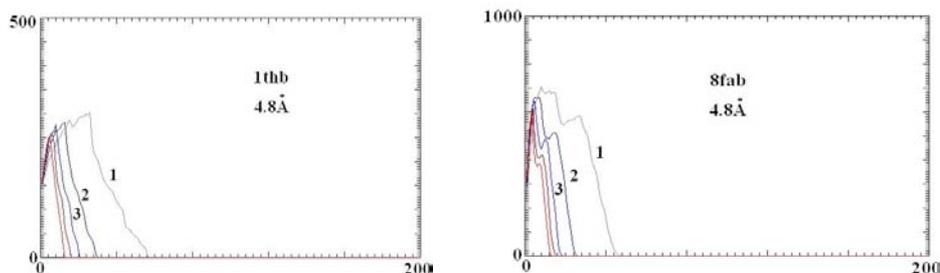


Fig.4 Topological distance distribution between two points for 1thb and 8fab

Fractal Body Created with a Designed Template Method

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Fractal is not only a key concept to understand irregular patterns in nature such as coast lines,¹⁾ but also a promising approach to create new functional materials such as super liquid-repellent surfaces (liquid = water & oil).²⁾⁻⁵⁾ The advantage of its application to material science is to theoretically allow us to make infinite surface area. Super liquid-repellent surfaces are yielded under the above framework. In this study, we tried to create a fractal body, which theoretically has infinite surface area and infinitesimal volume.

We designed experimental strategy as follows: First, we prepare fractal particles using alkylketene dimer (AKD), a material of super water-repellent surface, which forms fractal surface structure spontaneously. Next, we fill the template (the stacked particles in vessel) together with metal alcoxide solution and solidify it by a sol-gel synthesis. After that, we remove the template from the body by calcination. Fig. 1 shows a typical AKD particle after the formation of surface fractal structure, which was utilized as a template of a pore in fractal body. Fig. 2 is a SEM image of a fractal body with cross-sectional fractal dimension $D_{cs} = 1.87 \pm 0.03$. The fractal body is consisted of 15 % silica and 85 % air in vol % (volume fraction $f = 0.15$). Based on discussion of fractal geometry, the obtained D_{cs} and f , it has been found that the physical character of created fractal body has close to that of Menger sponge. We have thus experimentally succeeded in creating a fractal body.

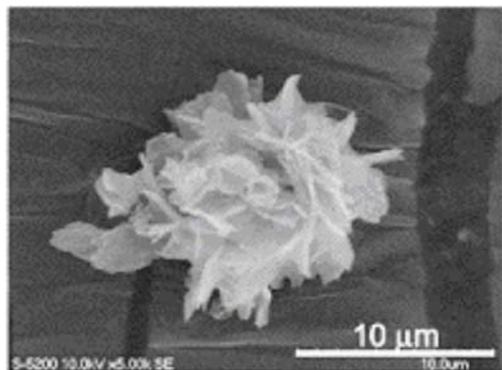
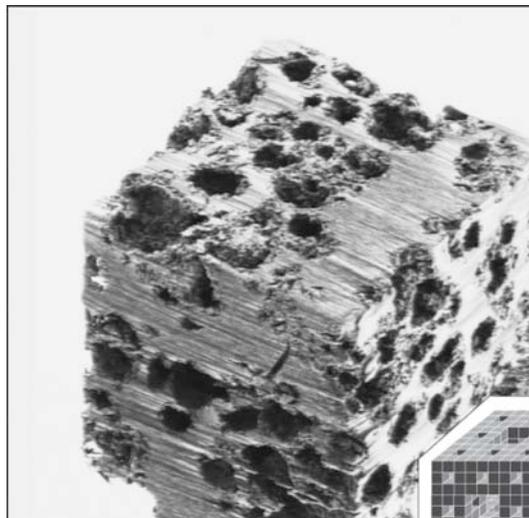


Fig. 1 AKD fractal particle



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Development of a Novel Preparation of Liposomes Using Supercritical Carbon Dioxide

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Many methods have so far been reported for preparation of liposomes such as the Bangham method, organic solvent injection method, reverse phase evaporation method, and so on. However, these methods need a large amount of organic solvents that are harmful to human body and environment. There have been very few methods that allow preparation of liposomes with a high trapping efficiency for water-soluble substances without using any organic solvent. When liposomes are used as drug carrier, use of organic solvent should be avoided as much as possible in their preparation because complete removal of remaining organic solvent is required. Although a method is known by which liposomes are formed through repeated freezing and melting of aqueous solution, this method consumes a large amount of energy as seen intuitively. All of these methods are not suitable to the mass production of liposomes since they consist of many steps.

Supercritical carbon dioxide (scCO₂), in particular, has attracted attention as an environment-friendly alternative solvent that can replace organic solvents since it has low critical temperature (T_c=31°C) and pressure (P_c=73.8bar) and is non-toxic, inflammable, and cheap.

We developed a process which uses scCO₂ as an alternative solvent to form liposomes with high trapping efficiency of water-soluble and oil-soluble compounds, and named the method as supercritical reverse phase evaporation (SCRPE) method. In this study, we report development of the improved SCRPE (ISCRPE) method to obtain the higher trapping efficiency with the simple process steps. Physicochemical properties of liposomes prepared by the Bangham, the SCRPE, and the ISCRPE method were compared with each other. As a result, maximum trapping efficiency of glucose reached to 36 % for 20 mM of L- α -dioleoylphosphatidylcholine (DOPC), while that of Bangham method was less than 5 %. Liposomes formed by the ISCRPE method were highly stable for one month of storage at room temperature. Freeze fractured TEM observation, osmotic shrinkage measurement, and DSC measurements revealed that the liposomes prepared by the ISCRPE method are the unilamellar vesicles with loosely packed phospholipids. Comparison of nitrogen with scCO₂ revealed that the existence of CO₂ is necessary for the formation of liposome.

Long Range Attraction between Hydrogen-Bonded Molecular Macroclusters Formed on Silica Surfaces

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Recently, we have found that alcohols, carboxylic acids and amides adsorbed on the silica surface in non-polar liquids such as cyclohexane and benzene form ordered structures extending to several tens of nanometer through hydrogen bonding between the surface silanol groups and the adsorbed molecules as well as between the adsorbed molecules (surface molecular macrocluster).¹ Surface forces measurement has revealed that the long range attraction appears from distances about twice of the macrocluster layer thickness, indicating that bridging of the adsorption layers brings about the long range attraction due to the interfacial energy between the adsorption layer of molecular macroclusters and the bulk solution. In this study, we derived the equation (1) which describes the long range interaction force caused by the contact of the adsorption layers based on the model shown in Fig. 1. In this model, the attraction term is the sum of the interfacial energy (γ) along the perimeter of the bridging. The short range repulsion can be attributed to the steric repulsion, and is approximated by a single exponential function. The measured interaction forces were analysed by equation (1) and the interfacial energies were estimated.

$$\frac{F_{total}}{R} = -\frac{2\pi\gamma\sqrt{(2t-D)(2R+D)}}{R} + A\exp\left(-\frac{D}{B}\right) \quad (1)$$

Fig. 2 shows the example of the surface forces measured in methanol–cyclohexane binary liquids together with theoretical curves. The interfacial energy between the adsorption layer of methanol macrocluster and the bulk solution (7.7 ± 0.4 mN/m) is much larger than that of methanol/cyclohexane interface in phase separation (0.6 mN/m, at ca. 8–90 mol% methanol). Other alcohols and carboxylic acids which are miscible with cyclohexane also give large interfacial energies through the molecular macrocluster formation (Table 1).

Table 1. The estimated interfacial energy (γ).

	methanol	ethanol	1-propanol	propionic acid	methanol/cyclohexane
Interfacial energy, γ (mN/m)	7.7 ± 0.4 (0.03–0.16 mol%)	2.9 ± 0.7 (0.1–0.6 mol%)	3.2 ± 1.1 (0.1–0.4 mol%)	3.0 ± 0.4 (0.1–5.0 mol%)	0.6 (ca. 8–90 mol%)

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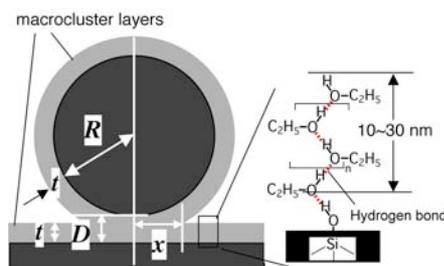


Fig. 1. Schematic illustration of bridging of macrocluster layers (ethanol macrocluster).

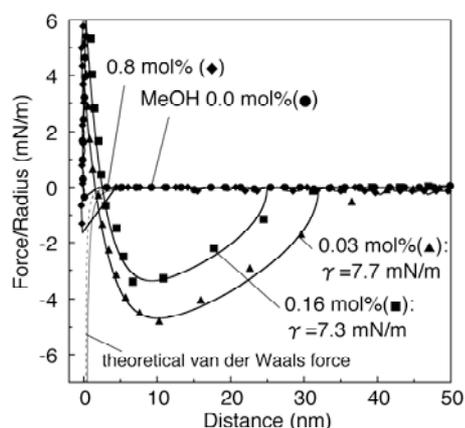


Fig. 2. Surface forces between glass surfaces in methanol–cyclohexane binary liquids and the fitting curves drawn by using equation 1.

Effect of Surfactants on the Transfer of Metal Ions Across Liquid-Liquid InterfacesWarren, D. B., Grieser, F., Perera, J. M. and Stevens, G. W.*Particulate Fluids Processing Centre, The University of Melbourne, Victoria, 3010, Australia*

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The effects of interfacial physicochemical properties on the extraction of nickel(II) by 2-hydroxy-5-nonylactophenone oxime in a two phase oil/water system was characterized using a total internal reflectance static transfer cell (TIRSTC). A two step reaction mechanism between nickel(II) and HNAPO satisfactorily explained the apparent initial reaction rate (R_{int}). The addition of neutral surfactants, non-ionic octa-ethyleneglycol mono-n-dodecyl ether ($C_{12}E_8$) and zwitterionic n-dodecyl-dimethyl-3-ammonio-1-propanesulfonate (DDSA), decreased R_{int} , which could be accounted for with a surface adsorption model. The presence of the anionic surfactant, sodium dodecyl sulphate (SDS), accelerated and then decelerated R_{int} , while the cationic surfactant, dodecyl trimethyl ammonium chloride (DTAC), caused a decrease. The effects of these charged surfactants were accounted for using a surface absorption model and the Boltzmann distribution of charged species.

Slurry Characterization by Hydrostatic Pressure Measurement -Analysis Based on Mass Flux Ratio-

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It is important to accurately evaluate the particle dispersion state of slurries in many industrial fields. In general the properties of slurries have been usually evaluated by a traditional gravitational or centrifugal sedimentation test although the experimental time was long. However a quicker and easier evaluation of the slurry properties is desirable for enabling its application in the industrial field. In our previous reports we proposed the hydrostatic pressure measurement which can evaluate the particle dispersion state in a slurry within a short period. It was also shown that the hydrostatic pressure at the bottom of the well dispersed slurry decreased more slowly compared to that of flocculated slurry. In this report the relationship between the results of the hydrostatic pressure measurement and final packing fraction of the sediment is discussed in detail.

In order to discuss the relation between the results of the hydrostatic pressure measurement and final packing fraction of the sediment, the mass flux ratio, U_b/U_u , was introduced. U_u is the settling mass flux of the particles, which denotes the particle flux settling below the interface between the slurry and supernatant. U_b is the deposition mass flux of particles, which denotes the particle flux deposited at the bottom. Figure 1 shows the time change of the mass flux ratio for alumina slurries prepared by pH adjustment. In this figure, the dashed lines represent the theoretically calculated values of U_b/U_u on the assumption that the hindered settling without the transient zone occurred. For the slurry with a pH of 4.3, U_b/U_u was the least among the prepared slurries and remained roughly constant during the settling. In addition, the experimental value was quite similar to the calculated value; therefore, the particles were well dispersed and settled. On the other hand, at the initial stage of settling for the slurry with a pH of 6.8, U_b/U_u obtained from the experiment was greater than the calculated value. Further, the value increased drastically after several hours. This means that the particles settled by a flocculate at the beginning of the settling and then formed the network structure, because the particles were strongly attracted to each other. In the case of slurries with pH values of 5.1, 5.5, and 6.2, U_b/U_u was close to the calculated value initially, suggesting that the particles were well dispersed at the initial stage of settling. However, at a certain settling time, particles began to flocculate, and this resulted in a rapid increase of U_b/U_u .

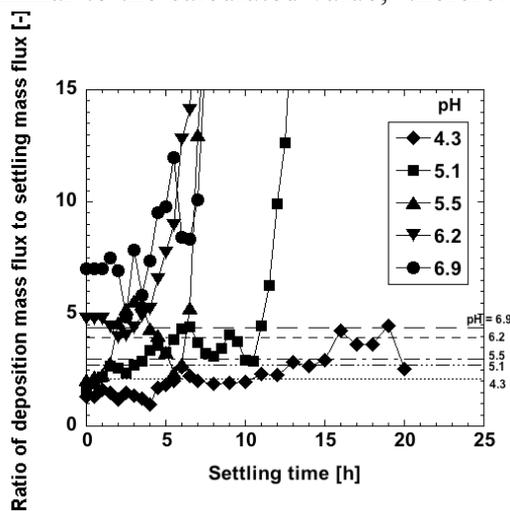


Fig.1 Time change of the mass flux ratio

Multivalent Cations Adsorption Effect on Friction between Silica Surfaces

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Lateral force measurements for interactions between a silica sphere attached to a rectangular cantilever and a flat silica wafer were performed using an atomic force microscope (AFM). The lateral force was measured as a function of applied normal loads and scan rate in solutions of divalent and trivalent electrolytes, chlorides and nitrates, with concentrations varying between 10^{-5} and 10^{-1} M. It is found that the friction coefficient is decreasing with the salt concentration increase for barium (Figure 1) and strontium salts. This effect is reversed for magnesium salts (Figure 2). In the group of alkaline-earth metal salts, friction in calcium chloride has a transitional behavior: friction coefficient is decreasing up to 3×10^{-3} M, and at 3×10^{-1} it is sharply increasing. This type of behavior is not encountered in the case of calcium nitrate, suggesting that the anion co-adsorption plays an important role in determining the tribological performance of the symmetrical silica-silica system. It is found that the friction force increases with the concentration of lanthanum chloride and nitrate increase.

The results indicate that the friction coefficients measured in chloride solutions have higher values compared with nitrate solution. Additionally, we have demonstrated specific dependence of the friction force on the sliding velocity.

These results imply that the tribological properties of silica in electrolyte solutions are the outcome of a combined effect of both, anions and cations, and their hydration properties. The friction trends behavior is discussed and a model is proposed.

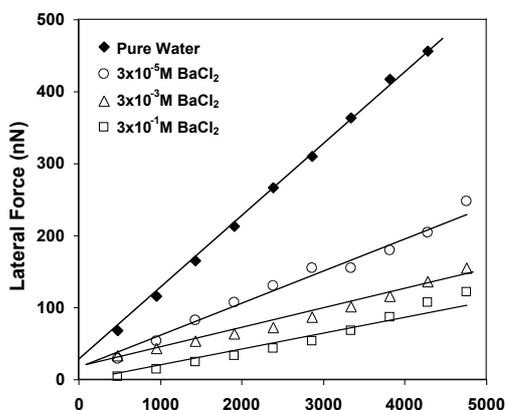


Figure 1. Lateral force dependence with loading force in water and BaCl₂ solutions

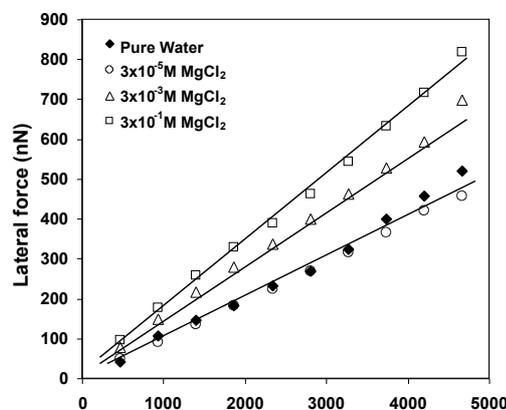


Figure 1. Lateral force dependence with loading force in water and BaCl₂ solutions

Shear Resonance Measurement on Liquids Confined between Non-transparent Substrates

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There are increasing interests in clear understanding of the structuring of confined liquids between solid surfaces. The shear resonance measurements have a high sensitivity for any change in the structure and fluidity of a thin liquid film between solid surfaces because of the large shear response around the resonance frequency¹.

We recently developed the twin path surface forces apparatus (SFA) for measuring the interactions between non-transparent substrates in liquids². In the present work, the shear unit was introduced in the twin path apparatus to investigate the shear response of confined liquids between non-transparent substrates (Fig. 1). The surface separation is controlled by the movement of the lower surface unit. The displacement of the lower disk holder was measured by the two beam (twin path) interferometry³. The upper surface is laterally oscillated with various frequencies by applying the sinusoidal voltage (U_{in}) to the four-sectored piezo tube. The movement of the upper surface is monitored by the capacitance probe, and the output voltage (U_{out}) was plotted as the amplitude ratio of U_{out}/U_{in} as a function of frequency. To obtain the shear resonance curve efficiently, we also developed a method using the Fourier transform of the relaxation process of the oscillation.

The shear resonance curves of the liquid crystal (6CB) confined between mica surfaces at various separations (Fig. 2) showed the similar results measured by the conventional shear resonance apparatus using the FECO interferometry for determining the surface separations.

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Optimising the drug delivery system for malignant melanoma cells

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In the drug delivery system (DDS), drugs designed to attack the malignant cell are embedded in a carrier with functionalities specific to the malignant cell. In this way, an accurate amount of the drug can be delivered at a pre-programmed rate to the desired location, so that only the targeted organ receives the drug and at concentrations required for effective treatment. In this way, the negative side-effects of the drugs affecting other cells can be minimized or eliminated. Several problems must be overcome, in order to realise such a DDS. The optimum conditions for administering the drugs are still not well known, and the question as to which carrier surface functionality groups are specific to a malignant cell needs to be answered. Here, we investigated these subjects with the atomic force microscope (AFM) by using functionalised cantilever colloid probes, which modelled the DDS carrier, and living malignant melanoma B16F10 cells as the substrate.

The force used in administering a drug, the position where the drug is administered on a cell, and the residential time of a drug at a cell have been thought to influence the success of a DDS. However, there appears to be no systematic study addressing these points. In order to address the first issue, we varied the pushing force of the colloid probe to the cell, and noticed its effect on the adhesion force. The result was that the magnitude of the pushing force was not observed to affect the adhesion, as long as the force was small enough not to damage the cell. Next, we investigated the difference in the adhesion force between the cell and colloid probe, when we measured at the cell nucleus and near the edge of the cell. We found no relation between the cell surface position and the adhesion force. Finally, the influence of the adhesion time of the probe at the cell surface was examined, by varying the adhesion time from 10 to 60 min. A large dependence was seen, where the largest adhesion was noted for longer times. Thus, the adhesion time appears to be the most influential condition in the DDS.

Next, the type of carrier was varied, in order to find the functionality with the highest specificity to the malignant cell. As carriers containing hydrophobic, polyethylene glycol (PEG), or positive surface groups appear to show specificity to benign cells, it was thought that a malignant cell may respond in a similar manner. However, as cancer cells differ from normal cells, e.g. they acquire altered differentiated functions, it is unclear as to which DDS functional group a malignant cell is most specific. Thus, we tested the effect of charge, hydrophobicity, and polymer presence on a DDS carrier on its degree of specificity to the melanoma cell. This was possible, as the maximum in the adhesive force upon decompression in the AFM force curves is related to the strength of the specificity of the DDS carrier to the malignant cell. We found that negatively charged surfaces, hydrophobic, and PEG modified surfaces all have similar low adhesive force values. Additionally, there was no observable dependence on the degree of hydrophobicity of the probe surface to a B16F10 cell, if the type of chemical structure was not varied. Only the particle that was modified to give a positive charge was seen to give strong adhesive forces with the B16F10 cell. Thus, DDS carriers with positive charges appear to have the highest specificity to malignant melanoma cells under these conditions.

In conclusion, the DDS particles must be carefully designed using the physicochemical properties we have shown here.

Ultrafast photoresponses and applications of polymer thin film containing gold nanorods

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We have been utilizing interactions of molecules and photons to make ultrafast all-optical signal processing by the guided wave mode (GWM) geometry with metal and polymer thin films (1,2). Ion-pair charge transfer complex polymers (3), extended porphyrin derivatives, and carbon nanotubes have been used as the best candidates showing ultrafast photoresponses in the visible to near infrared (NIR) regions. Very recently we have also proposed a new GWM device with a photoresponsive polymer and a low refractive index polymer (4). Gold nanorods show strong absorption in the visible to NIR regions depending on the aspect ratio with very fast photoresponses. In the present paper we will report photoresponses of gold nanorods (Mitsubishi Materials Co.Ltd.) in polymer composite thin films upon femtosecond (fs) laser excitation together with their photonics applications in the new GWM device.

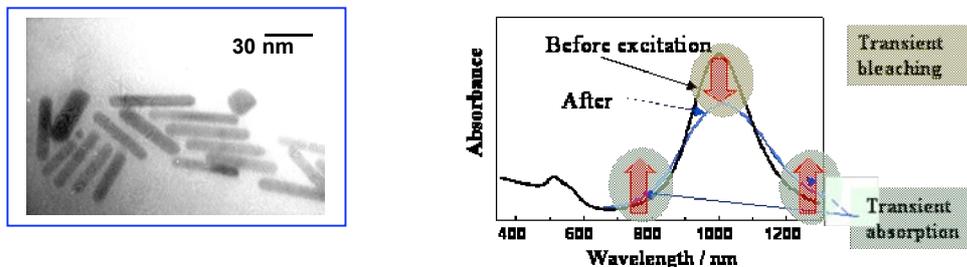


Fig. 1 TEM image of Au nanorods Fig. 2 Absorption spectral changes upon pulsed laser excitation

Electron micrograph of an example of nanorods employed in this study is shown in Fig. 1, which showed two absorption peaks at 512 and 1001 nm corresponding to the transverse and longitudinal plasmon bands, respectively. Upon excitation with a pulsed laser, transient bleaching and absorption were observed as schematically shown in Fig. 2 due to vibrationally excited free electrons; hot electrons. Recovery to the original state occurred due to several pathways with time constants from 1.0 to a few tens picosecond. These nanorods dispersed in polyvinylalcohol were spin-coated on a low refractive index polymer thin film to make the GWM device. In this geometry at specific incident angle larger than the total reflection, very sharp minimum reflectance is observed for a range of extinction coefficients, which strongly depends on the thickness values of the photoresponsive polymer and low refractive index polymer(4). Incident angle dependence of reflectance changed very sensitively according to the real and/or imaginary parts of complex refractive index, which can be utilized to make all-optical ultrafast modulation(4). The mode formation for these composite systems was confirmed by dips in the fs white light reflection spectra depending on the incident angle.

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Surface Forces of Colloidal Polystyrene Particle in Aqueous Solutions of Ionic Amphipathic Molecules

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Colloidal dispersions of polystyrene latex spheres are important in industrial process and have also been widely studied as model colloids. Surface structures and properties of the particles, which determine the physical properties of the latex, have been investigated; In particular, a behaviour of the polymer chain at a surface region in various solutions is focused and has been studied. Surface force measurement using an atomic force microscope (AFM) is one of the methods to obtain the force as a function of the separation between two surfaces. We investigated the surface forces between a polystyrene particle ($R = 5 \mu\text{m}$; negative charged surface) of latex and a flat silica plate in several concentrations of aqueous solution of ionic amphipathic molecule (hexadecyltrimethylammonium bromide; CTAB) by using AFM colloidal probe method [1]. Our purpose of this study is to reveal the surface structure and property of polystyrene particles from the surface force profiles.

The force-separation relationship in 5mM CTAB solution is shown in Fig. 1. Surface force between a silica particle ($R = 3.6 \mu\text{m}$) and a flat silica plate in the same condition is also shown [2]. At large separations, an electrical double-layer repulsive force was detected in both of the systems, which was induced by the charges of the adsorbed CTA^+ . On the other hands, at smaller separations, the surface force profiles were different from each other. For the silica particle, a jump-in phenomenon was observed at ca 6nm separation, an arrow in Fig.1, because of the adsorbed CTA^+ layers on both surfaces squeezed out by the pressure. For the polystyrene particle, instead of the jump-in phenomena, the repulsive force increased monotonously at separations closer than about 10nm. Linear force-separation relationship indicates that there would be a 10nm thick elastic region at the surface of the polystyrene particle. This elastic region may correspond to a hairy layer, which controlled the latex behaviour reported for many latex systems [3].

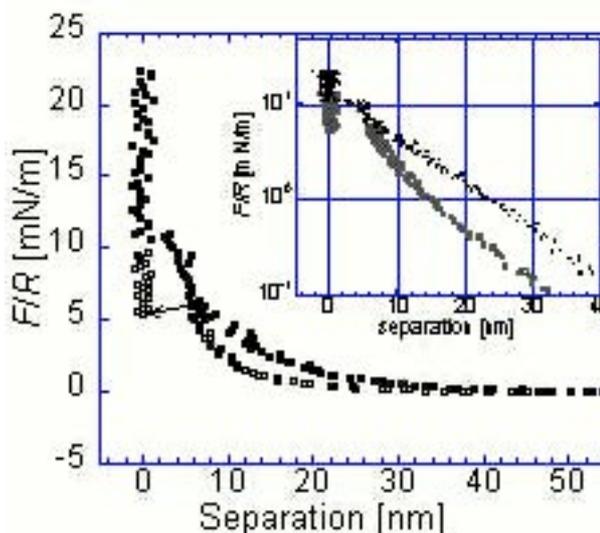


Fig.1 Normalized forces, F/R , between a polystyrene particle and a flat silica plate (—), and between a silica particle and a flat silica plate (---) in 5mM CTAB as a function of surface separation. Inserted figure shows the same on a logarithmic scale.

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Application of Self-assembly and Metal Nanoparticles: High density SPR Bio-Sensor

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In this paper, we report a new methodology to fabricate high density bio-sensor array (max. 10^4 dots/cm²) in combination with self-assembly, micro contact printing (μ -CP) and SPR imaging with metal nanoparticles. A novel COOH-terminated PEG-disulfides with *p*-carborane was synthesized to fabricate the first layer on gold substrates to achieve surface coupling reaction with amino-terminated DNA in high yield. The hybridization of the target-DNA modified gold nanoparticles on probe-DNA patterned surface was successfully demonstrated by the SPR imaging, where nonspecific adsorption was not observed to the array background. The gold nanoparticle arrays give quite high contrast even at low surface coverage ($\sim 10\%$) by the enhancement effect of optical signals based on nano-scale phenomena in the near field. This enhancement effect can be well demonstrated by the simulation based on Maxwell-Garnett (MG) theory and Fresnel's equation. As our new finding, when the density of the adsorbed particles increase until the particles come into contact, clear deviation arises from MG theory with the assumption that the dipole-dipole interaction between the particles is negligible, i.e., a coupling of local plasmon between particles could be determined in our SPR experiments.

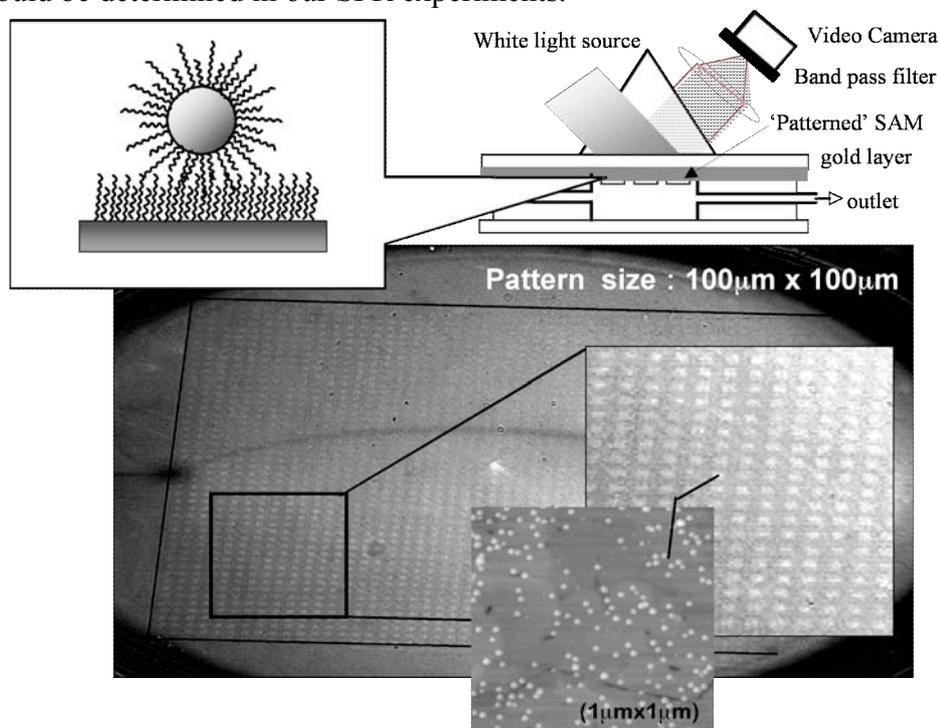


Figure. Detection of DNA hybridization by SPR imaging.

Fabrication of Sub-30-nm Metal Oxide Nanoline Patterns by Size Reduction Lithography Combined with the Surface Sol-Gel Process

Shigenori Fujikawa, Rie Takaki, Toyoki Kunitake

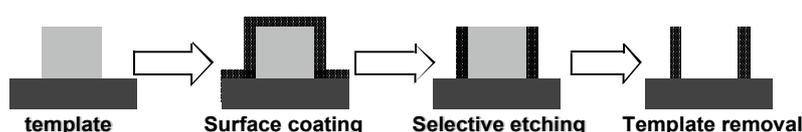
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Fabrication of nano patterns with dimensions of sub-50 nm has been actively studied, especially in semiconductor industry. Although photolithography-based fabrication is most process-friendly approach, it requires very high cost for processing equipments and large space. This approach is now getting close to technical and process limitation, and alternative methods are strongly desired for sub-30-nm fabrication. Recently, size reduction lithography was used to fabricate sub-50-nm wire arrays.¹⁾ This method is based on surface coating of nanoline templates and selective etching of the coating layer (Figure 1). Unfortunately, the surface coating employed chemical vapor deposition process to form silicon-based layers on templates, and, thus, the kind of coating materials are limited.

We herein report fabrication of metal oxide nanolines with sub-30 nm widths by size reduction lithography combined with the surface sol-gel process. Organic nanoline structures fabricated by photo-lithography technique were covered with ultrathin metal oxide layers with thicknesses of a few tens nm by the surface sol-gel process. Titanium alkoxide and silicon tetrakisocyanate were employed as precursor molecules. Scanning electron microscopy (SEM) and scanning transmission electron microscopy (STEM) results show that uniform silica layers were formed on the template surface after the surface sol-gel process. The top-side oxide layer on the template was selectively removed by etching, and then the organic moieties were removed by oxygen plasma process. Only the side walls were left behind on the solid substrate, and its width and heights were about 20 nm and 360 nm, respectively. The high aspect ratio (height/width= about 18) is noteworthy. Titania lines were also fabricated by the same approach.

In the surface sol-gel process, the film thickness is controllable with 1 nm precision by adjusting the number of the adsorption cycle. The width of the current lines corresponds to the film thickness of the metal oxide on the template, since the line was carved out as a part of the film. Therefore, the line width is controllable with 1 nm precision. In addition, the surface sol-gel process provides material variety in surface coating, and composite nanofilms of organic/inorganic and hetero-inorganic combinations can be employed. The current approach creates a remarkably rich methodology to fabricate nano-architectures in the sub 30-nm regime.



Figures 1. Schematic illustration of size reduction lithography

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Nano-Restricted Hydration Structure of Metal Ions Revealed by EXAFS

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New information about the ionic solution can be obtained, if we expose the ionic solution to the anisotropic field. Recently, we revealed the structural anomalies of hydration structure of ionic solution of RbBr and CuCl₂ confined in solid nanospaces (nanosolution; NSN) with EXAFS technique [1-5]. In this presentation, we show structural anomalies of NSNs of Sr, Cs, and Ba ions confined in activated carbon fibers (ACFs) by EXAFS technique. In addition, we studied the hydration structure around a Cu ion which is restricted in the liquid nanospaces formed within the reverse micelle of AOT (Aerosol-OT; dioctyl sulfosuccinate sodium salt) to discuss the nature of pore walls. Here, we call the ionic solution confined in the reverse micelle of AOT as nanodroplet (NDT).

The EXAFS measurements were performed on K-edges of each ion (Cu, Sr, Cs, and Ba) for NSNs and NDTs at the National Laboratory for High Energy Accelerator Research Organization (KEK) in Tsukuba and the SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI). The EXAFS spectra of the corresponding solutions were measured for comparison. The determination of hydration structure was carried out by the curve fitting of reverse Fourier transformed function of the 1st shell in each radial structure function (RSF) with the theoretical parameters calculated by FEFF code.

The coordination number of 1st hydration shell for NSN around a Sr ion was decreased compared with that of bulk aqueous solution. Also, the Debye-Waller factor for NSN of Sr ion was reduced. Then, the distances between a Ba ion and a water molecule obtained by a curve fitting are 0.271 and 0.276 nm in the nanospaces of 0.7 and 1.1 nm, respectively. Here, the literature value for bulk aqueous solution is 0.282 nm. These results indicate that the strong restriction effect can distort the hydration structure of NSN that depends on the average pore widths of ACFs. Therefore, the NSN in hydrophobic nanospaces have an incomplete dehydration structure because of an intensive restriction in the nanospaces.

We also determined the hydration structure of NDT for Cu ion. The results indicated that a mean hydration number and distance between a Cu ion and an oxygen atom of a water molecule for the NDT are 2.4 and 0.197 nm, respectively. Here, the hydration number for NDT is less than that of bulk phase, while the distance between a Cu ion and a water molecule is similar to that of bulk solution. These results strongly indicate that such a hydration structure around Cu ion in reverse micelle is strongly affected by the restriction effect, especially the geometrical restriction from the pore wall of AOT. However, the nano-confinement effect is not so strong compared with that in solid nanospaces that only the reduction of hydration number for NDT can be observed.

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Synthesis and Functions of Poly(*N*-isopropylacrylamide) Gel Trapping Polymeric Micelles

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Poly(*N*-isopropylacrylamide) (PNIPA) gel has attracted considerable attention, from both academic and technological aspects. At the phase transition temperature (ca. 34 °C), PNIPA gel undergoes an abrupt volume change, which can be utilized in several promising applications such as drug delivery systems and actuators.

PNIPA gel containing polymer surfactant poly(2-(methacryloyloxy)decylphosphate) (PMDP) was previously synthesized and was found to show rapid volume phase transition above its transition temperature (Fig. 1).¹ Interestingly, the phase transition temperature of the PNIPA-PMDP gel was equal to that of the PNIPA gel alone. The concentration gradient of PMDP within the PNIPA gel can be obtained by applying an electric field on the gel, similar to the gel electrophoretic technique. The PMDP-gradient PNIPA gel clearly demonstrated the prevention of skin formation and the acceleration of the phase transition rate of the PNIPA gel by PMDP.

Recently we have succeeded in synthesizing cylindrical microgels (0.8 μm in diameter, 5 μm in length) by a novel strategy where template-guiding synthesis and photochemical polymerization are combined.² The obtained microgels can be characterized in individual level by a laser-trapping/Raman spectroscopy.

Here we describe the feature of PNIPA-PMDP gel and the novel synthesis of the microgels. We also discuss potential applications of the PNIPA-PMDP gel as soft actuators³ and drug delivery systems.⁴

Acknowledgment:

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**Spontaneous Formation of Core/Shell Bimetallic Nanoparticles
by Mixing Metal Nanoparticles: Spectroscopic and Calorimetric Studies**

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Nanoparticles of noble metal have attracted much attention of late due to their wide applicability in “nanotechnology” or “nano-biotechnology”. They show some remarkable characteristics in optical, electrical, magnetic, physicochemical, and chemical properties and in some combinations of the above properties. More recently, particular interests are focused in bimetallic nanoparticles, which exhibit unique characteristics that are not just the addition of the two properties of the constituent metals. For example, Pd/Pt bimetallic nanoparticles have much higher catalytic activity than the mixture of the corresponding monometallic nanoparticles.

We showed recently that low-entropy core/shell structured nanoparticles form spontaneously from the physical mixture of a dispersion of polyvinylpyrrolidone(PVP)-protected Ag nanoparticles and that of another noble metal (Rh, Pd, or Pt) at room temperature. This spontaneous formation of bimetallic nanoparticles by mixing two kinds of metal nanoparticles was first found by disappearance of the plasmon absorption of Ag nanoparticles by addition of Rh nanoparticles in solution at room temperature. The core/shell structure of the produced bimetallic nanoparticles was suggested by the observation with energy filtered transmission electron microscopy (EF-TEM). The exact structure is now under investigation by an extend X-ray absorption fine structure (EXAFS) technique.

We also used isothermal titration calorimetry (ITC) and showed that the initial step of such a spontaneous process is strongly exothermic. When the alcohol dispersion of PVP-protected Rh nanoparticles (average diameter, $d_{av} = 2.3$ nm) was titrated into the alcoholic dispersion of PVP-protected Ag nanoparticles, a strong exothermic enthalpy change ΔH was observed; $\Delta H = -908$ kJ/mol for Ag(S) nanoparticle ($d_{av} = 10.8$ nm) and -963 kJ/mol for Ag(L) nanoparticles (average diameter, 22.5 nm). The strength of interaction increases in the order of Rh/Ag>Pd/Ag>Pt/Ag.¹⁾ This strong exothermic interaction is considered as a driving force to form low entropy bimetallic nanoparticles by simple mixing of two kinds of monometallic nanoparticles.

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Luminescence from CdSe Quantum Dots

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In this talk, we discuss the optical properties of small CdSe nanocrystals and the role of ligand adsorption on their optical properties, as well as the effect of core-shell syntheses on the photostability of such materials. We will demonstrate that chemisorption has strong effects on the luminescence quantum yield. Ligand adsorption-desorption kinetics play a key role in explaining the variability in particle brightness.

More recently, it has been found that the luminescence from a single quantum dot is not stable, but rather displays periodic fluctuations in brightness, termed blinking. We will discuss some recent experiments on the blinking behaviour of single nanocrystals. A key result is that blinking appears to be due to trapping into surface states, and this process is again drastically dependent upon the ligands present at the particle surface.

Together the ensemble and single particle results provide a generic platform for making photostable, intensely luminescent nanocrystals through classical colloid synthesis techniques.



Figure 1: CdSe quantum dots show size-tunable emission but the quantum yield depends strongly on the ligands present. This talk will try to explain why this is so.

Fabrication of Layered Nanostructures Composed of Inorganic Exfoliated Nanosheets and Rod-shaped Metal Complexes Toward Photoelectronic Devices

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The fabrication of inorganic multilayered films has attracted much attention due to their optical and electrochemical applications. Inorganic layered materials such as a lepidocrocite-type layered protonic titanate $H_xTi_{2-x/4}\square_{x/4}O_4 \cdot yH_2O$ ($x \sim 0.7$; vacancy sites were indicated by the box) or zirconium phosphonate can be exfoliated into colloidal single nanosheets. Recently, we have succeeded the preparation of densely packed exfoliated nanosheet films such as $Ti_{0.91}O_2$, $Ti_{0.8}M_{0.2}O_2$ ($M = Co, Ni$), $Ti_{0.6}Fe_{0.4}O_2$ and $Ca_2Nb_3O_{10}$ on solid substrates by the LB transfer method without any amphiphilic additives at the air-water interface.¹⁾ Nanosheet crystallites covered nearly 95 % on the solid surface with minimum overlapping of nanosheets. Since the $Ti_{0.91}O_2$ nanosheet holds the negative surface electric charge, alternating layer-by-layer fabrication method was generally applied to prepare multilayer films by use of electrostatic interaction between anionic nanosheets and cationic polyelectrolytes. Here, we present the novel fabrication method and the photoelectrochemical function of layered nanostructures based on the $Ti_{0.91}O_2$ nanosheets and simple organic phosphonate or Ru complexes with phosphonate groups by use of metal coordination.

We have synthesized a series of rod-shaped Ru complexes with phosphonate anchoring groups.^{2,3)} The phosphonate $-P(O)(OH)_2$ group is ionized to mono- or dianion in aqueous solution, therefore in general the phosphonate group is hardly immobilized on the negatively charged $Ti_{0.91}O_2$ nanosheets. In order to connect the Ru complex on the nanosheet surface, the simple metal cation such as Zn^{2+} acts as a junction between the negatively charged nanosheets and phosphonate groups in the Ru complex. The formation of alternating multilayer structure was confirmed by uv-vis spectra, AFM, and XPS measurements. The electrochemistry of Ru(II/III) couples in the films shows the strong dependence on the number of layers.

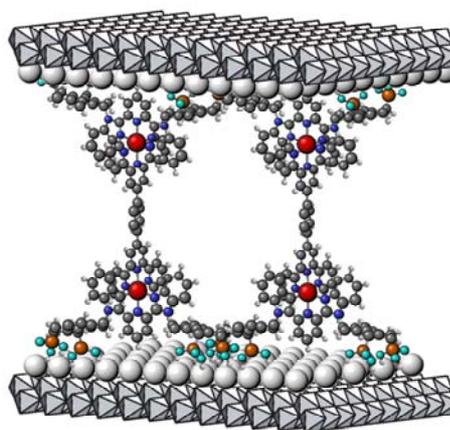


Fig. 1. Layered structure based on TiO_x nanosheets and Ru dinuclear complex with phosphonate groups on surface.

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Sonochemical Synthesis of Metal Nanocolloids for Fuel Cell Catalysts

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The primary processes that dictate the operation of the fuel cell are the oxidation of the fuel, hydrogen or methanol at the anode and the reduction of oxygen at the cathode. Both reactions require a precious metal catalyst usually platinum. In the case of methanol oxidation, the catalyst of choice is usually an alloy of platinum and ruthenium. Size control of the metal catalyst is expected to produce higher surface areas and thereby enhance oxidation. Synthesis of metal nanoparticles using a variety of methods has been widely reported in the literature^{1,2}. A number of groups, have shown that ultrasound irradiation of aqueous solutions containing noble metal salts produce the corresponding colloids of the noble metal.³

We will present data on the sonochemical reduction of Pt⁴⁺ and Ru³⁺ in the presence of a suitable stabilizer such as Nafion. Figure 1 shows the absorption spectrum of a 10⁻³ M solution of hexachloroplatinic acid in an (80:2) alcohol-water solution as a function of sonication time. The absorption bands arising from the Pt (IV) disappears with increasing sonication time. We obtain a featureless absorbance extending into the visible and is characteristic of colloidal platinum. The solution is centrifuged (1000 rpm) at this point to isolate the small Pt particles that still remain in the suspension. The Pt suspension of 2 nm diameter particles is a pale yellow solution and was used for electrophoretic deposition. This solution is stable up to a week, after this the solution gets progressively turbid as the colloidal particles begin to agglomerate and settle down. The high resolution TEM image of the sonochemically prepared colloidal solution reveals well dispersed ultra-small particles (~2 nm in diameter) of platinum.

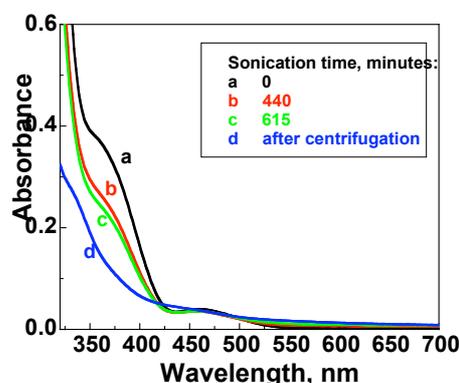


Figure 1: The absorption spectrum of a 10⁻³ M solution of hexachloroplatinic acid as a function of sonication time. Trace a-d corresponds to the sonication time in minutes.

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Control of Viscoelasticity using Photochemical Reaction

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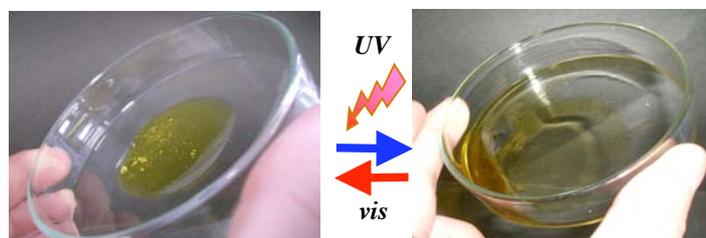
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Reversible control of interfacial properties and the formation and disruption of aggregates such as micelles and vesicles of surfactants in solution by external stimuli has attracted considerable attention. Recently, we reported the control of the viscoelasticity of worm-like micellar solution containing a redox-active ferrocenyl surfactant (FTMA) and sodium salicylate (NaSal) through the redox reaction of FTMA¹. This study deals with a “photo-responsive” viscosity system, based in part on our past report on the viscosity control using a ferrocenyl surfactant.

We used an azobenzene-modified cationic surfactant (4-butylazobenzene-4’-(oxyethyl)trimethylammonium bromide, AZTMA), which exhibits reversible *trans* – *cis* photoisomerization, as a “photo-switchable” agent. A small amount of *trans*-AZTMA (10mM) was added to worm-like micellar solution of 50mM cetyltrimethylammonium bromide (CTAB) containing 50mM NaSal to give a viscoelastic solution.

Figure 1 shows the photographs of an aqueous CTAB/NaSal/AZTMA mixture before and after UV-light irradiation, respectively. The viscosity of the mixture irradiated with UV-light was obviously lower than that of the non-irradiated one. We estimated their solution viscosity in terms of the zero shear viscosity (η_0). Addition of AZTMA (*trans*-form) to aqueous CTAB/NaSal solution increased its η_0 value from 60 Pa · s to 100 Pa · s. When UV-light was irradiated on the CTAB/NaSal/AZTMA(*trans*-form) solution, the η_0 value is decreased 4 orders of magnitude (0.1 Pa · s) over that of the *trans*-AZTMA solution. The following visible-light irradiation made the viscosity return to the value of the *trans*-AZTMA solution. This η_0 change was completely reversible between the *trans*- and *cis*-AZTMA solutions.

The drastic viscosity change reported here is likely to be attributed to a change in the aggregation state of surfactant molecules. *Trans*-AZTMA is easily incorporated into worm-like micelles. On the other hand, the bulky structure of *cis*-AZTMA is likely to destroy the network structure of worm-like micelles, and smaller aggregates (probably short-rods) are formed in the solution. AZTMA incorporated in worm-like micelles, even though it is minor component, permits a drastic change in solution viscosity through the *trans* – *cis* photoisomerization.



CTAB / *trans* -AZTMA/NaSal

CTAB/ *cis*-AZTMA/NaSal

Figure 1 Photoinduced viscosity change observed at CTAB / AZTAB / NaSal system.

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Hydrogels Deformed by Steady Magnetic Fields

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Hydrogels have been investigated from the viewpoint of not only scientific interests but also technological aspects such as drug delivery and actuator. Thus, it is very important to investigate the methodology for control of structures and physical properties of gels. A magnetic field is one of the attractive energies for orientation of hydrocarbon chains. Although the magnetic energy of a non-magnetic molecule in magnetic fields is much less than thermal energy, macromolecules having magnetic anisotropy and high molecular weight would orient under high magnetic fields. Therefore, magnetic fields may give one of useful methods for the structural control of gels. Magnetic anisotropy of a monomer is not enough to respond to magnetic fields, but polymer chains produced in the polymerization process may orient cooperatively. When the oriented polymer chains are cross-linked, a structured gel must be obtained. Gel properties depend on polymer chain distribution, cross-link density, and hydration. If we control these factors by magnetic fields, a novel gel would be produced.

Applying steady magnetic fields ($\leq 10\text{T}$) to gel preparation solution of e.g., *N*-isopropylacrylamide (NIPA), the structural anisotropy and induced volume phase transition of prepared gels appeared. Magnetic fields promoted dangling chain formation to decrease cross-link density and thus to make the gel softer¹⁾. This effect may arise from magnetic orientation of polymer chains and/or magnetic influence on radical polymerization process. Also, heat of the volume phase transition increased under magnetic fields, indicating that gel hydration should be affected by magnetic field.

The volume of a NIPA gel was increased by applying magnetic fields. This may be associated with increase in the heat of volume phase transition under magnetic fields. The volume change of NIPA gels due to magnetic fields was very fast, different from the thermal volume change. Moreover, the magnetic field-induced volume change via the phase transition was found in a certain condition.

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STM Studies of Self-Assembled Monolayers

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Growth processes and adsorption states of self-assembled monolayers (SAMs) were studied by scanning tunneling microscopy (STM), surface plasmon spectroscopy (SPS), thermal desorption spectroscopy (TDS), x-ray photoelectron spectroscopy (XPS), high-resolution electron energy loss spectroscopy (HREELS), and near edge soft X-ray absorption fine structure (NEXAFS) spectroscopy¹⁾. We confirmed for the very first time a completely new equilibrium state for alkanethiol SAMs. While the conventional final equilibrium state was interpreted as the homogeneous adsorption sites on three-fold hollow on Au(111), the existence of this new equilibrium state shows that there are three adsorption sites: hollow, bridge and on-top sites on Au(111), suggesting that the previously accepted phase exists under nonequilibrium conditions. As a result of this study, temporal development of interfacial reaction and dimerization problems were discussed in more detail²⁾.

Furthermore structural order and disorder processes during SAM formation were investigated, in dialkyl disulfide, dialkyl sulfide, and aromatic thiol systems. For example, molecularly resolved STM images clearly revealed that cyclohexanethiol (CHT) SAMs have an oblique unit cell consisting of three adsorbed molecules, which can be described as the $(5 \times 2\sqrt{10})R48^\circ$ superstructure (Fig.). The superstructure observed for CHT SAMs on Au(111) is comparable to that observed for the conventional alkanethiol or aromatic thiol SAMs. The formation of such a unique superstructure is attributed to the adsorption geometry with the stable chair conformations, i.e., the equatorial and axial chair conformations, for the flexible aliphatic ring in the CHT molecules. In this study, we revealed that the structural rigidity of the molecular backbone is an important parameter for determining the molecular packing structure of SAMs³⁾.

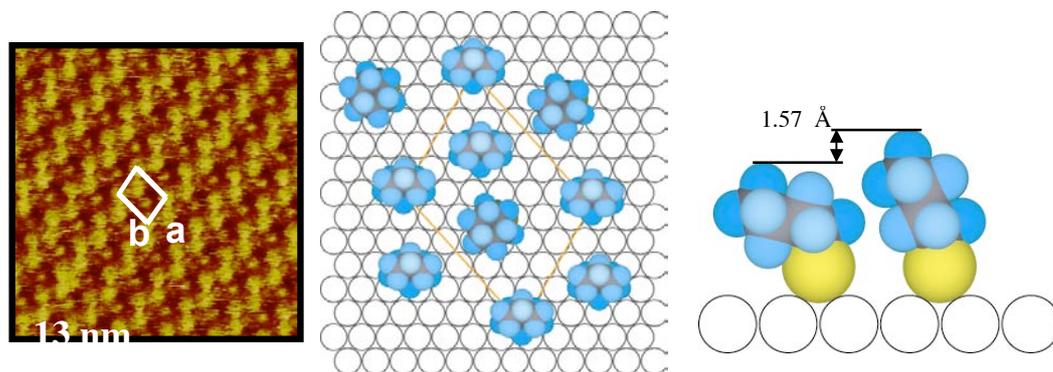


Fig. STM image and the model of the $(5 \times 2\sqrt{10})R48^\circ$ superstructure of CHT SAM on Au(111). Height contrast in STM was equal to the height difference (1.57 Å) between equatorial and axial chair conformations in isomers.

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Effect Of Different Parameters on the Quality of Oil/Water Emulsions

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To understand the process of emulsification and the effect of different parameters, four well-defined short chain (n-hexane, n-heptane, n-decane and kerosene) oils have been emulsified in water. The emulsification was carried out with and without the presence of sodium dodecyl sulphate (SDS) using ultrasonication. The resulting emulsion was characterized by surface tension, microscopic observation, turbidity, viscosity and conductance, measurements. The quality of the emulsion has been defined and discussed in terms of the size and number of droplets. It has been noted that the surface tension of an emulsion first decreases and then increases with an increase in oil content. The surface tension of SDS/oil/water system and the apparent CMC of SDS in an emulsion increases with the increase in oil content and is highest in the case of kerosene oil. This has been explained in terms of variation in the distribution coefficient of SDS between organic and aqueous phases. The number of droplets increases with the oil content and remains a maximum when SDS concentration is approximately equal to the CMC irrespective of oil contents and chain length. However, the droplet size shows an opposite trend to that of droplet number. Moreover, the distribution of droplets is narrow around the CMC. All the techniques employed confirm the above stated trend. Further, the turbidity and viscosity show a nice dependence over concentration of SDS. The variation in droplet number and the size of droplets is explained in terms of micellization of SDS, dissolution of oil in SDS micelles and variation in surface tension and viscosity in addition to electrostatic forces. To correlate the experimental data, number of droplets obtained irrespective of oil, oil contents and SDS concentration has been plotted as a function of surface tension and viscosity of the system. The data show a fairly good linear fit in each case, showing a strong dependence over these parameters. However, the number-viscosity seemed to be the best one. All these observations including CMC variation are in accord with the proposed mechanism of emulsification and prove that the quality of emulsion is governed by the equations proposed in this communication or earlier communications.

Bridging Interactions between Silica and Grafted PEO Surfaces

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The covalent coupling of polymer molecules onto surfaces in order to modify their surface properties has been quite widely utilized in recent years. In particular, grafting or adsorption of poly(ethylene oxide) onto biomaterial surfaces has been investigated as a means of reducing protein adsorption in blood contacting or ophthalmic applications such as contact lenses.

In this study, we have used a combination of X-ray Photoelectron Spectroscopy (XPS) and Atomic Force Microscopic (AFM) interaction force measurements to characterize surfaces with covalently grafted PEO layers of different grafting density and molecular weight. The surfaces were prepared using cloud point grafting¹ of aldehyde or active NHS ester terminated PEO molecules onto amine containing radio frequency glow discharge (r.f.g.d.) thin films deposited onto silicon wafers. Whilst one expects that densely grafted polymer layers should generate a steric repulsive force when compressed, the situation is not quite so clear cut when the grafting density is lower.

In cases where the grafting densities are such that the PEO molecules are not fully packed onto the surface, long range attractive polymer bridging forces were obtained between PEO coated surfaces and AFM tips modified with silica particles² in 0.15 M NaCl solutions. In this case, electrostatic forces were highly screened and therefore the forces of interest arose from the presence of the grafted polymer layers. The range and magnitude of the forces were correlated with the grafting density of the PEO molecules, lower densities giving longer ranged, more attractive forces, however, the range of the attractive forces were always within the fully stretched length of the grafted PEO molecules. The range of the attractive forces correlated also with the molecular weight of the covalently attached PEO molecules. The origin of the attractive forces appeared to relate to the adsorption of PEO molecules onto the silica surface on approach, with more molecules adsorbing at small separation distances.

When the chemistry of the opposing surface was changed from silica to, for example, another grafted PEO layer or a protein molecule (HSA), or if the end group of the PEO molecule was replaced with a protein molecule (NeutrAvidin), the attractive forces were removed and the measured interactions became purely repulsive. The form of the purely repulsive forces obtained in these instances was very similar to that obtained between silica and PEO surfaces with high grafting densities, suggesting that the measured forces were of steric origin, i.e. relating to compression of the attached layers.

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The Intrinsic Charge at the Oil/Water Interface

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When a hydrophobic surface is created in water the interface develops a negative charge arising from the enhanced autodissociation of water and the concentration of hydroxide ion at the surface. The magnitude of this charge can be measured by creating a large surface area, as in an emulsion, and measuring the quantity of hydroxide ion formed. This was done as a pH-stat experiment, measuring the amount of base required to maintain a constant pH of 7 (or 9) as an oil-in-water emulsion is formed by high-pressure homogenization. Simultaneously the droplet size was measured in the concentrated (2 or 5 vol%) emulsion by the electroacoustic technique, which allowed the surface area of the interface to be calculated. The surface charge was found to be 5-7 $\mu\text{C cm}^{-2}$, approximately independent of the identity of insoluble oils such as hexadecane, perfluoromethyldecalin or squalene.¹ The zeta potential of \sim -100 mV implies that most of the surface charge is compensated by sodium counterions inside the shear plane.

That hydroxide ion is the charge-determining ion was demonstrated in several ways with hexadecane emulsions. The pH dependence of the zeta potential as the emulsion was titrated towards its isoelectric point of pH 4 was independent of the identity of the anion of the 0.4 mM salt present among sodium perchlorate, sodium iodide and sodium chloride.¹ The reduction of the zeta potential through double-layer compression as salt is added to the dispersion from 0.1 to 10 mM at pH 9 is independent of the identity of the sodium salts of fluoride, chloride, bromide, iodide, perchlorate or iodate or of the chloride salts of lithium, sodium or caesium. The surface charge is also independent of the base used to form these surfactant-free emulsions among LiOH, NaOH or CsOH. These observations imply that dispersion forces are not significant in affecting the surface charge at low salt concentrations.²

The reason for the preferential 'adsorption' of hydroxide ion is obscure. One hypothesis is that there is dipole-dipole attraction between the water molecules oriented at the surface and the dipolar hydroxide ion. To test this idea, the salt dependence of the zeta potential was measured on addition of the dipolar anions thiocyanate, acetate or iodate. There was no difference from that caused by the non-dipolar anions.³ Hence dipole-dipole attraction is not a general explanation; the cause must relate to specific properties of the hydroxide ion.

These effects appear to be general for hydrophobic surfaces in water. Streaming potential measurements on polymer surfaces without functional groups show a similar pH dependence of the zeta potential with an isoelectric point of pH 4, as does the air/water interface.^{4,5} Such observations imply that the effects reflect the properties of water at hydrophobic interfaces.

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Stimulus-responsive emulsifiers based on nanocomposite microgel particles

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Colloidal particles have been used to prepare and stabilize emulsions (so-called ‘Pickering’ emulsions) for over a century.[1] Most of this literature is concerned with various types of *inorganic* particles such as silica, barium sulfate or calcium carbonate, although recently there have been several interesting examples of *organic* particles being used as emulsifiers. [2]

Herein we describe the synthesis of lightly cross-linked poly(4-vinylpyridine)-silica nanocomposite particles by copolymerizing 4-vinylpyridine with ethylene glycol dimethacrylate in the presence of an ultrafine aqueous silica sol and their evaluation as pH-responsive particulate emulsifiers for three different oils. Depending on the polarity of the oil phase, either oil-in-water or water-in-oil emulsions could be prepared using these nanocomposites as particulate emulsifiers at around pH 8-9. Rapid demulsification occurred below pH 3, since the addition of acid led to the protonation of the 4-vinylpyridine residues, which in turn imparted hydrophilic microgel-type character to the nanocomposite particles, hence promoting their desorption.

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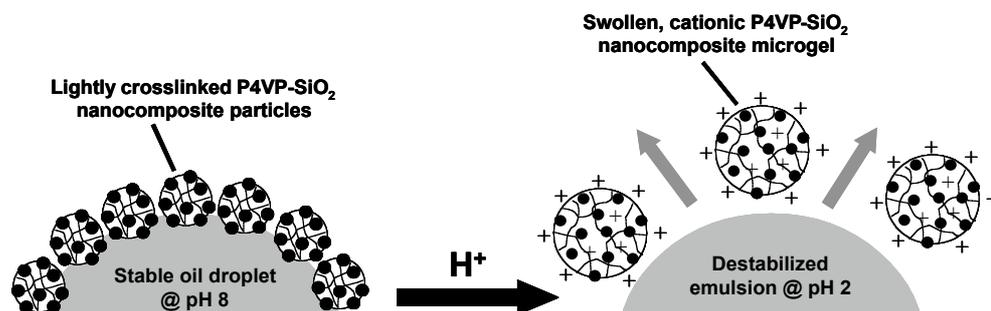


Figure 1. Schematic representation of pH-induced demulsification poly(4-vinylpyridine)-silica nanocomposites as particulate emulsifiers. Dewetting from the oil droplet surface occurs at low pH.

Surface modification of poly(ethylene terephthalate) by excimer ultraviolet light

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The 172 nm ultraviolet (UV) excimer light was exposed to poly (ethylene terephthalate) (PET) in ambient air. For experimental convenience, film, plate and fabric were used as PET samples. From surface analyses by X-ray photoelectron spectroscopy and atomic force microscopy, oxygen concentration and roughness at the PET film surface were found to increase after the UV exposure. As a measure of the wettability, the water contact angle was determined by the sessile drop and the Wilhelmy techniques. Considerable increase in wettability was accomplished by the UV exposure within a few tens of seconds. After the UV exposure, a decrease in the wettability, the hydrophobic recovery [1], was observed over a time period of several days. Even after the recovery, the wettability was sufficiently higher compared to that before the UV exposure. Capillary wetting and hygroscopicity of the PET fabric were evaluated from the change in electrical conductivity and resistance due to wetting and hygroscopic water, respectively [2]. It was found that the UV exposure increased capillary wetting and hygroscopicity of the PET fabric. Particle adhesion to the PET surface was investigated from the viewpoints of detergency.

The deposition of polyethylene particles onto the PET plate was examined, in situ, in water, water/ethanol mixture, ethanol and n-heptane. A considerable decrease in the deposition due to the UV exposure was confirmed in all liquids. The removal of polyethylene particles from the PET plate in aqueous surfactant solutions was found to be promoted after the UV exposure (Fig. 1). Conclusively, the exposure of UV excimer light to the PET surface can much improve its practical performance.

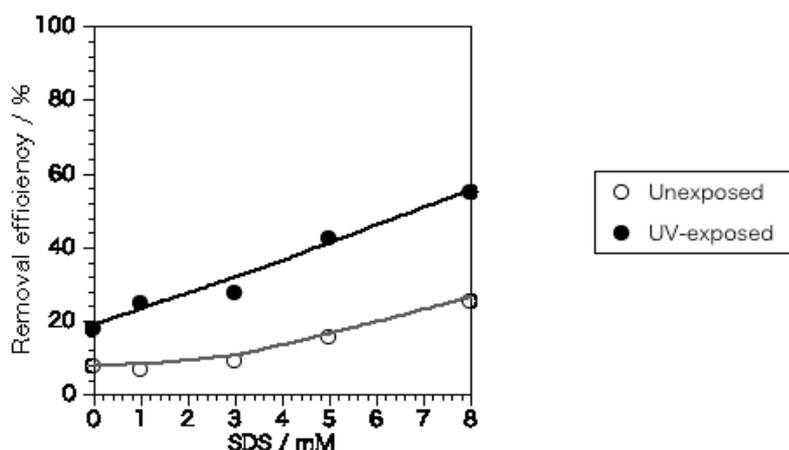


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Measurements of Static and Hydrodynamic Interaction Forces between Pluronic Stabilized Oil Droplets

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Pluronics, (PEO-PPO-PEO) tri-block co-polymers, are commonly used in a wide range of applications ranging from emulsion stabilization to drug delivery due to their low toxicity and cost. Understanding the behaviour of adsorbed Pluronics layers at the oil-water interface and their effect on interactions on the nanometer scale is crucial in controlling emulsion stability. However, measurements of interfacial forces at deformable interfaces are uncommon due to experimental challenges. In this work, we have employed a recently developed method using atomic force microscopy (AFM)^{1, 2} to study the static and hydrodynamic interactions between oil droplets in aqueous solution stabilized by a series of Pluronic co-polymers. Both electrostatic double layer and steric forces were observed in combination with pronounced hydrodynamic drainage forces. The effect of stabilizer length on both surface forces and hydrodynamic drainage will be discussed.

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Interacting Deformable Drops: Complex Shapes – Simple Forces

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The interaction between micron-size deformable drops are complicated by the fact that the geometry of the interacting bodies are not known a priori because the drops also deform as a result of the interaction. This change in drop geometry, especially in the vicinity of the interaction zone will in turn affect the force of interaction. For interacting drops in relative motion, colloidal surface forces and hydrodynamic forces together with the deformation characteristics of the drops all contribute to determine the force of interaction and the deformational behaviour of the drop surfaces.

Investigations of the interaction between deformable drops using the Atomic Force Microscope (AFM) between deformable decane drops ($\sim 50\mu\text{m}$) in aqueous electrolyte stabilized by SDS have observed and quantified separation- and velocity-dependent forces [1-3]. Accurate and detailed information about position- and time-dependence of deforming drop surfaces during interaction has been recorded using a modified Surface Force Apparatus (SFA). These measurement revealed complex and at times unexpected time dependent behaviour of the drop surfaces [4-5]. The AFM and SFA studies provided complementary information about the force of interaction and the deformational behaviour during interaction.

A theory that incorporates colloidal forces, hydrodynamic interactions and surface deformations has been developed [3] that can provide very good quantitative accounts of data obtained from the above AFM and SFA experiments. The theory also gives insight into aspects of the behaviour of interacting deformable drops that are otherwise not accessible experimentally [6]. A pleasing outcome of this study is that while the surface deformations are complex, a simple expression for the force vs displacement function can be obtained. This offers the possibility of being able to encapsulate the complexity of interacting deformable drops in relatively simple forms for future studies.

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Measurement of forces affecting the approach of an air bubble to a flat solid surface

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The physical interactions between air bubbles and solids are important in numerous situations such as separation processes (mineral flotation, plastic and paper recycling), froth and foam stability, and the nucleation and detachment of bubbles from surfaces. Considering the bubble as a colloidal object in an aqueous medium, two classes of force contribute to the interaction: equilibrium surface forces and hydrodynamic forces. Surface forces are expected to include double-layer forces and van der Waals forces, and possibly others such as hydration and steric forces. Hydrodynamic forces are generally discussed in the context of thin film drainage during the final stages of approach of an air bubble to another surface, which could be solid, liquid, another bubble, or a bulk gaseous phase.

We report measurements made using a modified surface force apparatus (SFA) in which a flat mica surface is pressed down on an air bubble that is attached to a fixed hydrophobic capillary tube and immersed in aqueous electrolyte solution. Optical interference measurements using the FECO technique in reflected light allow the thickness of the aqueous film that separates it from the mica to be measured with an accuracy of ~ 1 nm. The measurement also gives the precise shape of the bubble near its apex, or, equivalently, the profile of the aqueous film thickness as a function of radial distance from the vertical axis of cylindrical symmetry.

Measurements of the progressive deformation of the air bubble as it is approached by the mica have been analysed using a model based on the Young-Laplace equation augmented by the inclusion of an additional term to account for disjoining pressure, i.e., a term originating in surface forces acting between mica and the air/water interface. This term includes electrical double-layer and van der Waals forces. Measurements were made in a number of simple electrolyte solutions, and strenuous efforts were made to eliminate surfactants from the system.

The results show that the air-aqueous interface (viewed from the water side) has a small negative potential, with little or no variation between the different electrolytes investigated. The double-layer interaction is consistent with the air potential remaining constant independent of film thickness, which means that the charge of this surface can be reversed, becoming positive as it is pressed closer to the strongly negative mica surface. This creates a region of attractive double-layer force that pulls the bubble in until only a very thin wetting film, stabilized by van der Waals forces, remains on the mica. The approach to this configuration is very slow due to hydrodynamic resistance, and an unusual configuration of the draining film is observed. The attractive component of double-layer force also causes an "adhesion" between the air bubble and mica, so that a finite force is required to pull them apart.

Self-Assembly of pH-Responsive Diblock Copolymer Micelles at Solid/Aqueous Solution Interfaces

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A diblock copolymer poly(2-(dimethylamino)ethyl methacrylate)-*block*-poly(2-(diethyl amino)ethyl methacrylate) (PDMA-PDEA) can form pH-responsive micelles reversibly in aqueous solution: PDMA-PDEA exists as unimers under an acid condition, while in alkaline solution it can form core-shell micelles with the hydrophobic PDEA chains located in the cores and the hydrophilic PDMA chains forming the micelle coronas.¹ Interestingly, this solution behaviour is parallel to its adsorbed layer structure at the mica/aqueous solution and silica/aqueous solution interfaces.²⁻⁴ That is, (i) the adsorbed micelles at high pH are observed to “open” at low pH due to protonation of the hydrophobic PDEA chains; and (ii) the original core-shell adsorbed micelles appear to be reformed on returning to high pH. Although these observations provide possibilities for using the copolymer as nanomaterial building blocks, very little quantitative data has been obtained until now. In this research, we have studied adsorption for PDMA-PDEA at the silica/aqueous solution interface as a function of solution pH, block ratio, concentration and elapsed time, respectively. In addition, the effect of repeated exposure to acidic/alkaline water on the adsorbed mass and viscoelastic nature of the adsorbed micelles has been investigated. These adsorption characteristics were measured using a commercial quartz crystal microbalance with dissipation monitoring (QCM-D) and optical reflectometry (OR).

The applications of such adsorbed layers have also been investigated. Firstly, this new type of smart surface coating may provide an opportunity to encapsulate a wide range of hydrophobic molecules into the PDEA cores and then to release these molecules in response to an external stimulus. Based on this possibility, we have been studying the required conditions to develop the controlled capture and release applications. Secondly, such a core-shell micelle may act as a nanoreactor for preparing nano-ordered materials. In particular, it is accepted that the development of organic/inorganic hybrid materials using a self-assembled molecular layer is an exciting prospect. Thus, in our current work, we have been preparing metal nanoparticles encapsulated by a zwitterionic diblock copolymer poly(2-diethylamino) ethyl methacrylate-*block*-poly(methacrylic acid) (PDEA-PMAA) in order to organize the particles at solid/aqueous solution interfaces.

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Synthesis of Ribbon Shaped Mesoporous Silica using Novel Silica Precursor templated from ribbon phase surfactant self organization

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Tailored templating of liquid crystal (LC) structure of non-ionic surfactant with TEOS, $\text{Si}(\text{OCH}_2\text{CH}_3)_4$, is difficult as it is immiscible to water and requires acidic condition to be hydrolysed and initiate condensation. We have utilized novel glycol silicate, $\text{Si}(\text{OCH}_2\text{CH}_2\text{OH})_4$ (THEGS) (1) which is readily soluble and keep LC structure. We have successfully made mesoporous silica from several nonionic surfactants of which LC structure is well preserved.

Fig.2 shows the ribbon phase structure of mesoporous silica templated from ChEO_{10} ribbon phase (Fig.1) (2) at molecular assembly dimension. Resulted mesoporous silica exhibited ribbon type shape even at μm (Fig.3) and nm (Fig.4) level. This is a first example of ribbon shaped mesoporous silica built up from layered ribbon assembly, which would have practical advantage because of such sheet like structure.

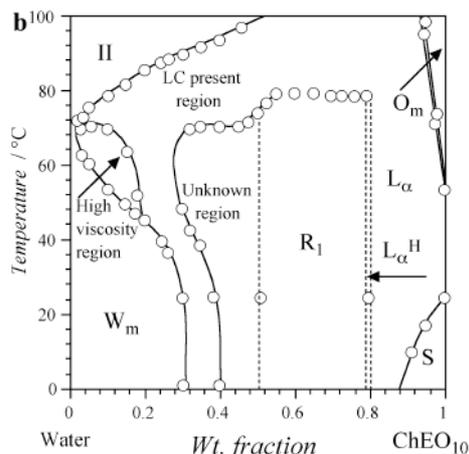


Fig.1 Phase diagram of ChEO_{10} /Water system (2)

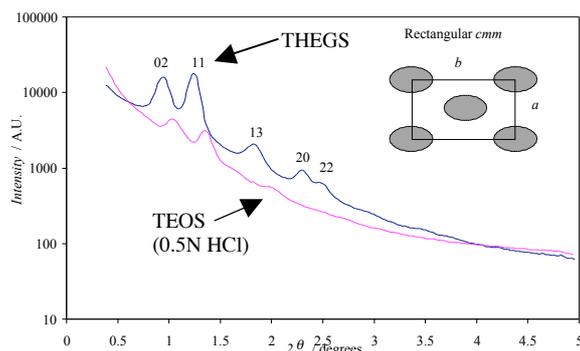


Fig.2 SAXS Pattern of mesoporous silica
Initial composition of synthesis mixture (wt%)
 ChEO_{10} 5%, Silicate monomer 5%, Water 90%

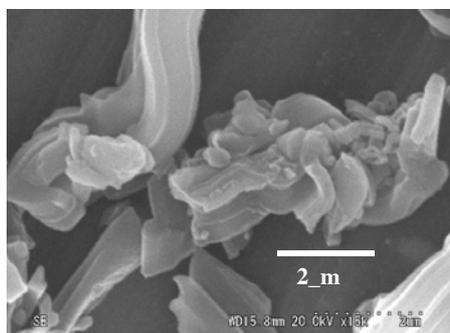


Fig.3 SEM image for THEGS mesoporous silica

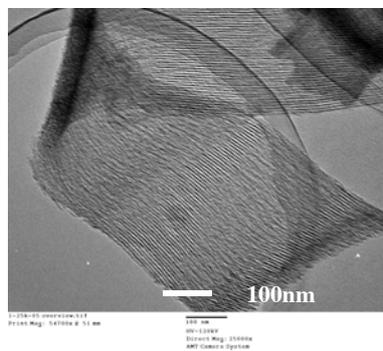


Fig.4 TEM image for THEGS mesoporous silica

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Silane-based Self-Assembled Monolayers for Water Treatment

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Water is one of the most abundant substances in the world. However, the conversion of water from various sources to potable and good quality drinking water can be a very demanding task for drinking water suppliers. Shrinking fresh water resources, increasing salinity of bore water, especially in arid areas of the world, and increasing demand in potable, drinking, and irrigation water requires the utilisation of even low quality water for fresh water supply.

The presented research project focuses the use of functionalised self-assembled monolayers (SAM) for water treatment. A SAM is a close packed, highly ordered array of chained hydrocarbon molecules containing three to seventeen CH_2 -units. Especially, long chained molecules (seventeen CH_2 -units, f. e. octadecyltrichlorosilane) are forming a highly ordered array of surfactant molecules due to stabilizing van der Waals forces between the molecules, whereas short chained molecules (three CH_2 -units, f. e. aminopropyltrimethoxysilane, are less perfectly arrayed. Hence, the length of the hydrocarbon molecules and the related thickness of the SAM varies between about 0.6 nm (three CH_2 -units) and about 2.5 nm (seventeen CH_2 -units). X denotes the 'surface group', chosen from among a number of possible species, such as hydroxyl ($-\text{OH}$), amine ($-\text{NH}_2$), and methyl ($-\text{CH}_3$), respectively. Immersed into aqueous solutions, some of the head groups like hydroxyl head groups tend to deprotonate and to form negatively charged surfaces. Head groups like NH_2 are able to deprotonate at high pH-values and to capture protons at low pH-values forming positively charged surfaces. Therefore, by carefully choosing of the SAM and pH-value of the solution, in which the SAM is immersed, negatively as well as positively charged surfaces can be obtained.

For the development of water treatment devices based on SAMs for the precipitation and deposition of metal oxide particles it is necessary to investigate and to quantify fundamental parameters, such as the type of functionalised end group of the SAM, temperature during precipitation, pH value, and cation concentration of the aqueous solution, because these parameters are eminent for the controlled precipitation and deposition of metal oxides.

Various SAMs have been applied for water treatment to study the efficiency of the method for removal of metal cations of several elements and also natural and artificial organic matter and results will be presented.

Functional Mesophase materials for the specific uptake and separation of biomolecules

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Lyotropic surfactant & lipid mesophase systems are attractive materials for solution based nanotechnology, since they possess nano-scale order which forms spontaneously via the self assembly process.

A limited number of examples of dilutable mesophase materials exist. Such materials exhibit nanostructure which does not reorganise or dissipate when exposed to an excess of aqueous solution. Instead, a stable 2-phase system comprising mesophase plus solution is formed.

The internal mobility and nano-scale porosity of mesophase materials offers a unique 'nano-environment' for the separation, solubilization and organization of solute species, in a manner which is distinct from conventional oil/water phases. Mesophase materials can therefore be used to encapsulate and stabilize solutes in a broad range of solution conditions. Further, high densities of specific ligand systems can be engineered within these structures, either synthetically, or through the integration of existing biological components. This offers the potential for selective uptake within the mesophase matrix. The ability to simply prepare stable colloidal dispersions based on these materials broadens their applicability from a processing perspective, and presents new opportunities for in vitro/in vivo uptake and delivery. Such mesophase particles have the advantage of considerable physico-chemical robustness when compared to emulsion / liposome systems.

This presentation explores recent progress in the synthesis, characterization and formulation of a range of novel, dilutable, surfactant / lipid mesophase systems. The chemical-structural requirements for dilutable mesophase behaviour will be discussed, with reference to existing synthetic and natural systems.

The application of these materials in the construction of nanoscale 3D matrices for the incorporation of biological receptor systems will be highlighted, and the use of such systems for the selective separation / remediation of bioactive molecules will be exemplified.

Influence of adsorbed/condensed cyclohexane between mica surfaces on stick-slip frictional behavior

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The stick-slip frictional behavior observed between mica surfaces under cyclohexane vapor with various relative vapor pressures was investigated with the Surface Force Apparatus (SFA).

The dynamic shear stress decreased with increasing the relative vapor pressure. When the relative vapor pressure reached 25%, stick-slip appeared but faded out with sliding time. At the relative vapor pressure greater than 50%, the stable stick-slip pattern was observed without fading. The dependence on relative vapor pressure of shear stress, pull-off force, and the stick-slip frictional behavior suggests that the stick-slip observed in cyclohexane vapor, especially at the low relative vapor pressure, is caused by non-equilibrium condition of cyclohexane adsorption inside and condensation outside of the contact area during sliding.

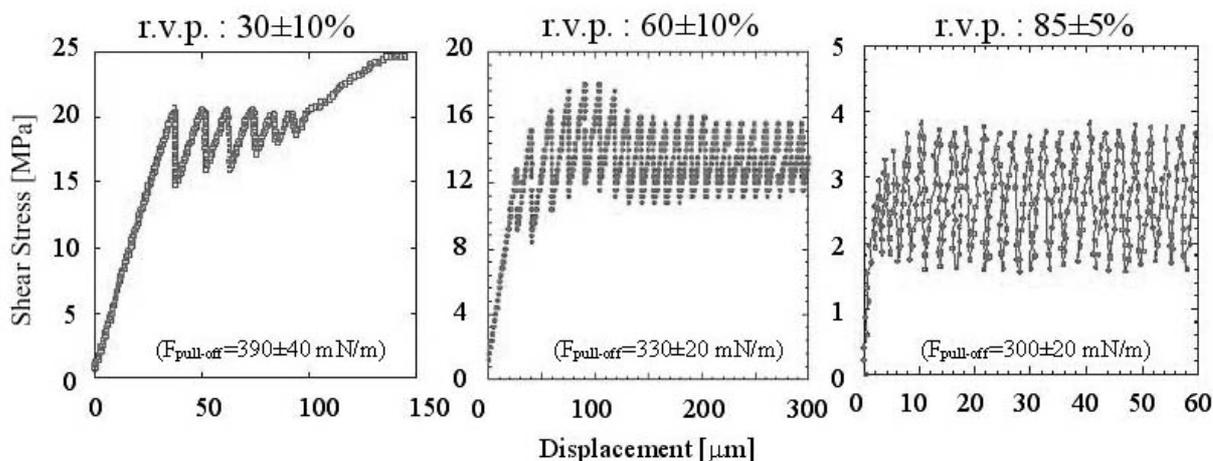


Figure Frictional behavior observed between mica surfaces in cyclohexane vapor

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Clathrate-Formation Mediated Adsorption of Methane on Cu-Complex Crystals

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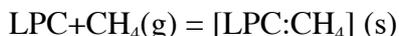
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Adsorption has been widely applied in separation and storage of gas, purification of liquids, pollution control, and catalysis. As nanopores have deep interaction potential wells, nanoporous systems occupy an essential role in adsorption.

A microporous metal organic framework (MOF) solid which is one of the nanoporous materials has a great merit for designing and construction of the porous framework appropriate for specific adsorption of the target molecules. Many researchers have studied adsorption properties of MOF solids^{1, 2}. Li and Kaneko found a vertical adsorption step (gate adsorption) of CO₂ on [Cu(4,4'-bipyridine)₂(BF₄)₂] (= LPC) with no apparent open porosity³. If we can apply this gate adsorption to gas storage or separation, a more efficient storage or separation is possible. As methane is quite important as a clean fuel, we studied gate adsorption of methane on LPC at different temperature.

The LPC crystals were pretreated at 373K and 1mPa for 2h. The high-pressure adsorption isotherms of methane were measured with gravimetric method at different temperature (258~303K).

Figure 1 shows methane adsorption isotherms. All adsorption isotherms exhibit the gate adsorption. The lower the measuring temperature the lower the gate pressure and the greater the adsorption amount. This is because the methane-LPC interaction becomes stronger with the lowering temperature. If we assume this gate adsorption stems from a clathrate formation reaction, the following chemical equilibrium should hold.



Here, [LPC:CH₄](s) is a new clathrate compound of LPC and CH₄. The Clapeyron-Clausius equation can be applied to the temperature dependence of the gate pressure, giving the enthalpy change of the clathrate formation. The logarithm of the gate pressure and the reciprocal of the measurement temperature had a linear relationship. The formation enthalpy of the clathrate from adsorption is $13.0 \pm 1.2 \text{ kJmol}^{-1}$ and the corresponding dissociation enthalpy of the clathrate is $12.5 \pm 1.2 \text{ kJmol}^{-1}$ ⁴. Consequently, LPC can adsorb methane with clathrate formation.

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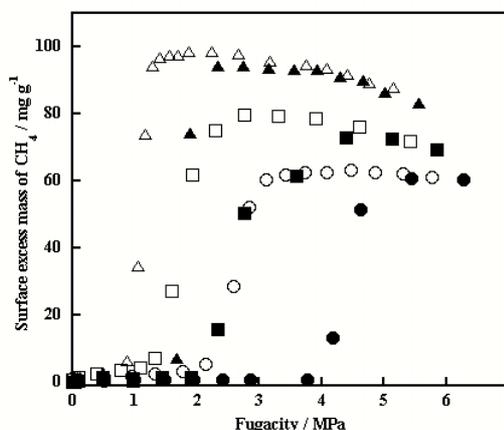


Figure 1. High-pressure adsorption isotherms of CH₄ on LPC:

(▲) 258K, (■) 273K, (●) 303K.
Solid symbol: Adsorption, Open symbol: Desorption

Posters

6 pm

Poster Session

- | | | |
|----|------------------|--|
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| 2 | Nobuo Maeda | Polymer adhesion and friction: Importance of the outermost molecular groups |
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Posters Continued

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|----|---------------------|---|
| 15 | Catherine
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and in Emulsions |
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Yaminsky | Hydrophobic Forces |
| 17 | Erica
Wanless | An in situ Investigation of the Swelling of Adsorbed Poly(2-
vinylpyridine) Microgel Latexes on Mica |
| 18 | Vincent
Craig | Measurement of Film Stress using a Cantilver bending
technique |

*7 pm**Conference Dinner*

Nanoparticle Suspension Rheology

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The study examines the effects of structural factors (particle size and volume fraction of solids) and surface chemistry conditions (pH, monovalent electrolyte cations and electrolyte concentration) on the rheological behaviour of Al₂O₃ nanoparticle suspensions. Additionally, the electrokinetic ζ -potential data of Al₂O₃ nanoparticle suspensions are determined as a function of pH using the electroacoustic technique to correlate with the shear yield stress (measured via the vane tool method) and steady-shear viscosity/stress experimental results. Three different types of Al₂O₃ powders with average particle sizes of 11 nm, 44 nm and 190 nm are used in this investigation. The findings indicate that the rheological properties such as shear yield stress, shear modulus and shear viscosity of attractive particle networks increase inversely with the square of particle size. This result is consistent with previous research on submicron alumina suspensions (200 to 800 nm)¹ but extends the relationship to the order of 10 nm for the first time. An explanation of the underlying physical parameters controlling the inverse square particle size dependence of the suspension rheological properties is presented. The rheological behavior was found to be a powerlaw function of the suspension volume fraction with the powerlaw exponent varying between 4.5 and 5.5 depending on the particular rheological parameter investigated.

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Polymer adhesion and friction: Importance of the outermost molecular groups

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Polymers are often used as adhesive and lubricant coatings to produce both high and low adhesion or friction. Characterization of the tribological and adhesive properties of polymers has therefore been of great interest for many years. Our recent work suggests that both adhesion and friction of such polymeric films are very sensitive to the physical state of the outermost molecular groups, with interpenetration of the polymer chains (or chain segments) across the contacting interface being a major factor. Thus, crosslinked polymer surfaces exhibit smooth and low friction and adhesion, whereas finely bond-broken polymer surfaces exhibit large friction and adhesion. We present our recent development of this work, namely the characterization of the effect of crosslinking and scission, complementary experiments using polymers of different molecular weight, and the effect of temperature in the vicinity of glass transition temperatures of the polymers.

Surfactant Aggregation in Ionic Liquids: Surface Self-Assembly and Microemulsion Formation

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Over the last decade or so there has been a dramatic increase in the use of room temperature ionic liquids (ILs), or molten salts, as solvents for chemical synthesis. However, the physical properties ILs have received comparatively little attention, particularly with regard to surfactant aggregation. In the first part of this study, we demonstrate by AFM imaging that nonionic alkyl oligoethyleneoxide (C_iE_j) surfactants self-assemble into hemicylindrical aggregates at the interface between graphite and the room temperature ionic liquid ethylammonium nitrate (EAN),¹ c.f Figure 1. Like aqueous systems, surfactant first adsorbs in a tail-to-tail monolayer arrangement along one of the three symmetry axes of graphite, templating subsequent self-assembly into adsorbed hemicylinders. Longer surfactant tails and higher concentrations are required to produce hemicylindrical aggregates in the ionic liquid than in aqueous solutions. Secondly, we show that microemulsions form in EAN-Oil- C_iE_j systems. The physical characteristics of these unusual microemulsions will be described as a function of composition and temperature.

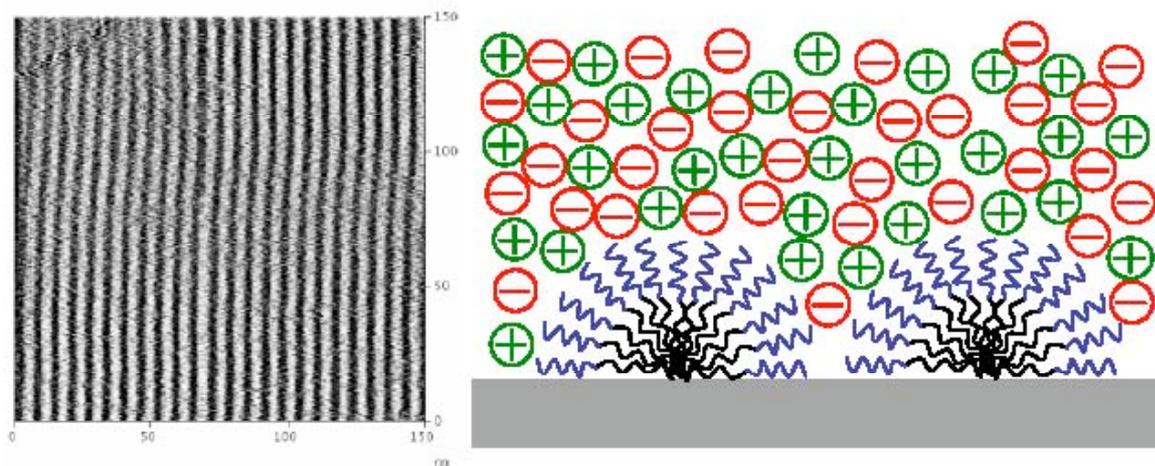


Figure 1. (left) Deflection image of 30 wt% $C_{16}E_6$ adsorbed at the graphite-EAN interface.¹ (right) Schematic representation on the adsorbed layer.

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Syntheses of shell cross-linked micelles using new ABC triblock copolymers and their application as pH-responsive particulate emulsifiers

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Colloidal particles have been used to prepare and stabilize emulsions (so-called 'Pickering' emulsions) for over a century.[1] Most of this literature is concerned with various types of *inorganic* particles such as silica, barium sulfate or calcium carbonate, although recently there have been several interesting examples of *organic* particles being used as emulsifiers. [2]

Herein we describe the synthesis of novel shell crosslinked micelles from the micellar self-assembly of new ABC triblock copolymers and their evaluation as pH-responsive particulate emulsifiers for a model oil, (1-undecanol), as shown in Figure 1. A1-undecanol-in-water emulsion (mean droplet diameter = 18 μ m) was obtained at pH 8-9 after homogenization and this emulsion could be readily demulsified by adjusting pH to 2-3, as shown in Figure 2. Our control experiments clearly demonstrate that shell crosslinking enhances the performance of these new organic nanoparticles, since the non-crosslinked ABC triblock copolymer micelles are much less effective pH-responsive emulsifiers (only partial demulsification occurs on acidification). It is noteworthy that these shell crosslinked micelles produce relatively fine *oil-in-water* emulsions compared to the larger *water-in-oil* emulsions produced by latex-based emulsifiers in conjunction with 1-undecanol.

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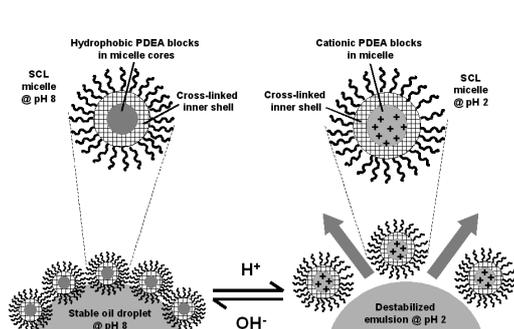


Figure 1. Schematic representation of pH-induced emulsification and demulsification using shell cross-linked micelles as particulate emulsifiers. Dewetting from the oil droplet surface occurs at low pH.

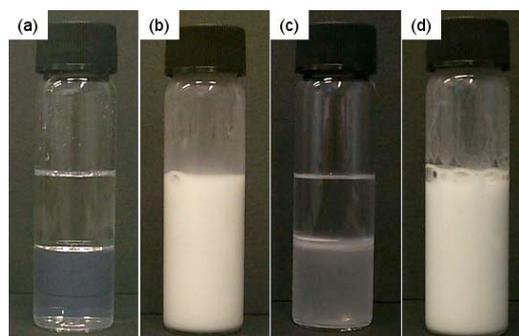


Figure 2. Digital photographs illustrating the reversible emulsification and demulsification of a 50:50 mixture of 1-undecanol and water using PEO-PSAGMA-PDEA-based shell cross-linked micelles: (a) before homogenization, (b) after homogenization at pH 9, (c) rapid macroscopic demulsification caused by the addition of one drop of 1 M aqueous HCl solution to the emulsion shown in (b), (d) after rehomogenization at pH 9.

**Synthesis and characterization of polypyrrole-coated sulfur-rich latex particles:
new synthetic mimics for sulfur-based micrometeorites**

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Over the last two decades there have been numerous reports of the deposition of air-stable organic conducting polymers such as polypyrrole (PPy), polyaniline or poly(3,4-ethylenedioxythiophene) onto colloidal substrates [1]. Conducting polymer-coated film-forming latexes have been evaluated as anti-static and/or anti-corrosion coatings [2]. Another application for these core-shell microparticles was recently established in collaboration with Burchell and co-workers [3]. Due to their electrically conductive overlayer, these coated latex particles easily acquire a high surface charge, and hence can be electrostatically accelerated up to hypervelocities ($> 1 \text{ km sec}^{-1}$) using a 1.5 MV Van de Graaf accelerator. Given their high carbon contents, low densities and narrow particle size distributions, these conducting polymer-coated latexes are expected to be excellent mimics for carbonaceous micrometeorites.

In this presentation, we describe the synthesis of submicrometer-sized polypyrrole (PPy)-coated sulfur-rich poly[bis(4-vinylthiophenyl)sulphide] (PMPV) latex particles by chemical oxidative seeded polymerization. The PPy-coated PMPV particles were extensively characterized using scanning electron microscopy, x-ray photoelectron spectroscopy, FT-IR spectroscopy, helium pycnometry, Raman spectroscopy and electrical conductivity measurements. Four-point probe measurements on pressed pellets indicate conductivities of around $6 \times 10^{-5} \text{ S cm}^{-1}$ for polypyrrole loadings of approximately 10 %. This suggests a somewhat patchy, non-uniform polypyrrole overlayer, which is consistent with our Raman spectroscopy studies. Given their high sulfur contents (ca. 28 %), these new electrically conductive latexes are expected to be interesting synthetic mimics for understanding the behavior of sulfur-based micrometeorites, whose existence has been postulated by planetary scientists investigating signs of volcanic activity on one of Jupiter's moons (Io).

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Polymerisation of Surfactant Structures at the Mica/Solution and Silica/Solution Interfaces

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We have investigated the polymerisation of surfactant structures at solid interfaces to render the morphologies that they form at solid interfaces resilient to rinsing. We used a cationic surfactant with a polymerisable counterion, tetradecyltrimethylammonium styrene sulphonate (TTASS), on both mica and silica. Polymerisation was followed by absorbance spectroscopy in the region 190 ~ 300 nm and morphological changes were studied with Atomic Force Microscopy (AFM).

Absorbance spectroscopy revealed that polymerisation went to completion after 1.5 ~ 2 hours. The presence of polymer at the surface of silica was spectroscopically confirmed by measuring the spectra after rinsing. Monitoring the peak at 225 nm as a function of rinsing, we observed that the polymerised films were significantly more stable than the unpolymersed films, which were not stable at all.

The morphology, prior to polymerisation, on both mica and silica is spheres (or possibly branched rods) with a centre to centre spacing, or correlation length, of ~8 nm on mica and ~10 nm on silica. It changes during polymerization to give long meandering rods on mica and shorter less ordered rods (or connected spheres) on silica.

After rinsing the surface with pure water the morphology at the surface is preserved.

**Wearing Characterization and Non-destructively Cleaning of Colloidal Probe
by Scanning Over Super-sharp Gratings**

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During colloidal probe force measurements, whenever the attached sphere is in hard contact with surface, relative motion between the sphere and substrate, can cause wear, contamination and even damage of the sphere. These problems can induce errors especially in adhesion force determination. Neto and Craig [1] have showed that super-sharp gratings are a powerful tool to characterise colloidal probes: both the sphere's radius and surface roughness can be determined by reverse imaging. Here we demonstrate that super-sharp gratings can also be use to successfully characterise the wearing of silica spheres (figure 1a-c) and clean minor adhered contaminants (figure 2a-b) that are not easily removed by UV ozone treatment.

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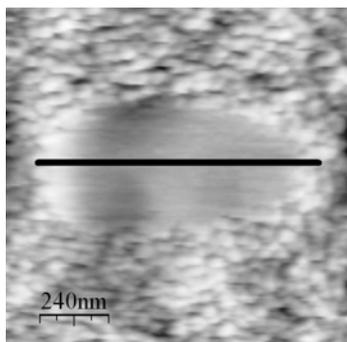


Fig. 1a

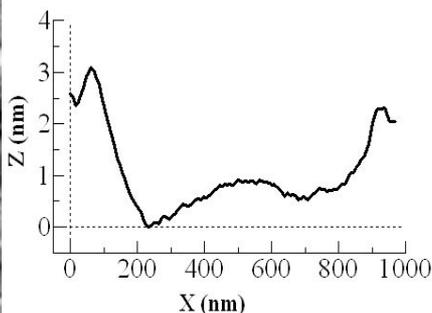


Fig. 1b

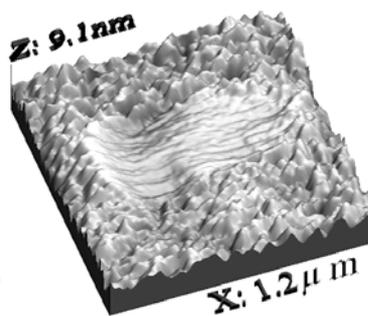


Fig. 1c

Fig.1 Reverse imaging of a silica sphere of 5 μm in diameter (Bangs Lab) showing that the part of the sphere touching a silica substrate was worn after force measurements in salt solution.(a) Surface morphology (1.2 μm by 1.2 μm); (b) sectional line profile; (c) perspective view.

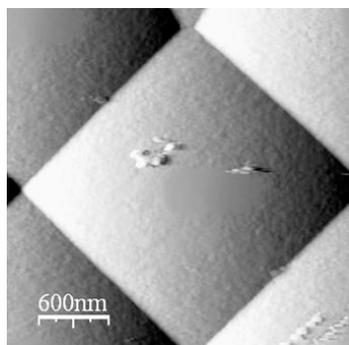


Fig. 2a

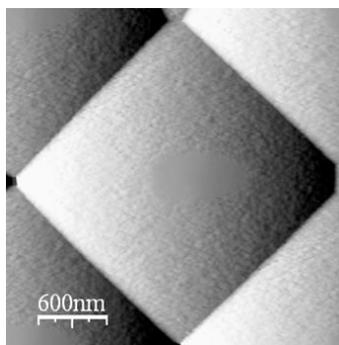


Fig. 2b

Fig. 2 (a) Contaminants were visible on the sphere's surface after repeated force measurements in salt solution; (b) contaminants were removed after scanning over gratings for a few runs. (Note: Gratings used are model TGT1 super-sharp gratings.)

Development of High Performance Cake-less Continuous Filtration System

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Filtration is widely used in many kinds of industrial fields to separate solid particles from a suspension. In general the flocculation aid is added before filtration in order to make particles flocculate, because the cake obtained from flocculate system has relatively high porosity, resulting in low filtration resistance. However, this means that the cake has much liquid in it. Therefore we incur much more energy and cost for drying. In addition the cake does not have fluidity, so the cake must be collected by a mechanical hand-scraping device.

In our previous researches, it was found that the condensed particle layer, obtained from the well dispersed system by a gravitational sedimentation test, still possessed fluidity even if the particle volumetric concentration reached approximately 40%. This result suggests that if we made particles well dispersed before filtration, a high concentration particle could be obtained continuously by some external force, such as centrifugal force, because of its fluidity.

In this study, it has been developed the high performance cake-less continuous filtration system, which can collect high concentration particle continuously without any mechanical hand-scraping device. Figure 1 shows the schematic illustration of cake-less continuous filtration equipment. The condensed particle layer on the rotating filter was expelled from the vessel by centrifugal force. Figure 2 shows the relation between the particle concentration of the condensed layer and the filtration time. The sample powder was sericite and a water glass was used as dispersant. It was shown that the condensed particle layer with a relatively high concentration of 35 vol% could be easily collected because of its fluidity.

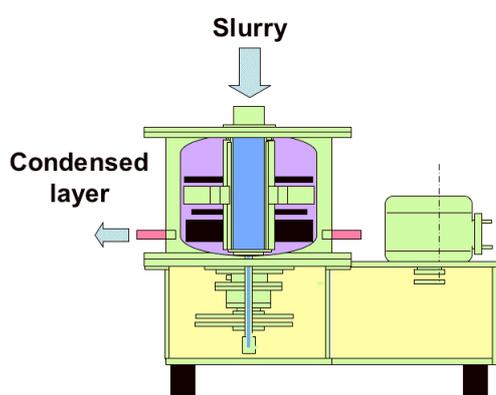


Fig.1 Experimental apparatus

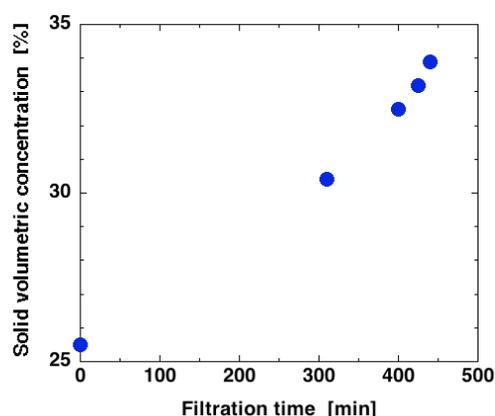


Fig.2 Experimental result

Exploring Metal Ion Adsorption onto Biological Substrates through Surface Spectroscopy

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Aqueous metals, released into the environment through industrial activities, tend to persist indefinitely, accumulating through the food chain. This is an increasingly important issue as it can ultimately lead to serious public health and environmental concerns, such as genetic malformation and/or death. One of the main causes of aqueous metal pollution is by the release of heavy metal-containing industrial effluent into waterways. This is often as a direct result of inefficiencies associated with existing heavy metal removal processes. Consequently, the efficient removal of heavy metals has become a significant problem for industry. Over the past few years, biological substrates - in particular, fungi -, have been investigated as potential adsorbents. This study examined the adsorption of selected aqueous metals onto biological adsorbents of fungal origin (*Rhizopus stolonifer*, *Mucor rouxii* and *Pycnoporus cinnabarinus*).

The pH-dependent adsorption of various divalent metals onto these substrates was investigated at both constant substrate surface area and constant mass. It was found that of all the substrates investigated, *M. rouxii* was the most effective in removing the divalent metals from solution, achieving a higher degree of adsorption (for a given pH) than the other substrates studied.

Surface characterisation of all fungal substrates was carried out in order to investigate the apparent 'unique' surface properties possessed by *M. rouxii* to result in this enhanced adsorption ability. The surface functionality of the fungi has been investigated using both Attenuated Total Reflectance Infra Red Spectroscopy (ATR-IR) and X-Ray Photoelectron Spectroscopy (XPS). Preliminary studies indicate that the amine functionality of the substrate appears to play a key role in achieving the enhanced levels of adsorption for a given pH.

Electrical Double Layers at Aqueous Non-polar Solid and Fluid Interfaces

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It has been known for many years that the surface charge or zeta-potential of non-polar solids, liquids and gasses in water is negative, suggesting a low, circa pH1-2 point-of-zero-charge (pzc) or iso-electric point (iep). Examples of these non-polar solid or fluid-water interfaces is provided by such materials as paraffin wax, molybdenite, stibnite, long chain alkane oils and air. Characteristically these interfaces are hydrophobic in the sense that they display a large non-wetting contact angle.

Most workers attribute this negative charge of such interfaces to the unusually strong or specific adsorption of hydroxyl ions. Further they conclude that the hydroxyl ion adsorbs in response to some as yet undefined H-bonding structures of water molecules present at the non-polar, hydrophobic material-water interface at the interface.

Our first approach to understanding hydrophobic material-water interfaces is to revisit the hydrophobic effect. We ask the question as to how to link the properties of a methylene group forced to be present in water to the properties of a long chain of methylene groups, similarly constrained to be in water. It may be that the optimum orientation of water a hydrophobic surface promotes in some way the strong adsorption of hydroxyl ions. In contrast, hydrophilic surfaces would promote a significantly different water structure.

Our other approach to resolving the dilemma posed by the specific adsorption of hydroxyl is to ask questions about how the so-called crystal field of materials will control the acid strength of water clusters at interfaces relative to the acid strength of water clusters in bulk water.

In this approach the non-polar solid or liquid or gas has a zero crystal field; in contrast materials such as titanium dioxide or alumina have large crystal field strengths. The interfacial field will influence the acid ionization, (proton release) from interfacial water clusters. The electrokinetic results suggest that the water clusters at non-polar interfaces are stronger acids than the clusters at ionic solid or polar oil –water interfaces.

Adsorption Properties and Characterization of Porous V-Ti Mixed Oxide Networks

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A series of vanadium/titanium mixed oxide networks with a porous structure have been synthesized by using a combination of sol-gel chemistry and an agarose-templating¹ technique. The morphology and adsorption properties of the samples have been characterized and the photocatalytic activity of the materials has been studied.

Scanning electron microscopy showed the inorganic samples to be porous and homogeneous in structure: Structure replication from the agarose gel template was clear. The surface area of the vanadium/titanium oxide networks initially increased with an increase in vanadium content, to a maximum of $71.2 \pm 0.4 \text{ m}^2/\text{g}$ for 7 mol% vanadium, then decreased for vanadium contents of 8 mol% or greater. The surface area change corresponded to a decrease then increase in the anatase crystal size and the c-axis lattice constant, as determined by X-ray diffraction. Vanadium ion incorporation into the titanium oxide was confirmed by Fourier transform infrared spectroscopy, powder X-ray diffraction and Raman spectroscopy. The UV-Vis reflectance spectra revealed a strong absorption in the visible-light range for the porous V-Ti mixed oxides and a red shift of 0.72 eV. The adsorption capability for methylene blue significantly increased with increasing vanadium content, and then remained constant for vanadium contents above 7 mol%. The photocatalytic behaviour of the materials as a function of V/Ti ratios will be discussed.

Measurement of surface forces between model wood biopolymer materials.

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Cellulose and lignin are the two most abundant biopolymers constituting wood. Cellulose is a linear polysaccharide consisting of repeat β -(1,4)-D-glucan units and both crystalline and amorphous forms are found within the cell wall of wood tracheids. Lignin can typically be described as a highly branched polymer with a phenylpropane base sub-unit with many different covalent linkages possible which varies heavily between tree species. Lignin is predominantly found within the secondary cell wall however the highest concentration is found in the mid-lamella or between the wood fibres.

Depending on the pulping process, either cellulose or lignin is the dominant chemical species at the surface of a wood-based fibre. Thus, an understanding of the surface chemistry of these biopolymers is essential for understanding the fundamental interactions between fibres which is of utmost importance in a number of industrial applications, not least paper-making and the preparation of composite materials. However, structural and chemical heterogeneities of real wood fibres often limit the ability to determine these interactions.

This presentation will outline the preparation of model crystalline and amorphous cellulose thin films as well as lignin thin films. These model surfaces have been optimised for the measurement of surface forces using the colloidal probe technique. Interaction forces between cellulose and lignin have been quantified and will be discussed in terms of their industrial relevance. Furthermore, the influence of introducing bulk and surface charge to the prepared thin films on the interaction force will be presented.

pH Dependent Friction Forces between Silica Surfaces measured by AFM

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The pH dependence of the friction between a silica particle and a silica wafer was investigated using lateral force microscopy. Measurements were done in the range of $3.6 \leq \text{pH} \leq 10.6$ in background electrolyte solutions of 10^{-3}M NaCl. Prior to the friction measurements, we have measured the normal interactions in different pH solutions. In the studied range of pH, we found that the electrostatic repulsion is always present between silica surfaces and decreases with the pH reduction.

The results for friction force versus loading force are shown in Figure 1. It is found that the friction is independent of the pH of solutions and increases linearly with the applied load, when the pH is between 3.6 and 8.6. On the other hand, once the pH is above 9.0, the friction becomes extremely small and the dependence on the applied load becomes non-linear. It is postulated that this transition is due to the development of a gel layer composed of polymer-like segments of silicic acid anchored on the surface. At the lower applied load, this layer acts as a boundary lubricant between the surfaces, but, at the higher applied load, the entanglements of these segments and more direct contact between two solid surfaces leads to the increase of the friction. The effects found here are expected to play an important role in elucidating the basic mechanism of the planarization process of silica wafers.

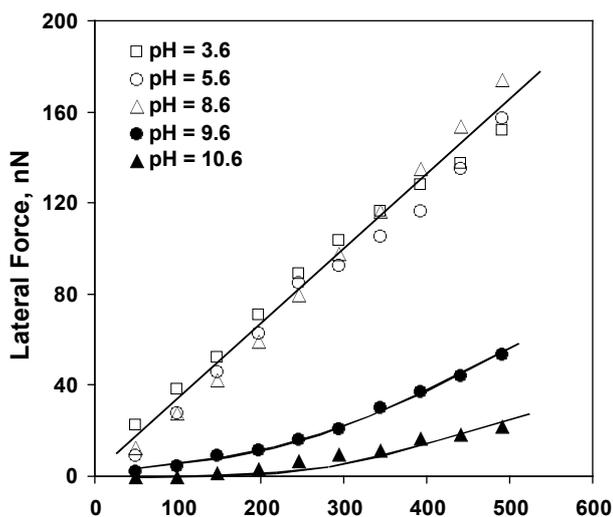


Figure 1. Silica – Silica friction in different pH

Interfacial Forces between a Captive Bubble and a Silica Particle

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Abstract

Interactions between an air bubble and a hydrophilic silica particle were measured using colloid probe Atomic Force Microscopy as a function of solution pH and indifferent electrolyte concentration. The experimental results revealed that interactions between the two surfaces can be attractive or repulsive, depending on the respective surface potentials of the two surfaces and the electrolyte concentration. At mildly acidic pH values and low salt concentration, a repulsive force was first seen on approach, followed by a small jump into an 'energy well', after which a second repulsion appeared. With increasing electrolyte concentration, the depth of the energy well is reduced and eventually disappears. The adhesion force is also significantly reduced, but not completely eliminated. At high pH (around 9), a repulsive force is observed and no adhesion force is detected. These results may be interpreted on the basis of classical DLVO hetero-coagulation theory.

Naturally Occurring Spore Particles at Planar Fluid Interfaces and in Emulsions

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Solid particles behave as emulsifiers by assembling at the oil-water interface into structures which stabilise emulsion drops. The free energy of adsorption of particles to interfaces can be orders of magnitude greater than thermal energy, making particle-stabilised emulsions highly stable to coalescence. Emulsions of oil and water have been stabilised using naturally occurring spore particles of *Lycopodium clavatum*.¹ The preferred emulsions, prepared from either aqueous or oil-borne dispersions of the spores (30 µm in diameter), were oil-in-water. Drops as large as several millimetres in diameter were found to be stable to coalescence indefinitely, despite low particle coverage of the interface. The influence of particle concentration, oil:water ratio and additives in the aqueous phase on the emulsions formed were studied. In the absence of shear, the spore particles assembled spontaneously on water drops from oil dispersions, but far less readily on oil drops from aqueous dispersions. The particles formed disordered aggregates in spread monolayers at planar oil-water interfaces.

1. B. P. Binks, J. H. Clint, G. Mackenzie, C. Simcock and C. P. Whitby, *Langmuir*, in press, 2005.

HYDROPHOBIC FORCES

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We trace in retrospective the evolution of a new scientific idea through the induction period, 60th – 70th, its extensive exploration with cumulating of knowledge over 80th and the subsequent activity decay. By paying tribute to the prophetic visions of Lord Rayleigh down in time, we highlight future developments in surface chemistry and biophysics with emphasizing semantic backgrounds of experimental and theoretical advances.

An in situ Investigation of the Swelling of Adsorbed Poly(2-vinylpyridine) Microgel Latexes on Mica

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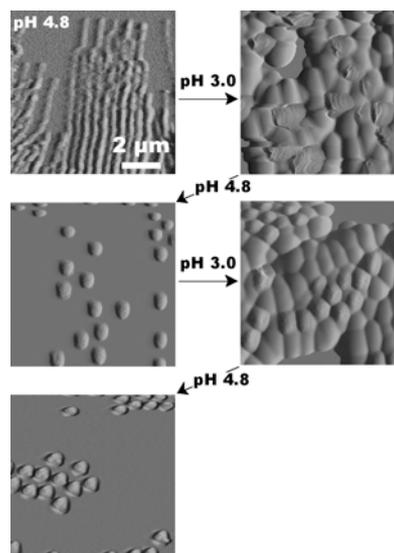
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We have studied the pH-responsive behaviour of a lightly cross-linked poly(2-vinylpyridinium) microgel latex prepared by emulsion polymerisation and stabilised with a combination of cationic and steric stabilisation. At neutral pH the latex has a hydrodynamic diameter of ~ 450 nm and a zeta potential of less than $+2$ mV. Between pH 4.5 and 4.0 the 2VP groups become protonated and the latex swells to a diameter of $1.3 \mu\text{m}$, while the zeta potential increases to $\sim +32$ mV.

The adsorption of the P2VP microgel latex particles to mica has been investigated using atomic force microscopy as a model coating system for high loading and subsequent pH-triggered release of molecules to solution. At pH 4.8 the latex (unswollen and uncharged) adsorbs onto negatively charged mica. The average diameter of the adsorbed latex particles is ~ 450 nm (equivalent to bulk). The low charge at this pH produces bound particles that are easily moved around on the surface, aligned or removed from the surface with an AFM tip. When the pH is reduced to pH 3.0 the adsorbed microgel particles become tightly bound to the surface through increased electrostatic attraction, swelling to form a closely packed film with the average diameter increasing to $\sim 1.1 \mu\text{m}$. Cycling back to pH 4.8 deswells the particles to an average latex diameter of ~ 800 nm, indicating that the surface constrains the microgel particle deswelling process. These partially deswollen particles can be removed at sufficiently high force. It is also possible to form patterns in the film, which remain during subsequent pH cycling.

The latex particles also adsorb to mica at pH 3.0 (i.e. when swollen and charged) with an average diameter of $\sim 1.3 \mu\text{m}$, again indicating minimal flattening. The particles are closely packed and adhere strongly to the mica. Thus the high charge on the particles does not prevent them from adsorbing as a close-packed film. Cycling between pH 4.8 (unswollen and uncharged) and pH 3.0 (swollen and positively charged) deswells and reswells the adsorbed microgel latex particles as was observed for the films deposition at pH 4.8.



Cycling between pH 4.8 and pH 3.0 produces swelling and deswelling of the microgel on the mica surface respectively.

Measurement of Film Stress using a cantilever bending technique

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The deposition of any coating onto a substrate will produce some degree of stress in the film. The degree of stress in the film is critical. If the stress is too large the substrate may warp or the film delaminate, therefore knowledge and control of film stress is important in many processes from the drying of paints to the production of Micro-Electro-Mechanical devices (MEMS).

The measurement of film stress using the Atomic Force Microscope and macroscopic surfaces will be described. Correct evaluation of the film stress requires knowledge of the bending mode of the cantilever under the action of the stress. Here we demonstrate that a significant number of measurements in the literature are based on methods of analysis that yield values of the film stress that are incorrect. How this data may be corrected is described and some examples of film stress measurements discussed.

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