14 - 01

Growth of Hierarchical Nanostructured Materials via Soft Solution Routes

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Nanostructured films have numerous applications including wetting, microfluidics, photonics, and other opto-electronic properties. Solution phase syntheses of nanostructured films provide the potential for cost effective, large scale manufacturing. In this talk, we will review recent progress at Sandia National Laboratories in using solution based, bottom-up approaches to synthesize oriented nanostructured films and complex nanostructures. First, the principles and applications of heterogeneous nucleation and growth will be highlighted. Next, a hierarchical growth method we recently developed to control structural ordering in a step wise manner will be discussed. Large arrays of complex, oriented and ordered architectures have been produced. Growth directing factors that influence crystalline morphologies will be discussed. Finally, we will demonstrate the wide applicability of the methods we developed in different systems.

14 - 02

Rare Earth Doped Nanocomposites for Photonic Applications

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The proliferation of optical systems for communications, defense, entertainment, automotive, and display applications has manifested the need for devices that can perform a greater number of tasks while being increasingly robust, take up less space, and use less power to operate. These increasingly more stringent requirements continue to spur international research efforts on materials that exhibit multiple optical functionalities. This talk will focus on approaches to achieving greater functionality and efficiency through the use of fluoropolymer nanocomposites. More specifically, theoretical and experimental studies on transparent rare-earth doped halide nanoparticles in unique fluoropolymer matrices will be presented as will potential applications.

14-03

Preparation of Nanoporous Silica and Sodium Fluoride from Hexafluorosilicic Acid and Sodium Silicate

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A process for the preparation of nanoporous silica and recovery of sodium fluoride from hexafluorosilicic acid and sodium silicate at the different molar ratios was studied. In

order to prepare the appropriate solutions of initial compounds the 25% hexafluorosilicic acid solution and the 18% sodium silicate solution were used. Obtained nanoporous silica and sodium fluoride have been investigated by XRD, BET, TGA, EDX and SEM methods.

14 – 04

Top-Down or Bottom-Up: New Approaches for the Fabrication of (Functional) Three-Dimensional Photonic Crystals

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Bottom-up self-assembly of colloidal sub-micron size spheres as well as top-down holographic laser lithography in photoresists are reliable tools for the inexpensive, large-scale fabrication of three-dimensional Photonic Crystals. To add functionality to these Photonic Crystals we follow different approaches: A lithographic method allows for reliable waveguide fabrication inside colloidal Photonic Crystals, while Direct Laser Writing (DLW) is the method of choice for holographically fabricated samples.

The crucial step for both methods is the final conversion into high index materials, e.g., silicon. As conventional silicon chemical-vapor deposition (CVD) can be used for bottom-up templates, no such technique is available for photoresist-based samples. Here we demonstrate the successful double-inversion of direct-laser written templates, combining silica and silicon CVD techniques.

Finally, a novel approach for the direct fabrication of three-dimensional Photonic Crystals will be presented, namely DLW in high index of refraction chalcogenide glasses with subsequent wet etching of the unexposed areas.

14 - 05

Colloidal Crystal Based 3-D Chemical Sensors and Optical Waveguides

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Colloidal materials offer interesting opportunities for scientific exploration and formation of functional materials and structures. After a brief introduction to the optical properties of colloidal crystals and photonic band gap materials, I will present our results on synthetic opal based devices. Device fabrication begins with the self-assembly of silica or polystyrene colloidal particles into a colloidal crystal, this colloidal crystal is then used to template a periodic 3-D structure into an optically active material. Colloidal crystals inherently have interesting optical properties, however by inverting the structure into a functional material, the optical behavior can be significantly enhanced. Using such an approach, we have created hydrogel inverse opal chemical and biological sensors. These sensors show rapid (~1 minute) diffusion limited responses to small changes in pH and glucose concentration, and were designed to have an optical diffraction based response that is detectable with the naked eye. The mechanical behavior of these structures turned out to be rather interesting. As the polymer swelled, the inverse opal transformed from fcc to $L1_1$ due to the strain field in the hydrogel inverse opal, and antiphase boundaries were observed to form. In contrast to photonic based sensors, which only require periodic structures, for a number of applications, incorporating aperiodic defects on the wavelength of light into an otherwise periodic structure will be critical. For example, a 3-D waveguide with a bend radius on the order of the wavelength of light could be created by embedding a waveguide structure inside of a photonic band gap material. We have been developing multiphoton polymerization of three-dimensional structures to do exactly this, and have demonstrated the writing of waveguide structures within colloidal crystals. A number of issues still must be dealt with to create an optical device, and I will highlight our latest results in this area.

14 - 06

Novel Types of Optical Gain Media Based on Photonic Crystals "Activated" with Semiconductor Nanocrystals

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The periodic variations of the dielectric constant in photonic crystals (PCs) give rise to photonic band structures analogous to those for electrons in semiconductors. Near the edges of the photonic band, the photonic density of states and group velocities are modified. In some cases, near zero group velocities are obtained leading to very large optical gains. Since PC properties are wavelength tunable through size variations, their properties can be tailored to match semiconductor nanocrystals (NCs) emissions, which are tunable across a wide spectral range through compositional and size variations. Here, we demonstrate NC incorporation into a variety of PC structures. In one example, we utilize self-assembled opals as a host for NC/sol-gel (NC/SG) nanocomposites. Despite an order-of-magnitude reduction in the NC volume fraction versus NC/SG films, we observe a two-fold reduction in the amplified spontaneous emission (ASE) threshold and an optical gain increase evidenced by the observation of ASE with a 30-? m excitation spot. We also discuss the impact of one-dimensional PC structures on the optical properties of NC/SG composites. Here, we incorporate the NC/SG material directly into a one-dimensional PC. The results presented here are steps toward low-threshold NC lasers that can be excited by a continuous wave source.

14 - 07

The Rate-controlled Synthesis of Doped Ferroelectric Nanoparticles under Conditions of Micro/Nanoreactors.

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Synthesis of nanoparticulate materials in micro/nanoscale reactors is widely used as a powerful and precise technique. One of the possible small-scale reactors is particulate intermediate product originating from thermal decomposition of unstable precursors. Scaling relationship between size of reactor and size of the specified nanoparticles is not well-understood one. The recently developed process, so called rate-controlled synthesis, is considered useful in manufacturing of nanosized powders from unstable precursors. The reaction rate-controlled processes (RCP) strongly differ from the conventional synthesis and sintering due to feedback established between transformation value and instantaneous temperature. During RCP, the transformation value is the dependent parameter whereas the temperature is the independent parameter, contrary to conventional processes. The chemical synthesis proceeds through the competition between new phase nucleation and nuclei growth. Both nucleation and growth have different thermal activation energies and, therefore, different rate, which is a function of temperature and heating rate. The competition of mechanisms results in possibility of particle size control. The rate-controlled mode allows flexible temperature-time regime and refinement of particles compared to conventional ramp-and-hold regimes. For instance, the rate-controlled decomposition of unstable precursors of barium titanate, zirconia and lanthanum-strontium manganate resulted in 1.2-2.0 times decrease of particle size compared to linear heating rate regimes. The nanosized barium titanate powders, both pure and doped, have been prepared through the modified Pechini process. The intermediate product of oxalate decomposition was impregnated with soluble precursors of dopants such as niobia, calcia, yttria and subsequently co-decomposed until synthesis of doped barium titanate. The morphological transformations within intermediate resin-like products have been studied by combination of FTIR, RAMAN and Kawazoe methods. The understanding of internal structure of nanoreactors allowed us to clarify features of rate-controlled non-linear heating rate synthesis compared with conventional process of ramp-and-hold.

14 - 08

Barium Titanate Based Nanocrystalline Ceramics: Preparation and Properties

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Barium titanate is the most widely used dielectric material in surface mount components and is presently under development for the mass production of submicron grain size ceramics. Over the next ten years, these dimensions will become nanoscale if present trends continue. With this view, most of the earlier research has focused on the dielectric properties of $BaTiO_3$ and considered these properties to enhance volumetric efficiency in multilayer ceramic capacitors. One of the major unknowns in these materials is the influence that nanosized grains may have on the reliability of future devices, which is typically controlled by the ionic migration of point defects under a direct bias. The production of fully dense nanocrystalline barium titanate ceramics is a difficult task due to enhanced grain growth during the final stage of sintering. To win this competition between densification and grain growth, the right combination of different factors should exist, such as powder particle size and pore size distribution in green body, sintering schedule and sintering atmosphere, and dopant type and dopant distribution. This work presents results of rate-controlled synthesis and sintering of doped barium titanate, as well as the size effect and its relation to reliability and dielectric properties. It is shown that rate-controlled synthesis by decomposition of thermal unstable precursors gives weakly agglomerated powder with an average particle size around 20 nm, which can be easily doped by modified sol-gel technique. Combining pressureless rate-controlled sintering with controlled atmosphere treatments and effective dopant concentrations yields a nano-grained fully dense ceramic with a grain size of less than 100 nm, with a 4÷5 factor of grain growth, which is 3÷5 times less than in traditional sintering modes. The lifetime and dielectric properties are studied based on grain size and dopant concentration. The prospects of using these results in multilayer ceramic capacitor technologies are discussed.

14 - 09

Nanoparticles as Functional Building Blocks: Size, Shape and Composition Control and Property

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Size, size distribution, shape and composition control of sphere, rod and multipods nanocrystals is pivotal in the development of new multifunctional nanomaterials. In this presentation, I will discuss our recent progress in the following areas: 1) size, shape (including monodisperse nanorods, cubes and multipods) and composition control of metals, metal alloys and metal oxides in both conventional solvents and ionic liquids; 2) composition and property of FePt and other alloy-containing magnetic nanocomposites made from core-shell nanoparticles; and 3) the electrode catalytic property of Pt-containing nanoparticles. This talk will cover several classes of nanomaterials including Pt, Ag, PtM (M=Co, Fe and Ni), Fe_2O_3 and a variety of magnetic core-shell nanoparticles. The emphases are on our understanding and the strategies on the controlled growth of colloidal nanocrystals, and the design of functional materials from nanoparticle building blocks, which possess interesting magnetic and electro-catalytic properties.

14 - 10

Alkaline Modified Calcium Doped Lead Titanate Film Humidity Sensor Formed Using Sol-Gel Method

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This research encompassed the fabrication, microstructural characterization, and moisture sensitivity of an alkaline modified, calcium doped, lead titanate thin film humidity sensing device. The active component for the humidity sensor is based on a $Li_yCa_xPb_{1-x}TiO_3$ (Li-CPT) ceramic (x = 0.35 to 0.50, y = 0.005 to 0.01). Films of Li-CPT were prepared by a sol-gel, spin-coating technique, and then followed by sintering at 550 to 900 ^{o}C for one hour. The films were structurally characterized by x-ray powder diffraction (PXRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), magnetic resonance force microscopy (MFM), and Raman spectroscopy (RS). Characterization results indicated the synthesized films were composed of a single perovskite phase with crystallite particles on the order of 30 – 50 nm. Humidity sensing measurement had been performed for Li-CPT using resistance measurements at different relative humidity (φ) range of 8% to 93%*RH* at room temperature. The variations of resistance values (R) were higher than three orders of magnitude over the working relative humidity range. The curves of Log R versus φ displayed excellent linearity, high sensitivity, minimal hysteresis and rapid response to the humidity change.

14 - 11

Dynamics of the Electrohydrodynamic Patterning of Thin Polymer Films

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We perform one and two-dimensional simulations of an electrohydrodynamic patterning process for a mask-air gap-polymer-substrate sandwich, which is a newly discovered patterning phenomenon. The simulations help us identify the intrinsic pattern resulting from nonlinear interactions to be hexagonal when the mask is unpatterned, consistent with experimental observations. The size of microstructures, periodicity and time for formation agree well with the experimental data. The dynamic evolution of the thin polymer layer under a patterned mask shows that the pillars start to form from corners, propagate along edges and then grow inwards. This growth sequence, identical to experimental observations, creates a square pattern under a square mask, a hexagonal pattern under a triangular mask, etc. Besides the hexagonal pattern, simulations indicate the conditions under which various different patterns that have been observed in experiments should form. The dynamic simulations are very helpful in understanding of the nonlinear dynamics of the patterning process, predicting the final pattern formation under different conditions, and providing insights for future experimental design.

14-12

Shape-Controlled Synthesis of Metallic Nanostructures

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Future nanotechnology applications, either in electronics, photonics, catalysis, or medicine, require nanostructure building blocks. I will present a solution phase synthesis that produces large quantities of silver, gold, platinum, and palladium nanostructures with controlled size, shape, monodispersity, and crystallinity. Some example nanostructures include silver nanowires and nanocubes, hollow gold nanotubes and nanocages, platinum nanowires and multipods, and palladium nanocubes and nanocages. By controlling nanostructure size and shape, one can tailor the photonic, plasmonic, electronic, and catalytic properties of metallic nanostructures for a given application.

14-13

Dynamic Tuning of Photoluminescent Dyes in Crystalline Colloidal Arrays

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A number of people in the group have been working on approaches to dynamically (i.e. in real time) tune the photoluminescent spectrum of dyes localized on crystalline colloidal arrays. Though a number of experimental studies have studied the suppression of the spontaneous emission of photoluminescent (PL) materials at frequencies inside the photonic bandgap of ordered dielectric structures, the majority of these experimental efforts have focused on sterically packed colloidal crystals composed of dye-labeled particles. Though these systems have offered a number of insights into this class of materials and have established that the emission spectrum of a dye may be controlled by the photonic lattice parameter, this control is usually exercised by fabricating samples of different particle diameters to alter the rejection wavelength.

The ability to dynamically (i.e., in real time) tune the emission characteristics of the dye through an in-situ modification of the rejection wavelength has not been previously demonstrated in colloidally-based crystals.

To this end, we focus on the exploitation of mechanochromic tuning to modify the emission spectra of hydrogel-encapsulated crystalline colloidal arrays composed of electrostatically self-assembled monodisperse polystyrene particles coated with the photoluminescent dye Rhodamine-B. The broad rejection wavelength tuning range, relatively narrow bandwidths, and non-hysteretic nature of the mechanochromism of these electrostatically based colloidal crystals suggest that these systems can be exploited to tune the emission characteristics of an PL dye coupled to a photonic crystal in a slew of optical/photonic based applications. The variation in the PL spectra of the system is presented in the adjacent graph as a stop band is mechanochromically tuned through the emission range; the approximate position of the rejection wavelength is indicated with the arrows.

14-14

Driving Tomorrow's Functional Electronics and Optics With Designer Nanopowders and Nanostructures

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Recent progress in the chemical synthesis of nanomaterials has created new opportunities for the application of ceramics in advanced structures and devices. Our laboratory is focused on developing low-cost and robust methods for the synthesis and processing of nanomaterials and on establishing structure-property relationships at the nanometer length scale. Hydrothermal crystallization is known to be a highly flexible process to prepare nanopowders and nanostructured films. Methods for engineering hydrothermal crystallization processes are being developed using traditional fundamental approaches based on thermodynamic and kinetic principles. However, the non-classical mechanism of hydrothermal crystallization has brought forward the importance of non-thermodynamic variables such as fluid hydrodynamics and precursor characteristics. These variables provide additional degrees of freedom for controlling the physical and chemical characteristics of designer particulates. Efforts are being dedicated towards understanding crystallization mechanisms and applying that knowledge to design and construct unique reactor systems. The availability of designer particulates enables new classes of functional materials not accessible with conventional commercial ceramic powder processes. For instance, various families of infrared optics based on transparent halide nanocomposites would not be possible without the availability of nanoparticles that can be dispersed at length scales below 100-nm. Dielectric materials based on titania or barium titanate at the 1-μm length scale require particle sizes less than 200-nm. However, the production of uniform and dispersible powders alone is insufficient to enable the fabrication of functional materials. Appropriate mixing and particle assembly methods are needed and being developed to address the homogeneity length scale requirements, with an emphasis on continuous processing. The ability to create advanced materials with controlled nanostructure has generated a technology pull for computational design of materials. Examples illustrating the steps along the path from particle synthesis to functional materials will be presented for the specific case of new dielectric and optical nanocomposites.

14-15

Engineering the Forces Between Nanocolloids: Challenges and Opportunities

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Bottom-up assembly of nanocolloids depends in large part on the forces between particles. Some forces – like the use of DNA as a "selective glue" – cause a desirable "directed" motion. But other forces – especially the van der Waaals (VDW) forces – cause a random and nonspecific aggregation of particles. A critical goal then is to minimize these nonspecific forces between particles so that aggregation occurs only by design. Traditional methods for calculating and measuring VDW forces between particles are not applicable to nanocolloids. In this talk we describe how we use Axilrod-Teller-Muto theory to help us calculate VDW forces between nanocolloids, and we will discuss our current approaches (e.g., particle force light scattering) to measuring interparticle forces for polystyrene and silica nanocolloids. The focus of the talk will be on bottlenecks to predicting nanocolloidal forces, possibilities for better models, and opportunities for bottom-up assembly.

14-16

High-Resolution, High-Sensitivity Particle Size Analysis of Concentrated CMP Slurries and other Nanoparticle Systems using the New Techniques of Focused Light Extinction and Scattering

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The technique of single-particle optical sensing (SPOS) is effective for assessing the quality of oxide “CMP” slurries used for semiconductor processing, ink-jet toners/pigments and a variety of other nanoparticle-based dispersions and suspensions. The large-diameter “tail” of the particle size distribution (PSD) can be measured effectively by combining the methods of light extinction (LE) and scattering (LS), called “LE+LS” (Pat.). However, this approach requires extensive sample dilution to achieve high sensitivity (> 0.5-um) and avoid PSD artifacts due to particle coincidences and background scattering. New techniques, called focused extinction (FX) and scattering (FS), have recently been developed (Pat.), which utilize a much smaller active sensing zone and novel signal processing methods. The resulting FX sensor requires much less sample dilution (often none), while still achieving excellent small-particle sensitivity not possible using conventional LE technology. The companion LS sensor produces PSD results of unprecedented resolution and sensitivity for particles as small as 0.1-um and concentrations exceeding 10 million/ml. The combined FX and FS capabilities permit accurate particle size measurement of many submicron systems that are poorly characterized using laser diffraction and other ensemble techniques.

14-17

Colloidal Self-Assembly, Multibeam Holography and Photonic Crystals

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Photonic crystals are materials that allow the manipulation of light in new and unexpected ways. Semiconducting materials played a tremendous role in microelectronics and we expect photonic crystals to revolutionize the world of microphotonics in a similar way. Colloidal self-assembly and multi-beam interference lithography are great tools to build crystals with interesting optical properties. I will review some recent progress towards constructing photonic band-gap materials.

14-18

Synthesis and Characterization of Polymer Encapsulated Nanoparticles for Microelectronic Applications

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There are two well-researched methods for constructing the core-shell morphology of particles. The shell can be produced by adsorption of preformed macromolecules onto core surfaces by electrostatic or by non-solvent deposition methods. An alternate method involves mixing core particles with monomers and then initiating polymerization. This procedure is more favorable for obtaining a uniform coating of each particle because of the substantially higher accessibility of the active surface of cores for molecules of a monomer compared to the corresponding macromolecules. However, the formation of an organic shell on extremely small silica nanoparticles (~ 20 nm) by the same method has received little attention. In the present work; we demonstrate a process of coating of such small colloidal silica particles with polymers in two layers; the first layer is PDVB (polydivinylbenzene) and the second layer is PHEMA (poly2-hydroxyethylmethacrylate). Results of several time based adsorption experiments are presented to verify the hypothesis of monomer adsorption on inorganic core with and without initiator. The presence of polymer encapsulating the silica surface was determined by FTIR spectroscopy, transmission electron microscopy(TEM) and ALV particle sizing instruments; while the amount of coated polymer on silica surface was assessed by thermogravimetric analysis(TGA). These polymer coated particles can be used as soft Abrasives in CMP application to mimimize defects.

14-19

Enlargement of Dye-sensitized Solar Cell by Using High Performance Transparent Electrode and Nano-porous TiO2 Film

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Dye-sensitized photoelectrochemical cell based on nano-porous semiconductor materials are gaining much attention as a promising solar energy conversion system. We have successfully developed a spray pyrolysis deposition technique to prepare high transparent conducting oxide and nano-structured TiO2 films for the fabrication of large-area dye-sensitized solar cell. Transparent conducting oxide film, in which tin-doped indium oxide (ITO) inner layer was covered with fluorine-doped tin oxide (FTO) outer layer, gave low resistivity 1.3 x 10-4 W cm and high optical transmittance about 80 %. TiO2 film, which is formed mainly from a mixed solution of Ti-containing compound and TiO2 sol, has much higher light-scattering properties and dye adsorption porosities. A solar cell consisted of dye-impregnated TiO2 porous film of an about 12 mm thickness and of a 7 x 4 cm2 active area, Pt counter electrode, and redox electrolyte. This solar cell showed short-circuit photocurrent (Isc) 9.89 mA cm-2, open-circuit voltage (Voc) 735 mV in AM-1.5 simulated sunlight (100 mW cm-2) with an efficiency of 5.08%.

14-20

Atomically-Flat Nanosurfaces: Flat Gold Nanoparticles as a Novel Substrate for STM and Photonic Studies

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Flat gold nanoparticles (FGNPs) can be used as atomically-flat gold substrates for STM studies. When supported on indium tin oxide (ITO) coated glass the FGNPs can also be

used as atomically-flat photonic substrates. Transmission electron microscopy (TEM) shows that FGNPs can be prepared 100–500 nm across with shapes that range from triangular to hexagonal with thicknesses of 15-25 nm. Dark-field optical microscopy is a convenient method for evaluating the FGNP arrays because the FGNPs and spherical gold nanoparticles are distinguished easily by their plasmon resonance spectra. Scanning tunneling microscopy (STM) reveals atomically flat terraces on the large {111} FGNP facets, which are flat to a few atomic layers over entire surface. No stepping (rounding) of the facet is observed even near the edges. STM images demonstrate that well-ordered alkanethiol self-assembled monolayers (SAMs) form on the FGNP/ITO substrates, thus they are excellent substrates for molecularly resolved STM imaging. Our results indicate that our FGNPs grow as single crystals, rather than by aggregation of smaller nanoparticles. An optimized method for growing the FGNPs and for depositing them on ITO coated glass with a high particle density is presented.

14-21

Liquid Crystal Molecule-Capped Metal Nanoparticles as Dopants for Liquid Crystal Display: Frequency Modulation and Fast Response

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Liquid crystal display (LCD) is a typical electronic display and ubiquitously used in the world. One of the most important problems to be solved in LCDs is the response rate of the switching. The response rate of commercial LCDs is about 15 ~ 20 ms, which is much slower than organic electroluminescent display (ELD) and plasma display (PDP).

Recently we have found that LCDs, which contain metal nanoparticles capped by liquid crystal molecules as a dopant for liquid crystal media, can switch the brightness not only by varying the applied voltage but also by varying the frequency. In other words, not only the amplitude modulation (AM) but also the frequency modulation (FM) mode can be effective for the metal nanoparticle-doped LCDs[1]. In addition, more interestingly, the response rate of LCDs doped with metal nanoparticles is expected to be faster than that of the presently commercialized LCDs[2].

Metal nanoparticles used here were prepared by reduction of the corresponding metal ions with ultra-violet light irradiation in a THF solution in the presence of 4-cyano-4'-pentylbiphenyl (5CB). Only 1 wt% of Pd monometallic or Pd/Ag bimetallic nanoparticles capped by 5CB were introduced to twisted nematic liquid crystal (5CB) media[3]. The effect of the kind and size of metal nanoparticles upon the electro-optic properties of twisted nematic LCDs will be discussed in the presentation.

14-22

Two Dimensional Arrangement of Gold Particles Less Than 10nm

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Monodisperse nanogold particles 2-5nm in diameter with standard deviation less than 0.4 have been prepared by using different methods. Many approaches to produce a homogeneous 2D arrangement have been attempted. A well ordered packing domain with area more than 1 μm^2 has been achieved on liquid and solid substrates by capillary force. Compare with the result which we obtained before, the area free from voids and quality of packing is much improved. The controlled factors and possible mechanism have been examined and discussed.

14-23

Computer Simulation Study on Behaviors of Surfactants at the Liquid/Liquid Interface

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Behaviors of surfactants at the interface play an important role in the industrial application, such as oil extraction, deterging process and material preparation. However, the detail information of interfacial region on a molecular level is scarce. Recently, computer simulation has become an effective tool for the study of complex interfacial systems on a detail molecular level, such as molecular dynamics (MD) simulations. However, the time and length scales accessible to ordinary MD simulations are not large enough to study some phenomena in surfactant system. Therefore, a mesoscopic level simulation named dissipative particle dynamics (DPD) is used to investigate the behaviors of surfactants at the water/oil interface.

Dissipative particle dynamics simulation bridges the gap between atomistic and mesoscopic simulations. The simulation strategy is to regard clusters of atoms as fluid particles or beads, some of which are connected by harmonic spring. Soft spherical beads interact through an effective pairwise interaction potential obtained from detailed atomistic molecular dynamics simulations, and thermally equilibrate through hydrodynamics.

The orientation of sodium dodecylsulfonate (DDS) and sodium dodecylsulfate (SDS) adsorbed at the water/carbon tetrachloride interface has been studied by considering the variation of root mean square (RMS) end-to-end distances of surfactants. An increase in the interface concentration of surfactants results in the increase in the orientation of surfactants before reaching a full monolayer. Strong hydrophilic head groups are beneficial to form a well-ordered configuration and appropriate salts make surfactant molecules more stretched and ordered, which may be interpreted as a reduction on gauche defects for them.

The synergistic effects of mixed surfactants sodium dodecylbenzene sulphonate (SDBS) and Triton X-100 (TX-100) at the oil/water interface has also been investigated. With the decrease in a_{HH} and a_{WE}, SDBS and TX-100 are driven to adsorb more at the interface and can decrease sharply the interfacial tension of the mixed system. Also we have observed that some cavities between SDBS clusters at the interface can be filled with TX-100 clusters. The inhomogeneous distribution helps to understand the mechanism of the synergism interaction and the decrease in the interfacial tension.

Therefore, computer simulation method might be an attractive method to provide effective information about behaviors of surfactants on a mesoscopic level.

14-24

High Dielectric Properties Ofnm-sized Barium Titanate Crystallites and its Origin

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BaTiO3 crystallites with various particle sizes from 20 to 1000 nm were prepared by the modified 2-step thermal decomposition method of barium titanyl oxalate. Investigation of impurity in these particles using both TG-DTAand FT-IR measurements revealed that no impurity was detected in the BaTiO3 lattice while hydroxyl and carbonate groups were detected only on the surface. Moreover, their relative densities werealways above 99%. The dielectric constants of these powders were measured using suspensions by a modified powder dielectric measurement method. As a result, the dielectric constant of BaTiO3 particles with a size of around 140 nm exhibited a maximum of around 6,000. Thus, we discussed the origin of high dielectric constant around 6,000 for BaTiO3 particles with a size of around 140nm. The crystal structure of the BaTiO3 particles with sizes below 100 nm was always assigned to cubic m-3m by a conventional X-ray diffraction measurement because of significant line broadening. Thus, using a synchrotron radiation X-ray powder experiment with imaging plate, the crystal structure of the BaTiO3 particles with sizes below 100 nm was investigate from 25? to 300?. As a result, in the BaTiO3 particles with sizes over 40 nm, itwas confirmed that their crystal structure at 25? was assigned to 4mm. This means that the c/a ratio decreased with decreasing particle sizes from 1000 nm to 40 nm. On the other hand, the local and dynamic crystal structure of the BaTiO3 particles with sizes below 1000 nm was assigned to tetragonal 4mm by a Raman scattering measurement. It should be noted that in the particlesize with a maximum dielectric constant of 6,000, its c/a ratio wassmaller than 1.011 as the same as single crystal value. Finally, to explain the origin of high dielectric constant, the model related to superparaelectric behavior was proposed.

14-25

Atomic Layer Deposition on Submicron ZrO_2 and $BaTiO_3$ Particles

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$BaTiO_3$ is a ferroelectric material with a large dielectric constant that is critical in the fabrication of multilayer ceramic capacitors (MLCs). Because of the ultrathin thickness of the dielectric layers in MLCs, submicron $BaTiO_3$ particles are used to fabricate the dielectric layers. In the past, $BaTiO_3$ particles could be mixed with other impurity particles to improve the properties of the dielectric layer. This approach is becoming increasingly difficult because the dielectric layer thickness is approaching the size of the individual particles. One solution is to coat the $BaTiO_3$ particles uniformly with ultrathin films to achieve homogeneous behavior in the thin dielectric layer.

Thin films can be deposited on particles using atomic layer deposition (ALD) techniques. ALD is performed using sequential, self-limiting surface reactions. ALD can achieve atomic layer controlled and conformal film growth. Our recent work has shown that ALD techniques can deposit conformal and atomic layer controlled films on various particles. Our examples in the literature are Al_2O_3 ALD on BN particles, SiO_2 ALD on BN particles and BN ALD on ZrO_2 particles. We have also recently demonstrated catalytic SiO_2 ALD on ZrO_2 and $BaTiO_3$ particles and ZnO ALD on ZrO_2 and $BaTiO_3$ particles. Our current research has focused on improving SiO_2 ALD on ZrO_2 and $BaTiO_3$ particles and developing new surface chemistry for Y_2O_3 ALD on ZrO_2 and $BaTiO_3$ particles. ZrO_2 particles are employed as model particles and yield excellent transmission electron microscopy (TEM) images.

The atomic layer deposition (ALD) of SiO_2 is very challenging. SiO_2 ALD can be accomplished using $SiCl_4$ and H_2O reactants at 600-800 K with large exposures of ~10^9 L or using TEOS and H_2O reactants at room temperature employing NH_3 as a catalyst with large reactant exposures of ~10^9 L. Recently, we have observed much more efficient SiO_2 ALD with $HSi[N(CH_3)_2]_3$ and H_2O_2 reactant exposures. $HSi[N(CH_3)_2]_3$ is tris-dimethylaminosilane (Tris-DMAS). SiO_2 ALD was studied using Fourier transform infrared (FTIR) spectroscopy to monitor the surface chemistry. The exposures required for the Tris-DMAS and H_2O_2 reactions were ~10^6L and ~10^7L, respectively. The SiO_2 thin films were deposited at temperatures ranging from 525-825 K. The maximum growth rate of 1.9 Å/cycle at 825 K was determined by measuring the SiO_2 film thickness by TEM. This talk will discuss our results for SiO_2 ALD and new results for Y_2O_3 ALD on ZrO_2 and $BaTiO_3$ particles.

14-26

Preparation and Characterization of the Cobalt Titanate $CoTiO_3$ Nanoparticles by Evaporation-Induced Self-Assembly

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The nanostructured photocatalyst of cobalt titanate, $CoTiO_3$ has been prepared by oxidation of $Co(OH)_2$ using titanium dioxide TiO_2 powder (P-25) as base material in cetyltrimethylammonium bromide (CTAB) micelle solutions, then followed the calcinations of the produced powders. These nanoparticles were investigated with X-ray powder diffraction (XRD), transmission electron microscopy (TEM), energy dispersive X-ray analysis (EDX), X-ray photoelectron spectroscopy (XPS) and thermogravimetric/differential thermal analysis (TGA/DTA) to determine the crystallite size and the phase composition. The spectroscopic characterizations of these nanoparticles were also down with UV-Vis spectroscopy and FT-Raman spectroscopy. XRD patterns show that $CoTiO_3$ phase was formed at calcinations temperature above 600 ^{0}C. The UV-Vis results showed that the $CoTiO_3$ nanoparticles have significant red shift to the visible region (400-700 nm). The new absorption peaks in FT-Raman also show the formation of Ti-O-Co bonds at above 600 ^{0}C and just not the mixtures of titanium dioxide with cobalt oxides.

14-27

Shrinking Composite Core-Shell Nanoparticles for Chemical Mechanical Planarization.

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The rate at which material is removed during Chemical Mechanical Planarization (CMP) and the degree of defectivity induced by this process are determined by the size, shape, concentration and hardness of the abrasives used in the polishing slurry. The tunable properties of polymer nanospheres, in particular size and hardness modulation, through synthesis design, make them particularly promising as cores in composite organic core/inorganic shell structures for application in CMP. In this work, monodisperse PMMA-based terpolymer particles were synthesized by suspension polymerization. Significant reaction parameters were varied in an effort to prepare particles with a wide and controllable range of size and polymer content. With the aim of understanding the effects of the amount of main monomer, MMA, we found that the average particle size increased within the range 250 to 550 nm with increasing amount in the feed as expected. The particle size distributions obtained were narrow, with a variation of ± 14 nm. The reaction temperature, varied in the range 60-80 °C, showed a significant impact on the polymerization rate and the final particle size and shape. Finally, the influence of the concentration of the initiator, 2,2'-Azobis(2-methylpropionamidine) dihydrochloride, is surprisingly less pronounced and the trend in the particle size behavior is ill-defined.