Colloid Chemical Approach to Nanotechnology

Janos H. Fendler

Center for Advanced Materials Processing, Clarkson University, Potsdam, NY 13699-5814, USA

Abstract – Colloid chemical methods for the preparation of nanoparticles and their self-assembly and organization into 2-dimensional arrays and three dimensional networks are surveyed. Potential applications of nanoparticles and nanostructured materials, fabricated by the wet colloid chemical approach, are also illustrated.

Key words: Colloids, Nanotechnology, Nanostructured Materials, Self-assembly, Nanoparticles

INTRODUCTION

The National Nanotechnology Initiative has been formally implemented in the United States in July 2000, with a $495 million budget request for fiscal 2001 [Schulz, 2000]. "The Initiative will develop the capacity to create affordable products with dramatically improved performance through gaining a basic understanding of ways to control and manipulate matter at the ultimate frontier - the nanometer - and through the incorporation of nanostructures and nanoprocesses into technological innovations. In addition to producing new technologies, the study of nanoscale systems also promises to lead to fundamentally new advances in our understanding of biological, environmental, and planetary systems" [http://www.nano.gov]. Efforts similar to the US National Natotechnology Initiative are underway in China, the European Community, Japan, Korea and other Countries.

Nanosized and/or nanostructured materials have dimensions, as their name implies, in the 1-100 nm range. Size quantization occurs in this region which manifests itself in physical and chemical properties which are distinctly different from those in the same bulk materials [Ozin, 1992; Weller, 1993; Markovich, 1999]. Exploitation of the size quantized nanoparticles and nanostructured materials is expected to lead to "breakthroughs in areas such as materials and manufacturing, nanoelectronics, medicine and healthcare, environment, energy, chemical, biotechnology, agriculture, information technology and national security [http://www.nano-gov]. There are two fundamentally different approaches to the fabrication of nanoparticles and nanostructured materials: "top down" and "bottom up" [Fendler, 1998]. Exhaustive grinding of bulk materials down to submicron particles illustrates the "top down" approach. Such industrial products as ferrofluids (liquid magnets) and components for photography are still fabricated by the ball-milling of bulk materials. The "bottom up" approach, based on the atom-by-atom or molecule-by-molecule assembly of nanoparticles, has the advantage of versatility and economy. Only the lack of our chemical knowledge and ingenuity limit the construction of nanoparticles and nanostructured materials by the "bottom up" method.

Colloid chemistry is particularly well suited for the "bottom up" fabrication of nanoparticles and nanostructured materials. It has suf-

ficiently matured to become quantitative and predictive thanks to recent instrumental and theoretical advances [Evans and Wennerstrom, 1994]. Furthermore, nanoparticles, by definition, are colloids and association colloids (micelles, microemulsions, vesicles, monolayers, bilayers) are often employed as templates and/or nanoreactors for the *in situ* generation of nanoparticles. Equally importantly, biomineralization, Mother Nature's construction of nanostructured materials, can be considered to be a colloidal process [Addadi and Weiner, 1991; Weiner and Addadi, 1997]. Indeed, the mimicking biomineralization has often provided a viable approach to the fabrication of nanoparticles and nanostructured materials [Fendler, 1992; Mann, 1996].

Attention is focused in the present review on the colloid chemical approach to nanotechnology. Specifically, nanoparticle preparations and their organization into two-dimensional arrays and three dimensional networks will be examined. Examples of potential applications of the nanoparticles and nanostructured materials, fabricated by a colloid chemical approach, will also be provided. No attempts will be made to cover the literature exhaustively. Instead, emphasis will be placed on general methodologies and on guiding the neophyte through the vast and diffuse literature.

COLLOID CHEMISTRY OF NANOPARTICLES

Dispersed colloidal particles have been around for over a century. Samples of beautiful deeply red colloidal gold dispersions prepared by Michael Faraday sometime in the eighteen-fifties are still stable and proudly displayed at the Royal Institution in London. The longevity of Faraday's colloidal gold dispersions rests upon the stabilization of the particles, probably by gelatin. In the absence of stabilizers the particles are attracted to each other by van der Waals forces (which increase inversely with the sixth power of the distance between the particle surfaces) and coagulate. Understanding the forces governing colloidal stabilities [Israelachvili, 1992] is an essential requirement for the preparation of colloidal nanoparticles. Stabilization of colloidal particles is, in fact, intimately involved in the preparation procedures.

Particles can be stabilized electrostatically and sterically (Fig. 1). The synergestic and concurrent particle preparation and electrostatic stabilization is illustrated by classical synthesis of 12 nm diameter gold particles [Turkevich et al., 1951]. The method involves the reduction of an aqueous gold chloride solution by sodium cit-
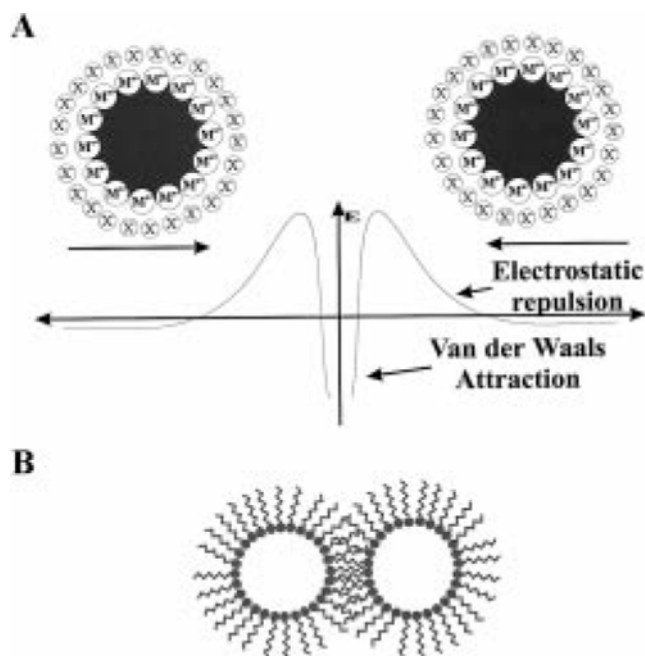
A

B

Fig. 1. Schematics of electrostatic (top) and steric (bottom) stabilization of particle dispersions. In the electrostatic stabilization attractive van der Waals forces are overcome by repulsive interactions between the ions (and associated counterions) adsorbed on the particles. Restricted motions of the polymers (adsorbed onto the particles) particles are responsible for their steric stabilization.

rate. The gold particles formed are coated by an electrical double layer (composed of bulky citrate ions, chloride ions and the cations attracted to them) responsible for the Coulombic repulsions which decays exponentially with increasing interparticle separations. There is a weak minimum in the van der Waals energy at an interparticle separation which approximately corresponds to the diameter of the stabilized gold nanoparticle. This minimum (where the attractive van der Waals forces are overcompensated by the repulsive electrostatic interactions) is responsible for the electrostatic stabilization of the gold colloids. However, compression of the electrical double layer (by increasing the ionic strength of the medium, or displacing the added ionic stabilizers) results in particle aggregation.

Steric stabilization is accomplished by adsorbing polymers and/ or surfactants onto the surfaces of colloidal particles. Intertwining of the adsorbed polymers (and/or surfactant) in the interparticle space restricts the conformational motion (entropy effect) and increases local polymer concentration (which has to be compensated by solvation=osmotic effect) which, in turn, results in the stabilization of the particle. It should be pointed out that stabilization of colloidal particles by long chain surfactants and/or polyelectrolytes involves *both* electrostatic and steric effects.

Coating (capping or derivatization) by molecules which form chemical bonds with or chemisorb onto the particles provides an extremely useful method of stabilization [Veinot 1997; Henglein and Meisel, 1998]. Thiols and dithiols have been demonstrated to be highly suitable capping-agents for metallic (particularly gold and silver) and semiconducting (CdSe, for example) nanoparticles (Fig.
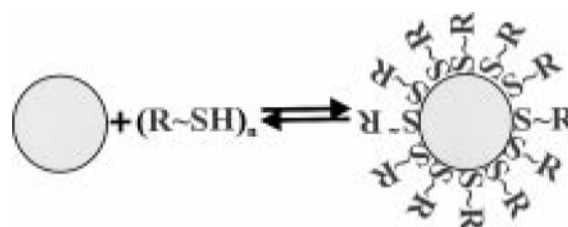

Fig. 2. Schematics of nanoparticle capping by alkylmercaptane molecules.

2). The capped nanoparticles can be separated from the dispersing solvent, stored as dried powders and redispersed on demand in a suitable solvent (polar solvent if the capping agent provides a hydrophilic surface and apolar solvent if the capping agent provides a hydrophobic surface) to form the same sized nanoparticles with the same degree of monodispersity [Steigerwald et al., 1998]. Nucleophilic reagents [Ko et al., 2000; Kim et al., 2000] have also been fruitfully employed as caps for nanoparticles. It should be remembered that capping (and stabilization by large ions, and/or surfactants and/or polymers) changes the surface states and surface properties of the nanoparticles.

Nanoparticles are also stabilized if they are *in situ* generated or trapped in (or on) templates or confined in the restricted volumes of nanoreactors. Once again, this way of stabilization is intimately connected to preparations and will be discussed, therefore, ion the subsequent section.

NANOPARTICLE PREPARATIONS

1. Precipitations in Homogeneous Solutions

Precipitation involves the nucleation of crystalline centers and subsequent growth of the incipient crystallites. In the absence of intervention bulk amorphous or crystalline materials are produced upon chemical precipitation. Control of the nucleation and growth is the requirements of forming monodispersed nanoparticles by precipitation [Matijevic, 1994]. In homogeneous solution this is accomplished by the judicious adjustment of the precipitating conditions (type, concentration, order and rate additions of the reagents and stabilizers or capping agents, stoichiometry, temperature, and solvent). Many submicron sized stable particle dispersions have been prepared by using the controlled double (or multi) jet precipitation process. Advantage has also been taken of ultrasonic power to form nanoparticles [Peters, 1996; Matai et al., 1999; Zhu et al., 2000; Kumar et al., 2000]. It is increasingly realized that the shapes as well as the electronic properties of the nanoparticles depend on the structure(s) of the capping (stabilizing) agents [Chemseddine, 1999].

2. Precipitation in and/or Incorporation onto (or into) Surfactant Aggregates and Templates

Such surfactant aggregates as aqueous micelles, reversed micelles, microemulsions (both oil-in-water, O/W and water-in-oil, W/O), surfactant vesicles and polymerized surfactant vesicles have been fruitfully employed as templates (and/or nanoreactors) for the *in situ* generation of nanoparticles [Fendler, 1982, 1992; Fox, 1991]. Alternatively, preformed nanoparticles have also been incorporated into surfactant aggregates. Aggregates referred to as aqueous mi-
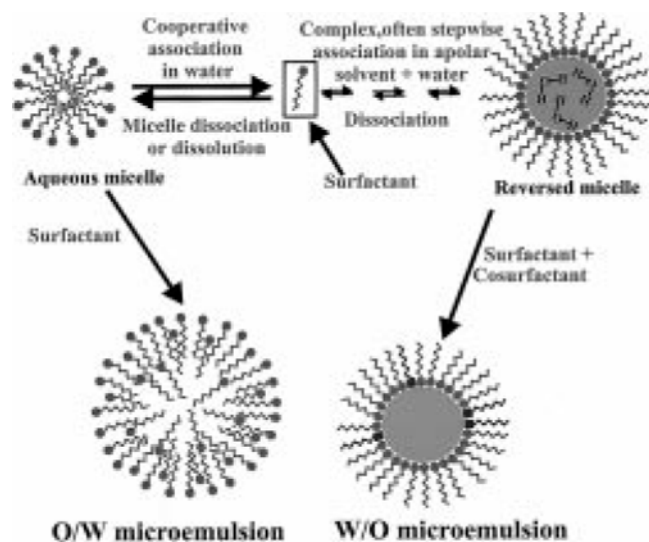
Fig. 3. Schematics of the formation of aqueous micelles, reversed micelles and of transformation, at higher surfactant concentrations, to oil-in-water (O/W) and water-in-oil (W/O) microemulsions.

celles are generated by the spontaneous association of *ca.* 50-100 surfactants (cationic, anionic, zwitterionic or neutral) above a characteristic concentration, known as the critical micelle concentration, (Fig. 3). The hydrodynamic diameters of aqueous micelles are on the order of 20-50 Å. Formation of aqueous micelles is a cooperative process. The opposing forces of repulsion between the polar headgroups and attraction between the hydrophobic chains of the surfactants are responsible for micellization. In general, the longer the hydrophobic tails are, the lower the CMC is. Micellar association is dynamic. Aqueous micelles rapidly break up and reform by two known processes. The first one, occurring on the microsecond time scale, corresponds to the release of a single surfactant from the micellar ensamble and subsequent reincorporation of it. The second process, taking place in the millisecond time-frame, corresponds to dissolution and subsequent reformation of the entire micelle. This very dynamic nature of aqueous micelles has limited their use as compartments for nanoparticle generation [Pileni, 1997].

Increasing the concentration of the surfactants in water above their CMC leads to the formation of rod-like micelles, oil in water microemulsions or liquid crystals. All these type of surfactant aggregates have been employed for nanoparticle generation [Tohver, 1997; Guo and Liu, 1997]. Of particular interest are the metallomesogens, the metal complexes of organic ligands which exhibit liquid crystalline behavior [Giroud-Godquin and Maitlis, 1991].

Surfactants having the appropriate hydrophobic - hydrophilic balance (sodium bis(2-ethylhexyl)sulfosuccinate, aerosol-OT or AOT, for example) undergo concentration dependent self-association in apolar solvents (hexane, for example) to form reversed or inversed micelles (Fig. 3) [Fendler, 1982]. Reversed micelles are capable of solubilizing a large number of water molecules ($[H_2O]/[AOT]=w=$ up to 60 for AOT, for example). This surfactant entrapped water pools in a bulk hydrocarbon solvent serve as the microreactor for the *in situ* generation of nanoparticles [Fendler, 1992; Pileni, 1997]. Reversed micelles are also dynamic; the water pools and their con-

tents are freely exchanging. This provides an opportunity for convenient nanoparticle preparations by mixing reactant precursors confined in two separate reversed micellar pools (a metal cation such as Cd^{2+} and Na_2S, for example). The possibility of controlling the water pool size (w) and the nature of the counterions also provide opportunities for controlling the size, shape and crystallinity of the incipient nanoparticles [Pileni, 1997]. Ultimate control is achieved, of course, by the prompt capping of the nanoparticles generated in reversed micelles.

Increasing the concentration of surfactant entrapped water results in the formation of larger aggregates which eventually become water-in-oil microemulsions (Fig. 3). At high surfactant and water concentrations the aggregate structures are best treated in terms of three (or multi) component phase diagrams.

Closed bilayer aggregates, formed from phospholipids (liposomes) or surfactant (vesicles) have also provided compartments for nanoparticles [Fendler, 1992]. Swelling of a thin lipid (or surfactant) films in water results in the formation of onion-like 100-800 nm diamter MultiLamellar Vesicles (MLV). Sonication of the MLV above the temperature at which they are transformed from a gel into a liquid (phase transition temperature) leads to the formation of fairly uniform Small (30-60 nm diameter) Unilamellar Vesiles (SUV; Fig. 4). SUV can also be prepared by injecting an alcohol solution of the surfactant through a small bore syringe into water, by detergent dialysis, by ultracentrifugation and by gel, membrane and ultrafiltration [Fendler, 1992]. Once formed, the SUV, unlike aqueous micelles, do not break down upon dilution. Surfactant vesicles, depending on composition and temperature of storage, remain stable for weeks to months. SUV can organize many guests in their compartments. Hydrophobic molecules may be distributed among the hydrocarbon bilayers and polar molecules may move relatively freely in the vesicle entrapped water pools, particularly if they are electrostatically repelled from the vesicle inner surface. The binding of small charged ions to the oppositely charged outer and/or inner vesicle surfaces is facile. Species with charges identical to those on the vesicle can be anchored onto the surfaces by
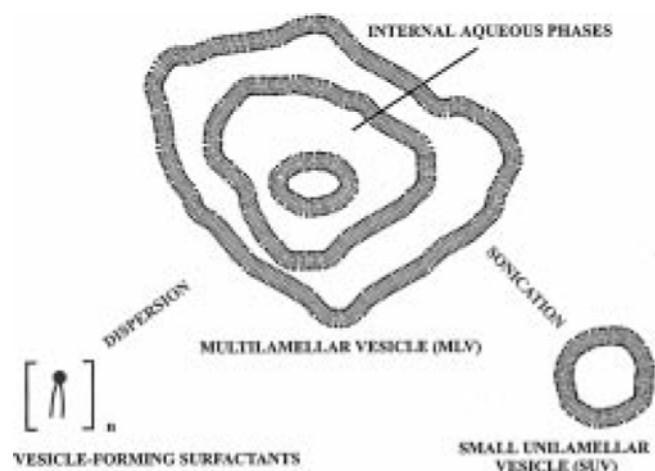

Fig. 4. Schematics of the formation of multilamellar surfactant vesicles (MLV) by the dispersion of a thin films of surfactant in water (by vortexing) and its subsequent transition to small single bilayer unilamellar vesicles (SUV) by sonication.

long hydrocarbon tails. This versatility permits a large variety of different approaches to the *in situ* generation of nanoparticles in SUV. Large (giant, *ca.* 1 μm diameter) Unilamellar Surfactant vesicles (LUV) have also been prepared.

SUVs have been stabilized by polymerization. Vesicle forming surfactants have been functionalized by vinyl, methacrylate, diacetylene, isocyano and styrene groups in their hydrocarbon tails or headgroups. Accordingly, SUV could be polymerized in their bilayers or across their headgroups. In the latter case, either the outer or the inner or both the outer and inner surfaces could be polymerized. Surfactant vesicles and polymerized vesicles have been extensively employed as compartments for the *in situ* generation of nanoparticles [Fendler, 1992; Kennedy et al., 1998; Correa et al., 2000].

Cadmium sulfide nanoparticles have also been generated in bacterial S-layer proteins [Shenton et al., 1997]. Nucleation was found to occur within the subunits in the and the resultant CdS nanoparticles arranged themselves in two-tier stacks. The structural diversity of the S-layer proteins opens the door to fabrication of a wide variety of 2D and 3D nanostructured materials.

Polymers have also been used as templates for the *in situ* generation or incorporation of nanoparticles. Particularly significant is the versatile use of dendrimers [Tomalia et al., 1990; Frechet et al., 1996; Percec et al., 1998; Sooklal et al., 1998; Fischer and Vigtle, 1999] and di- and tri-block copolymers [Bates et al., 1999; Leclere et al., 1998; Kane et al., 1999; Wang et al., 1999; Schrock et al., 1999; Spatz et al., 1996; Stupp, 1998; Rudoy et al., 1999; Colfen et al., 1999; Selvan et al., 1999; Nardin et al., 2000; Underhill and Liu, 2000]. Judicious selection of appropriate block copolymers in appropriate concentrations have resulted in the formation of large variety of self-assembled structures including those which resembled aqueous micelles, reversed micelles, microemulsions, surfactant vesicles and. All of these structure can, in principle, be used as templates for nanoparticle generation or incorporation.

The range of templates and/or compartment available for the *in situ* generation or incorporation of nanoparticles in controlled (or controllable) sizes and morphologies is limited only by the imagination and diligence of chemists and material scientists. Both natu-

rally occurring (zeolites, clay minerals, for example), naturally occurring but modified (pillared clay, for example) and artifical (porous glass, for example) have been employed. An interesting example is provided by using liquid crystal templating to form synthetic large pore zeolites (Fig. 5, Kresge et al., 1992): in the presence of silicate ions hexagonal arrays of cylindrical micelles are formed from surfactants with their polar groups in the exterior of the cylinders which are covered by silicates. Calcination results in the burning off the organic surfactants and leaves the inorganic silicate in the form of MCM-41 zeolites.

It should be remembered that rigid compartments and partial entrapping of nanoparticles therein obviate the need for surface coverage (ie., modification). Nanoparticles can be, therefore, examined (and employed) in their pristine states.

3. Soft Solution Processing-Hydrothermal Synthesis

Preparation of nanoparticles by Soft Solution Processing (ie., direct fabrication in aqueous solution at moderate temperatures and pressures) has increasing been gaining acceptance [Yoshimura and Livage, 2000]. Hydrothermal synthesis (hydrothermal technique) is a Soft Solution Processing which involves the heterogeneous reaction between powdered solids and water above ambient temperature and at pressure greater than 1 atm in a closed system [Byrappa and Yoshimura, 2000]. The relative ease (appropriate powdered reagents and water are placed in a teflon-lined autoclave and heated without stirring at moderate to high temperatures and pressures for the desired time) and the possibility of predicting optimum reaction conditions by electrolyte thermodynamics (in terms of phase diagrams) are the advantages of the hydrothermal synthesis [Lencka et al., 2000]. Hydrothermal reactions have also been carried out under microwave heating, ultrasonication, and applied electrical potential as well as employing solvent(s) under supercritical or near supercritical conditions [Yoshimura et al., 2000]. $BaTiO_3$, $SrTiO_3$, $LiNbO_3$, $LiNiO_2$, $LiCoO_2$, and PZT nanocrystalline thin films have been prepared by the hydrothermal synthesis [Yoshimura et al., 1999]. Remarkably, carbon coatings and carbide fibers [Gogotsi and Yoshimura, 1994] and even diamond [Zhao et al., 1997] have been prepared by this method.

4. Nanoparticle Formation in Aerosol Reactors

The term aerosol refers to a colloidal suspension of solid particles in a gas. Reacting nanoparticle precursors as aerosols at ambient and elevated temperature as well as in flames (flame pyrolysis) has been shown to be a suitable technique for the industrial production of metallic, semiconducting and ceramic particles and thin films therefrom [Pratsinis, 1998; Vallett-Regi et al., 1997; Valletregi et al., 1997; Kruis et al., 1998; Chow et al., 1998; Briesen et al., 1998; Jang and Friedlander, 1998; Kim and Park, 1999; Su and Choy, 2000]. Aerosol reactors have also been employed for the stabilization of nanoparticles by surface coating [Satoh and Kimura, 1989; Powell et al., 1997].

5. Electrodeposition

Electrochemical deposition of nanoparticles (or nanostructured films) is attractive since a high degree of control can achieved by the judicious employment of Faraday's laws (96,500 x n Coulumb results in the deposition of 1 gram mol of materials, where n is the number of electrons passed in depositing one mole of the deposit). Furthermore, composition, defect chemistry and shapes (along with thickness) is controllable at a reasonable cost. Both anodic and cath-
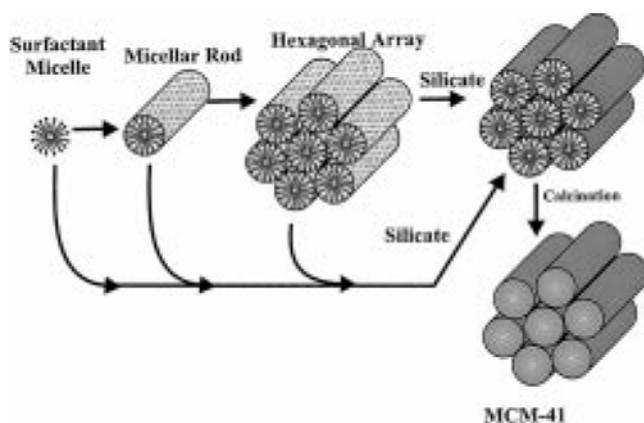

Fig. 5. Schematics of MCM-41 zeolite formation by the calcination of the silicate ions attached to the outer surfaces of hexagonal arrays of surfactants functioning as templates (modified from Kresge et al., 1992).

odic electrodepositions have been demonstrated. Anodic depositions are limited to metallic substrates since the process involves the electrolytic reduction of metal in the presence of the appropriate anions. Cathodic process is more versatile since both components of the semiconductor nanoparticles are both deposited from solution. Thus, for example, cadmium selenide nanoparticles were electrodeposited onto gold electrodes from hot dimethylsulfoxide solutions of Cadmium perchlorate, saturated by selenium at elevated temperatures [Hodes et al., 1998]. The method has been extended to the formation of composite Cd(Se, Te) and (Cd, Zn)Se nanocrystals. Interestingly, the size of the nanocrystallites did not depend on the temperature or current density but was related to mismatch induced strain [Golan et al., 1997]. Electrodeposition of MoS_2 [Ponomarev et al., 1997], ZnS [Mahamuni et al., 1999] nanoparticulate films, and CdS nanowires [Xu et al., 2000] have also been reported.

Particularly significant is the electrodeposition of nanostructured superlattices by pulsing either the applied current or potential of a solution containing precursors of *both* layers [Switzer, 1998]. Nanometer scale PB-Tl-O ceramic superlattice with a 0.3% mismatch was electrodeposited from aqueous solutions of 0.005 M, 0.005 M Tl(I) and 0.100 M Pb(II) in 5 M NaOH, for example [Phillips et al., 1997]. The defect composition was a found to be controllable by the overpotential; high overpotentials favored oxygen vacancies, low overpotential produced cation interstitials [Switzer, 1998].

ORGANIZATION OF NANOPARTICLES INTO 2D ARRAYS AND 3D NETWORKS

1. Generation of Nanoparticles and Nanostructured Materials Under Monolayers

Both chemical and electrochemical routes have been developed for the *in situ* generation of nanoparticles under monolayers [Fendler, 1992]. The experimental set-up used for the chemical generation and *in situ* monitoring of nanocrystalline particulate films is illustrated in Fig. 6. Typically, a surfactant monolayer is spread on an aqueous solution of the metal salt precursor of the nanoparticles and crystallization is induced by the injection of the reactant gas
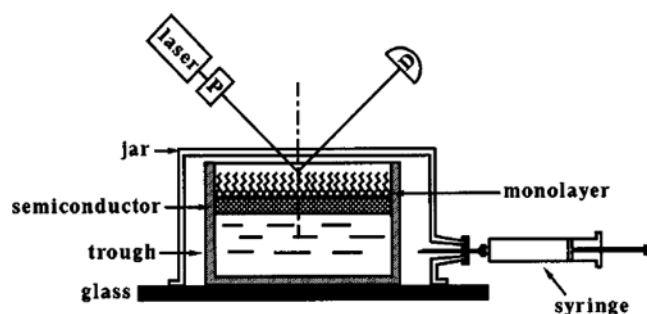

Fig. 6. **Schematics of the Langmuir through used for the** *in situ* **generation of nanoparticles and nanoparticulate films under monolayers. The aqueous phase contains a dilute aqueous solution of one of the precursors (cadmium perchlorate, for example) while the other precursor (H_2S, for example) is injected by the syringe. The growth of the nanoparticles can be monitored** *in situ* **(with Brewster angle microscopy using a laser, for example).**

into the closed system. Facilities are provided for determining surface pressure *vs.* surface area and surface potential *vs.* surface area isotherms in the film balance placed under the glass cover. Reflectivities, angle-dependent reflectivities, Brewster-angle and fluorescence microscopic images and non-linear optical parameters can also be monitored during the nanoparticle formation under the monolayer.

Nanoparticles have also been generated electrochemically under monolayers. A 1.0-mm-diameter, 3-cm-long silver electrode is immersed into the subphase (aqueous silver nitrate solution) and electrical connection is made through a 20-μm-diameter platinum electrode, floated (subsequent to monolayer formation) on the water surface at the middle of the trough. Ten to twenty minutes subsequent to monolayer formation, a potential of 1.8-1.9 V is applied across the electrodes (keeping Pt negative) by means of a DC power supply. With time, silver particles grow concentrically, forming larger and larger circles at the monolayer-water interface. The rate of this two-dimensional growth is typically 1-2 cm^2 per hour. Importantly, no silver particles are observed upon the application of the same potential to the water surface in the absence of surfactants or to monolayers prepared from positively charged surfactants. Negatively charged monolayers are essential to the electrochemical generation of silver particles; they prove binding sites for silver ions which are reduced at the cathodic surface. To-date, cadmium-sulfide, zinc-sulfide, lead-sulfide, cadmium-selenide, and lead-selenide semiconductor particulate and silver and gold metallic nanoparticulate films have been chemically grown, *in situ*, under monolayers in our laboratories [Kotov et al., 1993; Zhao et al., 1992; Yang et al., 1994, 1995; Yi et al., 1994; Yang and Fendler, 1995]. The formation of nanoparticulate films under monolayers by employing similar methodologies has been reported by other research groups [Pan et al., 1997; Liu, 1997].

Evolution of a nanocrystalline particulate film, as illustrated by the formation of sulfide semiconductor particulate films (Fig. 7), has been discussed in terms of the following steps: (a) formation of metal-sulfide bonds at a large number of sites at the monolayer-aqueous interface; (b) downward growth of well-separated nanocrystalline metal sulfide particles; (c) coalescence of clusters into interconnected arrays of semiconductor particles; (d) formation of the "first layer" of a porous sulfide semiconductor particuate film composed of 20- to 40-Å-thick, 30- to 80-Å-diameter particles; (e) diffusion of fresh metal ions to the monolayer head group area; (f) formation of a "second layer" of the porous sulfide semiconductor particulate film (by using steps a, b, and c); and (g) build-up of "subsequent layers" of the sulfide semiconductor particulate film (by using steps a, b, and c) up to a plateau thickness (ca. 300 Å for CdS and ca. 3,500 Å for ZnS) beyond which the film cannot grow.

The presence of a monolayer with an appropriate surface charge is essential to sulfide semiconductor particulate film formation. In the absence of a monolayer, infusion of H_2S over an aqueous metal-ion solution results in the formation of large, irregular, and polydispersed metal-sulfide particles which precipitate in the bulk solution before settling to the bottom of the trough.

The oriented growth requires the matching of the crystal lattice of the surfactants, constituting the monolayers, with that of the incipient nanocrystallites. Such epitaxial matching has been achieved by growing lead sulfide [12], lead selenide [13], and cadmium sul-
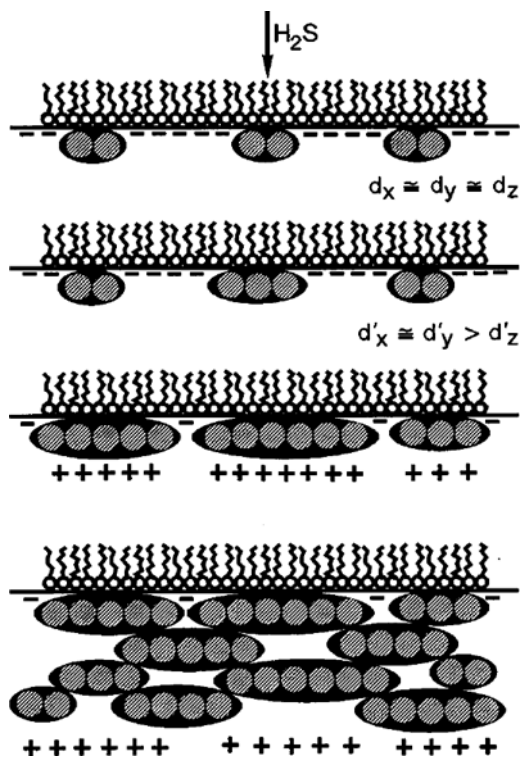
Fig. 7. Schematics of the growth of nanoparticulate films under monolayers. The time of infusion of H₂S gas is increased from top to bottom.

fide [14] under monolayers prepared from arachid acid (AA) and from mixtures of AA and octadecylamine (ODA). Differences in morphology between equilateral-triangular, right-angle-triangular PbS (epitaxially grown under monolayers, prepared from mixtures of AA and ODA in AA : ODA=1 : 0 and AA : ODA=1 : 1), and disk-shaped PbS (non-epitaxially grown under monolayers, prepared from hexadecylphosphate), manifested themselves in different spectroelectrochemical and electrical behavior [Zhao et al., 1992]. An important aspect of generating nanoparticles and nanoparticulate films under monolayers is that they can be transferred to substrates at any stages of their growth for *ex situ* characterizations and use as devices and sensors.

2. Incorporation into and *in situ* Generation of Nanoparticles and Nanostructured Materials between Langmuir-Blodgett Films

Langmuir-Blodgett (LB) films are now routinely and reproducibly formed by moving a clean plate through a monolayer, supported on an aqueous solution [Gaines, 1966; Fendler, 1982]. Hydrophobic substrates preferentially attract the tails of surfactants and the monolayer is transferred during immersion. Conversely, polar substrates favor the surfactant headgroups and monolayer transfer preferentially occurs during the withdrawal process. Repeated withdrawal and dipping of a hydrophilic substrate through the monolayer leads to the buildup of a substrate-head-tail-tail-head-head Y-type multilayer LB film. X-type multilayer deposition, in which the surfactants are organized substrate-tail-head-tail-head, or Y-type deposition, which is characterized by a substrate-head-tail-headtail arrangement, can be achieved by using alternative dippings.

Apposing surfactant headgroups in LB films, obtained by Y- or

X-type deposition, provide suitable sites for nanoparticles or nanoparticulate films. Indeed, size-quantized CdS [Smotkin et al., 1988; Grieser et al., 1992; Furlong et al., 1993; Xu et al., 1990; Moriguichi et al., 1994; Geddes et al., 1993; Peng et al., 1994; Pike et al., 1994; Luo et al., 1994; Urquart et al., 1994], CdSe [Grieser et al., 1992], CdTe [Grieser et al., 1992], CdSₓSe₁₋ₓ [Grieser et al., 1992], CdSₓTe₁₋ₓ [Luo et al., 1994], CdSeₓTe₁₋ₓ [Grieser et al., 1992], CoS [Luo et al., 1994], PbS [Peng et al., 1992], CdI₂ [Pike et al., 1994; Gao et al., 1994], CdBr₂ [Pike et al., 1994], and CdCl₂ [Pike et al., 1994], nanoparticles have been *in situ* generated by the exposure of the appropriate metal carboxylate(s) Y-type LB films to H₂S (or H₂Se, or H₂Te, or HI, or HBr, or HCl).

Alternatively, appropriately charged nanoparticle sols, dispersed in the subphase, can be electrostatically attracted to an oppositely charged monolayer surface and, thus, be inserted between LB films [Furlong et al., 1993; Xu et al., 1990; Peng et al, 1992; Tian et al., 1993]. The method is illustrated by the insertion of sodium hexametaphosphate- (HMP) stabilized CdS nanoparticles between the headgroups of LB films, formed from DODAB [Xu et al., 1990; Tian et al., 1993]. Stabilized Fe₃O₄ [64] and α-Fe₂O₃ [Zhao et al., 1990] nanoparticles have been similarly introduced into LB films.

3. Formation of Nanoparticles on Aqueous Subphases in a Langmuir Film-balance and their Layer-by-layer Transfer by the Langmuir-Blodgett Technique

Monoparticulate thick films can be formed at the air/water interface by dispersing surfactant-stabilized nanoparticles on an aqueous subphase which was contained in a Langmuir trough [Meldrum and Fendler, 1996]. The technique can be regarded as analogous to monolayer formation from simple surfactants. A similar approach has been applied to form monoparticulate layers from polystyrene microspheres [Pieranski, 1980; Robinson and Earnshaw, 1993; Armstrong et al., 1989], silylated glass beads [Horvolgyi et al., 1993], and organoclay complexes [Kotov et al., 1994]. There are many intrinsic benefits to this method. That the particles are prepared prior to their incorporation into the films enables their dimensions, physical properties, and the particle size distribution to be precisely controlled. Spreading the particles in a Langmuir trough provides a means for defining the interparticulate distances (Fig. 8) and facilitates subsequent transfer of the particulate films to a wide range of solid substrates by using standard Langmuir-Blodgett (LB) techniques. This may be contrasted with deposition techniques, where the quality of the film is highly dependent on the solid substrate itself.

Surfactant-coated cadmium sulfide, titanium dioxide, the magnetic iron oxide magnetite Fe₃O₄, ferroelectric barium titanate, lead zirconium titanate, platinum, palladium, and silver nanoparticles have been prepared to-date in our laboratories [Meldrum and Fendler, 1996]. Spreading of tryoctylphosphine-oxide-stabilized, nearly monodispersed CdSe nanoparticles [Daboussi et al., 1994] and Fe₂O₃ [Gao et al., 1994] microgels on water surfaces and their subsequent transfers to substrates by the LB technique have also been reported. In all cases, particulate films were spread on water in a Langmuir trough by dispersing solution aliquots from a Hamilton syringe. Physical properties of the monoparticulate films have been characterized, *in situ* on the water surface and subsequent to transfer to solid substrates, by using a range of physical techniques. The structures of the films on the water subphase have been examined
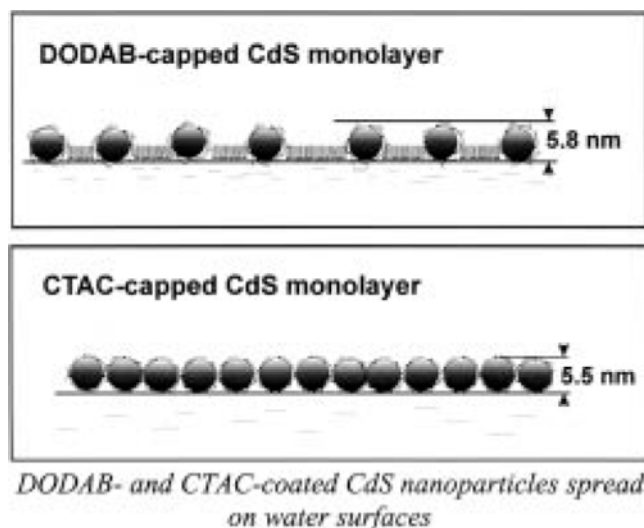
DODAB-capped CdS monolayer

5.8 nm

CTAC-capped CdS monolayer

5.5 nm

DODAB- and CTAC-coated CdS nanoparticles spread on water surfaces

Fig. 8. Schematics illustrating the control of interparticle distances in mono-particulate thick Langmuir films by different coatings.

on the micron scale by Brewster-angle microscopy (BAM) and at higher magnifications by transmission electron microscopy (TEM). Absorption spectroscopy and steady-state fluorescence spectroscopy can also be applied where appropriate and reflectivity measurements permitted the estimation of film thicknesses on water surfaces.

4. Self-assembly of Nanoparticles by Adsorption and Derivatization

Adsorption (either by physisorption of chemisorption) of nanoparticles onto substrate is the simplest method of fabricating self-organized 2D arrays and/or 3D networks. Adsorption is accomplished by dropping a few drops of dilute nanoparticle dispersion onto a suitable substrate (casting) and evaporating the solvent (usually slowly and in a controlled environment) [Brinker et al., 1999; Potter, 1999; Andres et al., 1996]. Alternatively, the substrate is immersed into a dilute nanoparticle dispersion (for a time optimized for the adsorption), withdrawn, rinsed and dried. Depending on the surface modifiers and on the dielectric constant of the medium TiO$_2$ particles self-assembled into cubic arrays [Brooks and Gratzel, 1998], or rodlike structures [Rajh et al., 1999]. Silver nanoparticles have been similarly deposited onto electrodes [Bright et al., 1998].

Crystallization of suitably derivatized nanoparticles into well ordered arrays have also been demonstrated [Chen et al., 1999; Yin and Wang, 1999; Park and Xia, 1999]. Differently sized alkanethiol derivatized gold nanoparticles, depending on experimental conditions, organized themselves into ordered bimodal arrays, size segregated regions of hexagonal close-packed monodispersed particles and random arrangements of pseudohexagonal lattices [Kiely et al., 1998]. Advantage has also been taken of capillary forces [Breen et al., 1999; Wei et al., 2000], temperature control [Boal et al., 2000] and dialysis [Adachi, 2000] to drive millimeter scale objects and gold nanoparticles into three dimensional crystalline arrays.

Nanoparticles can be capped (derivatized) and tethered to a substrate to form ordered two-dimensional networks and three dimensional arrays. Two different approaches have been used. The first

(and historically the earlier, Sagiv, 1980) approach involved the self-assembly of a bifunctional monolayer onto a substrate (ie., formation of a self-assembled monolayer, SAM) and then the subsequent attachment of the nanoparticles to the monolayers [Meldrum et al., 1997; Sato et al., 1997]. Nanoparticles themselves were derivatized by bifunctional molecules and then subsequently connected to each other and to substrates [Brust et al., 1998; Baum et al., 1999]. Thus, the formation of multilayer films have have been reported upon the deposition of 6 nm gold particles, stabilized by α,ω-dithiols onto glass substrates [Fan and Lopez, 1997; Brust et al., 1998]. Alternatively, decomposition of AuCl (NH$_2$R; R=C$_8$H$_{17}$; C$_{12}$H$_{25}$; C$_{16}$H$_{33}$) complexes resulted in the formation of self-organized fibrous material [Gomez et al., 2000].

5. Layer-by-layer Electrostatic Self-assembly

Self-assembly of alternating layers of oppositely charged polyelectrolytes and nanoparticles (or nanoplatelets) is deceptively simple (see Fig. 9). Self-assembly is governed by a delicate balance between adsorption and desorption equilibria. In the self-assembly of nanoparticles, for example, the efficient adsorption of one (and only one) mono-particulate layer of nanoparticles onto the oppositely charged substrate surface is the objective of the immersion step. Desorption of nanoparticles forming a second and additional layers (and preventing the desorption of the first added layer) is the purpose of the rinsing process. The optimization of the self-assembly in terms of maximizing the adsorption of nanoparticles from
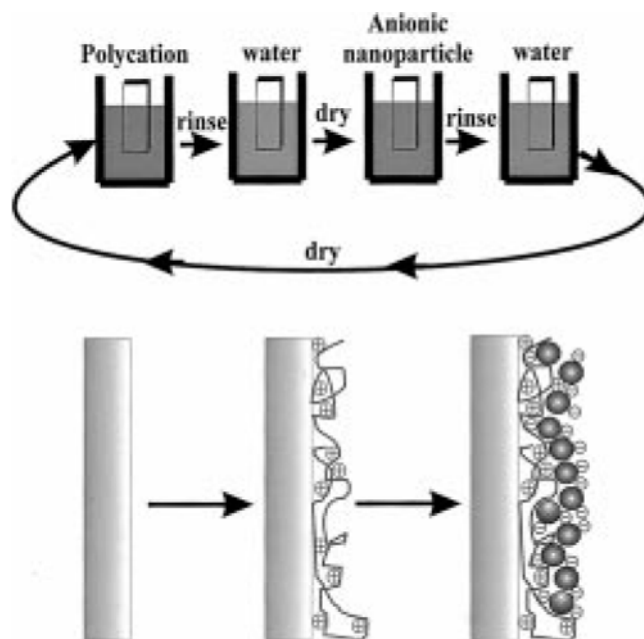
Fig. 9. Schematics of spontaneous self-assembly of a nanostructured film. A well cleaned substrate is immersed into a dilute aqueous cationic polyelectrolyte solution for a time optimized for the adsorption of a 2.0±0.5 thick polymer, rinsed and dried. Next the polycation coated substrate is immersed into a dilute dispersion of negatively charged nanoparticles for a time optimized for adsorption of a monoparticulate layer, rinsed and dried to form an organic-inorganic sandwich unit. Subsequent sandwich units are deposited analogously. The method is amenable to the fabrication of more complex superlattices.

their dispersions and minimizing their desorption on rinsing requires the judicious selection of stabilizer(s) and the careful control of the kinetics of the process.

Forces between nanoparticles (or nanoplatelets) and binder nanolayers (polyions or dithiols, for example) govern the spontaneous layer-by-layer self-assembly of ultrathin films. These forces are primarily electrostatic and covalent (for self-assembled monolayers, SAMs, of dithiol derivatives onto metallic surfaces) in nature, but they can also involve hydrogen bonding, π-π interactions, van der Waals attractions, hydrophobic and epitaxial or other types of interactions. It is important to recognize that polyionic binders must have *displaceable* counterions in order to electrostatically bind them to the oppositely charged surface. The use of dithiols is only relevant with building blocks which incorporate accessible metal atoms, M (Au- and Ag-nanoparticles, for example), or semiconducting nanoparticles (MS and MSe, for example where M=Cd, Zn, Pb) in which covalent M-S bonds can be formed. The properties of the self-assembled multilayers depend primarily on the choice of the building blocks used, their rational organization and integration along the axis perpendicular to the substrate.

Sequential adsorption of oppositely charged colloids was reported in a seminal paper in [Iler, 1996]. Self-assembly was subsequently "rediscovered" and extended to the preparations of multilayers of polycations and phosphonate anions [Lee et al., 1988; Decher and Hong, 1991; Lvov et al., 1993; Fendler, 1996], as well as to the layering of polyelectrolytes [Decher and Hong, 1991]. Construction of electrodes coated by polyelectrolytes, clays and other materials often involved self-assembly [Brumfield et al., 1992; Bard et al., 1992] albeit the method had not been called as such. Self-assembly are now routinely employed for the fabrication of ultrathin films from charged nanoparticles (metallic, semiconducting, magnetic, ferroelectric, insulating, for example) nanoplatelets, (clays or graphite platelets, for example), proteins, pigments, and other supramolecular species [Mallouk et al., 1996; Decher, 1996; Fendler, 1996; Correa-Duerte et al., 1998].

That any of these species in any order can be layer-by-layer adsorbed is the greatest advantage of self-assembly. The oppositely charged species are held together by strong ionic bonds and form long lasting, uniform and stable films which are often impervious to solvents. No special film balance is required for the self-assembly; indeed the method has been referred to as a "Molecular Beaker Epitaxy" [Keller et al., 1994]. Furthermore, self-assembly is economical (dilute solutions and dispersions are used and the materials can be recovered) and readily amenable to scaling-up for the fabrication of large area defect-free devices on virtually any kind and shape of surfaces.

NANOPATTERNING

Substrate patterning to submicroscopic length scale by soft lithography (chemical nanopatterning) have been demonstrated to provide a viable alternative to the fabrication of electronic and memory storage devices [Xia and Whitesides, 1998; Xia et al., 1999]. Attachment of 2D arrays self-organized nanoparticles to substrate provide a valuable lithographic mask [Fery and Herminghaus, 1997; Hayes et al., 1997; Hayes and Shannon, 1998; Brune et al., 1998]. Spinodal dewetting of thin polymer film mediated phase separa-

tion permits patterning without a template [Higgins and Jones, 2000]. Simple rubbing the surface results in patterns of well-aligned polymer lines whose width is controlled by the thickness of the polymer film.

POTENTIAL APPLICATIONS

Application of nanoparticles ranges from catalysts to additives, surface modifiers and controlled delivery agents. Perhaps the greatest benefits of 2D and 3D self-assembled nanoparticles will be in the optical (and electro-optical) and information industry. Well organized 2D and 3D colloidal (photonic) crystals [Shen et al., 2000; Benisty et al., 2000] have been shown to function as periodic materials [Asher, 1994], Bragg diffracting nanosecond optical switches [Pan et al., 1997], single domain spectroscopy [Vlasov et al., 2000] sensors [Holtz et al., 1998] and optical components [Halevi et al., 1999].

The information industry comprises computing, communication, measurement and data storage. According to industry projections computers by 2010 should be 256 times as capable as the current generation. Feature sizes of this computer will have to be well below the 100 nm range. It is increasingly recognized that current technologies will not be able to scale to this level and that the colloid chemical bottom up fabrication will become the only economically feasible approach to components in the 10 nm range. Our approach using nanoparticle self assembly for the fabrication of charge storage and electron transfer devices have been recently reviewed [Cassagneau and Fendler, 2001].

REFERENCES

Adachi, E., "Three-dimensional Self-assembly of Gold Nanocolloids in Spheroids Due to Dialysis in the Presence of Sodium Mercaptoacetate," *Langmuir*, **16**, 6460 (2000).

Addadi, L. and Weiner, S., "Control and Design Principles in Biological Mineralization," *Angewandte Chemie*, **31**, 153 (1991).

Andres, R. P., Bielefeld, J. D., Henderson, J. I., Janes, D. B., Kolagunta, V. R., Kubiak, C. P., Mahoney, W. J. and Osifchin, R. G., "Self-assembly of a Two-dimensional Superlattice of Molecularly Linked Metal Clusters," *Science*, **273**, 1690 (1996).

Armstrong, A. J., Mockler, R. C. and O'Sullivan, W. J., "Isothermal-expansion Melting of Two-dimensional Colloidal Monolayers on the Surface of Water," *Journal of Physics-Condensed Matter*, **1**, 1707 (1989).

Asher, S. A., Holtz, J., Liu, L. and Wu, Z., "Self-assembly Motif for Creating Submicron Periodic Materials. Polymerized Crystalline Colloidal Arrays," *Journal of the American Chemical Society*, **116**, 4997 (1994).

Barbour, K., Ashokkumar, M., Caruso, R. A. and Grieser, F., "Sonochemistry and Sonoluminescence in Aqueous AuCl₄-Solutions in the Presence of Surface-active Solutes," *Journal of Physical Chemistry B*, **103**, 9231 (1999).

Bard, A. J. and Mallouk, T., "Electrodes Modified with Clays, Zeolites, and Related Microporous Solids," in Molecular Design of Electrode Surfaces," R. W. Murray Ed., John Wiley & Sons, New York, 270 (1992).

Bates, F. S. and Fredrickson, G. H., "Block Copolymers - Designer

Soft Materials," *Physics Today*, 32 (1999).

Baum, T., Bethell, D., Brust, M. and Schiffrin, D. J., "Electrochemical Charge Injection into Immobilized Nanosized Gold Particle Ensembles: Potential Modulated Transmission and Reflectance Spectroscopy," *Langmuir*, **15**, 866 (1999).

Benisty, H., Weisbuch, C., Labilloy, D. and Rattier, M., "Photonic Crystals in Two-dimensions Based on Semiconductors: Fabrication, Physics and Technology," *Applied Surface Science*, **164**, 205 (2000).

Boal, A. K., Ilhan, F., DeRouchey, J. E., Thurn-Albrecht, T., Russell, T. P. and Rotello, V. M., "Self-assembly of Nanoparticles into Structured Spherical and Network Aggregates," *Nature*, **404**, 746 (2000).

Breen, T. L., Tien, J., Oliver, S. R. J., Hadzic, T. and Whitesides, G. M., "Design and Self-assembly of Open, Regular, 3D Mesostructures," *Science*, **284**, 948 (1999).

Briesen, H., Fuhrmann, A. and Pratsinis, S. E., "Electrically Assisted Aerosol Reactors using Ring Electrodes," Briesen, H., Fuhrmann, A., Pratsinis, S. E., Ed., Materials Research Society Proceedings, **520**, 3 (1998).

Bright, R. M., Musick, M. D. and Natan, M. J., "Preparation and Characterization of Ag Colloid Monolayers," *Langmuir*, **14**, 5695 (1998).

Brinker, C. J., Lu, Y. F., Sellinger, A. and Fan, H. Y., "Evaporation-induced Self-assembly: Nanostructures Made Easy," *Advanced Materials*, **11**, 579 (1999).

Brooks, K. and Gratzel, M., "Self-organization of TiO_2 Nanoparticles in Thin Films," *Chemistry of Materials*, **10**, 2419 (1998).

Brune, H., Giovannini, M., Bromann, K. and Kern, K., "Self-organized Growth of Nanostructure Arrays on Strain-relief Patterns," *Nature*, **394**, 451 (1998).

Brust, M., Bethell, D., Kiely, C. J. and Schiffrin, D. J., "Self-assembled Gold Nanoparticle thin Films with Nonmetallic Optical and Electronic Properties," *Langmuir*, **14**, 5425 (1998).

Byrappa, K. and Yoshimura, M., "Handbook of Hydrothermal Technology," William Andrews, LCC/Noyes Publications, Park Ridge, NJ (2000).

Cassagneau, T. and Fendler, J. H., "Electron Transfer and Charge Storage in Ultrathin Films Layer-by-Layer Self-assembled from Polyelectrolytes, Nanoparticles and Nanoplatelets," to be published in Electrochemical Approach to Nanoparticles, G. Hodes, Ed., VCH-Wiley, Weinheim (2001).

Chemseddine, A. and Moritz, T., "Nanostructuring Titania - Control over Nanocrystal Structure, Size, Shape, and Organization," *European Journal of Inorganic Chemistry*, 235 (1999).

Chen, Y. Y., Baker, G. L., Ding, Y. Q. and Rabolt, J. F., "Self-assembly through Stepwise Crystallization," *Journal of the American Chemical Society*, **121**, 6962 (1999).

Colfen, H., Schnablegger, H. and Antonietti, M., "Stabilization of Metal Nanoparticles in Aqueous Medium by Polyethyleneoxide-polyethyleneimine Block Copolymers," *Journal of Colloid and Interface Science*, **212**, 197 (1999).

Correa, N. M., Zhang, H. G. and Schelly, Z. A., "Preparation of AgBr Quantum Dots via Electroporation of Vesicles," *Journal of the American Chemical Society*, **122**, 6432 (2000).

Correa-Duarte, M. A., Giersig, M., Kotov, N. A. and Liz-Marzan, L. M., "Control of Packing Order of Self-assembled Monolayers of Magnetite Nanoparticles With and Without SiO_2 Coating by Microwave Irradiation," *Langmuir*, **14**, 6430 (1998).

Dabbousi, B. O., Murray, C. B., Rubner, M. F. and Bawendi, M. G., "Langmuir-blodgett Manipulation of Size-selected CdSe Nanocrystallites," *Chemistry of Materials*, **6**, 216 (1994).

Dantsin, G. and Suslick, K. S., "Sonochemical Preparation of a Nanostructured Bifunctional Catalyst," *Journal of the American Chemical Society*, **122**, 5214 (2000).

Decher, G. and Hong, J. D., "Buildup of Ultrathin Multilayer Films by a Self-assembly Process: II. Consecutive Adsorption of Anionic and Cationic Bipolar Amphiphiles and Polyelectrolytes on Charged Surfaces," *Berichte der Bunsen-Gesellschaft für Physikalische Chemie*, **11**, 1430 (1991).

Decher, G., "Layered Nanoarchitectures via Directed Assembly of Anionic and Cationic Molecules; in Comprehensive Supramolecular Chemistry," Sauvage, J.-P., Ed., Pergamon Press: Oxford, **9**, 507 (1996).

Dhas, N. A. and Gedanken, A., "A Sonochemical Approach to the Surface Synthesis of Cadmium-sulfide Nanoparticles on Submicron Silica," *Applied Physics Letters*, **72**, 2514 (1998).

Evans, D. F. and Wennerstrom, H., "The Colloid Domain. Where Physics, Chemistry and Technology Meet," VCH, New York (1994).

Fan, H. Y. and Lopez, G. P., "Adsorption of Surface-modified Colloidal Gold Particles onto Self-assembled Monolayers: A Model System for the Study of Interactions of Colloidal Particles and Organic Surfaces," *Langmuir*, **13**, 119 (1997).

Fendler, J. H., "Membrane Mimetic Approach to Advanced Materials," Springer-Verlag, Berlin (1992).

Fendler, J. H., "Nanoparticles and Nanostructured Films. Preparation, Characterization and Applications," Wiley-VCH, Weinheim (1998).

Fendler, J. H., "Membrane Mimetic Chemistry, Characterizations and Applications of Micelles, Microemulsions, Monolayers, Bilayers, Vesicles, Host-Guest Systems and Polyions," John Wiley, New York (1982).

Fendler, J. H., "Self-assembled Nanostructured Materials," *Chemistry of Materials*, **8**, 1616 (1996).

Fery, A. and Herminghaus, S., "The Formation of Nano-dot and Nano-ring Structures in Colloidal Monolayer Lithography," *Langmuir*, **13**, 7080 (1997).

Fink, J., Kiely, C. J., Bethell, D. and Schiffrin, D. J., "Self-organization of Nanosized Gold Particles," *Chemistry of Materials*, **10**, 922 (1998).

Fischer, M. and Vogtle, F., "Dendrimers: From Design to Application - A Progress Report," *Angewandte Chemie-International Edition*, **38**, 885 (1999).

Flagan, R. C., "Nanoparticles and Nanostructures - Aerosol Synthesis and Characterization," Flagan, R. C., Ed., Kluwer Academic Publ: PO Box 17, 3300 AA Dordrecht, Netherlands, 15 (1998).

Fox, M. A., "Semiconductor Particles Included within Supports," *Research on Chemical Intermediates*, **15**, 153 (1991).

Frechet, J. M. J., Hawker, C. J., Gitsov, I. and Leon, J. W., "Dendrimers and Hyperbranched Polymers: Two Families of Three- Dimensional Macromolecules with Similar but Clearly Distinct Properties," *Journal of Macromolecular Science- Pure and Applied Chemistry*, **a33**, 1399 (1996).

Furlong, D. N., Urquhart, R., Grieser, F., Tanaka, K. and Okahata, Y., "Size-quantised Cadmium Sulfide Particles in Langmuir-Blodgett Films: Film Thermal Stability," *Journal of the Chemical Society-Faraday Transactions*, **89**, 2031 (1993).

Gaines, G. L., "Insoluble Monolayers at Liquid-Gas Interfaces," Interscience, New York (1966).

Gao, M. Y., Peng, X. G. and Shen, J. C., "Polymer Langmuir-Blodgett-Film of Organic-Inorganic (Fe$_2$O$_3$) Composite Microgel," *Thin Solid Films*, **244**, 106 (1994).

Geddes, N. J., Urquhart, R. S., Furlong, D. N., Lawrence, C. R., Tanaka, K. and Okahata, Y., "Growth of CdS Particles in Cadmium Arachidate Films: Monitoring by Surface Plasmon Resonance, UV-Visible Absorption Spectroscopy, and Quartz Crystal Microgravimetry," *Journal of Physical Chemistry B*, **97**, 13767 (1993).

Giroud-Godquin, A.-M. and Maitlis, P. M., "Metallomesogens: Metal Complexes in Organized Fluid Phases," *Angewandte Chemie, International Edition in English*, **30**, 375 (1991).

Gogotsi, Y. G. and Yoshimura, M., "Formation of Carbon-Films on Carbides Under Hydrothermal Conditions," *Nature*, **367**, 628 (1994).

Golan, Y., Alperson, B., Hutchison, J. L., Hodes, G. and Rubinstein, I., "Electrodeposited Quantum Dots: Coherent Nanocrystalline CdSe on Oriented Polycrystalline Au Films," *Advanced Materials*, **9**, 236 (1997).

Gomez, S., Philippot, K., Colliere, V., Chaudret, B., Senocq, F. and Lecante, P., "Gold Nanoparticles from Self-assembled Gold (I) Amine Precursors," *Chemical Communications*, 1945 (2000).

Grieser, F., Furlong, D. N., Scoberg, D., Ichinose, I., Kimizuka, N. and Kunitake, T., "Size-quantised Semiconductor Cadmium Chalcogenide Particles in Langmuir-Blodgett Films," *Journal of the Chemical Society-Faraday Transactions*, **88**, 2207 (1992).

Guo, R. and Liu, T. Q., "The Synthesis of PbS Fine Particles in the Triton X-100/C$_{10}$H$_{21}$OH/H$_2$O Lamellar Liquid Crystal," *Colloids and Surfaces A- Physicochemical and Engineering Aspects*, **123**, 587 (1997).

Halevi, P., Krokhin, A. A. and Arriaga, J., "Photonic Crystals as Optical Components," *Applied Physics Letters*, **75**, 2725 (1999).

Hayes, W. A. and Shannon, C., "Nanometer-scale Patterning of Surfaces using Self-assembly Chemistry. 3. Template-directed Growth of Polymer Nanostructures on Organothiol Self-assembled Mixed Monolayers," *Langmuir*, **14**, 1099 (1998).

Henglein, A. and Meisel, D., "Spectrophotometric Observations of the Adsorption of Organosulfur Compounds on Colloidal Silver Nanoparticles," *Journal of Physical Chemistry B*, **102**, 8364 (1998).

Higgins, A. M. and Jones, R. A. L., "Anisotropic Spinodal Dewetting as a Route to Self-assembly of Patterned Surfaces," *Nature*, **404**, 476 (2000).

Hodes, G., Golan, Y., Behar, D., Zhang, Y., Alperson, B. and Rubinstein, I., "Electrodeposited Quantum Dots: Size Control by Semiconductor—Substrate Lattice Mismatch; in Nanoparticles and Nanostructured Films," Fendler, J. H. Ed., Wiley-VCH: Weinheim, Germany, 1 (1998).

Holtz, J. H., Holtz, J. S. W., Munro, C. H. and Asher, S. A., "Intelligent Polymerized Crystalline Colloidal Arrays - Novel Chemical Sensor Materials," *Analytical Chemistry*, **70**, 780 (1998).

Horvolgyi, Z., Nemeth, S. and Fendler, J. H., "Spreading of Hydrophobic Silica Beads at Water Air Interfaces," *Colloids and Surfaces A- Physicochemical and Engineering Aspects*, **71**, 327 (1993).

http://www.nano.gov, "National Nanotechnology Initiative: The Initiative and its Implementation Plan," pulled 10-31 (2000).

Iler, R. K., "Multilayers of Colloidal Particles," *Journal of Colloid and Interface Science*, **21**, 569 (1966).

Israelachvili, J. N., "Intermolecular Surface Forces," 2nd ed, Academic Press, San Diego (1992).

Jang, H. D. and Friedlander, S. K., "Restructuring of Chain Aggregates of Titania Nanoparticles in the Gas-Phase," *Aerosol Science and Technology*, **29**, 81 (1998).

Kamat, P. V. and Vinodgopal, K., "Sonochromic Effect in WO3 Colloidal Suspensions," *Langmuir*, **12**, 5739 (1996).

Kane, R. S., Cohen, R. E. and Silbey, R., "Synthesis of Doped ZnS Nanoclusters within Block Copolymer Nanoreactors," *Chemistry of Materials*, **11**, 90 (1999).

Keller, S. W., Kim, H. N. and Mallouk, T. E., "Layer-by-Layer Assembly of Intercalation Compounds and Heterostructures on Surfaces - Toward Molecular Beaker Epitaxy," *Journal of the American Chemical Society*, **116**, 8817 (1994).

Kho, R., Torres-Martinez, C. L. and Mehra, R. K., "A Simple Colloidal Synthesis for Gram-quantity Production of Water- soluble ZnS Nanocrystal Powders," *Journal of Colloid and Interface Science*, **227**, 561 (2000).

Kiely, C. J., Fink, J., Brust, M., Bethell, D. and Schiffrin, D. J., "Spontaneous Ordering of Bimodal Ensembles of Nanoscopic Gold Clusters," *Nature*, **396**, 444 (1998).

Kim, B. S., Avila, L., Brus, L. E. and Herman, I. P., "Organic Ligand and Solvent Kinetics During the Assembly of CdSe Nanocrystal Arrays using Infrared Attenuated Total Reflection," *Applied Physics Letters*, **76**, 3715 (2000).

Kim, K. Y. and Park, S. B., "Preparation of Nanosize SnO$_2$ Particles in an Aerosol Reactor by Pyrolysis of Tetra-n-butyl Tin," *Journal of Materials Science*, **34**, 5783 (1999).

Kotov, N. A., Meldrum, F. C., Fendler, J. H., Tombacz, E. and Dekany, I., "Spreading of Clay Organocomplexes on Aqueous-solutions - Construction of Langmuir-blodgett Clay Organocomplex Multilayer Films," *Langmuir*, **10**, 3797 (1994).

Kotov, N. A., Zaniquelli, E. D., Meldrum, F. C. and Fendler, J. H., "Two-dimensional Silver Electrocrystallization Under Monolayers Spread on Aqueosu Silver Nitrate," *Langmuir*, **9**, 3710 (1993).

Kresge, C. T., Leonowicz, M. E., Roth, W. J., Vartuli, J. C. and Beck, J. S., "Ordered Mesoporous Molecular Sieves Synthesized by a Liquid-crystal Template Mechanism," *Nature*, **359**, 710 (1992).

Kruis, F. E., Nielsch, K., Fissan, H., Rellinghaus, B. and Wassermann, E. F., "Preparation of Size-classified PbS Nanoparticles in the Gas-phase," *Applied Physics Letters*, **73**, 547 (1998).

Kumar, R. V., Diamant, Y. and Gedanken, A., "Sonochemical Synthesis and Characterization of Nanometer-size Transition Metal Oxides from Metal Acetates," *Chemistry of Materials*, **12**, 2301 (2000).

Leclere, P., Parente, V., Bredas, J. L., Francois, B. and Lazzaroni, R., "Organized Semiconducting Nanostructures from Conjugated Block Copolymer Self-assembly," *Chemistry of Materials*, **10**, 4010 (1998).

Lee, H., Kepley, L. J., Hong, H.-G. and Mallouk, T. E., "Inorganic Analogues of Langmuir-blodgett Films: Adsorption of Ordered Zirconium 1,10-decanebisphosphonate Multilayers on Silicon Surfaces," *Journal of the American Chemical Society*, **110**, 618 (1988).

Lencka, M. M., Oledzka, M. and Riman, R. E., "Hydrothermal Synthesis of Sodium and Potassium Bismuth Titanates," *Chemistry of Materials*, **12**, 1323 (2000).

Liu, J. Z., "Controlled Growth of the Ordered Cadmium Sulfide Particulate Films and the Photoacoustics Investigation," *Journal of Physical Chemistry B*, **101**, 9703 (1997).

Luo, X. Z., Zhang, Z. Q., Liang, Y. Q., "Structure of Cobalt Stearate and Cobalt Sulfide Stearic-acid Langmuir-Blodgett-Films," *Langmuir*, **10**, 3213 (1994).

Lvov, Y., Haas, H., Decher, G., Mohwald, H. and Kalachev, A., "Assembly of Polyelectrolyte Molecular Films onto Plasma-treated Glass," *Journal of Physical Chemistry B*, **97**, 12835 (1993).

Mahamuni, S., Borgohain, K., Bendre, B. S., Leppert, V. J. and Risbud, S. H., "Spectroscopic and Structural Characterization of Electrochemically Grown ZnO Quantum Dots," *Journal of Applied Physics*, **85**, 2861 (1999).

Mallouk, T. E., Kim, H.-N., Ollivier, P. J. and Keller, S. W., "Ultrathin Films based on Layered Inorganic Solids; in Comprehensive Supramolecular Chemistry, Vol VII: Solid State Supramolecular Chemistry: Two- and Three-Dimensional Inorganic Networks, part I. Layered Solids and Their Intercalation Chemistry," Alberti, G; Bein, T., Pergamon Press, Oxford, 189 (1996).

Mann, S., "Biomimetic Materials Chemistry," VCH, New York (1996).

Markovich, G., Collier, P., Henrichs, S. E., Remacle, F., Levine, R. D. and Heath, J. R., "Architectonic Quantum Dot Solids," *Acc. Chem. Res.*, **32**, 415 (1999).

Mastai, Y., Polsky, R., Koltypin, Y., Gedanken, A. and Hodes, G., "Pulsed Sonoelectrochemical Synthesis of Cadmium Selenide Nanoparticles," *Journal of the American Chemical Society*, **121**, 10047 (1999).

Matijevic, E., "Uniform Inorganic Colloid Dispersions. Achievements and Challenges," *Langmuir*, **10**, 8 (1994).

Mdleleni, M. M., Hyeon, T. and Suslick, K. S., "Sonochemical Synthesis of Nanostructured Molybdenum Sulfide," *Journal of the American Chemical Society*, **120**, 6189 (1998).

Meldrum, F. C. and Fendler, J. H., "Construction of Organized Particulate Films by the Langmuir-Blodgett Technique," in "Biomimetic Approaches in Materials Chemistry," (Mann, S. E., Ed.) VC H, Weinheim, 175-219 (1996).

Meldrum, F. C., Flath, J. and Knoll, W., "Chemical Deposition of PbS on Self-assembled Monolayers of 16- Mercaptohexadecanoic Acid," *Langmuir*, **13**, 2033 (1997).

Moriguichi, I., Hosoi, K., Nagaoka, H., Tanaka, I., Teraoka, Y. and Kagawa, S., "Stepwise Growth of Size-confined CdS in the Two-dimensional Hydrophilic Interlayers of Langmuir-Blodgett Films by the Repeated Sulfidation-intercalation Technique," *Journal of the Chemical Society-Faraday Transactions*, **90**, 349 (1994).

Nardin, C., Thoeni, S., Widmer, J., Winterhalter, M. and Meier, W., "Nanoreactors Based on (Polymerized) ABA-triBlock Copolymer Vesicles," *Chemical Communications*, 1433 (2000).

Okitsu, K., Bandow, H., Maeda, Y. and Nagata, Y., "Sonochemical Preparation of Ultrafine Palladium Particles," *Chemistry of Materials*, **8**, 315 (1996).

Okitsu, K., Yue, A., Tanabe, S. and Matsumoto, H., "Sonochemical Preparation and Catalytic Behavior of Highly Dispersed Palladium Nanoparticles on Alumina," *Chemistry of Materials*, **12**, 3006 (2000).

Ozin, G. A., "Nanochemistry: Synthesis in Diminishing Dimensions," *Advanced Materials*, **4**, 612 (1992).

Pan, G. S., Kesavamoorthy, R. and Asher, S. A., "Optically Nonlinear Bragg Diffracting Nanosecond Optical Switches," *Phys. Rev. Lett.*, **78**, 3860 (1997).

Pan, Z. Y., Shen, G. J., Zhang, L. G., Lu, Z. H. and Liu, J. Z., "Preparation of Oriented Cadmium-Sulfide Nanocrystals," *J. Mater. Chem.*, 7, 531 (1997).

Park, S. H. and Xia, Y. N., "Assembly of Mesoscale Particles over Large Areas and its Application in Fabricating Tunable Optical Filters," *Langmuir*, **15**, 266 (1999).

Peng, J. B. and Barnes, G. T., "The 2-Dimensional Hexatic-B Phase of Single Langmuir-Blodgett Monolayers Observed by Atomic-force Microscopy," *Thin Solid Films*, **252**, 44 (1994).

Peng, X., Zhang, Y., Yang, J., Zou, B., Xiao, L. and Li, T., "Formation of Nanoparticulate Fe{-2}O{-3}-stearate Multilayer through the Langmuir-blodgett Method," *Journal of Physical Chemistry B*, **96**, 3412 (1992).

Peters, D., "Ultrasound in Materials Chemistry," *Journal of Materials Chemistry*, **6**, 1605 (1996).

Phillips, R. J., Golden, T. D., Shumsky, M. G., Bohannan, E. W. and Switzer, J. A., "Electrodeposition of Textured Ceramic Superlattices in the Pb-Tl-O System," *Chemistry of Materials*, **9**, 1670 (1997).

Pieranski, P., "Two-dimensional Interfacial Colloidal Crystals," *Physical Review Letters*, **45**, 569 (1980).

Pike, J. K., Byrd, H., Morrone, A. A. and Talham, D. R., "Oriented Cadmium Dihalide Particles Prepared in Langmuir-Blodgett-films," *Chemistry of Materials*, **6**, 1757 (1994).

Pileni, M. P., "Nanosized Particles Made in Colloidal Assemblies," *Langmuir*, **13**, 3266 (1997).

Ponomarev, E. A., Albu-Yaron, A., Tenne, R. and Levy-Clement, C., "Electrochemical Deposition of Quantized Particle MoS_2 thin Films," *Journal of the Electrochemical Society*, **144** (1997).

Potter, D. I., "Particle Size Control and Self-assembly Processes in Novel Colloids of Nanocrystalline Manganese Oxide," *Journal of Physical Chemistry B*, **103**, 7416 (1999).

Powell, Q. H., Fotou, G. P., Kodas, T. T., Anderson, B. M. and Guo, Y. X., "Gas-phase Coating of TiO_2 with SiO_2 in a Continuous Flow Hot-wall Aerosol Reactor," *Journal of Materials Research*, **12**, 552 (1997).

Pratsinis, S. E., "Flame Aerosol Synthesis of Ceramic Powders," *Progress in Energy and Combustion Science*, **24**, 197 (1998).

Prozorov, R. and Gedanken, A., "Encapsulation of Nickel Nanoparticles in Carbon Obtained by the Sonochemical Decomposition of $Ni(C_8H_{12})(2)$," *Chemistry of Materials*, **11**, 1331 (1999).

Rajh, T., Thurnauer, M. C., Thiyagarajan, P. and Tiede, D. M., "Structural Characterization of Self-organized TiO_2 Nanoclusters Studied by Small Angle Neutron Scattering," *Journal of Physical Chemistry B*, **103**, 2172 (1999).

Robinson, D. J. and Earnshaw, J. C., "Initiation of Aggregation in Colloidal Particle Monolayers," *Langmuir*, **9**, 1436 (1993).

Rudoy, V. M., Yaminskii, I. V., Dement'eva, O. V. and Ogarev, V. A., "Formation of Ordered Structures from Metal Nanoparticles in the Surface Layer of Glassy Polymer," *Colloid Journal*, **61**, 800 (1999).

Sagiv, J., "Organized Monolayers by Adsorption. 1. Formation and Structure of Oleophobic Mixed Monolayers on Solid Surfaces," *Journal of the American Chemical Society*, **102**, 92 (1980).

Sato, T., Brown, D. and Johnson, B. F. G., "Nucleation and Growth of Nano-gold Colloidal Lattices," *Chemical Communications*, 1007 (1997).

Satoh, N. and Kimura, K., "Metal Colloids Produced by Means of Gas Evaporation Technique. V. Colloidal Dispersion of Au Fine Particles to Hexane, Poor Dispersion Medium for Metal Sol," *Bulletin of the Chemical Society of Japan*, **62**, 1758 (1989).

Sawai, S., Tanaka, H., Morimoto, K., Hisano, K. and Yamamoto, T., "Simultaneous Measurements of Specific Heat Capacity and Dielectric Constant of Ferroelectric $Ba_{1-x}Sr_xTiO_3$," *Ferroelectrics*, **242**, 59 (2000).

Schrock, R. R., Thomas, E. L., Rubner, M. F. and Bawendi, M. G., "Composite thin Films of CdSe Nanocrystals and a Surface Passivating/Electron Transporting Block Copolymer: Correlations Between Film Microstructure by Transmission Electron Microscopy and Electroluminescence," *Journal of Applied Physics*, **86**, 4390 (1999).

Schulz, W, "Crafting a National Nanotechnology Effort," C&EN News, p. 39, October 16 (2000).

Selvan, S. T., Hayakawa, T., Nogami, M. and Moller, M., "Block Copolymer Mediated Synthesis of Gold Quantum Dots and Novel Gold-polypyrrole Nanocomposites," *Journal of Physical Chemistry B*, **103**, 7441 (1999).

Shafi, K. V. P. M. and Gedanken, A., "Sonochemical Approach to the Preparation of Barium Hexaferrite Nanoparticles," *Nanostructured Materials*, **12**, 29 (1999).

Shen, Y. Z., Friend, C. S., Jiang, Y., Jakubczyk, D., Swiatkiewicz, J. and Prasad, P. N., "Nanophotonics: Interactions, Materials, and Applications," *Journal of Physical Chemistry B*, **104**, 7577 (2000).

Smotkin, E. S., Lee, C., Bard, A. J., Campion, A., Fox, M. A., Mallouk, T. E., Webber, S. E. and White, J. M., "Size Quantization Effects in Cadmium Sulfide Layers formed by a Langmuir-blodgett Technique," *Chemical Physics Letters*, **152**, 265 (1988).

Sooklal, K., Hanus, L. H., Ploehn, H. J. and Murphy, C. J., "A Blue-emitting CdS/Dendrimer Nanocomposite," *Advanced Materials*, **10**, 1083 (1998).

Spatz, J. P., Mossmer, S. and Moller, M., "Mineralization of Gold Nanoparticles in a Block-copolymer Microemulsion," *Chemistry-A European Journal*, **2**, 1552 (1996).

Steigerwald, M. L., Alivisatos, A. P., Gibson, J. M., Harris, T. D., Kortan, R., Muller, A. J., Thayer, A. M., Duncan, T. M., Douglass, D. C. and Brus, L. E., "Surface Derivatization and Isolation of Semiconductor Cluster Molecules," *Journal of the American Chemical Society*, **110**, 3046 (1988).

Stupp, S. I., "Self-assembly of Rodcoil Molecules," *Current Opinion in Colloid & Interface Science*, **3**, 20 (1998).

Su, B. and Choy, K. L., "Synthesis, Microstructure and Optical Properties of ZnS Films formed by Electrostatic Assisted Aerosol Jet Deposition," *Journal of Materials Chemistry*, **10**, 949 (2000).

Suslick, K. S., Fang, M. M. and Hyeon, T., "Sonochemical Synthesis of Iron Colloids," *Journal of the American Chemical Society*, **118**, 11960 (1996).

Suslick, K. S., Hyeon, T. W. and Fang, M. M., "Nanostructured Materials Generated by High-intensity Ultrasound: Sonochemical Synthesis and Catalytic Studies," *Chemistry of Materials*, **8**, 2172 (1996).

Switzer, J. A., "Electrodeposition of Superlattices and nanocomposites; in Nanoparticles and Nanostructured Films," Fendler, J. H. Ed., Wiley-VCH: Weinheim, Germany, 53 (1998).

Tian, Y. C., Wu, C. J. and Fendler, J. H., "Fluorescence Activation and Surface-State Reactions of Size-Quantized Cadmium-Sulfide Particles in Langmuir-Blodgett-Films," *Journal of Physical Chemistry B*, **98**, 4913 (1994).

Tohver, V., Braun, P. V., Pralle, M. U. and Stupp, S. I., "Counterion Effects in Liquid Crystal. Templating of Nanostructured CdS," *Chemistry of Materials*, **9**, 1495 (1997).

Tomalia, D. A., Naylor, A. M. and Goddard III, W. A., "Starburst Dendrimers: Molecular-level Control of Size, Shape, Surface Chemistry, Topology, and Flexibility from Atoms to Macroscopic Matter," *Angewandte Chemie, International Edition in English*, **29**, 138 (1990).

Turkevich, J., Stevenson, P. C. and Hillier, J., "A Study of the Nucleation and Growth Processes in the Synthesis of Colloidal Gold," *Discussion of the Faraday Society*, 55 (1951).

Urquhart, R. S., Furlong, D. N., Mansur, H., Grieser, F., Tanaka, K. and Okahata, Y., "Quartz-crystal Microbalance and UV-VIS Adsorption Study of Q-state CdS Particle Formation in Cadmium Arachidate Langmuir-Blodgett-Films," *Langmuir*, **10**, 899 (1994).

Vallet-Regi, M., Nicolopoulos, S., Roman, J., Martinez, J. L. and Gonzalez-Calbet, J. M., "Structural Characterization of ZrO_2 Nanoparticles Obtained by Aerosol Pyrolysis," *Journal of Materials Chemistry*, **7**, 1017 (1997).

Valletregi, M., Nicolopoulos, S., Roman, J., Martinez, J. L. and Gonzalezcalbet, J. M., "Structural Characterization of ZrO_2 Nanoparticles Obtained by Aerosol Pyrolysis," *Journal of Materials Chemistry*, **7**, 1017 (1997).

Veinot, J. G. C., Ginzburg, M. and Pietro, W. J., "Surface Functionalization of Cadmium Sulfide Quantum-confined Nanoclusters. 3. Formation and Derivatives of a Surface Phenolic Quantum Dot," *Chemistry of Materials*, **9**, 2117 (1997).

Vlasov, Y. A., Deutsch, M. and Norris, D. J., "Single-domain Spectroscopy of Self-assembled Photonic Crystals," *Applied Physics Letters*, **76**, 1627 (2000).

Wang, D., Bai, Y. B., Li, T. J. and Tang, X. Y., "Size Control of CdS Nanocrystals in Block Copolymer Micelle," *Chemistry of Materials*, **11**, 392 (1999).

Wei, Q. H., Cupid, D. M. and Wu, X. L., "Controlled Assembly of Two-dimensional Colloidal Crystals," *Applied Physics Letters*, 77, 1641 (2000).

Weiner, S. and Addadi, L., "Design Strategies in Mineralized Biological Materials," *Journal of Materials Chemistry*, 7, 689 (1997).

Weller, H., "Quantized Semiconductor Particles: A Novel State of Matter for Materials Science," *Advanced Materials*, **5**, 88 (1993).

Xia, Y. N. and Whitesides, G. M., "Soft lithography," *Annual Review of Materials Science*, **28**, 153 (1998).

Xia, Y. N., Rogers, J. A., Paul, K. E. and Whitesides, G. M., "Unconventional Methods for Fabricating and Patterning Nanostructures," *Chemical Reviews*, **99**, 1823 (1999).

Xu, D. S., Xu, Y. J., Chen, D. P., Guo, G. L., Gui, L. L. and Tang, Y. Q., "Preparation of CdS Single-crystal Nanowires by Electrochemically Induced Deposition," *Advanced Materials*, **12**, 520 (2000).

Xu, S., Zhao, X. K. and Fendler, J. H., "Ultrasmall Semiconductor Particles Sandwiched Between Surfactant Headgroups in Langmuir-Blodgett Films," *Advanced Materials*, **2**, 183 (1990).

Yang, J. P. and Fendler, J. H., "Morphology Control of PbS Nanocrystallites, Epitaxially Under Mixed Monolayers," *Journal of Physical Chemistry B*, **99**, 5505 (1995).

Yang, J. P., Meldrum, F. C. and Fendler, J. H., "Epitaxial-Growth of Size-quantized Cadmium-sulfide Crystals Under Arachidic Acid Monolayers," *Journal of Physical Chemistry B*, **99**, 5500 (1995).

Yang, J., Fendler, J. H., Jao, T. C. and Laurion, T., "Electron and Atomic-Force Microscopic Investigations of Lead Selenide Crys-

tals Grown Under Monolayers," *Microscopy Research and Technique*, **27**, 402 (1994).

Yi, K. C., Horvolgyi, Z. and Fendler, J. H., "Chemical Formation of Silver Particulate Films Under Monolayers," *Journal of Physical Chemistry B*, **98**, 3872 (1994).

Yin, J. S. and Wang, Z. L., "Preparation of Self-assembled Cobalt Nanocrystal Arrays," *Nanostructured Materials*, **11**, 845 (1999).

Yoshimura, M. and Livage, J., "Soft Solution Processing for Advanced Materials," *MRS Bulletin*, **25**, 12 (2000).

Yoshimura, M., Suchanek, W. L. and Byrappa, K., "Soft Solution Processing: A Strategy for One-Step Processing of Advanced Inorganic Materials," *MRS Bulletin*, **25**, 17 (2000).

Yoshimura, M., Suchanek, W. and Han, K. S., "Recent Developments in Soft, Solution Processing: One Step Fabrication of Functional Double Oxide Films by Hydrothermal- Electrochemical Methods," *Journal of Materials Chemistry*, **9**, 77 (1999).

Zhao, X. K., McCormick, L. D. and Fendler, J. H., "Preparation-dependent Rectification Behavior of Lead Sulfide Particulate Films," *Advanced Materials*, **4**, 93 (1992).

Zhao, X. K., Yang, J., McCormick, L. D. and Fendler, J. H., "Epitaxial Formation of PbS Crystals Under Arachidic Acid Monolayers," *Journal of Physical Chemistry B*, **96**, 9933 (1992).

Zhao, X. Z., Roy, R., Cherian, K. A. and Badzian, A., "Hydrothermal Growth of Diamond in Metal-C-H_2O Systems," *Nature*, **385**, 513 (1997).

Zhu, J. J., Koltypin, Y. and Gedanken, A., "General Sonochemical Method far the Preparation of Nanophasic Selenides: Synthesis of ZnSe Nanoparticles," *Chemistry of Materials*, **12**, 73 (2000).