Colloidal Stability by Surface Modification

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The study of colloids is important in the design of materials for uses ranging from pot making to petroleum refining. This review presents the reasons for instability and different methods for attaining stability in various systems of interest. In this context, both steric and electrostatic stabilization are discussed. Also discussed are surface modification in core-shell technology and the importance of surfactants in emulsions.

INTRODUCTION

In the 19th century, Robert Brown first observed the motion of dispersed particles.[1] However, Thomas Graham was the first to propose the name "colloid"—meaning gum-like. Among the various theories proposed, the DLVO theory by Derjaguin, Landau, Verwey, and Overbeek has been the most widely accepted in colloid science.[2] The main driving force for colloidal research lies in a wide range of applications,[1] from pot making to petroleum refining, water purification to beer manufacturing, cosmetics to chemical sensors. Currently, colloid systems are used for economical and room-temperature synthesis of nanomaterials[3,4] for novel applications in gas and chemical sensors.

However, achieving desired stability and rheological properties in colloids remain a challenge.[5] To exploit the size-dependent properties of nanomaterials,[6] it is necessary to avoid agglomeration.[7] Agglomeration deteriorates the rheological properties not only in nanomaterials but also in coarse-grained materials. With the advent of biotechnology, the study of colloids has increased, especially in drug delivery, where stable dispersions are required.[8] To tackle the problem of instability, researchers have mainly relied on various dispersants and surface-modification techniques.[5,9] Novel characterization techniques, such as mechanical spectroscopy,[10] neutron scattering,[11] photon correlation spectroscopy,[12] small-angle x-ray scattering, dynamic light scattering, and atomic-force microscopy have provided an impetus to the interface studies in the colloidal systems.[13] Analytical modeling is being carried out to predict various surface forces.[14]

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Table I. Classification of Colloid Systems[1]

Name	Dispersed Phase	Dispersion Medium	Applications	Example
Foam	Gas	Liquid	Froth	Fire extinguisher
Solid Foam	Gas	Solid	Insulating foam	Flame retardants
Sol, Paste, Latex	Solid	Liquid	Synthesis of particulate materials	Sol gel, microemulsion
Smoke, Aerosol	Solid	Gas	Spray	Cosmetics and paints
Emulsion	Liquid	Liquid	Dairy, pharmaceutical, nanotechnology	Milk products, body fluids

This article is an effort to analyze and correlate the basic phenomena in colloidal systems, and to emphasize the need for surface modification to impart stability and to retain desirable properties. Ceramic processing to nanomaterials synthesis have been exploiting surface modification to improve the properties of the system as a whole. This review is confined to the surface modification of inorganic materials using organic coatings[15] and core-shell technology.[16]

FUNDAMENTALS OF COLLOIDAL SYSTEMS

Colloids are a dispersion of one phase in another. The dispersed phase and medium can be solid, liquid, or gas (Table I).

Colloids are traditionally divided into two categories, lyophilic and lyophobic, depending on their ease of interaction with the solvent. The lyophilic colloids are thermodynamically stable, while the lyophobic colloids are unstable even at a concentration as low as 0.01M. Colloids with a combined nature are known as hydrophiles.[2]

Stability

The particles, when dispersed, are in a continuous jiggling motion known as Brownian motion.[1] As a result, uniform distribution of the particles is obtained through diffusion as described in Equation 1 (all equations are shown on page 53), where D_0 is the Stokes–Einstein diffusivity, k is Boltzmann's constant, T is temperature, t is time, a is particle size, Δr^2 is the mean square displacement, and μ is the solvent viscosity.[2] Particles in Brownian motion will collide with each other, which may lead to the formation of a doublet. With further collisions the doublet may become a triplet and with time this becomes a considerable mass,

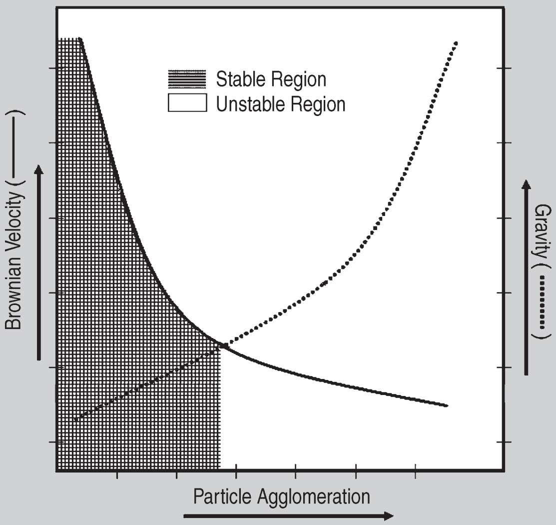

Figure 1. A schematic diagram showing the stable and unstable regions in a colloid system as a function of agglomeration.

Equations

$$\lim_{t \to \infty} < \Delta r^2(t) >= 6D_0 t = \frac{kTt}{\Pi \mu a} \tag{1}$$

$$W_{EL} = \frac{q_1 q_2}{4\varepsilon_0 \varepsilon_r \prod R_{12}} = \frac{\sigma_1 A_1 \sigma_2 A_2}{4\varepsilon_0 \varepsilon_r \prod R_{12}} \tag{2}$$

rendering instability to the system or causing precipitation. In order to prevent instability, different methods were proposed in various systems.

Figure 1 conceptually represents the two counteracting forces (Brownian motion and gravity) on the colloid particles. As the particles start agglomerating to reduce the surface energy, gravity effect initiates. At a critical agglomerate size, the gravity effect dominates, resulting in precipitation. This critical agglomerate size depends on the individual system and the nature of the dispersant.

Various stabilization techniques have been used, which can be broadly classified into two categories. In steric stabilization, the contact between the two colloid particles is physically avoided, while electrostatic stabilization uses the surface charge variation to attain stability. Core-shell technology[17] falls under the former, while the use of polar, non-polar solvents and dispersants belong to the latter.[15] The use of surfactants to form micelles in the micro- and nano-emulsion methods partially imparts both steric and electrostatic stabilization to the particles. A description of the science behind each of these techniques is beyond the scope of this article; however the reader is advised to consult various references.[1,2,4,9]

To achieve stability by manipulating the electrostatic surface charge on the colloid particles, a detailed knowledge of the stern layer, electric double layer, zeta potential, iso-electric point, and the potential-determining ion is necessary. Almost all of these aspects are dependent on the polarizability of the material under consideration. The various parameters are illustrated in Figure 2. The zeta potential is the potential at the interface between the stern layer and the diffuse layer. A colloid system will reach an iso-electric point, also known as the point of zero charge, just before the precipitation. Essentially there will be no more hindrance for the particles to agglomerate.

Three kinds of stabilities were proposed by Derjaguin:[18] phase, disperse composition, and aggregate. Research has concentrated primarily on aggregate stability. Highly stable disperse systems are of interest in microemulsion technology. Any stabilization mechanism involves the addition of an external agent to the system that can modify either the dispersing medium or the dispersed phase. When the particles transform from the micro- to nano-dimension, there is an inherent variation in the inter-particle interaction.[19]

The Brownian velocities of the particles are enough to overcome the gravity force, which might lead to increased stability. However, the process of Ostwald ripening is more pronounced in nanomaterials, increasing the possibility for agglomeration. The nanoparticles are significantly delocalized compared to the micrometer size, which influences the nucleation kinetics and the relative strength of the shear fields around them. As the particle size sets the range of potential interactions, Brownian motion and the inter-particle interactions are strongly dependant on the particle size. The increasing importance of nanomaterials in various applications demand the need for studying the colloidal stability at the nanoscale, and stability is strongly dependent on the nature of the inter-particle interactions. To achieve the most stable colloid system, a maximum electrostatic potential between the two adjacent particles is desired.

Electrostatic interaction between the two point charges at a distance of R_{12} can be quantified using the electrostatic potential, W_{EL}, where q_1, q_2 are the products of the charge densities

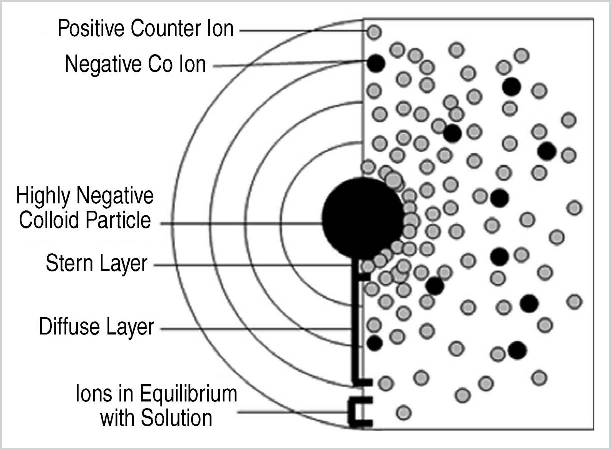

Figure 2. A schematic diagram showing the distribution of positive and negative ions around a charged colloid in solution.

(σ_1, σ_2) and the areas of contact at the interface (A_1, A_2) and ε_r is the dielectric constant of water. From Equation 2 it is possible to find where the particles will have the minimum and maximum interaction potentials, and the stability can be achieved by incorporating the appropriate conditions in Equation 2.[20]

Table II. Different Dispersion Systems in Ceramics

Ceramics/Oxides	Dispersant	Ref.
Zirconia	Darvan C Poly ethylene imine Diammonium citrate Ammonium polyacrylic acid	29
Barium Titanate	Ammonium polyacrylate Poly (acrylic acid-co-maleic acid)	9, 30
Alumina	Darvan C	31
Silica, Silicon Carbide	Poly ethylene imine	28
Silicon Nitride	Triethanolamine	12
Calcium Carbonate	Ammonium poly carbonates	24
Iron Oxide	Carboxymethyldextran	17

Surface Modification

A wide range of inorganic and organic stabilization agents and dispersants have been studied in the past few decades. However, inorganic systems with organic and inorganic coatings have generated interest in the materials community for the development of novel functional materials.[21] In the nano-regime, the synthesis of metallic oxide nanoparticles and semiconductor quantum dots has received the maximum attention. The stability in the solution is of great concern not only in view of exceptional properties but also in facilitating the self assembly of these nano-building blocks into three-dimensional super structures.[19]

MODIFICATION OF INORGANIC SURFACES WITH ORGANIC COMPOUNDS

In recent years, interest in dispersions of nanoparticles has grown due to their unique and diverse properties. The processing chemistry is found to be strongly dependent on the nature and the structure of the interface. Better thermal, chemical, and photochemical properties can be attained in stable nano-colloids. Hiroki and Osterloh[20] reported that inorganic particles are attractive building blocks for the construction of nanoarchitectures. They have clearly shown that CdSe, SiO_2, and gold, when modified with carboxylic acid and amines, change their stabilities and can form core-shell type structures. The nature of bonding between the nanoparticles decides the stability and the dynamics of particle clustering and their physical properties. Proposed[20] assembly and disassembly with pH clearly indicates the role of surface electrostatic forces and the adsorbed ions on the colloid stability. However, selecting an optimum organic polymer that can trap the nanoparticles without interfering with their inherent chemistry is critical to this type of synthesis. This, in turn depends on the functional groups, molecular weight and the chemical reactivity of the polymer at fixed molar concentrations and pH of the solvent.

The combinations of organic–inorganic structures are important in many biotechnology applications. The surfactant-based modification and nanocomposite formation were studied by Wang et al.[22] Valter[23] has critically reviewed the available synthesis routes for these hybrid materials and emphasized their application as opto-electronic materials, bio-mimetic composites, catalysts, and nano-fillers for composite film coatings.

Ceramic Processing

Researchers have tried to utilize the ancient example of ceramic pottery processing, where clays are dispersed in water, in modern-day ceramic synthesis. While processing the particles in a solvent, restricting aggregation, particle growth, and flocculation is imperative to obtain an even dispersion of the solids in the liquid.[5] Dispersing agents used in the processing of ceramics, such as $CaCO_3$,[24] Si_3N_4, Al_2O_3, and $BaTiO_3$[9,12,24–26] not only improve the stability of these ceramic slurries even at a very high solids loading, but also improve the rheological properties. The combined effect of all the factors, such as pH, zeta potential, and particle size is the key to achieving a stable colloid. Figure 3 shows the interdependence of zeta potential and pH with the addition of different surfactants in a zirconia system.[27]

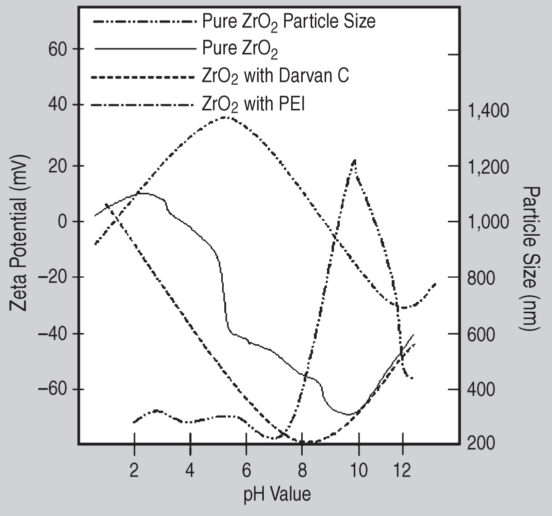

Figure 3. A variation of zeta potential and particle size of zirconia powder with pH in different surfactants: poly ethyleneimine (PEI), ammonium salt of poly methacrylic acid (Darvan C).[27]

It was mentioned that, in highly concentrated oxide suspensions, problems related to high viscosity, aging, and processing of multiphase systems can be drastically reduced by using polyelectrolytes as dispersants or deflocculants.[25] Proper colloidal processing of the ceramics can lead to increased green densities and more homogeneous green microstructures.[28] Table II presents different ceramic systems and the dispersants widely used. One major reason proposed for the enhanced dispersability of colloids is the increase in surface charge density. The increase in zeta potential leads to higher inter-particle repulsion.[29] Organic coatings are expected to increase the steric repulsion

Table III. Core-Shell Structures in Metallic/Semiconductor Nanoparticles

Core	Shell	Synthesis
Metallic Nanoparticles	Oxides	Seeded polymerization[36]
Dilute Magnetic Semiconductor Quantum Dots	Cadmium sulfide	Iso crystalline core-shell synthetic method[37]
Photo Stable Semiconductor Quantum Dots	Silica	Reverse microemulsion[38]

between the surfaces of two particles, thereby avoiding aggregation.[12]

MODIFICATION OF INORGANIC SURFACES WITH INORGANIC COMPOUNDS

The stabilization of colloids is achieved by surface modification[16] to enhance the double-layer properties or by adsorbing macromolecules that can form a physical barrier against the approaching particles. A wide range[32] of organic materials, such as long-chain polymers, surfactants, and chemically stabilized ligands can be used for the increased dispersability and stability of the colloids. Stabilization can also be achieved through compartmentalization in micelles and microemulsions, and immobilization in glasses and sol-gels. The inherent disadvantage of these methods, however, is their effect on the solid-state properties.[32] Another method of surface modification is the deposition of a homogeneous shell of inorganic materials (like SiO_2 encapsulation) to obtain a core-shell geometry. This inorganic shell essentially increases the distance between the two colloid particles and hinders agglomeration. In addition to the electrostatic stabilization, coatings can also reduce the interfacial energy of the nanoparticles, which otherwise might be very high. Encapsulation can be achieved using processes like hydration, condensation, and seeded polymerization.[16]

Interest is increasing in the synthesis of core-shell structures with the metal-metal, metal-semiconductor, and semiconductor-semiconductor colloid nanocomposites[33] because of their photocatalytic and optical properties. Kamath et al.[33] have reported the synthesis of Ag/Au and Au/TiO_2 nanocomposites. Researchers have tried to modify the Stöber method and have synthesized silver nanoparticles coated with silica.[33] Chang et al.[34] have reported the electroless deposition of silver on tin oxide and have increased the resistance to aggregation by the further coating of ten monolayers of tin silicate or tin oxide. Yu Lu et al.[35] have reported the synthesis and self assembly of $Au\text{-}SiO_2$ core-shell colloids for applications in photonic band-gap materials and wave guides. Coated inorganic materials have not only led to an improvement in the colloid stability but also have opened new avenues of research for novel applications. Table III gives some important examples of core-shell structures in various systems.

Mostly, the core-shell technology has been utilized for semiconductor quantum dots (QDs). Along with enhanced stability, it is necessary to retain the properties of the QDs such as photo luminescence, higher fluorescence lifetimes, and stable surface chemistry. Parameters such as thickness of the encapsulation, pH, concentration of the dispersion, and the uniformity of the coating shell on the core particles need precise control to achieve core shell stability.

EMULSION TECHNOLOGY

Emulsions are colloids with liquid dispersion in the liquids. The amphiphilic nature of surfactants has been utilized efficiently to form micelles and nanoreactors. Microemulsions are colloidal "nano-dispersions" and have been used to conduct chemical reactions to synthesize nanomaterials. The shape and size depends on the curvature free energy, which is determined by the elastic constant and the curvature of the surfactant film on the particles.[3,39] Further data regarding surfactants are available in a series of publications by Marcel Dekker Inc. The researchers have exploited the microemulsion practice for a multitude of industrial applications.[40]

Tadros et al.[41] have elaborately described the formation and stability of the nanoemulsions. The reasons for the stability of nanoemulsions and their use in personal care and cosmetics are:

- Their tiny size overcomes the gravity force by Brownian motion
- Weak flocculation can be prevented
- The particles are non-deformable and hence surface fluctuations are prevented
- Their large surface area makes their penetration easy
- Less surfactant concentration is sufficient

In addition to the previously mentioned applications, nano-sized particles are being used in high-efficiency heat-transfer fluids.[42] The main reason for their stability when compared to their coarse counterparts is the modified surface. Another important practical application of the colloidal system lies in the

Table IV. Tunable Nanostructures Using Colloid Systems[43]

Parameters	Influencing Factors	Type of Control*	Example
Nucleation	Monomer concentration	Ext	Solvent concentration can be used for controlling the rate of nucleation
	Crystal structure	Int	Isotropic seeds → isotropic crystals Anisotropic → anisotropic crystals
Stability	Thermodynamic	Ext/Int	Thermodynamic growth favors isotropic spherical powders
	Kinetic	Ext/Int	Kinetic growth favors anisotropic structures such as rods, tubes etc.
Crystalline Growth	Surface energy	Int	Selective thermodynamic growth along dense-packed planes
		Ext	Steric factors using organic surface modification can hinder growth along thermodynamic planes
	Temperature	Ext	CdS tetrapods below 250°C
	Steric control	Ext	Surface modifications using bulky organic groups can induce growth along different orientation resulting in rods, tubes, spheres, etc.

* Ext = external; int = internal

development of tunable nanostructures. Table IV emphasizes the importance of a highly stable colloidal system with surface modification. The shape of the nanostructures from colloids can be varied by external parameters such as temperature and steric control; hence, long-term stability of the colloid systems is needed over a range of temperatures and different additives to obtain selectivity in shape and size.

CONCLUSION

The field of colloid science is leading to new avenues in materials science, chemistry, and nano- and bio-technology. However, stability aspects are still a challenge. Both organic and inorganic materials are being used to impart stability. The dispersants, surfactants, and inorganic shells used to increase stability have also exhibited enhanced optical, electronic, and chemical properties. The semiconductor and biotechnology industries are major beneficiaries of colloidal nanocrystals. Numerous theoretical and modeling studies have been conducted from the DLVO theory to the latest review article by Manoharan and Pine.[44] More novel applications of these systems are found in various disciplines of science and engineering.

ACKNOWLEDGEMENTS

The authors acknowledge NASA Glenn Research Center, NASA-Kennedy Space Center, Florida Solar Energy Center-University of Central Florida, Florida Space Grant Consortium, Office of Naval Research–Young Investigator Award (ONR-YIP), National Science Foundation, National Institutes of Health, Department of Defense, Department of Energy, NASA, Department of Defense Small Business Innovation Research Program Phases I and II, Plasma Process Inc., Lockheed Martin, State of Florida, and Siemens Westinghouse for funding the current research in material engineering, functional coatings, and nanotechnology.

References

1. Robert J. Hunter, *Introduction to Modern Colloidal Science* (New York: Oxford University Press, 1993).
2. K.S. Birdy ed., *Handbook of Surface and Colloid Chemistry* (Boca Raton, FL: CRC Press, 2003).
3. M. Arthuro and Lopez-Quintela, *Current Opinion in Colloid and Interface Science,* 8 (2003), p. 137.
4. S. Shukla et al., *Journal of Nanoscience and Nanotechnology,* 5 (2005), pp. 1–11.
5. Ricardo H.R. Castro, Bruno B.S. Murad, and Douglas Gouvea, *Ceramics International,* 8 (30) (2004), pp. 2215–2221.
6. S. Deshpande et al., *Applied Physics Letters,* 87 (1) (2005), pp. 133113-1–133113-3.
7. Y. Andrew Wang et al., *Journal of American Chemical Society,* 10 (124) (2002), pp. 2293–2298.
8. Hidenori Otsuka, Yukio Nagasaki, and Kazunori Kataoka, *Advance Drug Delivery Reviews,* 55 (2003), pp. 403–419.
9. Carlos Gomez Yanez, Heberto Balmori Ramirez, and Froylan Martinez, *Ceramics International,* 26 (2000), pp. 609–616.
10. J. Mewis and G. Schoukens, *Faraday Discussions of the Chemical Society,* 65 (1978), pp. 58–64.
11. D. Cebula et al., *Faraday Discussions of the Chemical Society,* 65 (1978), pp. 76–91.
12. Rongcan Zhou et al., *Ceramics International,* 28 (2002), pp. 705–709.
13. Graeme Gillies and Clive A. Prestidge, *Advances in Colloid and Interface Science,* 108-109 (2004), pp. 197–205.
14. U. Gasser et al., *Science,* 292 (April 2001), pp. 258–262.
15. S. Shukla, S. Seal, and R. Vanfleet, *Journal of Sol Gel Science and Technology,* 27 (2) (2003), pp. 119–137.
16. S. Gu et al., *Journal of Colloid and Interface Science,* 279 (2004), pp. 284–287.
17. T. Goetze et al., *Journal of Magnetism and Magnetic Materials,* 252 (2002), pp. 399–402.
18. B.V. Derjaguin, *Faraday Discussions of the Chemical Society,* 65 (1978), pp. 306–312.
19. S.C. Glotzer, M.J. Solomon, and N.A. Kotov, *American Institute of Chemical Engineers,* 50 (12) (2004), pp. 2978–2985.
20. Hiroki Hiramatsu and Frank E. Osterloh, *Langmuir,* 19 (2003), pp. 7003–7011.
21. Wenzhuo Guo et al., *Journal of American Chemical Society,* 13 (125) (2003), pp. 3901–3909.
22. Yude Wang, Shuo Zhang, and Xinghui Wu, *Nano Technology,* 15 (2004), pp. 1162–1165.
23. Valter Castelverto and Cinzia De Vita, *Advances in Colloid and Interface Science,* 108-109 (2004), pp. 167–185.
24. G. Tari and J.M.F. Ferreira, *Ceramics International,* 24 (1998), pp. 527–532.
25. J. Wang and L. Gao, *Ceramics International,* 26 (2000), pp. 187–191.
26. A.U. Khan, P.F. Lukham, and S. Manimaran, *Journal of Materials Chemistry,* 7 (9) (1997), pp. 1849–1853.
27. Tang Fengqiu et al., *Ceramics International,* 26 (2000), pp. 93–97.
28. Jing Sun and Lian Gao, *Journal of European Ceramic Society,* 21 (2001), pp. 2447–2451.
29. Zhipeng Xie et al., *Ceramics International,* 30 (2004), pp. 219–224.
30. Jianling Zhao et al., *Ceramics International,* 30 (2004), pp. 1985–1988.
31. Bimal P. Singh et al., *Ceramics International,* 30 (2004), pp. 939–946.
32. Luis M. Liz-marzan, Michael Giersig, and Paul Mulvaney, *Langmuir,* 12 (1996), pp. 4329–4335.
33. Prashanth V. Kamath et al., *Colloids and Surfaces A,* 202 (2002), pp. 269–279.
34. H. Chang, C.H. Pitt, and G.B. Alexander, *Journal of Materials Science,* 28 (1993), p. 5207.
35. Yu Lu et al., *Nano Letters,* 7 (2) (2002), pp. 785–788.
36. Eiiche Mine et al., *Journal of Colloidal and Interface Science,* 264 (2003), pp. 385–390.
37. Pavle V. Radovanovic and Daniel R. Gamelin, *Journal of American Chemical Society,* 123 (2001), pp. 12207–12214.
38. Heesun Yang, Paul H. Holloway, and Swadeshmukul Santra, *Journal of Chemical Physics,* 121 (15) (2004), pp. 7421–7426.
39. S. Patil et al., *Nanoparticles Research,* 4 (2002), pp. 433–438.
40. Conxita Solans and Hironobu Kunieda, *Industrial Applications of Microemulsions, Surface Science Series,* vol. 66 (New York: Marcel Dekker, Inc., 1997).
41. T. Tadros et al., *Advances in Colloid and Interface Science*, 108-109 (2004) pp. 303–318.
42. Yimin Xuan and Qiang Li, *International Journal of Heat and Fluid Flow,* 21 (2000), pp. 58–64.
43. Young-wook Jun et al., *Journal of Physical Chemistry B,* 109 (31) (2005), pp. 14795–14806.
44. Vinothan N. Manoharan and David J. Pine, *MRS Bulletin,* 29 (2) (2004), pp. 91–95.

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