Surface modification and characterization for dispersion stability of inorganic nanometer-scaled particles in liquid media

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2010 Sci. Technol. Adv. Mater. 11 044304

(http://iopscience.iop.org/1468-6996/11/4/044304)

View the table of contents for this issue, or go to the journal homepage for more

Download details:
IP Address: 194.109.159.73
The article was downloaded on 11/03/2011 at 01:31

Please note that terms and conditions apply.
TOPICAL REVIEW

Surface modification and characterization for dispersion stability of inorganic nanometer-scaled particles in liquid media

Hidehiro Kamiya and Motoyuki Iijima

Institute of Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan
E-mail: kamiya@cc.tuat.ac.jp

Received 14 May 2010
Accepted for publication 11 August 2010
Published 10 September 2010

Abstract

Inorganic nanoparticles are indispensable for science and technology as materials, pigments and cosmetics products. Improving the dispersion stability of nanoparticles in various liquids is essential for those applications. In this review, we discuss why it is difficult to control the stability of nanoparticles in liquids. We also overview the role of surface interaction between nanoparticles in their dispersion and characterization, e.g. by colloid probe atomic force microscopy (CP-AFM). Two types of surface modification concepts, post-synthesis and in situ modification, were investigated in many previous studies. Here, we focus on post-synthesis modification using adsorption of various kinds of polymer dispersants and surfactants on the particle surface, as well as surface chemical reactions of silane coupling agents. We discuss CP-AFM as a technique to analyze the surface interaction between nanoparticles and the effect of surface modification on the nanoparticle dispersion in liquids.

Keywords: polymeric dispersants, silane coupling agents, nanoparticle synthesis, ligand exchange, colloid stability

1. Introduction

Because of their unique size-dependent electrical, magnetic, mechanical, optical and chemical properties, which largely differ from those of the bulk materials, nanoparticles have already become an indispensable material for many industrial fields [1–5]. Nanoparticles have different surface structures and surface interactions from those of the sub-micron sized particles; in particular, they show a much stronger aggregation tendency. For applications in functional materials and products, it is important to develop techniques of controlling the dispersion and aggregation of nanoparticles. Dispersion of nanoparticles in aqueous media can well be modeled with the theory by Deryagin, Landau, Verwey and Overbeek (DLVO). However, it is still a challenging task to manage high-concentration nanoparticle suspensions in organic media. Surface modification of nanoparticles is one of the most common methods to improve the dispersion stability of nanoparticles. It requires a design of the surface structure based on the type of nanoparticles and the liquid media. In our previous review [6], we introduced two approaches, namely post-synthesis and in situ surface modification, which, respectively, correspond to the surface modification of the manufactured particles and surface modification during the particle synthesis. Here, we only focus on the former technique. First, we discuss why nanoparticles aggregate so easily. Then, we review surface modification methods for dispersion of various nanoparticles in liquid media. For the
non-DLVO type surface interactions, such as steric and bridge forces originating from the surfactant adsorption and other surface modifications in organic solvents, a colloid probe atomic force microscopy (CP-AFM) is a useful method to analyze the nanoparticle dispersion. We also present some examples of the relationship between the surface interactions and dispersion behavior of nanoparticles.

2. Difficulties in handling nanoparticles

Brownian motion is essential for understanding the aggregation of nanoparticles. It results in a three-dimensional mean displacement ($\Delta x$) that can be expressed with equation (1), where $D_B$ is the Einstein’s Brownian diffusion coefficient and $\Delta t$ is the diffusion time. The diffusion coefficient in equation (1) can be evaluated with equation (2), where $k$ is the Boltzmann constant, $T$ is temperature, $\mu$ is viscosity of the medium and $d_p$ is the particle size. Equations (1) and (2) reveal that the displacement due to the Brownian motion increases with decreasing particle size, and thus that nanoparticles tend to move around and approach other nanoparticles. Because of the van der Waals attractive force acting among nanoparticles, generation of potential barriers is necessary to prevent their aggregation.

$$\Delta x = \sqrt{\frac{6 D_B \Delta t}{\pi}} \quad (1)$$
$$D_B = \frac{k T}{3 \pi \mu d_p} \quad (2)$$

The DLVO theory [7], which includes the van der Waals attractive forces and electrostatic interactions due to the electrical double layer, allows to evaluate the potential barrier between particles in aqueous media. It is relatively easy to control the dispersion stability of sub-micron particles with the electrical double layer, which can be tuned by the surface potential of particles and the counter ion concentration. As to nanoparticles, because of the relatively small potential barrier, it is difficult to improve their dispersion stability using only the DLVO interactions.

For concentrated suspensions, it is also important to take into account the distances between the surfaces of different particles. When the concentration of particles is high and their separation is smaller than this distance, the particles will be trapped by the van der Waals force and form aggregates. Figure 1(a) shows the relationships between the volume fraction of particles and the mean surface distance; the latter was calculated with equation (3) which was reported by Woodcock [8] and with equation (4) which is derived within the close-packing model of uniform spheres. In each equation, $h$ is the mean surface distance and $F$ is the volume fraction of particles in suspension. Both equations predict the mean particle surface distance of several nanometers when the concentration of sub-micron particles exceeds 60 vol%. However, the same distance will be reached for only 30 vol% of nanoparticles. An additional surface repulsive force, such as steric repulsive force, is necessary
to prevent aggregation of nanoparticles separated by this distance.

$$h = d_p \left( \frac{1 - \frac{5}{6} - 1}{\sqrt{\frac{1}{3} + \frac{\pi F}{3}}} \right),$$  \hspace{1cm} (3)

$$h = d_p \left[ \left( \frac{\pi}{3 \sqrt{2} F} \right)^{1/3} \right].$$  \hspace{1cm} (4)

Next, we discuss the relationship between the three-dimensional mean displacement ($\Delta x$) due to the Brownian motion and the mean surface distance calculated with equation (3). For this purpose, the effect of particle diameter on those values was calculated and plotted in figure 1(b). If the particle diameter exceeds $10 \mu m$ and the solid volume fraction is $20$ vol% then the mean surface distance is much larger than $\Delta x$. However, for the particles smaller than $100$ nm, the Brownian displacement is much larger than the surface distance. This estimation additionally illustrates the aggregation tendency of nanoparticles.

Nanoparticles possess different surface structure compared to the sub-micron sized particles [9, 10]. For example, we have synthesized SiO$_2$ particles with various diameters by sol–gel method, characterized their surface structure using Fourier transform infrared spectroscopy and found that the peak intensity of the free silanol groups increases with decreasing particle size. This result can be understood as the large curvature of nanoparticles increases the average distance between the silanol groups thereby decreasing the probability of hydrogenation. This difference of surface structure also strongly affects the surface force interactions and dispersion stability.

### 3. Surface modification of nanoparticles to improve their dispersion stability in liquid media

In section 2, we have described the difficulties of stabilizing nanoparticles in liquid media. To improve the dispersion stability of nanoparticles, it is necessary to modify the particle surface with polymeric surfactants or other agents in order to generate an effective repulsive force between the nanoparticles.

#### 3.1. Adsorption of polymeric dispersants

Adsorption of a polymeric dispersant on nanoparticles is one of the simplest surface modification techniques to improve the dispersion stability of nanoparticles in liquid media. When dispersing hydrophilic nanoparticles in aqueous media or in organic solvents with high polarities, anionic or cationic polymer dispersants are widely used to generate the steric repulsive force originating from the polymer chains and to increase the surface charge. Among anionic surfactants, various types of polycarboxylic acids and their salts including polyacrylic acid (PAA) [11–14], polyacrylic acid sodium salts (PAA-Na) [15–17] and co-polymers of polyacrylic acid and maleic acid [18] are used to disperse oxide nanoparticles such as BaTiO$_3$ [11], TiO$_2$ [15, 18], Al$_2$O$_3$ [12, 17], MgO [13] and Fe$_2$O$_3$ [16]. A common example of cationic surfactants is polyethyleneimine (PEI) [19, 20].

The relationships among pH of suspension, solid fraction of the suspension, dissociation ratio of polymer dispersant, molecular weight of polymer surfactant, surface charge of nanoparticles and the particle size affect the adsorption ratio of surfactants and the degree of steric repulsive force. Kakui et al [18, 19] reported the effect of particle size and the molecular weight of branched PEI on the viscosity of Al$_2$O$_3$ suspension in ethanol at a fixed solid concentration as shown in figure 2. They used four kinds of Al$_2$O$_3$ powder with the mean particle diameter varying between 7 and 600 nm. PEI with a certain molecular weight in the range 600–70,000 g mol$^{-1}$ was added into each suspension. The solid volume fraction of each Al$_2$O$_3$ powder was determined using the viscosity of suspension without PEI addition, which was almost constant at about 2.7 Pa.s. For sub-micron sized particles, the smallest viscosity was obtained when the molecular weight of PEI was 10,000. However, for 7 nm Al$_2$O$_3$ nanoparticles, the suspension viscosity reduced drastically when the molecular weight was 1800. As shown in figure 1, the mean surface distance drastically shortens, at a constant solid fraction, when the particle size is decreased from hundreds to tens of nanometers. Figure 3 shows the size distribution of PEI in ethanol determined with the dynamic scattering method [18]. It is expected that polymer surfactants with larger molecules (higher molecular weight) cannot freely move around nanoparticles and effectively adsorb on their surface; they therefore cannot improve the dispersion stability of the suspension. For example, if molecular weight is larger than 1800 g mol$^{-1}$, the mean size of PEI molecule exceeds 1 nm as shown in figure 3; such PEI cannot disperse nanosized alumina. Similar results were also reported for TiO$_2$ aqueous suspensions in terms of the effect of the solid fraction of TiO$_2$.
nanoparticles and the molecular weight of PAA-Na on the suspension viscosity [16]. Not only the molecular weight but also the structure of the polymer surfactant can affect the dispersion stability of nanoparticles. One example is the use of a polymer dispersant with a hydrophilic group and a hydrophobic group [21]. It is expected that the loop-train structure can be controlled by tuning the ratio of the hydrophilic and hydrophobic sites. Another example is the use of comb-type polymers such as PAA backbones with the polyethylene oxide chain [11, 17, 22]. These comb polymers are applied to improve the stability of various oxides, such as BaTiO$_3$ and Al$_2$O$_3$, and the particles decorated with these polymers are well stabilized in a wide range of pH and ion concentrations.

Copolymers with a hydrophilic group and a hydrophobic group are often used in anionic surfactants when dispersing hydrophobic nanoparticles, such as SiC, carbon nanotubes (CNTs), and coal, in aqueous media [23–25]. The hydrophobic segments facilitate adsorption of dispersant on hydrophobic particles; they may contain an aromatic compound such as styrene that improves the adsorption via hydrophobic and pi–pi interactions. The hydrophilic segments are added for compatibility with aqueous media; they also play an important role in the generation of an effective repulsive force by the electrical double layer. When using cationic polymers, PEI can be applied to hydrophobic particles to improve the stability of SiC and CNTs in aqueous media [26].

Recently, various aqueous colloidal suspensions with well-dispersed inorganic nanoparticles such as silica, TiO$_2$ and ZrO$_2$ have been marketed by several companies. There, the electrical charge on the nanoparticle surface and the formation of the double layer prevents the nanoparticle aggregation. In addition, we prepared a novel anionic surfactant shown in figure 4(a) to ensure the complete dispersion of nanoparticles, with high solid contents, in various organic solvents and polymers [27]. This surfactant was designed to have an anionic head group and organic chains that branched into a hydrophobic alkyl chain and a hydrophilic polyethylene glycol (PEG) chain. It was also designed to have a polymerizable vinyl group at the end of the hydrophilic PEG chain. The hydrophobic chain, hydrophilic chain and the polymerizable groups served to increase the affinity of nanoparticles modified with this surfactant to low polar solvents, polar solvents and polymerizable polymers, respectively. When this surfactant adsorbed on nanoparticles in aqueous solution, because of the hydrophobic group (R), nanoparticles formed aggregates and separated as sediments in aqueous solution. Those sediments were dried and re-dispersed in a wide range of organic solvents such as alcohols, nitriles, ketones and acetates. The obtained suspensions were stable over several months. Figure 4(b) demonstrates the stability of those surface-modified TiO$_2$ nanoparticles, dispersed at concentration of 3.0 wt% in four organic solvents with different polarities. The average size of their aggregates was several tens of nanometers, which is sufficiently small to yield a transparent suspension. The TiO$_2$ nanoparticles were dispersible in completely

![Figure 3](image-url)\[Figure 3.\] Size distribution of PEI in an ethanolic solution determined by the dynamic scattering method.

![Figure 4](image-url)\[Figure 4.\] (a) An anionic surfactant designed to have a hydrophobic alkyl chain, hydrophilic PEG chain and a polymerizable group. (b) A suspension of TiO$_2$ nanoparticles was modified with a surfactant and dispersed in four organic solvents: ethanol, tetrahydrofuran, methyl methacrylate and toluene.
different kinds of polymers such as radical-polymerized poly methyl methacrylate (PMMA) without strong aggregations. Interestingly, the TiO$_2$/epoxy composites were found to possess unique shape memory properties [27].

3.2. Chemical modification of the surface

Chemical modification of the particle surface is also a useful technique to improve the stability of nanoparticles in various liquid media. Silane coupling agents, which have 1–3 alkoxy groups and 3–1 organic functional groups, are used to modify the oxide nanoparticle surface since the 1960s. Metal-OH group on the particle surface is used as a reaction site. The first purpose of the silane coupling agents was to improve the compatibility of a hydrophilic particle surface with a hydrophobic polymer surface by functionalizing the particle with various organic groups. Since Plueddemann et al reported the concept of silane coupling agents [28], numerous researchers have modified the particle surface to improve the compatibility of particle/polymer surface and the properties of composite materials [29, 30]. The surface modification of nanoparticles by silane coupling agents also increases the dispersion stability in organic media. Typically, various reactive groups such as amines, epoxides and vinyls are first introduced on the particle surface by silane coupling agents, and then polymers are grafted from or grafted to the particle surface. In one example, the particle surface was modified by aminopropylsilane and then PEG chains were grafted to the particle using epoxy-terminated PEG [31]. Various radical polymers such as polyvinylpyrrolidone (PVP) can be attached to the vinyl-functionalized particle surface [32]. Radical polymer brushes such as PMMA can also be grafted from the amino-functionalized surface by reversible addition–fragmentation chain transfer polymerization (RAFT) [33–35].

Another technique is designing steric silane networks on the particle surface by controlling the reaction of silane alkoxides. Chaimberg et al have reported that the amount of silane coupling agent chemisorbed on the oxide surface differs drastically depending on the surface modification procedures [35]. The type of solvents, pH and amount of water adsorbed on particles largely affected the chemisorbed content of silane coupling agents. Using these results, we have modified the surface of fumed silica nanoparticles in methyl ethyl ketone (MEK) with addition of a small amount of pH-adjusted water [36]. The flow properties of a silica suspension in MEK, before and after the surface modification, are shown in figure 5. Compared to the suspension of raw silica nanoparticles in MEK, the viscosity reduced in all cases by the surface modification using silane coupling agents. It appeared that the organic functional groups as well as pH of the added water affected differently the dispersion stability. When 38.8 μmol m$^{-2}$ was treated with water of pH 12, the suspension viscosity did not reduce much; however, it decreased significantly for pH 4. Other MEK suspensions of modified silica particles also showed good dispersion stability and relatively low viscosity.

To analyze the interactions between silica nanoparticles modified by silane coupling agents, the changes of steric repulsive force and adhesion force on the surface of silica substrate in MEK were examined by CP-AFM [37]. The interaction between the colloid probe of silica and a sintered silica substrate was measured. The colloid probe was prepared by adhering a single spherical silica particle of 10 μm diameter on the commercial AFM tip, using a micromanipulation system as shown in figure 6(a) [36]. The spherical silica particles were prepared by spray-drying a silica nanoparticle suspension and sintering at 1223 K for 1 h in air. Such low-temperature heat treatment induces formation of a neck between the primary silica nanoparticles increasing the strength of the resulting granules. To adsorb the coupling agent on the silica substrate and on the spherical silica particle attached to the colloid probe, the silica substrate and the colloid probe were immersed into MEK with addition of coupling agents and pH-adjusted water. The content of MEK, silica nanoparticles, coupling agent and pH-adjusted water was the same as for the silica suspension in MEK. A sintered silica piece that was prepared in a similar manner to the

Figure 5. The flow property of silica suspension in MEK before and after surface modification using silane coupling agent [36].

| pH | µmol/m$^2$ |
|----|------------|
| pH 4 | 38.8 µmol/m$^2$ |
| pH 12 | 11.6 µmol/m$^2$ |
| non H$_2$O | 11.6 µmol/m$^2$ |

| pH | µmol/m$^2$ |
|----|------------|
| pH 4 | 11.6 µmol/m$^2$ |
| pH 12 | 38.8 µmol/m$^2$ |

Shear stress [Pa] 1000 100 10 1 0.1
Shear rate [1/s] 1000 100 10 1 0.1

```latex
\text{Figure 5. The flow property of silica suspension in MEK before and after surface modification using silane coupling agent [36].}
```
silica substrate was also immersed in MEK to control the amount of silica particles. When a small amount of acidic water was added to 3-glycidoxypropyl-trimethoxysilane, a relatively large steric repulsive force (pH = 4) was measured by CP-AFM, whereas small steric repulsive force (pH = 12) was observed, as shown figure 6(b), when base water was used. It was also reported that the MEK suspension of particles with large measured steric force had lower viscosity, and the silane network on the particle surface played an important role in improving the suspension stability.

Surface modification with mixed silane alkoxides is also a useful tool to improve dispersion of particles in various types of solvents. For an example, we have modified the surface of TiO$_2$ nanoparticles by mixed silane alkoxides with a hydrophobic group (decyltrimethoxysilane: DES) and a hydrophilic group (3-aminopropyl-trimethoxysilane: APTMS) [38]. When TiO$_2$ particles were modified by DES, they were only redispersible in low-polarity solvents such as toluene, but they could be dispersed in high-polarity solvents when treated with both DES and APTMS.

When chemically modifying hydrophobic particles such as those of carbides and carbon-related materials, it is necessary to add to the surface a reactive functional group. In case of carbon-related particles, the unsaturated hydrocarbons related to the defects of graphite rings are such useful functional groups. For example, we have modified the surface of SiC nanoparticles using various azo radical initiators such as 2,2′-azobisobutyronitrile (AIBN) and 2,2′-azobis (2-methylpropionamidine) dihydrochloride (AMPA) [39]. Various polymers can also be grafted on the particle surface using radical reactions at the surface of carbon-related particles. For example, radical initiators of atom transfer radical polymerization were first generated on the CNT surface and then PMMA was grafted from the surface [40].

There are also examples of surface modification techniques using a direct reaction with the graphite ring on the particle surface. It is reported that biradical groups such as those in nitrile compounds can be reacted with double bonds on carbon-related materials [41]. The particle surface can be tuned by applying various nitrenes with reactive functional groups such as amine, carboxyl and bromide groups [42]. The 1,3-dipolar cycloaddition of azomethine ylides, which can be generated by condensation of an R-amino acid and an aldehyde, can also be applied to functionalize carbon-related materials [43].

### 3.3. Physical dispersion method of nanoparticles

It is possible to improve the dispersion stability of nanoparticles in various solvents using post-synthesis surface modifications. The major difficulty with this method is aggregation of the particles when they are collected as dried powder. In order to redisperse this aggregated dry powder at the (nearly) primary particle size, a mechanical milling method using small beads has been developed recently [44]. The particles remained aggregated when using the beads larger than 100 µm in diameter. However, a redispersion of 10 nm particles with no aggregation was achieved when the bead size was decreased to 15–30 µm. This and other methods, such as ultrasonic irradiation, can be applied in combination with the surface modification discussed above to redisperse various nanoparticles in liquid media.

We have previously discussed [45] the effects of ultrasonic irradiation and ball milling on the size distribution of nanocrystalline TiO$_2$ aggregates in aqueous suspension containing polymer dispersant and on the suspension viscosity. Some of those results are presented in figure 7, namely the aggregate size distributions of two kinds of TiO$_2$.
nanoparticles suspensions, P25 and ST21, after ball milling or ultrasonic irradiation. When we used relatively large balls (5 mm), the size of the aggregates was significantly larger than that for ultrasonically irradiated TiO$_2$ nanoparticles. In that study, the combination of the surface modification and physical dispersion was important for the nanoparticle dispersion.

4. Conclusion

We have reviewed various surface modification techniques for dispersing nanoparticles and the associated difficulties. The post-synthesis surface modification has a benefit of easy processing and the treated nanoparticles can be redispersed in liquid media at their primary particle size. By selecting the surface modification procedure a nanoparticle suspension can be tailored for specific applications.

Acknowledgment

This review was compiled as part of a project supported by the Grant-in-Aid for Scientific Research (B) (20360346) from the Japan Society for the Promotion of Science.

References

[1] Marignier J L, Belloni J, Delcourt M O and Chevalier J P 1985 Nature 317 344
[2] Alivisatos A P 1996 Science 271 933
[3] Ozin G A 1992 Adv. Mater. 4 612
[4] Jun Y-W, Huh Y-M, Choi J-S, Lee J-H, Song H-T, Kim S, Yoon S, Kim K-S, Shin J-S and Cheon J 2005 J. Am. Chem. Soc. 127 5732
[5] Kimberly D, Dhanasekaran T, Zhang Z and Meisel D 2002 J. Am. Chem. Soc. 124 2312
[6] Iijima M and Kamiya H 2009 KONA Powder Part. J. 27 119
[7] Verwey E J W and Overbeek J Th G 1947 Theory of the Stability of Lyophobic Colloids (New York: Elsevier)
[8] Woodcock L V 1987 Lect. Notes Phys. 277 113
[9] Kamiya H, Mitsui M, Takano H and Miyazawa S 2000 J. Am. Ceram. Soc. 83 287
[10] Iijima M, Tsukada M and Kamiya H 2007 J. Colloid Interface Sci. 307 418
[11] Yoshikawa J, Lewis J A and Chun B-W 2008 J. Am. Ceram. Soc. 92 S42
[12] Plueddemann E P and Holmberg K 2008 Langmuir 24 9989
[13] Prabhakaran K, Kumbhar C S, Raghunath S, Gokhale N M and Sharma S C 2008 J. Am. Ceram. Soc. 91 1933
[14] Laarz E, Meurk A, Yanez J A and Bergstrom L 2001 J. Am. Ceram. Soc. 84 1675
[15] Sato K, Kondo S, Tsukada M, Ishigaki T and Kamiya H 2007 J. Am. Ceram. Soc. 90 3401
[16] Nisb F, Ayed N and Chevalier Y 2006 Colloids Surf. A 286 17
[17] Lyckfeldt O, Palmqvist L and Carlstroem E 2009 J. Eur. Ceram. Soc. 29 1069
[18] Kakui T 2004 Doctoral Thesis Tokyo University of Agriculture and Technology
[19] Kakui T, Miyayuichi T and Kamiya H 2005 J. Eur. Ceram. Soc. 25 655
[20] Tang F, Uchikoshi T, Ozawa K and Sakka Y 2006 J. Eur. Ceram. Soc. 26 1555
[21] Kamiya H, Fukuda Y, Suzuki Y, Tsukada M, Kakui T and Naito M 1999 J. Am. Ceram. Soc. 82 3407
[22] Kirby G H, Harris D J, Li Q and Lewis J A 2004 J. Am. Ceram. Soc. 87 181
[23] Xue C-H, Shi M-M, Yan Q-X, Shao Z, Gao Y, Wu G, Zhang X-B, Yang Y, Chen H-Z and Wang M 2008 Nanotechnology 19 115605
[24] Kakui T and Kamiya H 2004 Energy Fuels 18 652
[25] Deloazer D M, Watson K A, Smith J G Jr, Clancy T C and Mell J W 2006 Macromolecules 39 1731
[26] Zhang T, Zhang Z, Dong M, Zhang J, Lin Q and Jiang D 2007 J. Am. Ceram. Soc. 90 3748
[27] Iijima M, Kobayakawa M, Yamazaki M, Ohta H and Kamiya H 2009 J. Am. Chem. Soc. 131 16342
[28] Plueddemann E P, Clark H A, Nelson L E and Hoffman K R 1962 Mod. Plast. 39 135
[29] Owen M 2002 J. Adhes. Sci. Eng. 4 2 403
[30] Plueddemann E P 1970 J. Adhes. Sci. Eng. 2 1 184
[31] Emoto K, Alstine J M V and Harris J M 1998 Langmuir 14 2722
[32] Chainmberg M, Parnas R and Cohen Y 1989 J. Appl. Polym. Sci. 37 2921
[33] Li C, Han J, Ryu C Y and Benicewicz B C 2006 Macromolecules 39 3175
[34] Li C and Benicewicz B C 2005 Macromolecules 38 5929
[35] Chainmberg M and Cohen Y 1990 J. Colloid Interface Sci. 134 576
[36] Iijima M, Tsukada M and Kamiya H 2007 J. Colloid Interface Sci. 305 315
[37] Ducker W A and Senden T J 1992 Langmuir 8 1831
[38] Iijima M, Kobayakawa M and Kamiya H 2009 J. Colloid Interface Sci. 337 61
[39] Iijima M and Kamiya H 2008 J. Phys. Chem. C 112 11786
[40] Liu M, Zhu T, Li Z and Liu Z 2009 J. Phys. Chem. C 113 9760
[41] Holzinger M, Abrahaj J, Whelan P, Graupner R, Lay L, Henrich R, Kappes M and Hirsch A 2003 J. Am. Chem. Soc. 125 8566
[42] Gao C, He H, Zhou L, Zheng X and Zhang Y 2009 Chem. Mater. 21 360
[43] Georgakilas V, Kordatos K, Prato M, Guld M, Holzinger M and Hirsch A 2002 J. Am. Chem. Soc. 124 760
[44] Inkyo M, Tahara T, Iwaki T, Iskandar F, Hogan C J Jr and Okuyama K 2006 J. Colloid Interface Sci. 304 535
[45] Sato K, Li J-G, Kamiya H and Ishigaki T 2008 J. Am. Ceram. Soc. 91 2481

Topical Review