Intelligent Colloidal Hybrids via Reversible pH-Induced Complexation of Polyelectrolyte and Silica Nanoparticles

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Specific intermolecular interactions, such as hydrogen-bonding, acid−base interactions, and oppositely charged ionic interactions to prepare self-organized materials, have attracted much interest in academic researches as well as in important technologies, such as microelectronics and biotechnology. A variety of self-assembled systems have been reported, including polymer−polymer,[1] colloid−colloid,[2−5] and polymer−colloid.[6−9] Recently, Boal et al. have demonstrated the self-assembly of colloidal gold nanoparticles (∼2 nm) by the "bricks and mortar" approach through a hydrogen-bonding interaction.[6] So-called "intelligent" or "smart" materials that can sense signals and produce a definite dynamic response in the form of a change in shape, size, or structure are central to developments in various scientific fields.[10,11]
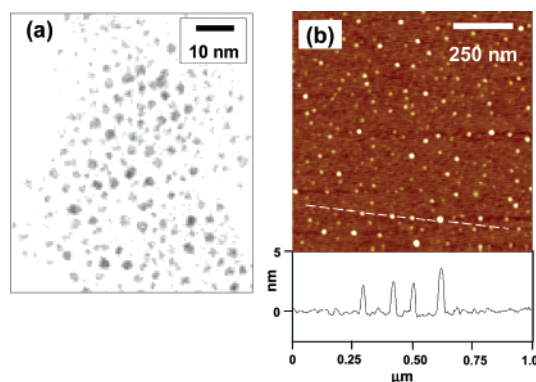
We present novel intelligent colloidal polymer/silica nanocomposites, in which the complexation of cationic silica nanoparticles and a weak anionic polyelectrolyte can be manipulated simply by pH change through a hydrogen-bonding interaction and ionic complexation caused by hydrogen-transfer interactions between the constituents. To provide an effective route for the controlled self-ordering of nanoparticles with polymers and for the achievement of characteristic stimuli-responsive properties in aqueous medium, we developed special silica nanoparticles which have two independent proton-accepting sites, oxygen or nitrogen atoms. Poly(acrylic acid) (PAA)[12] was selected as a weak polyelectrolyte, because the degree of ionization of carboxylic acids can be easily controlled by the pH value. Both the PAA and the silica in water were visually transparent, while a white turbid dispersion was obtained just after mixing the two solutions (see the Supporting Information).

The silica nanoparticles were prepared by the addition reaction of (aminopropyl)triethoxysilane and glycidol, followed by acidic condensation of the addition product (Scheme 1). The particle size

Scheme 1
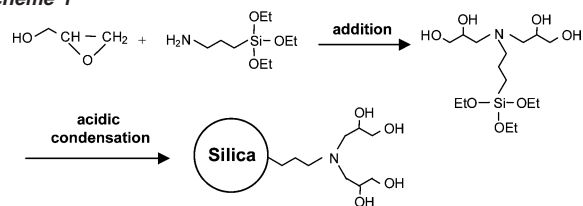
(diameter ≈ 3.0 nm) was confirmed by transmission electron microscopy (TEM) and scanning force microscopy (SFM), as shown in Figure 1. The preparation method can be referred to as a prefunctionalization approach, in which the silica precursor with an organic chain is directly used for the particle preparation. Nanometer size could be achieved by a careful choice of the organic

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Figure 1. (a) TEM and (b) SFM height images of the silica nanoparticles.

structure and condensation condition. A high density of functional groups could be attained because each silicon atom should be bound to one alkyl chain in the silica particles obtained by the condensation. Because of the tiny size and high functionality, the silica particles can be uniformly dispersed in water and behave as single dissolved molecules to form a transparent colloidal solution. These properties are significantly different from those of hydrophilic silica particles prepared by conventional methods.[13,14]

The complexation in water led to a milky white dispersion (pH ≈ 3.5), with no evidence of any microscopic precipitation. The turbid dispersion was completely dissolved by adding NaOH to pH ≳ 8.5. No insoluble complex was formed in alkaline solutions, where PAA is fully ionized, even when concentrated solutions were used. The clear transparent solution in the higher pH region became turbid by adding HCl. Further addition of HCl to the turbid dispersion of complexes led to a transparent solution at pH ≈ 2.2. Such transformations were observed reversibly and repeatedly, suggesting the existence of at least two different equilibrium states. The pH-induced complexation in water was also confirmed by the turbidity measurement (Figure 2a).
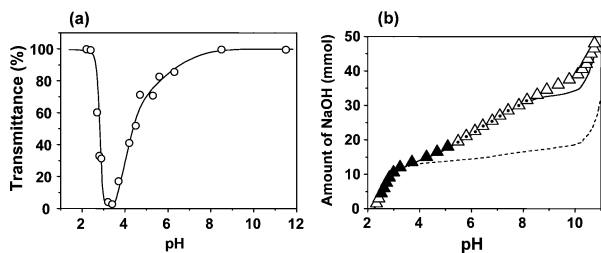
Figure 2b shows potentiometric titration curves for the PAA/silica complexes, in addition to those for PAA and the silica nanoparticles. By adding NaOH, we found that the complex in water shows three different transition points at pH = 2.3−2.5 (from transparent to white turbid), pH = 5.4−5.7 (to semitransparent), and pH = 8.2−8.5 (to transparent again). The second transition point corresponds to a pH where the hydrochloride/amino groups of the silica nanoparticles are deprotonated. The third transition point corresponds to the complete ionization point of PAA. The degree of ionization of PAA is >99% at pH = 8.2. The apparent pK_a values (taken as the pH at 50% ionization) of the PAA and the silica are 5.8 and 6.1, respectively.

Scheme 2 represents the postulated mechanism of the pH-induced complexation of the silica with PAA. At pH = 2.5−5.3, the complex is governed mainly by ionic complexation caused by

Figure 2. (a) Turbidity of the PAA/silica complexes ([silica] = [PAA] = 0.2 mg/mL) and (b) potentiometric titration curves for the complexes (△, △, ▲), PAA (—), and the silica nanoparticle (- - -); [silica] = [PAA] = 1.0 mg/mL. The symbols (△, △, ▲) indicate the regions where the solution was transparent, semitransparent, and white turbid, respectively.

proton-transfer interactions between the constituents. In the very acidic region (pH < 2.3), the nitrogen atoms are protonated by HCl instead of the carboxylic acid in PAA, leading to the dissociation of the ionic complex. In the intermediate pH region (pH = 5.8−8.0), PAA is partially ionized, and hydrogen bonds between the carboxylic acid and the hydroxy group are predominant. Only undissociated carboxylic groups are known to be capable of participating in hydrogen bonding, because the charged groups in polyelectrolytes are surrounded by small, oppositely charged counterions in aqueous solution. It means that a charged PAA chain in a higher pH region (pH > 8.5) leads to the breaking of the hydrogen bonding, resulting in the optically clear solution.

Scheme 2 [a]
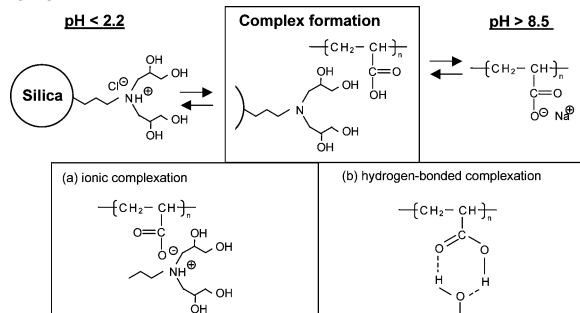
[a] Postulated mechanism of the reversible pH-induced association and dissociation behaviors of the silica nanoparticle with PAA through (a) ionic complexation and (b) hydrogen-bonded complexation.

To obtain structural information, the white turbid products were isolated by centrifugation and dried in vacuo. Comparison of the ^{1}H NMR spectra of the complexes formed in water and the mixture of the PAA and the silica (1/1 wt %) was conducted in DMSO-d_6. Both samples revealed resonances corresponding to the silica and PAA, and there was no significant difference in the composition. Elemental analysis indicated that the complexes contain 5.54% Si and 2.27% N, suggesting that the silica composition is about 50 wt % and is in good agreement with the composition in the feed. The FT-IR spectrum of the isolated complex revealed a carbonyl stretch vibration (1729 cm^{-1}) corresponding to the free carbonyl band of PAA and a typical broad band around 1100 cm^{-1} resulting from Si−O stretching on silica. In addition, a clear band was visible at lower wavenumbers (1560 cm^{-1}), which is attributed to the absorption of carboxylate anions. The appearance of the absorption band of the carboxylate anions in the complex, which may be a result of proton transfer from carboxylic groups in PAA to amine moieties in the silica, suggests that these complexes are stabilized by ionic COO$^-$−N$^+$ bonds at pH ≈ 3.5.
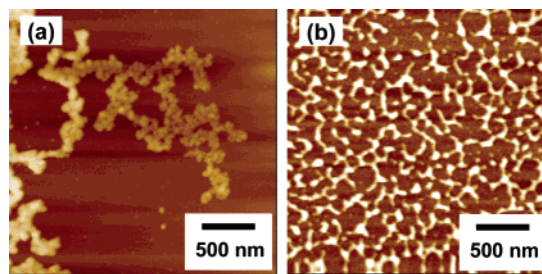
Figure 3. SFM images of the PAA/silica complexes obtained from turbid dispersion at pH ≈ 3.5: (a) dip-coated from 1 mg/100 mL, Z range 70 nm and (b) spin-coated from 1 mg/1 mL, Z range 10 nm.

Figure 3 shows tapping mode SFM images of the PAA/silica complexes obtained from water at pH ≈ 3.5. The aggregation structures are seen clearly in both cases. These results suggest that pH-induced complexation between the silica nanoparticles with PAA can be extended to a variety of novel assembled composites.

This discovery substantially broadens and extends the scope of intelligent colloidal nanocomposites, which reversibly form complexes in response to changes in the pH of environmental fluids. The reversible pH-induced colloid formation due to the complexation of the inorganic−organic nanomaterials can provide a viable route to the production of tailored materials with unique properties for various applications, such as controlled release, chemical sensing, and gene delivery systems.

Supporting Information Available: Synthesis of the silica nanoparticles, procedure of complex formation, instruments, and photographic demonstration of the complex formation (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) PAA (M_n = 7700, M_w/M_n = 1.15) was obtained by atom transfer radical polymerization of *tert*-butyl acrylate, followed by hydrolysis. See: Mori, H.; Chan Seng, D.; Lechner, H.; Zhang, M.; Müller, A. H. E. *Macromolecules* **2002**, *35*, 9270−9281.
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(14) A common method to prepare hydrophilic silica particles is the so-called postfunctionalization approach which is a modification of the silica particles with alkoxysilane (R′-Si(OR)$_3$) or chlorosilane (R′-SiCl$_3$) having organic R′ species. See: Sanchez, C.; de Soler-Illia, G. J.; Ribot, F.; Lalot, T.; Mayer, C. R.; Cabuil, V. *Chem. Mater.* **2001**, *13*, 3061−3083. By the method, it is actually impossible to attain nanometer size and high functionality, which are comparable to the silica nanoparticles developed in this study.

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