REVERSIBLE pH-INDUCED COMPLEXATION OF POLYELECTROLYTE AND WATER-SOLUBLE SILICA NANOPARTICLES AS INTELLIGENT COLLOIDAL HYBRIDS

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Introduction

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 numerous important technologies, such as biotechnology and advanced microelectronics. A variety of self-assembled systems have been reported, including polymer-polymer,[1] colloid-colloid,[2,3] and polymer-colloid.[4,5] Recently, Boal et al. have demonstrated the self-assembly of colloidal gold nanoparticles (~ 2 nm) by 'bricks and mortar' approach, in which complementarity between colloid and polymer was achieved using the diaminotriazine-thymine three-point hydrogen bonding interaction.[4] 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, is another central to developments in various scientific fields, such as shape-memory systems, drug-delivery system, and actuators. We present novel intelligent colloidal polymer/silica nanocomposites, in which the complexation of water-soluble cationic silica nanoparticles (diameter = 2.8 nm) and a weak anionic polyelectrolyte can be manipulated simply by pH change through hydrogen-bonded interaction and ionic complexation caused by hydrogen-transfer interactions between the constituents.

Experimental

Materials. Water-soluble silica nanoparticles were prepared by addition reaction of aminopropyltriethoxysilane and glycidol, followed by acidic condensation of the addition product. To 44.55 g (120.6 mmol) of the adduct dissolved in 200 ml methanol was added 6.727 g of aqueous HF solution (3.225 %) under stirring. The reaction mixture was stirred for additional 2 h at ambient temperature. Then water, ethanol, and methanol were removed in vacuum and the nanoparticles were dried at 40 °C at 8 mbar. Yield: 3.514 g (100 % of th.), $T_g = 32.2$ °C, η (23 °C) = 12.4 MPa*s. Linear poly(acrylic acid) was obtained by atom transfer radical polymerization of *tert*-butyl acrylate, followed by hydrolysis with an excess of trifluoroacetic acid.[6] M_n = 7700 (DP = 107); $M_w/M_n = 1.15$ (calculated from the molecular weights of poly(*tert*-butyl acrylate), before hydrolysis).

Complex formation. Linear PAA having low polydispersity and the water-soluble silica nanoparticles were employed for the complex formation. A representative example is as follows: To 4 mL of an aqueous solution of the silica nanoparticles (60 mg), 4 mL of an aqueous solution of PAA (60 mg) was added at room temperature. The mixed solution became turbid immediately. The product was isolated via centrifugation (4000 rpm, 20 min, 20 °C), and dried in vacuo at room temperature overnight to a give glassy material (Yield = 68 %). The product was characterized by FT-IR, ^{1}H NMR in DMSO-d_6. Elemental analysis indicated that the complexes contained 44.25 % C, 6.55 % H, 5.54 % Si, 2.27 % N. The pH value of the solution was adjusted by adding a proper amount of aqueous solution of NaOH or HCl. All experiments were conducted without adding salt.

Instrumentation. ^{1}H NMR spectra were recorded with a Bruker AC-250 spectrometer. FT-IR spectra were recorded on a Bruker Equinox 55 spectrometer. The elemental analyses were performed by Ilse Beetz Mikroanalytisches Laboratorium (Kulmbach). The potentiometric titration was conducted using a Schott CG840 pH meter equipped with a glass electrode. The turbidity measurement was conducted using a Perkin-Elmer Lambda 15 UV/VIS spectrophotometer at 450 nm. Bright field transmission electron microscopy (TEM) was performed using a Zeiss electron microscope (CEM 902) operated at 80 kV. The samples for TEM observation were prepared by applying a drop of a diluted DMF solution (10 mg/L) on carbon-coated Cu grids and allowed to dry in air. Scanning force microscopy (SFM) height and phase images were taken on a Digital Instruments Dimension 3100 microscope operated in Tapping Mode (free amplitude of the cantilever ≈ 30 nm, set point ratio ≈ 0.98). The samples were prepared on polished silicon wafers by dip-coating or spin-coating from DMF and aqueous solutions.

Results and Discussion

Synthesis of Water-soluble Silica Nanoparticles. Water-soluble silica nanoparticles used for the complexation were prepared by addition reaction of aminopropyltriethoxysilane and glycidol, followed by acidic condensation of the addition product. The resulting silica nanoparticle is directly soluble in water, methanol, DMF, and DMSO, while insoluble in most organic solvents, such as dichloromethane, acetone, etc. The particle size (2.8 nm) was confirmed using TEM, SFM (**Figure 1**), and SAXS.

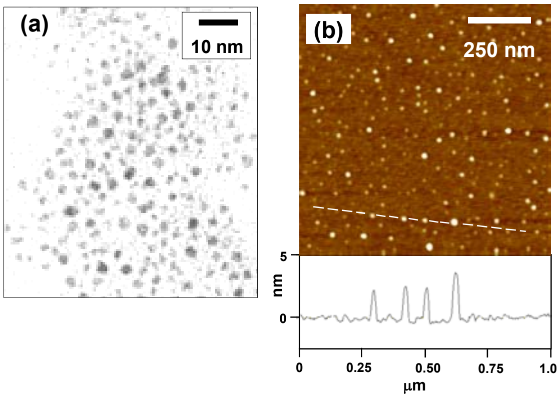


Figure 1. (a) TEM and (b) SFM height images of the water-soluble silica nanoparticles.

Complex Formation in Water. Both PAA and the silica nanoparticles were completely soluble in water, while a white turbid dispersion was obtained just after mixing the two solutions with the same concentration at room temperature. The complex formation in water was strongly affected by the pH value. **Figure 2** shows a representative demonstration of the reversible pH-induced complexation of the silica nanoparticle with PAA in aqueous solution. The complexation in water led to a milky white dispersion (pH ≈ 3.5), with no evidence of any microscopic precipitation. The turbid solution 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 at higher pH region became turbid by adding HCl. Further addition of HCl to the turbid solution 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 in this system. The pH-induced complexation in aqueous solution was also confirmed by the turbidity measurement (**Figure 3a**).

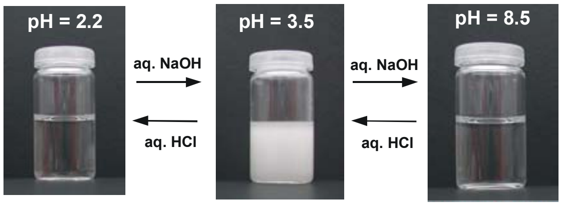


Figure 2. Demonstration of the reversible pH-induced complexation of the water-soluble silica nanoparticle with PAA in aqueous solution ([silica] = [PAA] = 7.5 mg/mL).

Figure 3b shows potentiometric titration curves for the PAA/silica complexes, in addition to those for PAA and the silica nanoparticles. By adding NaOH, the complex solutions show three different transition points at pH = 2.3 - 2.5 (from transparent to white turbid), pH = 5.4 - 5.7 (to semi-transparent), and pH = 8.2 - 8.5 (to transparent again). The second transition point corresponds to a pH, where the hydrochloride/amino groups of the water-soluble silica nanoparticles are deprotonated. The third transition point corresponds to the complete ionization point of PAA.

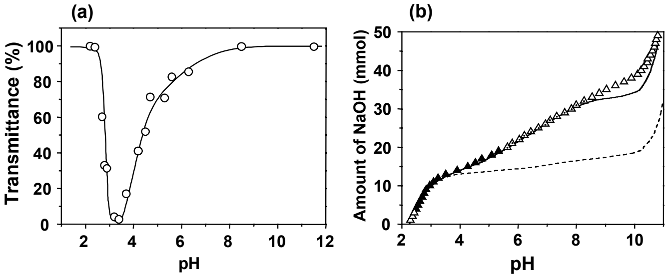
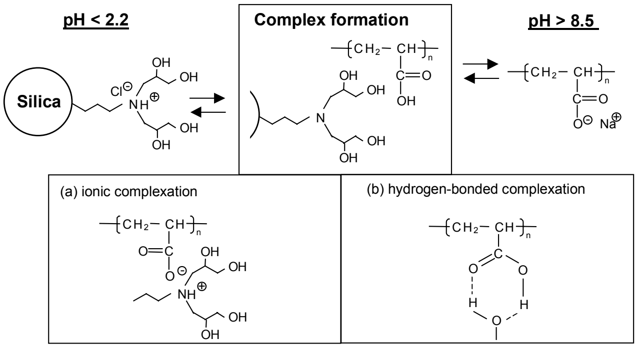


Figure 3. (a) Turbidity of the PAA/silica complexes ([silica] = [PAA] = 0.2 mg/mL) and (b) potentiometric titration curves for the complexes (Δ, ◬, ▲), PAA (—), and the silica nanoparticle (---); [silica] = [PAA] = 1.0 mg/mL. The symbols (Δ, ◬, ▲) indicate the regions where the solution was transparent, semi-transparent, and white turbid, respectively.

Scheme 1 represents the postulated mechanism of the reversible pH-induced association and dissociation behavior of the water-soluble silica nanoparticle with PAA. It is anticipated that two proton-accepting atoms, oxygen or nitrogen, on the silica nanoparticles play different roles to form complexes with PAA. At pH = 2.5 - 5.3, the complex is governed mainly by ionic complexation caused by proton-transfer interactions between the constituents. At 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 to participate 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 at higher pH region (pH > 8.5) leads to breaking the hydrogen bonding, resulting in the optically clear solution.



Scheme 1. Postulated mechanism of the reversible pH-induced association and dissociation behaviors of the water-soluble silica nanoparticle with PAA through (a) ionic complexation and (b) hydrogen-bonded complexation.

Characterization of the Complexes. In order to obtain structural information on the complexes, the white turbid products formed just after mixing of the corresponding solutions were collected 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 water-soluble silica (1/1 wt %) was conducted in DMSO-d_6. Both samples revealed resonances corresponding to the water-soluble silica and PAA, and there were no significant difference in the composition between the samples. Elemental analysis indicated that the complexes contained 5.54 % Si and 2.27 % N, suggesting that the composition of the silica nanoparticles in the complexes 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 free carbonyl band of PAA and a typical broad band around 1100 cm^{-1} resulted 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 as 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 $\approx$ 3.5.

Figure 4 shows tapping mode SFM images of the PAA/silica complexes obtained from aqueous solutions at pH $\approx$ 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 composites materials with well-defined three dimensional structures.

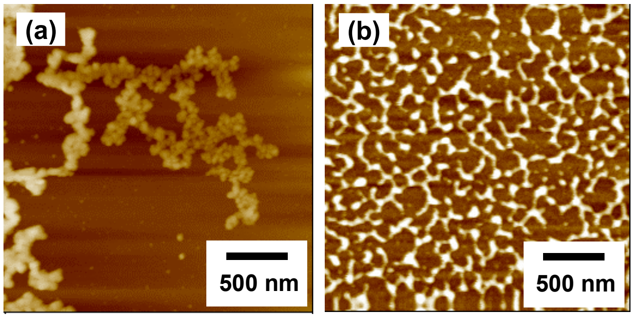


Figure 4. SFM images of the PAA/silica complexes obtained from aqueous solutions at pH $\approx$ 3.5: (a) dip-coated from 1mg/100mL, Z range: 70 nm and (b) spin-coated from 1mg/1mL, Z range: 10 nm.

Conclusions

This discovery substantially broadens and extends the scope of intelligent colloidal nanocomposites, which reversibly form complexes in response to changes in pH of environmental fluids. At least two different interactions between the water-soluble silica nanoparticles and polyelectrolyte appear to be a pre-requisite for the pH-responsive hybrid materials. The reversible pH-induced colloid formation due to the complexation of the inorganic-organic nanomaterials composed of the water-soluble silica nanoparticles and polyelectrolyte can provide a viable route to the production of tailored materials with unique properties for various bio-related applications.

Acknowledgements. The authors would like to thank the Deutsche Forschungsgemeinschaft (DFG) for financial support. The authors thank A. Göpfert for TEM measurement.

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