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Copper and copper compounds as coatings on polystyrene particles and as hollow spheres

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Submicron-sized anionic polystyrene latices have been coated with uniform layers of copper compounds by aging dispersions of the polymer colloid in the presence of aqueous solutions of $Cu(NO_3)_2$, urea, and poly(*N*-vinylpyrrolidone) at 85 °C. The thickness and morphology of the deposited layers can be altered by suitable adjustment of the reactant concentrations and the aging time. Hollow colloidal spheres of metallic copper and copper oxide were obtained by calcination of the coated polystyrene latices at elevated temperatures in nitrogen and air, respectively.

Introduction

Previous studies have provided successful procedures for the preparation of composite particles consisting of inorganic and organic cores covered with shells of other inorganic materials by controlled surface precipitation processes.[1–13] Such composite particles may be useful in many applications because the properties (magnetic, optical, electric, adsorptive *etc.*) of these particles can be altered by appropriate coatings. Other studies have also shown that these procedures can be used for the preparation of polymer particles covered with yttrium,[14] zirconium,[15] iron,[16,17] and titanium compounds[18] by controlled surface precipitation processes, which makes it possible to extend the use of these colloids to different areas of high technology.

Owing to their lower density, large specific surface area, and optical properties, hollow particles have been of interest as fillers, coatings, catalysts, capsule agents *etc.* In a novel approach, it was shown that hollow inorganic colloidal spheres of narrow size distribution can be obtained by thermal decomposition of the polymer core of polystyrene particles coated with yttrium,[19] zirconium,[15] iron,[16] and titanium compounds.[18]

The present work describes the application of the above-mentioned processes to other systems. Thus, under certain conditions, copper compounds can be deposited uniformly on submicron-sized polystyrene latices by precipitation using solutions of the corresponding salts in the presence of urea. Hollow metallic copper and copper oxide particles of a narrow size distribution can be obtained by calcination of particles coated in this manner at elevated temperatures in nitrogen and air, respectively.

Experimental

Materials

Cupric nitrate trihydrate (Wako), styrene (Wako), potassium persulfate (KPS, Wako), sodium dodecyl sulfate (SDS, Wako), poly(*N*-vinylpyrrolidone) (PVP, weight-average mol. wt. = 360 000, Aldrich), and urea (Wako) were used without further purification.

Preparation of particles

Polystyrene (PS) latex. An anionic polystyrene latex, which provided the core particles, was prepared by the batch polymerization method. For this purpose, 65 g of styrene, 373 g of distilled water, 0.65 g of KPS, and 0.20 g of SDS were added to a 500 cm^3 container and the mixture was purged with nitrogen to eliminate oxygen effects before the process was initiated. The polymerization was continued until the conversion exceeded 99%, as determined gravimetrically. Fig. 1a shows the polystyrene particles prepared by this procedure (Table 1). The mean particle size of the polystyrene latex was 0.42 μm.

Cupric basic carbonate [$Cu(OH)_2CuCO_3$]. As a first step in the preparation of coated particles, the nature of the precipitates obtained from solutions of cupric nitrate, in the absence of latex, was investigated. It has previously been shown that colloidal cupric basic carbonate consisting of spherical particles of a narrow particle size distribution can be obtained by aging copper salt solutions at elevated temperatures in the presence of urea.[9] Fig. 1b illustrates the uniform spherical particles consisting of cupric basic carbonate obtained by aging a solution 1.6×10^{-2} mol dm^{-3} in $Cu(NO_3)_2$ and 4.0×10^{-1} mol dm^{-3} in urea at 85 °C for 1 h in the presence of 0.3 wt% PVP.

Coated particles. The coating procedure consists of the controlled hydrolysis of aqueous solutions of $Cu(NO_3)_2$ in the

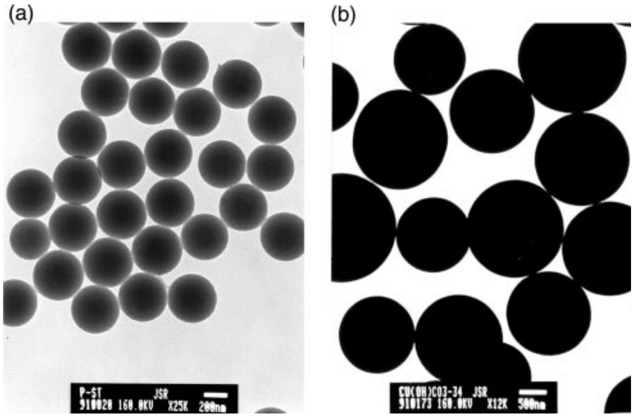

Fig. 1 TEM pictures of (a) polystyrene particles (Table 1) and (b) $Cu(OH)_2CuCO_3$ particles prepared by aging a solution 1.6×10^{-2} mol dm^{-3} in $Cu(NO_3)_2$ and 4.0×10^{-1} mol dm^{-3} in urea, containing 0.3 wt% poly(vinylpyrrolidone) (PVP) at 85 °C for 1 h.

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Table 1 Properties of spherical composite particles obtained by aging dispersions containing different amounts of $Cu(NO_3)_2$, urea, PVP, and 0.1 g dm^{-3} PS latex at 85 °C for different lengths of time

Sample	Cupric nitrate/mol dm^{-3}	Urea/mol dm^{-3}	PVP (wt%)	Aging time/h	Coated particle diameter/μm	System characteristic[a]
1	0.016	0.2	0.3	1.25		N
2	0.016	0.2	0.3	1.75	0.50	R
3	0.016	0.2	0.3	2.25	0.60	R
4	0.016	0.2	0.3	3	0.63	R
5	0.016	0.2	0.3	4		N, M
6	0.016	0.4	0.3	1	0.73	R
7	0.008	0.4	0.3	1	0.52	R
8	0.008	0.4	0.9	1	0.63	S
9	0.008	0.4	1.5	1	0.50	S
10	0.004	0.4	1.2	1	0.48	S

[a] S: smooth-coated spheres; N: no coating; R: rough-coated spheres; M: mixed systems consisting of PS and inorganic particles.

presence of polystyrene latex and PVP to prevent aggregation of the polystyrene particles. Thus, dispersions containing polystyrene latex, urea, $Cu(NO_3)_2$, and PVP were aged at 85 °C for 1–4 h. Then, the system was quenched in cold water to halt the reaction. The resulting dispersions were centrifuged at 3500 rpm for 25 min, the supernatant solutions discarded, and the particles resuspended in doubly distilled water in an ultrasonic bath. This process was repeated four times and the purified precipitates were dried in a desiccator.

Hollow particles. To produce hollow metallic copper and hollow copper oxide particles, the polymer coated with copper compound was heated at the rate of 10 °C min^{-1} and calcined in N_2 and air, respectively, in a furnace at 500 °C.

Characterization

The average size of the particles that were obtained was determined by transmission electron microscopy using a JEM-2000FX (JEOL) microscope. The coated and hollow particles were examined by infrared (IR) spectroscopy using a JIR-5500 (JEOL) spectrometer, X-ray diffraction (XRD) using a MXP[18] (Mac Science) diffractometer, and differential thermal analysis (DTA) and thermogravimetric analysis (TGA) using a TG/DTA300 (Seiko) analyzer. Electrokinetic measurements, using a DELSA 440 instrument (Coulter Electronics), were carried out with PS latex, cupric basic carbonate, and coated particles as a function of pH at a constant ionic strength (0.01 mol dm^{-3} $NaNO_3$).

Results and discussion

Preparation of coated particles

In order to determine suitable conditions for the coating of copper compounds on the surface of anionic polystyrene particles, several parameters were varied systematically. This was achieved in the presence of urea, while in the presence of Na_2CO_3 or CO_2 flow, the deposition of copper compound could not be controlled. In addition, it was found that PVP added to the system plays an important role in preventing aggregation of the core polymer and the coated particles without affecting the precipitation of the inorganic compounds.

Fig. 2 shows the results obtained in terms of $Cu(NO_3)_2$ and urea concentrations at constant amounts of the polystyrene latex (0.1 g dm^{-3}) and PVP (0.3 wt%). The dashed boundary delineates conditions yielding spheres with rough coatings. Outside this region, mixed dispersions consisting of non-coated latex and copper compounds were found. The formation of the surface coating may be explained by heterocoagulation between cupric basic carbonate precipitated *in situ* and the core PS particles, with the inorganic shell being built up from successive layers. The uniformity of the surface shell layers, therefore, depends not only on the precipitation rate of cupric carbonate, but also on the different surface charges of each particle which undergoes heterocoagulation. Table 1 shows the effect of aging time on the coating of a constant amount of PS latex (0.1 g dm^{-3}), $Cu(NO_3)_2$ (1.6×10^{-2} mol dm^{-3}), urea (0.2 mol dm^{-3}), and PVP (0.3 wt%) aged at 85 °C. Fig. 3 shows the TEM photographs of samples 2, 4, and 5 (aging time 1.75, 3.0, and 4.0 h respectively). The thickness of the coating layer increased to some degree with increasing aging time. When the aging time was over 4 h, however, mixed systems consisting of PS particles and black non-spherical inorganic particles were generated. It is thought that these arise from a change in the composition of the shell layer from cupric basic carbonate to copper oxide leading, in turn, to a change in morphology, which induced peeling of the copper compound from the surface on the polymer particles. When the other parameters, including the concentration of PVP and cupric nitrate in the system, were varied systematically, more smoothly-coated polystyrene particles were obtained (Table 1). When the concentration of PVP added to the system was increased (>0.9 wt%) (Table 1, sample 8, 9), a smooth coating layer was also formed (Fig. 3d and 6a). The effectiveness of the adsorption of the copper compounds generated on the surface of the polymer particles may increase with increasing PVP concentration in the system.

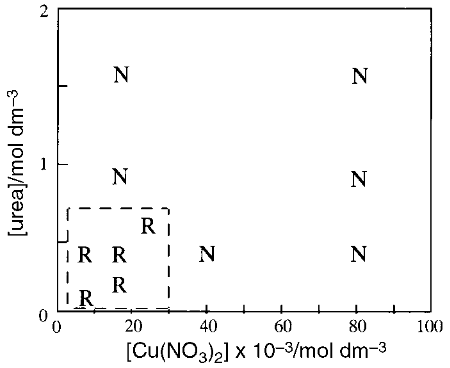

Fig. 2 Precipitation domain for systems containing varying amounts of urea and $Cu(NO_3)_2$ in the presence of 0.1 g dm^{-3} PS latex and 0.3 wt% PVP, aged at 85 °C for 2 h. R: rough-coated latex; N: non-coated systems.

Fig. 4 shows the infrared (IR) data for the polystyrene latex, coated particles and cupric basic carbonate particles. The IR spectrum of this latex (Fig. 4a) reveals well-defined bands (700, 750, 1050 and 3020 cm^{-1}) due to the phenyl group and a peak at 2920 cm^{-1} due to the CH_2 group. The spectrum of the cupric basic carbonate (Fig. 4b) shows a band due to OH stretching vibrations (3000–3500 cm^{-1}), as well as bands resulting from water of hydration (1650 cm^{-1}) and carbonate (1350–1600 and 860–880 cm^{-1}). Fig. 4c, obtained from sample 8 (Table 1), shows bands characteristic of polystyrene in addition to cupric

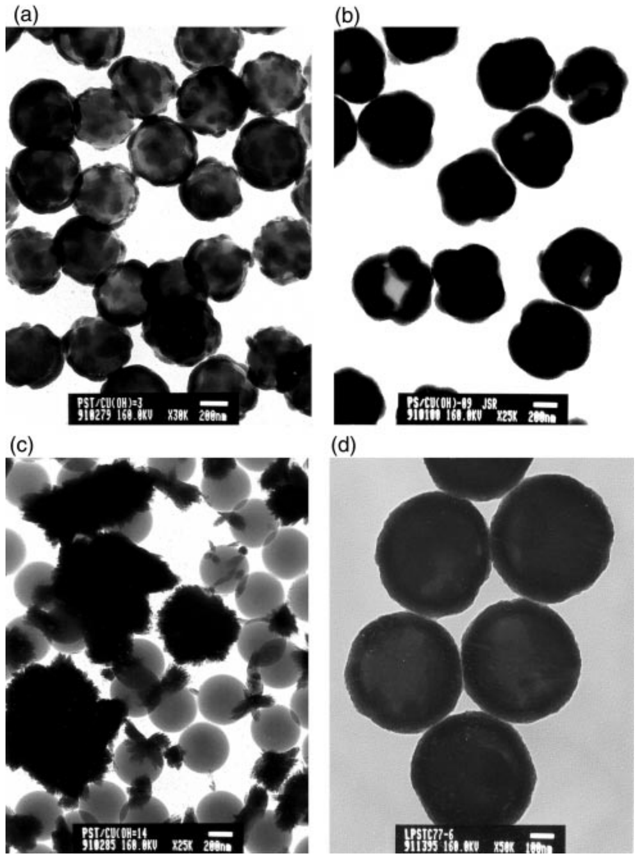

Fig. 3 TEM pictures of particles obtained: (a) sample 2, (b) sample 4, (c) sample 5, and (d) sample 9.

basic carbonate, demonstrating that sample 8 consists of coated particles.

Fig. 5 shows the mobilities of the coated polymer particles as well as the copper basic carbonate produced in the absence of PS latex. The isoelectric point (i.e.p.) of the composite particles (sample 8) was lower than that for the cupric basic carbonate, which leads to the conclusion that the polymer cores were not perfectly coated with copper compound, even if the coating layer was judged to be smooth by TEM (Fig. 6a).

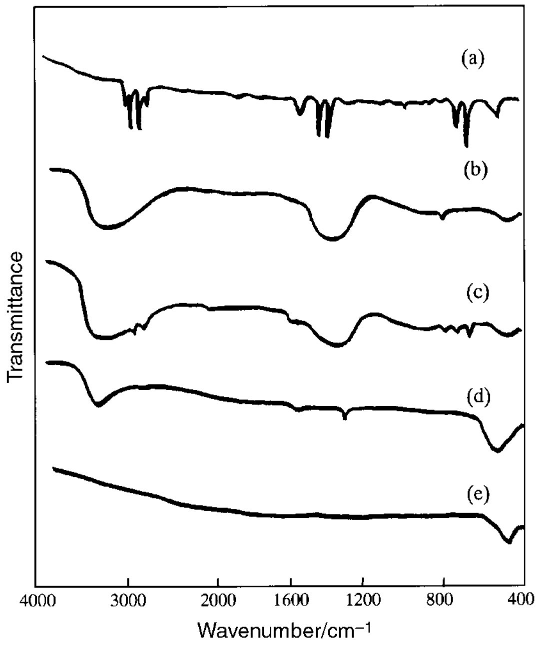

Fig. 4 IR spectra of (a) PS particles, (b) $Cu(OH)_2CuCO_3$, (c) sample 8 ($PS/Cu(OH)_2CuCO_3$), (d) sample 11 (void/CuO), and (e) sample 12 (void/Cu).

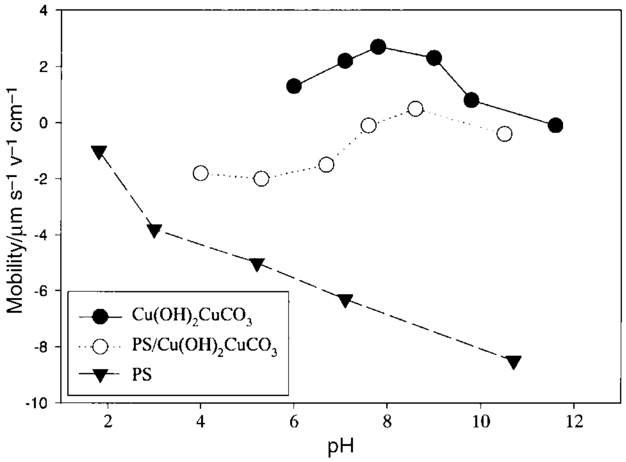

Fig. 5 Electrokinetic mobilities of dispersions consisting of PS, $Cu(OH)_2CuCO_3$, and $PS/Cu(OH)_2CuCO_3$ (sample 8) as a function of pH in 0.01 mol dm^{-3} $NaNO_3$.

Preparation of hollow particles

To obtain hollow particles, polymer particles coated with cupric basic carbonate were heated to 500 °C. The results are summarized in Table 2. The composition of the shell material depends on the calcination conditions. Hollow particles consisting of copper oxide resulted (Fig. 6b, sample 11) when the coated particles (sample 8) were calcined in air, whereas metallic copper shells were obtained (Fig. 6c, sample 12) when the coated particles were heated in an atmosphere of nitrogen, as ascertained by XRD (Fig. 7).

Fig. 8 compares the respective weight loss curves of coated particles, polymer particles, and cupric basic carbonate on heating to 500 °C in air. Fig. 8c, which refers to coated particles, show two inflection regions: the first at 150–250 °C and the second at 300–400 °C. These are associated with the

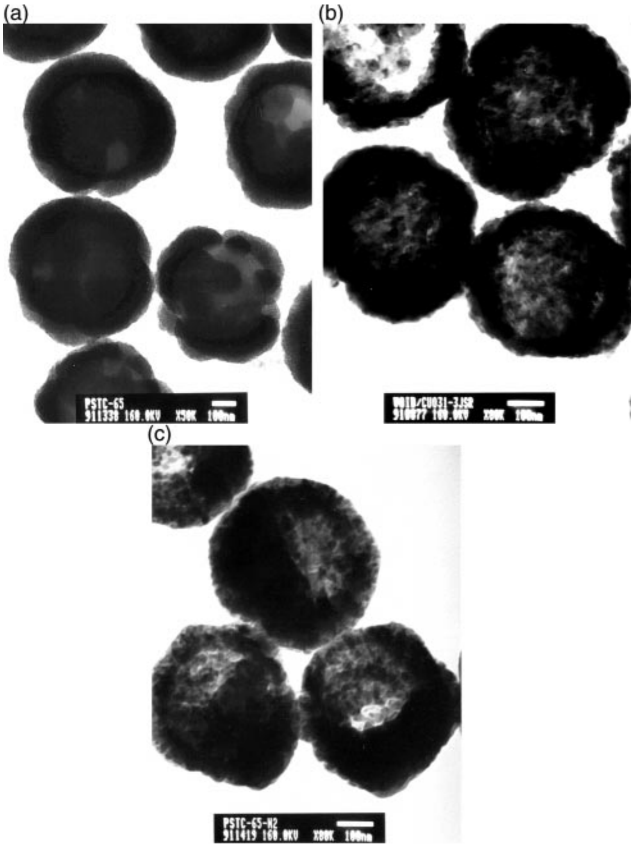

Fig. 6 TEM pictures of (a) composite particles (sample 8), (b) hollow CuO particles (sample 11), and (c) hollow Cu particles (sample 12).

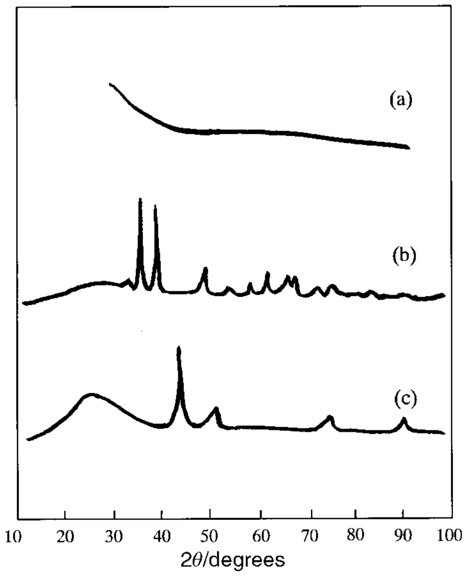

Fig. 7 XRD patterns of particles: (a) sample 8 (PS/$Cu(OH)_2CuCO_3$), (b) sample 11 (void/CuO), and (c) sample 12 (void/Cu).

Table 2 Properties of particles obtained by calcination of sample 8 at 500 °C in different atmospheres (heating rate = 10 °C min^{-1})

Sample	Calcination atmosphere	Particle diameter/μm		Composition	
		outer	inner	core	shell
11	Air	0.50	0.37	void	CuO
12	N_2	0.43	0.31	void	Cu

weight losses due to dehydration and decarboxylation of the inorganic shell to CuO and decomposition of polystyrene to CO_2 and H_2O, respectively. Weight losses when the same samples were heated in an atmosphere of nitrogen are compared in Fig. 9. The final weight loss of coated particles is 27% when calcined at 500 °C in air, and 39% when calcined in nitrogen. Fig. 9c, which refers to coated particles, shows two inflection regions as does Fig. 8c. But, in this case, the second inflection is due to the weight loss caused by the pyrolysis of polystyrene to H_2, CH_4, and so on. It is thought that the shells of the particles were reduced to metallic copper by these reductive gases when the coated particles were heated in nitrogen.

The IR spectra of powders of the coated particles calcined at 500 °C in air (Fig. 4d) and in an atmosphere of N_2 (Fig. 4e) reveal no spectral characteristics of polystyrene, confirming that the polymer core was decomposed by calcination at over 475 °C, which leads to the conclusion that these powders consist of hollow particles. Whereas Cu does not show absorption maxima in the IR region, a band at low frequency similar to that for PS/cupric basic carbonate (Fig. 4c) or the hollow CuO particles (Fig. 4d) is observed in the IR spectrum shown in Fig. 4e. This behavior seems to indicate that the layer is actually composed of a mixture, with the main component being metallic copper. The contaminant may be amorphous, since no other peaks were observed by XRD, although it has not been identified.

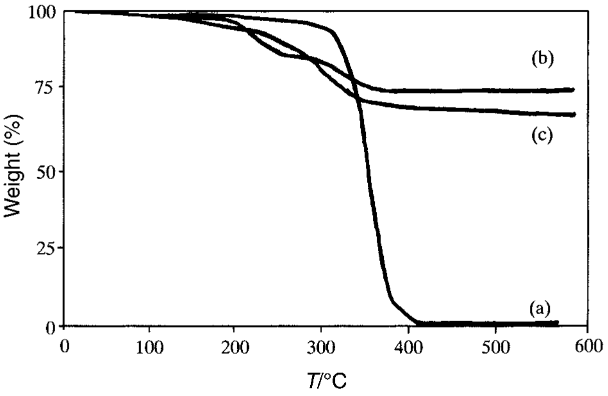

Fig. 8 The change in weight as a function of calcination temperature in air for (a) PS latex, (b) $Cu(OH)_2CuCO_3$, and (c) sample 8 (PS/$Cu(OH)_2CuCO_3$).

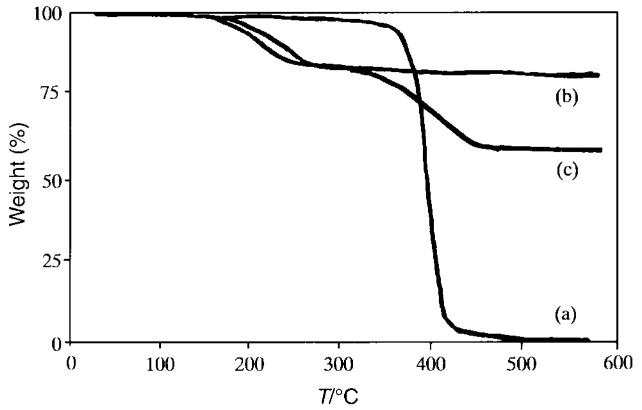

Fig. 9 The change in weight as a function of calcination temperature in nitrogen for (a) PS latex, (b) $Cu(OH)_2CuCO_3$, and (c) sample 8 (PS/$Cu(OH)_2CuCO_3$).

Conclusion

Submicron-sized anionic polystyrene particles can be coated with cupric basic carbonate by aging a solution containing cupric nitrate, urea, and PVP in the presence of PS latex. The thickness of the coating layer can be altered by variation of the aging time. Hollow particles of metallic copper and copper oxide were obtained by calcination of the composite powders at elevated temperatures in a flow of nitrogen and air, respectively, although some contaminant was included in the former particles.

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