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SHORT COMMUNICATION

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Preparation of electrically conducting particles consisting of a polymer core and a metallic copper shell

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Abstract Micron-sized composite particles consisting of spherical polymer cores and metallic copper shells were prepared. Basic cupric carbonate was coated on sulfonated polymer particles by pH-controlled hydrolysis of cupric nitrate. The thickness of the coating layer was controlled by the number of polymer particles. Addition of CO_2 during aging increased the shell thickness. Electrically conducting particles were obtained by reduction with hydrogen of the composite particles obtained.

Key words Copper · Particles · Coating · Core–shell

Introduction

Polymer colloids, commonly known as latexes, have been widely studied because of the many applications of these materials. To extend the uses of latexes in various fields of science and technology, it is often advantageous to coat the particles with layers of different chemical composition. Different methods for the preparation of such composite particles have been recorded [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13]. Particles covered with electrically conducting materials were used or proposed for use in electrically conducting inks, plastics fillers, microconnectors, and shielding agents of electromagnetic waves. Such powders covered with metal can be produced by electrochemical deposition [13, 14, 15]; however, these processes are somewhat tedious.

Here, we report a new concise process for producing electrically conducting materials consisting of monodispersed polymer particles covered with metallic copper. The composite particles were prepared by controlled hydrolysis of cupric nitrate in the presence of cross-linked polymer colloids and successive calcination in hydrogen.

Experimental

Materials

Cross-linked polymer powders [poly(divinylbenzene), particle diameter 4.60 and 6.26 μm, DYNO] were treated with concentrated sulfuric acid for 2 h in an ice-cold bath. The reaction mixture was pored into ice-cold water to discontinue the reaction. The resulting dispersions were allowed to stand for a while to separate. The supernatant was discarded, the residue was resuspended in doubly distilled water, and then the dispersion was centrifuged at 6,000 rpm for 20 min. This purification process was repeated four times. The treated particles were washed with 2-propanol, filtered, and dried in a desiccator.

Urea (Wako), poly(*N*-vinylpyrrolidone) (PVP; weight-average molecular weight 360,000, Aldrich), cupric nitrate trihydrate, sulfuric acid (Wako), and 2-propanol (Wako) were used without further purification.

Preparation of particles

Coated particles

The coating procedure consisted of controlled hydrolysis of aqueous solutions of $Cu(NO_3)_2$ in the presence of a polymer latex. Thus, a reaction mixture containing different numbers of sulfonated polymer particles, 5 g PVP, and 1 dm^3 distilled water was dispersed in an ultrasonic bath. The dispersion was heated to 85 °C with stirring, and then a solution containing 2.1×10^{-3} mol $Cu(NO_3)_2$, 8.3×10^{-2} mol urea and 50 g distilled water was added to the system. Fifteen minutes after the addition of $Cu(NO_3)_2$ and urea, a solution of cupric nitrate (1.7×10^{-2} mol) in distilled water (40 g) and a solution of urea (3.3×10^{-1} mol) in water (100 g) were added independently to the dispersion to keep the pH of the system between 5.0 and 5.3. The reaction mixture was aged for 75–90 min after the end of $Cu(NO_3)_2$ addition, then the system was quenched in a cold water bath. The resulting composite particles were separated from the reaction mixture by filtration. They were washed with distilled water and 2-propanol to remove PVP adsorbed on the surface of the particles, and then dried in a desiccator.

Calcination of the composite particles

In order to make the particles conductive, they were heated at 150–300 °C in an atmosphere of hydrogen for 1–3 h.

Analyses

The particle morphology was evaluated by scanning electron microscopy (JEOL JEM-2000FX microscope). The composite particles were examined by X-ray diffraction with a MXP^{18} (Mac Science) diffractometer, differential thermal analysis, and thermogravimetric analysis with a TG/DTA300 (Seiko) analyzer. The electric conductivity of the particles was measured as follows: powders were put into a glass tube with a diameter of 3 mm and pressed slightly by copper sticks inserted into the glass tube from the both sides of the tube, and then measured using a multimeter.

Results and discussion

Heat-resistant cross-linked polymer particles were used as the core material taking into account the subsequent calcination treatment. The polymer powders used in this study could not be dispersed in water without a dispersing agent, probably because their surfaces were hydrophobic. The powders were, therefore, treated with concentrated sulfuric acid to generate hydrophilic sulfonated groups on the surface. The so-treated particles could be dispersed in water. A good coverage by the copper compound was achieved, while no coating could be deposited on the nontreated polymer latex.

The coating procedure consisted of hydrolysis of an aqueous solution of $Cu(NO_3)_2$ in the presence of the pretreated polymer latex. In order to prevent aggregation of core particles during the course of the coating reaction, PVP was added to the system as in previous studies [3, 4, 16, 17, 18, 19]. PVP covered the surfaces of the precipitated inorganic particles and the composite particles.

We have previously established the optimum condition for coating submicron-sized polymer particles by a copper compound with a batch method [16]. This technique was modified for the coating the micron-sized polymer particles. The optimum condition was established when the pH of the system was kept between 5.0 and 5.3 by the intermittent addition of $Cu(NO_3)_2$ and urea solutions. The addition of $Cu(NO_3)_2$ solution and the hydrolysis of $Cu(NO_3)_2$ led to a pH decrease in the system. On the other hand, urea decomposes at elevated temperature according to [20]

$$CO(NH_2)_2 \rightleftharpoons NH_4^+ + NCO^-$$

$$NCO^- + OH^- + H_2O \rightleftharpoons NH_3 + CO_3^{2-}$$

which increases the pH. As a result, the pH in the system could be kept constant in a narrow range by controlled addition of $Cu(NO_3)_2$ and urea solutions. The polymer particles used as a core and the composite particles are shown in Fig. 1.

The surface charge of the polymer particles was negative at $pH < 2$. The isoelectric point of basic copper carbonate $Cu_2(OH)_2CO_3$ was 11.2 [16]; therefore, heterocoagulaton occurs between the polymer particles and the basic copper carbonate, which is followed by the growth of the shell.

When the pH in the system was maintained above 5.3, the color of the dispersions changed from green to dark brown during the course of the reaction owing to the formation of crystalline particles, mostly rodlike or spindlelike cupric oxide. In this case, separated copper compounds were generated without coating the polymer surface, although coated particles were formed in the early stage of the reaction. The morphology changed because crystallization of the coating layer induced peeling off of the shells. A similar phenomenon was previously observed in another system [21]. When the pH in the system was below 5.0, blue crystals were formed without coating the polymer particles. X-ray diffraction showed that this material contained crystal-

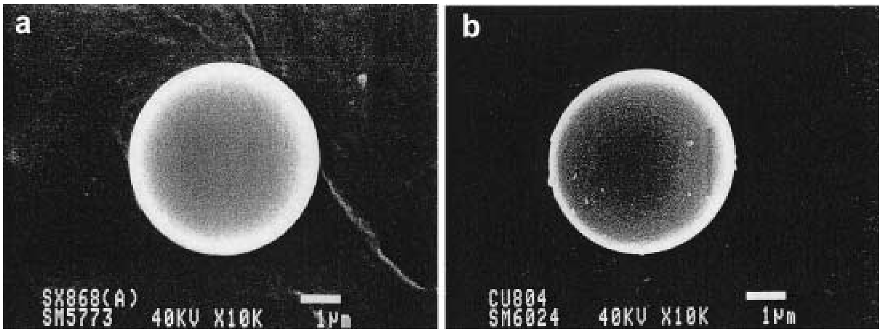

Fig. 1 Scanning electron micrographs of **a** poly(divinylbenzene) particles (4.60 μm) and **b** particles obtained by heating a solution at 85 °C with 4.6 gdm^{-3} $Cu(NO_3)_2$ and 25 gdm^{-3} urea (90 min, pH 5.0, 85 °C)

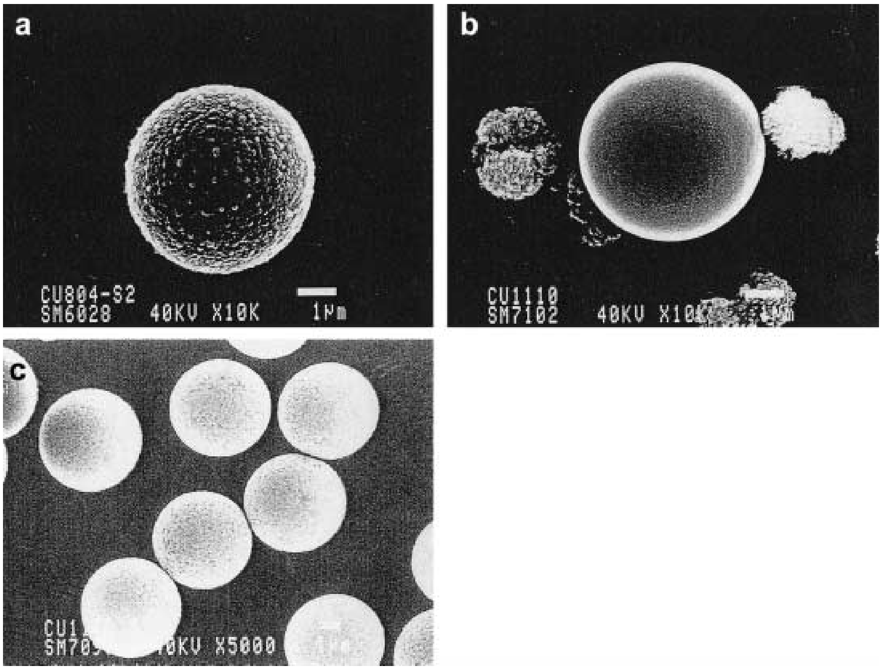

Fig. 2 Scanning electron micrographs of particles of **a** thinly coated particles (entry 3), **b** pealed-off particles (entry 3 after pH drop), and **c** thickly coated particles (entry 4)

Table 1 Thermogravimetric analysis for composite particles (a dispersion of different numbers of polymer particles and 0.5 wt % was heated at 85 °C and 4.5 g m^{-3} Cu(NO$_3$)$_2$ was added to the dispersion to keep the pH at 5.0) consisting of a polymer core (4.60 μm) and a Cu$_2$(OH)$_2$CO$_3$ shell, heated to 900 °C in air

Entry	Polymer latex added to the system (g dm^{-3})	Particle diameter (μm)	Weight loss of the composite particles after calcination at 900 °C in air (%)	Calculated yield of copper (%)[b]
1	10	4.61	98.7	4
2	5	4.62	95.5	14
3	1	4.63	92.1	26
4[a]	1	4.86	77.1	91

[a] CO$_2$ was bubbled into the dispersion for 15 min after the addition of Cu(NO$_3$)$_2$

[b] Based on the weight of Cu(NO$_3$)$_2$ added to the system and the weight loss after thermal decomposition of the composite particles to CuO

line Cu$_2$(OH)$_3$NO$_3$; therefore, a strong pH control is required to obtain smooth coated particles, as observed in another system [18].

Even when the pH was between 5.0 and 5.3 at the beginning, it dropped and the coverage peeled off (Fig. 2) during aging after the end of the addition of the incremental amounts of Cu(NO$_3$)$_2$. The uncontrollable pH drop is due to the change in the chemical composition of the precipitated copper compound from Cu$_2$(OH)$_2$CO$_3$ to Cu$_2$(OH)$_3$NO$_3$ accompanied by crystallization. In the first stages, amorphous basic cupric carbonate covered the polymer cores. Separated Cu$_2$(OH)$_2$CO$_3$ and uncoated poly(divinylbenzene), particles were not observed before the pH drop.

When the quantity of the polymer particles added to the system was increased, the coating layer decreased as the total surface area of the polymer particles increased. This was ascertained by the thermogravimetric analysis for the composite particles (Table 1). It is interesting that the yield of copper increases in spite of a decrease in the total surface area of the polymer particles.

When CO$_2$ was bubbled in the dispersion during aging, the generation of Cu$_2$(OH)$_2$CO$_3$ was accelerated at the expense of Cu$_2$(OH)$_3$NO$_3$. As a result, the thickness of the coating and the yield of the reaction increased (Fig. 2, Table 1). When NaHCO$_3$, instead of CO$_2$, was added, a good coating was not obtained because the pH increased above 5.3.

The coated particles were reduced in an atmosphere of hydrogen (Fig. 3, Table 2). The morphology of the coating layer became slightly rough when heated to 300 °C. The shell material was metallic copper as ascertained by X-ray diffraction. Good electric conductivity was attained by moderate calcination at 150 °C for 1–3 h at a hydrogen flow rate of 0.2 dm^3 min^{-1}. At a hydrogen flow rate of 0.05 dm^3 min^{-1}, the electric conductivity was lower because of the partial reduction of the shell. Calcination at 300 °C reduced the electrical

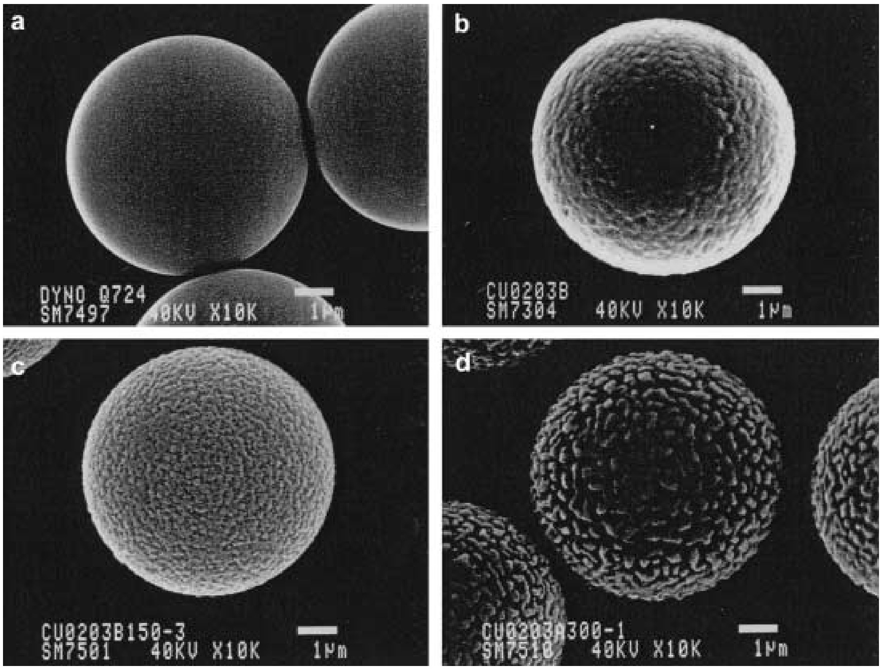

Fig. 3 Scanning electron micrographs of **a** polymer particles (6.26 μm), **b** composite particles, and **c** particles reduced at 150 °C for 1 h and **d** at 300 °C for 1 h

Table 2 Reduction of composite particles consisting of polymer cores and $Cu_2(OH)_2CO_3$ shells. The composite particles (6.38 μm, Fig. 3b) consisted of 6.26-μm poly(divinylbenzene) cores (Fig. 3a) and basic cupric carbonate shells

Entry	Reduction temperature (°C)	Reaction time (h)	Hydrogen flow rate ($\times 10^{-3}$ dm^3 min^{-1})	Electric resistivity (Ω cm)
5	150	1	50	2.0×10^2
6	150	3	50	3.3×10^3
7	150	1	200	2.6×10^{-2}
8	150	3	200	3.7×10^{-2}
9	300	1	200	$> 1.0 \times 10^{10}$

conductivity. The shells cracked into smaller fragments under the hard reduction condition and porous and less electrically-conducting particles were generated.

Conclusion

Electrically conducting particles consisting of a polymer core and a metallic copper shell were obtained by a simple method which includes pH-controlled hydrolysis of cupric nitrate in the presence of a polymer latex and a reduction of the composite particles with shells of basic cupric carbonate in hydrogen. The thickness of the coating layer was altered by the number of polymer particles added to the system. It could be increased when CO_2 was bubbled into the dispersion during aging. The electric conductivity was changed by the calcination conditions.

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