

# Synthesis of metallic copper nanoparticles coated with polypyrrole

Yoshio Kobayashi · Satoshi Ishida · Kazuaki Ihara ·  
Yusuke Yasuda · Toshiaki Morita · Shinji Yamada

Received: 10 March 2009 / Revised: 15 April 2009 / Accepted: 30 April 2009 / Published online: 16 May 2009  
© Springer-Verlag 2009

**Abstract** This paper describes a method for polypyrrole (PPy) coating of metallic Cu nanoparticles in aqueous solution in atmosphere. Colloid solution of Cu nanoparticles was prepared by reducing Cu ions with the use of hydrazine in an aqueous solution dissolving citric acid and cetyltrimethylammonium bromide as stabilizers. The PPy coating was performed by polymerizing pyrrole with the use of hydrogen peroxide as an initiator in an aqueous colloid solution of the Cu nanoparticles. Ultraviolet–visible extinction measurements, transmission electron microscopy observation, and X-ray diffraction measurements revealed that the metallic Cu nanoparticles with a size of  $27.6 \pm 11.1$  nm were coated with PPy. The obtained PPy-coated Cu particles were chemically stable even in atmosphere.

**Keywords** Copper · Nanoparticle · Coating · Polypyrrole

## Introduction

Metallic Cu nanoparticles are attractive materials fundamentally and industrially because they give unique properties over catalysis, electronics, and photoelectronics [1–6], and their

cost is low compared with other metallic materials such as gold and silver. The practical use of Cu nanoparticles faces at the main difficulty that arises from their instability toward oxidation in air. In addition, colloidal instability of nanoparticles brings about aggregation of the nanoparticles, which spoils the unique properties of nanoparticles. Various methods for stabilizing the Cu nanoparticles have been reported. Several researchers have proposed the use of nonaqueous liquid such as organic compounds as solvent or dispersing media, which does not dissolve oxygen gas and prevents it from contacting Cu nanoparticles, so that the Cu surface oxidation would be minimized [7–11]. Though their methods could avoid oxidation of Cu nanoparticles, harm and hazard of organic compounds are matter of concern.

Protection of Cu nanoparticles with a stabilizer such as surfactant can be given as another stabilization method, and various methods using the stabilizer have been previously reported [4, 12–15]. The nanoparticles are surrounded with the stabilizer by hydrophilic interaction between the nanoparticles and the stabilizer and/or coordination of functional groups of the stabilizer to metal atoms. However, the stabilizer may not prevent oxidation and aggregation of nanoparticles enough because of their molecular motion.

Coating of metallic nanoparticles can also be another approach for the stabilization because physical barrier of coating materials will prevent the nanoparticles from contacting oxygen molecules and aggregating and control interparticle interactions. Several works on coating with silica have been reported [16–22]. The silica coating has the following advantages: exceptional stability of aqueous dispersions and easy surface modification that allows the preparation of nonaqueous colloids. We have developed a technique for silica coating of Co nanoparticles prepared through reduction

Y. Kobayashi (✉) · S. Ishida · K. Ihara  
Department of Biomolecular Functional Engineering,  
College of Engineering, Ibaraki University,  
4-12-1 Naka-narusawa-cho, Hitachi,  
Ibaraki 316-8511, Japan  
e-mail: ykoba@mx.ibaraki.ac.jp

Y. Yasuda · T. Morita · S. Yamada  
Materials Research Laboratory, Hitachi Ltd,  
7-1-1 Omika-cho, Hitachi,  
Ibaraki 319-1292, Japan

of cobalt inorganic salts in aqueous solution [23]. The nanoparticles were chemically stable even after being heated at high temperature in air. In addition, we also performed silica coating of metallic Cu nanoparticles prepared from aqueous solutions of inorganic salts, and oxidation of the nanoparticles did not progress even 1 month after preparation [24].

Polymers have been also used for coating metallic nanoparticles. Mandal et al. fabricated polymethylmethacrylate-coated Au nanoparticles by living radical polymerization [25]. The polymerization was confined on the Au particle surface because of Br termination of the Au particles. Kang and Taton reported a study on polystyrene-block-poly(acrylic acid) coating of Au nanoparticles using interaction between amphiphile of the block copolymer and nanoparticle surface [26]. Structure of the coated particles was varied with a relative ratio of the amount of polymer to available surface area of Au particles. Kim and Lee proposed a method for hydrogel coating of Au nanoparticles by surfactant-free emulsion polymerization of *N*-isopropylacrylamide and acrylic acid [27]. The produced particles revealed a response to temperature and pH. Quaroni and Chumanov prepared polystyrene/methacrylate-coated Ag nanoparticles via emulsion polymerization [28]. The obtained particles could adsorb protein (bovine serum albumin) due to carboxylate functionality derived from methacrylic acid monomers. Apart from these polymers, electro-conducting polymers such as polypyrrole (PPy) and polyaniline (PA) have also been used as shell materials. In the electro-conducting polymers, charge transfer might be expected at the interface, and the optical functions of both materials should be quite different from the corresponding bulk materials because the conducting polymers provide an effective route for the flow of electronic charges [29, 30]. Liu and Chuang synthesized Au nanoparticles coated with PPy by a simple mixing of pyrrole (Py) monomer and  $\text{AuCl}_4^-$ -containing aqueous solution, in which polymerization of PPy took place through reduction of  $\text{AuCl}_4^-$  to elemental Au [31]. Ye and Lu fabricated PPy-coated Ag nanoparticles with polymerization of PPy using  $\text{FeCl}_3$  as an initiator [32]. Optical properties of the produced particles were investigated on the basis of the classical Mie theory. Du et al. proposed a method for preparing Ag nanoparticles coated with PA with a reaction between  $\text{AgNO}_3$  and aniline [33]. According to a series of comparative experiments, it was found that both the reaction temperature and  $\text{AgNO}_3$  concentration had a profound effect on macrostructure of particles.

In the present paper, we propose an alternative method for polymer coating of Cu nanoparticles, which stabilizes Cu nanoparticles chemically. Cu ions were reduced with hydrazine in the presence of citric acid and CTAB to generate Cu metallic nanoparticles, which were PPy-coated with polymerization of Py in the presence of Cu nanoparticles.

## Experimental

### Chemicals

Copper chloride dihydrate ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ; >99%) was used as copper precursors. Cetyltrimethylammonium bromide (CTAB; 99%) and citric acid monohydrate (>99.5%) were used as stabilizers. Hydrazine monohydrate (>98.0%) was used as a reducing reagent. Py (>99%) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ; 30.0–35.5%) were used for PPy coating. HCl solution (35.0–37.0%) was used for adjusting pH of solution in the PPy coating. All chemicals were purchased from Kanto Chemical and were used as received. Water that was ion-exchanged and distilled with Shimadzu SWAC-500 was used in all the preparations and was deaerated by bubbling with  $\text{N}_2$  gas for 30 min prior to preparation of aqueous solutions of  $\text{CuCl}_2$  and hydrazine.

### Preparation

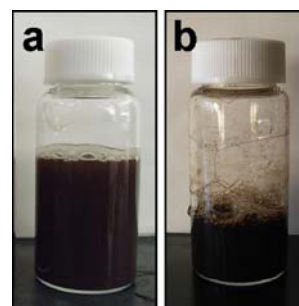
Colloids of Cu nanoparticles were prepared by mixing of  $\text{CuCl}_2$  and hydrazine. Freshly prepared 10 ml of 2 M hydrazine aqueous solution containing 0.0005 M citric acid and 0.005 M CTAB was added to 10 ml of 0.02 M  $\text{CuCl}_2$  aqueous solution containing 0.0005 M citric acid and 0.005 M CTAB under vigorous stirring at room temperature. The reaction time was 3 h. A dark-red and muddy colloid solution was produced, as shown in Fig. 1a.

PPy coating for the Cu nanoparticles was performed by polymerization of Py in the presence of the Cu nanoparticles. Ten microliters of the HCl solution was added to 10 ml of the Cu colloid. Then, 10 ml of 0.17 M Py solution and 0.32 ml of 12.4 M  $\text{H}_2\text{O}_2$  was added to the colloid in turn. The reaction time for the PPy coating was 24 h. The obtained colloid solution is shown in Fig. 1b. A dark-red colloid solution was also produced.

### Characterization

The PPy-coated Cu (Cu/PPy) nanoparticles were characterized by ultraviolet (UV)–visible (VIS) spectroscopy, X-ray diffractometry (XRD), and transmission electron microscop-

**Fig. 1** Colloid solutions of Cu nanoparticles (a) and Cu/PPy particles (b)



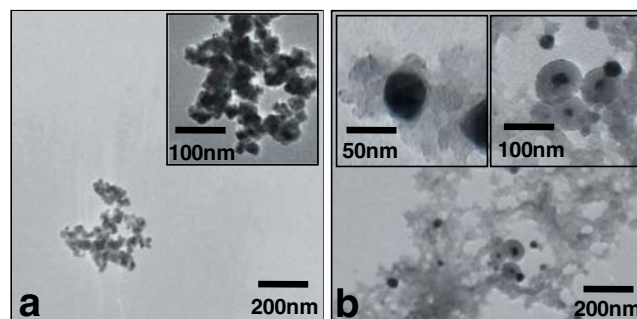
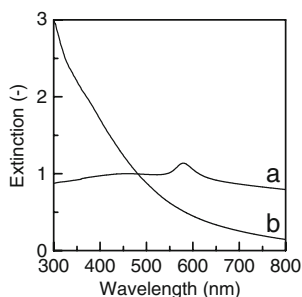
py (TEM). UV–VIS extinction spectra were measured with a Hitachi UV-3010 spectrophotometer using a quartz cuvette with a light-path length of 1 cm. Samples for UV–VIS spectroscopy were prepared by diluting as-prepared colloid solution with water by 2.5 times. An XRD chart was recorded with an X-ray diffractometer (Rigaku RAD-C) operated at 20 kV and 40 mA with  $\text{CuK}\alpha$  radiation. Samples for XRD were prepared by centrifugation of the colloid solutions at 12,000 rpm for 1 h, removal of supernatant, and drying sediment. TEM was performed with a JEOL JEM-2000FX II microscope operated at 200 kV. Samples for TEM were prepared by dropping and evaporating the nanoparticle suspensions on a collodion-coated copper grid.

## Results and discussion

### Cu nanoparticles

Figure 2 (a) gives extinction spectrum of Cu nanoparticle colloid. The background intensity of the solution itself was as high as ca. 1, which was derived from the muddiness of the colloid solution. This result provided speculation that aggregates or flocculates, which scattered UV–VIS light, were produced in the solution. A peak was observed at 577 nm on the background. According to Refs. [12, 16, 34], the peak was attributed to surface plasmon resonance of Cu nanoparticles, which provided evidence for not only the production of aggregates or flocculates but also generation of Cu particles. Figure 3a shows TEM image of the Cu nanoparticles. Submicron-sized aggregates composed of particles irregular in shape were observed. This observation indicated that the production of aggregates resulted in the strong background intensity shown in Fig. 2 (a). Figure 4 (a) shows XRD pattern of the Cu nanoparticles. The pattern showed peaks at 43.3, 50.5, and 74.1 degree, which were attributed to those of metallic Cu (JCPDS card no. 4-0836). Besides the metallic Cu peaks, several peaks, which were assigned to  $\text{Cu}_2\text{O}$  (JCPDS card no. 5-0667), were strongly detected at 36.7, 42.4, and 61.4 degree.

**Fig. 2** UV–VIS extinction spectra of colloid solutions of Cu nanoparticles (a) and Cu/PPy particles (b)

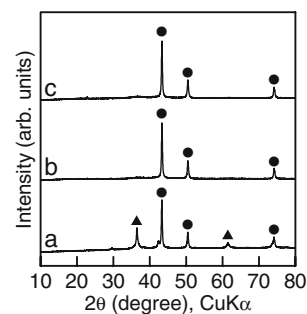


**Fig. 3** TEM images of Cu nanoparticles (a) and Cu/PPy particles (b)

### Cu/PPy particles

Figure 2 (b) shows extinction spectrum of Cu/PPy particle colloid. Extinction of the spectrum gradually increased as the wavelength became shorter, and a peak due to the surface plasmon resonance was not observed. Figure 3b shows TEM image of the Cu/PPy particles. Darker and lighter parts of particles correspond to copper and PPy, respectively, since the electron density of copper is significantly higher. Cu nanoparticles were coated with PPy shell (high magnification images in Fig. 3b). Some Cu nanoparticles incorporated in large gel-like structure were also observed. The Cu particle size was  $27.6 \pm 11.1$  nm. Figure 4 (b) shows XRD pattern of Cu/PPy particles. The pattern was measured a few days after preparation of the particles. The pattern gave clear peaks attributed to metallic Cu appeared at 43.3, 50.5, and 74.2 degree. The UV–VIS measurement (Fig. 2 (b)) could not provide evidence of production of metallic copper since no peak due to the surface plasmon resonance was observed. Strong scattering from the PPy shell possibly screened the surface plasmon peak. Figure 4 (c) shows XRD pattern of Cu/PPy particles, which was measured 50 days after preparation of the particles. The XRD pattern did not change even 50 days after preparation. This indicated that the PPy coating prevented the Cu nanoparticles from being oxidized even in air, compared with the uncoated Cu nanoparticles, which is evidence of the protection that the PPy exerts against

**Fig. 4** XRD patterns of Cu nanoparticles (a) and Cu/PPy particles (b). (c) stands for a pattern of Cu/PPy particles, which was measured 50 days after preparation. Circles metallic Cu, triangles  $\text{Cu}_2\text{O}$



oxidation of the Cu core. Thus, quite stable Cu nanoparticles could be fabricated with PPy coating.

## Summary

A method for PPy coating of metallic Cu nanoparticles in aqueous solution was proposed. To coat the Cu nanoparticles with PPy, polymerization of Py was performed in the presence of the Cu nanoparticles, which were prepared using hydrazine, citric acid, and CTAB in water in air. The present method fabricated PPy-coated metallic Cu nanoparticles, which were chemically stable even in air, compared to uncoated Cu nanoparticles.

**Acknowledgments** We express our thanks to Dr. T. Noguchi and Mr. M. Hayashi in College of Science of Ibaraki University, Japan for their help for TEM observation and to Mr. Hirano in Materials Research Laboratory, Hitachi Ltd., Japan for his help for XRD measurements.

## References

- Lambert S, Cellier C, Gaigneaux EM, Pirard JP, Heinrichs B (2007) Ag/SiO<sub>2</sub>, Cu/SiO<sub>2</sub> and Pd/SiO<sub>2</sub> cogelled xerogel catalysts for benzene combustion: relationships between operating synthesis variables and catalytic activity. *Catal Commun* 8:1244–1248
- de Oliveira AM, Crizel LE, da Silveira RS, Pergher SB, Baibich IM (2007) NO decomposition on mordenite-supported Pd and Cu catalysts. *Catal Commun* 8:1293–1297
- Wang LC, Liu YM, Chen M, Cao Y, He HY, Wu GS, Dai WL, Fan KN (2007) Production of hydrogen by steam reforming of methanol over Cu/ZnO catalysts prepared via a practical soft reactive grinding route based on dry oxalate-precursor synthesis. *J Catal* 246:193–204
- Huang HH, Yan FQ, Kek YM, Chew CH, Xu GQ, Ji W, Oh PS, Tang SH (1997) Synthesis, characterization, and nonlinear optical properties of copper nanoparticles. *Langmuir* 13:172–175
- Johnson RC, Li J, Hupp JT, Schatz GC (2002) Hyper-Rayleigh scattering studies of silver, copper, and platinum nanoparticle suspensions. *Chem Phys Lett* 356:534–540
- Liu Z, Bando Y (2003) A novel method for preparing copper nanorods and nanowires. *Adv Mater* 15:303–305
- Lisiecki I, Pileni MP (1993) Synthesis of copper metal clusters using reverse micelles as microreactors. *J Am Chem Soc* 115:3887–3896
- Qi L, Ma J, Shen J (1997) Synthesis of copper nanoparticles in nonionic water-in-oil microemulsions. *J Colloid Interface Sci* 186:498–500
- Song X, Sun S, Zhang W, Yin Z (2004) A method for the synthesis of spherical copper nanoparticles in the organic phase. *J Colloid Interface Sci* 273:463–469
- Park BK, Jeong S, Kim D, Moon J, Lim S, Kim JS (2007) Synthesis and size control of monodisperse copper nanoparticles by polyol method. *J Colloid Interface Sci* 311:417–424
- Anžlovar A, Orel ZC, Žigon M (2007) Copper (I) oxide and metallic copper particles formed in 1, 2-propane diol. *J Europ Ceram Soc* 27:987–991
- Lisiecki I, Billoudet F, Pileni MP (1996) Control of the shape and the size of copper metallic particles. *J Phys Chem* 100:4160–4166
- Wu SH, Chen DH (2004) Synthesis of high-concentration Cu nanoparticles in aqueous CTAB solutions. *J Colloid Interface Sci* 273:165–169
- Zhang X, Yin H, Cheng X, Hu H, Yu Q, Wang A (2006) Effects of various polyoxyethylene sorbitan monooleils (Tweens) and sodium dodecyl sulfate on reflux synthesis of copper nanoparticles. *Mater Res Bull* 41:2041–2048
- Khanna PK, Gaikwad S, Adhyapak PV, Singh N, Marimuthu R (2007) Synthesis and characterization of copper nanoparticles. *Mater Lett* 61:4711–4714
- Liz-Marzán LM, Giersig M, Mulvaney P (1996) Synthesis of nanosized gold-silica core-shell particles. *Langmuir* 12:4329–4335
- Marinakos SM, Shultz DA, Feldheim DL (1999) Gold nanoparticles as templates for the synthesis of hollow nanometer-sized conductive polymer capsules. *Adv Mater* 11:34–37
- Hardikar VV, Matijević E (2000) Coating of nanosize silver particles with silica. *J Colloid Interface Sci* 221:133–136
- Hall SR, Davis SA, Mann S (2000) Cocondensation of organosilica hybrid shells on nanoparticle templates: a direct synthetic route to functionalized core-shell colloids. *Langmuir* 16:1454–1456
- Cho G, Fung BM, Glatzhofer DT, Lee JS, Shul YG (2001) Preparation and characterization of polypyrrole-coated nanosized novel ceramics. *Langmuir* 17:456–461
- Tago T, Hatsuta T, Nagase R, Kishida M, Wakabayashi K (2001) Preparation of silica-coated Co-Fe<sub>3</sub>O<sub>4</sub> nanoparticles and their magnetic properties. *Kagaku Kogaku Ronbunshu* 27:288–290 (in Japanese)
- Wang H, Nakamura H, Yao Y, Maeda H, Abe E (2001) Effect of solvents on the preparation of silica-coated magnetic particles. *Chem Lett* 11:1168–1169
- Kobayashi Y, Horie M, Konno M, Rodríguez-González B, Liz-Marzán LM (2003) Preparation and properties of silica-coated cobalt nanoparticles. *J Phys Chem B* 107:7420–7425
- Kobayashi Y, Sakuraba T (2008) Silica-coating of metallic copper nanoparticles in aqueous solution. *Colloids Surf A* 317:756–759
- Mandal TK, Fleming MS, Walt DR (2002) Preparation of polymer coated gold nanoparticles by surface-confined living radical polymerization at ambient temperature. *Nano Lett* 2:3–7
- Kang Y, Taton TA (2005) Controlling shell thickness in core-shell gold nanoparticles via surface-templated adsorption of block copolymer surfactants. *Macromolecules* 38:6115–6121
- Kim JH, Lee TR (2004) Thermo- and pH-responsive hydrogel-coated gold nanoparticles. *Chem Mater* 16:3647–3651
- Quaroni L, Chumanov G (1999) Preparation of polymer-coated functionalized silver nanoparticles. *J Am Chem Soc* 121:10642–10643
- Godovski DY (1995) Electron behavior and magnetic properties of polymer nanocomposites. *Adv Polym Sci* 119:79–122
- Selvan ST, Hayakawa T, Nogami M, Möller M (1999) Block copolymer mediated synthesis of gold quantum dots and novel gold-polypyrrole nanocomposites. *J Phys Chem B* 103:7441–7448
- Liu YC, Chuang TC (2003) Synthesis and characterization of gold/polypyrrole core-shell nanocomposites and elemental gold nanoparticles based on the gold-containing nanocomplexes prepared by electrochemical methods in aqueous solutions. *J Phys Chem B* 107:12383–12386
- Ye S, Lu Y (2008) Optical properties of Ag@polypyrrole nanoparticles calculated by Mie theory. *J Phys Chem C* 112:8767–8772
- Du J, Liu Z, Han B, Li Z, Zhang J, Huang Y (2005) One-pot synthesis of the macroporous polyaniline microspheres and Ag/polyaniline core-shell particles. *Micro Meso Mater* 84:254–260
- Yeh MS, Yang YS, Lee YP, Lee HF, Yeh YH, Yeh CS (1999) Formation and characteristics of Cu colloids from CuO powder by laser irradiation in 2-propanol. *J Phys Chem B* 103:6851–6857