Preparation of Core–Shell Organic–Inorganic Nanocomposite Particles Based on Phase Separation of a Polymer Blend

Hiroshi Yabu,*[1,2] Kazutaka Koike,[3] Kiwamu Motoyoshi,[3] Takeshi Higuchi,[4] and Masatsugu Shimomura[1,4]
[1]*Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University,*
2-1-1 Katahira, Aoba-ku, Sendai 980-8577
[2]*Precursory Research for Embryonic Science and Technology (PRESTO), Japan Science and Technology Agency (JST),*
5 Sanbancho, Chiyoda-ku, Tokyo 102-0075
[3]*Graduate School of Engineering, Tohoku University, 6-6 Aramaki-Aza, Sendai 980-8579*
[4]*WPI-Advanced Institute for Materials Research (AIMR), Tohoku University,*
2-1-1 Katahira, Aoba-ku, Sendai 980-8577

(Received July 27, 2009; CL-090700; E-mail: yabu@tagen.tohoku.ac.jp)

Polymer nanoparticles with phase-separation structures can be prepared by simple solvent evaporation process from block copolymer or polymer blend solution (self-organized precipitation (SORP)). In this report, core–shell organic–inorganic nanocomposite particles were prepared by combination of block copolymer stabilizing Au nanoparticles and polymer blend. Block copolymer stabilizing Au NPs were prepared by reduction of Au ion in their micelles. Nanocomposite particles of poly(methyl methacrylate) (PMMA) and block copolymer stabilizing Au NPs are successfully prepared by using the SORP method.

Nanostructured polymer particles received great interest due to their potentials for various applications in the photonics, electronics, and biotechnologies.[1] There are several methods for preparing nanostructured polymer particles including seed polymerization,[2] emulsion polymerization by using microfluidic channels,[3] and precipitation.[4] We have reported that phase-separated polymer particles can be prepared by evaporating good solvent from the solution of block copolymers or polymer blends containing poor solvent.[5] Unique nanostructured polymer particles including one-dimensionally stacked lamellae, onion, Janus, and core–shell structures have been prepared by using this simple evaporation method.[6]

Metal–polymer nanocomposite materials are also key materials in the nanotechnology. By using high conductivity, reflectivity, and mechanical stability of metals, polymer materials are functionalized with nanoscale hybridization of metals. Metal nanoparticles (NPs) show unique optical and electronic properties based on their quantum and plasmonic effects.[7] Especially, Au NPs show local plasmonic absorption in the visible light wavelength region depending on their sizes and shapes.[8] The arrangement and spacing between the Au NPs strongly affect the plasmonic absorption. Thus, control of arrangement of particles is important to realize their unique optical properties.

In many methods for preparing Au NPs, reduction of Au ion in the block copolymer micelles is a simple way to obtain size-controlled Au NPs stabilized with polymers. Spatz et al. reported that poly(styrene-*block*-4-vinylpyridine) forms micelles in their toluene solution, and several metal particles were prepared by simple reduction of metal ions complexed with pyridine moieties.[9] By using this method, polymer stabilizing Au NPs can be prepared.

In this report, we show the preparation of Au NPs stabilized by block copolymers and preparation of Au NPs and polymer composite particles with phase-separation structures by using the SORP method. Control of inner structures of Au NPs–polymer composite particles is discussed.

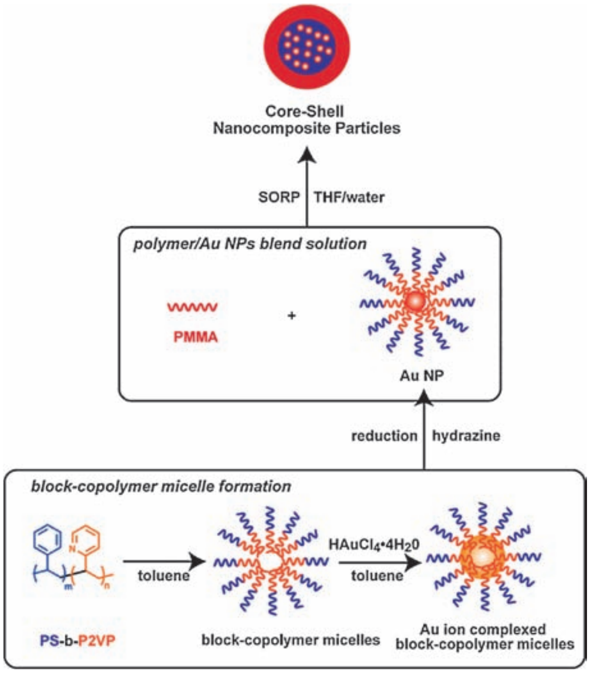

Figure 1. A schematic illustration of the core–shell nanocomposite particles.

Figure 1 shows a schematic illustration of preparation of Au NPs and composite particles. Poly(styrene-*block*-2-vinylpyridine) (PS-*b*-P2VP, $M_n(\mathrm{PS}) = 17.5\,\mathrm{kg\,mol^{-1}}$, $M_n(\mathrm{P2VP}) = 9.5\,\mathrm{kg\,mol^{-1}}$, $M_w/M_n = 1.10$), PMMA ($M_n = 15.8\,\mathrm{kg\,mol^{-1}}$, $M_w/M_n = 1.06$) were purchased from Polymer Source Inc., USA. Hydrogen tetrachloroaurate (III) tetrahydrate ($HAuCl_4{\cdot}4H_2O$) and hydrazine hydrate were purchased from Wako Chemical Industry, Japan. Dehydrated toluene and tetrahydrofran (THF) were also purchased from Wako Chemical Industry, Japan and used without further purification.

Au NPs embedded in the block copolymer micelles were prepared according to the literature.[10] PS-*b*-P2VP ($5\,\mathrm{mg\,mL^{-1}}$) and $HAuCl_4{\cdot}4H_2O$ (mol equivalent to 0.5 pyridine unit) were dissolved in toluene. The solution was degassed in a three-neck glass flask equipped with nitrogen inlet, vacuum pump, and sealing septum by three cycles of pump–thaw–evacuate. After degassing, the atmosphere was filled with dry nitrogen.

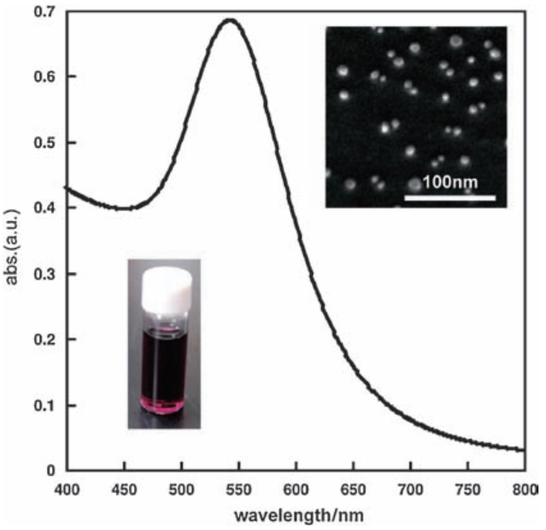

Figure 2. Visible light spectrum of PS-*b*-P2VP stabilizing Au NPs. The inset images show a photograph of toluene solution of Au NPs and a TEM image of them.

The solution was stirred overnight to form block copolymer micelles. Hydrazine (0.1 mL) was dissolved in 20 mL of toluene, and degassed the same as the micelle solution. The micelle solution was poured into the vigorously stirred hydrazine solution. After addition of micelle solution, the solution color suddenly changed from yellow to deep red. This color change indicates that nanosized Au particles having local plasmonic absorption bands were formed. The PS-*b*-P2VP stabilizing Au NPs were characterized by UV–vis spectroscopy and transmission electron microscopy (TEM, H-7650, Hitachi).

Figure 2 shows the UV–vis spectrum of Au NPs in toluene. Absorption at 530 nm attributed to the plasmon resonance of the Au NPs is clearly observed. The inset photograph shows the red-colored toluene solution of Au NPs. A TEM image of Au NPs on a Cu grid covered with a collodion membrane is shown in the inset of the Figure 2 (right side). The image shows that 10.1 ± 2.7 nm Au NPs have been prepared.

The toluene was evaporated from the solution of PS-*b*-P2VP stabilizing Au NPs and then dissolved in THF to prepare 0.1 $\mathrm{mg\,mL^{-1}}$ solution. PMMA was also dissolved in THF at the same concentrations. Four milliliters of water was added into 1 mL of THF solution of a 1:3 mixture of Au NPs and PMMA. After evaporation of THF at room temperature, an aqueous dispersion of particles was obtained.

Inner structures of the particles were observed by using a transmission electron microscope (TEM) or a scanning transmission electron microscope (STEM, S-5200, Hitachi). The average particle size was 393 ± 70 nm calculated from TEM image. Figures 3a and 3b show a SEM (a) and a dark field STEM image (b) of the composite particles. The particle has spherical shape with densely packed Au NPs located internally. The white shell of the particle is attributed to the PMMA moiety, which has lower electron density than Au NPs. These images indicate that a clear core–shell phase-separation structure has formed. The cross-sectional TEM image (Figure 3c) shows that the core part of the particle is filled with Au NPs. The average size of core was 339 ± 78 nm.

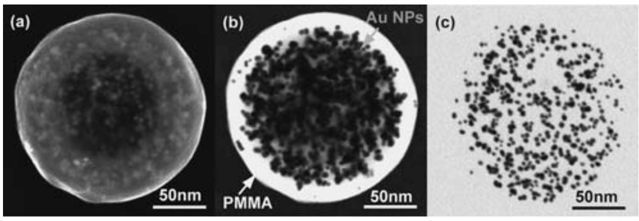

Figure 3. A SEM mode (a), a dark field STEM mode (b) image, and a cross-sectional TEM image (c) of a core–shell type nanocomposite particle.

In a previous report,[11] we found that the phase-separation structures in the polymer blend particles were governed by hydrophobicity of the blended polymers. During the formation process of the particles, the water content of solution increased with evaporation of THF. As a result, hydrophilic PMMA domain encapsulated the hydrophobic PS-*b*-P2VP stabilizing Au NPs as protective colloids.

We have shown that core–shell nanocomposite particles can be formed by using the SORP method. This method can be applicable to form various kinds of metal particles and polymer blend systems. Moreover, these nanocomposite particles with unique phase-separation structures can be applicable to a wide variety of applications in the fields of electronics, photonics, and biotechnology.

References and Notes

1 *Colloids and Colloid Assemblies*, ed. by F. Caruso, Wiley-VCH, Weinheim, **2004**.

2 M. Okubo, T. Fujibayashi, A. Terada, *Colloid Polym. Sci.* **2005**, *283*, 793.

3 T. Nisisako, T. Torii, T. Takahashi, Y. Takizawa, *Adv. Mater.* **2006**, *18*, 1152.

4 a) R. Takekoh, W.-H. Li, N. A. D. Burke, H. D. H. Stöver, *J. Am. Chem. Soc.* **2006**, *128*, 240. b) G. Zhao, T. Ishizaka, H. Kasai, H. Oikawa, H. Nakanishi, *Chem. Mater.* **2007**, *19*, 1901. c) T. Onodera, Z.-Q. Tan, A. Masuhara, H. Oikawa, H. Kasai, H. Nakanishi, T. Sekiguchi, *Jpn. J. Appl. Phys.* **2006**, *45*, 379.

5 H. Yabu, T. Higuchi, K. Ijiro, M. Shimomura, *Chaos* **2005**, *14*, 047505.

6 a) H. Yabu, T. Higuchi, M. Shimomura, *Adv. Mater.* **2005**, *17*, 2062. b) T. Higuchi, H. Yabu, M. Shimomura, *J. Nanosci. Nanotechnol.* **2007**, *7*, 856. c) T. Higuchi, H. Yabu, M. Shimomura, *Koubunshi Ronbunshu* **2007**, *64*, 177. d) T. Higuchi, H. Yabu, S. Onoue, T. Kunitake, M. Shimomura, *Colloids Surf., A* **2008**, *313–314*, 87. e) T. Higuchi, A. Tajima, H. Yabu, M. Shimomura, *Soft Matter* **2008**, *4*, 1302.

7 M. W. Knight, Y. Wu, J. Britt Lassiter, P. Nordlander, N. J. Halas, *Nano Lett.* **2009**, *9*, 2188.

8 Q. Zhang, J. Ge, T. Pham, J. Goebl, Y. Hu, Z. Lu, Y. Yin, *Angew. Chem., Int. Ed.* **2009**, *48*.

9 T. Lohmueller, E. Bock, J. P. Spatz, *Adv. Mater.* **2008**, *20*, 2297.

10 J. P. Spatz, S. Mössmer, C. Hartmann, M. Möller, *Langmuir* **2000**, *16*, 407.

11 a) A. Tajima, T. Higuchi, H. Yabu, M. Shimomura, *Colloids Surf., A* **2008**, *313–314*, 332. b) K. Motoyoshi, T. Higuchi, H. Yabu, M. Shimomura, *Adv. Funct. Mater.*, submitted.

Published on the web (Advance View) September 5, 2009; doi:10.1246/cl.2009.964