

Metal Nanoparticle/Polymer Hybrid Particles: The Catalytic Activity of Metal Nanoparticles Formed on the Surface of Polymer Particles by UV-Irradiation

Toshiyuki Tamai,^{*1} Mitsuru Watanabe,¹ Tomohiro Teramura,² Noboru Nishioka,² Kimihiro Matsukawa¹

Summary: Polymer particles decorated with metal nanoparticles were prepared by UV-irradiation of polystyrene particles incorporating polymethylphenylsilane (PS/PMPS) and P[S-co-NIPAM]/PMPS particles (NIPAM: N-isopropyl acrylamide) in the presence of metal salts. The metal nanoparticle/polymer hybrid particles were used as a catalyst for the reduction of 4-nitrophenol with NaBH₄. The Pd- and Ag-P(S-co-NIPAM)/PMPS hybrid particles had larger metal nanoparticles and the lower catalytic activity than those of Pd- and Ag-PS/PMPS, respectively. The surface functional group of the polymer particles affected the formation of the metal nanoparticles and their catalytic activity.

Keywords: catalysts; emulsion polymerization; latices; metal nanoparticle; photochemistry

Introduction

Metal nanoparticles have become attractive key materials in both academic and industrial area because of their unique chemical and physical properties.^[1] Polymer particles decorated with metal nanoparticles (metal-nanoparticle/polymer hybrid particles) are utilized in sensing- and imaging-materials^[2,3] and catalyst.^[4–8] It was reported that metal-nanoparticle/polymer hybrid particles can be obtained by immobilizing metal nanoparticles on the surface of polymer particles prepared by emulsion polymerization and be applicable to catalyst in water.^[9,10] We have already reported the preparation of polymer particles decorated with metal nanoparticles by UV irradiation of polystyrene particles incorporating polymethylphenylsilane (PS/PMPS).^[11] It was considered that the metal nanoparticles are formed on the polymer particle

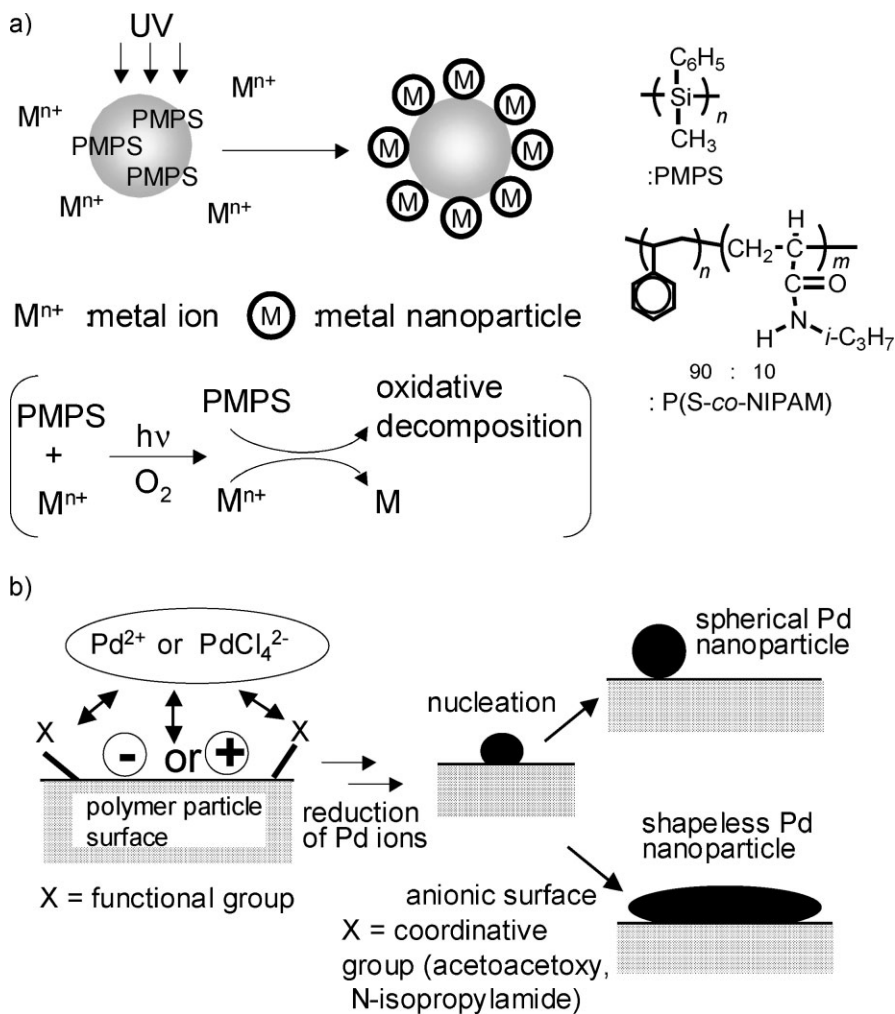
surface due to the reduction of the metal ions accompanied by the photoinduced oxidation of PMPS, as shown in Scheme 1a. The interaction between the polymer surface and the metal ions could affect the formation and the growth of the metal nanoparticles. We now report the catalytic properties of the metal nanoparticles on the surface of polymer particles. The surface functional group of the polymer particle played an important role in the catalytic properties. We also studied photo-induced metal-nanoparticle formation on the surface of polymer particles that do not incorporate PMPS and are dispersed in ethanol.

Preparation of Metal-Nanoparticle/Polymer Hybrid Particles by UV Irradiation of PS/PMPS

Polystyrene emulsions (**1-2**) incorporating PMPS ($M_n = 1.68 \times 10^4$, $M_w/M_n = 2.35$, 1.9 mol % vs. PS) were synthesized by miniemulsion polymerization (Table 1). UV irradiation (>280 nm, a high pressure Hg-arc lamp, a Pyrex glass filter) of emulsion **1** (0.1 wt%) that contained Na₂PdCl₄ (0.058 mmol) under air at room temperature

¹ Osaka Municipal Technical Research Institute, 1-6-50 Morinomiya, Joto-ku, Osaka 536-8553, Japan
E-mail: tositama@omtri.city.osaka.jp

² Osaka Electro-Communication University, Hatsucho, Neyagawa, Osaka 572-8530, Japan

**Scheme 1.**

(a) Metal nanoparticle formation on the surface of polystyrene particles incorporating polysilanes by UV-irradiation. (b) Interaction between polymer particle surface.

afforded palladium-nanoparticle/polymer hybrid particles as described recently.^[11] Similar irradiation of **2**, which has an N-isopropylamide group, also afforded the

hybrid particles. UV irradiation of emulsion **1-2** that contained $AgNO_3$ and $HAuCl_4 \cdot 4H_2O$ afforded silver- and gold-nanoparticle/polymer hybrid particles,

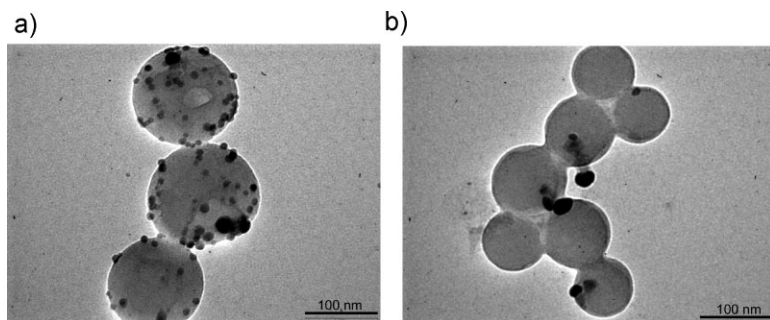
Table 1.

Polystyrene Emulsion Incorporating PMPS.

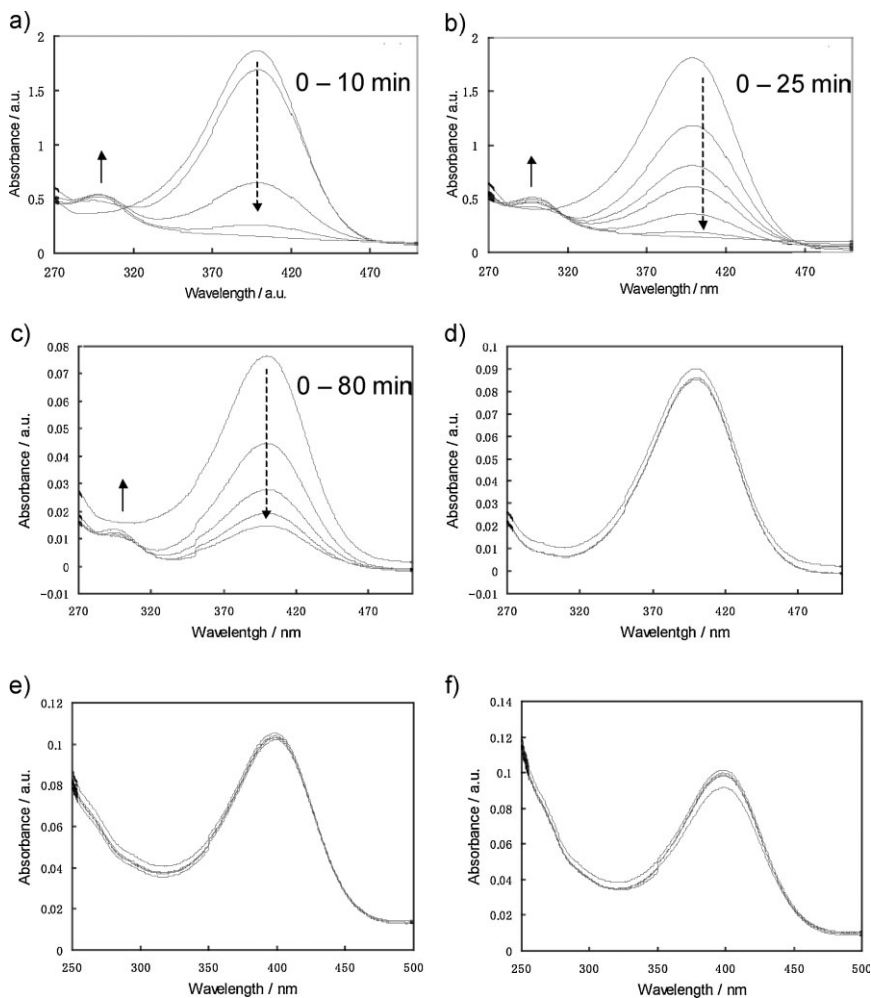
| emulsion | Polymer (ratio of monomer ^{a)}) | PMPS (mol % vs. styrene) | surface charge | diameter ^{b)} (nm) |
|----------|---|--------------------------|----------------|-----------------------------|
| 1 | PS | 1.9 | Anionic | 169 |
| 2 | P[S-co-NIPAM] (90:10) | 1.9 | Anionic | 256 |
| 3a | PS | – | Anionic | 171 |
| 3b | PS | – | Cationic | 160 |
| 4 | P[S-co-NIPAM] (90:10) | – | Cationic | 182 |

^{a)}Ratio based on mol of the monomers used for the polymerization.

^{b)}Measured by dynamic light scattering (DLS).

**Figure 1.**

TEM images of the metal nanoparticle/polymer hybrid particles prepared from: (a) $\text{AgNO}_3/1$, (b) $\text{AgNO}_3/2$. Emulsions 1–2 incorporate PMPS and are dispersed in water.

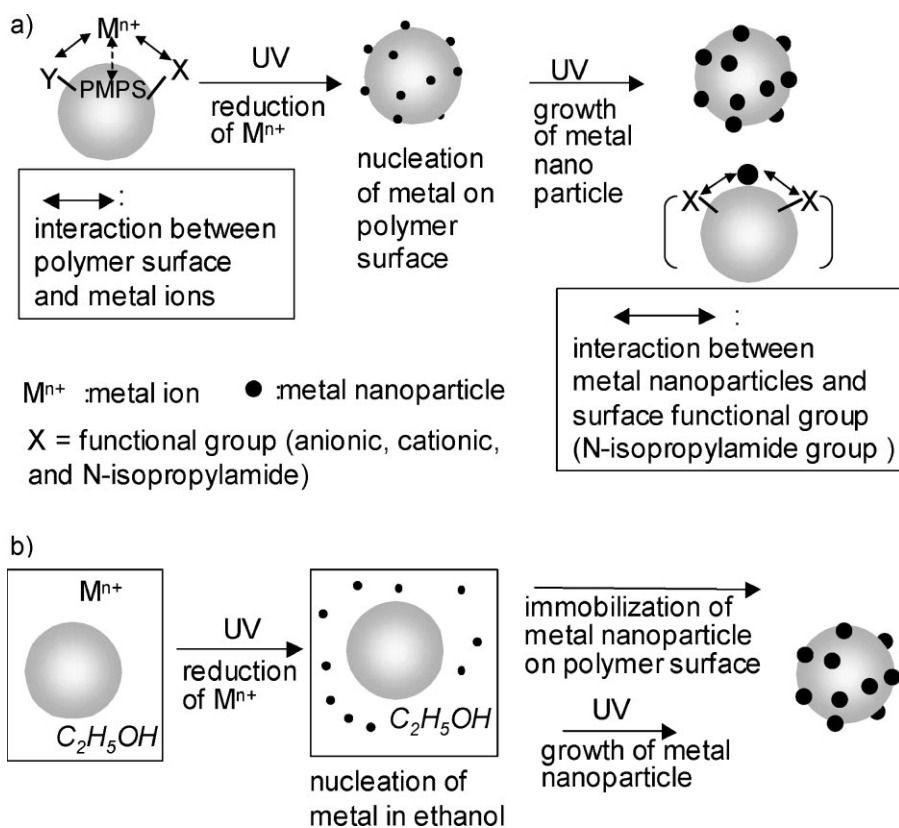
**Figure 2.**

Reduction of 4-nitrophenol by NaBH_4 ; UV-vis spectra of the solutions containing the hybrid particles as a catalyst at different times: (a) $\text{Pd}/1$, 0, 1, 5, 8, 10 min. (b) $\text{Pd}/2$, 0, 5, 8, 10, 15, 20, 25 min. (c) $\text{Ag}/1$, 0, 20, 40, 60, 80 min. (d) $\text{Ag}/2$, 0, 0, 20, 40, 80 min. (e) $\text{Au}/1$, 0, 30, 60, 90, 180 min. (f) $\text{Au}/2$, 0, 30, 60, 90, 180 min.

respectively. TEM image (Figure 1) indicated that silver-nanoparticles (black particle) were immobilized on the surface of the polymer particle (gray particle). The interaction between the polymer surface and the metal ions would affect the formation of the metal nanoparticles (Scheme 1b). The larger and fewer palladium and silver nanoparticles were formed on the surface of polymer particle (2) having N-isopropylamide group, which can coordinate to the palladium and silver ions. In contrast, formation of gold nanoparticle was not affected by N-isopropylamide group as described in our previous report.^[11] The hybrid particles were purified by dialysis in pure water for a week and their catalytic properties were investigated as shown in the following section.

Catalytic Activity of Metal-Nanoparticles on the Polymer Particle Surface

Palladium-, silver-, and gold-nanoparticles were immobilized on the surface of **1** and **2** as shown above. Those hybrid particles (Pd/**1-2**, Ag/**1-2**, Au/**1-2**) were used as a catalyst for the reduction of 4-nitrophenol.^[9] An aqueous solution (3 mL) of 4-nitrophenol (0.3 μmol) and NaBH_4 (18 μmol) was stirred in a sample tube and then the hybrid particle (0.04 mg) was added. The pH was adjusted to 10 with NaOH. The process of the reduction was monitored by observing UV-vis spectrum of the mixture (Figure 2). The characteristic peak of 4-nitrophenol at 400 nm decreases with time, and a new peak at 290 nm due to 4-aminophenol appears. The reaction catalyzed by Pd/**1** was completed in shorter time (for 10 min) than that



Scheme 2.

(a) Metal-nanoparticle formation on the surface of polymer particles incorporating PMPS. (b) Metal-nanoparticle formation on the surface of polymer particles that do not incorporate PMPS and are dispersed in ethanol.

of Pd/**2** (for 25 min) as shown in Figure 2a,b. This shows the catalytic activity of Pd/**2** was higher than that of Pd/**1**. Ag/**1** also catalyzed the reduction, but Ag/**2** did not (Figure 2c,d). Neither Au/**1** nor Au/**2** catalyzed the reduction (Figure 2e,f). The catalytic activity depended on the metals and also the surface functional group of polymer particles. The N-isopropylamide group on the surface of **2** could interact with the surface of palladium- and silver-nanoparticles and decrease their catalytic activity (Scheme 2a). In conclusion, the surface

functional group of the polymer particle played an important role in the formation and the properties of the metal nanoparticles on polymer particle surface.

Preparation of Metal-Nanoparticle/ Polymer Hybrid Particles by UV irradiation of Polymer Particles in Ethanol

Polystyrene emulsions (**3-4**), which do not incorporate PMPS, were synthesized by miniemulsion polymerization. UV irradiation of emulsion **3a** (dispersed in water) that contained $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ for 2 h did

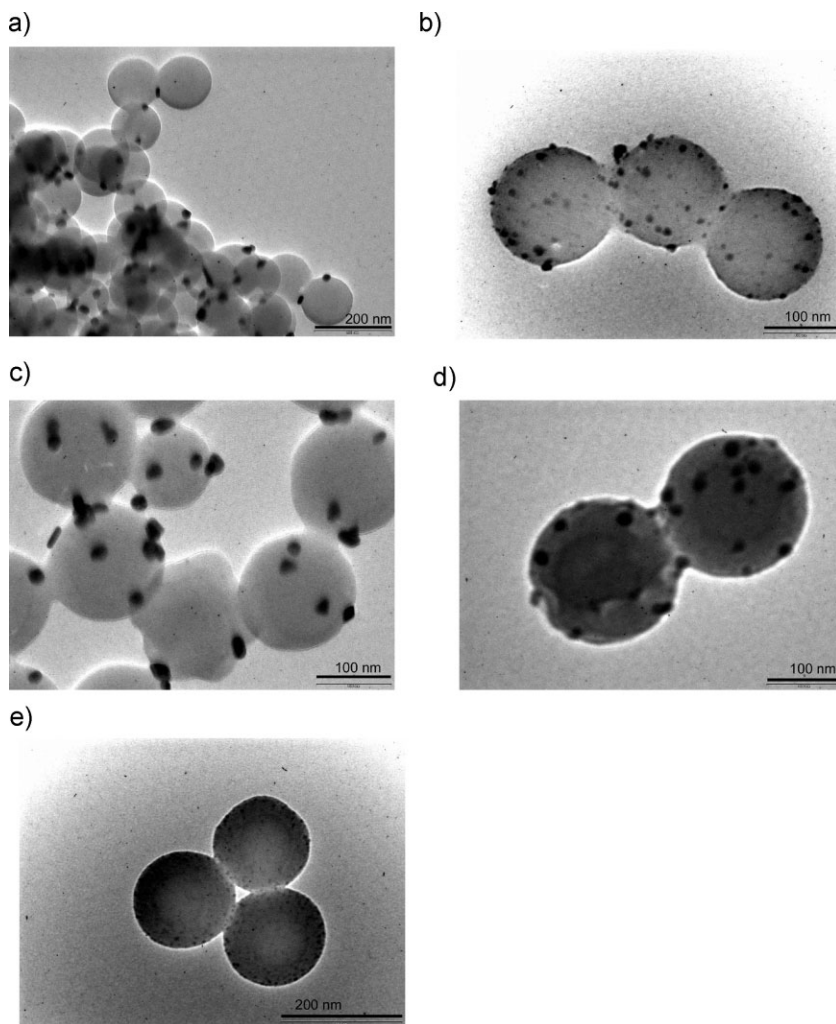


Figure 3.

TEM images of the metal nanoparticle/polymer hybrid particles prepared from: (a) $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}/\mathbf{3a}$, (b) $\text{Na}_2\text{PdCl}_4/\mathbf{3a}$, (c) $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}/\mathbf{4}$, (d) $\text{AgNO}_3/\mathbf{3b}$, (e) $\text{PdCl}_2/\mathbf{3b}$. Emulsions **3a-b**, **4** do not incorporate PMPS and are dispersed in ethanol.

not afford metal nanoparticles. Emulsions **3–4** were centrifuged (15000 rpm) and then re-dispersed in ethanol at least twice. Anionic emulsion **3a** dispersed in ethanol contained $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ was stirred for 30 min in the dark under air at room temperature. It retained its milky white color. Then the mixture was irradiated for 90 min and its color turned deep wine-red. TEM image indicated the formation of gold-nanoparticle/polymer hybrid particles (Figure 3a). This showed that the UV irradiation of AuCl_4^- in ethanol resulted in the formation of gold nanoparticles. The irradiation of anionic emulsion **3a** dispersed in ethanol-water (9:1) contained Na_2PdCl_4 afforded palladium-nanoparticle/polymer hybrid particles (Figure 3b). The irradiation of cationic emulsion **4** in ethanol contained $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ also afforded hybrid particles (Figure 3c). The irradiation of cationic emulsion **3b** dispersed in ethanol contained cationic metal ions Ag^+ and Pd^{2+} (AgNO_3 , PdCl_2) also afforded hybrid particles (Figure 3d,e). This is contrast to the result that UV-irradiation of cationic polymer emulsions (dispersed in water) incorporating PMPS in the presence of cationic metal ions did not afford the hybrid particles.^[11] Because, on the surface of polymer particle incorporating PMPS, the metal ions are reduced accompanied by the photoinduced oxidation of PMPS and afford the metal nanoparticles (Scheme 1, 2a). The reduction of the cationic metal ions can be inhibited by the electrostatic force between the cationic polymer surface and the cations (Scheme 1b). In the irradiation of ethanol emulsion as shown in Scheme 2b, metal nanoparticles will be formed in ethanol phase and then be immobilized to the surface of the polymer particles, therefore, the interaction between the cationic polymer surface and the cationic metal ions did not affect the metal nanoparticle formation. These contrasting results of the UV-irradiation of

cationic emulsions contained cationic metal ions would be due to the difference in the site of metal-nanoparticle formation between polymer emulsions incorporating PMPS (Scheme 2a) and emulsions **3–4** dispersed in ethanol (Scheme 2b).

Conclusion

Metal nanoparticles were immobilized on the surface of polymer particle by photo-induced reduction of the metal ions to afford metal-nanoparticle/polymer hybrid particles. The surface functional group of the polymer particle played an important role in the formation and the catalytic properties of the metal nanoparticles. Polymer particles are suitable for supporting metal nanoparticles and the advantages of the photoinduced reduction are a simple operation and ease of controlling the growth of the metal nanoparticles. The metal-nanoparticle/polymer hybrid particles are expected to be applicable to the catalyst for a variety of reactions in water.

- [1] M. Daniel, D. Astruc, *Chem. Rev.* **2004**, 104, 293.
- [2] D. Suzuki, H. Kawaguchi, *Langmuir* **2006**, 22, 3818.
- [3] Y. Wang, S. Alexandra, A. S. Angelatos, F. Caruso, *Chem. Mater.* **2008**, 20, 848.
- [4] C. Chen, T. Serizawa, M. Akashi, *Chem. Mater.* **1999**, 11, 1381.
- [5] A. B. R. Mayer, J. E. Mark, *Angew. Makromol. Chem.* **1999**, 268, 52.
- [6] S. Pathak, M. T. Greci, R. C. Kwong, K. Mercado, G. K. S. Prakash, G. A. Olah, M. E. Thompson, *Chem. Mater.* **2000**, 12, 1985.
- [7] Y. Li, E. Boone, M. A. El-Sayed, *Langmuir* **2002**, 18, 4921.
- [8] F. Wen, W. Zhang, G. Wei, Y. Wang, J. Zhang, M. Zhang, L. Shi, *Chem. Mater.* **2008**, 20, 2144.
- [9] Y. Mei, Y. Lu, F. Polzer, M. Ballauf, M. Drechsler, *Chem. Mater.* **2007**, 19, 1062.
- [10] W. Liu, X. Yang, W. Huang, *J. Colloid. Interface Sci.* **2006**, 304, 160.
- [11] T. Tamai, M. Watanabe, Y. Hatanaka, H. Tsujiwaki, N. Nishioka, K. Matsukawa, *Langmuir* **2008**, 24, 14203.