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

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Summary: Polymer particles decorated with metal nanoparticles were prepared by UV-irradiation of polystyrene latex 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 $NaBH_4$. 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 as 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 photoinduced 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 latex particles (**1**-**2**) incorporating PMPS ($Mn = 1.68 \times 10^4$, $Mw/Mn = 2.35$, 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 diluted **1** (0.1 wt%) that contained Na_2PdCl_4 (0.058 mmol) under air at room temperature afforded palladium-nanoparticle/polymer

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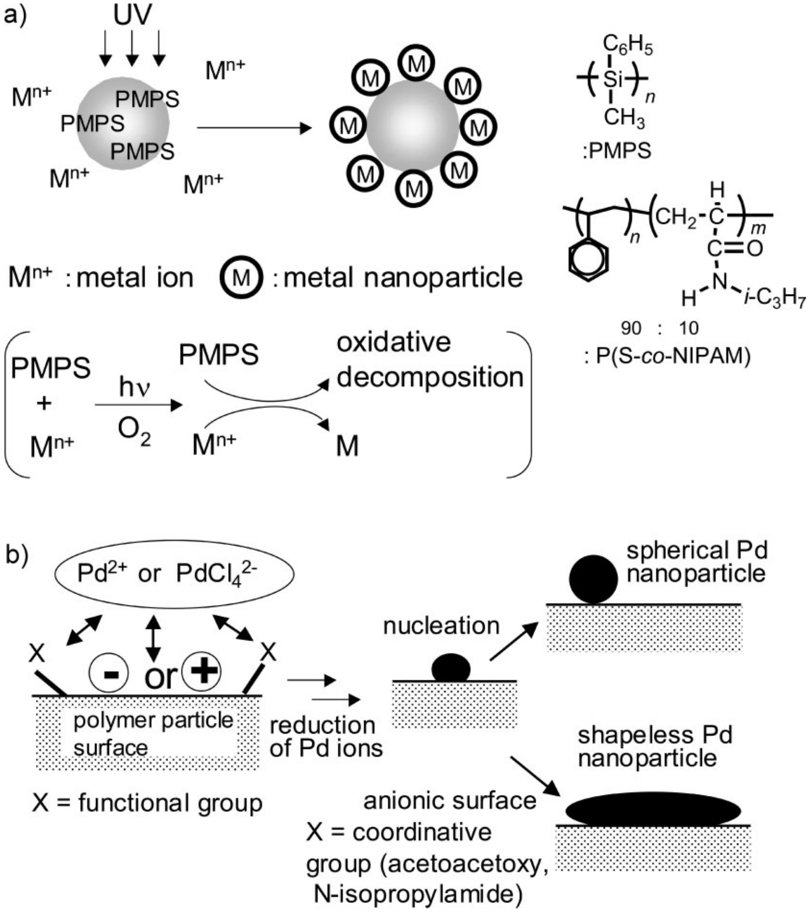


Scheme 1.
(a) metal nanoparticle formation on the surface of polystyrene particles incorporating polysilanes by UV-irradiation (b) interaction between polymer particle surface and Pd ions.

hybrid particles as described recently.[11] Similar irradiation of **2**, which has an N-isopropylamide group, also afforded the hybrid particles. UV irradiation of **1**-**2** that contained $AgNO_3$ and $HAuCl_4 \cdot 4H_2O$ afforded silver- and gold-nanoparticle/polymer hybrid particles, respectively. TEM image (Figure 1) indicated that

Table 1.
Polystyrene Latex Particles Incorporating PMPS.

particles	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).

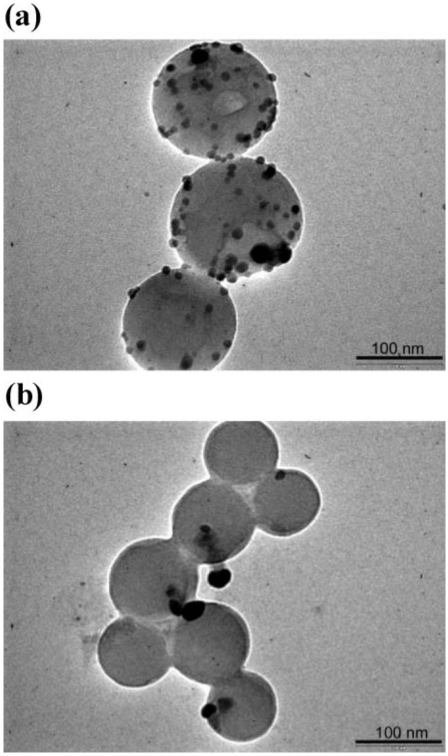


Figure 1.
TEM images of the metal nanoparticle/polymer hybrid particles prepared from: (a) $AgNO_3$/**1**, (b) $AgNO_3$/**2**. Polymer particles **1-2** incorporate PMPS and are dispersed in water.

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 by Pd/**2** (for 25 min) as shown in Figure 2a,b. This shows the catalytic activity of Pd/**1** was higher than that of Pd/**2**. 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). On the other hand, Pd/**2** and Ag/**2** have larger and fewer palladium- and silver-nanoparticles (Figure 1), which will result in the smaller surface areas of the nanoparticles compared to those of Pd/**1** and Ag/**1**, respectively. These smaller surface areas could also decrease their catalytic activity. 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 the polymer particle surface.

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

Polystyrene latex particles (**3**-**4**), which do not incorporate PMPS, were synthesized by miniemulsion polymerization. UV irradiation of **3a** (dispersed in water) that

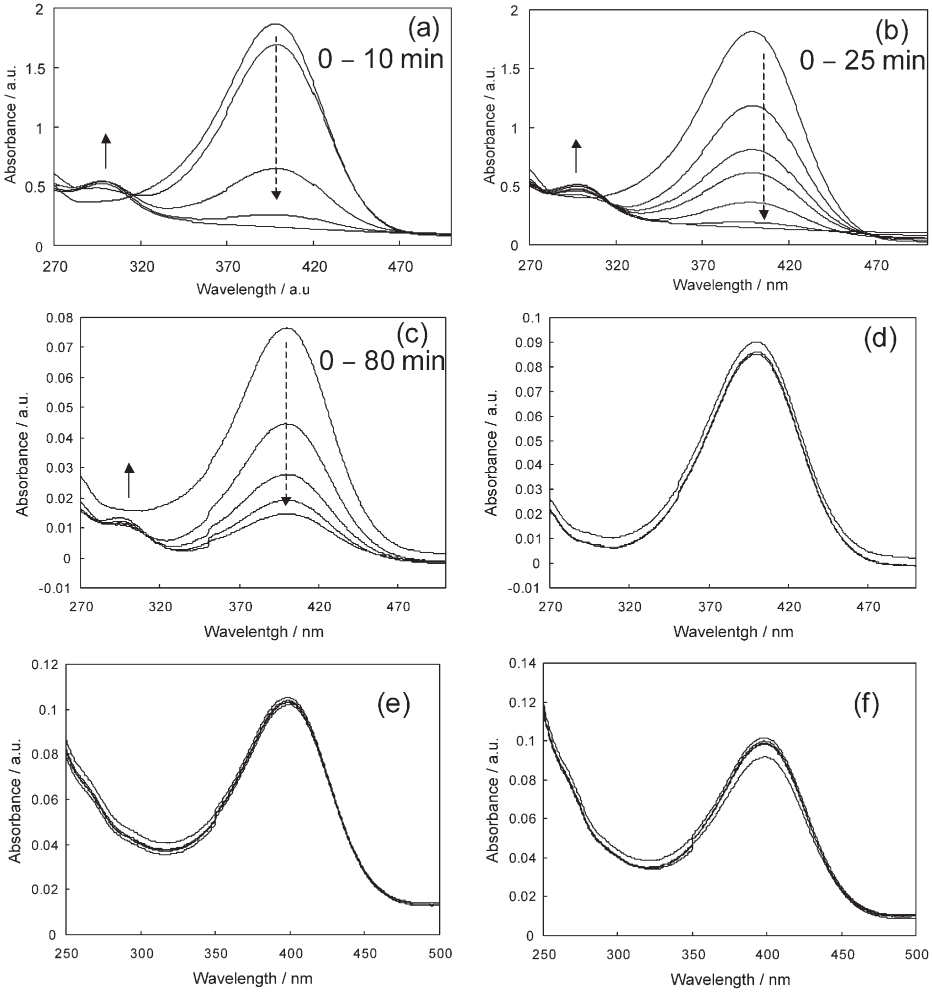
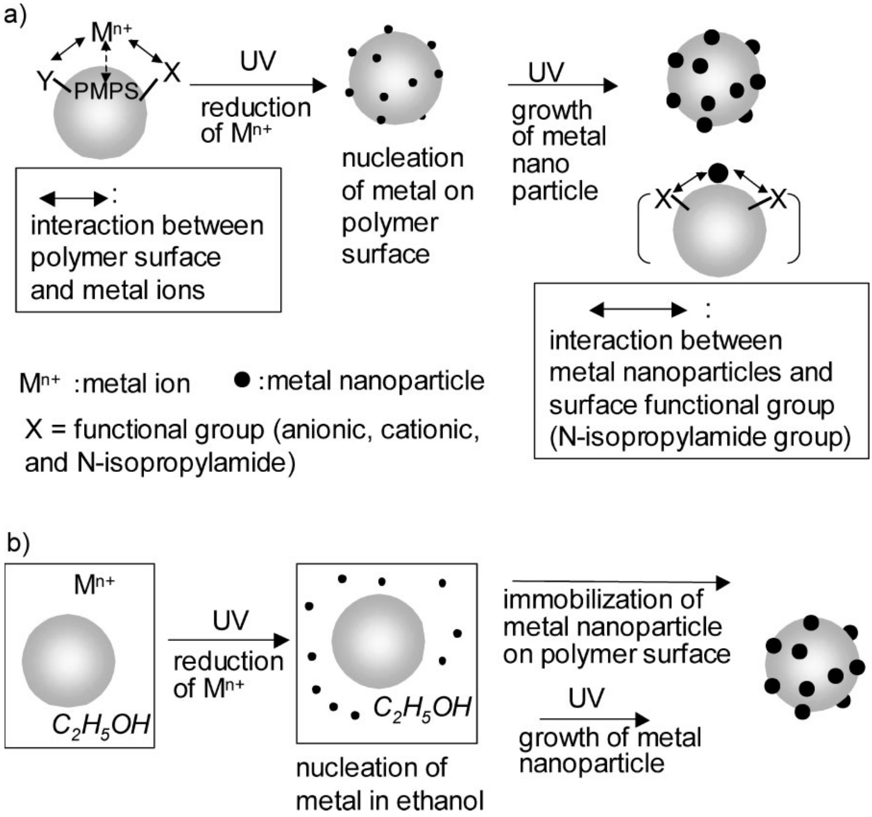


Figure 2.
Reduction of 4-nitrophenol by $NaBH_4$; UV-vis spectra of the solutions containing the hybrid particles as a catalyst at different times: (a) Pd/**1**, 0, 1, 5, 8, 10 min. (b) Pd/**2**, 0, 5, 8, 10 15, 20, 25 min. (c) Ag/**1**, 0, 20, 40, 60, 80 min. (d) Ag/**2**, 0, 20, 40, 80 min. (e) Au/**1**,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

contained $HAuCl_4 \cdot 4H_2O$ for 2h did not afford metal nanoparticles. Polymer particles **3**-**4** (dispersed in water) were centrifuged (15000 rpm) and then re-dispersed in ethanol at least twice. Anionic polymer particles **3a** dispersed in ethanol contained $HAuCl_4 \cdot 4H_2O$ 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 polymer particles **3a** dispersed in ethanol-water (9:1) contained Na_2PdCl_4 afforded palladium-nanoparticle/polymer hybrid particles (Figure 3b). The irradiation of cationic polymer particles **4** dispersed in ethanol contained $HAuCl_4 \cdot 4H_2O$ also afforded hybrid particles (Figure 3c). The irradiation of cationic polymer particles **3b**



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.

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 particles (dispersed in water) incorporating PMPS in the presence of cationic metal ions did not afford the hybrid particles.[11] Because, on the surface of the 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 cationic metal ions (Scheme 1b).

In the UV-irradiation of ethanol-dispersion 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 the cationic polymer particles with the cationic metal ions would be due to the difference in the site of metal-nanoparticle formation between the polymer particles incorporating PMPS (Scheme 2a) and polymer particles **3-4** dispersed in ethanol (Scheme 2b).

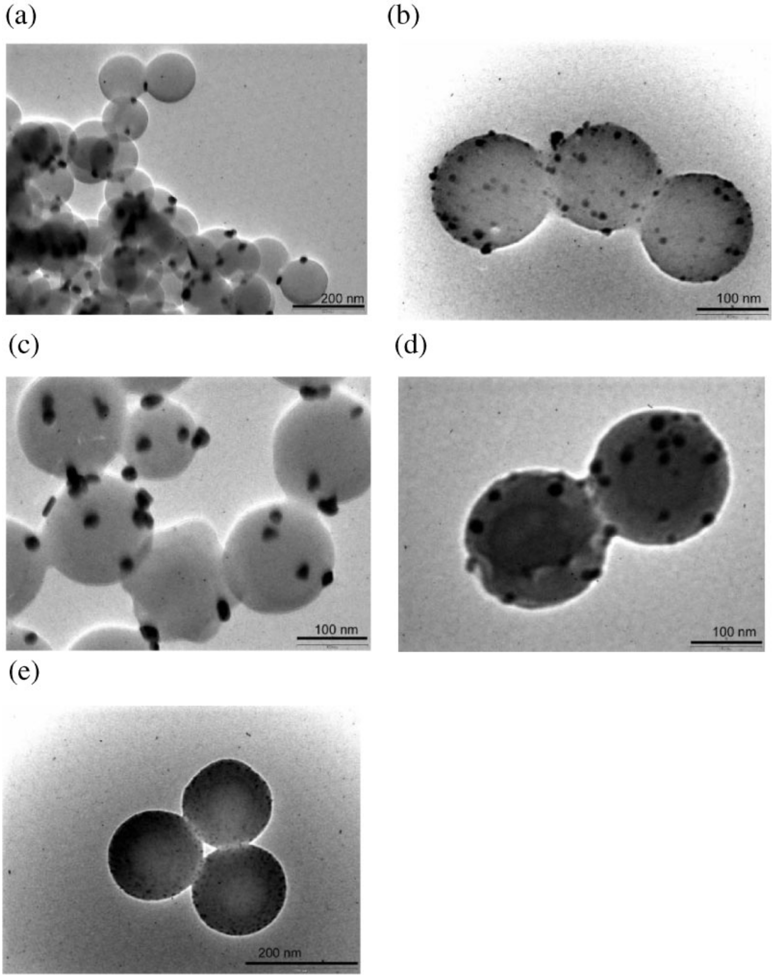


Figure 3.
TEM images of the metal nanoparticle/polymer hybrid particles prepared from: (a) $HAuCl_4 \cdot 4H_2O$/**3a**, (b) Na_2PdCl_4/**3a**, (c) $HAuCl_4 \cdot 4H_2O$/**4**, (d) $AgNO_3$/**3b**, (e) $PdCl_2$/**3b**. Polymer particles **3a-b**, **4** do not incorporate PMPS and are dispersed in ethanol.

Conclusion

Metal nanoparticles were immobilized on the surface of polymer particle by photoinduced 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 as the catalyst for a variety of reactions in water.

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