

# Monodisperse Polymer/Metal Composite Particles by Electroless Chemical Deposition: Effect of Surface Functionality of Polymer Particles

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**ABSTRACT:** Micron-sized polymer particles were coated with layers of nickel compounds by plating electrolessly in the presence of aqueous solutions of nickel chloride, sodium hypophosphite, sodium citrate, and ammonium chloride at elevated temperature. The uniform functional polymer particle could be obtained by seeded polymerization. To investigate the effect of surface functionality on the conditions for nickel deposition, the polymer particle was functionalized

with the thiol group. From morphological observation, it was found that the mode of nickel deposition was greatly dependent on the surface functionality of the polymer particle. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 420–424, 2003

**Key words:** composites; polymer particle; electroless plating; surface functionality; core-shell polymers

## INTRODUCTION

Polymer-metal composite particles within the size range of 1–10  $\mu\text{m}$  or greater have gained a widening interest in such fields as medial science, catalytic applications, and some electronic packaging technologies.<sup>1–3</sup> In all applications, particle monodispersity plays a crucial role in meeting their material efficiency.

The metallization of polymer has usually been carried out by physical vapor deposition and electroless plating.<sup>4,5</sup> The electroless plating of polymers by nickel or copper is possible on the condition that catalytic sites are created on the surface to be metallized. These sites usually contain palladium nuclei chemisorbed from solution. Different methods have been proposed to perform this chemisorption. The conventional two-step process involves the successive exposure of the substrate to a solution of  $\text{SnCl}_2$  and  $\text{PdCl}_2$ .<sup>6–8</sup> The one-step process, on the other hand, uses a mixture of  $\text{SnCl}_2$  and  $\text{PdCl}_2$  solutions.<sup>9,10</sup> It is often proposed that  $\text{Sn(III)}$  ions are needed to reduce  $\text{Pd(II)}$  ions to colloidal particles. For conventional polymers, palladium chemisorption cannot be achieved directly in the absence of  $\text{SnCl}_2$  sensitization because of the low reactivity of substrate surfaces. Additionally,  $\text{CrCl}_3$  treatment of polymeric substrate is often required to give

surface roughness for effective chemisorption of palladium colloid before the sensitization process.

From a practical point of view, there are numerous manipulation steps for the metal finishing of polymer and preparation of composite material thereof in electroless plating. On the other hand, thiol-functionality has been known to complex with noble metal ions containing Au, Ag, Hg, Ni, Zn, and so on.<sup>11</sup> Both chemisorption and self-assembly of alkanethiol on Au and/or Ag surface have also been described.<sup>12–15</sup> It was found that the thiol moiety had a good ability to complex with the above-mentioned metallic substrates or ions in aqueous and nonaqueous media. Thus, in the present study, we are proposing a useful method to produce the polymer-metal core-shell particle by an electroless plating process in which no sensitization step is required. For effective electroless plating, the thiol group was introduced onto the particle surface. We investigated the effectiveness of the surface functionality of polymer particles on metal deposition.

## EXPERIMENTAL

### Materials

Inhibitors in styrene (St; Junsei Chemical Co., Japan), hexanedioldimethacrylate (HDDM, Junsei), and divinylbenzene (DVB, 55% divinylbenzene isomers; Aldrich Chemical Co., Milwaukee, WI) were extracted from the removal column (Aldrich). Chloromethylstyrene (CMS, 90% *para*-isomer; Aldrich) was treated with 0.1% NaOH solution to remove inhibitors. Other

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TABLE I  
The Standard Recipe for the Preparation of the Monodisperse Polymer Particle<sup>a</sup>

Symbol	Styrene	CMS <sup>b</sup>	HDDM <sup>c</sup>	DVB <sup>d</sup>	$D_n$ ( $\mu\text{m}$ )	PSD	Remarks
P1	5.85	2.70	0.45	—	11.1	1.01	Uniform
P2	8.55	—	—	0.45	10.7	1.01	Uneven surface

<sup>a</sup> The seed particles were swollen with the 1-chlorododecane before monomer swelling process. 1.5 wt % of benzoyl peroxide was dissolved with monomer mixture. The polymerization was carried out under N<sub>2</sub> inlet with stirring at 150 rpm for 10 h (unit: gram).

<sup>b</sup> Abbreviation of chloromethylstyrene monomer.

<sup>c</sup> Abbreviation of hexanedioldimethacrylate crosslinker.

<sup>d</sup> Abbreviation of divinylbenzene crosslinker.

<sup>e</sup> Particle size distribution,  $D_w/D_n$ .

reagents including polyvinylpyrrolidone (PVP K-30,  $M_w = 4.0 \times 10^4$  g mol<sup>-1</sup>; Aldrich), poly(vinyl alcohol) (PVA,  $M_w = 8.8\text{--}9.2 \times 10^4$  g mol<sup>-1</sup>, 87–89% hydrolyzed; Kuraray Co., Ltd., Japan), thiourea (Aldrich), nickel chloride (Aldrich), sodium hypophosphite (Aldrich), sodium citrate (Aldrich), and ammonium chloride (Samchun, Korea) were used as received. Benzoyl peroxide (BPO; Aldrich) was recrystallized from methanol before use.

#### Preparation of monodisperse functional polymer particles

Highly monodisperse functional polymer particles could be achieved by a two-stage swelling of PS seed and sequential polymerization.<sup>16–19</sup> The PS seed was obtained by dispersion polymerization.<sup>19</sup> The swelling and polymerization were carried out in the four-neck glass reactor equipped with a stirrer, a reflux condenser, thermocouples, and nitrogen gas inlet system. The PS seed particles redispersed in SLS (sodium lauryl sulfate) aqueous solution by sonification were swollen with 1-chlorododecane (CD) emulsified by ultrasonic homogenizing in 0.25% SLS aqueous solution. Then, the mixture of monomers (St, crosslinking agent, and/or CMS) and BPO (1.5 wt % to the total monomers) was emulsified by the same method as CD and poured into the reactor. The swelling was continued for another 10 h at 30°C. The swollen particles were stabilized with PVA aqueous solution. After removal of air with N<sub>2</sub>, the polymerization was carried out at 70°C for 16 h. The particles produced were repeatedly washed by decantation in water and ethanol and dried under vacuum at ambient temperature. The experimental details can be found in our previous works.<sup>16,19</sup> Two types of particles were prepared by changing the monomer composition. The composition of the monomer mixture of each type of particles is listed in Table I.

The surface chloromethyl-group of P1 particle was changed into a thiol group by reacting the particles with the thiourea solution in excess.<sup>20</sup> The reaction was carried out in the one-neck flask equipped with reflux condenser. At first, 0.5 g of P1 particles was dispersed

in 50.0 g water by sonication. Then, 25.0 g of 0.1M thiourea ethanol/water 50/50 solution were poured into the flask. The reaction was carried out at 45°C for 3 h. After the reaction, particles were recovered by centrifugation, which were then allowed to react with 0.05M ammonium chloride solution. The particles obtained were named TP1.

#### Chemical metal deposition

Electroless plating was carried out without a sensitization process. The typical procedure was as follows: 0.25 g of each of the TP1 and P2 particles was dispersed in a plating bath, composed of nickel chloride, sodium citrate, and ammonium chloride. The bath was heated to 70°C and the reducing agent sodium hypophosphite in aqueous solution was introduced. The reaction was continued for 30 min at this temperature. The color of the solution rapidly turned dark. After the electroless plating, the composite particles were separated by filtration, washed with methanol, and dried at room temperature.

#### Characterization

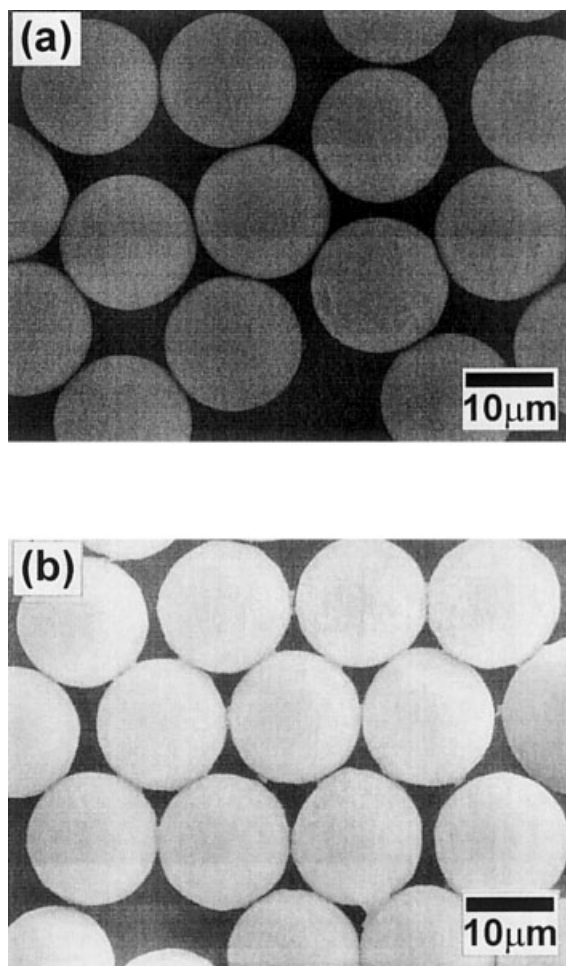
The size and morphology of the copolymer microspheres and the composite particles were investigated by an optical microscope (OM; Nikon Microphot Fax, Tokyo, Japan) and a scanning electron microscope (SEM, JSM-6300; JEOL, Peabody, MA). Both chloromethyl groups and thiol groups at the surface of the P1 and TP1 were confirmed by X-ray photoelectron spectroscopy (XPS). Spectra were recorded by use of magnesium K<sub>α</sub> radiation (1253.6 eV) at a potential of 10 kV and an X-ray current of 15 mA. The pressure in the measurement chamber was about  $8 \times 10^{-10}$  Torr. XRD pattern was measured by an X-ray diffractometer. Particles was powdered by freeze-drying and stored *in vacuo*. The dried particles were pelletized with a hydraulic compressor (Carver, model 4040) into a disk-type specimen.

## RESULTS AND DISCUSSION

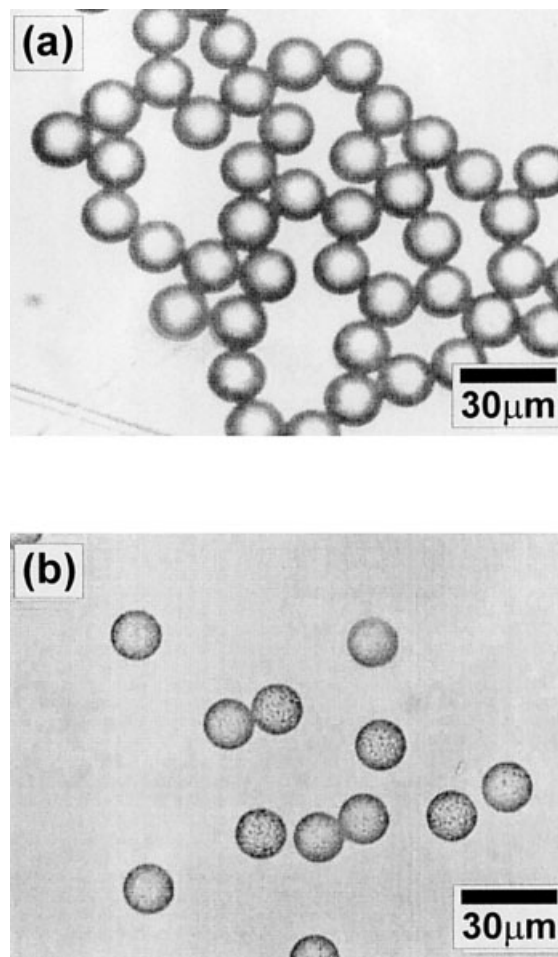
The particles produced displayed monodisperse size distribution and a spherical shape, as shown in Figure

1. The characteristic of each particle is also listed in Table I. Figure 2 displays the OM images of the P1 and P2 particles, respectively. Unlike P1, interestingly, P2 showed somewhat uneven surfaces. The difference in surface roughness between P1 and P2 can be accounted for by the different characteristics of the crosslinking agents, HDDM and DVB. HDDM consists of a hexamethylene unit in its molecular backbone, which is expected to give a relatively low degree of crosslinking density compared with the same amount of DVB. Furthermore, high reactivity of DVB during polymerization will produce considerable elastic retractile forces, resulting in the formation of wrinkles or shrinkage on particle surfaces.<sup>16</sup>

Figure 3 shows the  $Cl_{2p}$  and  $S_{2p}$  core-level spectra obtained for P1 and TP1, respectively. In  $Cl_{2p}$  spectra, shown in Figure 3(A), it is clear that the intensity of  $Cl_{2p}$  peaks was lowered after the reaction with the thiourea solution. Alternatively, this indicates that the concentration of chloromethyl groups on the particle surface definitely decreased. Moreover, the high intensity of  $S_{2p}$  peaks in  $S_{2p}$  spectra shown in Figure 3(B)



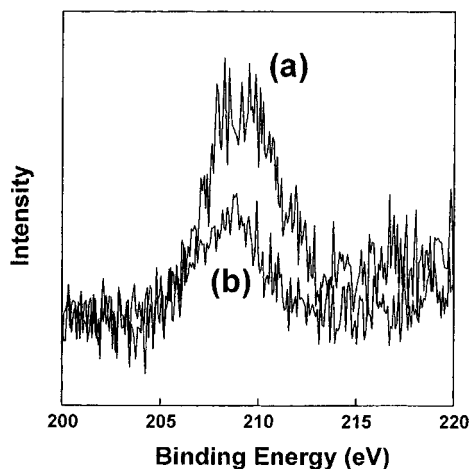
**Figure 1** Scanning electron microscopic images of the particles: (a) P1 and (b) P2.



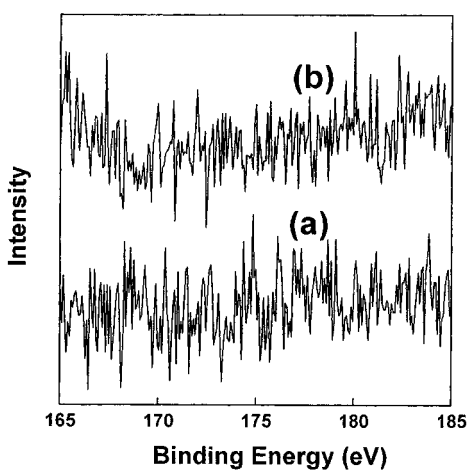
**Figure 2** Optical microscopic images of the particles: (a) P1 and (b) P2.

confirms again the presence of thiol groups on the surface of TP1 particles.

Polymer/Ni composite particles were prepared under conditions in which the surface sensitization process was omitted. Typical SEM photographs for P2/Ni and TP1/Ni composites are shown in Figure 4. As can be seen, there was a clear difference in surface coverage mode. In the case of P2/Ni [Fig. 4(a)], small Ni particles or Ni aggregates were closely attached to the surface of the polymer microsphere. Because the microsphere P2 has only some unevenness on its surfaces, as shown in Figure 2(b), these Ni colloidal particles were physically adsorbed onto the polymer particle. Moreover, there also were free Ni aggregates that were not adsorbed on the substrate, indicating that the physical adsorption between polymer particles and Ni colloids led to the formation of these polymer/Ni composites. However, in the case of TP1/Ni composite particles in Figure 4(b), a continuous Ni domain was developed on the polymeric particle surfaces. Moreover, there were no free Ni colloidal aggregates in the reaction medium, indicating that all the reduction of Ni ion occurred entirely on the particle sur-



A

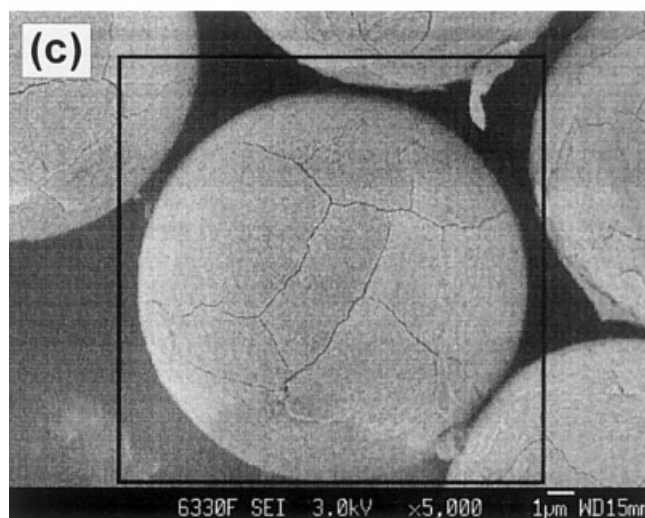
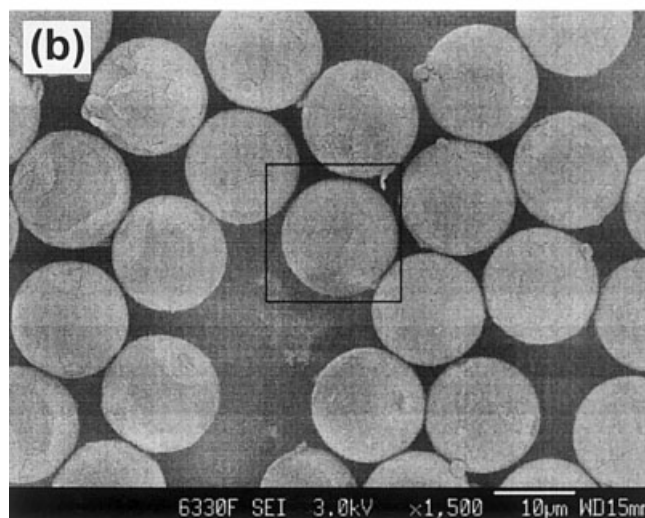
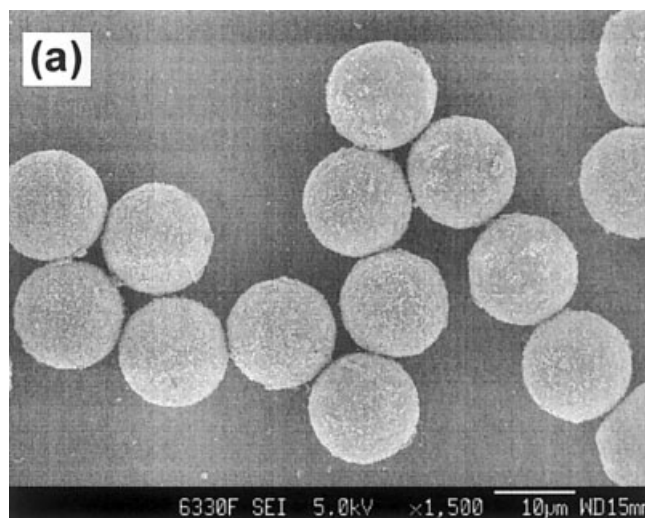


B

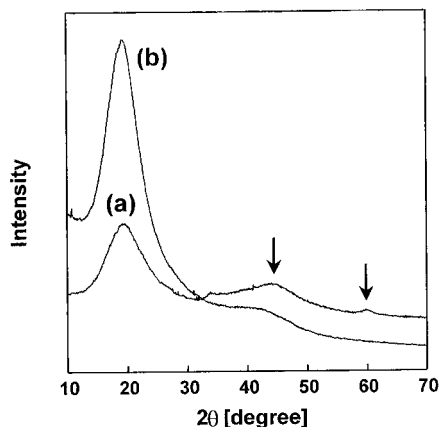
**Figure 3** (A) XPS  $C_{1s}$  spectra for the particles: (a) P1 and (b) TP1. (B) XPS  $S_{1s}$  spectra for the particles: (a) P1 and (b) TP1.

faces. Figure 4(c) shows the magnified SEM image of the TP1/Ni composite particle, where metallic domain formed on the particle surfaces can be clearly seen. From the above-mentioned images, a possible explanation might be suggested for the formation of polymer/Ni core-shell composite particles. It is believed that the thiol-functional group on the polymer particle surfaces provided the sites at which Ni ions can complex before the reduction. Therefore, at the early stage of reduction, chemisorption between nuclei of Ni colloidal particles and the surface thiol group would occur. As the reduction proceeded, a nickel domain would be grown from these nuclei of Ni, which itself has catalytic activity for the reduction of Ni ions.

XRD patterns of the TP1/Ni composite and TP1 particles are shown in Figure 5. Compared with the XRD profile of TP1 microspheres [Fig. 5(b)], peaks at



**Figure 4** Scanning electron microscopic images of the polymer/metal composite particles: (a) P2/Ni particles, (b) TP1/Ni particles, and (c) magnification of sample (b) at resolution  $\times 5000$ .



**Figure 5** X-ray diffraction (XRD) profiles of (a) TP1 polymer particles and (b) TP1/Ni composite particles.

$2\theta$  values of  $44.4$  and  $60.6^\circ$  are observed for the TP1/Ni composite particles. These peaks are attributable to the (1 1 1) and (2 0 0) planes of zerovalent nickel, respectively. The results confirm the formation of zerovalent Ni domains on the surface of the TP1 microspheres during the chemical metal deposition.

### CONCLUSIONS

Polymer/Ni composite particles may be obtained by chemical metal deposition without a surface sensitization process. This was possible by introducing the thiol group onto the particle surface as a site for coordinating with Ni ions. Actually, it was found that physically adsorbed polymer/Ni composite particles were also possible on the uneven particle surfaces. However, the deposition mode was largely different from that of the functional particle/Ni composite.

From SEM images and XRD patterns, it was confirmed that polymer/Ni core-shell particles could be achieved by chemical metal deposition.

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