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ORIGINAL ARTICLE

Preparation of polymer-protected NiMoPt alloy nanoparticles dispersible in water over a wide pH range by a hot-soap method and ligand-exchange reaction

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The reduction of bis(acetylacetonato)platinum(II), nickel(II) acetate tetrahydrate and molybdenum(II) acetate dimer in a mixed solvent of oleylamine and diphenyl ether using 1,2-hexadecanediol resulted in the production of oleylamine-protected ternary alloy nanoparticles (nickel–molybdenum–platinum ternary alloy nanoparticles (NiMoPtNPs)). A ligand-exchange reaction with 50% *N*-methylated linear poly(ethyleneimine-*co*-*N*-methylethyleneimine) (poly(EI-*co*-NMEI)) in chloroform yielded poly(EI-*co*-NMEI)-protected NiMoPtNPs. The resultant nanoparticles had average diameters of 1.9–2.5 nm and could be dispersed in water at pH levels ranging from −1 to 14. The average radii of the NiMoPtNPs decreased when the protecting polymer was changed from oleylamine to poly(EI-*co*-NMEI). Energy-dispersive X-ray spectroscopy of the poly(EI-*co*-NMEI)-protected NiMoPtNPs was performed to confirm the formation of polymer-protected alloy nanoparticles of nickel, molybdenum and platinum.

INTRODUCTION

Platinum is a highly durable and high-activity catalyst[1–4] that is widely used in both synthetic organic chemistry and environmental science. Platinum nanoparticles (PtNPs) are also used as an environmental catalyst to clean the exhaust gases from vehicles and factories.[5,6] However, the high cost of platinum metal limits its applications, and the substitution of a highly catalytic metal in the place of platinum is thus desirable to mitigate the cost of platinum and to preserve this natural resource.

A nickel–molybdenum–platinum alloy was found to show higher activity than platinum in the hydrogenation of an organic compound. The most significant advantage of this system is the lower platinum content required because this lowers the cost of the catalyst. The next stage in the development of this system is the preparation of nanoparticles of a ternary metal alloy.

In our previous study,[7] we prepared poly(ethyleneimine-*co*-*N*-methylethyleneimine) (poly(EI-*co*-NMEI))-protected PtNPs by reduction in an aqueous phase, and poly(EI-*co*-NMEI) was shown to be a good protecting polymer for the dispersion of PtNPs in water over a wide pH range. In addition, our preliminary experiments revealed that the poly(EI-*co*-NMEI)-protected NiPtNPs could be obtained by the reduction of nickel(II) chloride and

chloroplatinic(IV) acid with sodium borohydride; however, nickel(II) chloride is not reduced by sodium borohydride. Thus, we chose a hot-soap method to reduce the nickel source. Ahrenstorf *et al.*[8] reported the preparation of oleylamine-protected NiPtNPs by a hot-soap method in which nanoparticles are formed at high temperature and under inert conditions. Consequently, it is easy to reduce the starting materials to metals and the oxidation of alloy nanoparticles is prevented, in contrast to what is observed using the aqueous-phase method. We therefore attempted to prepare poly(EI-*co*-NMEI)-protected NiPtNPs by this method and found that poly(EI-*co*-NMEI) decomposed at high temperature, that is, 200 °C. In the present study, we prepared oleylamine-protected nickel–molybdenum–platinum ternary alloy nanoparticles (NiMoPtNPs) and then changed the protecting ligand to poly(EI-*co*-NMEI) as shown in Scheme 1. We determined the particle size, metal composition and dispersibility of the resultant nanoparticles.

EXPERIMENTAL PROCEDURE

Reagents

Bis(acetylacetonato)platinum(II), nickel(II) acetate tetrahydrate, oleic acid, oleylamine, 1,2-hexadecanediol, diphenyl ether, *o*-dichlorobenzene, ethanol

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and chloroform (Wako Pure Chemical Co., Osaka, Japan) were used as received. Molybdenum(II) acetate dimer (Sigma-Aldrich Co., St. Louis, MO, USA) was also used as received. In all, 50% N-methylated poly(EI-co-NMEI) (M_W 2500) was synthesized by the Eschweiler–Clarke reaction according to the method described in the literature.[9]

Preparation of oleylamine-protected NiMoPtNPs

In a 200-ml three-neck flask, 41.6 mg (0.167 mmol) nickel(II) acetate tetrahydrate, 35.8 mg (0.083 mmol) molybdenum(II) acetate dimer, 43.1 mg (0.167 mmol) 1,2-hexadecanediol, 0.20 ml (0.631 mmol) oleylamine, 0.20 ml (0.608 mmol) oleic acid and 10 ml diphenyl ether were charged and heated under reduced pressure (3 Torr) at 80 °C for 30 min. Then, argon gas was injected into the flask, and the mixture was heated to 200 °C, followed by the injection of 65.5 mg (0.167 mmol) bis(acetylacetonato)platinum(II) dissolved in 1.0 ml o-dichlorobenzene and 1 h of reflux. After cooling to 25 °C, 5 ml chloroform and 30 ml ethanol were added, and the precipitate was recovered by ultracentrifugation. The resultant particles were subjected to evaporation to yield oleylamine-protected NiMoPtNPs as a black powder.

Other oleylamine-protected NiMoPtNPs were prepared by changing the molar ratio of nickel(II) acetate hydrate to bis(acetylacetonato)platinum(II) from 2 to 10.

Preparation of poly(EI-co-NMEI)-protected NiMoPtNPs

Oleylamine-protected NiMoPtNPs, 50% 150 mg (0.060 mmol) N-methylated poly(EI-co-NMEI) and 10 ml chloroform were charged in a 20-ml vial container and heated on a hot plate to 100 °C until the chloroform was completely evaporated. The resultant viscous liquid was dispersed in 10 ml ethanol and subjected to ultrafiltration and evaporation to yield poly(EI-co-NMEI)-protected NiMoPtNPs as a black viscous liquid.

Evaluation of the dispersibility of poly(EI-co-NMEI)-protected NiMoPtNPs in water

Poly(EI-co-NMEI)-protected NiMoPtNPs were mixed in a vial container with hydrochloric acid or an aqueous sodium hydroxide solution, and the pH was adjusted over the range of −1 to 15. Samples were left to stand at room temperature and the state of the solution was evaluated by visual inspection.

Measurement and analysis

[1]H nuclear magnetic resonance (NMR) spectra were recorded using a JEOL JNM ECP-300 or JNM ECP-500 (JEOL, Tokyo, Japan) NMR spectrometer. Chloroform-d and D_2O were used as the solvents, and tetramethylsilane and 4,4-dimethyl-4-silapentane-1-sulfonic acid were used as the internal standards to determine chemical shifts.

Thermogravimetric-differential thermal analysis (TG-DTA) was performed using a TG-DTA 2020S analyzer (Mac Science Co., Yokohama, Japan) in air. The heating rate was 10 °C min^{-1}.

Inductively coupled plasma emission spectrometry (ICP) was performed with an ICPE-9000 spectrometer (Shimadzu, Kyoto, Japan).

Transmission electron microscopy (TEM) was performed with a High-Technologies H-7650 unit (Hitachi, Tokyo, Japan).

Energy-dispersive X-ray spectrometry (EDS) was performed with a JEOL JED-2300 T unit.
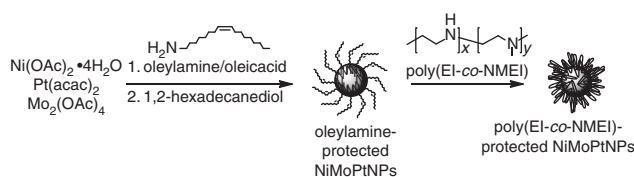
Scheme 1 The preparation of polymer-protected ternary alloy nanoparticles (NiMoPtNPs).

RESULTS AND DISCUSSION

Preparation of oleylamine-protected NiMoPtNPs

Oleylamine-protected NiMoPtNPs (nos. **1**–**6**) were prepared by a hot-soap method and obtained as a black powder. The results of the preparation of oleylamine-protected NiMoPtNPs are summarized in Table 1. The initial molar ratio of nickel, molybdenum and platinum, Ni:Mo:Pt, was set to 1:1:1–5:1:1 or 10:1:1. The resultant nanoparticles were analyzed by ^{1}H NMR, TG-DTA, ICP and TEM. Although nos. **1**–**4** dispersed in chloroform and hexane, nos. **5** and **6** did not disperse in any organic inorganic solvent because of their high nickel content. The TG-DTA of nos. **1**–**4** showed a decrease in weight due to the combustion of oleylamine, whereas an exothermic peak due to the oxidation of nickel was observed for nos. **5** and **6**. The results of the ICP analysis are shown in Table 1. The contents of molybdenum and platinum in the nanoparticles decreased with the increasing content of nickel. The nanoparticles contained no molybdenum when the molar ratio of nickel to molybdenum was > 5. This is because the reduction of nickel(II) species was accelerated due to the large content of nickel compound compared with that of molybdenum compound. The ^{1}H NMR spectra of oleylamine-protected NiMoPtNPs (no. **1**), oleylamine and oleic acid are shown in Figure 1. The spectra show the disappearance of the signals due to the carbon–carbon unsaturated bond, amino group and the methylene protons next to the amino group, indicating that metal-ligand coordination was established. A TEM image of no. **2** is shown in Figure 2. The size of the nanoparticles was evaluated by measuring the diameter of the nanoparticles in the TEM images; the average sizes of these nanoparticles are summarized in Table 1. The average size was 2.1–6.8 nm, which increased with the increasing content of nickel.

Table 1 Results of the preparation of oleylamine-protected NiMoPtNPs

No.	Infeed molar ratio (Ni:Mo:Pt)	Yield (mg)	Metal content[a] (%)	Molar ratio[b] (Ni:Mo:Pt)	Average size[c] (nm)
1	1:1:1	64.9	53	24:22:54	2.1 ± 0.3
2	2:1:1	52.8	62	31:8:61	2.5 ± 0.3
3	3:1:1	52.8	66	40:6:54	2.6 ± 0.3
4	4:1:1	109	48	63:9:28	4.3 ± 0.9
5	5:1:1	86.2	–	78:0:22	5.8 ± 0.4
6	10:1:1	47.8	–	85:0:15	6.8 ± 0.7

[a]Analyzed by TG-DTA.
[b]Determined by ICP analysis.
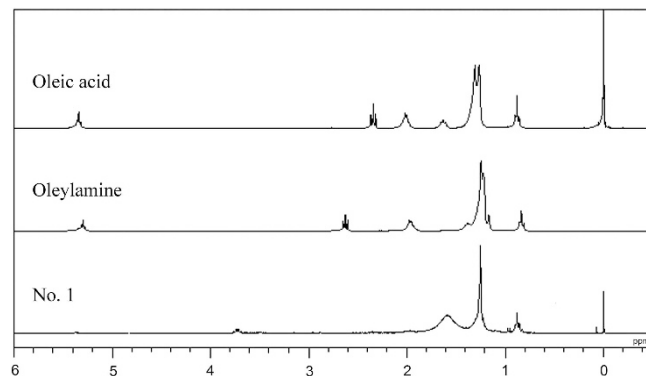[c]Calculated based on the TEM image.

Figure 1 ^{1}H NMR spectra of oleylamine-protected NiMoPtNPs (no. **1**), oleylamine and oleic acid (solv.: chloroform-d, ref.: tetramethylsilane).

Preparation of poly(EI-co-NMEI)-protected NiMoPtNPs

Many methods for the ligand exchange of organically protected metal nanoparticles have been reported. For example, the exchange between a hydrophobic and a hydrophilic ligand using oleic acid-protected FePtNPs and 2-aminoethanethiol in methanol at room temperature for 10 min has been described.[10] In this study, we conducted a ligand exchange from oleylamine-protected NiMoPtNPs to *N*-methylated poly(EI-co-NMEI) in water, methanol, ethanol or chloroform with heating or ultrasonication. Ligand exchange was accomplished only in chloroform. We confirmed the ligand exchange of NiMoPtNPs by confirming their dispersion in ethanol after heating. As a result,
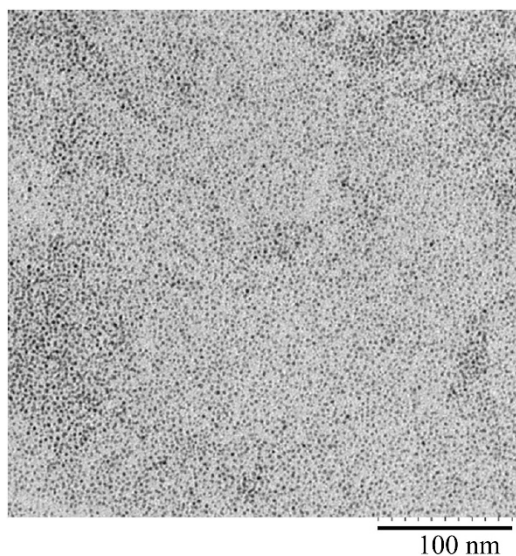
poly(EI-co-NMEI)-protected NiMoPtNPs were obtained as a black viscous liquid.

The results of the preparation of poly(EI-co-NMEI)-protected NiMoPtNPs are summarized in Table 2. In nos. **1–3**, the ligand was successfully exchanged to yield NiMoPtNPs **1′–3′**, respectively, as a black and viscous liquid. The ^{1}H NMR spectra of poly(EI-co-NMEI)-

Figure 4 TEM image of no. **2′**.

Figure 2 TEM image of no. **2**.

Table 2 Results of the preparation of poly(EI-co-NMEI)-protected NiMoPtNPs in nos. 1′–3′

No.	Yield (mg)	Metal content[a] (%)	Molar ratio[b] (Ni:Mo:Pt)	Average size[c] (nm)
1′	127	12	27:36:37	1.9 ± 0.2
2′	197	11	9:16:75	2.4 ± 0.3
3′	97.6	15	40:4:56	2.5 ± 0.3

[a]Analyzed by TG-DTA.
[b]Determined by ICP analysis.
[c]Calculated based on the TEM image.

Figure 5 TEM image of **2′** (**a**) and EDS spectrum of the marked position (**b**).

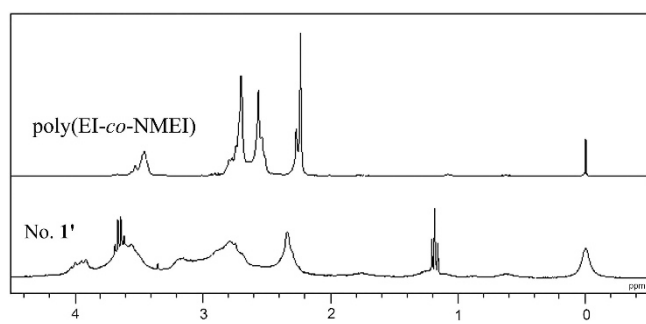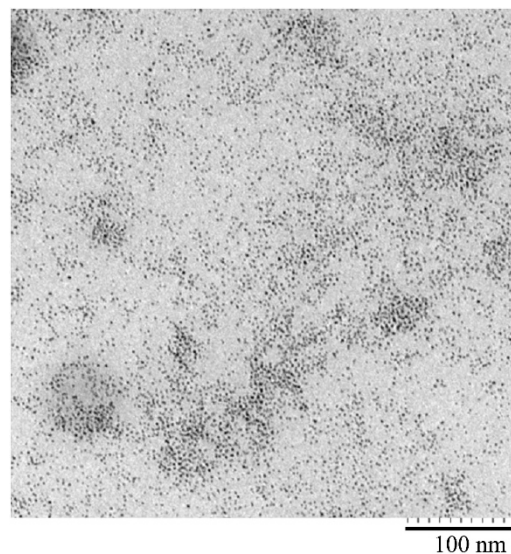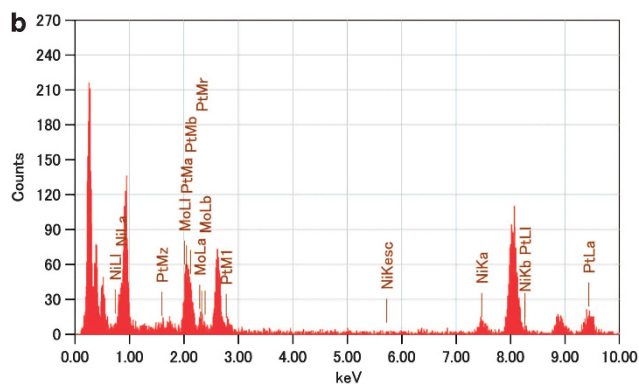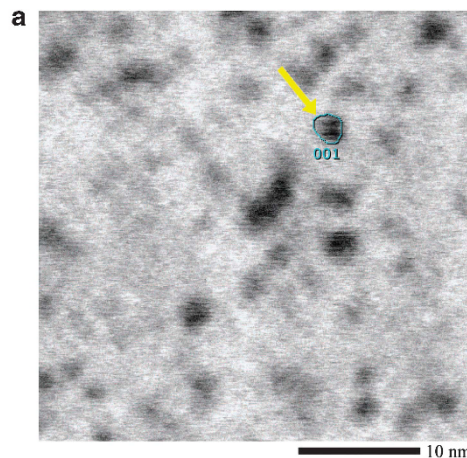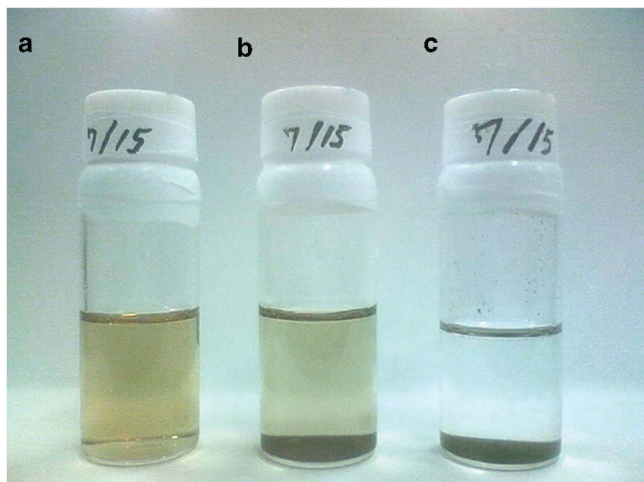**Figure 3** ^{1}H NMR spectra of poly(EI-co-NMEI)-protected NiMoPtNPs (no. **1′**) and poly(EI-co-NMEI) (solv.: D_2O, ref.: 4,4-dimethyl-4-silapentane-1-sulfonic acid).

Table 3 Results of the EDS analysis for no. 2′

Element	Weight %	Atomic %	Error %
Ni	3.44	9.02	0.88
Mo	18.34	29.38	0.33
Pt	78.21	61.60	0.08

Figure 6 Dispersibility of poly(EI-co-NMEI)-protected NiMoPtNPs at pH = −1 (**a**), pH 14 (**b**) and pH 15 (**c**).

protected NiMoPtNPs (no. **1′**) and poly(EI-co-NMEI) are shown in Figure 3. The disappearance of the signals due to oleylamine, the broadening of the signals and the shift in the signal due to the methyl group from 2.23 to 1.09 p.p.m. suggest the coordination of poly(EI-co-NMEI) to nanoparticles. The metal contents of nos. **1′–3′** were determined to be 12, 11 and 15%, respectively, by thermogravimetric analysis. Compared with those of the oleylamine-protected NiMoPtNPs, these contents were lower, but oxidation was not observed. The metal molar ratios of nos. **1′–3′** were measured by ICP analysis. The metal compositions were altered to some degree by the ligand exchange. No relationship was observed between the metal compositions of the oleylamine-protected NiMoPtNPs and the poly(EI-co-NMEI)-protected NiMoPtNPs, which suggests that nickel is oxidized more easily than molybdenum or platinum. A TEM image of no. **2′** is shown in Figure 4. The size of the nanoparticles was evaluated by measuring the diameter of the nanoparticles in the TEM images; the average sizes of these nanoparticles are summarized in Table 2. The average sizes of nos. **1′–3′** were smaller than those of nos. **1–3** because some metal atoms were lost during the ligand exchange. These metal losses were also observed in the metal yields of the nanoparticles. In contrast, no ligand exchange was observed for nos. **4–6**. The ligand exchange was affected by nickel because nickel is more easily oxidized than platinum, which resulted in the decomposition of nanoparticles during the ligand exchange. In other words, oleylamine-protected NiMoPtNPs with a nickel ratio over 63% failed to exchange the ligand.

EDS was carried out for a particle of no. **2′**, indicated in the TEM image by an arrow. The spectrum and the corresponding analytical data are summarized in Figure 5 and Table 3, respectively. The average

composition of no. **2′** was Ni:Mo:Pt = 9:29:62 in atomic ratio, which is relatively close to the composition of 9:16:75 determined by ICP. EDS mapping revealed that three metals were distributed uniformly in each particle. Metal atoms of Ni, Mo and Pt were mixed uniformly to form a trimetallic random alloy.

Nos. **1′–3′** were mixed with hydrochloric acid or aqueous sodium hydroxide solution to observe their stability at various pH values, as shown in Figure 6. Nos. **1′–3′** were well dispersed in water over pH levels ranging from −1 to 14 immediately after mixing and were precipitated at pH 14 after standing for 1 week, whereas the PtNPs were dispersed in water at pH levels ranging from −1 to 15, as we have reported.[7] In light of the stability of the nanoparticles over these pH ranges, it is apparent that a slight decrease in dispersibility would be induced by alloying platinum with nickel and molybdenum to lower the reducibility due to nickel.

CONCLUSION

Novel oleylamine-protected NiMoPtNPs were prepared by a hot-soap method using oleylamine. A ligand-exchange reaction with 50% N-methylated linear poly(EI-co-NMEI) yielded poly(EI-co-NMEI)-protected NiMoPtNPs. When the content of nickel was high, the ligand-exchange reaction of oleylamine with poly(EI-co-NMEI) did not proceed. In addition, the contents of molybdenum and platinum decreased with the increase in the content of nickel. Poly(EI-co-NMEI)-protected NiMoPtNPs were dispersed in methanol, ethanol and water over a pH range of −1 to 14. TEM images revealed that the sizes of the nanoparticles were smaller than 3 nm and increased slightly with the increase in the content of nickel. EDS analysis showed that poly(EI-co-NMEI)-protected NiMoPtNPs are composed of a ternary metal alloy.

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