Synthesis and Stabilization of Ni Nanoparticles in a Pure Aqueous CTAB Solution

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Ni nanoparticles (7–20nm) were synthesized by hydrazine reduction in a pure aqueous solution at 25 °C using CTAB as a capping agent and an appropriate amount of bases as catalysts. No organic solvents and extra inert gases were necessary. It was suggested that Ni nanoparticles were stabilized by a bilayer structure of CTAB.

In the past two decades, considerable attention has been devoted to the synthesis of metal nanoparticles because of their unusual properties and potential applications in optical, electronic, catalytic, magnetic materials, and so on. Among various kinds of metal nanoparticles, the preparations of some metal nanoparticles such as Ni, Cu, and Fe are relatively difficult because they are easily oxidized. Ni nanoparticles have attracted much attention because of their applications as catalysts and conducting and magnetic materials. Until now, only few works on the preparation of Ni nanoparticles have been reported and they usually were performed in organic media to avoid the formation of nickel oxide or hydroxide.[1–3]

The synthesis of Ni nanoparticles in pure aqueous solutions is attractive because of the absence of organic pollution. Recently, we have reported the preparation of Ni nanoparticles in aqueous solution of cationic surfactants cetyltrimethylamonium bromide/tetradodecylammonium bromide ($CTAB/TC_{12}AB$),[4] which was usually used for the syntheses of rod-like or fiber-like Au, Ag, CdS, and CdSe nanoparticles.[5–10] However, an elevated reaction temperature and the addition of acetone were necessary. In this work, we prepared Ni nanoparticles in a pure aqueous CTAB solution at 25 °C. The role of CTAB was also examined.

In general, for the synthesis of Ni nanoparticle, an aqueous solution of 10 mL was first prepared by dissolving CTAB (0.01 M) and nickel chloride (0.005–0.05 M) in water. Then, hydrazine (0.25–2 M) and NaOH solutions (0.02 M) were added in sequence. At 25 °C, Ni nanoparticles were formed after about 20 h in a capped bottle.

Figure 1 shows the typical transmission electron microscope (TEM), electron-diffraction pattern and high-resolution TEM (HRTEM) images of Ni nanoparticles. The TEM image indicated that these particles essentially were very fine and monodispersed with a mean diameter of 15.4 nm and a standard deviation of 1.9 nm. This revealed that the presence of CTAB indeed restricted the growth of Ni nanoparticles efficiently. The electron-diffraction pattern showed three fringe patterns with plane distances of 2.03, 1.76, 1.02 Å. They related to the (111), (200), (222) planes of pure face-centered cubic (fcc) Ni. From HRTEM, the interreticular distance was found to be 2.06 Å. It related to the (111) plane of pure fcc Ni. In addition, the X-ray diffraction (XRD) analysis also indicated three characteristic peaks for Ni ($2\theta = 44.5, 51.8$, and 76.4), corresponding to their indices ((111), (200), and (222)). No oxides or hydroxide such as NiO, Ni_2O_3, and $Ni(OH)_2$ were formed. Accordingly, it could be concluded that the nanoparticles prepared in this work were pure Ni of fcc structure.

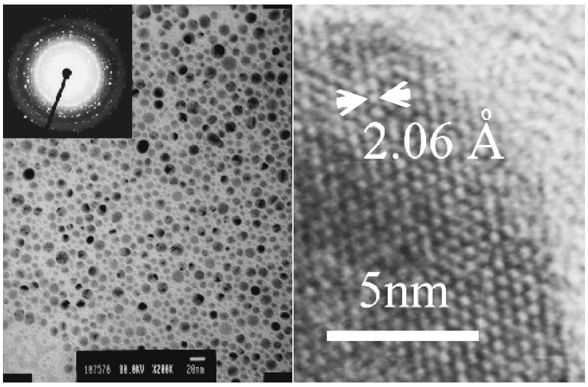

Figure 1. TEM, electron-diffraction pattern, and HRTEM images of Ni nanoparticles. $[NiCl_2] = 25\,mM$; $[N_2H_5OH] = 0.25\,M$; $[CTAB] = 0.01\,M$; 25 °C.

Similar to our previous work,[3,4] it was notable that the addition of NaOH was necessary for the formation of Ni nanoparticles. In this work, it was found that other bases such as KOH, $Ba(OH)_2$, or tetraethylammonium hydroxide also led to the same result. The additions of these bases resulted in the increase of solution pH from 10.2 to 10.6. However, no Ni nanoparticles were formed if much more hydrazine was added to raise the solution pH up to 10.6. This reveals that theses bases probably acted as catalysts instead of a simple role to adjust the solution pH. Further investigation is necessary.

Furthermore, no matter whether the synthesis reaction was performed in an inert atmosphere (N_2 gas) or not, only metallic Ni nanoparticles were obtained. Since N_2 gas might be generated to create an inert atmosphere automatically via the formation reaction and the catalytic decomposition of excess hydrazine by the resultant Ni nanoparticles,[3] the input of extra N_2 gas was not necessary.

By a superconducting quantum interference device (SQUID) magnetometer, the saturation magnetization (M_s), remanent magnetization (M_r), and coercivity (H_c) of the resultant Ni nanoparticles at 25 °C were determined to be 31.8 emu/g, 1.86 emu/g, and 26.8 Oe, respectively. In addition, at an applied field of 10 kOe, the magnetization of Ni nanoparticles increased with the decrease of temperature at 5–400 K owing to the decrease in thermal energy. All these magnetic properties reflected the nature of nanoparticles.[2–4]

The size of Ni nanoparticles decreased with decreasing nickel chloride concentration or increasing hydrazine concentration. When $[N_2H_5OH] = 0.4\,M$, the mean diameters of Ni nanoparticles (20–9 nm) decreased with the decrease of nickel chloride concentration (0.05–0.01 M) and remained unchanged at $[NiCl_2] < 0.01\,M$. At $[NiCl_2] = 0.025\,M$, the mean diameters of Ni nanoparticles (15–10 nm) decreased with the increase of hydrazine concentration (0.25–0.5 M), and remained at 10 nm when [hydrazine] $>$ 1.0 M. Both the concentration effects revealed that the size of Ni nanoparticles was not affected by hydrazine concentration when $[N_2H_5OH]/[NiCl_2] > 40$. These phenomena were similar to those observed in other media.

Since CTAB is a cationic surfactant, nickel ions would not be adsorbed on the micelles. Hence, it was suggested that Ni nanoparticles were capped by CTAB molecules after they were formed. First, the Fourier transform infrared (FTIR) spectrum of the resultant Ni nanoparticles and free CTAB were studied. The resultant Ni nanoparticles were washed several times with alcohol and water to remove free CTAB before the measurement. As shown in Figure 2, the resultant Ni nanoparticles and free CTAB had the similar absorption bands. Since Ni has no characteristic absorption bands in the examined wavenumber range, this revealed that CTAB was indeed capped on the surface of Ni nanoparticles. In addition, the resultant Ni nanoparticles did not exhibit any absorption bands different from those of free CTAB. This implied that CTAB might be just adsorbed on the surface of Ni nanoparticles, not decomposed catalytically by Ni nanoparticles as observed in the case of ethylene glycol.[3] For the synthesis of metal nanoparticles in ethylene glycol, extra protective polymers were usually necessary because ethylene glycol was not an efficient surfactant or capping agent and could be used just as a solvent or a reducing agent. In the case of Ni nanoparticles, the adsorbed ethylene glycol was decomposed catalytically by Ni nanoparticles and self-created a protective layer on the surface.[3,11] Thus, compared to ethylene glycol, the surfactant CTAB could be used directly as an efficient capping agent for the synthesis of metal nanoparticles.

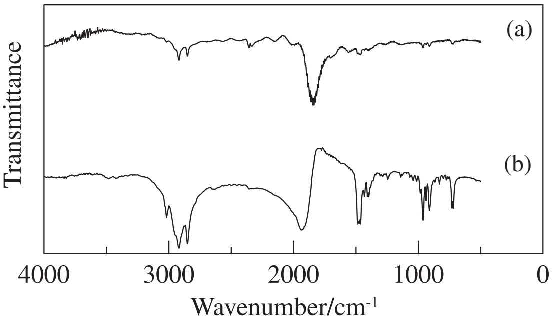

Figure 2. FTIR spectra of the resultant Ni nanoparticles (a) and free CTAB (b).

To further investigate the stabilization mechanism of Ni nanoparticles by CTAB, thermogravimetric analysis (TGA) was conducted. The TGA curves for CTAB and CTAB-capped Ni nanoparticles are indicated in Figure 3. In the case of CTAB, the weight loss occurred sharply from 250 to 350 °C, revealing CTAB molecules were decomposed thermally within this temperature range. However, in the case of CTAB-capped Ni nanoparticles, the TGA curve shows two weight loss steps. The first weight-loss step occurred sharply within 250–400 °C and the second one appeared gradually from 400 to 500 °C. This implied that CTAB molecules were present on the surface of Ni nanoparticles in two different forms. Thus, it could be suggested that a bilayer structure of CTAB was formed: the inner layer was bound to the Ni surface via the headgroups and was connected to the outer layer, whose headgroups were in the aqueous solution, through hydrophobic interaction. On the basis of the suggestion, the first and second weight-loss steps in the TGA curve might be attributed to the releases of the outer and inner layers, respectively. Similar phenomenon and suggestion were also reported in the assembly of cationic surfactants on the surface of Au nanorods.[12]

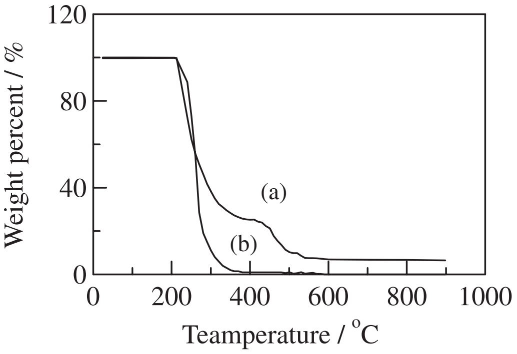

Figure 3. TGA curves for CTAB (b) and CTAB-capped Ni nanoparticles (a) obtained at $[NiCl_2] = 0.025$ M, $[N_2H_5OH] = 0.25$ M, and [CTAB] = 0.01 M.

In conclusion, Ni nanoparticles were synthesized in a pure aqueous solution at 25 °C. No extra inert gases were necessary and the formation of a bilayer structure of CTAB was suggested. Compared to our previous works,[2–4] both elevated temperature and organic solvent were unnecessary. Also, CTAB was used directly as an efficient capping agent, not to form micelles or reverse micelles for the stabilization of Ni nanoparticles. The simple method will be helpful for the production of Ni nanoparticles.

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