Research Letter Synthesis of Ag or Pt Nanoparticles by Hydrolysis of Either Ag₂Na or PtNa

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Ag and Pt nanoparticles have successfully been synthesized by hydrolysis of either Ag_2Na or PtNa at room temperature. The oxidation of sodium in the Pt-Na pellets was much faster than that in the Ag-Na pellets since Pt is a catalyst for H_2O formation reaction from hydrogen and oxygen at room temperature. The hydrolysis byproduct, NaOH, has a high solubility and easily is removed. This method offers a simple method of preparing transition metal nanoparticles. The Ag and Pt nanoparticles prepared by this method were crystalline in nature, and spherical in shape with a mean size of around 10 nm.

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1. INTRODUCTION

Transition metal nanoparticles have attracted considerable attention since they have unique catalysis, magnetism, and optical properties, and have great potential for use in chemical synthesis [1] and fuel cells [2]. Although a variety of preparation methods have been developed to synthesize transition metal nanoparticles [3–5], and some of these synthesis methods are, in certain ways, reaching maturity, an economical synthesis method that is capable of being scaled up to large volume production is still required.

Recently, we have found that Mg_2Ni spontaneously undergo hydrolysis in water and forms Ni nanoparticles, $Mg(OH)_2$, and hydrogen. After the hydrolysis product, $Mg(OH)_2$ was carefully removed using an acid, pure Ni nanoparticles were obtained [6]. Cu, Ag, and Au nanoparticles have also been produced by hydrolysis of their magnides [7, 8]. On further investigation, certain aluminides such as Al_3Ni were shown to exhibit a similar hydrolysis behavior in water at room temperature [9]. However, due to the chemical characteristics of $Al(OH)_3$, including its low acidity, chemically active transition metal nanoparticles, such as Fe, Co, and Ni, cannot be produced by using dilute hydrochloric acid to remove $Al(OH)_3$.

In this study, the hydrolysis behavior of Ag-Na or Pt-Na intermetallics in water at room temperature was investigated.

The Ag and Pt nanoparticles prepared by hydrolysis of the Ag-Na or Pt-Na intermetallics were characterized in detail.

2. EXPERIMENTAL

Ag₂Na or PtNa were synthesized by in situ reaction of mixtures of Ag or Pt powders with a weight ratio (Ag or Pt to Na) of about 1:4 at 600°C for 2 hours. Small Ag₂Na and PtNa pellets (about 0.05 g each) were placed, one by one, into 500 mL distilled water in a matrass. After about 12 hours, the Ag and Pt nanoparticles started to deposit on the bottom of the matrass. The solid products were rinsed three times using distilled water, and then three times using ethanol.

The phase compositions of the small Ag-Na and Pt-Na pellets were characterized using a Philips X-ray powder diffractometer. The morphology of Ag and Pt particles and the chemical composition were characterized by a TEM. The size of the Ag and Pt particles (no drying) was analyzed using a Zetasizer 3000 HS instrument.

3. RESULTS AND DISCUSSION

 Ag_2Na , Na, and NaOH were observed in the XRD patterns for the Ag-Na pellets prepared at 600°C for 2 hours (see Figure 1(a)). No Ag peaks were observed, which shows that all the Ag powder in the initial materials was totally converted



FIGURE 1: XRD powder diffraction patterns for (a) the Ag_2Na pellets and (b) the PtNa pellets.



FIGURE 2: XRD powder diffraction patterns for (a) the Ag nanoparticles and (b) the Pt nanoparticles.

to Ag_2Na after the conventional melting and casting processing. The presence of NaOH suggests that Na in the pellets reacted with moisture, rather than oxygen in air, during in situ synthesis, storage, and testing.

Na, PtNa, NaOH, and Pt diffraction peaks were observed in the XRD patterns for the Pt-Na pellets prepared at 600° C for 2 hours (see Figure 1(b)). The Pt peaks in Figure 1(b) were fairly broad, which reflects the fact that the crystallite size of Pt particles was extremely small (much smaller than the size of the initial Pt particles (500 nm)). The XRD result (see Figure 2(a)) indicates that the solid product in the Ag-Na sample, after rinsing in distilled water and ethanol, only consisted of Ag particles. Discrete Ag nanoparticles were observed (see Figure 3(a)) by TEM.

There are two intermetallic compounds in the Na-Pt binary system [10]. It has been reported that Pt-Na with an atomic ratio of 1:1 is totally converted into PtNa at 350–400°C, and a lower transformation temperature can be achieved when the Pt concentration is less than 50 atomic percent [11]. According to the compositions of the initial materials in the Na-Pt sample, a homogeneous liquid alloy melt would be generated at 600°C. In other words, Pt should be completely converted into PtNa after cooling down. Therefore, the Pt particles in the Pt-Na pellets should not come from the initial Pt powders. In addition, the Pt

diffraction peaks in Figure 1(b) were fairly broad, which reflects the fact that the crystallite size of the Pt particles was extremely small. Hence, the Pt particles in the Pt-Na ingot pellets must result from the dissociation of PtNa.

Only a part of the Na was oxidized in the Ag-Na pellets during storage. In comparison with the Ag-Na pellets, the Pt-Na ingot pellets exhibited a more severe oxidation behavior in air with a rapid change in color from metallic to gray, and then to black.

The oxidation product of sodium in both the Ag-Na and Pt-Na samples was NaOH. A possible oxidation reaction for Na in moist air is as follows:

$$2Na(s) + 2H_2O(g) \longrightarrow 2NaOH(s) + H_2(g), \qquad (1)$$

where *s* and *g* in brackets denote the solid and gas states, respectively.

Pt is a catalyst for the formation reaction of H_2O from hydrogen and oxygen at room temperature [12]. The hydrogen formed in Reaction 1 could react with oxygen in air and form water again. Thus, Pt is able to accelerate the oxidation of sodium in the Pt-Na pellets.

When the Ag-Na or the Pt-Na pellets were dropped into a matrass, which contained 500 mL distilled water, the reactions were very fast, and sometimes were accompanied by slight explosions or combustion. Water in the matrass instantly became a colloid.

The reactions of Na₂Ag and PtNa in water can be written as follows:

$$2Ag_2Na(s) + 2H_2O(l) \longrightarrow 2NaOH(l) + 4Ag(s) + H_2(g),$$

$$2PtNa(s) + 2H_2O(l) \longrightarrow 2NaOH(l) + 2Pt(s) + H_2(g),$$

(2)

where *l* in brackets denotes the liquid state.

After about 12 hours, the colloids started to deposit on the bottom of the matrass. The solid products were rinsed three times using distilled water, and then three times using ethanol. Ag and Pt nanoparticles were obtained.

The Ag nanoparticles were predominantly spherical in shape and had a size of around 10 nm, which agrees with the results of the particle size analysis (see Figure 4(a)). The size of the Ag nanoparticles ranged from 5.4 nm to 17.2 nm with a mean size of 8.3 nm. The high-resolution TEM image for individual nanoparticles (see Figure 3(b)) shows that the spacing for the lattice fringe of the indicated nanoparticles is 0.230 nm. This is close to the interplanar spacing for the (111) planes of Ag (0.2259 nm). In addition, the fringes for individual particles indicate that some of the small Ag nanoparticles are single crystals. No significant oxygen and Na was detected by EDS. This result suggests that the Ag nanoparticles are resistant to oxidation from both the dissolved oxygen in an aqueous solution and the oxygen in flowing air.

XRD (Figure 2(b)) shows that the solid final product in the Pt-Na sample consisted only of Pt particles. The morphology of the Pt nanoparticles (see Figure 3(c)) was similar



FIGURE 3: Morphology of the Ag nanoparticles (a) TEM image and (b) HRTEM image, and the Pt nanoparticles (c) TEM image and (d) HRTEM image.



FIGURE 4: Particle size distribution of (a) the Ag nanoparticles and (b) the Pt nanoparticles.

to that of the Ag nanoparticles (spherical in shape and a size of around 10 nm). The high-resolution TEM image for individual nanoparticles (see Figure 3(d)) shows that the spacings for the lattice fringes of the indicated nanoparticles are 0.235 nm. This is close to 0.2265 nm, the interplanar spacing for the {111} planes in Pt. The results for the particle size analysis (see Figure 4(b)) shows that Pt nanoparticles ranged in size from 5.6 nm to 17.9 nm with a mean size of 8.7 nm. The size of the initial Pt particles for preparing the Pt-Na pellets ranged from 150 nm to 500 nm, much larger than above results, which confirmed that these Pt nanoparticles resulted from the dissociation of the Pt-Na intermetallic compounds.

No significant oxygen and Na was detected by EDS, which indicates that Pt nanoparticles are resistant to oxidation from both the dissolved oxygen in an aqueous solution and the oxygen in flowing air.

Compared with the hydrolysis of magnides, the reaction byproduct, NaOH, has a high solubility and is easily removed. This method offers a simple method of preparing transition metal nanoparticles. In addition, the shape and size of both Ag and Pt nanoparticles could be easily modified by chemical methods since these nanoparticles were prepared in an aqueous solution. The drawback of this method is the difficulty in controlling the reaction rate. Besides the sodium intermetallic compounds, there are many other alkali metal or alkali earth metal intermetallic compounds. Due to their high chemical activity, they also could exhibit a similar hydrolysis behavior in water. Hence, they could also have the potential to produce transition metal and semiconductor element nanoparticles.

4. SUMMARY

The oxidation of sodium in the Pt-Na pellets in air was much faster than that in the Ag-Na pellets since Pt is a catalyst for formation reaction of H_2O from hydrogen and oxygen at room temperature. The hydrolysis byproduct, NaOH, has a high solubility and is easily removed. This method offers a simple method of preparing transition metal nanoparticles. The Ag and Pt nanoparticles prepared by the hydrolysis of either Ag₂Na or PtNa were crystalline in nature, had a spherical shape with a mean size of around 10 nm.

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