

Synthesis and formation mechanism of Ag–Ni alloy nanoparticles at room temperature

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ABSTRACT

Ag–Ni nanoparticles were prepared with a chemical reduction method in the presence of polyvinylpyrrolidone (PVP) used as a stabilizing agent. During the synthesis of Ag–Ni nanoparticles, silver nitrate was used as the Ag⁺ source while nickel sulfate hexahydrate was used as Ni²⁺ source. Mixed solutions of Ag⁺ source and Ni²⁺ source were used as the precursors and sodium borohydride was used as the reducing agent. Five ratios of Ag⁺/Ni²⁺ (9:1, 3:1, 1:1, 1:3, and 1:9) suspensions were prepared in the corresponding precursors. Ag–Ni alloy nanoparticles were obtained with this method at room temperature. Scanning electronic microscope (SEM), energy dispersive spectrum (EDS), high resolution transmission electron microscope (HRTEM) were used to characterize the morphology, composition and crystal structure of the nanoparticles. The crystal structure was also investigated with X-ray diffraction (XRD). In all five Ag/Ni ratios, two kinds of particle structures were observed that are single crystal structure and five-fold twinned structure respectively. Free energy of nanoparticles with different crystal structures were calculated at each Ag/Ni ratio. Calculated results revealed that, with identical volume, free energy of single crystal particle is lower than multi-twinned particle and the difference becomes smaller with the increase of particle size; increase of Ni content will lead the increase of free energy for both structures. Formation of different crystal structures are decided by the structure of the original nuclei at the very early stage of the reduction process.

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1. Introduction

Metallic nanoparticles have received great attention due to their unique optical, electronic, magnetic, and catalytic properties [1–3], which are highly dependent on the particle size, content, and structure. Both Ag and Ni nanoparticles have been studied a lot since they all have very valuable properties [4–7]. Silver and nickel are immiscible, mainly because of the lattice mismatch and lower surface energy of Ag. However, synthesis of Ag–Ni alloy nanoparticles and related theoretical calculations have been studied widely in recent years [8,9]. It is known that most of the Ag–Ni nanoparticles are core@shell structure because of the reduction

of Ag⁺ to Ag⁰ is much faster than Ni²⁺ to Ni⁰ and the 14% lattice mismatch between the two metals. To overcome the large lattice mismatch and synthesize Ag–Ni alloy nanoparticles is a common purpose for related researchers [9–13]. For example, Mukesh et al. [9] synthesized Ag–Ni alloy nanoparticles by reducing nickel nitrate hexahydrate and silver nitrate in the present of hexadecylamine in 1-octadecene solution at 250 °C. A five-fold twinned morphology of the particles was obtained. Quasi-sphere particles about 20 nm in diameter were confirmed to have excellent and unique catalytic and magnetic properties. Van et al. [12] used laser ablation for production of Ag–Ni thin film on amorphous substrates. Though Ag–Ni film was obtained, both pure Ag and pure Ni were detected in the film, also Ag content was lower than expected. Zhang et al. [13,14] used radiolysis to reduce Ag and Ni ions at room temperature. Particles with different Ni content were studied. They found that with the Ni content growth, average particles size decreased from 7.4 nm to 4.0 nm. Using density functional theory and other characterization methods, they confirmed that the formation of the particles is determined by kinetic

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rather than thermodynamic reaction process. Tabatabaei and Sadrnezhaad [15] developed a one-step method to synthesize Ag–Ni nanoparticles at room temperature by a simple chemical method. To be specific, silver nitrate and nickel nitrate were dissolved in deionized water, then NaBH_4 was added to the solution. It is believed that particles were formed when the solution become gray. Srivastava et al. [8] also synthesized Ag–Ni nanoparticles with co-reduction method in water medium. Analysis on a single particle level was taken. They found that size distribution of the particles was wide, but the composition distribution was fairly narrow. Size composition correlation analysis showed that the bigger particles in the dispersion were primarily Ag rich, whereas the smaller particles (< 7 nm) had compositions lying in the broad range of 10–90 at% Ag. These previous researches demonstrate that the formation of Ag–Ni alloy nanoparticles is viable. However, the structural information and the formation mechanism of the nanoparticles are still ambiguous and related thermodynamic calculations are not all-sided. In this paper, Ag–Ni nanoparticles with different initial $\text{Ag}^+/\text{Ni}^{2+}$ ratios were prepared at room temperature. Thermodynamic calculations for particles with different crystal structures were carried out. Formation mechanisms of the particles were discussed from the viewpoint of both kinetics and thermodynamics based on the particle size, morphology and crystal structure. We expect that this research could provide direct insight into formation mechanism of bimetallic nanoparticles with different elements.

2. Experimental section

2.1. Materials

The source materials AgNO_3 , NaBH_4 , $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and polyvinylpyrrolidone (PVP, K-30, average MW ≈ 40000) were obtained from Sinopharm Chemical Reagent Co. Ltd., and all are in analytical purity without further purification.

2.2. Synthesis of Ag–Ni alloy nanoparticles

About 1 g PVP was dissolved in 100 ml aqueous solutions with Ag^+ and Ni^{2+} ions, and the mixed solution was used as reaction solutions. The total mole concentration of Ag^+ and Ni^{2+} was set to be 20 mM, the ratios of $\text{Ag}^+/\text{Ni}^{2+}$ were 9/1, 3/1, 1/1, 1/3, and 1/9, respectively. NaBH_4 was dissolved in distilled water and used as the reduction solution. Sufficient NaBH_4 solution was dripped into the stirring reaction solution. To avoid hydrolysis of NaBH_4 , all NaBH_4 solutions were fresh made for each ratio of $\text{Ag}^+/\text{Ni}^{2+}$. Once NaBH_4 was added, the solution turned to light yellow, a few seconds later the reacting solution became black and large amount of foam was observed. The solution was kept stirring for 30 min until the reaction was finished. To separate the nanoparticles, 100 ml acetone was added in the reacted solution. After 12 h, the solution was obviously double layered, transparent clear liquid at top and black precipitate at bottom. After removed the clear liquid, the black precipitate was re-dispersed in distilled water and then centrifuged at 4000 rotations per minute for 10 min, and such centrifuge process was repeated for 5 times until the extra surface agent and salt were washed away. To the end, the precipitate was dried at room temperature to get the Ag–Ni nanoparticles powder. The whole process was performed at room temperature (25 °C). For contrast, pure Ag nanoparticles were synthesized in the same situation mentioned above.

2.3. Sample characterization

Drops of ethanol re-dispersed sample were dripped on clean silicon chip and Cu grid respectively. After the ethanol was

evaporated, the silicon-chip sample was used for scanning electronic microscope (SEM) observation and energy dispersive spectroscopy (EDS) characterization, which were performed by using a Hitachi S-4800 equipped with an energy dispersive spectroscopy attachment operated at 10 kV, While the Cu-grid sample was used for high resolution transmission electron microscope (HRTEM) observation, which was carried out by using a Jeol 2010 TEM with an accelerating voltage of 200 kV. The crystal structure and purity of as-prepared alloy nanoparticles were characterized by powder XRD on a Bruker D8 Advance X-ray diffractometer by using Cu K α as a radiation source at room temperature.

3. Result and discussion

Phase composition of Ag/Ni alloy nanoparticles synthesized with different conditions and pure Ag were examined by powder XRD measurements. Fig. 1 represents the XRD patterns of as prepared Ag/Ni and pure Ag nanoparticles. It can be clearly seen that all patterns revealed the *fcc* structure of the samples. For pure Ag sample, five characteristic peaks corresponding to (111), (200), (220), (311), and (222) planes were obtained and all these peaks are in good agreement with standard Ag powder XRD sample (ICSD code 44387). For alloy samples, characteristic peaks corresponding to the (111), (200), (220), and (311) planes were also obtained as shown in Fig. 1. It is observed that all alloy sample peak positions resembling the (111), (200), (220), and (311) planes of pure Ag nanoparticle sample but with slight deviation from the actual 2θ at 38.14, 44.31, 64.49, and 77.42°. For (111) peak with increasing of Ni content, the intensity is getting weaker, the FWHM (full width at half maximum) is getting wider and the peak position is shifted toward higher 2θ values. Similarly decrease on the intensity and broaden on the FWHM of other peaks can be detected for (200), (220), and (311) planes with the increasing of Ni content. The deviation of peak positions can be attribute to the decrease of the lattice constant while the decrease of intensity and broaden on the FWHM would be caused by the decline of crystallinity. The peak position of (200) plane for Ag is at 44.31° which is close to (111) plane for Ni at 44.83°, however, for all binary metallic nanoparticle samples, no (200) plane for Ni at 52.15° was detected. This observation is consistent with other Ag–Ni alloy particles synthesized using different method [9]. In other words, all peaks resemble the Ag *fcc* structure and there is no characteristic peak of Ni. So, it can be confirmed that the alloy nanoparticles are formed by Ni atoms present in Ag matrix. To analyze Ag–Ni

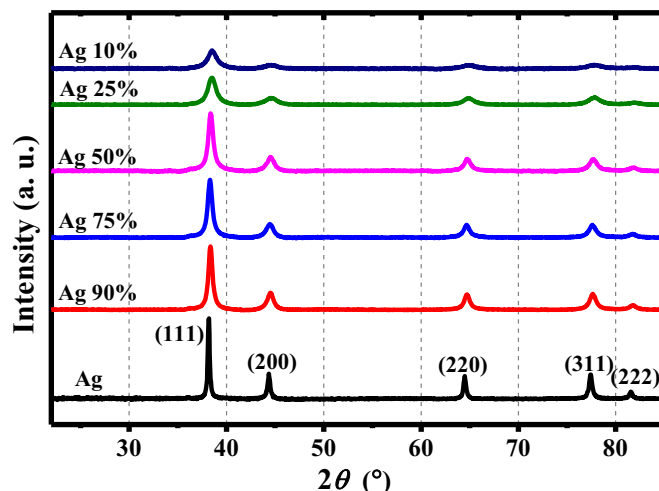


Fig. 1. XRD patterns of Ag nanoparticles and Ag–Ni alloy nanoparticles.

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