



Ag-catalyzed synthesis of ultrafine nickel nanoparticles: A facile way to size control

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ABSTRACT

We report here a facile strategy, Ag-catalyzed reduction of Ni²⁺ ions, for the synthesis of metallic nickel nanoparticles. The phase structure and morphology of particles were analyzed by means of X-ray diffraction and scanning electron microscopy. It was found that the resultant Ni nanoparticles had narrow size distribution, and the control of particle size could be easily achieved through manipulation of the molar ratio between nickel salts and silver seeds. XRD analysis of the final particles showed the crystalline nickel structure and the presence of metallic Ag, which was influenced by the Ni/Ag molar ratio. The effects of reduction temperature on the final particle size were also investigated.

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1. Introduction

During the last two decades, Ni nanoparticles (NPs) have attracted much attention, looking in particular for a high degree of control over size and shape, because of the potential application in magnetic and electrical devices [1,2]. For instance, Ni NPs are now regarded as anode materials for rechargeable batteries, ethanol fuel cells, and a fine substitute for noble metal Pd or Pd/Ag used in the internal electrodes of multilayer ceramic capacitors (MLCCs) [3]. The most successful procedure for the synthesis of monodisperse Ni NPs is that wet chemical reduction of Ni²⁺ ions in aqueous or organic solution usually containing cationic surfactant, such as cetyltrimethylammonium bromide (CTAB) and poly(vinylpyrrolidone) (PVP). In these syntheses, the reaction parameters relevant to the control of particle size include time, temperature, driving force of the hydroxide, the concentration of precursor, and the nature of surfactants serving as the capping agent or steric stabilizer. Each of the parameters has complex effects on final particle properties and is difficult for manipulation in view of desired particle size. Besides, the correlations between the parameters make the reaction rather intractable for control, although various particles with their size tunable to a certain extent can be synthesized. Take the case of MLCCs for example, which continues towards miniaturization with higher capacitance, Ni particles with their size in the order of ~100 nm, or even smaller, would be desired. However a number of

papers have reported the particles synthesized by usual wet chemical process are several hundred nanometers in size [4,5]. Although tiny Ni NPs with very small sizes (<10 nm) have been synthesized via a surfactant-assisted chemical reduction in dilute solution [6–9], the inefficient yield and the difficulty for preparing a thick enough layer retard their application in the internal electrode layer.

Recently, a seed-mediated growth method, with a fine control of the particle size, has been proposed. Various NPs, such as self-seeded iron oxide [10,11], self-seeded gold [12], Ag-seeded gold [13], and Pt-seeded nickel [14], have been successfully synthesized with this approach. Usually, the seeded growth goes through a two-step procedure, in which the seeds should be first synthesized and dispersed subsequently in another solution to catalyze the growth. To the best of our knowledge, there have been few reported on the synthesis of Ni NPs using Ag-seeded wet chemical method. In this work, ultrafine Ni NPs have been synthesized via Ag-seeded, surfactant-free chemical reductions of nickel (II) sulfate with hydrazine. Instead of the inconvenient two-step procedure, a one-pot process has been employed here. The final particle size can be adjusted simply by varying the Ni/Ag molar ratio.

2. Experimental details

All chemicals were of reagent grade and used without further purification. In a typical synthesis, 0.03 mmol of 97% silver acetate (AgAc) was dissolved in 40 ml of 98% ethylene glycol (EG) solution at room temperature, and the obtained solution was moved to an oil bath keeping stirring for 1 h. A given amount of nickel sulfate hexahydrate (NiSO₄·6H₂O) was added into the Ag-contained EG solution; the molar ratio of Ni to Ag was fixed in the range of 5–200.

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Then, 1 ml of 5 M NaOH aqueous solution and 1 ml of 98% hydrazine monohydrate were poured in sequence. After reduction, the resulting products were magnetically collected after washing repeatedly with distilled water and methanol.

The phase structure was identified by X-ray diffraction (XRD, Rigaku Geigerflex) using Cu K α radiation with a graphite monochromator. The particle size and morphology analyses were per-

formed using field emission (FE-) scanning electron microscopy (SEM, Hitachi S-4500, with accelerating voltage of 20 kV).

3. Results and discussion

In the seed-mediated synthesis, it is widely considered that small metallic seeds are formed when the organometallic salts are reduced by the reducing agent, then promoting metal reduction on the in situ seeds, which act as catalysts. And the

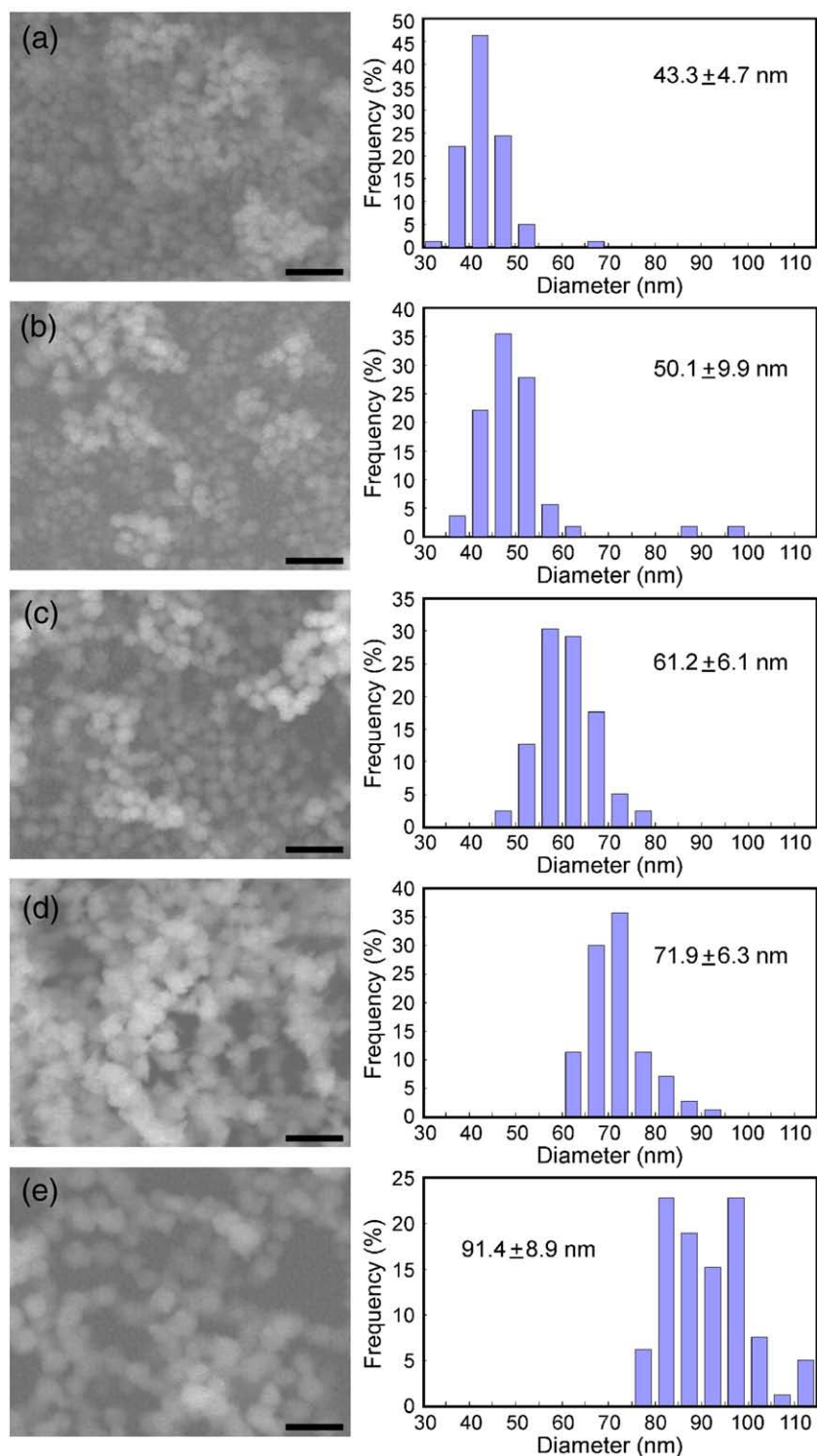


Fig. 1. SEM images and particle size distribution of Ni particles synthesized at 120 °C as a function of Ni/Ag molar ratio: (a) 5, (b) 20, (c) 40, (d) 60, and (e) 200. Scale bar=200 nm.

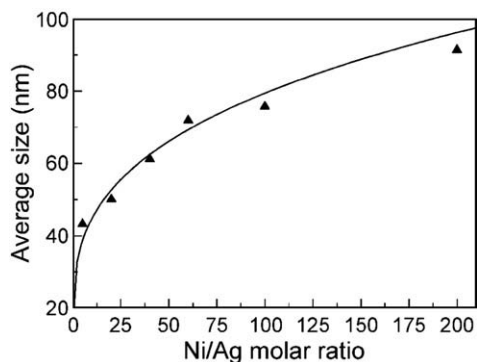


Fig. 2. Dependence of Ni/Ag molar ratio (x) on the average size of particle synthesized at 120 °C. The curve is calculated from Eq. (1) with d_{Ag} at 15 nm.

addition of nucleation agent not only accelerates the nucleation but also leads to the formation of smaller particles with lower polydispersity [14]. Herein, Ag seeds were produced by alcohol [15,16] or hydrazine reduction. At 120 °C, we used identical reaction conditions for the preparation of Ag seeds, while varying the amount of Ni salt. The SEM images in Fig. 1 illustrate the morphology of resultant particles obtained with different molar ratios between nickel and silver, as indicated in the caption. The particle size distributions are also presented correspondingly. Apparently, fine Ni NPs with narrow size distribution were obtained. The particle size increased steadily from 43.3 nm (Ni/Ag=5) to 91.4 nm (Ni/Ag=200). This is attributed to the amount of nickel available for particle growth per Ag seed increases with increasing the Ni/Ag molar ratio, resulting to forming larger sized particles. At the same time, it was found that the size distribution became broader with the increase in Ni content.

Taking the Ag/Ni core/shell structure into consideration, the final particle size (d) can be approximately given with the Ni/Ag molar ratio (x) as follows.

$$d = d_{Ag} \left(1 + \frac{1.62}{1.75} x^{\frac{1}{3}} \right) \quad (x \gg 1) \quad (1)$$

where d_{Ag} is the diameter of Ag seed; the atom radius ratio of Ni to Ag (1.62/1.75) is used as a modifying factor. Fig. 2 presents the dependence of Ni/Ag molar ratio on the average size of particles synthesized at 120 °C. Although the one-pot process did not allow us to obtain reliable information about the diameter of Ag seeds, we assumed diameters around 15 nm in view of those reported for Ag seeds [16], and the calculated results fitted well with observed from SEM images. This analysis suggested that a continue increase of particle diameter could be achieved through gradually increasing the amount of Ni salt, which was previously observed for the seeded-growth of gold NPs [12].

Fig. 3 indicates the XRD patterns of the particles obtained with different Ni/Ag molar ratios. For [Ni]/[Ag]=5 and 20, four main characteristic peaks for the Ag (111), (200), (220) and (311) planes at $2\theta=38.1^\circ$, 44.3° , 64.4° and 77.5° were observed, which matched well with the pattern for face-centered cubic (fcc) Ag. The characteristic peaks for the (111) and (220) planes of fcc Ni at $2\theta=44.8^\circ$ and 76.8° were overlapped with those for (200) and (311) planes of Ag, but the (200) and (311) planes of fcc Ni at $2\theta=52.1^\circ$ and 92.7° could be found. With the increase of Ni amount, the intensities of Ni peaks increased while those of Ag turned weaker, even nearly

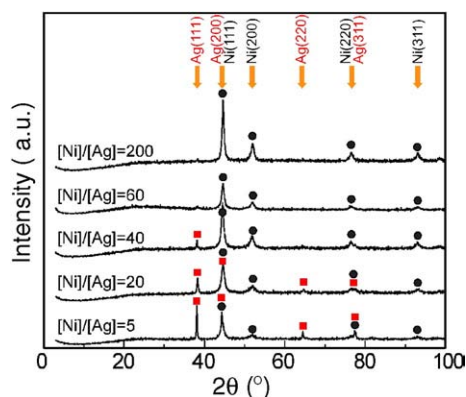


Fig. 3. XRD patterns of the particles synthesized at 120 °C.

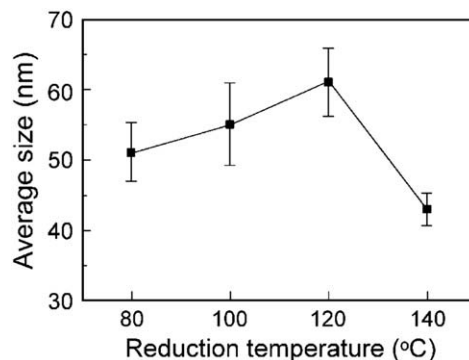


Fig. 4. Dependence of reduction temperature on average particle size with the Ni/Ag molar ratio at 40.

quenched at [Ni/Ag]>60. This revealed that the resultant composite NPs were indeed composed of Ni and Ag. Also, both Ag cores and Ni shells had an fcc structure.

As mentioned above, the size of Ag seeds is determined by multifold parameters in the wet chemical reduction. The effects of reduction temperature were investigated briefly. With a fixed Ni/Ag ratio at 40, the reductions were carried out at different temperature. The average sizes of the particles obtained are shown in Fig. 4. A decrease in final size of Ni NPs at 140 °C means a larger number of, i.e. smaller sized, Ag seeds are formed. The largest Ag seeds were obtained around 120 °C. It should be noted that a majority of Ni NPs synthesized at 80 °C assembled to form large aggregates. At temperature lower than 80 °C, the reduction medium remains light blue in color, implying that the nickel ions do not undergo reduction.

4. Conclusion

In summary, we have demonstrated that the catalytic activity of Ag seeds can be used for the uniform seeded growth, environment-friendly reduction of nickel by hydrazine in EG solution. For the given Ag seeds, the final particle size could be easily controlled in a range between 43.3 and 91.4 nm by variation of Ni/Ag molar ratio. Analyses of XRD indicated the presence of crystalline Ni and Ag, both in fcc phase. The reduction temperature played an important role in determining the Ag seed size.

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