

X-ray synthesis of nickel–gold composite nanoparticles

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Received 9 June 2005; received in revised form 13 December 2005; accepted 5 January 2006

Abstract

We developed a novel approach to prepare Ni–Au composite nanoparticles using synchrotron radiation X-rays. Ni–Au particles dispersed in aqueous solutions were synthesized with two different irradiation strategies. The first is by exposing to X-rays a mixed electroless solution of Ni and Au at two different temperatures, trying to nucleate Ni nanoparticles homogeneously at room temperature and to deposit Au subsequently on them at the high temperature of 70 °C. The second strategy is to change the pH value of the mixed solution, directly leading to the formation of Ni–Au nanoparticles. In both cases, the Ni–Au composite nanoparticles were successfully formed, as confirmed by the observed ferromagnetic behavior and by the evolution of the Au surface plasmon resonance band.

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Keywords: Ni–Au composite nanoparticles; Synchrotron radiation X-rays; X-ray induced nucleation; Synthesis

1. Introduction

X-ray induced nucleation in solution has been used in several cases to obtain dispersed nanoparticles [1–4], but has not been tried yet to produce composite materials. We show that composite nanoparticles can indeed be obtained by synchrotron X-ray irradiation without transporting them from one to another solution. The test was performed on Au–Ni nanoparticles, a potentially important system for biotechnology [5,6], e.g., for targeted drug delivery. Our new fabrication process is fast – a few seconds of X-ray exposure – and is very simple to control the process. Another advantage is that the possible core oxidation, which could occur when the core and the coating are fabricated in two different baths, is greatly reduced by maintaining the particles in the same bath throughout the process.

Au-based nanocomposites have several good properties for applications: biocompatibility [7], excellent drug-delivery capa-

bilities [8] and easy surface deposition of functional bimolecular groups [9]. Furthermore, it is easy to monitor the structural evolution of Au-based composites based on the particle size dependence of the Au surface plasmon resonance [10]. Functionalized magnetic particles such as Ni, Fe or magnetite can be also incorporated in Au-based nanoparticles to enhance the effectiveness and flexibility of the drug treatment with an external magnetic field [11].

Chemical process in solution is a favorite choice to produce nanoparticles and nanocomposites because of its simplicity, good compositional control and excellent homogeneity. The process can be easily stimulated by external assistances such as ultrasound [12], electromagnetic fields [13], laser [14,15] or gamma-ray sources [16,17]. Recently, irradiation by synchrotron X-rays was also employed to synthesize nickel [3] or gold nanoparticles [18]. However, no report has been presented on the use of this approach to fabricate composite nanoparticles.

We show here that Ni–Au nanoparticles can be obtained by synchrotron irradiation on a mixed electroless solution of Ni and Au based on the dependence of the nucleation process on the temperature and on the solution acidity. Since the growth rate

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is higher for Ni than for Au, Ni nanoparticles are first obtained. With the depletion of Ni in the solution, Au is later deposited on Ni nanoparticles by raising the solution temperature or changing its acidity.

2. Experimental

The bath was a mixture of precursor solutions for Au and Ni: $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ and $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ with $\text{NaPH}_2\text{O}_2 \cdot \text{H}_2\text{O}$ (where $\text{NaPH}_2\text{O}_2 \cdot \text{H}_2\text{O}$ was the reducing agent for Ni). In the first strategy, the pH value was set at 8.9 using ammonia solution. The solution was then exposed to an unmonochromatized X-ray beam from the 7B2 bending magnet beamline [19] at the 2.5 GeV storage ring of PLS (Pohang Light Source, Pohang, Korea). The photon energy of the broad band X-rays from the 7B2 beamline was approximately between 5 and 15 keV. The synchrotron X-rays were exposed first at room temperature and then at 70 °C. The exposure times at the high temperature were varied from 2 to 4 min at a storage ring current of ~ 100 mA. Additional tests were also performed at the B1A bending magnet line of the 1.5 GeV storage ring of National Synchrotron Radiation Research Center (NSRRC, Hsinchu, Taiwan). And the results were the same regardless of the storage rings within our detection limits as long as the total power of synchrotron radiation to the samples is adjusted to the same level by the exposure time. In addition to monitoring the color changes of the solution by a CCD camera, we also monitored the formation of the particles in real time in the solution using synchrotron X-ray microscopy [20,21].

In the second strategy, Ni nanoparticles were first formed by X-ray irradiation of the mixture of the precursor solutions at room temperature. Then, more $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ was added together with NaOH to change the pH value, followed by 5 min of X-ray exposure at room temperature, trying to produce Au coating on the Ni nanoparticles.

The pH of the solution was measured with an Orion 720A pH-meter. The morphology of the composite particles was observed with a field-emission scanning electron microscope (FESEM, JEOL JSM-6330F). Elemental analysis was performed with an energy dispersive X-ray spectrometer (EDX) in the FESEM. The average particle size was derived from micrographs obtained with a transmission electron microscope (TEM, JEOL JEM2010F FEEM).

The room-temperature magnetic nanoparticle properties were investigated with an alternating gradient magnetometer (AGM, Princeton Measurements). The magnetization of the composite particles was measured by cycling the susceptometer between +4000 and -4000 Oe. The optical absorption spectra in the ultraviolet and visible ranges were measured with a GBC170C spectrometer.

3. Results and discussions

3.1. Temperature-based strategy

A 30-s X-ray exposure on the mixed Ni–Au solution at room temperature produced a large amount of Ni particles, darkening the bath, while the production of Au particles was quite limited.

The reduction of Au in the same mixed solution was enhanced by raising the temperature to 70 °C as a second step. By the Au reduction the bath color was changed from dark to reddish.

FESEM micrographs of the resulting nanoparticles as a function of the second-step exposure time are shown in Fig. 1. The size of the composite particles increased from 30 to 50 nm as the exposure time increased from 2 to 4 min, suggesting that the Ni particles might be progressively coated with Au.

The Ni and Au atomic concentrations of the composite particles were measured using EDX as a function of the solution temperature for the second-step irradiation of 2 min, as shown in Fig. 2. The fraction of Ni was significantly reduced as 3% after

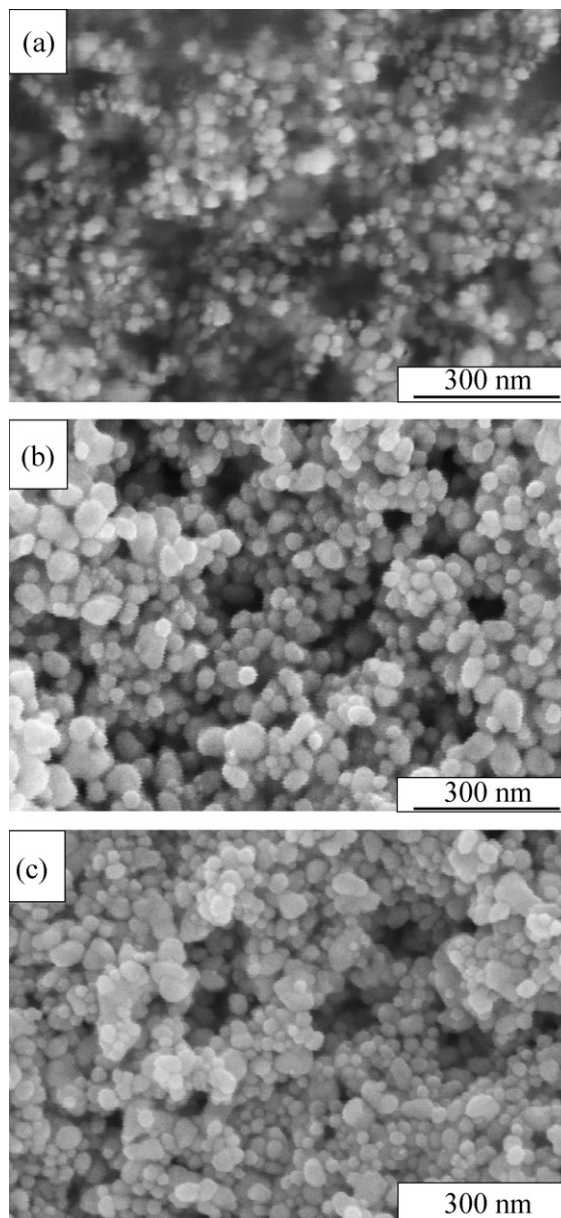


Fig. 1. FESEM micrographs of Ni–Au nanoparticles produced with the temperature-based strategy for three different second-step exposure times: (a) 2 min; (b) 3 min; (c) 4 min.

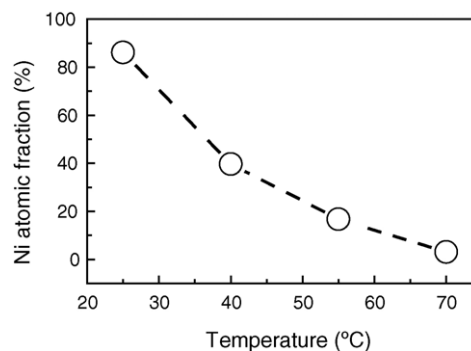


Fig. 2. Ni atomic fraction of Ni–Au composite nanoparticles produced with the temperature-based strategy as a function of the electroless solution temperature in the second step. The second-step exposure time was 2 min.

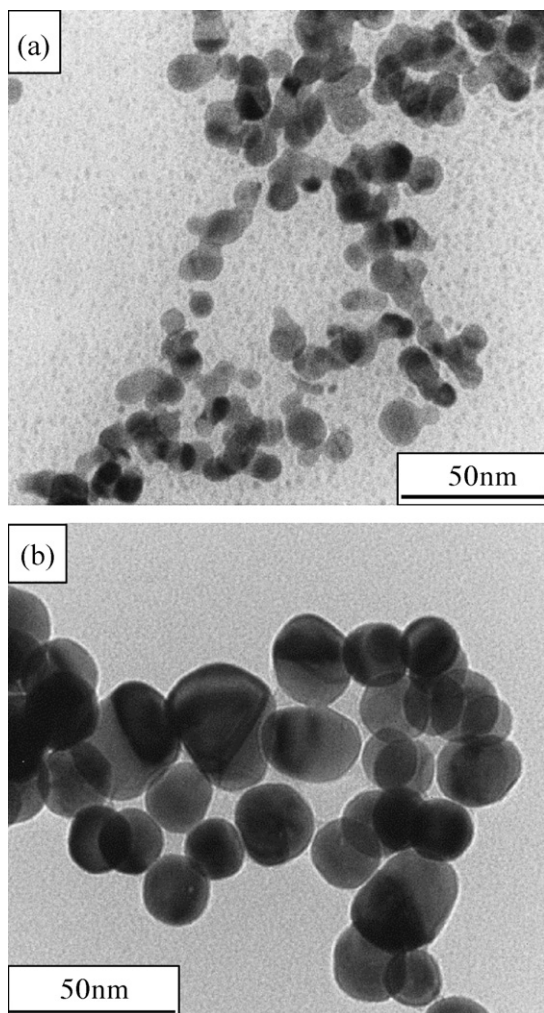


Fig. 3. TEM micrographs of Ni–Au composite particles produced at room temperature (a) and particles produced with the temperature-based strategy (b). The second-step exposure time was 2 min.

the irradiation at 70 °C, while it was 86% before raising the temperature. Since EDX is a somewhat surface-sensitive tool, we concluded that Ni might exist mostly inside the composite nanoparticles formed, as a core with Au shell outside.

TEM micrographs of the composite particles are shown in Fig. 3. The figure shows particles before (a) and after (b) the second step at the temperature of 70 °C. The particle sizes in the (a) case were about 15 nm but they increased to 30 nm in the (b) case. The TEM results are thus consistent with the trend of Fig. 1. The difference in the sizes observed in TEM and FESEM data is due to the agglomeration of composite particles in FESEM data.

To further corroborate the existence of a Ni core in the composite particles, magnetic measurements were performed after drying them. The data shown in Fig. 4 reveal ferromagnetic characteristics, as indicated by the coercivity (126 Oe) and the remanence (0.07 emu g^{-1}). This magnetic property confirms the existence of the ferromagnetic Ni phase in the core since Au would not contribute to the magnetization and Au mostly exists on the particle surface according to the EDX results.

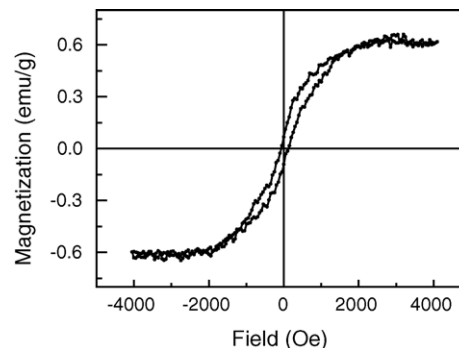


Fig. 4. Room-temperature magnetization vs. magnetic field for Ni–Au nanoparticles obtained with the temperature-based strategy.

3.2. pH-based strategy

Temperature increase may be undesirable in some applications. We thus tested a second strategy. The Ni core particles were first formed by the irradiation at room temperature using a solution with an acidity favorable to Ni nucleation [4]. Then, the acidity was changed so as to produce Ni–Au composite particles under further exposure to synchrotron X-rays.

The relevant parameters in this second strategy are the molar ratio of Ni/Au, the pH of the mixed solution, the Au/NaOH ratio and the exposure time. We tested indeed different Ni/Au ratios (1:1, 5:1, 1:5), pH values (4, 7, and 10), Au/NaOH ratios (1:1, 1:2, 1:5) and exposure times (1 min for the first step and 1, 2, 5, 10 min for the second step).

We empirically found an optimal set of parameters as Ni/Au = 1:5; pH 4; Au/NaOH = 1:5 and a second-step exposure time ≥ 5 min. In the first step, after 1 min of irradiation, Ni nanoparticles formed and the initially transparent solution changed to slightly gray color. In the second step the HAuCl₄ + NaOH solutions were added in the solution. After several minutes of irradiation, the color of the solution became reddish. This again suggested the formation of composite nanoparticles of Ni core with gold shell coating, as confirmed by the following tests.

UV and visible absorption spectra of the aqueous solution with the Ni–Au nanoparticles is shown in Fig. 5. After 1 min of the second-step exposure, only a sharp absorption peak was

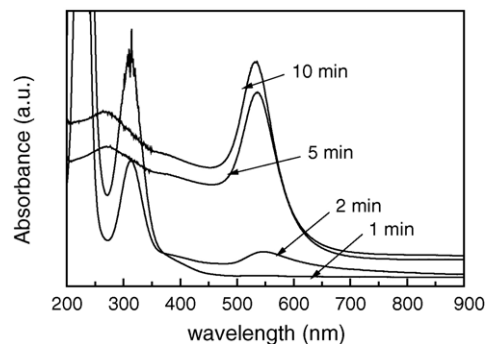


Fig. 5. UV and visible absorption spectra of the Ni–Au nanoparticles obtained with the pH-based strategy as a function of second-step exposure time (1–10 min).

observed at 320 nm. This is attributed to AuCl_4^- ions in the solution. For 2 min of exposure, an additional peak appeared at ~ 545 nm. This is due to the characteristic surface plasmon resonance of Au nanoparticles [22]. Conversely, the intensity of the AuCl_4^- peak rather decreased, indicating that Au ions were reduced to Au atoms. After increasing the exposure time to 5 min, the AuCl_4^- features further weakened whereas the plasmon feature strength increased. Additional exposure did not make any substantial change in the spectra.

4. Conclusions

We developed and successfully tested two methods to synthesize Ni–Au composite nanoparticles using synchrotron radiation X-rays. In the first strategy, Ni–Au particles dispersed in aqueous solutions were prepared by directly irradiating a mixed Ni–Au electroless solution first at room temperature and then at a higher temperature of 70°C . Ni nanoparticles homogeneously nucleated in the first step and played as a precursor for the Au deposition in the second step. In the second strategy, the crossover from the Ni growth to the Au coating was achieved by changing the pH of the solution at room temperature. The formation of Ni–Au nanocomposite was optimized by adjusting the parameters such as the molar ratio and the pH values. The production of Au–Ni nanoparticles was confirmed by detecting the ferromagnetic behavior and the evolution of the Au surface plasmon resonance band. From a practical point of view, the resulting nanocomposites were well dispersed and free from air oxidation. Such characteristics are important in view of possible applications.

Acknowledgements

We wish to thank G.M. Chow for the stimulating discussion in characterizing the samples. This work was supported by MOST(KOSEF) through the National Core Research Center (Systems Bio-Dynamics) and SKORE-A projects, by the Strategic National R&D Program of Ministry of commerce, industry and energy (MOCIE), by the BK21 Project, by the National Sci-

ence Council (Taiwan), by the Academia Sinica (Taiwan), by the Swiss Fonds National de la Recherche Scientifique and by the EPFL.

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