

Formation of magnetic Ni nanoparticles in x-ray irradiated electroless solution

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Abstract

Magnetic nanostructures are attracting tremendous interest as regards application in high-density data storage devices and magnetic fluids. We have prepared magnetic nanoparticles (~ 7.5 nm) by x-ray irradiation of electroless solutions and furthermore have investigated their structural and magnetic properties. Interestingly, we find that the formation of these Ni nanoparticles occurs spontaneously, during the room temperature process, dominantly at electrolyte pH of 8.2. The hydrated electrons produced during the irradiation of electroless solution seem to play a decisive role in the spontaneous formation and growth of nanoparticles. The possible surface alloying and/or coating over these pure Ni cores occurs only upon longer irradiation of high-P-content solutions. This suggests a possible catalytic behaviour of these nano-Ni surfaces in relation to P counter-ions in the irradiated solutions. The magnetic properties of these 'as-received' particles have been studied using a vibrating sample magnetometer. The saturation magnetic moment per gram for the Ni particles is 9.38 emu g^{-1} , which is 17% of the saturation moment of bulk ferromagnetic Ni at room temperature; this can be attributed due to the size effect of these magnetic domains. The symmetric hysteresis loop about the zero-field axis showing negligible loop shift ($\Delta H_c \sim 3\text{--}10 \text{ Oe}$) suggests that Ni particles are free from oxide layers.

1. Introduction

Magnetic metal nanofabrication is attracting tremendous interest due to the potential future prospects of magnetic nanostructures in high-density data storage devices, magnetic fluids and magnetic refrigeration [1]. The size and surface controlled properties of these nanoscale materials can be easily tuned to meet requirements by the proper control of different synthesis parameters. In particular, in photochemical methods,

metal nanoparticles as well as nanostructured films can be fabricated by photo-irradiation of metal precursor solutions. The nanostructure size tuning can be easily achieved by selecting the photon energy, photon flux, irradiation time and irradiation area. These parameters give direct control over the photo-dynamics in the irradiated solution [2]. Recently our laboratory has successfully fabricated Ni composite nanoparticles by synchrotron x-ray irradiation of electroless Ni solutions [3]. There has been no previous report on preparing magnetic Ni nanoparticles by this method. This method has been used earlier [4] for the preparation of non-magnetic metal

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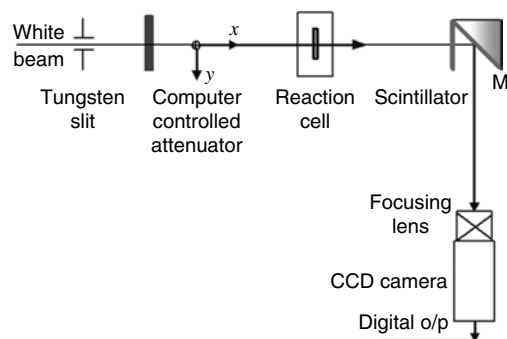


Figure 1. A schematic diagram of the experimental set-up, which is a modified synchrotron x-ray microscope, used to carry out the synchrotron x-ray induced reaction. Automated x - y - z motion is possible for the reaction cell. M is an Au coated mirror on one face of the prism.

(Au, Ag) nanoparticles. We report here an extension of this method for generating magnetic Ni nanoparticles at room temperature.

Magnetic metal nanoparticles are severely affected by the issues of chemical stability, dispersion and surface functionalization. Due to the large surface to volume ratio, these particles are prone to attack by oxidative or corrosive environments which leads to surface disorder and is thereby responsible for the degradation of the physico-chemical properties. This obstacle can be tackled in general by forming a protective coating around the particles or growing the particles in some host matrix (silica). Among the coating materials, graphitic carbon and purposely oxide-passivated coating [5, 6] have been reported on, showing their effects on (i) unidirectional anisotropy induced by exchange coupling and (ii) other magnetic properties such as the magnetic moment and coercivity. There are also reports of intentional coatings with other non-oxide layers of Pd and N [7, 8], which increase the coercivity (H_c) of core particles. However, there have been no reports on the use of P to coat the metal nanoparticles to the best of our knowledge.

In this paper, we report an extension of the x-ray method for generating magnetic Ni nanoparticles at room temperature. The salient feature of the work is the effort to use P as a coating or host material for the thus produced magnetic Ni nanoparticles.

2. Experimental details

The magnetic Ni nanoparticles were synthesized by x-ray irradiation of the Ni and P precursor containing electroless solution. The aqueous electroless solutions were prepared in Nanopure *deionized* water by mixing powders of nickel sulfate hexahydrate and sodium hypophosphate monohydrate yielding specific P:Ni molar ratios of solutions. We describe here the work on samples A and B. For samples A and B, respectively, 0.1 and 1.0 M P precursor solution were dissolved in the 0.1 M Ni precursor solution. Upon mixing the two salts, the pH of the electroless solution obtained was raised to ~ 8.2 by using NaOH. The finally obtained mixture was exposed to x-ray irradiation using an unmonochromatized beam [9] from the 5C1 and 7B2 beamlines at PLS (Pohang Light Source, Pohang, Korea) operating at 2.5 GeV. The x-ray irradiation time in the

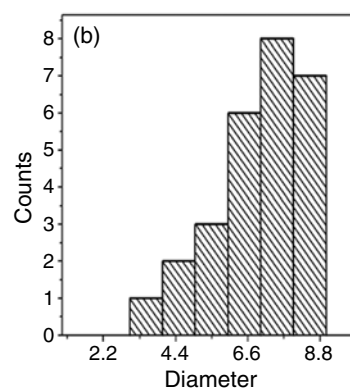
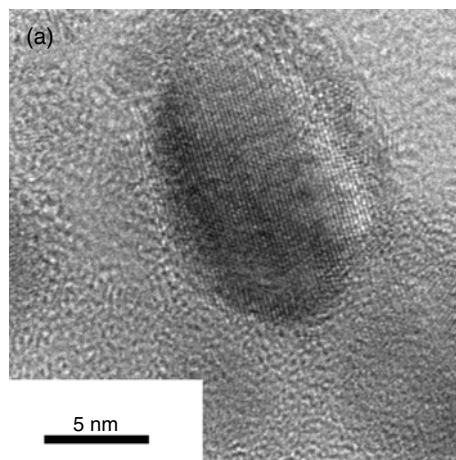


Figure 2. (a) The HREM image of sample A showing Ni nanoparticles with amorphous coating. (b) The size distribution histogram for the Ni nanoparticles.

room temperature ($\sim 25^\circ\text{C}$) reaction was 2 and 20 min for samples A and B respectively. The reaction was carried out using the specially designed set-up shown in figure 1. The precipitate obtained after the irradiation was extracted and washed with ammonia, deionized water and ethyl alcohol to remove the unreacted species and later air dried to obtain the free-standing nanoparticles. The free-standing nanoparticles were used for further structural and magnetic studies. The pH of the solution was measured by an electronic pH-meter, Orion model 720A. The structural investigations were carried out by means of x-ray diffraction (XRD) and a transmission electron microscope (TEM), while for elemental analysis an in-built energy dispersive x-ray spectrometer (EDX) in the TEM was utilized. The diffractometer, MP18, XG M18 XCE MAC SCIENCE Co. Ltd, with $\text{Cu K}\alpha$ (1.542 \AA) radiation, was used for the XRD study. Model JEOL JEM 2010 F FEEM (200 kV) was used for the TEM study of free-standing particles. The magnetic properties of the nanoparticles were investigated at room temperature by using a vibrating sample magnetometer (Toei's VSM-5) in a magnetic field of 16 kOe.

3. Results and discussion

The high-resolution electron micrograph (HREM) of typical particles of sample A, obtained from the respective solution after 2 min of irradiation, is shown in figure 2(a). Nanoparticles of mean diameter of 7.5 nm are formed, as seen in the particle

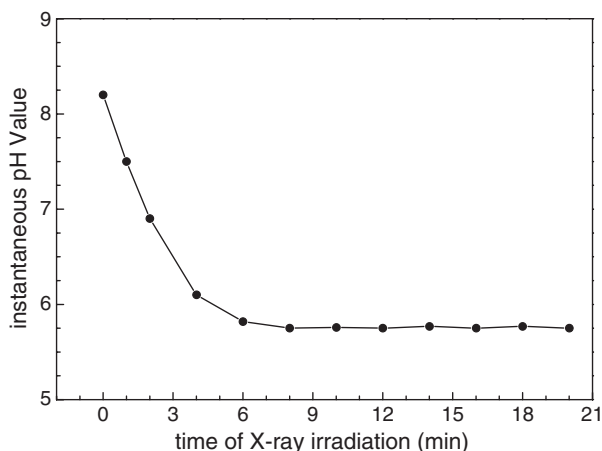


Figure 3. The instantaneous pH variation in the electroless solution with x-ray irradiation time observed during preparation of sample A. The drastic pH decrement suggests a high rate of reduction of Ni ion during the first few minutes of irradiation.

Table 1. The incorporated phosphorus concentration in the particles and corresponding ΔH_c values estimated from the hysteresis loops.

Sample name	P:Ni in solution (molar ratio)	Incorporated P (wt%)	H_c (Oe)	ΔH_c (Oe)
A	1.0	2	55.6	3.1
B	10.0	10 ± 2	56.5	10.0

size distribution curve of figure 2(b). The crystalline phase of the resultant particles is clearly visible (figure 2(a)); it shows planes corresponding to Ni(111) in the cubic unit cell. A simultaneous EDX measurement of the lattice shows the existence of Ni in the particles. This reveals the spontaneous formation of Ni nanoparticles in the irradiated solution. Further, figure 2(a) also shows an amorphous shell over the cubic Ni core surface, suggesting possible surface alloying due to the P, which is observed during the EDX study at the particle surfaces. We correlate the spontaneous particle formation with the higher Ni reduction rates attained due to radiolytic generation of hydrated electrons. Like in our earlier report [11], we observed a drastic decrease in the instantaneous pH with irradiation time, as shown in figure 3. This is attributed to the spontaneous formation of Ni nanoparticles, as observed in the HREM (in figure 2). The radiolytically generated species, namely e_{aq}^- , H^+ , H , OH and OH^- [2], facilitate the Ni^{2+} reduction leading to Ni particle formation. Though the HREM image of the nanoparticles clearly shows the existence of a cubic Ni lattice, we further utilized XRD to statistically investigate the structure of these nanoparticles. Figure 4 shows a typical XRD spectrum for sample A. The spectrum shows the existence of cubic Ni phase matching with the standard JCPDS data (JCPDS file 4-850). The diffraction peaks show a trend of broadening, which is a consequence of the reduced size of the particles, and is in accordance with the Debye–Scherrer relation. This proves that pure Ni nanoparticles are formed. Sample A does not show the existence of crystalline NiO and NiP phases. The EDX measurement also reveals the existence of Ni cores. We used sample B prepared in a high-concentration P solution to check the effect of phosphorus on the structure and composition of

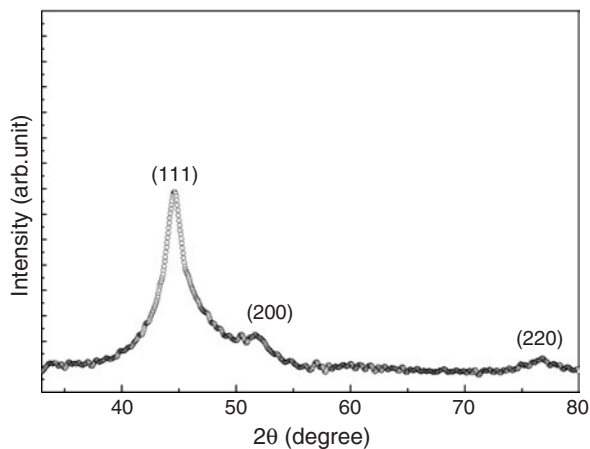


Figure 4. The x-ray diffraction spectrum of sample A showing reflection from the cubic Ni phase.

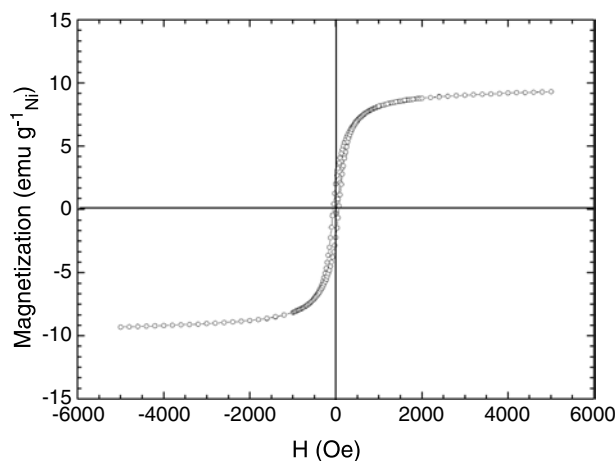


Figure 5. The magnetization curve as a function of the applied field for sample A, recorded at room temperature.

particles and their surfaces. In both Ni samples A and B, NiO and NiP phases are not detected by means of XRD; however, the EDX measurement performed during the TEM study, at the surface of the nanoparticles, reflects sample B containing more phosphorus, 10 ± 2 P wt% (see table 1), than sample A. This suggests that the photochemical reaction performed in high-P-content solutions (as in the case of sample B) yields an amorphous P coating/host around the particles, protecting the nanosized magnetic domains.

The observation of high P concentration in the EDX of sample B (table 1) also suggests that the longer irradiation time (~ 20 min) favours the catalytic nature of Ni nano-core surfaces in relation to P. It is known that an autocatalytic reaction is responsible for the nickel deposition in the conventional electroless process [12]. However, the reaction occurs only after a period of incubation (20–40 min). This is true in the case of sample B. Thus all the above discussion proves that longer irradiation of a high-P-content solution yields an amorphous coating over Ni cores.

The magnetic measurements on samples A and B revealed further the effect of phosphorus at the surface of the magnetic domains. Figure 5 shows the $M-H$ curve for sample A at room temperature, showing the ferromagnetic

characteristic of Ni single domains with the magnetization (M_s) value of $9.38 \text{ emu g}_{\text{Ni}}^{-1}$, far from saturation for bulk Ni ($55 \text{ emu g}_{\text{Ni}}^{-1}$) [13]. This decrease in M_s can be attributed to the size and surface effects of nanosized magnetic domains [10, 13]. However, exploring the finer details of the issue needs further detailed temperature and field dependent magnetic studies. We also observe that the M_s and H_c values remain unchanged for samples A and B, indicating that the low P concentrations do not affect their magnetic properties. The amorphous P coatings, which act as magnetically dead layers, seem to play a vital role in surface protection. The following discussion proves the validity of this statement. The metal nanoparticle surfaces are easily oxidized in air, thus leading to the formation of an oxide layer on the particle surface. The thus formed metal/metal oxide interface exhibits an exchange bias due to the presence of exchange interactions at the interface. The magnitude of the exchange bias can be estimated from the shift in the hysteresis loop with respect to the zero-field axis, in the following way [14]:

$$\Delta H_c = (H_c^+ + H_c^-)/2,$$

where H_c^+ and H_c^- are the coercive fields with increasing and decreasing fields respectively. The shift in the hysteresis loops, i.e. the ΔH_c values for samples A and B (table 1), are very small: 3–10 Oe, compared with 80–700 Oe for the NiO–Ni nanowire system [15]. Thus the symmetry in the exchange bias about the zero-field axis indicates the absence of particles with NiO–Ni morphology. This is consistent with the data from HREM and XRD characterization. The ΔH_c value for sample B being a little higher than that for sample A can be attributed to the surface disorder occurring due to the large P concentration. The magnetic study strongly suggests that the present photo-induced irradiation method results in significantly less oxidized Ni nanoparticles being produced in a very short time of irradiation.

In conclusion, we have demonstrated the room temperature formation of magnetic Ni nanoparticles by x-ray irradiation of alkaline electroless solution. The hydrated electrons produced during the x-ray irradiation of the solution seem to play a decisive role in the spontaneous formation and growth of nanoparticles. The possible surface alloying and/or coating over these pure Ni cores occurs only upon longer irradiation of high-P-content solutions. This suggests possible catalytic behaviour of these nano-Ni surfaces in relation to P counter-ions in the irradiated solutions. The magnetic

properties of these ‘as-received’ particles are studied using a vibrating sample magnetometer. The saturation magnetic moment per gram for the Ni particles is 9.38 emu g^{-1} , which is 17% of the saturation moment of bulk ferromagnetic Ni at room temperature; this can be attributed to the size effect of these magnetic domains. The symmetric hysteresis loop ($\Delta H_c \sim 3\text{--}10 \text{ Oe}$) about the zero-field axis suggests that Ni particles are free from oxide layers. This approach is expected to open the way to easy and faster nanofabrication of transition metals.

Acknowledgments

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