Complexant-assisted Fabrication of Football-like Nickel Architectures Covered by Hexagonal Nanoplatelets

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Novel football-like nanostructures of metallic nickel with surfaces covered by hexagonal nanoplatelets were fabricated through a simple chemical reduction route with 2-hydroxy-4-(1-methylheptyloxy)benzophenone oxime in anti form (N530) as complexing agent. Formation of the unique nanostructures was reasonably ascribed to the special complex precursor and variation of the reaction rate at different stages. Magnetic properties of the nickel nanostructures were compared with other shaped counterparts.

Magnetic metal nanoparticles with various shapes and organizations are desired for their attractive applications in the fields of catalysis, electronics, magnetism, etc.[1–3] In particular, metallic nickel, as one of the most used elements, shows applications spanning over almost all sizes and fields. Its uses today and in the future would benefit from materials designed with nanosize and novel morphologies. To date, many efforts have been paid to the preparation of nickel nanostructures with various shapes. Among them, solution chemical synthesis presents the advantages of simplicity and low cost compared with physical approaches. However, the fabrication of nickel nanoparticles with anisotropic shapes by liquid process is an interesting challenge because in most cases the isotropic shapes minimize their surface energy in solution.[4] In order to control the shape of the nickel nanoparticles grown from solution, structure-directing agents are always introduced, such as complexing agents, surfactants, and polymers.[5–7] In particular, the complexing agent, which can coordinate with Ni^{2+} ions and form relatively stable complex precursors, decreases the free Ni^{2+} concentration in solution, resulting in a relatively slow rate of generation of nickel atoms, and facilitates the production of anisotropic nanocrystals.[5] Meanwhile, the complexant may selectively absorb on a crystal surface during the crystal growth and finally leads to special shaped product, for example, nickel nanobelts fabricated with sodium tartrate, prickly nickel nanowires prepared with the assistance of triethanolamine, tartrate, or citrate.[5,8] Previously, we prepared nickel hexagonal nanoflakes using dimethylglyoxime as complexant, which showed a unique role for the formation of nickel nanoplatelets.[9] In this manuscript, we report the shape-controlled preparation of metallic nickel with another oxime ligand of 2-hydroxy-4-(1-methylheptyloxy)benzophenone oxime in anti form (donated as N530), which also leads to the production of hexagonal platelets. The morphological details, possible formation mechanism and magnetic properties of thus-prepared football-like nickel nanostructures, were studied.

A typical experiment was as follows: 10 mL of ethanol solution containing 0.72 g of N530 was added dropwise into 25 mL of aqueous solution containing 1 mmol $NiCl_2$. Then 1 mL of $N_2H_4 \cdot H_2O$ and a certain amount of aqueous solution of NaOH were added. The mixture was sealed into a 40-mL Teflon-lined autoclave and maintained at 120 °C for 10 h. The resulting precipitate was collected, rinsed with distilled water and ethanol, and finally vacuum dried at 50 °C for 4 h.

An X-ray diffraction (XRD) pattern was recorded on a Philips X'pert diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å). Fourier transform infrared (FTIR) spectra were recorded using a Bruker EQUINOX55 Fourier transform spectrometer. Morphology of the samples was studied with field emission scanning electron microscopy (FE-SEM, JEOL JSM-6300F) and transmission electron microscopy (TEM, Hitachi H-800). The *M–H* hysteresis loops were recorded with a model BHV-55 vibrating sample magnetometer.

Figure 1 shows the XRD pattern of a sample, which could be indexed as face-centered cubic (fcc) Ni. No peaks of nickel oxide and hydroxides were observed, indicating that pure fcc nickel was obtained under such experimental conditions. The inset in Figure 1 is the corresponding FTIR spectra of the sample, in which neither N or C signals were detected, indicating that no N530 ligand residue was absorbed on the nickel product.

Morphology of the nickel sample was studied by SEM and TEM. Figure 2a showed that the sample consisted of microspheres with a diameter of about 1 µm. The magnified images of Figures 2b and 2c showed that the surface of the sphere was covered with hexagonal platelets, which looked like footballs. However, the surface covering hindered further observation of inner structures of the spheres. Therefore, TEM study of sample was adopted. From Figures 2d and 2e, we can see that the spheres are polypod with each rod headed with a bigger hexagonal platelet. Figure 2f gives the TEM image of an isolated platelet and the corresponding SAED pattern with the electron beam perpendicular to the platelet surface, which could be proved single crystalline with the top–bottom surface of (111) planes of fcc nickel.[10,11]

To investigate the possible formation process of the special nickel nanostructures, SEM images of the product obtained at different stages were compared (Figure 3). It was found that the initial products were spherical particles assembled by nano-

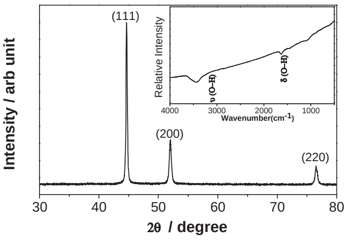

Figure 1. XRD pattern of a nickel sample, inset is the corresponding FTIR spectrum.

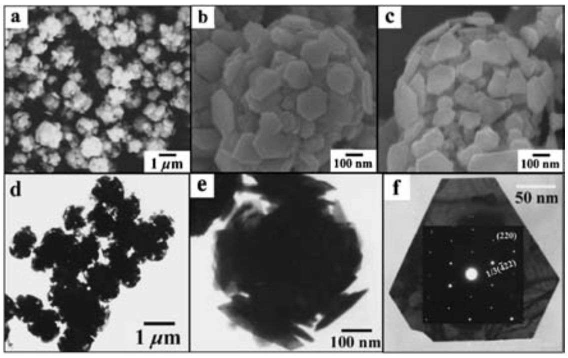

Figure 2. (a) Panoramic SEM image of as-prepared nickel sample, (b) and (c) were magnified SEM images of two typical spheres, (d) TEM image of the spheres, (e) magnified TEM image of a sphere. (f) TEM image and the corresponding SAED (inset) of a hexagonal platelet.

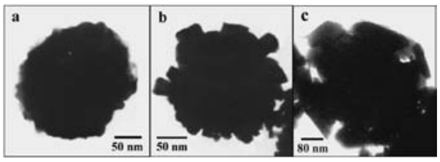

Figure 3. SEM images of the product obtained at different reaction stages. (a) 4, (b) 6, and (c) 10 h.

particles. With time, nanorods began to grow out from the particle surface, as shown in Figure 3b. Finally, hexagonal platelets formed at the head of each rod.

It was found that N530 and the alkali concentration played important roles in determining the morphology of the final structures. In the absence of N530 or replacing N530 with another complexant of pyridine or quinoline, no such nickel nanostructures could be obtained. N530 as oxime ligand can coordinate with Ni^{2+} in a square mode, provided spacial limitation for the growth of nickel particles, and resulted in the anisotropic growth of fcc nickel into platelets.[12,13] Nevertheless, the presence of oxime ligand is not sufficient, and a proper concentration of sodium hydroxide was also necessary. Contrast experiments showed that the football-shaped nickel architectures could only be prepared in a narrow range of alkali concentration of 0.1 to 0.15 M under the present conditions. Higher alkali concentration resulted in irregular particles, while at lower alkali concentration the reduction could not proceed completely. Based on the above results, formation of the special football-like structure could be explained by the influence of the growth rate on product shape. It is known that the reducing power of hydrazine varied with the concentration of hydroxide ions in solution. In the initial reaction stage with higher concentration, a relatively fast reaction rate resulted in spherical particles assembled by nanoparticles to minimize the surface energy (Figure 3a). Then with OH^- consuming, the reaction rate decreased correspondingly, and nanorods emerged from the initially formed spheres.[14] At the end of the reaction stage, hexagonal nanoplatelets were formed owing to the further reduced reaction rate in the presence of N530.[2] But the real mechanism is not clear and a relative study is underway.

Magnetic properties of the nickel nanostructures were studied at room temperature, as seen in Figure 4. For comparison, two other samples were also studied (products obtained at 4 and 6 h with shapes shown in Figures 3a and 3b, denoted as sample a and b). It was found that the football-like spheres (denoted as sample c) displayed the highest coercivity of 224 Oe, much higher than that of the other samples of 168, 196, and 198 Oe of discrete hexagonal nanoplates, which could be ascribed to smaller size and special hierarchical configuration.[9,15] Howerver, this value was still less than that of the one-dimensional nanobelts, possibly for its low shape anisotropy.[5]

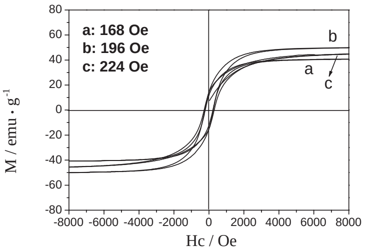

Figure 4. Magnetization-hysteresis loops of the three samples. (a) particles, (b) flowers, and (c) thus-prepared spheres.

In summary, we reported a simple complexant-assisted method for the fabrication of football-like nickel architectures with the surface covered by single crystalline hexagonal nanoplatelets. The complexant of 2-hydroxy-4-(1-methylheptyloxy)-benzophenone oxime in anti form (N530) and alkali concentration played important roles for the formation of the unique nanostructures. Thus-prepared nickel spheres exhibited ferromagnetic characteristics with a coercivity of 224 Oe. The work presented a simple route to the shape-controlled fabrication of nickel nanostructures by complexant directing and kinetic control, which may be extended for preparation of other nanomaterials.

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