Synthesis of Nickel Nanocrystallites with Hexagonal Flake-like Morphology from Nickel Dimethylglyoximate

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Nickel nanocrystallites with hexagonal flake-like morphology with a side length of 200–400 nm and a thickness of 20–30 nm were prepared by reduction of nickel dimethylglyoximate with hydrazine hydrate in a solution. Selected area electron diffraction (SAED) pattern revealed that the flakes were single crystals. It was found that the precursor, nickel dimethylglyoximate, played an important role for the formation of these flakes. Magnetic properties of the product were measured by a vibration sample magnetometer (VSM).

Considerable attention has been drawn to the morphology control of nanocrystals because of the intimate relationship between the property and morphology of nanomaterials.[1] A lot of methods have been exploited to fabricate nanoparticles with various morphologies, such as anode aluminium oxide (AAO), mesoporous silica, carbon nanotubes, microemulsion, surfactants, and polymers.[2–7] In addition to these techniques, recently coordination chemistry method, avoiding complicated process and special instruments, has been widely used to control the morphology of nanomaterials.[8] For example, Xiong and coworkers succeeded in preparing Cu_2O nanowires employing the linear complex of $[Cu_3(dmg)_2Cl_2]_n{}^{2n+}$; Stibnite boundle rods were synthesized by thermal decomposition of $Sb(DDTC)_3$; Hollow spheres of ZnO and nanotubes of Sb were both created using organic metal complexes as reactants.[9–12] In this synthetic route, morphology of the desired materials showed close association with the structure and shape of the complex precursors.

Nanosized nickel crystals show wide applications in the fields of magnetic recording, medical diagnosis, catalysis, electronics, and conduction.[13–15] Because of its highly symmetric cubic lattices, the anisotropic growth of nickel has been a challenging issue. Although several morphologies of nickel nanoparticles have been achieved by template-based methods, such as nanowires templated by AAO, hollow spheres resulted from microemulsion and nanorods assisted by mixed surfactants.[16–18] However, there have been seldom reported on the synthesis of hexagonal nickel nanoflakes to the best of our knowledge.

Here, we put forward a facile method to prepare single crystalline nickel nanoflakes by reduction of nickel dimethylglyoximate. The role of the precursor for the formation of nanoflakes was investigated. Compared with other template methods, this synthetic route proved to more simple and convenient.

All reagents were analytical grade. A typical experimental process could be described as following. First, 8 mmol of diacetyldioxime was dissolved into 13-mL of ethanol to give a homogenous solution. Then this solution was added dropwise into 25-mL of aqueous solution containing 4 mmol of $NiCl_2$. Red flocculates emerged in the system, indicating the formation of nickel dimethylglyoximate. Subsequently, 2-mL of $N_2H_4 \cdot H_2O$ (80%) was added under continuous stirring and pH of the system was adjusted above 12 using the solution of sodium hydroxide. Then the red mixture was transformed into a 50-mL Teflon-lined autoclave. The clave was sealed, maintained at 110 °C for 10 h and then allowed to cool to room temperature. The resulting black powders were collected and washed, and finally dried in a vacuum at 50 °C for 4 h.

The X-ray diffraction (XRD) patterns were collected on a Japan Rigaku Damax γA diffractometer with graphite monochromized Cu Kα radiation ($\lambda = 0.15418$ nm). Transmission electron microscope (TEM) was performed by a Hitachi model H-800 transmission electron microscope with an accelerating voltage of 200 kV. The M–H hysteresis loop was recorded by a model BHV-55 vibrating sample magnetometer.

X-ray diffraction (XRD) was used to examine the phase composition of the product. Figure 1 was a typical XRD pattern of the sample. Three peaks at $2\theta = 44.6°$, $51.8°$, $76.2°$ could be indexed to the face-centered cubic nickel and the corresponding Miller indices were marked for each diffraction peak. No peaks of metal hydroxides or other impurities were detected, suggesting the complete reduction of nickel dimethylglyoximate. The strong and sharp peaks revealed that nickel particles were well crystalline.

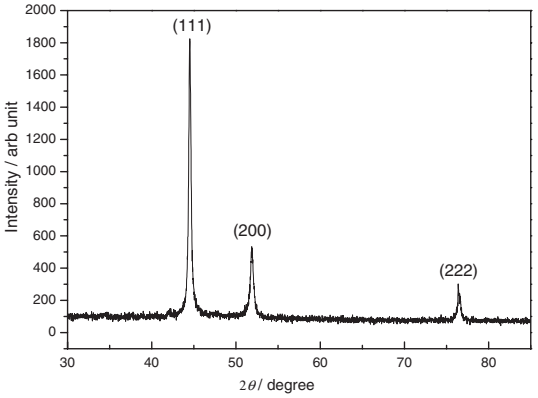

Figure 1. XRD pattern of the sample.

Morphology and size of the product were studied by TEM. Figure 2a showed that as-prepared sample mainly consisted of hexagonal flakes with the side length of 200–400 nm. From some standing nanoflakes shown on the TEM image, the thickness of the flakes was estimated to be 20–30 nm. Figure 2b gave a typical hexagonal nanoflake and the corresponding SAED pattern (inset in Figure 2b). The diffraction spots suggested that the flake was single crystalline. ED patterns recorded on each individual nanoflake were essentially the same, implying the single crystalline nature of these flakes.

It was known that Ni^{2+} could be coordinated by dimethylglyoxime and formed nickel dimethylglyoximate, which had a

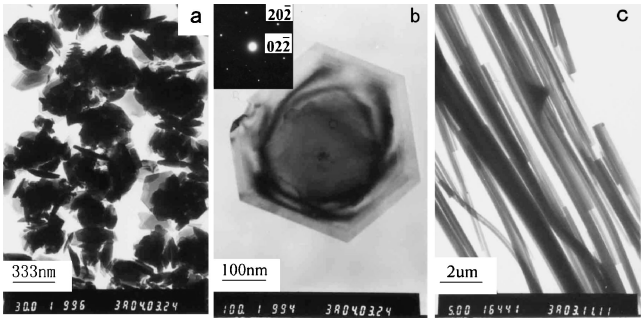

Figure 2. a) TEM images of the sample. b) A typical hexagonal nickel nanoflake and the corresponding ED pattern (inset in Figure 2b). C) TEM image of the precursor of nickel dimethylglyoximate.

square planar structure. We proposed that the flake-like morphology of our product related to the planar structure of the precursor. To illustrate the puzzle, we attempted to replace the ligands with other N-complexing agents such as ethylenediamine, hydrazine, and pyridine which all combined with Ni^{2+} in a octahedral structure, keeping the other reaction conditions equal. Results showed that no flake-like particles could be obtained and the products were only nickel nanocrystallites with no definite geometric shapes, proving the unique role of nickel dimethylglyoximate for the formation of nickel nanoflakes. To examine further the effect of precursor on the shape of the final product, we studied the morphology of nickel dimethylglyoximate. The TEM image of Figure 2c showed that the precursor was ribbon-like with a diameter of 300–500 nm and length of dozens of microns, which exhibited a characteristic of planar morphology. On the basis of the above facts, we deduced that the formation of nanoflakes was related to the template effects of the complex precursor.[19] During the reaction, it was possible that the reduced nickel atoms were confined on a plane by the specially shaped precursor, inducing the oriented growth of nickel nanocrystals. As a result, flake-like single crystals of nickel were obtained. It was likely that the planar ribbon-shaped precursor provided orientation for the growth of nickel particles. Meanwhile, the slow release of Ni^{2+} from the complex precursor may also be favorable for the growth of single crystalline nickel particles.[20] However, why these flakes appeared at a hexagonal shape was still not clear and the related research was under way.

Magnetic measurements on thus-prepared nanoflakes were conducted and the M–H hysteresis loop was presented in Figure 3. The coercivity reached 198.8 Oe, much enhanced compared with that of bulk nickel (100 Oe), possibly for their novel morphology and nanosize.[21] Owing to that the particle size exceeded the single magnetic domain size of nickel, the product did not show superparamagnetization.[22] The saturation magnetization (Ms) and remnant magnetization (Mr) were 48.4 and 14.86 emu g^{-1}, respectively.

In conclusion, hexagonal nickel flakes with a side length of 200–400 nm and a thickness of 20–30 nm were prepared via the reaction between nickel dimethylglyoximate and hydrazine hydrate. The planar precursor showed a significant influence on the formation of flake-like nickel nanocrystals. To the best of our knowledge, this is the first report of the preparation of single crystalline nickel with hexagonal flake-like morphology. The resultant nickel nanoflakes may provide interesting possibilities

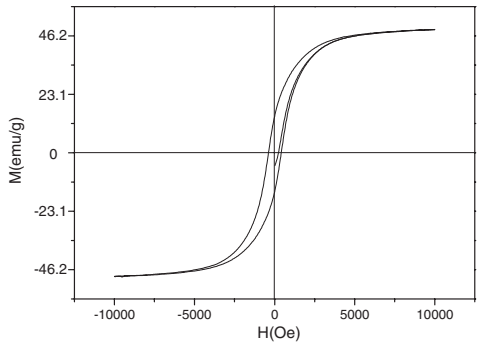

Figure 3. M–H (Magnetization–Hysteresis) loops of as-prepared nickel nanoflakes measured at room temperature.

for further applications in the magnetic, photonic, catalysis, and electronic fields.

References

1 A. P. Alivisatow, *Science*, **271**, 933 (1996).
2 H. O. Cao, Z. Xu, H. Sang, D. Sheng, and C. Y. Tie, *Adv. Mater.*, **13**, 121 (2001).
3 K. S. Napolsky, A. A. Eliseev, A. V. Knotko, A. C. Lukahsin, A. A. Vertegel, and Y. D. Tretyakov, *Mater. Sci. Eng., C*, **23**, 151 (2003).
4 Y. Zhang and H. Dai, *Appl. Phys. Lett.*, **77**, 3015 (2000).
5 S. Mishima, M. Kawamura, S. Matsukawa, and T. Nakajima, *Chem. Lett.*, **2002**, 1092.
6 X. Zheng, Y. Xie, L. Zhu, X. Jiang, and A. Yan, *Ultrason. Sonochem.*, **9**, 311 (2002).
7 L. Qi, J. Li, and J. Ma, *Adv. Mater.*, **14**, 300 (2002).
8 K. Soulantica, A. Maisonnat, F. Senocq, M. C. Fromen, M. J. Casanove, and B. Chaudret, *Angew. Chem., Int. Ed.*, **40**, 2984 (2001).
9 Y. Xiong, Z. Li, R. Zhang, Y. Xie, J. Yang, and C. Wu, *J. Phys. Chem. B*, **107**, 3679 (2003).
10 C. H. An, K. B. Tang, Q. Yang, and Y. T. Qian, *Inorg. Chem.*, **42**, 8081 (2003).
11 Z. Li, Y. Xie, Y. Xiong, and R. Zhang, *New J. Chem.*, **27**, 1518 (2003).
12 H. Hu, M. Mo, B. Yang, M. Shao, S. Zhang, Q. Li, and Y. Qian, *New J. Chem.*, **27**, 1161 (2003).
13 V. F. Puntes, K. M. Krishnan, and A. P. Alivisatos, *Science*, **291**, 2115 (2001).
14 M. P. Pileni, *Adv. Funct. Mater.*, **11**, 323 (2001).
15 W. X. Zhang, C. B. Wang, and H. L. Lien, *Catal. Today*, **40**, 387 (1998).
16 J. Bao, C. Tie, Z. Xu, Q. Zhou, D. Shen, and Q. Ma, *Adv. Mater.*, **13**, 1631 (2001).
17 J. Bao, Y. Liang, Z. Xu, and L. Si, *Adv. Mater.*, **15**, 1832 (2003).
18 N. Coydente, M. Respaud, F. Secocq, M. J. Casanove, C. Amiens, and B. Chaudret, *Nano Lett.*, **1**, 565 (2001).
19 C. Chen, C. Zhu, L. Hao, Y. Hu, and Z. Chen, *Chem. Lett.*, **33**, 898 (2004).
20 Z. Liu, S. Li, Y. Yang, S. Peng, Z. Hu, and Y. Qian, *Adv. Mater.*, **15**, 1946 (2003).
21 J. H. Hwang, V. P. Dravid, M. H. Teng, J. J. Host, B. R. Elliott, D. L. Johnson, and T. O. Mason, *J. Mater. Res.*, **12**, 1076 (1997).
22 D. H. Chen and S. H. Wu, *Chem. Mater.*, **12**, 1354 (2000).

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