High-yield Synthesis of Nickel Flowers from Nickel Hydroxide Precursor

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High-yield synthesis of a new type of flowerlike nickel nanostructure was reported. The method involved the growth of β-$Ni(OH)_2$ flowers from the alkali solution of $Ni(dmg)_2$ (nickel dimethylglyoximate), followed by reduction in hydrogen atmosphere at 450 °C for 1 h. Compared with that of bulk nickel, thus-prepared nickel flowers showed a much enhanced coercivity.

Shape control of inorganic nanomaterials has attracted much attention for its vital role in determining their magnetic, electrical, optical, and some other properties.[1] Among the current shape-controlling techniques, there are many factors affecting the product shapes, such as the internal structure of product, external conditions of solvents, temperature, concentration of the reactants, the kinds of surfactants, etc.[2] In addition to these, shape of the precursor also showed great influence on that of the target product. Taking the approach of calcination for example, the morphology of the precursor often can be basically inherited by the calcined product. NiO nanosheets, α-Fe_2O_3 nanorods and ZnO nanobelts were all created by calcining the isomorphological precursors.[3–5] In the case of solution synthesis, morphology of the product was also tightly associated with that of the precursor. For example, Cu_2O nanowires were resulted from a linear complex precursor of $[Cu_3(dmg)_2Cl_2]_n^{2n+}$,[6] ribbon-like nickel dimethylglyoximate yielded hexagonal nanoflakes of nickel,[7] ZnO superstructures with ring-like nanosheets standing on spindle-like rods originated from platelike precursor of $Zn_5(OH)_8Cl_2 \cdot H_2O$,[8] while branched spindles and prismatic whiskers of ZnO derived from sheet-shaped $Zn_3(OH)_2V_2O_7 \cdot H_2O$.[9] Generally, in order to endow the target product with desired shapes, a proper precursor with special morphology is vital besides a rational reaction route.

Nickel was an important inorganic material whose applications span over catalysis, magnetic record, electronic, and conduction.[10] Many differently shaped nickel nanocrystals had been prepared from different precursors by various methods, such as nanowires electrodeposited in AAO templates, nanobelts assisted by complexing agent and surfactant, hollow spheres templated by microemulsion and nanorods created by thermal decomposition of organic compounds.[11–14] However, to the best of our knowledge, flowerlike crystallites of nickel have not been seen up to date.

Herein, we reported a hydrogen reduction route for the synthesis of nickel flowers from β-$Ni(OH)_2$ crystallites which served as the self-sacrificing templates. The whole process included two procedures, in which β-$Ni(OH)_2$ flowers were first prepared by the reaction between $Ni(dmg)_2$ and NaOH, and then reduced in hydrogen flow at 450 °C for 1 h. Magnetic properties of the nickel flowers at room temperature were studied.

All reagents were analytical grade. In a typical experimental, $Ni(dmg)_2$ was prepared first by adding 13-mL of ethanol solution containing 1 wt % dmgH into 0.4 mmol of $NiCl_2 \cdot 6H_2O$ solution. Subsequently, 0.06 mol of NaOH was added and then the mixture was hydrothermally treated at 120 °C for 5 h. The resulted green powder was rinsed with distilled water and ethanol, and then dried in a vacuum at 105 °C for 4 h. Part of the powder was heated in H_2 flow (30 mL min^{-1}) at 450 °C for 1 h in a fixed-bed reactor and further kept in H_2 current until the temperature was decreased to room temperature.

X-ray diffraction (XRD) patterns of the samples were recorded on a Philips X'pert diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å). The morphology and structure of the sample were studied with field emission scanning electron microscopy (FESEM, JEOL JSM-6300F) and transmission electron microscope (TEM, Hitachi, H-800) with an accelerating voltage of 200 kV. The hysteresis loop (M–H loop) was measured by a BHV-55 vibrating sample magnetometer at room temperature.

Figure 1a and 1b were the XRD patterns of the as-prepared precursor and product, which could be indexed as β-$Ni(OH)_2$ (JCPDS 14-0117) and face-centered cubic (fcc) Ni (JCPDS 4-850), respectively. No impurities were detected, indicating that two pure samples were created under such conditions. Compared with that of the standard pattern, Figure 1a shown about 4 times strengthened intensities of (00*l*) peaks, suggesting an abundance of (00*l*) plane in the β-$Ni(OH)_2$ sample.

Morphology of the β-$Ni(OH)_2$ sample was revealed by the FE-SEM and TEM image in Figure 2. Flowerlike crystallites with diameters of 2–4 μm were shown and the yield was above 99% by SEM observations. Each flower was composed of dozens of flakes, which were connected with each other. The selected electron diffraction (SAED) pattern revealed that the flake-like petals were single crystalline with top/bottom surfaces of {0001} planes and the side surfaces of {1010} planes. ED patterns recorded on different flakes were essentially the same, which agreed well with the intensified (00*l*) peaks in XRD pattern.

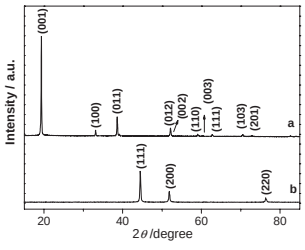

Figure 1. XRD patterns of as-prepared β-$Ni(OH)_2$ precursor (a) and Ni flowers (b).

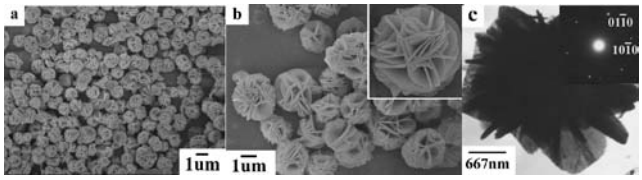

Figure 2. FE-SEM images of the β-Ni(OH)$_2$ flowers (a), inset in Figure 2b was a typical flower; TEM image of a typical flower, inset in Figure 2c was the SAED pattern of a petal.

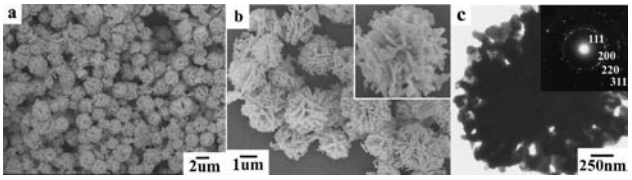

Figure 3. FE-SEM images of the nickel flowers (a) and (b), inset in Figure 3b was a typical flower; TEM image of a typical flower (c), inset was the corresponding SAED pattern.

Figure 3 presented the FE-SEM and TEM images of the as-prepared nickel. A panoramic image in Figure 3a shown that flowerlike Ni crystallites were produced and the yield was estimated above 99%. These Ni flowers well inherited the size and morphology of the β-Ni(OH)$_2$ precursor. However, the magnified image in Figure 3b showed that the details had changed. The former compact and flat flakes now exhibited a reticular skeleton consisted of interconnected particles with sizes of about 30–50 nm. Such characteristics were further illustrated by the TEM image of Figure 3c, and the corresponding ED pattern revealed the crystalline nature of the particulate subunits. Formation of the reticular flakes was possibly ascribed to the release of H and O atoms during the thermal reduction process that destroyed the former compact petals and resulted in a lot of nanoparticles and gaps or pores between the particles. However, the removal of the H and O atoms did not damage the regular geometrical shape, which was probably due to the nanocontact between each particle that stabilized the flowerlike structure mechanically against collapse or fracture.[15]

Nickel widely used as magnetic material, whose magnetic properties were greatly affected by the sample size, shape, crystallinity, etc. Figure 4 gave the magnetic hysteresis loop of the resultant nickel flowers measured at 25 °C in an applied field of 5000 Oe, showing a coercivity (Hc), saturation magnetism (Ms) and remnant magnetism (Mr) of ca. 184.3 Oe, 49.2 emu g^{-1} and of 13.4 emu g^{-1}, respectively. Relative to that of the bulk nickel (100 Oe, 55 emu g^{-1}, 2.7 emu g^{-1}), a much enhanced coercivtiy was shown, probably for its nanosized subunits.[16] The decreased value of Ms may be resulted from the increased interactions between the nanocontacted subunits, which reduced the total magnetic moment.[17]

In summary, a novel new type of flower-shaped nickel nanostructure was prepared using the β-Ni(OH)$_2$ flowers as precursor. The hydrogen reduction made the former compact petals turn into reticular skeleton with interconnected nanoparticles, but did not damage the flowery shape of the precursor. As-prepared peculiar nickel flowers are expected to find applications in the fields of magnetism, catalysis, conduction, etc.

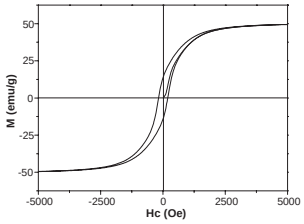

Figure 4. Magnetic hysteresis loop of the resultant nickel flowers measured at 25 °C.

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