微波辅助的多元醇法合成 CoNi 纳米材料

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摘要: 利用微波辅助的多元醇法合成出纳米线和海胆状结构 $\text{Co}_{0.8}\text{Ni}_{0.2}$, 采用 X 射线衍射和透射电镜技术对该材料合成过程中的结构变化进行了详细的研究. 根据晶体的成核与生长速率阐述了 $\text{Co}_{0.8}\text{Ni}_{0.2}$ 纳米结构的形成机理. 结果表明, $\text{Co}_{0.8}\text{Ni}_{0.2}$ 纳米材料在丙三醇氢解反应中的催化性能与其形貌和粒径密切相关.

关键词: 微波加热; 多元醇合成; 钴; 镍; 纳米线; 海胆状结构; 丙三醇氢解

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Microwave-Assisted Polyol-Synthesis of CoNi Nanomaterials

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Abstract: $\text{Co}_{0.8}\text{Ni}_{0.2}$ nanourchins and nanowires were fabricated by microwave-assisted polyol-synthesis. Their structural evolution was monitored by powder X-ray diffraction and transmission electron microscopy measurements. The nucleation and growth rates of the crystals in their formation mechanism were discussed. Their catalytic activity for glycerol hydrogenolysis depended on their anisotropic shape and particle size.

Key words: microwave-heating; polyol-synthesis; cobalt; nickel; nanowire; nanourchin; glycerol hydrogenolysis

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Bimetallic CoNi nanoparticles have attracted increasing attention for their potential applications in ultra-high density magnetic recording, magnetic resonance imaging, and catalysis [1–3], where their performance strongly depend on the chemical composition, size, and morphology. Compared with conventional spherical particles, CoNi nanorods and nanowires exhibited enhanced activities due to the high shape anisotropy [4,5], which clearly demonstrated that the morphology of the bimetallic nanoparticles is an essential parameter determining the magnetic properties. Spherical CoNi nanoparticles were previously reported to be highly active for methane drying reforming [6] and for growing single-walled carbon nanotubes [7], but CoNi nanoparticles with anisotropic shapes as the catalyst has not been reported.

The control of the size and morphology during the synthesis of CoNi nanostructures has emerged as one of the most popular topics in materials science because of their magnetic and catalytic properties. CoNi nanorods [4], nanowires [5], nanochains [8], nanoneedles [9], nanotube arrays [10], nanodumbbells [11], nanorings [12], and nano/micro-flowers [13] have been fabricated in the liquid phase with the aid of soft and hard templates. These advanced but, in many cases, complicated preparative techniques have greatly facilitated the shape control of CoNi nanomaterials, but they usually use conventional heating and the unavoidable temperature gradient adversely affected the particle size distribution and product yield [14].

In contrast to conventional heating methods, microwave irradiation has been applied for the rapid synthesis of metal-

lic nanostructures with very narrow size distributions [15,16]. CuNi [17], AuAg [18], PdPt [19], AuNi [20], and NiCo [21] spherical or core-shell nanoparticles with rather narrow size distributions have been obtained by the microwave heating technique. We have previously synthesized CoNi nanorods/nanowires by a conventional hydrothermal process, but the synthesis required up to 12 h [3]. In this work, we used a microwave-assisted polyol procedure to fabricate CoNi nanourchins and nanowires in a very short time and the morphology was effectively controlled by simply tuning the temperature and heating rate.

1 Experimental

1.1 Materials synthesis

Microwave heating was carried out using a multimode 2.45 GHz microwave apparatus (MARS-5, CEM Corporation). The temperature of the reaction solution was measured by a fiber optic thermometer that was directly inserted into the solution. The CoNi nanoparticles with the molar ratio of 4:1 were prepared by a heterogeneous nucleation method in 1,2-propanediol described elsewhere [3]. In a typical synthesis, 0.8 g $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, 0.2 g $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, and 0.2 g NaOH were dissolved into 50 ml 1,2-propanediol, followed by the addition of 0.27 g (0.95 mmol) stearic acid and 0.02 g (0.18 mmol) $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (35 wt% Ru) dissolved in 5 ml 1,2-propanediol. Subsequently, the mixture was transferred into a flask (100 ml) and heated to the desired temperatures (140–170 °C) at 10 °C/min and kept at that temperature for 2 h. The black powders obtained was centrifuged, thoroughly washed with ethanol, and dried at 50 °C for 5 h under vacuum. The key parameters of the temperature, heating rate, and synthesis time were studied.

1.2 Characterization

Powder X-ray diffraction (XRD) patterns of the particles were recorded on a D/MAX 2500 diffractometer (Rigaku, Japan) using nickel-filtered $\text{Cu } K_\alpha$ radiation at 40 kV and 200 mA. The mean crystallite size, L_m , was calculated from the (100) and (002) lines using the Scherrer equation [4]. Transmission electron microscopy (TEM) images were recorded on a Philip Tecnai G² Spirit microscope operating at 120 kV. High resolution transmission electron microscopy (HRTEM) images were taken using a FEI Tecnai F30 G² Spirit microscope operated at 300 kV. The samples were ultrasonically dispersed in ethanol and a drop of the suspension was deposited on a carbon enhanced copper grid and then dried in air. Field emission scanning electron microscopy (FESEM) images were recorded on a Philips Fei Quanta 200F instrument operated at 20 kV. The sample was

placed on conductive carbon tape on an aluminum sample holder. The elemental analysis of the particles was performed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on a ICPS-8100 instrument.

1.3 Glycerol hydrogenolysis

CoNi nanomaterials (0.05 g) were added to 40 g of 10 wt% glycerol aqueous solution in an autoclave (100 ml). After purging with hydrogen, the reaction system was pressurized to 3 MPa of hydrogen and heated to 220 °C. The reaction was conducted for 7 h under stirring. The products were identified by a mass spectrometer and quantitatively analyzed by a gas chromatograph equipped with a flame ionization detector.

2 Results and discussion

2.1 Effect of temperature

Figure 1 shows the XRD patterns of the CoNi nanoparticles synthesized at 140 to 170 °C. The MW-140 sample exhibited diffraction lines at 2θ values of 41.5°, 44.4°, 47.3°, 62.4°, and 75.7°, corresponding to the (100), (002), (101), (102), and (110) planes, respectively, of the hexagonal close packed cobalt structure (JCPDS 89-4308). The minor diffraction at 51.4° was assigned to the (200) plane of the face centered cubic structure (JCPDS 65-380 (Ni) or 15-0806 (Co)). With increasing synthesis temperature, the intensity of the *fcc* (200) diffraction weakened significantly and disappeared at 170 °C, indicating the formation of a pure *hcp* phase. The crystallite sizes estimated from the (100) and (002) diffraction lines decreased with the increase

Fig. 1. XRD patterns of the CoNi nanomaterials. The solution was heated to the desired temperature at 10 °C/min and held there for 2 h. (1) MW-140; (2) MW-150; (3) MW-160; (4) MW-170.

in the temperature. These are listed in Table 1. The crystallite size (L_{100}) calculated from the (100) diffraction was smaller than the crystallite size L_{002} calculated from the (002) diffraction, indicating that the crystallite was anisotropic in shape and the nanoparticles grew preferentially along the c -axis of the hcp structure.

Table 1 Structural properties and catalytic activity in glycerol hydrogenolysis of the CoNi nanomaterials

Sample	Co/Ni mole ratio	L_m /nm		Glycerol conversion (%)	1,2-Propanediol selectivity (%)
		(100)	(002)		
MW-140	4.3	21.0	25.7	17.6	34.7
MW-150	4.0	19.2	21.4	59.1	50.4
MW-160	3.9	16.4	22.0	71.1	48.2
MW-170	3.8	13.1	18.4	96.3	36.5

Figure 2 shows the TEM and SEM images of the CoNi nanomaterials. When the synthesis was performed at 140 °C, the CoNi sample was urchin-like in shape with needles that randomly grew on spherical particles of about 100 nm in diameter. The needles had a diameter of about 15 nm and a length of 100–300 nm with a conical head of 30 nm. The MW-150 sample was CoNi nanowires having a diameter of 10 nm and lengths of several micrometers. These were apparently formed because of the enhanced reduction rates of Co^{2+} and Ni^{2+} . Each nanowire had a cone head of about 35 nm. At the synthesis temperature of 160 °C, the nanoparticles were partially aggregated into irregular shapes but they were easily re-dispersed into nanowires upon ultrasonic treatment. The length of the nanowire was decreased to 1 μm with a similar diameter of 10 nm, while the diameter of the cone head was decreased to 25 nm. When the synthesis

was conducted at 170 °C, hollow microspheres of 1–2 μm in diameter were formed (Fig. 2(e)). The microsphere was assembled by nanorods with length of 100–300 nm and diameter of 10 nm. The cone head of the nanorods were further decreased to 20 nm.

We have previously fabricated CoNi nanowires using a conventional hydrothermal method at 140 °C for 12 h [3]. Here, with the aid of microwave-heating, CoNi nanourchins and nanowires were successfully prepared at the same temperature but in a very short time (~2 h). This confirmed that microwave irradiation greatly expedited the reduction rates of Co and Ni, showing the advantage of microwave synthesis in fabricating bimetallic nanomaterials. Under the current microwave-assisted polyol-synthesis conditions, the decrease in the head size and the increase in the length from 140 to 160 °C indicated that the conical heads were formed at the end of the reaction due to the very slow reduction rate of Co^{2+} and Ni^{2+} [5]. The formation of microsphere self-assembled by CoNi nanorods at 170 °C implied that both the reduction of the metal ions and growth of metal crystals occurred very quickly at that synthesis temperature.

2.2 Effect of heating rate

The influence of heating rate during the microwave assisted polyol-synthesis on the structure of the CoNi nanomaterials were studied at 140 °C with the synthesis time of 10 h. As shown in Fig. 3, at the lower rate of 4 °C/min, CoNi nanourchins with isotropic cores below 150 nm were formed. These were composed of needles with a diameter of 15 nm and length of 200–500 nm. When the synthesis system was heated at a rate of 10 °C/min, nanourchins were

Fig. 2. TEM (a, b, d, f) and SEM (c, e) images of CoNi nanomaterials synthesized at 140 °C (a), 150 °C (b), 160 °C (c, d), and 170 °C (e, f). The solution was heated to the desired temperature at 10 °C/min and held there for 2 h.

Fig. 3. TEM and HRTEM images of CoNi nanomaterials synthesized at 140 °C for 10 h with a heating rate of 4 °C/min (a, b), 10 °C/min (c–f), and 20 °C/min (g, h).

still obtained, and the length of the needles was decreased to 100–300 nm but the diameter of the needles was increased to 10–30 nm. The crystallography of an individual needle was investigated by HRTEM observation. The diffraction patterns demonstrated the single crystalline nature of the CoNi nanourchins. The crystallographic *c* axis was parallel to the stacking direction and the CoNi nanomaterials grew anisotropically along the (100) plane, which was confirmed by the XRD pattern. When viewed along the [010] direction, the lattice spaces of 0.210, 0.205, and 0.198 nm were ascribed to the (100), (002), and (101) planes of the *hcp* Co phase. The nanoneedle exposed the (001) planes and the anisotropic growth was parallel to the [002] orientation. On further increasing the heating rate to 20 °C/min, CoNi nanowires were formed with a mean diameter of 10 nm and average length of 1–2 μm .

It was observed that the heating rate also played an essential role in determining the morphology. This has been previously reported for metallic cobalt nanorods [22]. The morphology of the CoNi nanomaterials was mainly determined by the relative rates of nucleation and growth during heterogeneous nucleation in polyols [5]. A lower nucleation rate and higher growth rate favored the formation of anisotropic shape such as rods, wires, and urchins. A higher nucleation rate favored the formation of isotropic shapes such as spherical particles and platelets [5,23]. With increasing heating rate, the morphology changed from nanourchins to nanowires, indicating that both the nucleation and growth rates were enhanced simultaneously but was more pronounced for the initial nucleation step, which thus induced the CoNi nanomaterials to grow along the one dimensional

direction.

2.3 Formation mechanism

The chemical composition and shape evolution during the synthesis of CoNi nanourchins were monitored by XRD measurements (Fig. 4) and TEM observations (Fig. 5). A solid phase was immediately formed in the mixed solution just before the synthesis. The XRD pattern of this solid precursor indicated the formation of cobalt and/or nickel stearates with an irregular layered structure, which were aggregated to form large blocks (Fig. 5(a)). The interlayer

Fig. 4. XRD patterns of the solid intermediates during the synthesis of CoNi nanourchins at 140 °C with heating rate of 10 °C/min. (1) 0 h; (2) 1 h; (3) 1.5 h; (4) 4 h.

Fig. 5. TEM images of the solid intermediates during the synthesis of CoNi nanourchins at 140 °C with a heating rate of 10 °C/min for 0 h (a), 1 h (b), 1.5 h (c), and 4 h (d).

distance was calculated to be 4.8 nm for the (002) plane, which was equal to the inter-layer distance (about 5 nm) of cobalt and nickel stearates [24]. When the synthesis was conducted for 1.0 h, the solid product still showed typical diffractions of cobalt and nickel stearates but spherical nanoparticles with diameters of 20–50 nm were formed (Fig. 5(b)). When 1.5 h was used, distinct diffraction lines at $2\theta = 41.5^\circ$, 44.4° , and 47.3° emerged, indicating the formation of the *hcp* crystal phase. Meanwhile, urchin-like nanoparticles were formed but these were still wrapped by an irregular layered matrix (Fig. 5(c)). The component needles had a diameter of 10 nm and length of 200 nm and grew randomly on isotropic cores with diameters of 40–80 nm. With further increase of the synthesis time, the cobalt and nickel stearates phases with the irregular layered shapes disappeared and the intensity of the *hcp* crystal phase in the XRD patterns was significantly stronger. The diameter of the nanoneedle increased while the length decreased, implying the occurrence of Ostwald ripening.

The chemical compositions of the CoNi nanoparticles during the structural evolution under the microwave-assisted polyol-synthesis conditions were analyzed by ICP. When the synthesis was conducted for 1 h, the Co/Ni molar ratio was 3.2, and it increased to 4.3 at 2 h, which was very close to the feed ratio of 4.0. This was quite different from the conventional hydrothermal synthesis where the obtained CoNi nanowires/nanorods had quite different Co/Ni molar ratios from the initial feed ratio [3]. The deviation was caused by the relative slower reduction rate of Ni^{2+} ions compared with the cobalt species in the polyol solution [25]. However, under the current microwave-assisted poly-

ol-synthesis conditions, CoNi nanourchins and nanowires with the desired feed ratios were obtained, which further demonstrated that microwave irradiation increased the reduction rate of Co and Ni species. Therefore, microwave synthesis has an advantage in synthesizing bimetallic nanomaterials as compared with the conventional hydrothermal process.

2.4 Glycerol hydrogenolysis

Table 1 compares the catalytic activity of the CoNi nanomaterials for the hydrogenolysis of glycerol. For the MW-140 sample, the glycerol conversion was 17.6% and the selectivity for 1,2-propanediol was 34.7%. On the sample synthesized at 150 °C, the conversion of glycerol increased to 59.1% while the selectivity towards 1,2-propanediol approached 50.4%. On the MW-160 and MW-170 samples, the conversion of glycerol further increased but the selectivity for propanediol decreased. Obviously, the different catalytic performance was dependent on the anisotropic shapes and particle sizes of the CoNi nanostructures, as shown in Table 1. Compared with the CoNi nanowires prepared by the conventional polyol-synthesis, the conversion of glycerol was generally increased but the selectivity for propanediol was lower under the same reaction conditions [3]. This could be due to the improved reduction of Co and Ni nanoparticles by microwave-heating that gave more Ni species on the surface of the CoNi nanowires. Since nickel has a higher activity in breaking the C–C bond than cobalt [26], the Ni-rich surface catalyzed glycerol cracking instead of hydrogenolysis, resulting in a lower propanediol selectivity.

3 Conclusions

$\text{Co}_{0.8}\text{Ni}_{0.2}$ nanostructures were prepared by microwave-assisted polyol-synthesis in a very short time. The effects of the temperature and heating rate used were studied. Fast heating led to the formation of nanowires while slow heating resulted in $\text{Co}_{0.8}\text{Ni}_{0.2}$ nanourchins. With increasing temperature, the aspect ratio of the $\text{Co}_{0.8}\text{Ni}_{0.2}$ nanowires decreased due to the fast growth rate. In glycerol hydrogenolysis, the activity and selectivity were strongly dependent on the shape and size of the $\text{Co}_{0.8}\text{Ni}_{0.2}$ nanomaterials.

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