



Surfactant-assisted hydrothermal synthesis of 3D urchin-like cobalt-nickel microstructures

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ABSTRACT

Novel urchin-like CoNi alloy microstructures with diameter of $7.5 \pm 0.8 \mu\text{m}$ were successfully prepared by a hydrothermal route at 120°C for 10 h, in which cationic surfactant cetyltrimethylammonium bromide (CTAB) and anionic surfactant sodium dodecyl benzenesulfonate (SDBS) were used. The samples were characterized by XRD, SEM, TEM, and SQUID techniques. It was found that the ratio of surfactants (CTAB/SDBS) and reaction temperature have great effects on the size and shape of the final CoNi alloys. The magnetic measurements reveal that the urchin-like CoNi microstructures display ferromagnetic behavior with coercivities of 177.2 and 149.8 Oe at 2 and 300 K, respectively, which are higher than those of the bulk counterpart. These urchin-like CoNi alloy are expected to have significant potential applications in the fields of catalysis and magnetic storage.

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1. Introduction

In recent years, micro/nano-scale materials have attracted increasing interest due to their unique physical and chemical properties and potential applications in many fields. It is well known that many properties of micro- and nanomaterials are closely related to their size, morphology and spatial organization [1]. Especially, three-dimensional (3-D) functional materials have received considerable attention because they generally yield collective properties, depending on their sizes, spacing, and high-order structures [2]. Hence, they may provide a good opportunity to explore novel properties and possible applications of the nanomaterials with complex architectures.

As an important transition metal alloy, CoNi alloy has been widely used in magnetic recording and magnetic resonance imaging, biomedical microdevices, catalysis, microwave absorbers, and micro-electromechanical systems (MEMS) [3–5]. Various methods have been developed in the past decade to fabricate CoNi nanostructures with different size and shapes, such as CoNi nanoparticles, wires, needles, chains, rings, and so on [6–10]. However, to the best of our knowledge, the synthesis of 3D CoNi alloy micro- and nanostructures with well-organized shapes by the wet-chemical reduction approach is still a challenge and has been rarely reported. This is partly due to the different reduction rates of Ni^{2+} and Co^{2+} in solution, as well as the different crystal growth characteristics of Co and Ni, which will result in difficulty

in forming regular 3D CoNi architectures with homogeneous element distribution.

Herein, novel 3D urchin-like CoNi hierarchical microstructures with diameter of $7.5 \pm 0.8 \mu\text{m}$ were synthesized through a surfactant-assisted hydrothermal method. The surface of the CoNi alloy microspheres consist of many thorns with length up to $0.5 \mu\text{m}$. It was found that the ratio of surfactants (CTAB/SDBS) and reaction temperature have great effects on the size and shape of the final CoNi alloys. The magnetic measurements show that the coercivities of such urchin-like CoNi microstructures are 177.2 and 149.8 Oe at 2 and 300 K, respectively, which are higher than the values of some CoNi nanostructures reported previously.

2. Experimental procedure

All reagents were analytical grade and were used without further purification. In a typical procedure, 0.48 g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, and 0.48 g of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 0.36 g of CTAB, and 0.12 g of SDBS were dissolved in 30 mL of distilled water with magnetic stirring. Then 3 mL of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ (80 wt%) was introduced into the above solution, and the mixture was transferred into a Teflon-lined stainless-steel autoclave with a 50 mL capacity. The autoclave was sealed and maintained at 120°C for 10 h. Finally, it was cooled down to room temperature, and the products were collected, rinsed, and then dried for characterization.

XRD pattern was recorded on a Bruker D8 focus diffractometer with $\text{Cu K}\alpha$ radiation. FESEM images were taken on a JEOL JSM6300F scanning electron microscope equipped with X-ray energy dispersive spectrometer (EDS), and HRTEM image was

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obtained by a JEOL JEM2100F transmission electron microscope with an accelerating voltage of 200 kV. Magnetic hysteresis loops were measured using a Quantum Design magnetic property measurement system (SQUID-VSM) with a magnetic field up to 10 kOe.

3. Results and discussion

The phase and purity of the sample obtained at 120 °C for 10 h was determined by X-ray diffraction, as shown in Fig. 1a, the three feature peaks at $2\theta=44.42$, 51.71 , and 76.30° matched the (111), (200), and (220) characteristics of a face-centered cubic (fcc) structure, respectively. No peaks of impurities were detected, indicating that the completion of the reduction reaction and the formation of CoNi alloy.

The morphologies of the as-synthesized product have been studied by SEM and TEM. Fig. 1b is the overall shape of the sample, which indicates that the product consists of large-scale microspheres with diameter of $7.5 \pm 0.8 \mu\text{m}$. The magnified SEM image in Fig. 1c clearly reveals that the surface of individual CoNi alloy microspheres is quite rough, and it presents a fine hierarchical nanostructure. Many thorns with length of about $0.5 \mu\text{m}$ were found to be radiated from the core, namely, urchin-like structures were formed. These 3D urchin-like CoNi alloy are very stable, even long time ultrasonication can not destroy the thorns, suggesting the structures are actually integrated. The EDS spectrum (not shown here) of the urchin-like CoNi microstructures indicated that the atomic ratio of Co/Ni is about 51.53:48.47, which is very close to 1:1 for CoNi. The shape of the sample was further determined by TEM as shown in Fig. 1d, which is consistent with that observed by SEM. High resolution transmission electron microscope (HRTEM) image in the inset shows that a typical thorn is mainly of the same lattice spacings with a lattice spacing of 0.207 nm ,

corresponding to the interplanar distance of (111) planes and consistent with previous reports on CoNi nanostructures.

The surfactant played an important role for the synthesis of nanomaterials. Generally, it is considered to kinetically control the growth rates of different crystallographic facets of nanostructures through preferentially adsorbing and desorbing on these facets. However, there is rarely report about the use of aqueous cationic/anionic surfactant mixtures for the shape control of nanostructures. PbS and gold nanocrystals with various morphologies have been prepared in the solution contained CTAB and sodium dodecylsulfonate (SDSn) mixture [11,12]. In this work, when no or only a small amount of CTAB (0.06 g) was used, the samples were microspheres with rough surface (Fig. 2a and b). If we kept the total amount of CTAB and SDBS with a given value (0.48 g), and adjusted the CTAB to 0.24 g, the product was mainly dominated by urchin-like CoNi alloys. The thorns were not obvious at this stage, and small quantity of irregular microparticles coexisted (Fig. 2c). Perfect assembled thorns were developed in the solution consisted of 0.36 g of CTAB and 0.12 g of SDBS. Once the CTAB was further increased to 0.42 g, the thorns grew very densely on the surface of CoNi particles (Fig. 2d). Although the detailed mechanism for the formation of urchin-like CoNi microstructure using binary surfactants needs more investigation, the mixture of CTAB and SDBS can surely play special roles in crystal nucleation and growth of CoNi nanocrystals owing to the synergistic interaction of the binary surfactants with metal ions, as well as specific crystal planes. Some work related to the mechanism is currently under way.

Temperature was another important factor in controlling the morphology of CoNi alloy. The reaction proceeded slowly if the experiment was conducted below or at 90°C , and it is also difficult to obtain CoNi with very high purity. Urchin-like structures and some small nanoparticles were produced when the reaction was carried out at 100°C (Fig. 3a). microparticles were formed if the

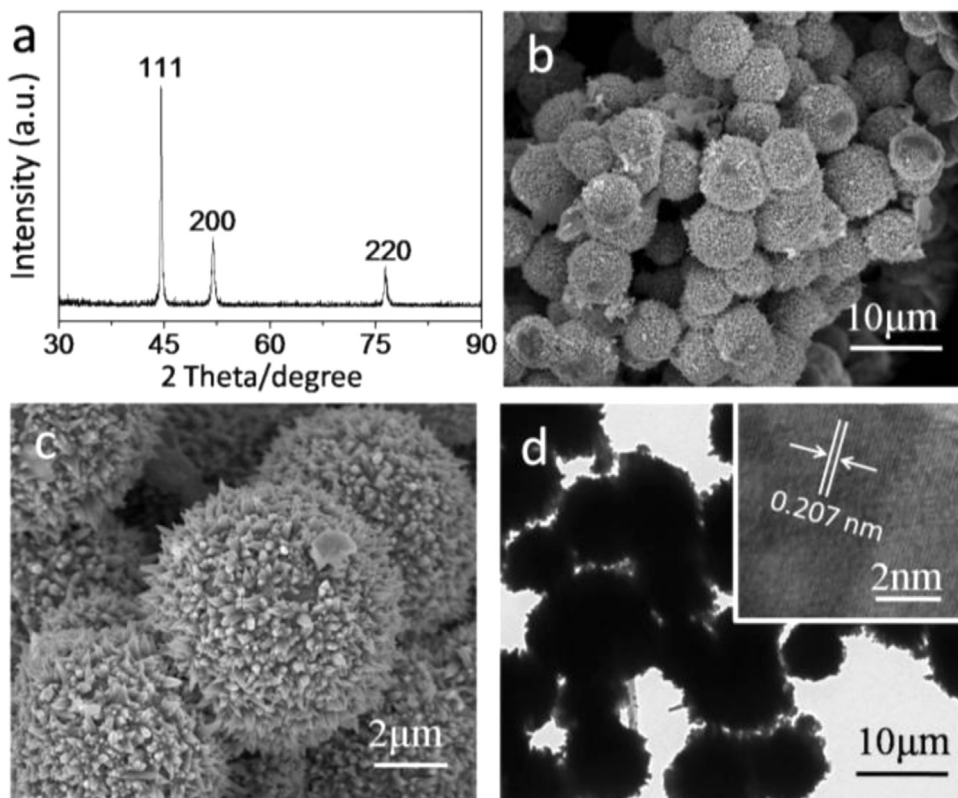


Fig. 1. (a) XRD pattern, (b–c) SEM images, and (d) TEM image of the obtained sample. Inset of (d) is the HRTEM image.

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