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Novel chain-like cobalt–nickel microstructures fabricated by a CTAB-assisted hydrothermal method

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ABSTRACT

CoNi chains with length up to a few hundred micrometers have been synthesized via a cetyltrimethylammonium bromide (CTAB)-assisted hydrothermal approach. The product was characterized by means of XRD, SEM, TEM, and VSM techniques. The effects of CTAB amount and reaction time on the resulting CoNi were investigated by a series of assistant experiments. It was found that the CTAB molecule played an important role for the formation of such novel CoNi microchains. These chains assembled by CoNi particles possessed face-centered cubic (fcc) structure. The magnetic property investigation of the obtained CoNi chains illustrated that they display ferromagnetic behavior with significantly enhanced coercivity of 223.3 Oe.

1. Introduction

One-dimensional (1D) nanostructured materials including nanowires, nanorods, nanotubes, and nanochains play an important role in the field of nanoscience and nanotechnology because of their novel physical properties and potential applications as interconnects in future generations of nanoscale electronics or electrochemical devices [1]. Among these 1D nanostructures, nanochains exhibit distinct optical, magnetic, and electrical properties due to their intricate nanostructures such as small length scale, low dimensionality, and interplay among constituents [2,3].

Several methods including magnetic-field-induced (MFI) assembly [4], dipole-directed assembly [5], and template-synthesis [6–8], have been developed so far to synthesize chain like structures. MFI assembly is a versatile method to prepare magnetic chains. However, the ordered structures can hardly be maintained after removal of the external field due to the weak anisotropic dipolar interaction between the magnetic building blocks. Template-synthesis has been experimentally demonstrated elsewhere. For example, Lu et al. reported the synthesis of iron-nickel nanochains via a CTAB-mediated solution route, and found that the CTAB molecules served as the “cross-linkers” to link two neighboring iron-nickel particles [7]. Zhang et al. prepared chain-like cobalt microstructures using poly(vinylpyrrolidone) (PVP) as a soft template [8]. However, the detailed mechanism for the formation of these chains is still very unclear, and it is also challenging to prepare chain-like structures with controlled length and diameter.

As a magnetic alloy, CoNi has drawn increasing attention due to its potential applications in ultra-high-density magnetic recording, biomedical microdevices, catalysis, and microwave absorbers. Over the past several years, CoNi with different shapes such as nanoparticles, wires, rings, chains, flowers, and etc, were prepared by various methods [9–15]. It is still necessary to seek a general approach to large scale fabricating of magnetic CoNi chains with controllable size. Herein, we report a CTAB-assisted hydrothermal method to batch synthesis of magnetic CoNi chains assembled by particles. It was found that the CTAB amount and reaction time were important for the formation of chainlike CoNi structures. The formation mechanism was proposed, and magnetic properties were also investigated.

2. Experimental procedure

2.1. Materials and method

All reagents were analytical grade and were used without further purification. In a typical experiment, 0.48 g of $CoCl_2 \cdot 6H_2O$, 0.48 g of $NiCl_2 \cdot 6H_2O$, and 0.24 g of CTAB were dissolved in 30 mL of distilled water, and the mixture was strongly stirred for 20 min to ensure that the reagents were dispersed homogeneously in the solution. Then 3 mL of $N_2H_4 \cdot H_2O$ (80 wt%) was added, and the mixture was transferred into a Teflon-lined stainless-steel autoclave with a 50 mL capacity. The autoclave was sealed and maintained at 200 °C for 10 h. After being cooled to room temperature, the precipitates were collected and washed with distilled water

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and ethanol for several times, and then dried for characterization.

2.2. Characterizations

The phase purity of the product was examined by X-ray powder diffraction (XRD) using a Bruker D8 focus diffractometer with Cu Kα radiation. FESEM images were taken on a JEOL JSM6300F scanning electron microscope and HRTEM image was obtained by a JEOL JEM2100F transmission electron microscope with an accelerating voltage of 200 kV. Magnetic measurement was carried out at room temperature with a VSM (Lakeshore 7307, USA) by saturating the sample powder in a maximum magnetic field of 10 kOe.

3. Results and discussion

The phase and purity of the sample formed at 200 °C for 10 h was determined by XRD, as shown in Fig. 1a for 2θ angle values of 20–100°. All the feature peaks matched the characteristics of a face-centered cubic (FCC) structure of CoNi alloy. No peaks due to the impurities of elemental Ni, Co, hydroxide or oxide were detected, indicating that the as-obtained product was pure and confirmed the formation of an alloy.

The morphology of the product was investigated by FESEM firstly. A panoramic FESEM image in Fig. 1b demonstrated that the sample contained a large scale of CoNi microchains with a length up to a few hundred micrometers. Magnified image in Fig. 1c showed that the chains possessed linear, branched and zig–zag-like shapes. Such structure was formed by CoNi spheres ranging in size from 3 to 4 μm and they were closely conjoined with each other. A typical TEM image (Fig. 1d) clearly showed the shape of chain-like assemblies with high branches. HRTEM image was taken on the surface of an assembled particle, and the distance between two adjacent planes was measured to be 0.205 nm, which corresponded to the lattice spacing of (111) planes of FCC CoNi. Experiment further demonstrated that such microchains could keep unbroken even under vigorous ultrasonication, suggesting the stable characteristic of the chain-like structures.

It was found that CTAB played an important role for the formation of CoNi chains. Isolated irregular particles with size of 0.5–1.5 μm were produced without using any CTAB (Fig. 2a and b). When small amount (0.12 g) of CTAB was employed, the product was composed of a few chains and a large scale of particles (Fig. 2c). The length of the chains could reach 100 μm with branched and zig–zag-like morphology. Perfect CoNi chains could form when 0.24 g of CTAB was added (Fig. 1b), and these chains tangled together. Further increasing the amount of CTAB to 0.48 g, interestingly, all the CoNi chains tangled seriously and the connected position between the adjacent particles was not obvious any more (Fig. 2d). At the same time, the diameter increased a little accordingly. To form chain-like structure, external magnetic fields are often required as those reported previously. Surfactant was often used in the synthesis of nanomaterials to protect the particles from aggregation. Herein, CoNi chains were obtained just in the presence of CTAB, and hence we believed that CTAB was crucial to produce the CoNi microchains.

The initially generated CoNi nuclei carried net negative surface charges in basic solution, and created a strong repulsive force inhibiting the aggregation of the nuclei. As a cationic surfactant, CTAB molecule has a positively charged oleophilic head-group, which would absorb on the negatively charged surface of CoNi particles to decrease the "ζ potential". Therefore, the total repulsive force on the surface of nanoparticles was reduced, leading to the aggregation of particles. As the concentration of CTAB was very low, the negative charges could not be completely neutralized, and the formation of anisotropic distribution of the residual surface charges is beneficial to produce a permanent electric dipole moment on each CoNi particle. Chain-like structure was easily formed via electric dipole–dipole interaction between the

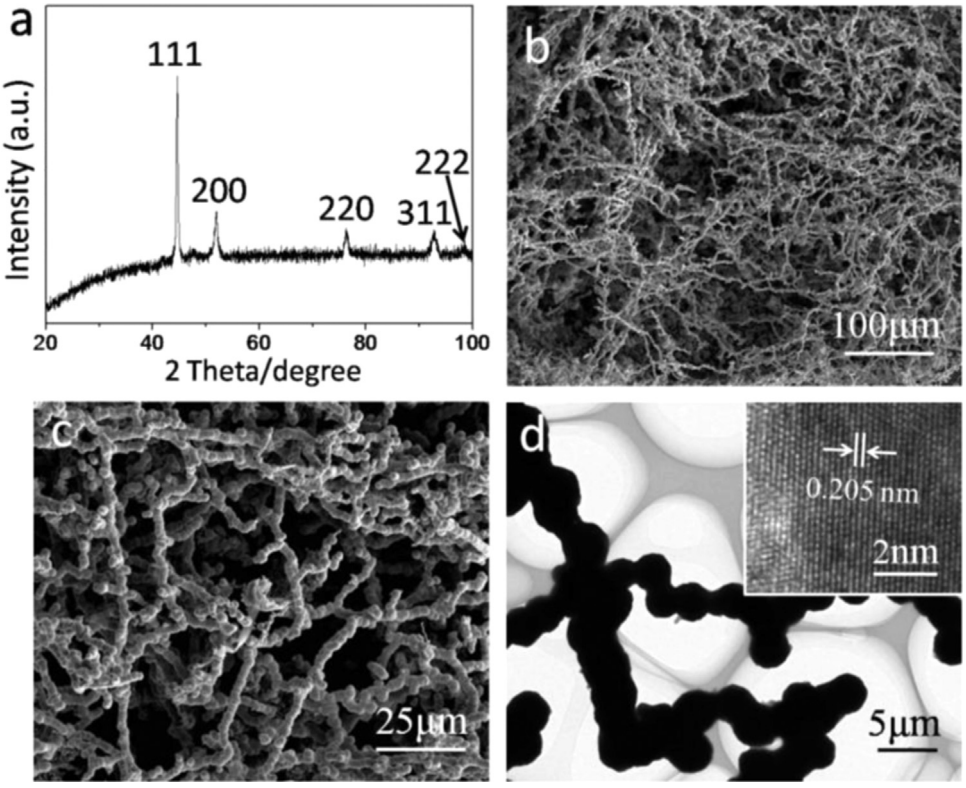

Fig. 1. (a) XRD pattern, (b–c) SEM images, and (d) TEM image of the CoNi chains. Inset of (d) is the HRTEM image.