Materials Chemistry and Physics 201 (2017) 235–240

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

The synthesis of ultra-long cobalt chains and its outstanding catalytic performance on the thermal decomposition of ammonium perchlorate

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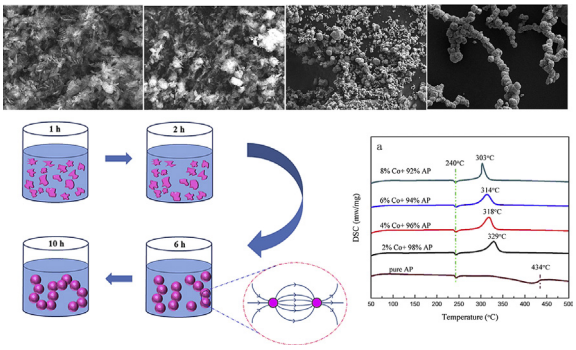
HIGHLIGHTS

- Ultra-long cobalt chains were synthetized.
- The growth mechanism was explored by controlling the reaction time.
- Elevated ferromagnetic property relies on the preferred orientation and shape anisotropy of cobalt chains.
- A synergistic effect mechanism for excellent catalytic performance was proposed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 2 December 2016
Received in revised form
21 July 2017
Accepted 21 August 2017
Available online 24 August 2017

Keywords:
Ultra-long cobalt chains
Hydrothermal
Magnetization
Thermal decomposition of AP

ABSTRACT

A simple method without assisted of external magnetic field or surfactant soft templates was utilized to fabricate ultra-long cobalt chains. The formation mechanism was investigated by time dependent experiment, and it was considered that the link of adjacent spherical particles were through dipolar interaction. Due to the preferred orientation and shape anisotropy of the chain structure, the coercively (H_c) value was about 84.5 Oe and saturation magnetization value was up to 149 emu/g at room temperature. To develop its further practical application, the products with regard to accelerate the thermal decomposition of ammonium perchlorate revealed that it exhibited an outstanding performance of reducing the thermal decomposition temperature. This excellent performance has great practical significance on the development of solid rocket fuels. The mechanism of the excellent performance probably ascribed to the synergistic effect of cobalt and cobalt oxide was proposed.

1. Introduction

The synthesis of magnetic nanomaterials was significantly due to their applications in magnetic storage devices, magnetic

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http://dx.doi.org/10.1016/j.matchemphys.2017.08.057
0254-0584/

refrigeration systems and magnetic carriers for drug targeting [1–3]. Magnetic products including Fe, Co and Ni metals have been studied for many years. Strong magnetic interactions in these particle systems make it difficult to form stable colloids [4]. Uncontrolled agglomeration of the magnetic particles often makes it impossible to separate, and thus could not meet the requirement of many applications, such as magnetic recording [5]. By far, there were two feasible approaches to increase the magnetic anisotropy. One was to modify the shape of the nanoparticles, and the other was to assemble nanocrystals into multidimensional morphologies [6–9].

It has been found that magnetic properties of nanomaterials depending on the size and morphology widely. Based on the excellent physical and chemical properties, the relevant research activities about one-dimensional (1D) structures have increased dramatically [1–3,10]. Compared with other 1D structure such as wires, rods, and tubes, the chain-like structure was especially special. The coupling interactions between the adjacent particles could give rise to some novel properties. Virtually all types of methods have been employed to synthesize 1D chain, such as linear templates and physical methods like magnetic-field alignment. However, there were several intrinsic disadvantages [4,11]. When the templates were removed through physical or chemical method, the morphological of the products would be varied. In addition, the large-scale magnetic field could not avoid intrinsic disorder in the chains, and consequently the efficiency of the devices would be decreased obviously [12,13].

In addition, One-dimensional (1D) structures present excellent performance in catalytic field as well. Compared with other structures, 1D structure would facilitate the formation of 3D net so as to increase the reaction active sites [14,15]. Ammonium perchlorate (AP) is the most common oxidant in composite solid propellants since its thermal decomposition characteristics directly influence the combustion behavior of the propellant. In the past decades, metal oxides acting as catalysts have a significant role in promoting the thermal decomposition of AP [16–20]. However in comparison to metal oxide nanoparticles, the corresponding metals exhibited superior properties on thermal decomposition of AP and the employ of rocket propellants [21,22]. The metal nanoparticles contain many defects in their crystal lattice, and atoms on the defects tend to be saturated by combining with surplus electrons on its surface. Coincidentally, the nitrogen atoms of AP contain surplus electrons, thus the *N-X* bond would be easily broken due to the absorption of metal atom. This is favorable for the decomposition of AP. Especially, the cobalt metal revealed excellent catalytic performance compared with other kinds of metals [17].

In current work, a simply and environmentally method was employed to prepare the ultra-long cobalt chains. The growth mechanism was proposed through investigating the SEM images and Raman spectra of the products at different reaction time. The obtained one-dimensional cobalt chains with preferred orientation and shape anisotropy exhibited elevated ferromagnetic property. In addition, the decomposition temperature region of ammonium perchlorate (AP) could be significantly decreased by the presence of chain-like cobalt. The ultra-long cobalt chains showed a promising potential application in the field of high-energy fuel.

2. Experimental

2.1. Synthesis method

In a typical procedure, 20 mL of $CoCl_2 \cdot 6H_2O$ ethylene glycol solution (0.714 g) was added to 20 mL of NaOH ethylene glycol solution (3.75 g) under vigorous stirring at room temperature. After 30 min of reaction, the final products were put into a 50 mL Teflon-lined stainless steel autoclave. The sealed tank was incubated at 200 °C for 10 h, and then cooled to room temperature naturally. Finally, the products were washed with alcohol several times and dried at 60 °C for 10 h.

2.2. Characterization

The phase structure of the as-synthesized products were examined by X-ray diffraction (XRD, D8/ADVANCE diffractometer, Cu Kα λ = 1.5418 Å). The morphology analysis was characterized by scanning electron microscopy (SEM, LEO-1530, Oberkochen, Germany) and transmission electron microscope (TEM, JEM-2100F). The room temperature magnetic characterization of the products was performed by a vibrating sample magnetometer (VSM, BHV-50 HTI). The properties of products concerning on reducing the thermal decomposition of AP were tested with a Thermo Gravimetric Analyzer (N33-TG 209F3). The chemical valence of the products was measured by XPS (PHI QUANTERA-II SXM) with an Al Kα radiation source (1486.6 eV). Raman scattering was excited using the 633 nm radiation from He-Ne laser and was collected by a micro-Raman spectrometer in the 100–2000 cm^{-1} range at room temperature.

3. Results and discussion

The SEM images in Fig. 1 displayed disparate magnifications morphologies and assembled structures of the product. Fig. 1a and b indicated that the length for the large proportion of products ranged from 100 to 200 μm and the diameter was about 5 μm. There were also some short-chains and spherical particles spreading in the products. A closer observation in Fig. 1c displayed that some small pompon-like particles with different size attached on the product surface. X-ray powder diffraction pattern (Fig. 1d) displayed that two phases were formed in the product including hexagonal close-packed (hcp) and face-centered cubic (fcc). The reported data of the two phases were PDF#05–0727 ($a = 2.514$ Å, $c = 4.105$ Å) and PDF#15–0806 ($a = b = c = 3.545$ Å) respectively. The two phases were both close-packed structures but differed on the stacking sequence of (111) direction atomic planes. Low activation energy on stacking faults often led to the formation of two phases under high-temperature crystallization techniques [5,23]. However, the relative intensities of diffraction peaks did not agree well with the PDF card (JCPDS 05–0727). In the PDF card, the diffraction peak of (101) was the strongest while the (002) peak was weaker. However, the relative intensity of the (002) peak significantly increased in the product. This phenomenon was closely related with the anisotropic of the products.

Transmission electron microscopy (TEM) was employed to figure out the microstructure of the cobalt chains. From the bright field TEM image (Fig. 2a), a small amount of nanosheets could be found. The crystallinity and the corresponding SAED pattern of an isolated nanosheet were illustrated at Fig. 2b and c. The nanosheet was in the state of polycrystalline, and the planar spacing was 0.2169 nm and 0.2050 nm which corresponded well to the H (100) and F (111) plane. The planar spacing obtained from the pattern were 2.030, 1.930, 1.477, 1.250 and 1.150 nm which corresponded to the (002), (101), (102), (110), and (103) planes of hexagonal cobalt respectively and the 1.750 nm corresponded to (200) plane of cubic cobalt phase.

To investigate the growth process, the shape evolution of the product at various stages was investigated by SEM. Fig. 3 exhibited the SEM images of the products which obtained from different reaction times after reaching 200 °C. Seen from Fig. 3a, the reaction solution was comprised of many uniformly petals-shaped particles. As the reaction time was extended to 1 h, the flowery crystals