

Synthesis of Self-assembled Magnetite (Fe₃O₄) Chain-like Core–Shell Nanowires by a Facile One-step Process

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A robust hydrothermal route has been designed for synthesis of uniform Fe₃O₄@carbonaceous core–shell nanowires with self-assembled Fe₃O₄ nanowires as the core component and carbonaceous matter as shell. The formation mechanism of the self-assembled Fe₃O₄@carbonaceous core–shell nanowires is investigated in detail.

One-dimensional nanostructured materials including nanotubes, nanorods, and nanowires have attracted intensive interest owing to their potential applications in molecule-based electronic devices,¹ magnetic sensors, and their unique properties.² As one of the most important spinel-type materials, magnetite (Fe₃O₄) has gained more and more attention in materials science because of its potential application in various fields such as hyperthermic treatment, magnetic resonance imaging, and cancer cell targeting and imaging.³ A great deal of research has been focused on the investigation of one-dimensional magnetite nanostructures such as anodic aluminum oxide (AAO). Hard MgO template processes,⁴ soft lecithin templates,⁵ and hydrothermal methods⁶ have been developed for the preparation of one-dimensional magnetic metals, alloys, and metal oxides.

Recently, the organization of magnetic nanoparticles has had a great impact on numerous branches of applied sciences. Due to their intricate nanostructures, extremely small length, low dimensionality, and interplay among constituents, assembly magnetic nanoparticles often exhibit new and enhanced properties over their bulk counterparts.⁷ A number of techniques have been developed to obtain ordered magnetic nanoparticle arrays, including spin coating,⁸ vertical depositions,⁹ and applying external electric fields¹⁰ or external magnetic fields.¹¹ Although the process toward assembly of magnetite nanoparticles into ordered structures has achieved exciting success,^{12,13} the development of a facile method for the preparation of high-quality self-assembled magnetite nanoparticles is still intriguing topic.

Recently, we have proposed an efficient one-pot route for the large-scale synthesis of luminescent self-assembled Fe₃O₄@phenol formaldehyde resin (PFR) nanowires.¹⁴ Herein, we examine the versatility and capability of this approach and explore whether other organic reductants such as glucose can be used to form new self-assembled magnetic nanostructures. The results have demonstrated that self-assembled Fe₃O₄@carbonaceous core–shell nanowires can also be synthesized by controlling the reaction conditions.

Figure 1 shows an X-ray diffraction (XRD) pattern of the products obtained by this hydrothermal approach. All peaks are well indexed as spinel magnetite, and the (210) and (211) peaks of maghemite are not observed in the XRD patterns, which are in good agreement with the standard literature data (JCPDF card

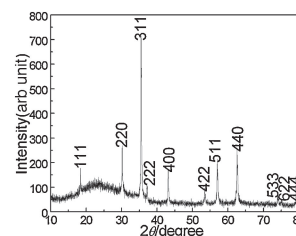


Figure 1. XRD pattern of Fe₃O₄@carbonaceous core–shell nanowires.

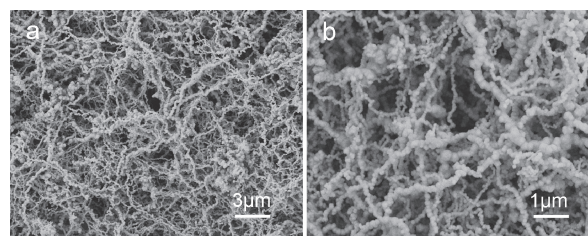


Figure 2. (a) and (b) SEM images of self-assembly Fe₃O₄@carbonaceous core–shell nanowires synthesized at 180 °C for 48 h.

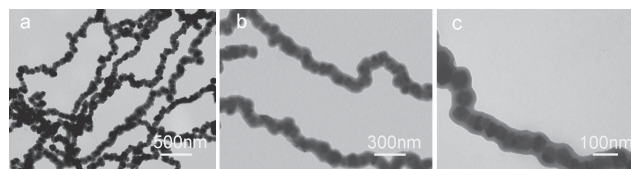


Figure 3. (a) and (b) TEM images of self-assembly Fe₃O₄@carbonaceous nanowires. (c) TEM of an individual nanowire that was taken from the sample.

number: 86-1354). Additionally, there is an obvious broadening peak at about 22° that corresponds to amorphous carbon, considering the carbonization of carbohydrates under the present reaction conditions.

Figure 2 shows the SEM images of self-assembly Fe₃O₄@carbonaceous core–shell nanowires. It is indicated clearly that self-assembled Fe₃O₄ nanowires with a width ranging from 100 to 150 nm and 20–30 μm in length can be produced. Figure 3 shows typical TEM images of self-assembled Fe₃O₄@carbonaceous core–shell nanowires. The TEM image (Figure 3c) of an individual nanowire clearly reveals that the Fe₃O₄ nanochain is assembled by nanoparticles 60–70 nm in diameter in order and that the organic coating has a uniform thickness over the entire surface of each chain-like Fe₃O₄ nanowire.

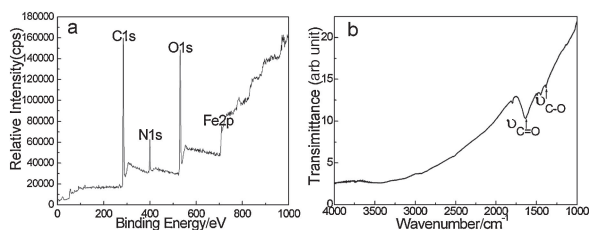


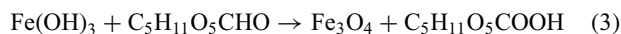
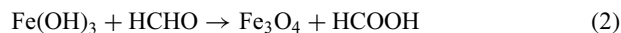
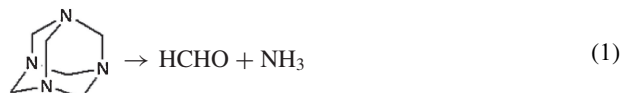
Figure 4. (a) XPS spectrum of the Fe₃O₄@carbonaceous nanowires. (b) FTIR spectrum the Fe₃O₄@carbonaceous nanowires.

The high-resolution transmission electron microscopy (HRTEM) image further confirms a single Fe₃O₄ nanowire has characteristics of ordered nanochain assemblies (Figure S1¹⁸). The lattice fringe observed in the images is 0.485 nm, corresponding to (111) plane in the inverse spinel structure. The two neighboring linked discrete particles present different characteristics (Figure S1b¹⁸), while particles with the same characteristics also appear (Figure S1c¹⁸). Therefore, the particles in the chains are partially linked together mechanically driven by magnetostatic interaction with random crystal orientations and partially assembled by oriented attachment.¹⁵

The XPS spectrum in Figure 4a indicates that C1s and O1s binding energies of the obtained sample are 284.59 and 531.11 eV, respectively. However, the binding energy at 709.98 eV for Fe2p cannot be detected, implying that almost all self-assembly magnetite (Fe₃O₄) nanowires are all confined within shells. The quantitative analysis of the sample shows that the molar contents of C, O, N, and Fe are 73.96%, 22.21%, 3.01%, and 0.82%, respectively. Obviously, the molar ratio of C to O (about 3:1 based on elemental analysis) in the product increased markedly, compared to the value for pure glucose (about 1:1). It can be inferred that the change in C/O molar ratio is due to the carbonization of glucose.

To further testify the shell composition, the FTIR spectrum of the obtained nanowires has acquired, which is shown in Figure 4b. It indicates that there is no strong absorption peak from 3500 to 3400 cm⁻¹ and from 2400 to 2100 cm⁻¹, which can be assigned as the absorption peak of ν(N-H) and ν(C≡N), respectively. The trace amount of nitrogen indicated by XPS possibly comes from the hexamethylenetetramine (HMT) or NH₃ released from HMT, which can bind the carbonaceous surface layer through hydrogen bond or VDW (van der Waals' force) interactions. In contrast, that FTIR spectra have characteristic C=O stretches at 1650 cm⁻¹ and C-O stretches at 1300 cm⁻¹. Therefore, it can be confirmed that the shells of self-assembled Fe₃O₄ core-shell nanowires are carbonaceous matter.¹⁶

According to the experimental conditions, the reaction mechanism of the self-assembly Fe₃O₄@carbonaceous core-shell nanowires is investigated. During the early stage of the preparation, f iron(II) (Fe²⁺) can react with OH⁻ from HMT to form f iron(II) hydroxide; the f iron(II) hydroxide is mostly oxidized by O₂ in air to form f iron(III) hydroxide. After that, f iron(III) hydroxide is partially reduced by HCHO released from HMT to form Fe₃O₄ in the proper pH and temperature according to eqs 1 and 2. Furthermore, f iron(III) hydroxide also can be reduced by -CHO from glucose to form Fe₃O₄ under similar conditions according to eq 3.¹⁷ Simultaneously, glucose is carbonized in the reaction system, which is responsible for the formation of the shell.¹⁶



In fact, we have proposed that the formation of such self-assembly Fe₃O₄@PFR core-shell nanowires is controlled by a so-called synergistic soft-hard template mechanism (SSHM).¹⁴ The self-assembly of magnetic particle chains is a complex process that involves numerous competitions, magnetostatic interactions, and particle sizes and shapes. Here, these chain-like core-shell nanowires are formed directly in the reaction solution due to the cooperation of dipole-directed self-assembly and the stabilization of amorphous carbon. In a word, both the carbonization of glucose and magnetic dipole interaction play important roles in the formation of nanowires and their assemblies.

In summary, the uniform self-assembled Fe₃O₄@carbonaceous core-shell nanowires have been synthesized by a facile one-step hydrothermal approach in large scale. The formation mechanism of the self-assembled Fe₃O₄@carbonaceous core-shell nanowires is investigated in detail. This approach may provide a facile route for the production of high-quality Fe₃O₄ nanostructure with various interesting properties that have potential application in biotechnology.

This work was supported by the CREST program of the Japan Science and Technology Agency (JST), the National Natural Science Foundation of China (Nos. 50873042 and 21001048), the Natural Science Foundation of Jiangsu Province (No. BK2009651) and the Scientific Research Program of HuaiHai Institute of Technology (Nos. KQ08029 and KX08020).

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