Polyoxometalate-assisted One-step Fabrication of Porous Nanorods of β-FeOOH and the Facile Transition to Hematite

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Uniform porous β-FeOOH nanorods of 10–20 nm have been controllably fabricated by direct hydrothermal treatment of $FeCl_3$ and dilute tungstophosphoric acid $H_3PW_{12}O_{40}$ (PW12) solution. N_2 adsorption–desorption properties of the nanorods were studied. Hematite nanorods with the same morphologies and interesting weak ferromagnetic properties were obtained by annealing these β-FeOOH nanorods.

Iron oxides, which have many practical applications both in industry and laboratory, represent a very important family in materials science.[1] Among various iron oxides, β-FeOOH, a semiconductor with the band gap of 2.12 eV,[2] is widely used as pigment, catalysts, adsorption material and raw material for the synthesis of magnetic iron oxides[3] and is also a promising active materials for lithium batteries.[4] One-dimensional (1D) structures of β-FeOOH are of especially great interest because of their easy formation, and many iron-based anisotopic magnetic materials used in industry are fabricated from FeOOH 1D structures. Much effort has been paid to the facile synthesis of nanorods, nanospindles, and nanowires of α-[5] and β-FeOOH recently.[4c,6] However, there is few report on the direct synthesis of hollow β-FeOOH nanostructures, which may have superior properties in catalysis and lithium batteries owing to the high surface area and structure superiority.[4b]

Hematite is another important iron oxide used widely in catalysts, pigments, and sensors.[1] Recent work focused on the syntheses and improved properties of hematite nanotubes,[7a–7c] hollow nanowires,[7d] and porous nanorods.[7e] On the other hand, recent researches on FeOOH 1D nanostructures also included the convenient phase transition to hematite.[5,6] Especially, Xie's group reported synthesis and catalytic property of hollow hematite nanowires by vacuum pyrolysis of β-FeOOH nanowires.[7d] However, this procedure needs vacuum equipments and precise control of pyrolysis parameters. Furthermore, morphology-controlled synthesis of magnetic materials has been a long time goal for the application in magnetic devices and biological systems.[5b,7a,7c] Simply obtaining hollow hematite nanostructures from FeOOH nanostructures will be of practical interests.

Polyoxometalates are one class of widely used inorganic metal–oxygen cluster compounds, especially as excellent catalysts owing to their unique electronic characteristics and structural robustness.[8] Recently, they were also introduced into the morphology-controlled fabrication of nanostructures employing the adsorption of POMs on nanoparticle surface and have become more and more remarkable in the rational synthesis of nanomaterials.[9] In this paper, uniform porous β-FeOOH nanorods were controllably fabricated by a polyoxometalate-assisted one-step hydrothermal process. And porous hematite nanorods could be obtained from direct pyrolysis of the β-FeOOH nanorods.

In a typical synthesis of the β-FeOOH nanorods, 10 mL of mixed solution of 0.1 M $FeCl_3$ (containing 0.002 M HCl) and 1.5×10^{-4} M PW_{12} was sealed into a Teflon-lined stainless-steel autoclave with capacity of 15 mL. The autoclave was maintained at 180 °C for 8 h. The parameters that are essential for the formation of β-FeOOH nanorods were also studied. Detailed parameters of experiments and characterizations are given in Supporting Information.[11]

Figure 1 shows typical TEM images of the β-FeOOH nanorods. The product of 0.1 M $FeCl_3$ and 1.5×10^{-4} M PW_{12} reacted for 8 h is composed of porous nanorods with diameter of about 15 nm and length of 80–120 nm as shown in Figure 1a (inset is the corresponding SAED pattern). Elongation of the reaction time to 48 h resulted in the formation of porous nanorods with the similar size but with large pores (Figure 1b). All peaks in the corresponding XRD patterns shown in Figure S1[11] can be indexed as β-FeOOH (JCPDS card 34-1266).

The porous structure of the nanorods in Figure 1a is further studied with N_2 adsorption–desorption (Figure 2). The Brunauer–Emmett–Teller (BET) surface area is 89.02 m^2/g. The nanorods have pores mainly below 25 nm with average pore diameter of 14.85 nm, indicating the porous structure and uniformity. The large calculated diameter of 14.85 nm may be due to the poor crystallinity of the nanorods.

A series of experiments indicate that concentration of PW_{12} and reaction time played a key role in the formation of the porous β-FeOOH nanorods. Only hematite submicrospheres could be obtained with a low concentration of PW_{12} (4×10^{-5} M) or without it (Figure S2[11]). The whole phase evolution under other conditions was shown in Figure S3.[11] Nanorods without pore were obtained with 1.5×10^{-4} M PW_{12} reacted for 2 h. And nanorods with a poorer wall structure could be obtained with

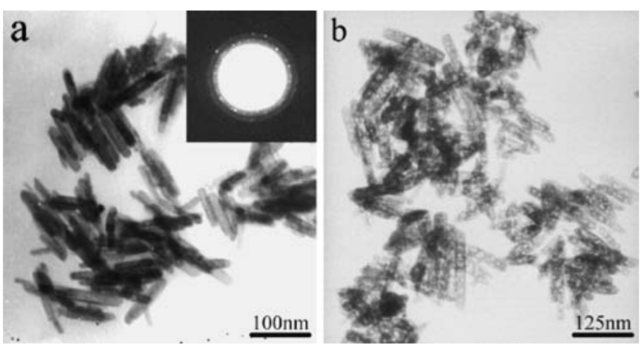

Figure 1. TEM images of the β-FeOOH nanorods with different pores prepared with 1.5×10^{-4} M PW_{12} for 8 h (a) and 48 h (b).

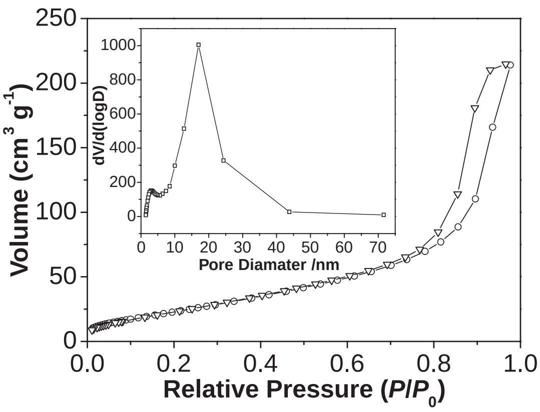

Figure 2. Nitrogen adsorption–desorption isotherm of the porous β-FeOOH nanorods. The inset is the BJH pore-size distribution curve.

4×10^{-4} M PW_{12} for 8 h. A mixture of destroyed nanorods and nanoparticles formed with 4×10^{-4} M PW_{12} for 48 h. Further increasing PW_{12} to 8×10^{-4} M resulted in the destruction of the nanorods.

Recently, Jia et al. reported rational synthesis of single-crystalline hematite nanotubes by a coordination-assisted dissolution process with $FeCl_3$ and $NH_4H_2PO_4$, in which formation of the tubular structure is attributed to the selective adsorption of phosphate ions on the surfaces of hematite particles and their ability to coordinate with Fe^{3+}.[7a] Formation of the hollow β-FeOOH nanorods may also be attributed to the selective adsorption[9] and the coordination chemistry of the POMs.[10] The growth control of iron oxide particles in the hydrolysis process of Fe^{3+} has been extensively studied, in which β-FeOOH is a favorable phase with a high concentration of chloride.[1,3b] However, in our hydrothermal process, only hematite submicrospheres could be obtained without PW_{12}, which may be ascribed to the adsorption of PW_{12} on the nanorods surface that inhibits their further growth into hematite microspheres. And the formation of porous structure of the β-FeOOH nanorods may be ascribed to the coordination-assisted dissolution process that is time-dependent (Figure 1 and Figure S3[11]).

Porous hematite nanorods were obtained by annealing the corresponding porous β-FeOOH nanorods at 450 °C.[6] Figure S5[11] shows the corresponding TG curve. Figure 3 shows TEM images of the porous hematite nanorods with the same morphology and size. The annealed nanorods can be identified as pure phase α-Fe_2O_3 (JCPDF No. 33-664) from the XRD patterns (Figure S4[11]). Bulk hematite shows weak ferromagnetic behavior above its Morin transition temperature 263 K. Recent studies indicate that magnetic properties of the hematite nanostructures strongly depend on their shape and structure.[5b,7c] Figure S6[11] shows the magnetic hysteresis loop curve of the hollow hematite nanorods measured at 300 K in which the values of remnant magnetization and coercivity are 0.00959 emu/g and 691 Oe, respectively.

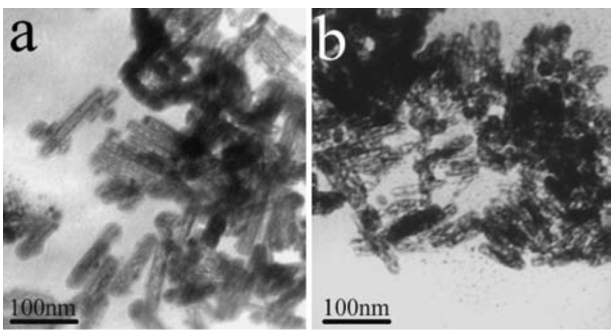

Figure 3. TEM images of the porous hematite nanorods annealed from the nanorods in Figures 1a and 1b, respectively.

In summary, uniform porous β-FeOOH nanorods were controllably fabricated by a one-step hydrothermal process. The polyoxometalate PW_{12} played a key role in the formation of the porous nanorods. Hematite nanorods with similar morphologies can be obtained by direct annealing of them. The porous nanorods with a narrow pore size distribution and no organic group may have potential uses in catalysis and lithium batteries. This convenient and low-cost process provides a rational synthesis alternative for the preparation of porous nanorods of β-FeOOH and hematite. This method may be applied to other oxides, and the work is still ongoing.

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11 Supporting information is available electronically on the CSJ-Journal Web Site, http://www.csj.jp/journals/chem-lett/index.html.

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