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The effect of hydrogen treatment on magnetic property of porous iron oxides nanorods

Hyun Gil Cha, Tae Wan Kim, Young Soo Kang*

Korea Center for Artificial Photosynthesis, Department of Chemistry, Sogang University, Seoul 121-742, Republic of Korea

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1. Introduction

Iron based one dimensional (1D) nanostructure have become the focus of intense research because of their great potential for use in magnetic information storage devices, magnetic refrigerants, oxidation/reduction catalysts, biological and environmental sensors, and biomedical applications [1-6]. One of the crucial problems in obtaining nanostructured iron oxide systems is that their high surface energy and surface/volume ratio make them be pyrophoric when it was put in contact with atmospheric air, they were burned to form hematite, α -Fe₂O₃. One of the approaches to stabilize iron nanoparticles is encapsulation in matrices such as silica or alumina [7–11]. However, this methodology is not appropriate for applications because of either a low magnetic moment (dilution with non-ferromagnetic matrices such as silica or alumina decreases this value significantly) or the presence of phases containing only iron atoms is required. Thus, the other approach to stabilize iron nanoparticles is through passivation with an oxide protective coating by exposing the particles to a well-controlled Ar/air or N₂/air mixture at room temperature. The protecting layer is generally formed by one of the four possible candidates: hematite (α -Fe₂O₃), maghemite (γ -Fe₂O₃), magnetite (Fe₃O₄), wustite (FeO), or a mixture of all these phases. These oxides often exhibit very small diameter, poor crystallinity, and impurities, which makes it hard to elucidate the nature of the oxide layer [12-14].

Recently, several studies [15,16] have been carried out to acquire knowledge of the surface composition, structural order,

* Corresponding author. E-mail address: yskang@sogang.ac.kr (Y.S. Kang).

http://dx.doi.org/10.1016/j.matlet.2014.08.043 0167-577X/© 2014 Elsevier B.V. All rights reserved. and the thickness of the oxide layer and its magnetic interaction with the core, to optimize the magnetic properties of these materials for specific applications. Therefore, we investigated the inherent electronic effects at the interface of metal and metal oxide nanostructures i.e. influence of interface crystal phase in the interaction between the iron oxide and reduced iron oxide. This was carried out by hydrogen treatment to have an effect on the exchange-bias [17] and magnetization values.

2. Experimental

Iron chloride hexahydrate (98%, Aldrich), sodium hydroxide (93%, Duksan, Korea) and 1-butyl-3-methylimidazolium chloride (98%, C-TRI, Korea) were obtained from commercial sources. All chemicals were generally regent grade and used without further purification. Porous α -Fe₂O₃ nanorods were synthesized via solution chemical route involving two steps: (1) Synthesis of α -FeOOH nanorods: 2 mmol of FeCl₃ · 6H₂O and 20 mmol of NaOH were put into 20 mL of deionized water under stirring to form a homogeneous solution. Subsequently, 6 mmol of the ionic liquid 1-nbutyl-3-methylimidazolium chloride ([BMIM][Cl]) was added into the above solution under continuous stirring. After stirring for 20 min, the mixed solution was transferred into a Teflon-lined stainless-steel autoclave with a capacity of 23 mL, sealed and heated at 423 K for 6 h without shaking or stirring during reaction time. When the reaction was completed, the autoclave was cooled to room temperature naturally. The resultant products were collected and washed with deionized water and anhydrous ethanol for several times until the solution was neutral. The final red product was dried in a vacuum at 353 K for 3 h. (2) Transformation









We demonstrated that magnetic properties of porous iron oxide nanorods obtained by hydrogenation of hematite nanorods at several annealing temperature (523, 573, 623, and 673 K). The iron oxide and reduced iron oxide layer in iron oxide nanocomposite nanorods show porous iron oxide nanorods consisted with two phase formation and crystal structure affect on the magnetism via exchange bias originated from the strong magnetic interface coupling of a ferromagnetic with an antiferromagnetic or ferrimagnetic species.

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from α -FeOOH nanorods to porous α -Fe₂O₃ nanorods by heat treatment at 623 K for 3 h in air. Different oxidation states of porous iron oxide nanorods were fabricated by annealing α -Fe₂O₃ nanorods at different temperatures for 4 h under a continuous Ar/H₂ (5%) mixture gas flowing (H1–H4). After H₂ reduction, the color of sample was changed from red to black. The prepared samples are summarized in Table 1, where the obtained iron oxide nanorods have been named as H1, H2, H3, and H4. The collected solid products stored in cyclohexane under freezer (243 K) to protect oxidation.

The morphology and size of samples (H1-H4) were observed by scanning electron microscopy (SEM, Hitachi S-430, 20 kV), and transmission electron microscope (TEM, JEM 2100F, 200 keV) images. The structural analysis of the samples was carried out by powder X-ray diffraction (XRD, Rigaku D/MAX-2500/pc) and selected area electron diffraction (SAED). Magnetic measurements were performed using a Quantum Design SQUID-VSM dc magnetometer. The hysteresis was recorded for powdered samples of porous hematite nanorods in gelatin capsule. The temperature was varied between 5 and 350 K according to a zero field cooling (ZFC) and field cooling (FC) procedure at 1 kOe, and the hysteretic loops were obtained in a magnetic field up to +70 to -70 kOe.

3. Results and discussion

The experimental observations of H1–H4 (see Table 1 for details) indicate that porous iron oxide nanorod crystal was

Table 1

Experimental condition used to produce iron oxide nanorods by hydrogenation. Ratio of crystal structure was observed from XRD data by the Rietveld refinement method using FullProf suite. Pore size/volume were measured by BET data for different heating temperatures under H_2 +Ar.

Sample	Crystal structure [%]*	Pore size [nm]	Pore volume [cm³/g]	Heating temperature for hydrogenation [K]
H1	H:M=20.2 (15):77.7(11)	21.78	1.03	523
H2	M:I=82.3 (5):17.70(19)	21.76	1.12	573
H3	M:I=41.2 (7):58.8(13)	21.74	1.30	623
H4	M:I=20.6 (7):79.4(4)	21.77	1.02	673

* H: hematite, M: magnetite, I: iron metal.

reduced by hydrogen treatment. Two reactions are occurring by a controlled heating temperature range from 523 to 673 K:

- Reduction of hematite with hydrogen

$$3Fe_2O_3 + H_2 \leftrightarrow 2Fe_3O_4 + H_2O \tag{1}$$

- Reduction of magnetite with hydrogen
- $Fe_{3}O_{4} + 4H_{2} \leftrightarrow 3Fe + 4H_{2}O \tag{2}$

Fig. 1(a) reveals a typical SEM image of the prepared porous α -Fe₂O₃ nanorods. It can be clearly seen that α -Fe₂O₃ rod-like particles with a diameter range of 48-83 nm and length range of 340-850 nm are obtained on a large scale. XRD pattern of synthesized α -Fe₂O₃ nanorods in Fig. 1(b) shows that all peaks can be indexed to the rhombohedral structure α -Fe₂O₃ (space group: *R*-3*c*, no. 167) with structural parameters of a=b=5.035 Å and c=13.74 Å, $\alpha=\beta=90^{\circ}$, and $\gamma=120^{\circ}$, which is in agreement with the literature, i.e., JCPDS card 33-0664 [18]. No characteristic peak was observed for other impurities such as α -FeOOH, Fe₃O₄, and γ -Fe₂O₃ and other metal ions. XRD patterns of H1 in Fig. 2 (a) demonstrated the mixed crystal structures consisted with α -Fe₂O₃ and Fe₃O₄ phases (JCPDS card no. 19-0629) [19]. In case of H2 and H3, XRD patterns in Fig. 3(b and c) matched with Miller indices (220), (311), (400), (422), (511), and (440) planes come from cubic crystal structure according to Fe₃O₄ and additional two peaks from XRD pattern are also found. These can be indexed to α-Fe according to the data. (JCPDS card no. 85-1410) [20]. A small amount of α -Fe was consisted in sample H2. As increasing annealing temperature from 573 to 623 K, the portion of α -Fe in H3 also increases (Fig. 2(c)). The XRD peaks of Fe₃O₄ phase are almost disappeared but still remained as increasing reduction temperature corresponding to α -Fe in H4 (Fig. 2(d)).

Figs. 3 and 4 are representative SEM and TEM images of H1–H4 (α -Fe₂O₃@Fe₃O₄ and Fe₃O₄@Fe). It reveals that the size and morphology are still sustained after annealing at 523, 573, and 623 K under Ar+H₂ (5%) condition except H4 (673 K). It is clearly seen that the nanorods have an average diameter of ~60 nm and length ~650 nm. The SAED pattern shows that the space between neighborhood lattices is 0.37 nm and 0.21 nm, corresponding to (012) planes of α -Fe₂O₃ (see I line) and (400) planes of Fe₃O₄ (see II line), respectively. This indicates that the nanorods are consisted with two crystal phases such as α -Fe₂O₃ and Fe₃O₄, which was corresponded to XRD data (Fig. 2(a)). It means that some part of porous α -Fe₂O₃ nanorods were transformed



Fig. 1. SEM image and XRD spectrum of synthesized α-Fe₂O₃ nanorods.

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