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Microscopic studies of a SnO_2/α-Fe_2O_3 architectural nanocomposite using Mössbauer spectroscopic and magnetic measurements

Naoaki Hayashi [a,*], Shigetoshi Muranaka [a], Shinpei Yamamoto [b], Mikio Takano [b,1], Dong-Feng Zhang [c], Ling-Dong Sun [c], Chun-Hua Yan [c]

[a] Graduate School of Human and Environmental Studies, Kyoto University, Yoshida-nihonmatsu, Sakyo, Kyoto 606-8501, Japan
[b] Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan
[c] State Key Lab of Rare Earth Materials Chemistry and Applications, & PKU-HKU Joint Lab in Rare Earth Materials and Bioinorganic Chemistry, Peking University, Beijing 100871, China

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ABSTRACT

A SnO_2/α-Fe_2O_3 architectural nanocomposite, which was evidenced as SnO_2 nanorod arrays assembled on the surface of α-Fe_2O_3 nanotubes in our previous study, was investigated microscopically by means of Mössbauer spectroscopic and magnetic measurements. It was found for the SnO_2 nanorods that Fe^{3+} ions substituted slightly to $Sn_{0.998}Fe_{0.002}O_2$. Concerning the α-Fe_2O_3 tubes, the Morin transition, which was completely suppressed in the mother, SnO_2-free α-Fe_2O_3 nanotubes, was found to be recovered locally. We speculate that it takes place in the interface area as a result of structural modification needed for the connection with the SnO_2 nanorods.

1. Introduction

As promising candidates for nanodevice construction, nanocomposites with complex structures have become a research focus in recent years. Mentioning some examples, ZnO/In_2O_3 hierarchical structures with different symmetries [1], GaP/GaP and GaP/GaAsP tree-like arrays [2], Cd*E* (E = S, Se, and Te) heterostructures with linear and branched morphologies [3], and ZnO- and TiO_2-based nanoblocks assembled into brush-like architectures [4] have been reported. Spontaneous or designed organization of building blocks is of the greatest interest in these studies, but it should be kept in mind that the blocks themselves may be more or less modified through the organizing processes.

The magnetism of α-Fe_2O_3 is quite interesting [5]. A drastic spin flipping takes place at $T_M = 263$ K, which is called the Morin transition. In the high-temperature (high-T) phase, the atomic spins lie within the (001) plane of the hexagonal structure, while they are aligned perpendicular to the plane in the low-T phase. The high-T phase is a spin-canted weak ferromagnet, while the low-T phase is a simple antiferromagnet without any spin canting. Of special interest from the viewpoint of nanoscience is that the Morin transition can be suppressed, or the weak ferromagnetism can be preserved down to low temperatures by decreasing the particle size, for example [6]. Driven by potential physical and chemical applications and also as a challenge in morphology control approach, SnO_2 nanorods were assembled on the surface of hexagonal α-Fe_2O_3 nanotubes and their structural matching was studied as reported previously [7]. In this paper, we will report the magnetism and related microstructural aspects studied by means of Mössbauer spectroscopic and magnetic characterizations.

2. Experimental

The detailed assembling process is described elsewhere [7]. Briefly, α-Fe_2O_3 nanotubes grown along the c-axis were first synthesized by a coordination-assisted dissolution process [8], and were then dispersed in a $Sn(OH)_6^{2-}$-containing solution and converted to the SnO_2/α-Fe_2O_3 hierarchical architectures by a hydrothermal process.

The compositional analysis of the product was carried out with inductively coupled plasma (ICP, Vario EL, Elementar), and the morphology was investigated by scanning electron microscopy (SEM, DB-235 focused ion beam system). Magnetic measurements were carried out using a SQUID magnetometer (Quantum Design, MPMS2) on field cooling (FC) and also on heating after zero-field cooling (ZFC) at a magnetic field of 100 Oe in a temperature range

* Corresponding author.
E-mail address: hayashi@sou.mbox.media.kyoto-u.ac.jp (N. Hayashi).
[1] Present address: Institute for Cell-Material Integrated Sciences, Kyoto University, c/o Research Institute for Production Development, 15 Morimoto, Shimogamo, Sakyo, Kyoto 606-0805, Japan.

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of 5–300 K. The field dependence was studied at certain fixed temperatures up to 10 kOe. Mössbauer spectra were measured in transmission geometry using $^{57}Co/Rh$ and $Ca^{119m}SnO_3$ as the γ-ray sources. The velocity scale and the isomer shift were determined by using α-Fe and $CaSnO_3$ as the control samples, and the resulting spectra were least-squares-fitted using the Lorentzian function.

3. Results and discussion

Fig. 1 shows a typical SEM image of the SnO_2/α-Fe_2O_3 architecture. It can be seen that the composites are essentially of 6-fold symmetry with secondary SnO_2-nanorod arrays of 10–15 nm in diameter and 70–100 nm in length. The original α-Fe_2O_3 nanotubes were 90–100 nm in outer diameter, 40–80 nm in inner diameter, and 250–400 nm in length. Based on an HRTEM characterization, the interfacial orientation relationship was determined as SnO_2 (101)//α-Fe_2O_3 (110) [7].

Fig. 2(a) shows the ^{57}Fe Mössbauer spectra, which consists of components characterized by the parameters listed in Table 1. At room temperature, the sextet (component II) coincides with the pattern of the high-*T* phase of normal α-Fe_2O_3, while the doublet, component I, was the new presence that had not been detected from the mother α-Fe_2O_3 nanotubes. This component could not be attributed to the formation of very fine, superparamagnetic α-Fe_2O_3 particles because the quadrupole splittings (QSs) of this doublet are considerably larger than expected and also because the previous TEM observations did not detect such particles anywhere in the sample, either in the SnO_2/α-Fe_2O_3 interface region or within the SnO_2 nanorods [7]. According to the report by Castro et al. on 2–30 mol% Fe-doped SnO_2 nanoparticles synthesized by a polymeric precursor method [9], the spectrum generally consisted of a pair of paramagnetic doublets having different QSs of ~0.7 and ~1.6–1.2 mm s^{-1}, the smaller QS-component being assigned to Fe^{3+} ions distributed in the inner part of the SnO_2 crystal, and the larger QS-component to Fe^{3+} ions concentrated in the surface area where the SnO_2 lattice was distorted as a result of the segregation of excess Fe ions beyond the solubility limit. Therefore, the portion of the former doublet

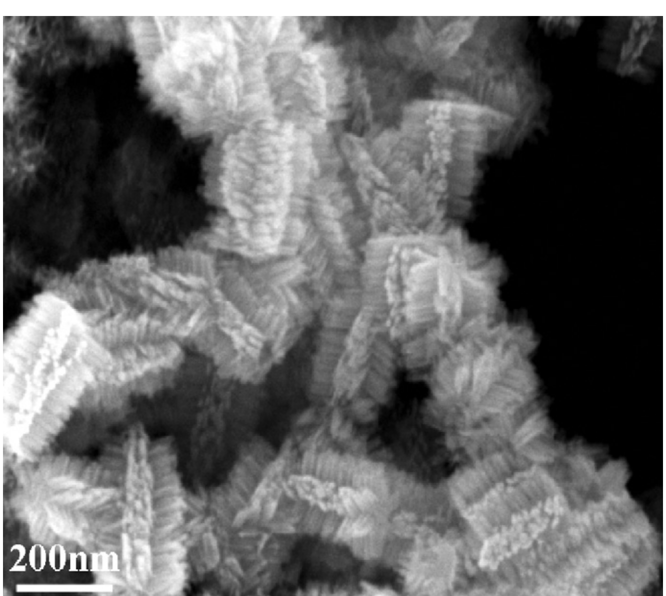

Fig. 1. SEM image of the SnO_2/α-Fe_2O_3 architecturral nanocomposite.

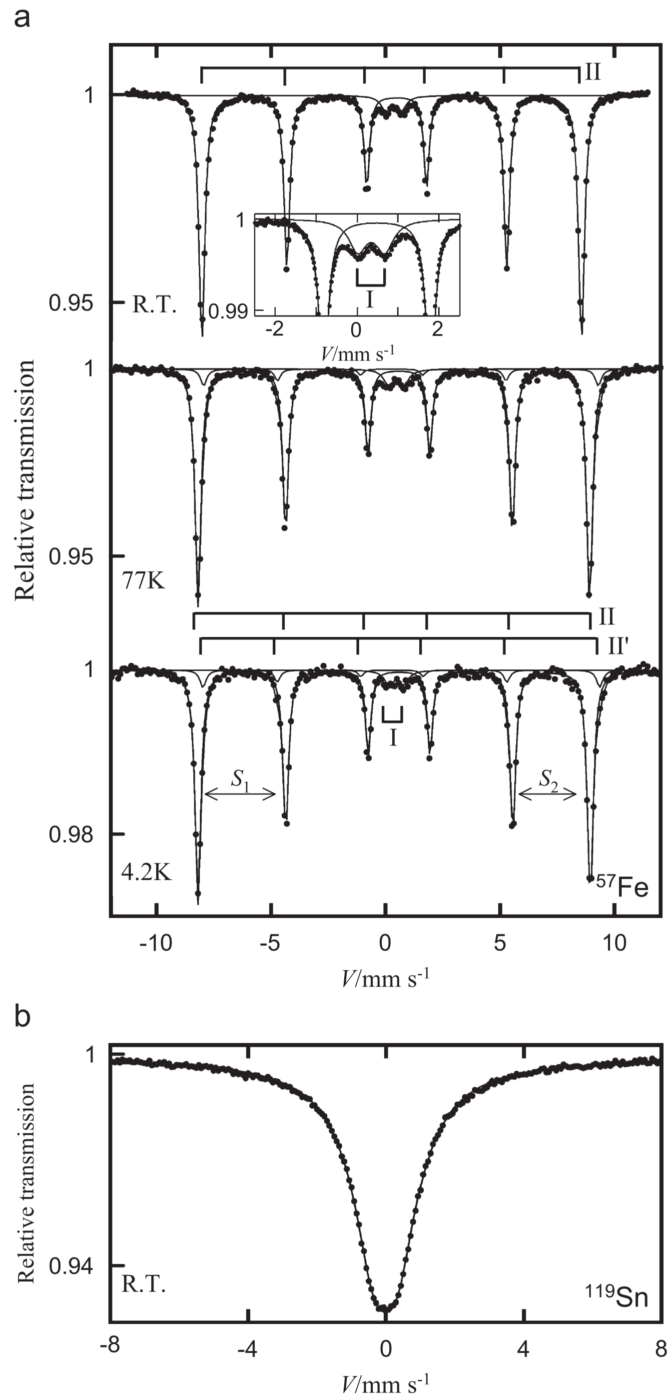

Fig. 2. (a) ^{57}Fe Mössbauer spectra of the SnO_2/α-Fe_2O_3 architectural nanocomosite. Inset shows the spectrum expanded in a narrow velocity range. (b) ^{119}Sn Mössbauer spectrum of the SnO_2/α-Fe_2O_3 architecture.

decreased with increasing Fe concentration. Concerning the present case, all the Fe ions may be concluded to be dissolved in the SnO_2 rods homogeneously, without being segregated locally, considering the facts that the single doublet has a relatively small QS of ~0.65 mm s^{-1} and that the Fe content is so small as ~0.2 mol% as will be described later. It is very likely that the original α-Fe_2O_3 nanotubes partially dissolved and the ferric ions formed were incorporated into the growing SnO_2 nanorods in the hydrothermal assembling process. Fig. 2(b) shows the ^{119}Sn spectrum at room temperature, which has been assigned to the