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Magnetic behavior of Fe_3O_4 nanostructure fabricated by template method

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Abstract

One dimensional nanostructured magnetic materials are interesting because of their enhanced magnetic properties and potential applications such as information storage and biosensor. To prepare uniform nanostructure with controlled diameter, we have utilized porous anodic alumina template (AAT). The nanowire arrays are prepared by incorporation of monosized 10 nm magnetite nanoparticles into AAT, accompanied by thermal annealing. Transmission electron microscope and field emission scanning electron microscope showed that the nanoparticles were changed to the polycrystalline nanowire phase in AAT. The annealing procedure, which improved crystallinity of the nanoparticles and caused clustering of nanoparticles into nanowires, had a dramatic effect on their magnetic properties. For example, coercivity measured at cryogenic temperature increased from 350 to 8000 Oe after annealing. Clustering of the nanoparticles had also significant effect on the Faraday rotation spectra of the material. For example, inter-valence charge transfer transition of isolated magnetite nanoparticles vanished in wire assembles. It might be due to significant improvement of crystallinity of the wires, which might consists of enlarged Fe_3O_4 nanoparticles lined up in quasi-1D wires.

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In recent years, research on one-dimensional (1D) nanostructured materials, such as nanorods and nanowires, has been one of the most interesting and remarkably advanced fields of materials science. It was stimulated by the fundamental interest in these materials but also by the potential applications of the fabrication of nanodevices [1]. In particular, ordered 1D magnetic nanowire arrays have been extensively exploited for their potential utilization in high-density magnetic recording and spintronics [2]. It has been well established that for magnetic nanowires, their shape magnetic anisotropy affects the shape of the magnetic hysteresis loops. When measured in a field applied parallel to the wire's axis the hysteresis loop is more rectangular than that of isotropic quantum dots. Therefore, the fabrication of 1D nanostructured magnetic nanowires remains a challenge to prepare free-standing 1D magnetic nanowires in high yield.

To date, various approaches have been developed for the preparation of 1D magnetic materials, one of the most progressive improvements is using the anodic alumina template (AAT) [3]. Nanowires prepared in such templates present an assembly of geometrically and chemically uniform objects, in terms of diameter, length, and composition. In the present work, we applied the concept of building blocks by organizing Fe_3O_4 nanoparticles in a template to fabricate nanowire arrays.

Hexagonally ordered porous AAT was formed by anodization process as described previously [3]. Fe_3O_4

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nanoparticles were produced by a wet chemical technique that involves organic solution-phase decomposition of the iron precursor at high temperature [4]. To prepare Fe_3O_4 nanowire, 10 mL of Fe_3O_4 nanoparticle solution was filled by vacuum suction within alumina template under applied fields. To form the nanowire, annealing was performed under Ar gas (99.999%) in quartz tube at 600 °C for 2 h.

The structure of the Fe_3O_4 nanomaterials was characterized by electron microscopy and X-ray diffraction spectrometry. The XRD patterns indicated a phase of cubic spinel-type structure. The average particle size calculated by the Scherrer formula is about 10 nm, which is consistent with the transmission electron microscope (TEM) image (Figs. 1(a) and (b)). Fig. 1(c) is the TEM image of the sample prepared after annealing and the measured diameter of the nanowires corresponds closely to the pore diameter. The TEM diffraction pattern, shown in the inset of Fig. 1(c), indicates that the Fe_3O_4 nanowire is polycrystalline phase. The Fe_3O_4 nanowire arrays were uniformly assembled into the ordered nanochannel of AAT.

Magnetic properties were studied using a Quantum Design MPMS 5S SQUID magnetometer at 5 and 300 K. Magnetic field was applied along the AAT pore direction. Magnetic hysteresis loops for the nanoparticles before and after annealing are shown in Fig. 2. It is worth to note that the particles before annealing reveal superparamagnetic behavior at 300 K. With temperature decreasing ferromagnetic behavior appears. This is due to the blocking process of the superparamagnetic particles [5]. Annealing at 873 K for 2 h causes a dramatic change of the shape of the hysteresis loops. The coercivity increases to 350 Oe at 300 K and 8000 Oe at 5 K. Also the magnetization at low temperature is not fully saturated for annealed samples. Another interesting fact is the extremely high coercive field. It is know that Fe_3O_4 in bulk is a ferrimagnet with coercivity 115–150 Oe [5]. The coercivity of the bulk material is governed by domain wall movements. Because of the small size of aggregates and their complex structure formation of domains will be restricted compared to the bulk. Therefore, magnetization rotations are expected to dominate the magnetization processes in nanoparticles. Improved crystallinity of the annealed wires gives rise to enhancements of the anisotropy and the coercivity. Also the shape anisotropy of the nanowires contributes to increase of the coercivity at room temperature. Exceptionally large coercivity at low temperature can be interpreted in terms of the spin structure of the nanoparticles following the model proposed by Kodama et al [6]. They reported extremely high coercivity values for spinel type $NiFe_2O_4$ nanoparticles [6]. Also, at low temperature, the magnetization did not saturate in fields up to 160 kOe. Such behavior was explained using a model that takes into account interplay of the magnetic properties of ferromagnetic core and spin-glass-like disordered states on the surface of the particles. Surface spin disorder arise from broken exchange bonds and reduced coordination on the particle surface. At low temperatures, the surface spins freeze in spin-glass phase, having random orientations with respect to the core magnetization. The magnetic coupling between frozen surface spins and the core spins gives rise to huge coercivity.

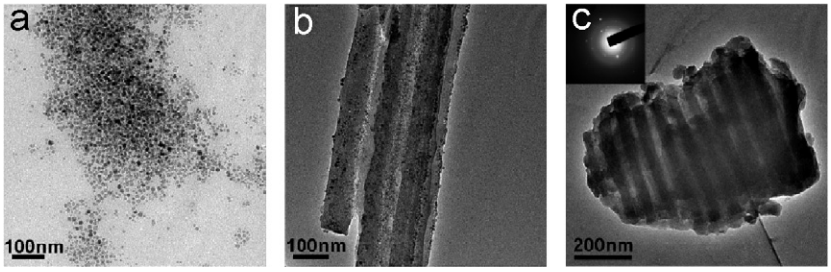

Fig. 1. TEM image of (a) Fe_3O_4 particles, (b) Fe_3O_4/AAT composite structure before annealing and (c) Fe_3O_4/AAT composite structure after annealing (inset shows TEM diffraction pattern).

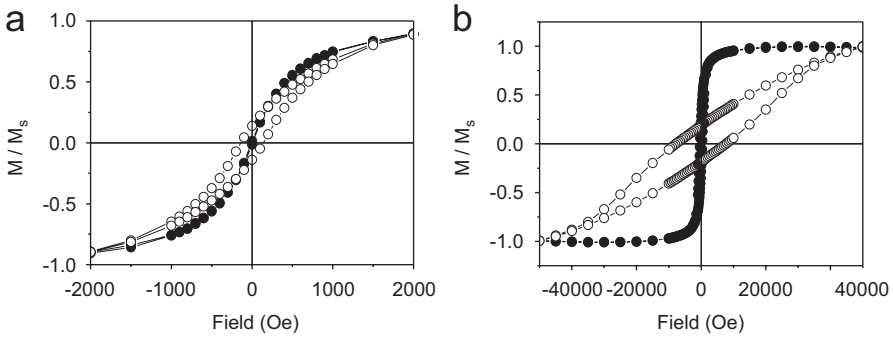

Fig. 2. Hysteresis loop of Fe_3O_4/AAT composite structure before (a) and after annealing (b), measured at 300 K (solid circle) and 5 K (open circle).

Some similarities with magnetic properties have been observed in magneto-optical studies of formed nanowires, namely Faraday rotation. In this study, the presence of inter-valence charge transfer (IVCT) peak at 465 nm for 10 nm incorporated nanoparticles is seen. This is in consistence with our previous studies of Fe_3O_4 nanoparticles incorporated into polymer film [7]. The annealing at 873 K of magnetic nanoparticles in AAT membrane results in a significant reduction of IVCT peak intensity and appearance of some sharp bands in the UV range of spectrum. Previously, it was shown that IVCT peak in bulk Fe_3O_4 was in the range 600–650 nm [8]. The observed result, taking into account the essential particles growth at high temperature can be interpreted by the formation of agglomerates larger than initially incorporated nanoparticles, which are physically confined into AAT channels. Moreover, the surface states of each building block of polydisperse magnetic rod can be strongly disordered and together with anisotropy of quasi-1D geometry is responsible for observed drastic changes in magnetic properties of formed wires.

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