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ScienceDirect
Solid State Communications 141 (2007) 431–435
solid state communications
www.elsevier.com/locate/ssc

Anomalous ferromagnetic behavior of CuO nanorods synthesized via hydrothermal method

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Received 4 December 2006; accepted 5 December 2006 by E.V. Sampathkumaran
Available online 20 December 2006

Abstract

Copper monoxide (CuO) nanorods of 30–40 nm in diameter and 100–200 nm in length were successfully synthesized using a hydrothermal reaction method in the presence of sodium citrate. On the basis of the morphology observation and X-ray diffraction patterns of the samples, a possible growth mechanism of the CuO nanorods was proposed. The magnetic properties of CuO nanorods were studied using a SQUID magnetometer and a vibrating sample magnetometer. It was interesting to note that the as-synthesized CuO nanorods showed an anomalous ferromagnetic behavior. The coercive force (H_c) for the CuO nanorods at $T = 5$ K and $T = 300$ K were estimated to be 331.39 and 175.88 Oe, respectively. The anomalous ferromagnetic behavior of the as-synthesized CuO nanorods was discussed in terms of the effect of the peculiar morphology.

PACS: 75.75.+a; 76.75.+I; 75.30.Gw; 81.16.Be

Keywords: B. Chemical synthesis; B. Nanorods; D. Exchange and superexchange

1. Introduction

Copper monoxide (CuO) based materials are well known due to their relevance to high-temperature superconductivity and semiconducting antiferromagnetism. CuO is a narrow band gap p-type semiconductor and has been recognized as an industrially important material for a variety of practical applications, such as catalysis, batteries, magnetic storage media, solar energy conversion, gas sensing and field emission [1–5]. In recent years, there has been considerable effort in the fabrication of nanostructured CuO with various morphologies to enhance its performance in currently existing applications [6–14]. Among the various methods developed for fabrication of nanostructured CuO, the hydrothermal process has been considered as the most promising route due to its advantages of low temperature, simplicity and large-scale production [6,9].

Moreover, recently as an important biological ligand for metal ions, citrate has been widely employed as a reductant and capping agent in synthesis of elemental Ag, Au, and Ag–Au alloy nanoparticles [15]. It also serves as a shape controller and stabilizer in the synthesis of $Ni(OH)_2$, calcite, coated CdSe colloids, doughnut-shaped ZnO microparticles, titanium and CuI crystals [16]. In this study, sodium citrate will be employed for the first time to synthesize CuO nanorods using the hydrothermal process.

The magnetic nanostructures are of great interest mainly because of their diverse industrial applications. CuO occupies a special place among the semiconductor 3d oxides because it has some unique physical properties. Unlike NiO, CoO, FeO and MnO, CuO has a low symmetry monoclinic crystal structure and a magnetic susceptibility temperature behavior that is unusual for 3d antiferromagnets. In nanoparticles with an antiferromagnetically ordered core, the surface spins are expected to dominate the measured magnetization because of their lower coordination and uncompensated exchange couplings [17]. Thus, considerable variations of the magnetic properties with change in particle sizes are expected because

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0038-1098/$ - see front matter
doi:10.1016/j.ssc.2006.12.005

of the associated changes in the relative number of surface spins. As a result, the weak ferromagnetic behavior of CuO nanoparticles with a diameter < 10 nm has been observed whereas the antiferromagnetic behavior of the particles with size ≥ 10 nm resembles that of bulk CuO [17–20]. It seems that the diameter of 10 nm is a critical particle size for nanostructured CuO to show ferromagnetic behavior. On the other hand, it is well known that the magnetic properties of nanostructures depend not only on particle size but also on particle anisotropy for one-dimensional nanostructures [21]. Study of the magnetic behavior of one-dimensional CuO nanorods is thus one of the objectives of the present work and the nanorods would be expected to show anomalous ferromagnetic behavior to examine the effect of particle aspect ratio.

In this paper, the hydrothermal reaction method is employed to synthesize CuO nanorods in the presence of sodium citrate. The influence of reaction time and temperature on the microstructure of the CuO nanorods is examined. The magnetic susceptibilities of the as-synthesized CuO nanorods in the 5–400 K range were studied. Their magnetic properties at room temperature were also investigated using a vibrating sample magnetometer. It is interesting to note that the CuO nanorods with a much larger diameter than 10 nm exhibit anomalous ferromagnetic behavior which has never been reported previously, demonstrating the effect of their peculiar morphology.

2. Experimental

2.1. Preparation

The chemical reagents including $CuSO_4 \cdot 5H_2O$, sodium citrate ($C_6H_5O_7Na_3 \cdot 2H_2O$) and sodium hydroxide (NaOH) were of analytical grade and used without further purification.

CuO nanorods were synthesized through the hydrothermal process in the presence of sodium citrate. The synthesis process of CuO nanorods is as follows: 1.3 mmol of $CuSO_4 \cdot 5H_2O$ and 1.3 mmol sodium citrate were dissolved in 40 ml of distilled water, and the solution was kept for 15 min under constant stirring. Then 5.3 mmol NaOH were added to the above mixture solution. After 2.5 h constant stirring, the final solution was transferred to a 50 ml Teflon-lined autoclave. The autoclave was sealed into a stainless steel tank and kept at the experiment condition. Afterwards, the reactor was cooled to room temperature naturally. The resulting samples were collected and washed with de-ionized water and dried at 50 °C in air. The effect of reaction temperature (100–180 °C for 12 h) and reaction time (20 min to 12 h at 160 °C) on the CuO products was studied.

2.2. Characterization

X-ray diffraction (RINT 2000 Wilder-angel goniometer with Cu Kα radiation and $\lambda = 1.5406$ Å) and energy dispersive X-ray spectroscopy (SEM-EDS, EDAX, PV9100) were used to characterize the molecular structure of the CuO sample.

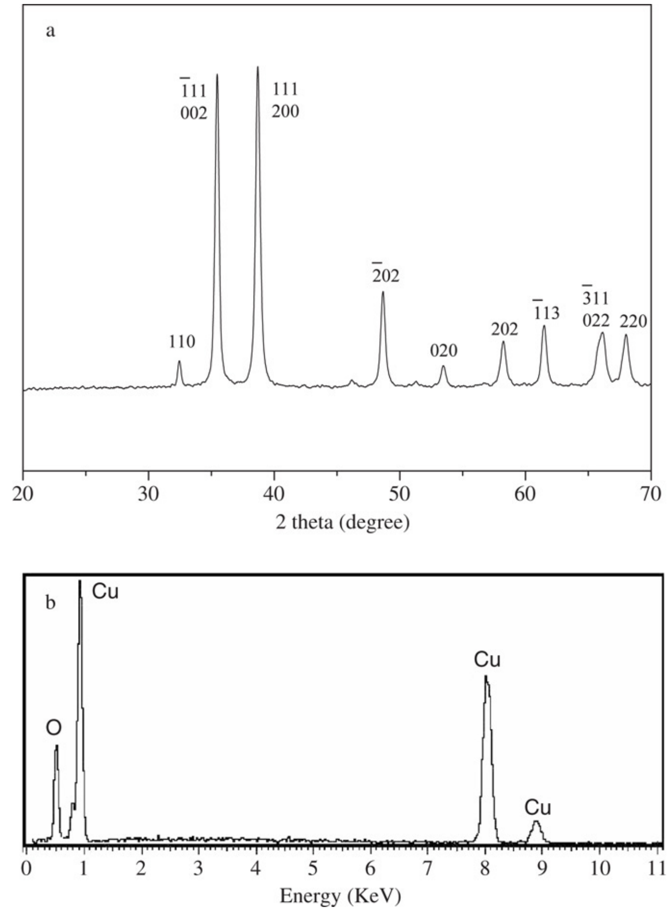

Fig. 1. Structural characterization of the as-synthesized CuO nanorods: (a) XRD and (b) SEM-EDS element analysis.

Morphology of the CuO sample was measured by transmission electron microscopy (Hitachi H-600 with an accelerating voltage of 200 kV). Magnetic properties of CuO nanorods in the 5–400 K were measured using a commercial Quantum Design SQUID magnetometer under the zero-field-cooled (ZFC) and field-cooled (FC) conditions, respectively. A vibrating sample magnetometer was also employed to measure the magnetic properties at room temperature.

3. Results and discussion

3.1. Crystal structure, morphology and formation mechanism

The structure and chemical composition of the CuO samples were measured by means of XRD and SEM-EDS, where synthesis conditions are as follows: reaction temperature = 160 °C and reaction time = 12 h. As shown in Fig. 1a, all peaks in the XRD patterns of the CuO are consistent with the JCPDS (5-0661) data of the copper oxide with a monoclinic phase [22]. The atomic ratio of Cu to O was estimated to be 1:1 by SEM-EDS elemental analysis (Fig. 1b).

The effect of the reaction temperature on morphology of the resulting CuO was examined. As shown in Fig. 2a–d, the morphology of the products is highly dependent upon the hydrothermal temperature. At 120 °C (Fig. 2a), there are many large nanoplates and few nanorods in the product. As