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NiO core–shell nanostructure with ferromagnetic-like behavior at room temperature

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ABSTRACT

We report on ferromagnetic-like magnetic properties, at room temperature, of spherical nickel oxide core–shell nanoparticles synthesized by sol–gel combustion method. The sample is characterized by using transmission electron microscopy (TEM), selected electron area diffraction (SAED), energy-dispersive X-ray spectroscopy (EDX), Raman spectroscopy (RS) and superconducting quantum interference device (SQUID) magnetometer. The SAED, EDX and RS show high quality and purity of the sample. The TEM images point to core–shell NiO nanostructure with a well crystallized NiO core and surface disorder shell. The size of the nanoparticles of about 5 nm and thickness of the surface shell below 1 nm are estimated from the TEM and HRTEM measurements. The measurements of the magnetization reveals ferromagnetic-like behavior of the sample at room temperature with remanent magnetization $M_r = 0.0087$ emu/g and coercive field $H_C = 115$ Oe. These magnetic properties are quite different than in NiO bulk materials and uncommon for nanosized NiO materials. These results also indicate that the synthesized NiO core–shell nanostructure is suitable for spin-valve applications.

1. Introduction

The 3d transition-metal oxides (e.g. NiO, Fe_2O_3, Fe_3O_4, Mn_3O_4, CoO and Co_3O_4) exhibit a wide variety of magnetic structures, including canted, disordered, ferrimagnetic and antiferromagnetic. Recently, there has been renewed interest in antiferromagnetic NiO nanoparticles due to their novel properties and applications [1–36]. NiO has been extensively reported in the literature. Very few reports deal with magnetic studies of NiO nanoparticles with ferromagnetic-like magnetic features at room temperature, however [2,4,6,14,28,29,35].

NiO is an intriguing magnetic material which in bulk exhibits antiferromagnetic properties below Neel temperature $T_N = 523$ K [37]. When NiO is prepared in nanoparticle form novel magnetic properties have been observed [10–38]. This possibility of new and distinct magnetic properties motivates our investigation of these NiO nanoparticles. Furthermore, a detailed understanding of the chemical and magnetic structure of NiO nanomaterials is important for understanding the behavior of magnetic nanomaterials and has widening their use. Different models have been proposed to explain this weak ferromagnetism in small antiferromagnetic nanoparticles [38]. It has been proposed that surface and finite size effects in NiO nanoparticles are the cause of novel and interesting magnetic properties [10–38].

All of applications of magnetic nanoparticles require a specific particle size, morphology and the narrow particle size distribution, i.e., the particles should have uniform physical properties. However, producing particles with the desired size, acceptable size distribution and without particle agglomeration has been a constant problem. The preparation of antiferromagnetic nanomaterials with ferromagnetic-like properties at room temperature is very important for applications in magnetic devices. Recently, various methods for preparing NiO nanomaterials have been developed such as solvothermal method [1,35], electron beam evaporation [2], hydrothermal [3,10,29], organic solution-phase reaction [4], sonochemical method [5], metallographic [6], anodic arc plasma method [7], sol gel [8,14,27], sol–gel spin-coating method [9], infrared heating evaporation [11], thermal decomposition [12,22,26,28], polymer precursor [13], magnerton sputtering method [16],

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combustion [17], co-precipitation [23], sol–gel combustion [25,31], electrospinning method [34] and precipitation [36].

The present work relates to a method for synthesizing monodisperse nanoparticles of NiO with peculiar magnetic properties. The results show high purity spherical NiO nanostructures with ferromagnetic-like magnetic properties at room temperature with coercivity $H_C = 115$ Oe and remanent magnetization $M_r = 0.0087$ emu/g. The final goal of this investigation is to establish interesting magnetic characteristics of NiO nanoparticles, which may lead to applications in spin-valve systems.

2. Experimental

The NiO nanoparticles in a silica matrix were prepared by utilizing sol–gel combustion (SGC) method. The starting point for the synthesis of a targeted system was a solution prepared by mixing tetraethoxysilane (TEOS, Aldrich), distilled water, ethanol, nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$, Aldrich) and citric acid monohydrate (CA, Aldrich). Nickel nitrate was added to the initial solution in such a proportion as to provide the 30 wt.% of nickel oxide in the final dried powder. The mole ratios of ethanol to TEOS, water to TEOS and nickel nitrate to CA were 4:1, 12:1, and 1:1.1, respectively. The pH of the mixture was adjusted to about 2.5 after an hour of stirring. The sol was dried for about 20 h at 50 °C temperature. Afterward, the gel was heated in air at 500 °C for 2 h and autoignited automatically.

Element components were determined using energy-dispersive X-ray spectroscopy (EDX, Oxford Instruments, INCA PentaFETx3) provided in the scanning electron microscope (SEM, JEOL 840 A). The nanostructure, size and selected electron area diffraction of the nanoparticles were observed by a transmission electron microscope (JEOL 2010 F) operating at 200 kV. The room temperature measurements of the Micro-Raman spectra of the hematite (NiO) were obtained using the Chromex Micro Raman 2000 single-grating spectrometer system. The excitation source was $\lambda = 532$ nm doubled Nd:YaG laser. The laser power on the sample was about 1 mW with the 40× microscope objective which prevented sample degradation. Acquisition times were 250 s with five exposures on the average. The spectral resolution was about 2.4 cm^{-1}. Magnetic measurements were performed on a commercial Quantum Design MPMS-XL-5 SQUID-based magnetometer in an applied DC fields up to 5 T.

3. Results and discussion

In order to confirm crystallization and the phase composition of the sample, selected area electron diffraction (SAED) was carried out by TEM. The SAED pattern shown in Fig. 1(a) consists of diffraction spots/rings that were indexed in correspondence with the NiO structure. Fig. 1(b) shows the EDX spectrum of the NiO/SiO_2 nanostructure, where Ni, Si and O are the main components. Their atomic ratios are in good agreement with those expected from synthesis conditions. The C, Zn, Cu and Au peaks in the EDX spectrum originate from the holder and paste (Dotite XC-12) which was used in the preparation of the sample for EDX observation. These peaks are not labeled in the Fig. 1(b). No other impurities have been identified. Raman spectroscopy is very sensitive to the microstructure of nanocrystalline materials and it is also used here to clarify the structure of the NiO nanostructure. Raman spectrum of the sample (Fig. 2) shows two obvious Raman peaks located at around 500 and 1050 cm^{-1}. The Raman shifts are consistent with those of nanosized NiO which is also in agreement with the SAED measurements [2,3,34].

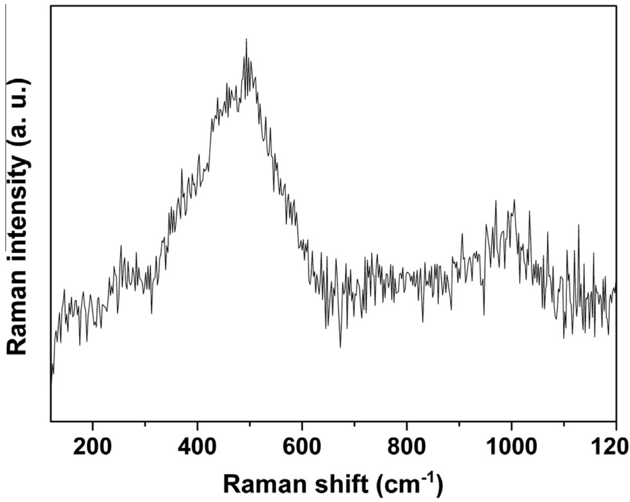

Fig. 2. Raman spectrum of as-synthesized NiO/SiO_2 nanostructure.

The structure of the sample was further characterized by TEM measurements. The TEM micrographs (Fig. 3) indicate formation of spherical nanoparticles of an average size of about 5 nm, and it also shows their uniform size and shape. The TEM images did not show evidence of significant particle agglomeration. Fig. 4 shows the HRTEM images of the sample. This HRTEM examination clearly reveals the nanoparticle core–shell nanostructure. It can be seen from Fig. 4 that the particle has a defect-free core and a disordered surface layer. The thickness of the disordered surface shell can be estimated from the HRTEM images. We obtained a value of $t \approx 0.6$ nm. Moreover, the clear lattice image indicates a high crystallinity and single-crystalline nature of the core–shell NiO nanostructure (Fig. 4). A lattice spacing of 0.24 nm for the (1 1 1) planes can be readily resolved.

A surprising magnetic property was observed such as magnetic hysteresis at room temperature, i.e., the coercivity field of $H_C = 115$ Oe and remanent magnetization $M_r = 0.0087$ emu/g, which is quite different than in NiO bulk material [37]. Observation of hysteresis and coercivity in magnetic isotherms at room temperature indicates the presence of a ferromagnetic component associated with magnetic ordering [10–36,38]. Measurements of the magnetization as a function of the applied field at 300 K are shown in Fig. 5. The continuous increase of the magnetization should be noticed even at the largest field ($H = 5$T), indicating a superposition of an antiferromagnetic core and surface effects. The magnetization and coercivity in the NiO nanoparticles are due to the disorder surface shell and uncompensated surface spins [10–36,38]. This

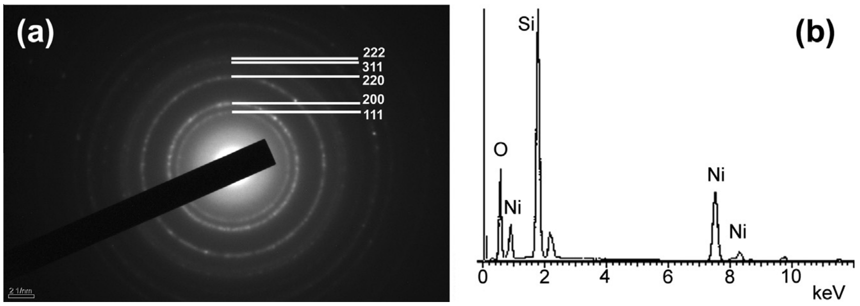

Fig. 1. (a) SAED pattern of the NiO/SiO_2 nanostructure; (b) EDX spectrum of the sample.