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Structure and magnetic properties of Co_3O_4/SiO_2 nanocomposite synthesized using combustion assisted sol-gel method

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ABSTRACT

This paper reports on novel cobalt oxide nanoparticles (NPs) embedded in an amorphous silica (SiO_2) matrix, synthesized using a modified sol-gel method. SEM and TEM images show as-synthesized particles to aggregate in the shape of spheres and less than 5 nm in size, while XRD and SAED analysis both point to well crystallized cubic spinel cobalt oxide phase with an average crystallite size of about 4.6 nm. Raman analysis confirms the formation of cobalt (III) oxide (Co_3O_4) NPs. As-synthesized Co_3O_4 single-nanocrystallite has magnetic properties that correlate with finite size effects and uncompensated surface spins. Temperature dependence of ZFC-FC magnetization curves reveals a sharp peak around 10 K which corresponds to the blocking temperature. A Curie-Weiss behavior of magnetization above 25 K shows lower Néel temperature of the sample compared with its bulk counterpart $T_N = 40$ K (possibly due to crystal defects and nano-dimensionality of the particles). The magnetic measurements exhibit high magnetization at low temperatures ($M_S = 54.3$ emu/g) which can be associated with random canting of the particles' surface spins and uncompensated spins in the core which tends to interact ferromagnetically at low temperatures. The initial magnetization curve falls out from the hysteresis loop at 5 K, which could be also the effect of surface spins.

1. Introduction

Low-dimensional magnetic materials show better properties for industrial applications compared to their bulk forms, for example like when used in data storage, spintronics, biomedicine or telecommunications [1]. Spinel cobalt oxide (Co_3O_4) nanomaterial stands out among others because of its multifunctional applications: as heterogeneous catalysts, solid-state sensors, anode materials in Li-ion rechargeable batteries, in electrochromic devices, solar energy absorbers, pigments etc. [1–6]. Co_3O_4 nanostructures have been synthesized so far via a variety of methods such as precipitation, sol-gel, combustion, solvothermal, hydrothermal [1–13], all in attempt to control its particle size and morphology i.e. its properties. The combustion assisted sol-gel method has allowed so far considerably faster synthesis of nanoparticles, especially magnetic NPs with higher magnetization and particle magnet moment, compared to NPs obtained by a conventional sol-gel method [14,15]. It is desirable to embed magnetic NPs in an amorphous matrix to prevent agglomeration since the investigation and understanding of magnetic NPs properties is much simpler when there is weakly or no interaction between the particles. Silicon dioxide (silica) is especially suitable as matrix for this purpose because of its nontoxicity, high biocompatibility, non-magnetic properties. Also, silica has well-defined size and geometry of the cavities that are regularly arranged in space [15] which creates a possibility to change the intensity of the magnetic inter-nanoparticle interactions by changing the NPs distance in the matrix. It is well known that besides interesting optical and structural characteristics, the magnetic features of Co_3O_4 nanoparticles are of a particular interest [1,8,13–19]. The magnetic moment of antiferromagnetic (AFM) nanoparticles originate from incomplete magnetic compensation between spins in sublattices, while the bulk AFM is magnetically compensated and has zero net magnetic moment in zero applied magnetic field [8,13]. In small structures, the surface-to-volume ratio becomes large enhancing the contribution to the magnetization by uncompensated spins at the surface of the particles. It is expected that structural imperfections and strain in the nanoparticles induce distortion and site inequivalence on the crystallographic structure, resulting in an extra increase of magnetization in antiferromagnetic nanoparticles. The bulk Co_3O_4 material is antiferromagnetic with a Néel temperature about 40 K. It was reported that in the normal spinel structure

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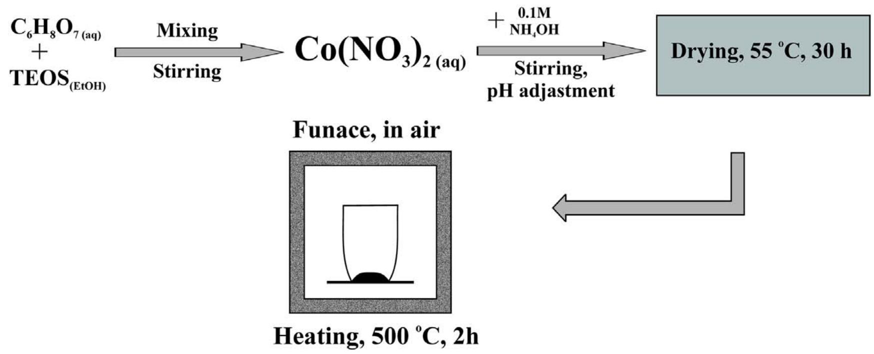

Fig. 1. Flow chart for preparation of Co_3O_4/SiO_2 nanocomposite.

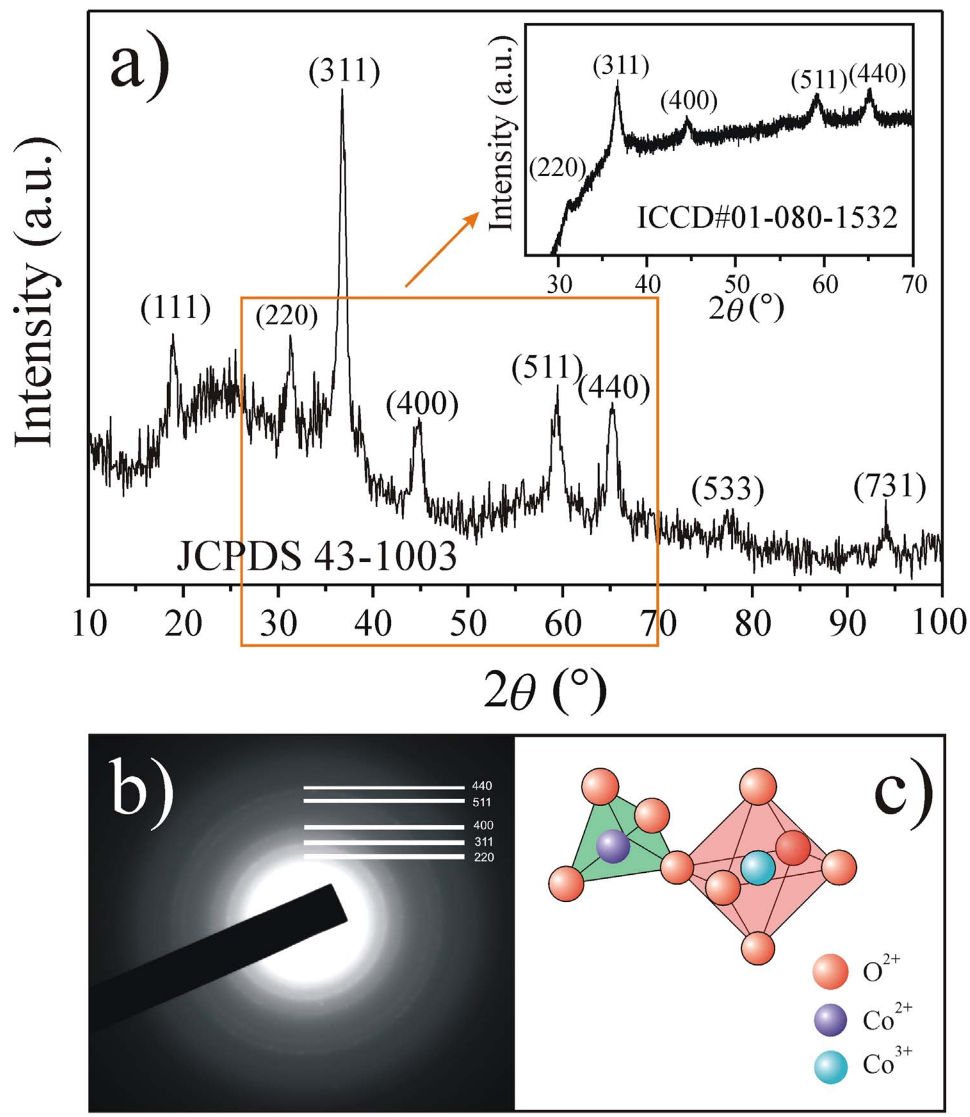

Fig. 2. Microstructural characterization of Co_3O_4/SiO_2 nanocomposite: (a) XRD pattern; inset is a high-quality experimental diffraction pattern in the indicated area, (b) SAED pattern, (c) The ions schedule in the spinel Co_3O_4 crystal structure.

only Co^{2+} ions in the tetrahedral sites have magnetic moment while Co^{3+} ions in the octahedral sites have no permanent magnetic moment. Chen et al. reported octahedral Co_3O_4 nanoparticles synthesized in an aqueous ammonia solution using hexagonal β–$Co(OH)_2$ nanoplates as starting material [18]. They found antiferromagnetic ordering below 10 K, with a paramagnetic Curie temperature of 3 K and a paramagnetic susceptibility that is double that expected for high-spin Co^{2+}. Shen et al. prepared well-aligned Co_3O_4 nanotubes in porous anodic alumina membranes using a single-source chemical vapor deposition method [19]. Magnetic measurements of nanotubes revealed a strong antiferromagnetic interaction with Weiss constant $\theta = -248$ K, whereas the field dependence of the magnetization at $T = 1.8$ K showed a small hysteresis loop with a coercivity of ~98 Oe.

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