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Surfactant-free synthesis and magnetic property evaluation of air-stable cobalt oxide nanostructures

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Abstract

We report the synthesis of metastable cobalt oxide (CoO) nanostructures via the low-temperature microwave-assisted solvothermal (MAS) process. An alcoholic solution of cobalt (II) acetylacetonate in a sealed vessel was irradiated with microwaves at a temperature $<150\,°C$ and a pressure below 100 psi. As-synthesized powder material was characterized in terms of its structure and morphology. X-ray diffractometry (XRD) indicates the formation of well-crystallized CoO nanoparticles without the need for post-synthesis annealing. The mean crystallite size of the nanoparticles was estimated to be 41 nm. The morphology of the as-prepared powder sample was evaluated by field-emission scanning electron microscopy (FESEM), which revealed the formation of densely packed nanospheres of diameter <100 nm. The CoO nanospheres were obtained without the need for any surfactants or capping agents; they were found to be quite resistant to oxidation in ambient air over several months. We attribute the stability of CoO nanospheres to their dense packing, the driving force being the minimization of surface energy and surface area. Fourier-transform infrared (FT-IR) spectroscopy and Raman spectroscopy confirm the formation of phase-pure CoO nanostructures. The deconvolution of the active modes in Raman spectra obtained at room temperature reveals the O_h symmetry in rock-salt CoO produced by the MAS route. We have analyzed its effect on the magnetic characteristics of the CoO nanostructures. Isothermal field-dependent magnetization (MH) and inverse magnetic susceptibility measurements show a phase transition from antiferromagnetic to ferromagnetic interactions in the CoO nanostructures at around 10 K. The results indicate that the phenomenon of magnetic phase transition as a function of temperature is unique to CoO nanoparticles. This finding reveals the magnetic behavior of CoO nanostructures and presents opportunities for its possible application as an anisotropy source for magnetic recording.

Introduction

Transition metal (TM) oxide nanoparticles and other types of nanostructures [1] have attracted significant attention due to their unique properties for energy storage [2], gas sensing [3], photovoltaics [4], catalysis [5], semiconductor memory devices [6], and antimicrobial devices [7]. Specifically, the synthesis of stable TM-monoxides with controlled size and morphology is of great technological interest. As cobalt is a ferromagnetic TM, and oxides of cobalt are dielectrics and semiconductors, which exhibit multiplet structures that demonstrate fascinating magnetic and semiconducting properties [8]. The band gap of cobalt oxides spans a wide range, making them suitable for a number of applications, including use in energy storage [9] and optoelectronic devices [10]. Co_3O_4 exhibits a spinel structure and a band gap of 1.4–1.5 eV [11]. CoO crystallizes

in the rock salt structure, with a wide band gap of 2.2–2.8 eV [12]. It should be noted that the controlled synthesis of air-stable CoO nanoparticles is a technical challenge due to the greater thermodynamic stability associated with Co_3O_4 as well as the immediate reducibility of CoO to metal Co. Thus, CoO nanoparticles are susceptible to surface oxidation and are often contaminated with Co_3O_4 or metal Co.

The synthesis of CoO nanoparticles has been accomplished by several growth techniques, such as sol–gel [13], hydrothermal [14], solvothermal [15], thermal decomposition [16], and electrochemical deposition methods [17]. Capping agents such as polyvinylpyrrolidone (PVP) [18], urea [19], and cetyltrimethylammoniumbromide (CTAB) [20] are often employed in these processes. Most of these methods require harsh reduction conditions, toxic chemicals, and high processing temperatures. Even so, high-temperature annealing is often employed to eliminate the capping agents, surfactant, polymer, and other by-products. However, such high-temperature treatment processes can induce significant side effects, such as the formation of multiple phases in a sample. Furthermore, high-temperature processing can destroy the magnetic ordering in the material [21]. Additionally, conventional ceramic synthesis routes lead to a non-uniform particle size distribution.

On the other hand, the microwave irradiation-assisted solvothermal synthesis (MAS) technique has emerged as a promising technique for the synthesis of nanometric powders and thin films. As such, MAS has attracted significant recent attention owing to its simplicity and reduced processing time [22, 23]. Moreover, microwave irradiation facilitates a high rate of contactless heating at the molecular level, leading to a steady rise in temperature; as such, this process is efficient and reproducible [24]. The functionality of a material synthesized via the MAS technique can be suitably tuned by controlling the choice of precursor materials and solvents, microwave power, duration, and temperature of the reaction [25]. In particular, MAS facilitates the growth of TM-oxides at a relatively low temperature, offers great control over stoichiometry, and can yield products with enhanced properties. Here, we report a novel and simple route to synthesize cobalt oxide (CoO) nanostructures through the microwave-assisted irradiation process. The nanostructures so formed are found to be air-stable and resistant to oxidation for several months. To the best of our knowledge, this is the first report on surfactant-free and low-temperature synthesis of well-crystallized air-stable CoO nanostructures without employing any post-synthesis heat treatment. We discuss the structural, morphological, and magnetic characteristics of the CoO nanostructures obtained using this approach.

Experimental

Unlike in traditional inorganic synthesis, we have employed a β-diketonate cobalt complex (acetylacetonate) as the precursor. Acetylacetonates are excellent candidates for the preparation of highly connected framework due to their versatile bridging characteristics as well as potential hydrogen bonding donors and acceptors. Further, the metal-oxygen bond present in acetylacetonates makes them suitable for the synthesis of metal oxide powders and the deposition of thin films [26].

Commercial-grade powder of cobalt (II) aacetylacetonate $(Co(acac)_2)$ [99.9%, Sigma Aldrich] was used without further purification. To synthesize CoO, 1 mmol of $Co(acac)_2$ was dissolved in a solvent mixture of ethanol (15 ml, HPLC-grade) and ethylene glycol (25 ml, AR-grade). The resulting solution was stirred until the solution became clear. The solution was subsequently transferred to an 80-ml sealable reaction vessel, which was subsequently irradiated for 15 min by microwave energy in a hydrothermal-like arrangement (2.45 GHz, 300 W, Discover- SP, CEM Corp., Charlotte, NC USA). Due to microwave irradiation, the temperature and pressure in the reaction vessel rose to 150 °C and 100 psi. The irradiated solution was centrifuged at 7500 rpm for 15 min. The powder that precipitated from the solution was double-washed with ethanol and then dried at 60 °C overnight.

Characterization

The crystallinity and the phase composition of the powder sample were examined by powder x-ray diffractometry (p-XRD, Smart Lab, Rigaku, Tokyo, Japan) using Cu-K_α radiation. Fourier-transform infrared spectroscopy (FT-IR) (Perkin Elmer, Billerica, MA, USA) was used to evaluate the purity of the sample. About 15 mg of the powder sample was used for XRD and FTIR measurements. The morphology of the sample was examined by field-emission scanning electron microscopy (FESEM, Ultra-55, Carl Zeiss, Oberkochen, Germany). Elemental analysis of the powder sample was performed using energy-dispersive x-ray spectroscopy in the FESEM. Raman spectroscopy (LabRAM-HR (UV), HORIBA, Kyoto, Japan, $\lambda = 532$ nm) was employed to obtain qualitative evidence for the formation of CoO. Magnetic measurements were undertaken using a SQUID magnetometer (Quantum Design MPMS, San Diego, CA, USA) in fields up to 5 T. The M-H measurements were performed at 5 K, 10 K, 50 K, 100 K, 200 K, 300 K, and 350 K at a field of 5 T. Zero-field cooled and field-cooled

Figure 1. Powder XRD pattern of as-prepared CoO nanostructures.
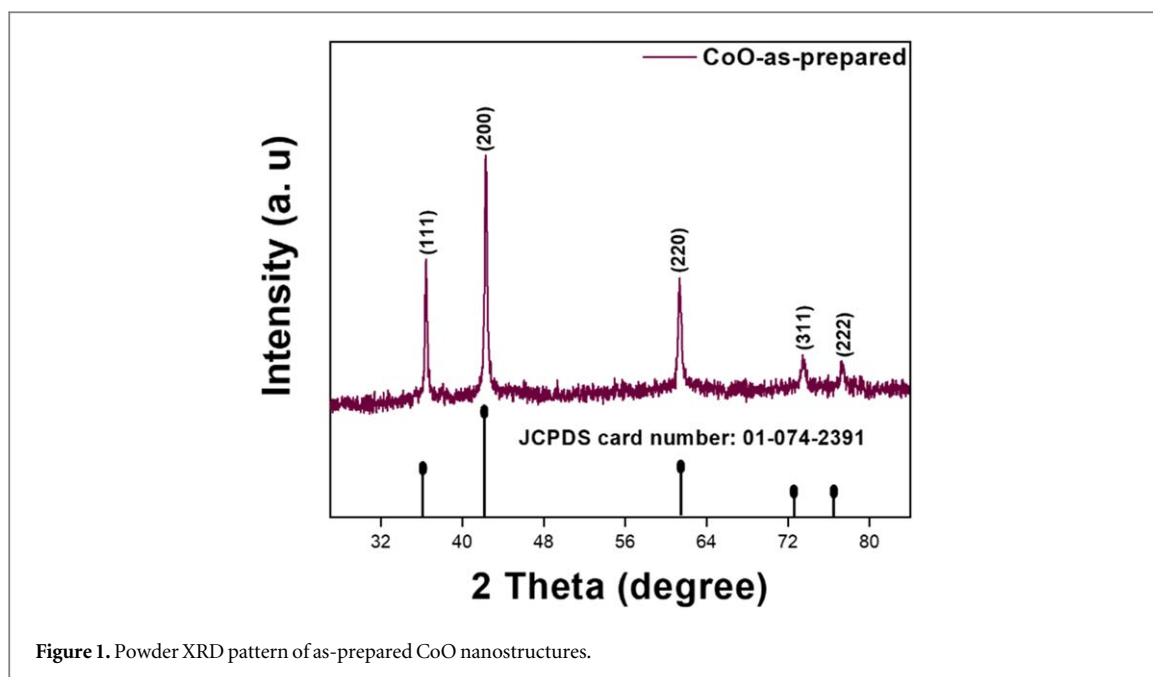
measurements were undertaken from 5 K to 350 K at a field of 1 T. All of the measurements were undertaken using the as-synthesized cobalt oxide powder sample.

Results and discussion

XRD studies

The x-ray diffraction pattern of the powder (shown in figure 1) corresponds to the CoO of the cubic rock salt structure; it was indexed using the JCPDS file number 01-074-2391. Peaks corresponding to (111), (200), (220), (311), and (222) facets were observed (figure 1); this result was consistent with previous reports on the solvothermal synthesis of cubic CoO [18, 27]. The strong and relatively broad peaks in the pattern indicate the formation of well-crystallized nanostructures. The mean crystallite size was calculated using the Debye–Scherrer equation, given by
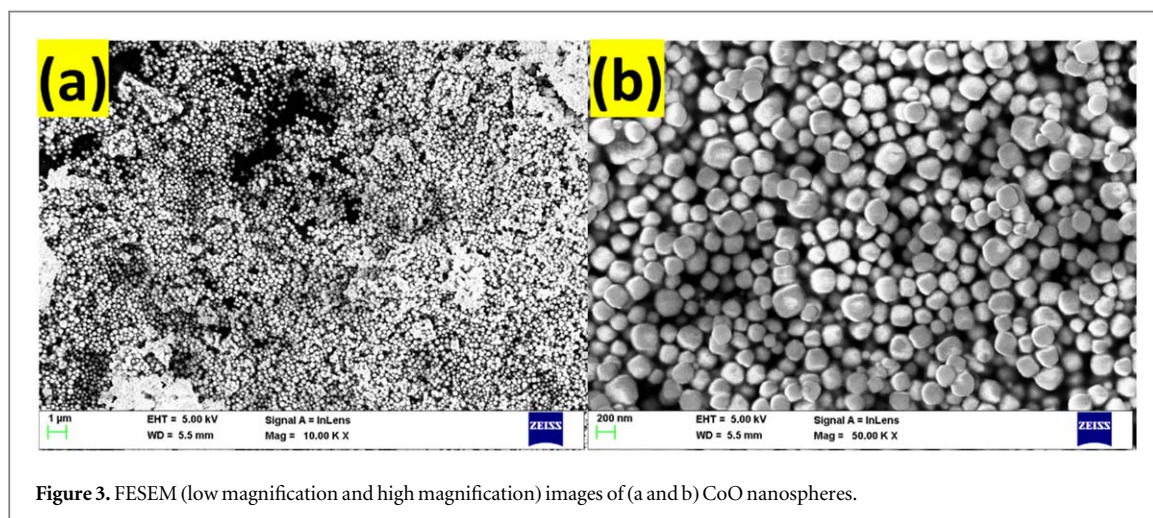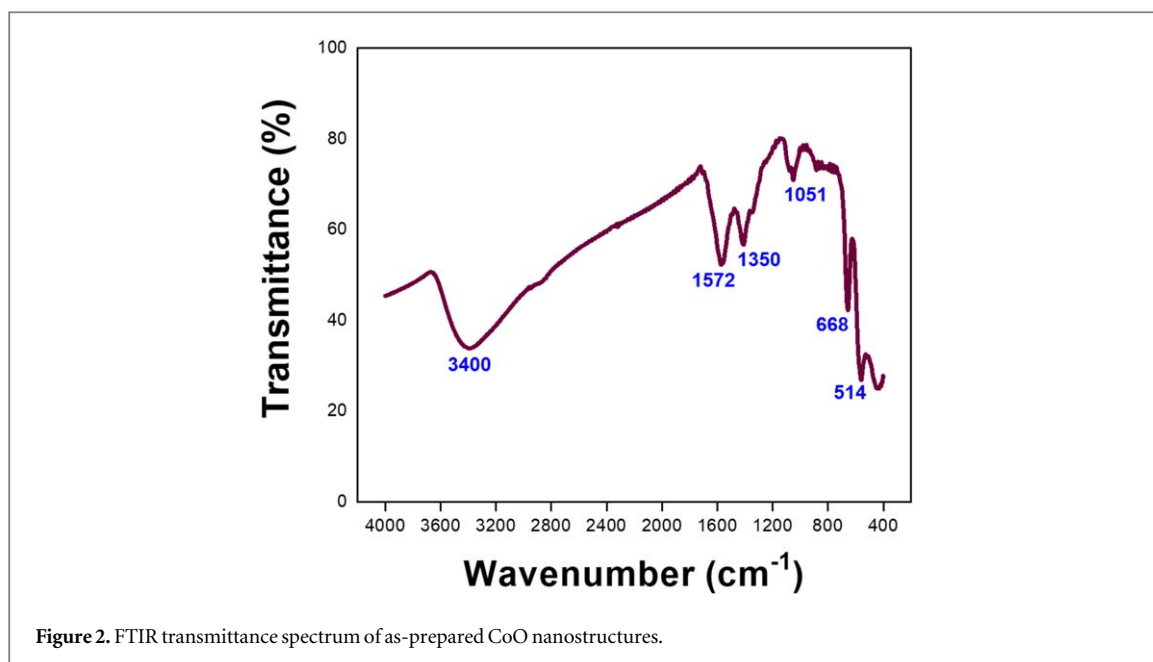
$$D = \frac{K\lambda}{B\cos\theta} \tag{1}$$

where D is the absolute crystallize size, K is a constant dependent on the shape of the crystal (0.91), λ is the x-ray wavelength (1.540 Å), B is the full width at half-maximum (FWHM) of the peak considered, and θ is the scattering angle. The mean crystallite size, considering the (200) peak, was determined to be 41 nm. The absence of other peaks besides CoO implies that the sample is phase-pure.

FTIR studies

The composition and quality of the material were determined by analyzing the FTIR spectrum of cobalt oxide in the range 4000–400 cm^{-1} (figure 2). The broad bands centered around 1572 and 3400 cm^{-1} were attributed to O–H stretching and bending modes of water, respectively [28]. The two sharp peaks located at 668 and 514 cm^{-1} are assigned to the metal-oxygen (Co–O) stretching vibration modes of CoO. Peaks around 1050 cm^{-1} and 1350 cm^{-1} are characteristic vibrations of carbonate species, which are formed by the adsorption of CO on CoO nanoparticles [29]. Based on the XRD and FTIR data, it can be concluded that microwave-assisted synthesis results in the formation of phase-pure cobalt monoxide.
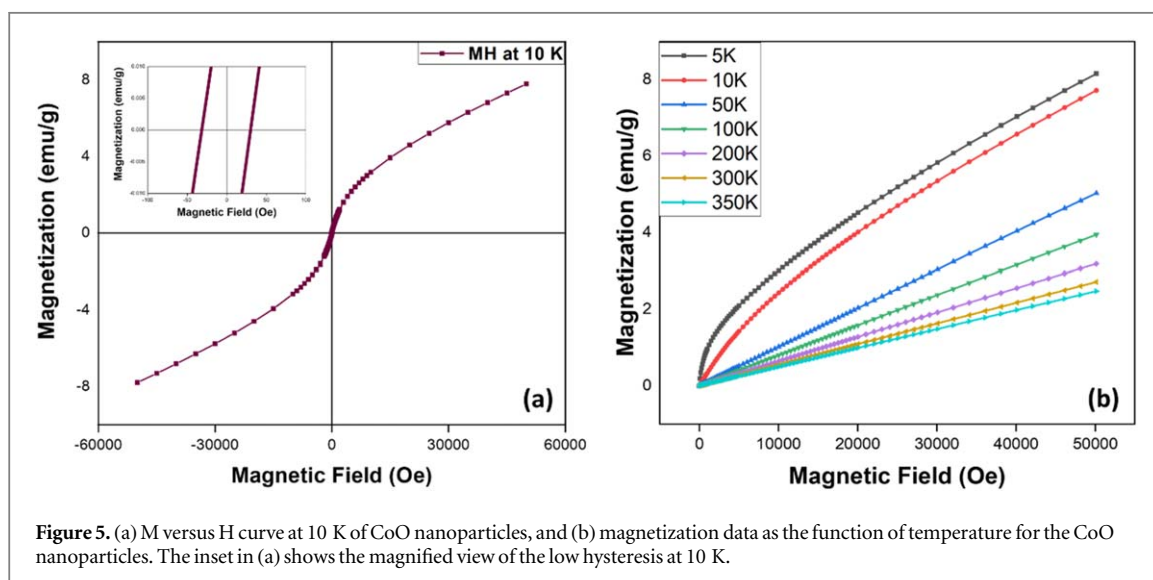
SEM-EDS

The morphology of the as-prepared CoO powder sample examined by FESEM is shown in figure 3. It can be readily seen from figure 3(a) that the as-prepared material consists of densely packed, polydisperse spherical entities of micrometer dimensions. A high magnification SEM image (figure 3(b)) indicates that it is made of a large number of nanoparticles that measure less than 100 nm, which is consistent with the crystallite size (41 nm) that was determined from the XRD data. The mechanism of formation of oriented CoO nanostructures, the evolution of their microstructure, and the structure–property relationship are highly dependent on the synthesis technique [22, 25]. In the current case, the solvents with high dielectric constant, such as the ones used

Figure 2. FTIR transmittance spectrum of as-prepared CoO nanostructures.

Figure 3. FESEM (low magnification and high magnification) images of (a and b) CoO nanospheres.

in the synthesis of CoO nanostructures (ethanol and ethylene glycol) via the MAS technique, produce a larger heating effect, resulting in the aggregation of molecules [25]. The dielectric heating in the MAS technique is homogeneous and rapid, due to which the nucleation of species happens everywhere in the solution; this process results in a high degree of crystallization of CoO [22, 30]. This result is, however, not possible through synthesis techniques involving conventional heating processes. In addition, Kahmei *et al* have shown that the heating rate in a microwave-assisted process can be used to modulate the position of cationic sites in complex oxide nanostructures, thereby altering the magnetic anisotropy in a material [31]. The uniform heating of the solution in the MAS process, as well as the reducing character of ethylene glycol, leads to the formation of cobalt monoxide crystallites with a fairly narrow size distribution. These results indicate that the present solution-based growth process, which utilizes a microwave irradiation-assisted chemical reaction, is a powerful and straightforward approach for obtaining CoO nanostructures of reasonably uniform size distribution with unique magnetic properties, which are difficult to obtain because of the higher stability of Co_3O_4. Furthermore, the EDS spectrum of CoO nanospheres (Fig. S1) indicates that the crystallites are composed of Co and O. The sample has an oxygen peak at 0.53 keV and a cobalt peak at 6.94 keV, indicating the formation of CoO.

Raman spectroscopy

The CoO nanostructures were also examined further using Raman scattering. In fcc-CoO, the Co^{2+} ions are octahedrally coordinated with six O^{2-} ions. It should be noted that the O_h symmetry should lead to the formation of at least three Raman-active modes (referred to as A_{1g}, E_g, and T_{2g}) at room temperature [32, 33]. The Raman spectrum of CoO (figure 4) shows a small peak at 469 cm^{-1} and two prominent peaks at around

Figure 4. Raman scattering spectrum of the as-prepared CoO nanostructures.

Figure 5. (a) M versus H curve at 10 K of CoO nanoparticles, and (b) magnetization data as the function of temperature for the CoO nanoparticles. The inset in (a) shows the magnified view of the low hysteresis at 10 K.
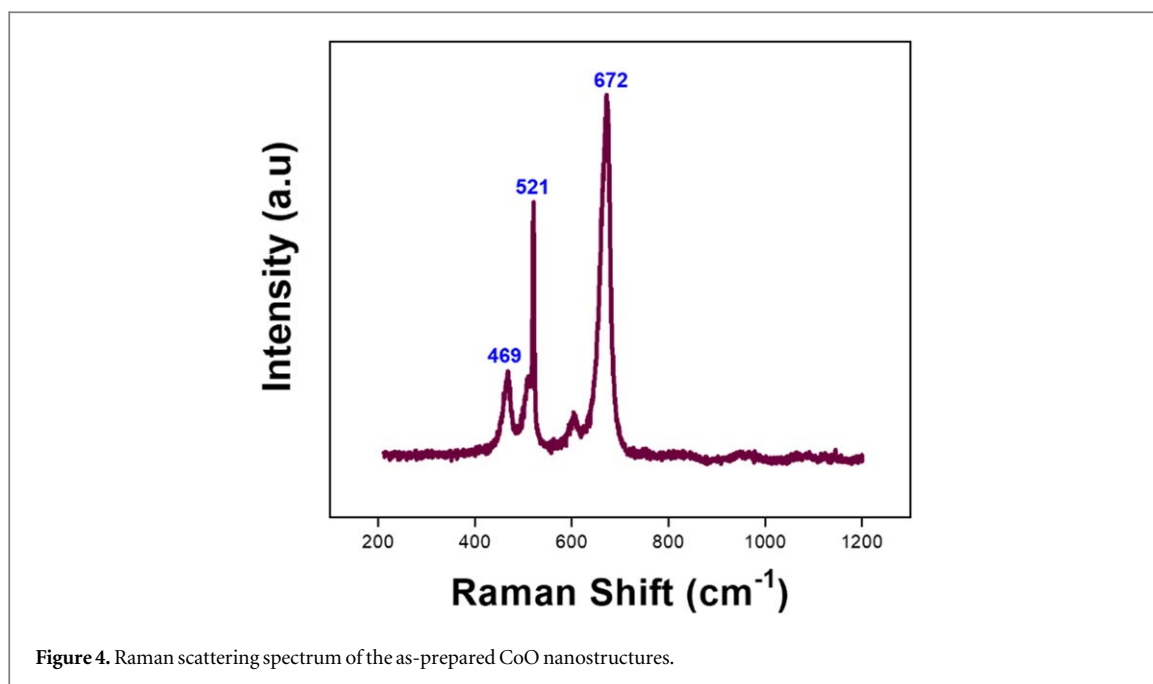
521 cm^{-1} and 672 cm^{-1}, which were identified as the E$_g$, T$_{2g}$, and A$_{1g}$ modes, respectively [34]. The shoulder peaks centered around 482 and 590 cm^{-1} were assigned to Co-O stretching vibration [35]. Thus, the Raman spectrum further confirms the phase purity of the CoO nanospheres.

Magnetic characterization

Figure 5(a) shows the M-H data for CoO nanostructures measured at 10 K in a field of 5 T. The curve shows hysteresis at low temperature. The temperature dependence of the magnetization characteristics of the sample (figure 5(b)) indicates that hysteresis occurs only at a temperature $\leqslant$10 K, indicating ferromagnetic (FM) interactions in nano-CoO occur at low temperatures. This result is generally suspected to be a consequence of the presence of Co clusters and Co^{3+} ions in the CoO lattice [36]. However, our XRD results and Raman spectra confirm that the as-synthesized nanoparticles are phase-pure with no contamination. Thus, ferromagnetic interactions in CoO nanostructures are intrinsic to the nanoparticle system. Furthermore, Néel *et al* have shown that antiferromagnetic particles exhibit ferromagnetism with permanent magnetic moments [37]. Given that CoO is reported to be antiferromagnetic (AFM) in its bulk form (T$_N$ ~ 298 K) [38], this phenomenon is believed to be a consequence of the uncompensated spins at the surface of the smaller nanoparticles [39]. In addition, Makhlouf *et al* attribute the origin of permanent magnetic moments in nanoscale antiferromagnetic materials to

Figure 6. The temperature dependence of the dc magnetic susceptibility data (χ) and the inverse magnetic susceptibility data (χ^{-1}) for the CoO nanostructures. Arrow shows the broke point around 300 K.
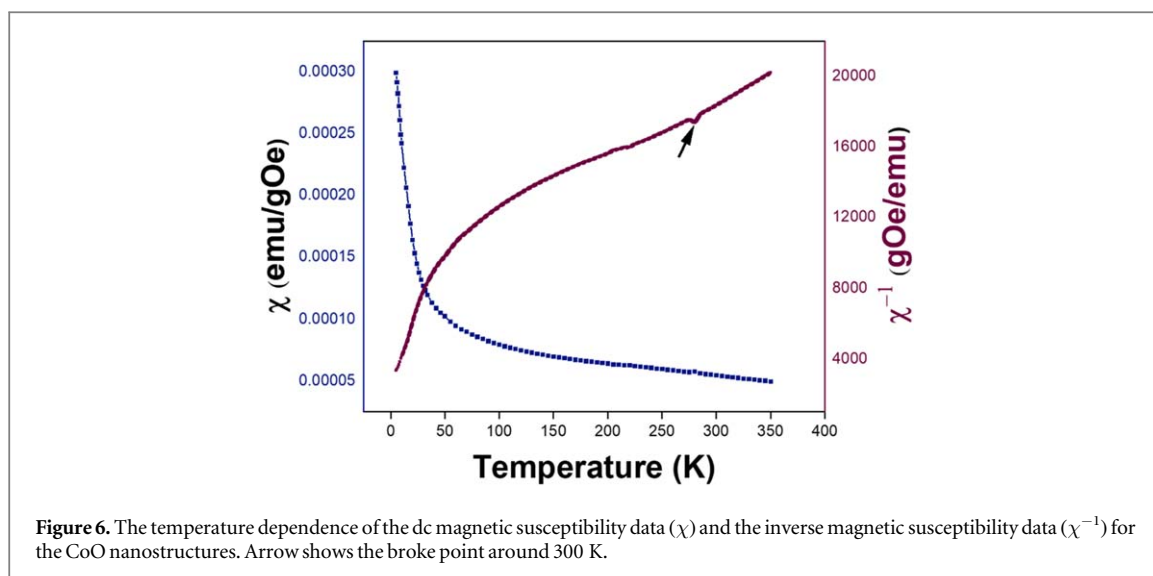
broken symmetry at the surface [40]. Thus, ferromagnetism in cobalt oxide nanostructures at low temperatures could be correlated with the surface anisotropy of the nanostructures [36].

Temperature dependence associated with the dc magnetic susceptibility (χ) and the inverse magnetic susceptibility (χ^{-1}) for the CoO nanostructures is provided in figure 6. A 'broke point,' which was noted around 300 K in the inverse susceptibility data, indicates the transition to the antiferromagnetic (AFM) state from the paramagnetic (PM) state near room temperature. The transition to AFM is not noticeable at lower temperatures, possibly due to increased FM interactions in the sample. Bulk Co_3O_4 is reported to show an AFM transition at 33 K; however, nano-Co_3O_4 shows ferromagnetic features (including hysteresis) below 10 K [41]. Thus, the phenomenon of magnetic phase transition from FM to AFM as a function of temperature is unique to cobalt oxide nanoparticles. This result suggests the possibility of cobalt oxide nanoparticles serving as potential anisotropic materials for magnetic recording and other memory devices.

Conclusions

We report a novel, rapid, and simple route to synthesize air-stable cobalt monoxide nanostructures with the rock salt structure. The structural and compositional features of these magnetic nanostructures have been systematically studied using XRD, SEM-EDS, FTIR, Raman spectroscopy, and SQUID magnetometry. The results indicate that the as-prepared CoO nanostructures are phase-pure and well-crystallized with the rock salt structure. The materials are resistant to oxidation and are chemically stable; moreover, they exhibit unique magnetic properties that can be tuned as a function of temperature. We envisage that these well-characterized and stable cobalt oxide nanostructures hold promise for magnetic recording-related applications.

Acknowledgments

Data availability statement

All raw or processed data required to reproduce these findings are included in the paper. The data that support the findings of this study are available upon reasonable request from the authors.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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