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Spectroscopic and structural studies of isochronally annealed cobalt oxide nanoparticles

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ABSTRACT

X-ray absorption near edge structure (XANES) spectroscopy, X-ray photoelectron spectroscopy (XPS), and Synchrotron X-ray diffraction (SXRD) techniques are used to study as synthesized and isochronally annealed samples of cobalt oxide nanoparticles (NPs) grown using the wet chemical route. Quantitative phase composition determined using Linear Combination Fitting (LCF) on XANES data is found to be in reasonably good agreement with that obtained from Rietveld refinement on SXRD data. XPS data qualitatively indicate that Co_3O_4 concentration increases with increase in the annealing temperature, in confirmation with SXRD and XANES data. Larger shifts in the satellite peaks from the main peaks compared to these in bulk suggest larger crystal field splitting in nanoparticles as compared to the bulk.

1. Introduction

Mixed oxidation state of transition metal oxides (TMO) is the root cause of unusual physical, chemical and magnetic properties [1]. This makes the study of mixed oxidation state of TMOs important from fundamental as well as application point of view. For example, cobalt oxide nanoparticles (NPs) have wide range of applications such as catalytic oxidation of carbon monoxide (CO) [2], water oxidation under mild conditions [3], magnetic materials [4], electro chromic devices [5], high temperature solar selective absorber [6] and gas sensors [7] etc. Magnetic NPs also have biomedical applications such as drug delivery and contrast enhancement agents for magnetic resonance imaging (MRI) [8]. The spinel structure of cobalt oxide (Co_3O_4) can act as an efficient catalyst in the heterogeneous chemical processes [9]. Cobalt oxides are formed in five different oxidation states of Co. CoO_2, Co_2O_3, CoO (OH), CoO and Co_3O_4 are the oxides of Co with different oxidation states. Out of these, Co_3O_4 (oxidation state +8/3) and CoO (Oxidation state +2) are stable oxides. Bulk Co_3O_4 has a cubic spinel structure in which the Co^{2+} ions occupy the tetrahedral (8*a*) site whereas Co^{3+} ions at octahedral (16*d*) one [10]. Co^{3+} ions are in a diamagnetic t_{2g}^6 (low spin, $S=0$) state due to strong octahedral cubic field and large crystal-field splitting between t_{2g} and e_g levels in the 3d orbitals, while Co^{2+} ions at the 8*a* site are in a high spin state $e_g^4\ t_{2g}^3$ with $S=3/2$. As a result, Co^{3+} ions are not magnetic and the antiferromagnetism posses by Co_3O_4 are mainly due to the weak coupling between nearest neighbor Co^{2+} ions [10]. Bulk CoO is also antiferromagnetic in nature and it has simple cubic structure in which Co^{2+} ions occupy the octahedral site.

In this paper, spectroscopic and structural investigation of mixed oxidation states on as grown as well as isochronally annealed cobalt oxide NPs samples are carried out. Spectroscopic method (e.g. X-ray absorption spectroscopy (XAS)) generally measures the response of a system as a function of energy. X-ray absorption near edge structure (XANES) spectroscopy and X-ray photoelectron spectroscopy (XPS) are two spectroscopic tools which are sensitive to bulk and surface of the samples respectively. Information obtained are also complementary in the sense that XPS gives information about occupied density of states (DOS) below the Fermi level, whereas XANES that for unoccupied DOS just above the Fermi level. In XANES spectra, features such as K-edge, pre-edge and near edge provide detailed information on the oxidation state, the coordination environment and the unoccupied DOS respectively. However, the information on the coordination environment is an average of various possible coordination. In XPS, main peak positions, peak separation and position of other special features like shake up satellites are used for classification of different chemical states of an element in that particular sample. Herein, Rietveld refinement on powder SXRD data are carried out to obtain the composition of mixed phase samples and their lattice parameters. The composition analysis has also been done using Linear Combination Fitting (LCF) on XANES data. Quantitative approach used in XANES experiments is based on statistical

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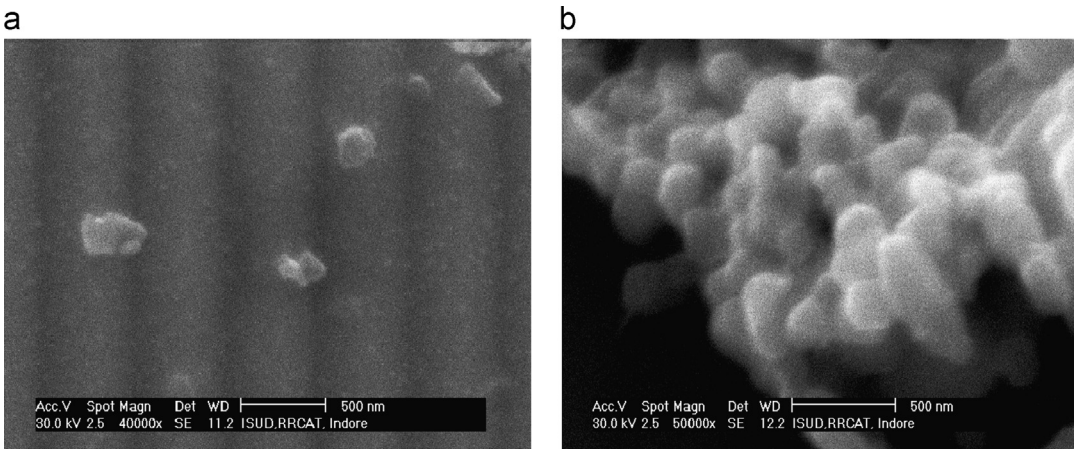

Fig. 1. SEM image of two samples (a) H1 and (b) H4.

goodness-of-fit and does not explain the accuracy of the components obtained from the LCF fittings [11]. In this work, we show that a good agreement between the composition obtained from the XRD and XANES ensures the validity of LCF on XANES data.

2. Experimental

Cobalt oxide nanoparticles were synthesized using the wet chemical route. The reactants used were cobalt nitrate $Co(NO_3)_2 \cdot 6H_2O$ as a precursor, 2-pyrrolidone as solvent, oleic acid and trioctylphosphine oxide (TOPO) as surfactants. The chemicals used were of analytical grade and were procured from Sigma Aldrich. 0.5 g (1.72 mM) $Co(No_3)_2 \cdot 6H_2O$ was dissolved in 25 mL (0.33 M) 2-pyrrolidone. 2 mL (6.2 mM) oleic acid and 2.4 g (6.2 mM) trioctylphosphine oxide were mixed with the above solution at 50 °C and stirred for 30 min. The reaction took place in two steps. After heating at 50 °C and stirring the mixture for ~30 min, the solution changed to transparent pink color. This indicates the completion of the first phase. The solution was heated in air at 200 °C for 1 h and a black solution was observed. The solution was then cooled to the room temperature and diluted with methanol. Black powder was separated from the solution using centrifuge. The powder was dried at 65 °C for about 10 h in the oven. More details of the synthesis are given elsewhere [12]. For this work, the synthesis is done at higher temperature (280 °C) and for longer time compared to that reported in our earlier work [12]. The base sample (as grown) was further annealed at various temperatures from 300 °C to 800 °C for ~2 h in air. We have chosen four samples (1) H1: as grown, (2) H2: annealed at 300 °C for 2 h, (3) H3: annealed at 500 °C for 2 h, and (4) H4: annealed at 800 °C for 2 h for spectroscopic and structural studies. Obtained samples were characterized using scanning electron microscopy (SEM) to investigate the typical size of nanoparticle. SEM images were obtained using Phillips microscope (model XL30CP, 30KV). For SEM measurements, NPs were dispersed in methanol and were ultrasonicated for 15 min. These particles were dispersed dropwise on cleaned Si wafer. The samples were then dried under lamp light. A 100 Å thick gold layer was deposited on the samples to nullify the charging effect while performing SEM. Spectroscopic and structural studies have been done using the XANES, XPS and SXRD techniques. XPS measurements were performed at room temperature with an OMICRON 180° hemispherical analyzer (model EA 125) using Al Kα (photon energy = 1486.7 eV) source [13]. The hemispherical analyzer was operated in constant-pass energy mode and its overall energy resolution with pass energy of 50 eV was estimated to be 0.8 eV. The measurements were carried out with a photoelectron take-off angle of 45° and the pressure in the spectrometer chamber during the measurements was $\sim 10^{-10}$ mbar. XANES and SXRD measurements were performed at angle dispersive X-ray diffraction (ADXRD) beamline (BL-12) [14] on Indus-2 synchrotron source [15]. The beamline consists of a Si (111) based double crystal monochromator and two experimental stations namely a six circle diffractometer with a scintillation point detector and Mar 345 dtb image plate area detector. SXRD measurements were carried out using the image plate. The X-ray wave length used for the present study was accurately calibrated by doing X-ray diffraction on LaB_6 NIST standard. Data reductions were done using Fit2D software [16]. XANES measurements were carried out in transmission mode at room temperature. Absorption by the samples was measured by measuring incident intensity before and transmitted intensity after the sample using two ionization chambers around the Co K-edge (7.709 keV). Photon energy was calibrated by measuring the XANES spectra of standard cobalt metal at Co K-edge. Energy resolution ($\Delta E/E$) and energy reproducibility were estimated to be 1.5×10^{-4} and 0.2 eV respectively.

3. Results and discussion

3.1. Scanning electron microscopy (SEM)

Fig. 1a and b shows SEM images for as grown (H1) and sample annealed at 800 °C (H4) respectively. The average size of the particle is ~180 nm (Fig. 1b). SEM image shows that annealing has lead to the coalescence of nanoparticles (Fig. 1b). In case of as grown sample and sample annealed at 300 °C, weak type II magnetic contrast is seen due to the some leakage field above the cobalt nanoparticles surface. This also verifies the Rietveld refinement result which shows the presence of Co metallic nanoparticle phase in two samples H1 and H2 (to be discussed in Section 3.4).

3.2. XANES

XANES spectroscopy is an element specific technique and is highly sensitive to the oxidation state, local coordination and hybridization effects of orbitals of that specific element. Generally XANES measurements (where absorption edge is being probed) are performed to study oxidation state, local surroundings and electronic states of specific metal site [17–19]. However in this work, XANES measurements on all the samples have been performed to investigate the composition of mixed phase. Fig. 2 shows the normalized Co K-edge XANES spectra of nanoparticles