Impact of Isochronal Annealing on Phase Transformation of Cobalt Oxide Nanoparticles

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Abstract. The present paper elicits the phase transformation in cobalt oxide nanoparticles with alteration in annealing temperature for constant time period. The Cobalt oxide nano particles were successfully synthesized using ASH supported technique followed by annealing for 2 hours at various temperatures between 300°C and 800°C. It was observed using X-ray diffraction (XRD) that the as grown sample of cobalt oxide nanoparticles has mixed phases while at 700°C it is in pure CO_3O_4 phase. Particle size and phase of the nanoparticles were around ~ 40 nm. Phase and particle size of nanoparticles were also confirmed using Transmission Electron Microscopy (TEM). The EDAX study shows the presence of pure cobalt oxide (CO_3O_4) at 700°C.

INTRODUCTION

Co3O4 is a magnetic p-type semiconductor having direct band gaps at 1.48 and 2.19 eV [1] with potential applications as heterogeneous catalyst, anode material in lithium ion batteries [2], gas sensors [3], electrochemical devices [4], solar energy absorbers [5], magnetic material [6] and memory storage devices [7]. A momentous research work exists on the magnetic and optical properties of Co3O4, exhibiting dependences on the size of the nano crystallites. Due to their miniscule size, nanoparticles exhibit unique material properties that are inevitably different from those of their bulk counterparts. Thus properties of Co3O4 nanoparticles are invincibly dependent on their size and morphology. Therefore, it is of elite interest to know the particle size of synthesized Co3O4 nano particle before determining any physical properties. The phase and particle size of nanoparticles depends on fabrication techniques. Among various synthesis techniques ASH SUPPORTED method has been used which is very simple, ecofriendly and cost effective [8, 9]. The present work portrays the structural properties of cobalt oxide nanoparticles. Also, the effect of isochronal annealing on phase and particle size of nanoparticles has been observed.

EXPERIMENTAL

Cobalt oxide nanoparticles have been synthesized using ASH supported method [9]. Obtained nanoparticles (as prepared sample) were further annealed in air at various temperatures from 300^{o}C to 800^{o} C. Samples assigned as 300^{o}C (sample #1), 400 ^{o}C (sample #2), 500 ^{o}C (sample #3), 600 ^{o}C (sample #4), 700 ^{o}C (sample #5) and 800 ^{o}C (#6). The sample so formed, were analyzed by X- Ray Diffraction (XRD) using angle dispersive X-ray diffraction (ADXRD) beamline (BL-12) on Indus-2 synchrotron radiation source, India [10]. The beamline is based on a Si (311) based double crystal monochromator. The Photon beam (0.3mm X 0.3mm) of energy ~11keV was used. For further phase confirmation and estimation of average sizes of the nanoparticles, Transmission Electron Microscopy (TEM) and EDAX were performed using Tecnai-G2 20 TEM installed at UGC-DAE-CSR Indore. The wavelength of electron beam is much shorter (only 0.025 Å at 200 kV) than those of X-rays (1.54 Å of Cu Kα) and neutron (~ 1-2 Å).

RESULTS

Structural Characterization (XRD Analysis)

An analysis of XRD pattern shows that the as-prepared nanoparticles annealed at 700°C (sample #1) exhibit polycrystalline nature and contains at least two crystalline phases. The peaks marked as B in Fig. 1 are due to CoO phase with cubic face centered structure [(JCPDS #71-1178; Fm3m (225)]. The peaks marked as **A** are due to Co_3O_4 phase [(JCPDS # 78-7969; Fd3m)] also having cubic face centered structure (space group: Fd3m) called as a major phase. On isochronal annealing of as-prepared samples, it is clear from the Fig. 1 that peaks B corresponding to CoO (minor phase) tends to disappear with increase in temperature while peaks A corresponding to Co_3O_4 tends to become more prominent with the increment in temperature. Annealing after 400°C, only peaks A remains while peaks B completely disappears. Particle sizes of the nanoparticles are calculated using XRD. The average particle size of the cobalt oxide nanoparticles is ~ 43 nm.

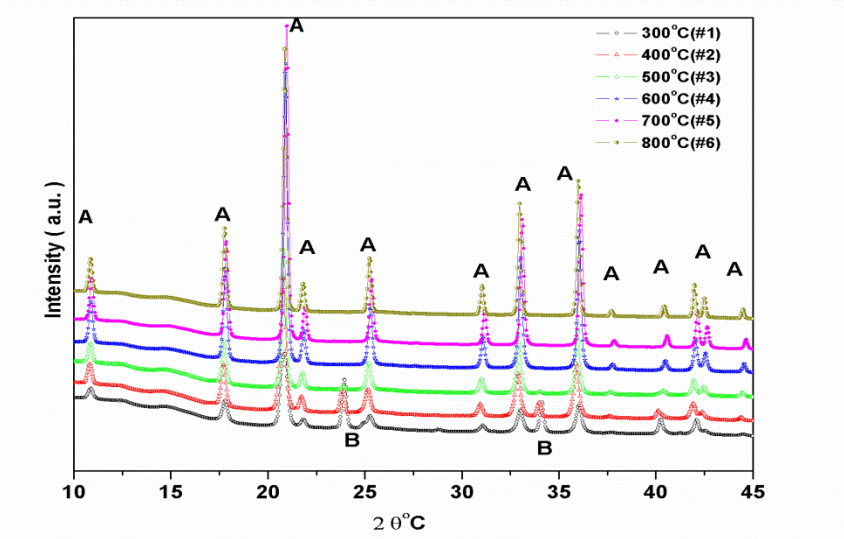
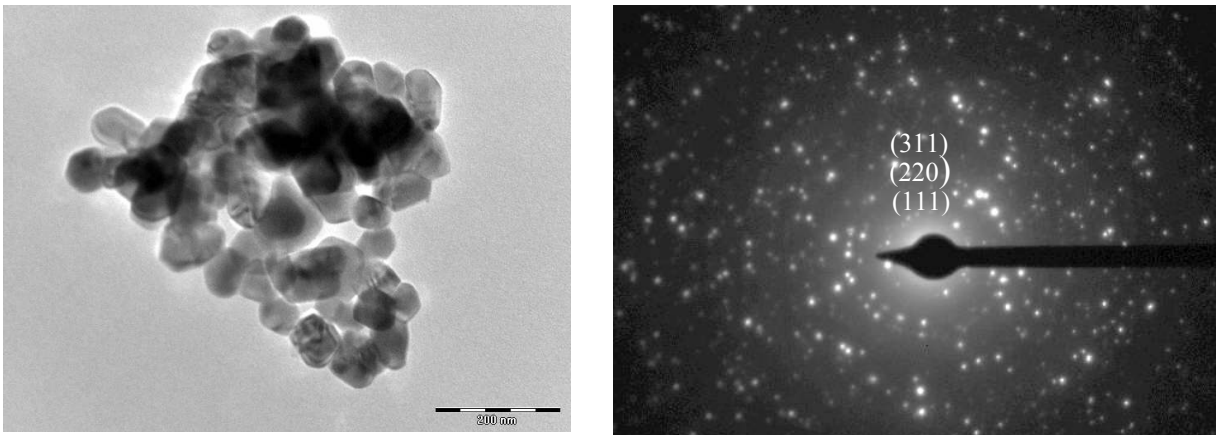


FIGURE 1. X-Ray Diffraction patterns for samples (#1 to #6) of cobalt oxide annealed in air at various temperatures. Samples (#1 to # 3) show mixed phase whereas (#4 to #6) show single phase. CoO and Co_3O_4 phases are represented by symbol B and A, respectively.

Transmission Electron Microscopy (TEM)

Fig. 2(a) and (b) shows the electron micrographs and selected area diffraction (SAD) pattern of cobalt oxide nanoparticles annealed at 700°C (sample #5). The sizes of nano particles are determined using the Image J software. From the various electron micrographs, it is confirm that the size of nano particles is in 40-110 nm range. Further, the SAD pattern of studied system has been used to index the different planes of crystal structure by measuring the d spacing. The calculated d-spacing of first, second and third planes are 4.616, 2.86 and 2.424 Å respectively. By matching the d-spacing with the PCPDF database, the rings can be index as (111), (220), (311) planes. Similarly other rings can also be index in the same manner. The (hkl) indexes of diffracted planes are neither fully odd nor even but are the combination of both. Therefore, it is clear from the diffraction patterns, that the possible crystal structure is cubic for the studied nano particle which is reported in several research papers.



(a) **(b)**

FIGURE 2. (a) Confirm the formation of Co_3O_4 nano particles. (b) The Selected area diffraction pattern of nano particles confirms the phase formation.

Energy Dispersive X-ray Analysis (EDAX)

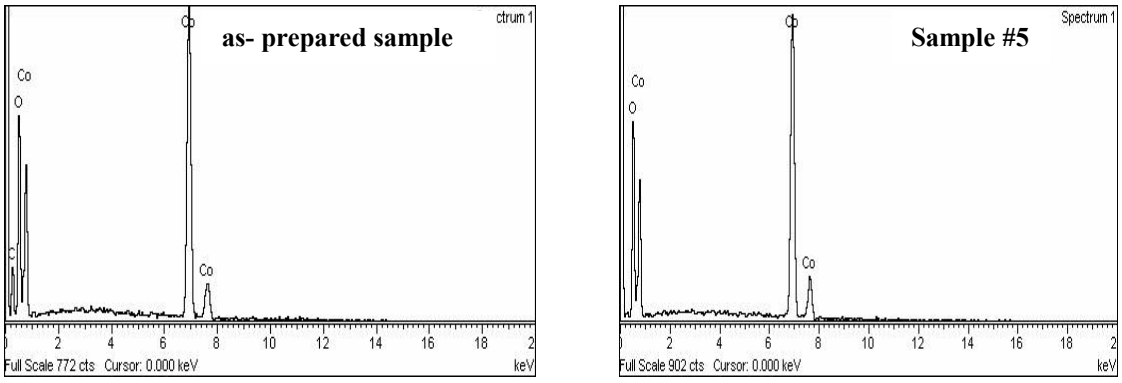
The present work illustrates the EDAX measurement of the as-prepared sample and cobalt oxide nanoparticles annealed at 700°C (sample #5) to observe the effect of annealing on elemental composition. For perfect stoichiometric sample, the atomic percentage of cobalt and oxygen can be calculated as:-Atomic weight % of Co = no. of Co element / no. of total elements

$$\frac{3*100}{3+4} = \frac{3}{7}*100 = 42.857\%$$

Atomic weight of oxygen = no. of oxygen element / no. of total elements

$$\frac{4*100}{3+4} = \frac{4}{7}*100 = 57.14\%$$

Fig. 3 (a) & (b) shows the K-edge EDAX spectra of as-prepared sample and sample #5 (annealed at 700°C). In the as- prepared sample, apart from the main elements i.e. cobalt and oxygen, some content of extra carbon has also been found.



(a) **(b)**

FIGURE 3. (a): K-edge EDAX spectra of as-prepared sample (b) sample #5 (annealed at 700°C)

The K-edge EDAX spectra of annealed cobalt nano particles is present in fig. 3(b). Unlike, the as prepared samples, there is no impurity phase of carbon. Probably at high temperature, the formation of carbon dioxide takes

place and it evolves below 700°C. Table 1 shows the atomic weight % of all the three element cobalt, oxygen and carbon in as-prepared sample and in sample #5. From the table it is clear that the atomic weight % of Co and O are 41.73 and 58.27 % which approximately matches with the theoretical value (Co-42.857% and O-57.14%).

Also, it is clear that for as- prepared sample, experimentally observed atomic percentage of oxygen and cobalt are slightly lower than the expected values because of the presence of extra carbon impurity present in the sample.

TABLE 1: Atomic weight percentage of constitute atoms in as-prepared sample and in sample #5

Element	Conc.	Intensity	Atomic Weight%
As Prepared			
C	3.38	0.433	13.69
O	49.14	1.1963	54.17
Co	81.87	0.9117	32.14
Sample #5			
O	53.93	1.3482	58.27
Co	98.32	0.9320	41.73

CONCLUSIONS

Present work concludes that XRD study exhibits that the as-prepared sample is in mixed phase of CoO (minor phase) and Co_3O4 (major phase). Minor phase disappears with the increase in annealing temperature. Beyond 400°C it is only the major phase that remains i.e. pure Co_3O_4 phase. The phase and particle size of the annealed sample are in agreement with XRD results. The EDAX analysis also confirms the presence of extra carbon in as-prepared nano particles whereas at 700°C annealed nano particles are perfectly stoichiometric.

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