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Effect of annealing on cobalt oxide nanoparticles for concentrated solar power system

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ABSTRACT

Cobalt Oxide nanoparticle is a suitable material for concentrated solar power system (CSP) that has high efficiency and can withstand high temperatures. Cobalt oxide nanoparticle is synthesized by hydrothermal method followed by annealing to induce crystallization. The presence of Co_3O_4 nanoparticles are observed in FTIR spectrum and confirmed by X-ray diffraction pattern and observed phase changes as the temperature varies. The size of the Particle increases with increase in temperature. The SEM observations showed that the size of the particles is in a few hundreds of nanometers. At higher temperatures the size and shape of the nanoparticles varies which are suitable for concentrated solar power system. From the UV-visible spectrometer the band gap was found to be 2.21eV at all high temperatures.

KEY WORDS: Cobalt Oxide, Annealing, CSP system, Crystallization.

1. INTRODUCTION

With the expeditious development of the economy and society, the consumption of fossil fuels such as coal, natural gas and oil are reaching far beyond its availability. In order to satisfy the basic needs a renewable energy required. Among them solar energy is an efficient and alternative source (Crabtree, 2007). One of the main advantages of this unique system is inexpensive energy storage using thermal energy storage system (TES). It can be hybridized with other energy systems but Levelized cost of energy of CSP is higher than the other alternative energy technologies (Hernandez, 2012). To reduce the cost of CSP, it is essential to increase the system power conversion efficiency. Hence the materials which are used in CSP should have operating temperature more than 600°C and thermally stable for longer duration (Kolb, 2011). Nanostructured metal oxides are nontoxic and thermally stable at high temperatures in air (Kunihito, 2006). Many synthesis methods have been employed to prepare cobalt oxide nanostructures such as microwave assisted precipitation, hydrothermal synthesis, solvothermal synthesis, chemical bath deposition (Vijayakumar, 2006; Meher, 2011; Wang, 2009; Yang, 2013). In the present work, a simple, low cost, shape and size controllable hydrothermal method is adopted followed by annealing to get a crystalline nanoparticles (Yixin, 2011). The increase in size of the particle by annealing from 450°C to 650°C is suitable for CSP systems.

2. MATERIALS AND METHODS

2.1 Synthesis of materials: Co $(NO_3).6H_2O$, KOH and ethanol were all of an Analytical grade and used as raw materials without further purification. Co_3O_4 nanoparticles were synthesized by hydrothermal method. 0.1M of Co $(NO_3).6H_2O$ was dissolved in deionized water, and the pH of the solution was adjusted to 13 by adding KOH. After ultrasonic stirring, the solution was transferred into a Teflon autoclave for hydrothermal treatment kept at a temperature of 200°C for 24hrs. After the autoclave was gradually cooled to room temperature and the obtained solid products were washed with deionized water and ethanol and subsequently dried overnight (Yang, 2010).

2.2 Characterization: Phase identification and the crystal structure were determined by X-ray powder diffraction (XRD) using a XRD diffractometer (D8 Advanced) with Cu Kα radiation. The obtained data ranges between 10° and 80° in 2θ with 0.02° step. The morphology was observed with scanning electron microscopy (SEM, JEOL JSM-6700F) at 20 kV and images were obtained. The optical properties of the Co_3O_4 nanoparticles were characterized by UV-vis spectroscopy. The band gap of the Co_3O_4 nanoparticle was determined by UV-vis spectroscopy, using a Lambda 35 UV-vis spectrometer. FTIR spectrophotometer has been used to determine the formation of the nanoparticles from the precursor.

3. RESULTS AND DISCUSSION

3.1 Structural Studies: The cobalt oxide nanoparticles are prepared and annealed at 450°C, 550°C and 650°C for 4hrs. The powder XRD pattern reveals that the prepared nanoparticles are crystalline in nature. The powder XRD pattern of cobalt oxide and annealed samples are as shown in figure 1. The synthesized nanoparticle is confirmed by X-ray diffraction analysis, which is one of the polymorphs of cobalt oxide. Synthesizing pure cobalt oxide is very difficult, as it combines with oxygen readily forming higher level oxides. Co_2O_3 can also be formed when

compounds are annealed at low temperature. If the temperature is increased more than 600°C, a stable and higher level oxide Co_3O_4 occurs (Cao, 2006; Chen, 2003; Shinde, 2006). The diffraction peaks can be assigned to a cubic phase of Co_3O_4 according to JCPDS card no 43-1003, indicating the formation of spinal structure. The diffraction peaks could be readily indexed to crystalline Cubic phase of Co_3O_4 with a lattice constant of a = 8.084 Å, which is consistent with the standard value of a = 8.065 Å. The optimal size for absorbing visible and near infra-red light is around a few hundreds of nanometers. Small size particles will not trap the light effectively. Therefore the samples were annealed at higher temperature (Jaeyun, 2015).

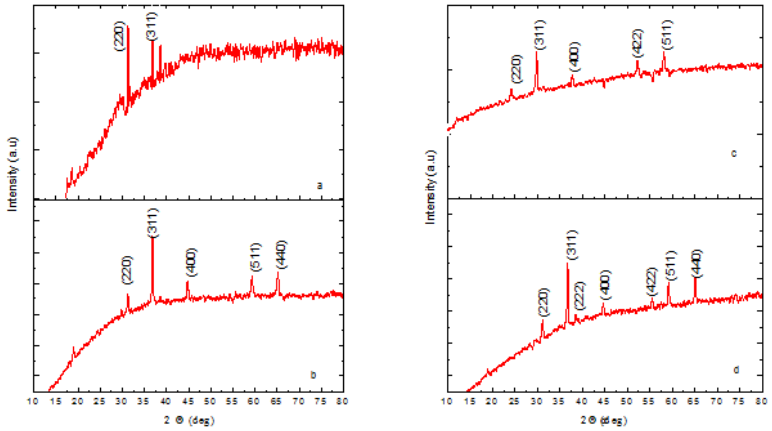

Fig.1.Powder XRD pattern of (a) Synthesized (b, c, d) annealed at 450°C, 550°C, 650°C

The grain sizes of the as-synthesized sample was calculated from the major diffraction peaks of the base of (3 1 1) using the Scherrer formula

$$D = K\lambda / \beta\cos\theta \text{ --- (1)}$$

Where K is a constant (K=0.94), λ is the wavelength (1.5418 Å). θ is the Bragg angle; β is full width half maximum that is, broadening due to the crystallite dimensions. The average particle size of the prepared and annealed cobalt oxide samples at 450°C, 550°C, 650°C are 38,42, 67, 105 nm respectively. It is observed that clear that as the annealing temperature increases the average particle size increases, indicates that the size of the crystallites can be controlled by temperature. Hence this material is suitable for high temperature CSP systems.

3.2.Morphological Studies: Synthesized and annealed cobalt oxide nanoparticles were examined with scanning electron microscopy as shown in figure 2. Material shows a sphere like morphology with uniform homogeneity and good connectivity between the grains. SEM images shows that annealing leads to coalescence of cobalt oxide nanoparticles (Harishchandra, 2014).The grain size of the particles lies in the range of a few hundreds of nanometers. Hierarchical structure could not be obtained as KOH sufficiently supply OH^- anion that leads to the uniform nucleation and growth of uniform small size cobalt oxide nanoparticles (Xu, 2015)

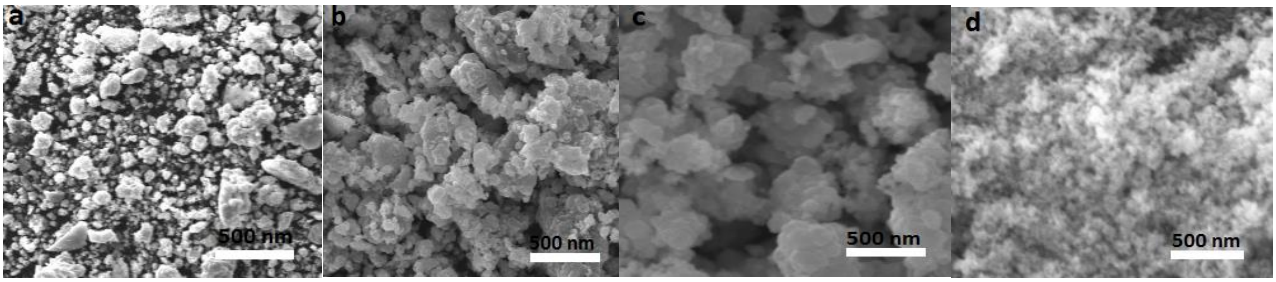

Fig 2. SEM image of (a) Synthesized (b, c, d) annealed at 450°C, 550°C, 650°C

3.3 Optical Studies: The optical properties of Co_3O_4 nanoparticles were characterized by UV-vis spectroscopy. Figure 3a shows the UV-visible spectrum of Co_3O_4 nanoparticles. The optical band gap of Co_3O_4 is strongly influenced by the size, shape, and dimension of materials (Guoxiu, 2009). There are two absorption peaks in the spectrum at 691 nm and 429 nm indicates ligand–metal charge-transfer such as O(II) to Co(III) and O(II) to Co(II) respectively (Masoud, 2009).

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The band gap E_g can be calculated from the equation

$$(\alpha h\nu)^n = B\,(h\nu - E_g) \qquad \text{--- (2)}$$

Where α is the absorption coefficient, *hν* is the photon energy, *B* is constant, and *n* can be either 1/2 or 2 for indirect and direct transition respectively. The $(\alpha h\nu)^2$ versus h*ν* curve is shown in figure 3b and it is found to be 2.21 eV.

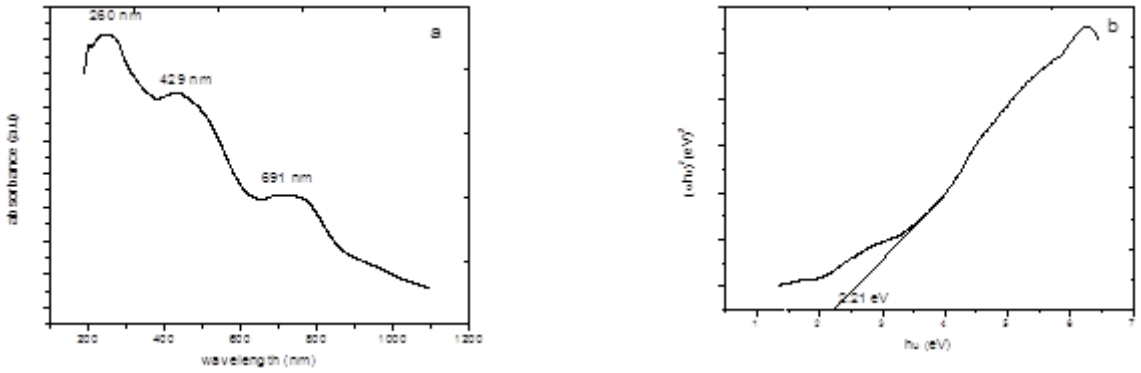

Fig.3.(a) UV –vis spectrum of Co_3O_4 Nanoparticle (b) band gap determination

3.4 Functional Group Studies:

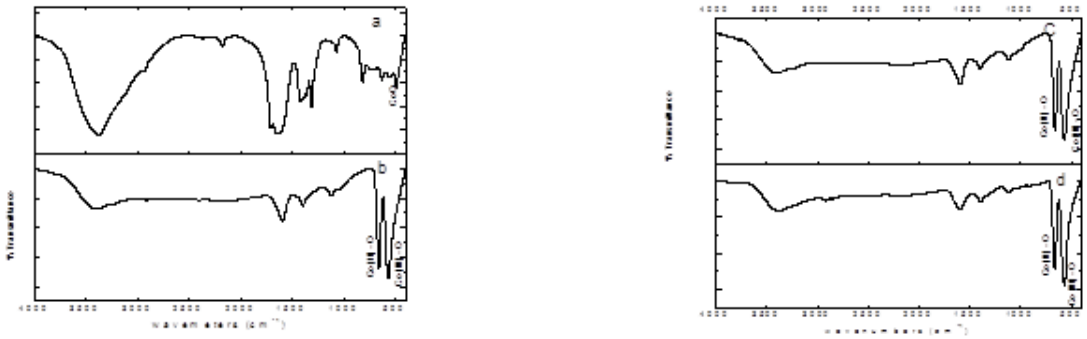

Fig.4.FTIR Spectrum of (a) cobalt oxide and (b, c, d) at 450°C, 550°C, 650°C

The formation of Co_3O_4 phase from the precursor was further ascertained by IR spectroscopy are as shown in fig 4. The characteristic stretching bands of NH_3, CO_3, and NO_3 are observed at 3,368 to 3,500, 1,500, and 1,399 cm^{-1} respectively. The Absorption peak obtained at 2921 and 2852 cm^{-1} corresponds to the C–H stretching vibrations. In the case of Co_3O_4 nanoparticles sharp absorptions of Co(III)–O and Co(II)–O stretching vibrations at 567 and 664 cm^{-1} are observed (Masoud Salavati-Niasari, 2009; Rina Tannenbaum, 2006). It is noted that the bands at 3,572 and 1,590 cm^{-1} in the FTIR spectrum of some samples should be assigned to the stretching and bending vibrations of the water molecules.

4. CONCLUSION

Co_3O_4 nanoparticles were synthesized by hydrothermal method at different annealing temperatures to get crystalline material. The samples were chemically stable even at high temperatures and the average particle size was increased with increase in temperature which is suitable for CSP systems. As the band gap energy of cobalt oxide is 2.21 eV, it absorbs the entire visible region. Hence the cobalt oxide can be coated as thin film for applications in concentrated solar power system.

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