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Synthesis, characterization and optical properties of Co₃O₄ by Precipitation method

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Abstract: Precipitation method has been used as an efficient technique to synthesize Co₃O₄ at low temperature. The prepared products were characterized by thermal analysis (TGA-DTA), powder X-ray diffraction (XRD), Fourier transformer Infrared spectroscopy (FTIR), Scanning electron microscope (SEM) and UV-Visible diffuse reflectance spectroscopy (DRS). X-ray diffraction pattern confirmed the formation of single phase Co₃O₄. SEM images indicates the obtained samples are micro porous sphere like morphology and its grain size will be in the range of 100-300nm. Optical properties of Co₃O₄ ceramic shows an energy band gap as 3.50eV.

Keywords: cobalt oxide, semiconductor, precipitation method, optical property.

1. Introduction

Inorganic materials have more attention because of the vast application as electrical, optical and magnetic properties. Cobalt oxide is a well-known p-type semiconducting material of its electronic and electro-optic properties. Its optical properties have attracted considerable attention and many experimental and theoretical reports have been published [1-3]. Typically, Co₃O₄ powders are synthesized by a solid state reaction requires repeated mechanical mixing and extensive heat treatment at high temperatures to achieve the desired phase purity. Sol gel method has some disadvantage due to its less homogeneity and product obtained only at high temperature. It has been accepted that the wet-chemical process offers advantages of good mixing of the starting materials and excellent chemical homogeneity of the final product [3-4]. Cobalt oxide plays an efficient role in memory storage devices. The cobalt oxide nanoparticles play an important role as a catalyst in water electrolysis process [4]. In the present investigation, reporting synthesise of Co₃O₄ by simple precipitation method at low temperature method and study its optical property.

2. Experimental Details

Fig.1. shows the schematic representation of preparation method. The analytical grade reagents cobalt nitrate and ammonium oxalate are used. The aqueous (0.02M) cobalt nitrate solution with vigorous stirring. Then the precipitating agent 0.02M of ammonium oxalate added into the cobalt solution then, it suddenly forms purple precipitate. The purple cobalt oxalate precipitate was filtered, washed with double distill water and with ethanol then dried in the air at room temperature then decomposed at 400°C for 2h, it forms the black oxide product Co₃O₄.

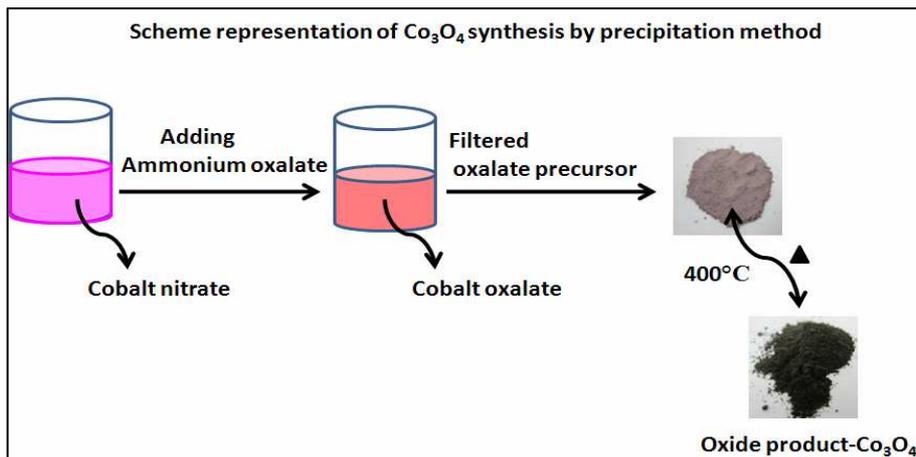


Figure.1. Scheme representation of Co_3O_4 prepared by precipitation method

3. Results and Discussion

Fig.2. (a) Shows the decomposition of oxalate precursor and product formation was investigated by TGA-DTA. Thermogravimetry differential thermal analysis was carried out from room temperature to 400°C in a nitrogen atmosphere at a heating rate of $4^\circ\text{C}/\text{min}$. Fig.1.shows the thermal analysis of oxalate precursor. The precursor decomposed at 400°C it forms stable product of Co_3O_4 and phase identification by XRD it proves the product formation. **Fig.2.(b)** shows the XRD pattern of the obtained Co_3O_4 product. The XRD pattern proves the Co_3O_4 stable single phase formed as cubic normal spinel structure and its lattice parameters $a=b=c=8.072\text{\AA}$ and space group of $Fd3m$, which are consistent with those reported (JCPDS card No 76-1802). Using the XRD diffraction data, the crystallite sizes of samples were able to be estimated using the Scherer Eq.(1).

$$D = K\lambda/\beta\cos\theta \quad (1)$$

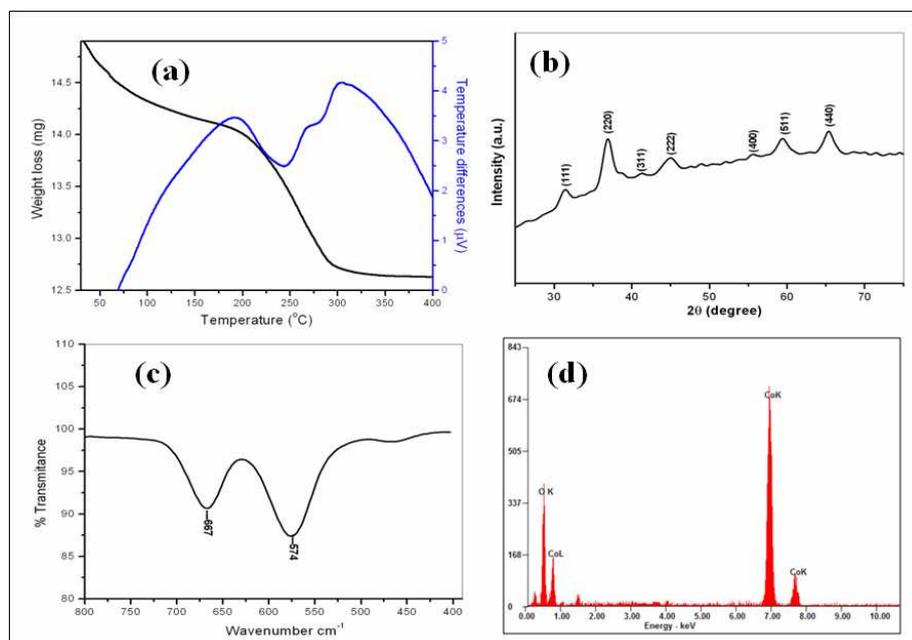


Figure.2. (a) TGA-DTA pattern of product formation of Co_3O_4 (b) XRD patterns of Co_3O_4 (c) FTIR spectra of Co_3O_4 , (d) EDX spectra of Co_3O_4

In this equation, D is the crystallite size (nm); K is the so-called shape factor, which usually takes a value of about 0.9; λ is the X-ray wavelength; β is the full width at half maximum of the diffraction peak at θ is the diffraction angle. Since the peak from the most intense (220) plane diffraction was selected to calculate the average crystallite size of Co_3O_4 as $\sim 50\text{-}100\text{nm}$. FTIR absorption band in the range of $4000\text{-}400\text{cm}^{-1}$ are usually assigned to vibration of ions in the crystal lattice were recorded using KBr disc method. Fig.2.(c) Shows the

FTIR spectra of Co_3O_4 shows peak at 574cm^{-1} corresponds to vibration in the Co^{3+} in octahedral hole and 667cm^{-1} stretching vibrations in the Co^{2+} in tetrahedral hole it shows the presence of single phase face centered cubic structured nanoparticles [1-6]. Fig.2.(d) shows the energy dispersive X-ray spectrometry (EDX) used to quantify the elements exist in the sample by taking a selective portion of SEM image in the form of peaks.

Fig.3 (a) shows the SEM image of nanoparticles of Co_3O_4 . The figures represent higher and lower magnifications. In order to investigate the morphology evolution of the samples, the material shows a sphere like morphology and is composed of agglomerated assembled spheres indicate a uniform homogeneity and good connectivity between the grains.

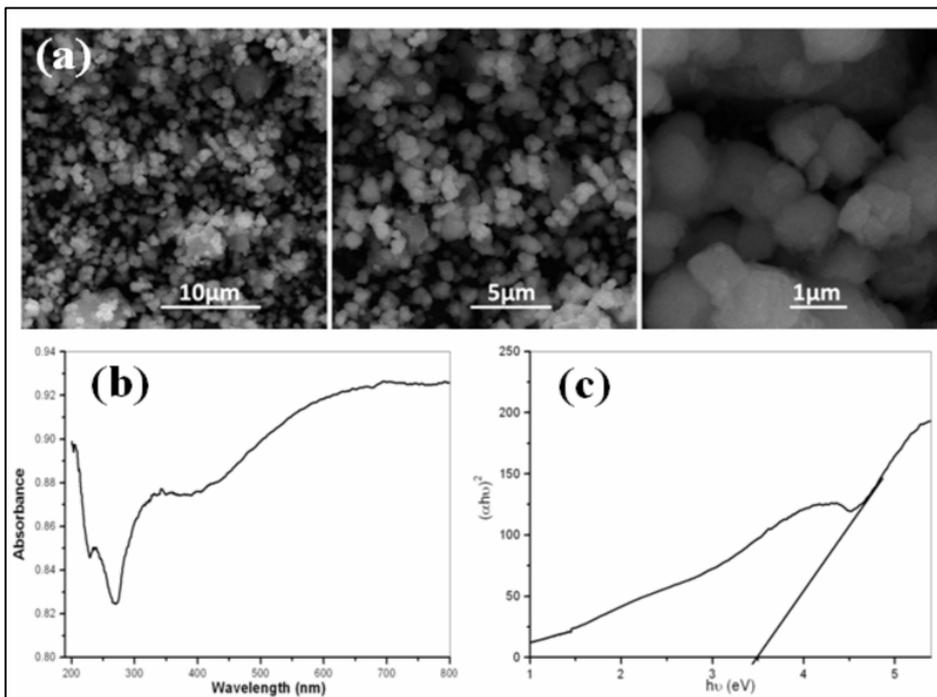


Figure.3. (a) SEM images of higher and lower magnification of Co_3O_4 , (b)UV-absorbance spectra of cobalt oxide (Co_3O_4), (c) DRS band gap of cobalt oxide (Co_3O_4)

Fig.3.(b) shows the absorbance at 250 to 350cm^{-1} and 400 - 580cm^{-1} , the first absorption at due to O^{2-} to Co^{2+} the ligand to metal charge transfer and the band at 580cm^{-1} corresponds to O^{2-} to Co^{3+} charge transfer [2]. The cubic phase Co_3O_4 behaves as a p-type semiconductor. The spectrum can be explained in terms of charge transfer in transition metal (TM) oxides. The relationship between the absorption coefficients α is an incident photon energy $h\nu$. In order to calculate the optical band gap of sample by using Tauc's relation in Eq.(2)

$$(\alpha h\nu)^n = A(h\nu - E_g) \quad (2)$$

Where α denotes the absorption coefficient, A is constant, E_g is band gap and exponent n depends on the type of transition. Fig.3.(c) shows the optical band gap was calculated using Tauc relation by plotting $(\alpha h\nu)^2$ against $h\nu$, by extrapolating the curve to photon energy axis. Calcium cobaltite prepared in this work, cobalt exists in the octahedra of oxygen ions with Co^{3+} (high spin $e_g^2 t_{2g}^4$ / low spin $e_g^0 t_{2g}^6$) ions occupying tetrahedral and octahedral sites, respectively. Hence the optical energy band gap at $E_g=3.5\text{eV}$, due to the electron creates positive hole in the valence band to the conduction band. Hence d-d charge transfer takes place in the Co_3O_4 system it shows p-type semiconducting material.

4. Conclusion

Simple precipitation method used to synthesize nanocrystalline Co_3O_4 ceramic powder. X-ray diffraction pattern confirmed the formation of single phase Co_3O_4 . SEM image indicates the obtained samples are sphere like morphology and its grain size will be in the range of 50 - 100nm . Optical properties of Co_3O_4 ceramic shows a band gap in the energy range of 3.50eV behave as a p-type semiconducting material.

References

1. Y.Ni, X. Ge, Z. Zhang, H. Liu, Z. Zhu, Q. Ye, A simple reduction-oxidation route to prepare Co_3O_4 nanocrystals, *Mater. Res. Bull.*, 2001, 36, 2383–2387.
2. S. Farhadi, J.Safabakhsh and P. Zaringhadam, Synthesis, characterization, and investigation of optical and magnetic properties of cobalt oxide (Co_3O_4) nanoparticles, *Journal of Nanostructure in Chemistry*, 2013, 3,69.
3. M. S. Niasari, A. Khansari, F.Davar, Synthesis and characterization of cobalt oxide nanoparticles by thermal treatment process, *Inorg Chim Acta*, 2009, 362, 4937–4942.
4. Y. Li, J.Zhao, Y .Dan, D .Ma, Y .Zhao, S.Hou, H.Lin, Z.Wang, Low temperature aqueous synthesis of highly dispersed Co_3O_4 nanocubes and their electrocatalytic activity studies, *Chem Eng J*, 2011, 166, 428–434.
