Characterization of manganese/cobalt oxide composites synthesized by chemical co-precipitation method

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Abstract. Composite materials have emerged as new class of materials which presented unique and enhanced applications in the nanotechnology field. In this study, Cobalt oxide-manganese oxide composites have been prepared by chemical co-precipitation method. Cobalt oxide particles were first prepared and used as seeds for making composites with manganese oxide. These composites have been characterized by XRD, SEM, UV-Vis spectroscopy and FTIR. Characterization tools confirmed the formation of Manganese/Cobalt oxide composites. XRD results presented the diffraction peaks for cobalt oxide, manganese oxide and MnCo₂O₄ compounds. FTIR spectrum also indicated the formation of bonds between Mn, Co and O especially at 461 cm⁻¹ shows MnCO₂O₄ bonding. These composite materials absorb visible light of wavelength 682 nm and can be used in light activated photocatalytic activity for the degradation of toxic dyes.

1. Introduction
Nanoscale materials are the synthetic materials linked through noncovalent and covalent bonds. They may have the properties of organic, inorganic and bioactive materials which makes them versatile in nature. Their unique properties give opportunities to develop vast varieties of advanced materials of multiple functions and well-developed structures [1]. The properties of composites may be beneficial to many disciplines such as electronics, optical, catalysis, sensing, coating, energy storage and biomaterials [2]. Composites are attracting the attention of the researchers now a days due to the ever-growing interest, versatility and a path to the development of desired materials [3]. The composites are the atomic or molecular level composition of two different materials. These materials have chemical bonds between their different particles. Composites can be synthesized by variety of protocols including sol-gel methods, blending processes, coordination methods, intercalation, photo-polymerization, electrochemical preparation and synthetic routes of surface-grafting. Composite materials are providing multifunction in a single nano-system and consequently could be used to perform more than one function at a time [4]. Composites have potential application in biomedical field for combinational therapy e.g. gold-iron oxide nanocomposites are useful for both magnetic hyperthermia and plasma thermotherapy [5].

The bioinorganic hybrids are responsible for the development of biological and scientific materials. These are usually able to demonstrate the functions including drug delivery and molecular functioning of the drugs. The enzyme-clay nanohybrids and bio-materials related to the inorganic structures are
used for the biosynthesis applications. The anionic exchange characteristics, versatile structure and wide chemical composition of nanocomposites makes the immobilization of biomolecules possible. For the immobilization of biomolecules, the double layered hydroxides are the most appropriate materials [6]. Manganese oxide nanoclusters with diameters of only 5 to 10 nm have the tendency towards the ferromagnetic behavior. This behavior is shown towards the phase transition between the paramagnetic and other magnetic phases. The abnormal behavior shown by MnO may arise from the effects of cluster size of the material [7].

The anisotropy energy which is usually deformation dependent, outweighs the other anisotropy energies of Cobalt oxide. This property of CoO determines the direction and dimension of the magnetization which is to be directed towards the tetragonal deformation axis [8]. In this research, manganese-cobalt oxide composites were prepared by simple seed mediated co-precipitation method. The obtained composites have been characterized by x-ray diffraction, scanning electron microscopy, UV-Vis spectroscopy and FTIR for structural, morphological, optical and bonding properties.

2. Methodology

2.1. Chemical and components
All the chemicals were bought in pure form and used without any additional treatments. CoCl$_2$.6H$_2$O, MnCl$_2$.4H$_2$O and NaOH were used for the preparation of the composites. Distilled water was used as solvent and for other reactions throughout the experiment. Reaction was based on two steps; first cobalt oxide was formed then used the cobalt oxide particles as seeds for the formation of composite materials.

2.2. Preparation of cobalt oxide powder
For cobalt oxide preparation, 0.4 M of each cobalt chloride hexahydrate and sodium hydroxide was taken and dissolved in 100 ml distilled water separately. NaOH solution was added drop wise into CoCl$_2$.6H$_2$O solution with the help of burette. The colour of solution was first blue then turns into green and finally changes into dark brown. The pH of the solution was adjusted to 11. Then solution was magnetically stirred for two hours. The obtained precipitates were filtered, washed and dried in oven at 80 °C for 24 hours. The so formed cobalt oxide powder was used for further synthesis of composite materials.

2.3. Procedure for preparing composites
After measuring, the CoO (0.74g), MnCl$_2$ (7.91g) and NaOH (1.99g) were dissolved in 25 ml, 100 ml and 125 ml distilled water respectively. MnCl$_2$.4H$_2$O solution were then mixed with CoO solution and sonicate it for 15 minutes. Then NaOH solution was added drop wise into the mixture of two solutions. The formed solution was magnetically stirred for 24 hours to produce composite materials. The obtained precipitates were separated by centrifugation, placed in a crucible for drying in hot air oven at 80 °C and ground into a fine powder using mortar and pestle to get the powdered form cobalt-manganese oxide composites. The obtained powder was then calcinated at 300 °C and 900 °C for 2 hours.

The obtained composite materials have been characterized by XRD [Philips Xpert X-ray diffractometer with Cu Kα radiation (λ= 0.15406 nm)] for analysing phase purity of synthesized powder in the angle 2θ range of 20° to 70°. SEM (VEGA3 TESCAN) was used to observe the morphology of the structures. UV-vis spectrometer was used for optical properties and FTIR was used for bonding structures between different elements.

3. Results and discussion

3.1. X-ray diffraction analysis
The synthesized materials were characterized by X-ray diffraction (XRD). Figure 1 is showing XRD pattern of as synthesized composites and treated at 300 °C and 900 °C. There is only one prominent peak was observed at 29.5° which belongs to the (202) plane of cobalt oxide. As temperature rises up
to 300 °C, two additional peaks were appeared at 25.3° and 35.8°. Diffraction peak at 35.8° belongs to (222) plane of Manganese oxide whereas 25.3° belong to pure Mn phase with JCPDS # 032-0634 as no such diffraction angle was observed in the different phases of cobalt oxide, manganese oxide and its composites. When temperature is elevated to 900 °C, number of diffraction peaks are increased at different diffraction angles. These peaks and their corresponding planes are presented in table 1. These diffraction peaks belong to both cobalt-manganese oxide composites having cubic crystal structure. From these observations, it can be concluded that rise in temperature improved the crystalline order in the materials and presented more stable composite behaviour at higher calcination temperature.

Figure 1. X-ray Diffraction pattern of CoO-MnO composites at different calcination temperature.

Table 1. Peaking matching of sample calcinated at 900 °C.

| Sr. # | Peak (2θ) | Planes | Compound |
|-------|-----------|--------|----------|
| 1     | 30.3297   | (220)  | MnCo₂O₄  |
| 2     | 34.0208   | (311)/(111) | MnO/CoO |
| 3     | 35.7275   | (222)/(311) | MnO/MnCo₂O₄ |
| 4     | 43.5245   | (400)  | MnCo₂O₄  |
| 5     | 57.4356   | (511)/(220) | MnCo₂O₄/CoO |
| 6     | 63.0822   | (440)  | MnCo₂O₄  |
| 7     | 66.695    | (531)  | MnCo₂O₄  |

3.2. Morphological analysis

Figure 2 shows SEM images of the samples calcinated at 300 °C and 900 °C at different magnifications. Low magnification image presents high yield of structures in both temperature values. SEM images of sample calcinated at 300 °C show larger aggregates and some flake like particles. Whereas, in case of 900 °C, more homogenous distribution of spherical particles is observed. High resolution images show that particles are present and existed in spherical shape. These particles have size in the range from 225 nm to 350 nm. SEM images at 900 °C shows better transformation of composite materials.
3.3. UV-visible spectroscopy

UV-vis spectroscopy is a useful technique to study the optical properties of the material. Visible light spectrum of the composites calcinated at 900 °C was recorded as shown in figure 3. The absorption edge of cobalt oxide-manganese oxide composites was obtained at 682 nm wavelength, indicating the potential use of these structures in visible light driven applications especially in photocatalytic degradation and thermotherapy.

3.4. Fast transform infrared spectroscopy

FTIR spectrum of CoO-MnO composites has been computed between the ranges 400-1100 cm\(^{-1}\) wave number region and composed of many close bands. Bands are observed at 461 cm\(^{-1}\), 493 cm\(^{-1}\), 553 cm\(^{-1}\), 591 cm\(^{-1}\) and 611 cm\(^{-1}\). The bands at 493 cm\(^{-1}\), 591 cm\(^{-1}\) and 611 cm\(^{-1}\) attributes to Mn-O bonding for its different oxide types [9, 10]. The band at 553 cm\(^{-1}\) is related to the Co-O vibrations at the octahedral site [11]. Whereas band at 461 cm\(^{-1}\) corresponds to MnCo\(_2\)O\(_4\) compound [12]. FTIR analysis confirms presence of cobalt oxide, manganese oxide and bond between cobalt and manganese indicating the formation of composite particles.

Figure 2. SEM images at different magnifications of composites calcinated at 300 °C (a-c) and 900 °C (d-f). Magnifications: (a) 2400x, (b) 5000x, (c) 8000x, (d) 8980x, (e) 13800x, (f) 23700x.
4. Conclusion
The co-precipitation technique was effectively employed for the preparation of manganese cobalt oxide composites. Cobalt oxide powder was used as seed and manganese was allowed to grow on these seeded particles. XRD results confirm the formation of composites and present cubic crystal structure. SEM and UV-vis spectroscopy were used for morphological and optical properties. Particle size around 300 nm and absorption band at 682 nm wavelength was observed. Finally, FTIR spectrum also indicate the bonding between cobalt, manganese and oxygen which further asserted the results obtained from XRD analysis. These visible lights activated composites can be good candidate for photocatalytic degradation of organic dyes.
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