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Magnetic and electrochemical behaviour of cobalt doped tungsten oxide (WO_3) nanomaterials by microwave irradiation method

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ABSTRACT

Nanocrystalline $WO_3 \cdot H_2O$ nanopowders, doped with cobalt (2 and 5 wt%) have been synthesized using $CoCl_2 \cdot 6H_2O$ and $Na_2WO_4 \cdot 2H_2O$ in a facile microwave irradiation process, followed by the annealing process. The samples were characterized with powder X-ray diffraction, field emission scanning electron microscopy, UV-VIS diffusion reflectance spectroscopy, photoluminescence spectroscopy and cyclic voltammetry (CV). X-ray diffraction patterns showed both undoped and Co doped $WO_3 \cdot H_2O$ crystallized with orthorhombic phase. Annealing h-WO_3 at 600 °C 6 h in air resulted in the different products, $W_{17}O_{47}$ (monoclinic) for undoped, WO_3 orthorhombic for 2 wt% Co doped and WO_3 (monoclinic) for 5 wt % Co doped. FE-SEM micrographs suggested that the dopants are able to influence the growth rate and morphology of the prepared nanopowders. UV-VIS-DRS spectra revealed that the dopant (Co ion) is incorporated in the intermediate energy level. Blue emissions (450–550 nm) were verified using PL at room temperature for the annealed samples ($W_{17}O_{47}$ and WO_3) with excitation wavelength 390 nm. The difference in peak intensity observed through PL spectra attributed to the possible distortions in WO_4^{2-} tetrahedron group during microwave irradiation process. Electrochemical studies showed the possible enhanced catalytic behaviour of cobalt doped (5 wt%) as prepared samples than that of others. The temperature dependent magnetic susceptibility (300 K–2 K) and isothermal magnetization measurements showed the enhancement in magnetic behaviour of the samples for diamagnetic to antiferromagnetic nature which is clearly shows the incorporation of Cobalt ion at tungsten lattice site and in determining the resultant magnetic behaviour of the samples.

1. Introduction

Nanosized materials have attracted great attention as a result of exhibiting unique surface to volume ratio. In particular, high surface area materials have been of great interest in a wide range of applications such as catalysis, chemical and biosensors, fuel cell electrodes and so on [1]. As a well known inorganic oxide, WO_3 is a promising candidate for many applications such as electrochromic [2], photocatalytic [3], photoluminescent [4] and as a gas sensor device [5] due to their existence of various structural polymorphs and easily tunable oxygen content of the end product by varying the growth atmosphere. In fact, the optical and electrical properties of this compound strongly depend on size and morphology of the corresponding end product. Accordingly, the recent scenario for many practical applications is mainly based on morphology and size distribution of the nanoparticles. This can be done by varying the synthesis procedure and growth atmosphere which influence the morphology and size distribution of the nanoparticles.

On the other hand, dopants have offered relatively better morphology and high surface to volume ratio of the nanoscale materials. To date, the following methods have been adopted to synthesis pure and doped WO_3 in the form of powders; vapour deposition [6], hydrothermal route [7], sol-gel [8], acidification method [9], electro spinning method [10], electro deposition method [11] etc. However, the above mentioned techniques are more time consuming and cost effective. Great efforts are being

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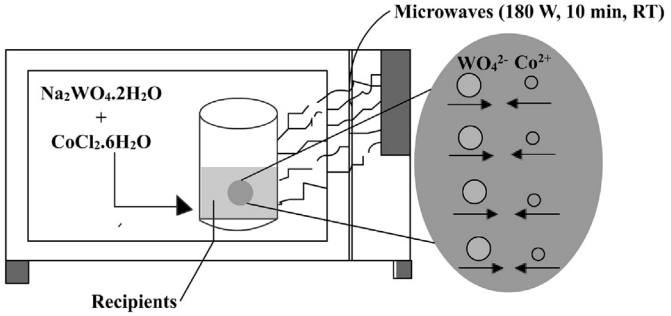
taken to explore new synthesis methods to control the morphology and size distributions to satisfy certain applications. Recently, most of the works focused on the preparation of doped nanocrystalline WO_3 following their successful applications. Zhu et al. [12] have prepared Cu-doped WO_3 materials with photonic structures using combined sol-gel templating and calcinations method for the detection of various volatile organic gases. They suggested that the photonic crystal of Cu-doped WO_3 replica sensor has a much higher response as well as selectivity when compared to that of pure one due to their different morphologies. Cheng et al. [13] fabricated Zn-doped WO_3 thin films and found the enhanced behaviour of Zn doped WO_3 with a suitable amount in the case of photocurrent and photo-activity. Zamani et al. [14] have synthesized Cr-doped mesoporous WO_3 nanomaterial by chemical route for the detection of amines and tetra methyl amines. Finally they summarized the product showed low sensitivity to NH_3 and TMA was detected more efficiently. Xia et al. [15] have prepared pure and Au-doped WO_3 nanopowders by a colloidal chemical method. They concluded that proper Au loading on WO_3 is suitable for the detection of NO_2 at relatively low temperature. Kalidindi et al. [16] studied Ti-doped WO_3 films on Si(100) wafers using sputtering technique and found that the electrical conductivity of Ti-doped samples at room temperature is more than that of pure sample.

The aim of this paper is to synthesize cobalt doped $WO_3 \cdot H_2O$ nanopowders with different W/Co (0.02 and 0.05) ratios using simple, efficient straight forward microwave irradiation method. The procedure reported here, to the best of our knowledge, is the first demonstration in the synthesis of cobalt doped $WO_3 \cdot H_2O$ nanopowders using microwave irradiation method. The time required for the synthesis was around 10 min and the reaction process was also very simple and the results are reported in this paper.



Schematic illustration of synthesis of cobalt doped $WO_3 \cdot H_2O$ in microwave atmosphere.

2. Experimental details

$W_{1-x}Co_xO_3$ (x ≈ 0, 0.02 and 0.05) nanopowders were prepared by microwave irradiation method at room temperature [17,18]. Analytical grade of 4.98 g of tungstic acid (H_2WO_4) was dissolved in 20 mL of sodium hydroxide (NaOH) with one molar ratio. The resultant solution was stirred for 20 min. The yellow colored hydrated sodium tungstate solution was formed; this may be due to proton exchange protocol process [19]. Subsequently, 2 wt% and 5 wt% of cobalt hexa chloride ($CoCl_2 \cdot 6H_2O$) was mixed along with the total amount of tungstic acid into a 20 mL of deionized water. Both the solution was mixed together slowly and the final solution was stirred again for 20 min. The pH of the solution was found to be neutral (≈7.0) and it was adjusted up to 1 by adding few drops of HCl because it can act as a precipitating agent and also medium for the product to have desired morphology [20]. In addition, in the above solution 5 ml of double distilled water (i.e. 50 vol % of precursor solution) was added in order to respond microwave quickly. The final mixture was transferred into a microwave oven (2.45 GHz and maximum power of 900 W) and kept the mixture at 180 W for 10 min. After microwave treatment the yellow precipitate was finally collected. The obtained powders were annealed in a tubular furnace at 600 °C for 6 h in air in order to remove the sub products and to improve the crystallinity.

3. Results and discussion

3.1. Powder XRD analysis

Fig. 1a shows the powder XRD spectra of undoped and cobalt doped $WO_3 \cdot H_2O$ nanopowders. The results confirmed that both products crystallize in orthorhombic structure in accordance with JCPDS card no: 43–0679. A small shift in lower Bragg angle side for Co-doped (≈2 wt%) sample indicates the incorporation of Co ion into $WO_3 \cdot H_2O$ lattice, which could be attributed to atomic radius of Co ion (1.16 p.m.) compared to that of tungsten ion (1.5 p.m.). In case of 5 wt% doped sample, the XRD peaks correspond well with that of undoped parent phase $WO_3 \cdot H_2O$. Fig. 1b shows the variation of crystallite size as a function of cobalt concentration along (020) and (111) planes estimated using Debye Scherrer's formula. The shrinkage of crystallite size for 5 wt% cobalt doped sample nearly to the value of undoped sample along (020) plane clearly suggested the incorporation of Co ion in WO_4^{2-} (020) tetrahedron structure but not in water molecule site along (111).

Fig. 2 presents the corresponding XRD patterns of the annealed undoped and cobalt doped tungsten oxide nanopowders at 600 °C in air for 6 h. The XRD pattern of h-WO_3 is transformed into $W_{17}O_{47}$ phase with monoclinic structure in accordance with the JCPDS card no: 79–0171. On the other hand Co (2 and 5 wt%) doped h-WO3 (WO3·H2O) have been reduced to stoichiometric WO3 with orthorhombic (JCPDS card no: 89–4480) and monoclinc (JCPDS card no: 8–4479) structure revealed the excess of oxygen content counteracts the hole doping behaviour. The excessive oxygen atom may intercalate into the WO_4^{2-} tetrahedron site due to high hole density created by Co-ion [21]. As the cobalt concentration (Co ≈ 0.05) increased further, it attains the saturation point which then it is difficult to accommodate excess of oxygen atom into the crystalline structure which exhibited the phase memory process.

3.2. Microstructural analysis (FE-SEM)

Fig. 3a and b show the FE-SEM images of un doped and Co doped $WO_3 \cdot H_2O$ samples. Fig. 3a indicates platelet like morphology in the order of 0.1–0.29 μm along longer axis and 0.1–0.22 μm in shorter axis; moreover, the white appearance in FE-SEM is due to charging phenomenon. Formation of elongated particles indicated the prepared samples growth along (020) plane. A careful examination of the particles shows the edge effects, which is attributed to charge transfer between 'W' and 'O' ions (Fig. 3a). Conversely, co doped (5 wt%) smaller particle may be attributed to the faster nucleation process under the same conditions due to the presence of Co ions in the growth environment.

Fig. 3c and d show the micrographs of annealed pure and doped (Co ≈ 5 wt%) $WO_{3-\delta}$ nanopowders. Pure sample revealed the formation of large quantity of particles with agglomerate and poly disperse nature that appears sheet like morphology of the order of 0.23–0.37 μm in lateral axis and 0.047–0.066 μm in longitudinal axis. As it can be seen from Fig. 3c, the agglomeration is due to fast and rapid collision between the particles during the recrystallization process from $WO_3 \cdot H_2O$ to $WO_{3-\delta}$ through annealing. On the other hand, Fig. 3d shows the formation of cubic like particles with the dimensions of the order of 0.188–0.37 μm range for cobalt