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Synthesis and characterization of Manganese doped Tungsten oxide by Microwave irradiation method

Mohammed Harshulkhan Sayed Abhudhahir [a,*], Janaki Kandasamy [b]

[a] Vinayaka Mission's Kirupananda Variyar Engineering College, Department of Physics, Salem 636308,Tamil Nadu, India
[b] Government Arts College for Women, Department of Physics, Salem 636008,Tamil Nadu, India

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ABSTRACT

The aim of this article is to synthesis tungsten oxide (WO_3) nanoparticle along with Manganese (3 wt% and 10 wt%) by Microwave irradiation method. The physical properties of the synthesized Manganese doped Tungsten oxide materials were characterized by X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Transmission Electron Microscope (TEM), UV-Diffuse Reflectance Spectroscopy, SEM-EDAX and Photoluminescence studies. The predominant peaks obtained in X-ray diffraction pattern reveal the crystalline nature of the nanoparticles and the structure belongs to Monoclinic for pure and Mn doped WO_3. FTIR analysis shows the presence of Tungsten and oxygen in the synthesis material and verified with EDAX. TEM analysis shows both pristine and Mn doped WO_3 nanopaticles. They are having spherical shaped morphology with average particle size from 35 to 40 nm. UV-DRS revealed that the bandgap energy for pure and Manganese doped WO_3 are discussed in this article. The Scanning Electron Microscope analysis shows the plate like morphology for pure WO_3 and the morphology were decreased by doping Manganese. The defects and oxygen deficiencies were analysed by photoluminescence spectroscopy.

1. Introduction

The heterogeneous photocatalysis attracted a considerable attention due to elimination of organic pollutants in water [1–4] and semiconductor photocatalysts drew attention due to low cost and environmental friendliness. Because of low cost and stability towards corrosion. TiO_2 is used as commercial photocatalytic material. The bandgap energy for TiO_2 is 3.2 eV [5] limits further application in the visible light region.

Tungsten oxide is the important n-type semiconductor material. Due to the novel character, it is used in various fields like optical, electrical and semiconductor industries. Tungsten oxide was first studied in seventeenth century for its electrochromic properties in amorphous state. Due to this property it is used for various applications like flat panel devices, smart windows and anti glare rear mirrors for automobiles. Tungsten oxide shows high response to the gases like O_2, O_3, NO_2, H_2S and H_2 and it is used in solid state sensors [6]. The band gap energy of the tungsten oxide is 2.5–3 eV [7,8]. WO_3 is a visible light responsive photocatalyst that absorbs radiation in the region upto 480 nm [9]. WO_3 is an inexpensive material with high stability in aqueous solution and under acidic condition which makes it an attractive material for photocatalytic applications. There are several additives and metallic dopants like Cu [10], Sn [11], Pd [12] which can improve the photocatalytic performance of WO_3. The doping element which can modify the electronic structure of semiconductors and surface properties which extends their visible light absorbance. Cong and Lin [13] have successfully prepared Eu^{3+} doped WO_3 nanoparticles for the photocatalytic decomposition of rhodamine B (RHB). Madhan et al. prepared Zn doped WO_3 for the photo degradation of methylene blue and rhodamine B [14]. The different concentrations of various transition metals (Fe, Co, Ni, Cu and Zn) effect on the photocatalytic activity of WO_3 for splitting of water into hydrogen and oxygen was studied but only under UV laser irradiation [15].

Several synthesis processes like Sol–gel method, Chemical precipitation method, hydrothermal process, sputtering technique and Microwave irradiation method are available to produce tungsten oxide. Among these methods Microwave irradiation method is very simple due its operation, less consumption of time, purity of the material when compared to other methods.

In the recent study, it has been reported that the tungsten oxide synthesis was found along with the water molecule ($WO_3 \cdot H_2O$) by Microwave irradiation method [16]. In the present research work the pure and Manganese doped Tungsten oxide without hydrate group were synthesized by Microwave irradiation

* Corresponding author.
E-mail address: harshulkhan21@gmail.com (M.H. Sayed Abhudhahir).

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method. For the first time the study yielded the pure and Manganese doped Tungsten oxide directly from the Microwave irradiation method without hydrate group (H_2O). In both the cases, the time taken to complete the synthesis was around 5 min and the reaction process is very simple.

2. Experimental procedure

2.1. Material synthesis

The precursor solution was prepared by adding tungstic acid in 10 ml of sodium hydroxide (NaOH) solution. It results in a yellow color solution due to proton exchange process [17]. Then Hydrochloric acid (HCl) is added drop by drop till it attains a pH value of 1. Hydrochloric acid acts as a precipitating agent and also as the medium for the required product to have desired morphology [18]. After attaining the desired pH value, 5 ml of distilled water is added for quick response of microwave with precursor solution. The final solution was placed into the microwave oven (2.45 GHz) under optimum power of 360 W in air atmosphere. After the irradiation process, the resultant substance was dried in convection mode at 100 °C for 5 min. The Mn–WO_3 was synthesized by adding tungstic acid and Manganese sulfate at molar ratio (0.03 and 0.10) in 10 ml of sodium hydroxide (NaOH) solution. The above procedure was repeated to obtain the final product. The final product was pale green in color for pure WO_3 and pale yellow color for Mn doped WO_3.

2.2. Characterization techniques

The surface morphology, structural and chemical state of the obtained Nanomaterial was characterized by using X-ray diffraction method (X-ray Diffractometer-XPERT PRO) and FTIR (Spectrum RX I-Perkin Elmer). Transmission Electron Microscope and Selected-area electron diffraction were recorded with JEM2100. High resolution electron microscope were recorded with a accelerating voltage of 200 kV. Optical measurements were carried out in UV–vis Spectroscopy (SHIMADZU 3600 UV–vis Spectrometer), surface morphology was studied by Scanning Electron Microscopy (FEIQUATA250), Elemental analysis were performed by EDAX (FEIQUATA250) and PL spectra were recorded by LS 45 Fluorescence spectrometer.

3. Results and discussion

3.1. XRD analysis

The microstructure of the prepared sample was analyzed by X-ray diffraction (XPERT PRO) using the Cu Kα wavelength of 1.5405 Å. Fig. 1 shows the X-ray diffraction (XRD) pattern for synthesized pure and Mn doped WO_3. From the figure it is observed that the pure WO_3 exhibit the diffraction peak at 2θ=23.123, 23.594 and 24.371 related to (002), (020),(200) reflection of monoclinic phase of WO_3. Lattice parameter of the synthesized pure and Mn doped WO_3 are a=7.300, b=7.538, c=7.689 and β=90.892 (JCPDS Card no.: 83-0950). It is also observed that no diffraction peak for MnO due to lower concentration of Manganese atom into WO_3. The full width at half maximum (FWHM) of the diffraction peak of the WO_3 is increased in Mn doped WO_3. The increase of peak width indicates the decrease in the crystallite size of the Mn doped WO_3. The crystalline size (D) of the pure and Mn doped WO_3 was calculated by using Debye Scherrer's relation [19,20].

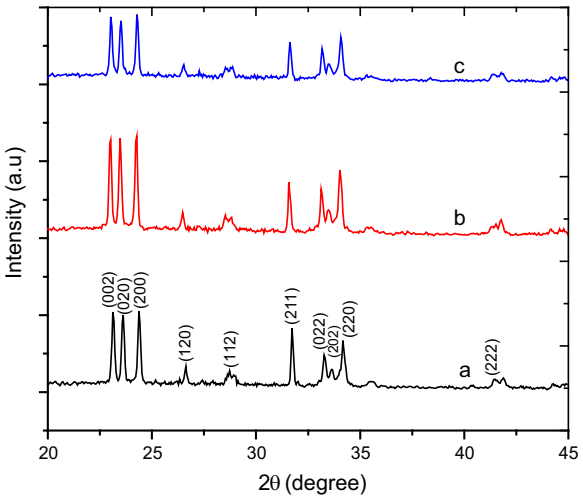

Fig. 1. XRD pattern for (a) pure WO_3, (b) 3 wt% Mn and (c)10 wt% Mn.

Table 1
Crystalline size for pure and Mn doped WO_3.

Material	Average crystalline size (nm)
Pure WO_3	46.35
3 wt% Mn	43.97
10 wt% Mn	31.87

$$D = \frac{0.9\lambda}{\beta \cos\theta}\text{nm}$$

where β is the full width at half maximum, λ is the X-ray wavelength (0.15406 nm), and θ is the diffraction angle. The crystalline size of the pure and Mn doped WO_3 are shown in the Table 1. The XRD results reveals that the crystalline size has increased in Mn doped WO_3.

3.2. FTIR analysis

Fig. 2 shows the FTIR spectra of pure and Mn doped WO_3. The observed wave number, relative intensities obtained from the recorded spectra and the assignments were listed in Table 2. The

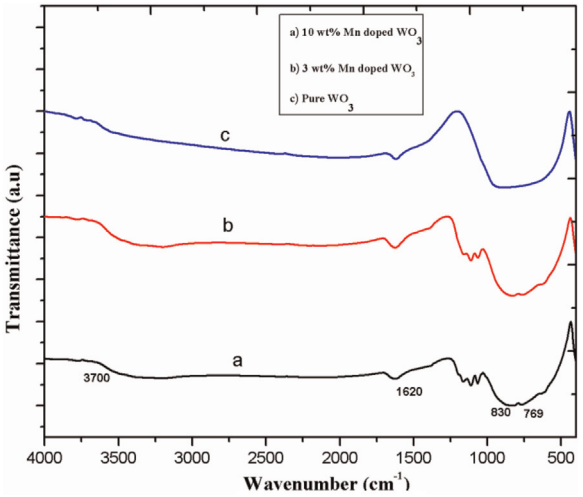

Fig. 2. FTIR spectrum of (a) 10 wt% Mn doped WO_3 (b) 3 wt% Mn doped WO_3 (c) Pure WO_3.