

# Effect of temperature on aluminum doped WO<sub>3</sub> nanoparticles prepared by solvo thermal method

N. PRABHU<sup>a,\*</sup>, S. AGILAN<sup>b</sup>, N. MUTHUKUMARASAMY<sup>b</sup>

<sup>a</sup>Department of Physics, Nandha Engineering College, Erode, 638052, India

<sup>b</sup>Department of Physics, Coimbatore Institute of Technology, Coimbatore, 641014, India

Aluminum (Al) doped Tungsten oxide (WO<sub>3</sub>) nanoparticles have been successfully synthesized by the simple solvo thermal cum chemical method and annealed for different temperatures like room temperature (RT), 100°C and 400°C respectively. The nanoparticles have been characterized by number of techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive x-ray analysis (EDXA). The XRD results point out that all the Al doped WO<sub>3</sub> nanoparticles are in monoclinic form and that aluminum ions are successfully integrated into the WO<sub>3</sub> lattice. The SEM images used to identify the grain size of the 400°C Al doped WO<sub>3</sub> nanoparticles was smaller than that of room temperature (RT) Al doped WO<sub>3</sub> nanoparticles. It was also specific that a film with a spherical porous structure was successfully fabricated. The EDXA spectra of the Al doped WO<sub>3</sub> nanoparticles confirmed the presence of Al, W and O.

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## 1. Introduction

Tungsten oxide (WO<sub>3</sub>) is one of the d<sup>0</sup> transition metal oxides, has many attractive optical, electrical, structural, and defect properties. The work on WO<sub>3</sub> has encouraged extensive research on a number of other transition metal oxides, and several books [1,2] and review articles have been written on this issue [3,4]. Among all the materials studied thus far, WO<sub>3</sub> has emerged as the most widely studied material, not only for chromo genies, but also for a variety of other device applications. Beyond the technology development, massive work on the physical and chemical properties of WO<sub>3</sub> as a prototypical material has been done that is of immense scientific interest [5]. WO<sub>3</sub> is a semiconductor oxide material with a band-gap of 2.6–3.0 eV [6], and it is becoming the focus of research attention due to its unique electronic properties. In particular, various WO<sub>3</sub> nanostructures (nanoparticles, nanoplatelets, nanorods, and nanowires) are of special interest as promising candidates for photocatalyst [6], solar cell [7] electrochromic devices [8, 9], and gas sensors [10,11] because of their high surface area and novel properties [12].

Many physical properties of WO<sub>3</sub>, such as piezoelectricity, electrical conductivity and defect structures, are greatly predisposed by the presence of impurities. Several dopants such as Fe, Cr, Al, Cu, Co, Mn, Mg, S, P, N etc. can lead to an increase in the surface area of the WO<sub>3</sub> based nano powders. Doping with other elements can greatly advance the performance of Metal oxide [13]. Among these doped metal oxide materials, aluminum (Al) doped WO<sub>3</sub> (AWO<sub>3</sub>) nanoparticles have received significant attention [14-18]. And also have the advantage of abundant and cheap raw materials. However,

the application range of Al doped WO<sub>3</sub> nanoparticles have been limited by the limitation of particles characteristics.

Several methods including hydrothermal [19], sol-gel [20], chemical vapor deposition (CVD) [21] and sputtering [22] have been used to prepare metal oxide nanoparticles. For efficient photo catalytic activity, nanomaterials need to be crystalline, that is, should be grown at high temperatures or at very slow rates. In general, different synthesis routes of nanostructures usually result in amorphous structures but, solvo thermal cum chemical method [23] has the advantage in this regard as it produces self- crystallized nanostructures due to high temperature caused by joule heating. Moreover, compared with other techniques, solvo thermal cum chemical method is an attractive method because of simplicity of experimental set up, lack of need for complicated equipments, low impurity, less production steps leading to a high-throughput and cost-effective procedure to generate a high yield of nanoparticles. Also the plainness of this method allows scaling up for mass production.

The aim of the present study is to synthesize the aluminum (Al) doped tungsten oxide (WO<sub>3</sub>) nanoparticles by simple solvo thermal cum chemical method. The prepared Al doped nano particles are annealed by different temperatures like room temperature, 100°C and 400°C respectively. And the doped nano particles are followed by structural characterizations using X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDS).

## 2. Experimental

Tungsten chloride (Sigma Aldrich 99.99%) and Cyclohexanol were used as a precursor. 40 mg of

Tungsten chloride was slowly dissolved in 15 ml of Cyclohexanol to obtain a consistent solution with the help of magnetic stirrer. Then the solution was centrifuged and washed with distilled water until to reach neutral pH of the solution. After the centrifuge, the solution was subjected to slow evaporation to remove the excess solvent present in the solution at room temperature. After evaporation we got WO<sub>3</sub> nanoparticles. To prepare Aluminum (Al) doped WO<sub>3</sub> nanoparticles, we used the paste preparation method. In paste preparation method, the paste was produced by mixing of 5.0 g of Aluminum powders and 15 g of WO<sub>3</sub> nanoparticles with a mixture consisting of 15.0 g of  $\alpha$ -terpineol, 2 g of cellulose, and 25 ml of ethanol, which was sonicated for 60 hrs at 1200 Wcm<sup>-2</sup>. By using the prepared paste thin films were prepared by coating the paste on a FTO conducting glass plate (Hartford FTO, ~30 $\Omega$  cm<sup>-2</sup>, 80% transmittance in visible region) using the doctor blade technique. The Al doped WO<sub>3</sub> nanoparticles are prepared at different temperature like room temperature, 100°C and 400°C respectively.

X-ray diffraction method using CuK $\alpha$  radiation has been used to study the structure of the synthesized nanoparticles. This study was carried out by employing a Bruker Axs D8 Advance X-ray diffractometer with CuK $\alpha$  ( $\lambda=1.5406$ ) radiation using a tube voltage and current of 40kV and 30mA respectively. The sample was scanned from 10° - 80° in 2 $\theta$  with step size of 0.5° in 2 $\theta$  and scan speed of 0.5° per second. Surface morphology of the synthesized nanoparticles were studied using scanning electron microscopy (SEM; Philips XL 40), and the atomic compositions of the nanoparticles were measured by energy dispersive x-ray analyses (EDXA; Inca, oxford instruments) operated at 120 kV.

### 3. Results and discussion

The XRD pattern of Aluminum (Al) doped WO<sub>3</sub> nanoparticles with different temperatures like Room temperature (RT), 100°C and 400°C as shown in Figure 1. All the annealed Al doped WO<sub>3</sub> nanoparticles displayed a monoclinic, polycrystalline WO<sub>3</sub> structure with a main peak at 24.4° consequent to the (1 0 0) plane. The XRD patterns for the Al doped WO<sub>3</sub> samples were found to be the same as those for the room temperature, suggesting that the aluminum ions were well integrated into the WO<sub>3</sub> lattice. No additional peaks were detected even for 400°C, indicating that the temperature did not change the crystalline structure of the WO<sub>3</sub> nanoparticles. However, the intensity of the main WO<sub>3</sub> peaks decreased as the temperature increased, suggested that the increasing temperature may manipulate the crystalline at which WO<sub>3</sub> changes from amorphous to crystalline state. The line augmentation of the peak is related to the size of the monoclinic crystalline phase [24]. The average crystallite size  $D$ , of each sample can be calculated using the Scherrer equation [25],

$$D = K\lambda / FWHMCos\theta$$

Where  $K$  is the shape factor of the average crystallite (expected shape factor is 0.94),  $\lambda$  is the wavelength in nanometer, FWHM is the full width at half maximum in radians, and  $\theta$  is the peak position. The crystallite size of room temperature based on the (1 1 2) peak was found to be 16.7 nm. The crystallite size decreased with increasing temperature. The crystallite size was reduced to 9 nm under 400°C. This is because of the increasing temperature, the atomic sites enhanced inter granular cohesion and induced lattice eccentric. Therefore, the direct relation between particles was inhibited, and crystal growth was slowed down. However, SEM measurements indicated that the particle size was reduced at 400°C temperature. This is due to the agglomeration of the particles with insignificant crystal growth.

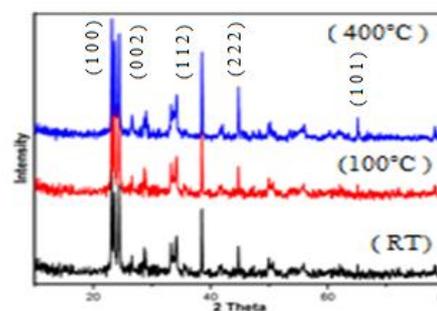


Fig. 1. X-ray diffraction pattern of Al doped WO<sub>3</sub> nanoparticles annealed at Room temperature (RT), 100°C and 400°C.

The scanning electron microscope (SEM) images of the Al doped WO<sub>3</sub> nano particles prepared at different temperatures are shown in Fig. 2 (a), 2 (b), and 2 (c).

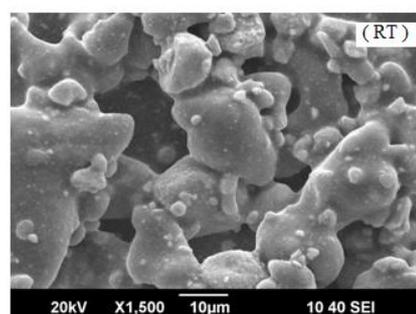


Fig. 2. (a) SEM image of Al doped WO<sub>3</sub> nano particles at room temperature (RT).

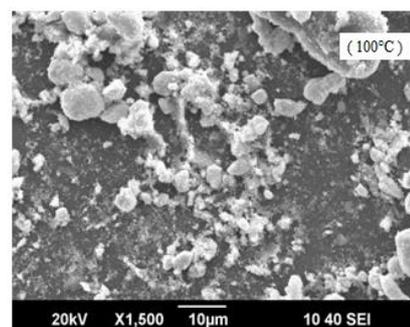


Fig. 2. (b) SEM image of Al doped WO<sub>3</sub> nano particles at 100°C.

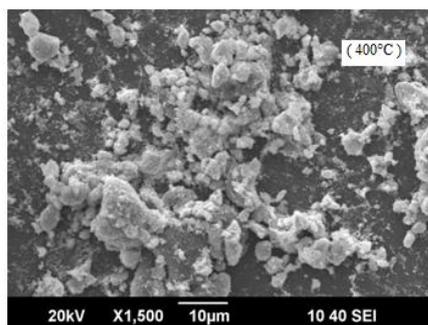


Fig. 2. (c) SEM image of Al doped  $WO_3$  nano particles at  $400^\circ C$ .

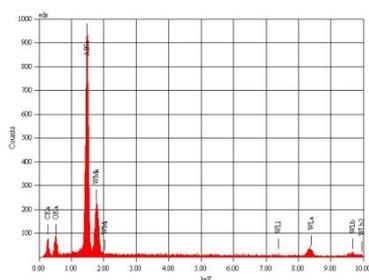


Fig. 3. (a) EDS image of Al doped  $WO_3$  nano particles at Room temperature.

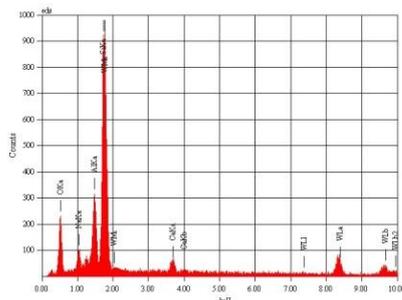


Fig. 3. (b) EDS image of Al doped  $WO_3$  nano particles at  $100^\circ C$ .

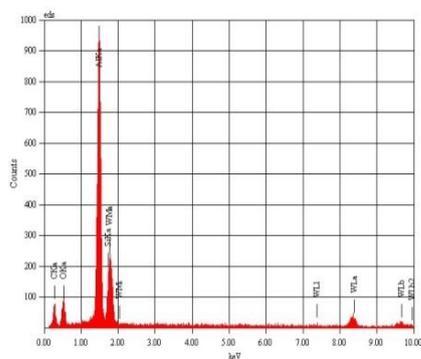


Fig. 3.(c) EDS image of Al doped  $WO_3$  nano particles at  $400^\circ C$ .

Fig. 2(a), 2(b), and 2(c) presents SEM images of Al doped  $WO_3$  nanoparticles annealed at different temperatures like room temperature (RT),  $100^\circ C$  and  $400^\circ C$ . For room temperature (RT) of Al doped  $WO_3$  nanoparticles with a diameter of 10nm and a uniform array were observed. The spherical particles suggested that the organic compounds used in the synthesis were effectively eliminated during the annealing process. The morphology of  $400^\circ C$  Al doped  $WO_3$  nanoparticles were different from that of room temperature (RT) Al doped nanoparticles. Compared with  $400^\circ C$  Al doped  $WO_3$  nanoparticles, room temperature (RT) Al doped nanoparticles [Fig. 2 (c) & Fig. 2 (a)] verified that increasing temperature presents to the agglomeration and grain growth of the Al doped  $WO_3$  particles, leading to an rough particle surface. The grain size of the  $400^\circ C$  Al doped  $WO_3$  nanoparticles was smaller than that of room temperature (RT) Al doped  $WO_3$  nanoparticles. It was also definite that a film with a spherical porous structure [26] was successfully fabricated. The porosity of the film is a key factor because a large surface-to-volume ratio means an increase of dye absorption, which facilitates the photocurrent enhancement [27].

The chemical composition and concentration of the aluminum doping were investigated by energy-dispersive x-ray analysis (EDXA) as well as by solvo thermal cum chemical method [Fig. 3 (a), 3 (b), and 3 (c)]. The EDXA spectra of the Al doped  $WO_3$  nanoparticles confirmed the presence of Al, W and O. According to EDXA, Al/W ratios of different temperatures were obtained with a formal Al doped nanoparticles provided in the combination of preliminary materials. Although  $Al^{3+}$  is integrated and the real ratio correlates with the formal one, a significant percentage of the  $Al^{3+}$  clearly remains in solution so that the real doping of the solid nanomaterials is lower than expected.

#### 4. Conclusion

This article described the preparation of Al doped  $WO_3$  nanoparticles annealed at different temperatures like room temperature (RT),  $100^\circ C$  and  $400^\circ C$  by solvo thermal cum chemical method, using Tungsten chloride (Sigma Aldrich 99.99%), Cyclohexanol and Aluminum as early materials. The XRD results indicate that all the Al doped  $WO_3$  nanoparticles are in monoclinic form and that aluminum ions are successfully incorporated into the  $WO_3$  lattice. The SEM images used to identify the grain size of the  $400^\circ C$  Al doped  $WO_3$  nanoparticles was smaller than that of room temperature (RT) Al doped  $WO_3$  nanoparticles. It was also specific that nano particles with a spherical porous structure were successfully fabricated. The EDXA spectra of the Al doped  $WO_3$  nanoparticles confirmed the presence of Al, W and O. The characterizations concluded that increasing temperature changes the structural and morphological effects on Al doped  $WO_3$  nanoparticles.

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\*Corresponding author: prabhu761984@gmail.com