Hydrothermal Synthesis of tailored Tungsten Oxide (WO_3) Nanoparticles for Versatile Functionalities[1]

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ABSTRACT

The Nanocrystalline tungsten oxide(WO3) is synthesized on fluorine-doped tin oxide (FTO) glass substrates employing hydrothermal technique. The structure, phase and morphology of these WO3 thin films were characterized using X-ray diffraction (XRD), UV-Vis Transmittance, scanning electron microscopy(SEM), Energy dispersive spectra (EDX). The Hydrothermal deposition technique can be potentially used to obtain uniform nanocrystalline WO3 films on a considerably larger area..The synthesized WO3 nanocrystalline is excellent substitute for various application and these films are equally comparable to the ones obtained by other sophisticated methods such as, vacuum or plasma deposition techniques.

Keywords: *Hydrothermal deposition, self-assembly, tungsten oxide, photocatalytic*

INTRODUCTION

Tungsten oxide (WO_3) nanoparticles, have gained researchers attention in various fields of science and technology due to their unique properties and potential applications. Some of the important applications of tungsten oxide nanoparticles are photocatalysis [12], electrochromic devices, gas sensors, energy storage devices, super capacitor, photovoltaics, hydrogen generation[22] anti-reflective coatings, drug delivery, biomedical imaging. Among many materials tungsten oxide has emerged as promising materials on account of low cost and acidic stability [6]. [5] [11][12] [16][17].These nanoparticles can change their optical properties in response to an applied voltage , making them valuable for controlling the amount of incident sunlight and heat entering the buildings i.e electrochromic devices [15][17]. Since Tungsten is a transition metal with oxygen acquire sensitivity to sense various gases including hydrogen, methane and volatile organic compounds, because of this property tungsten oxide nanoparticles can be employed in industrial and environmental monitoring [8][9] [16]. They can be used as anode materials and is used in energy storage applications, especially in lithium-ion batteries. The unique structure of nanoparticles can enhance the performance of batteries [5]. Even these particles can be employed as electron transport materials in pervoskite solar cells, increasing their efficiency and stability [10][18][22]. When these particles are incorporated into coatings can reduce reflection and glare from surfaces, such as solar panels and optical lenses [20]. With their controllable size and tunable surface properties researchers have explored tungsten oxide nanoparticles in targeted drug delivery system, control release, biomedical imaging such as magnetic resonance imaging (MRI) and computed tomography(CT) scans. In photocatalytic water purification tungsten oxide nanoparticles play a major role in removing the contaminants and pollutants from water sources when exposed to light [9][18]. The ability in absorbing light in visible and near IR region is high which makes them valuable in optical and electronic devices [18]. Their unique properties and versatility make them a subject of ongoing research and development in various scientific and industrial fields.

Various physical and chemical methods are reported to synthesis nanocrystalline tungsten oxide like sputtering, physical vapor deposition (PVD), spray pyrolysis, electrodeposition, Sol-gel [2-13]. Among them hydrothermal synthesis is one step and simple method to execute the functionalities efficiently including structural modification (tailored), elemental doping to create effective composites. Hydrothermal synthesis technique used to create wide range of materials, including metals, ceramics, semiconductors, nanoparticles and organic compounds under high temperature and high pressure conditions in an aqueous environment. With this technique researchers could adjust parameters such as

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temperature, pressure and reaction time to tailor the physical and chemical properties [11][13][18]. This technique is particularly useful in synthesizing nanoparticles with uniform size and shape which enhances the performance of nanoelectronics. This method involves aqueous system which can facilitate the recycling of certain materials and environment friendly compared to some organic solvents contributing to sustainable practices. The tailored tungsten nanoparticles is used in developing the materials for energy storage and energy conversion (fuel cells) and to increase their efficiency and durability[17][18].The unique tailored tungsten oxide nanpoarticles can be used to capturing the greenhouse gases and removing pollutants in waste water.

In the present study the nanocrystalline tungsten oxide are synthesized using simple hydrothermal techniques for different applications. The structural properties were studied using X-ray Diffractometer (XRD) with Cu K_α radiation of wavelength 1.542 Å. X-ray diffraction data were used to identify the phases present in the films and to find out the lattice parameters, if any. The surface morphology of the films was studied using scanning electron microscopy (FESEM).

MATERIALS

Sodium tungstate dihydrate ($Na_2WO_4 \cdot 2H_2O$), hydrochloric acid (HCl) were purchased from SIGMA company and are used as received.

Synthesis of Nanoparticle: 0.5 gm of Sodium tungstate, 1 ml conc.HCl (Cold), 50 mL deionised water are added by adjusting the pH between 1 and 2. kept at 120^0 C for 12 hours in autoclave named as sample 1 . 0.5 gm of Sodium tungstate, 1 ml dil .HCl (Room temperature), 50 mL deionised water are added by adjusting the pH between 1 and 2 kept at 120^0 C for 12 hours in autoclave named as sample 2.

Characterization: The phase structure and purity of the samples were characterized by powder X-ray diffraction(XRD) using a Bruker/D-8 advance diffractometer with Cu K_α radiation at 40 kV and 150 mA scanning range of $20^0 – 80^0$ (2θ).The morphology and nanostructure were investigated by field-emission scanning electron microscopy and elemental composition of the samples were studied by Energy Dispersive spectrum (EDS).

RESULT AND DISCUSSION

X-ray diffraction (XRD: The X-ray diffraction pattern recorded in the θ-2θ scan mode. The purity of the sample material is confirmed by the lack of other peaks in the XRD patterns. The average crystal size of tungsten oxide was determined from the Scherer equation, $d = \frac{k\lambda}{\beta \cos\theta}$ cos , where 'k' is a dimensionless shape factor of the crystallite (a typical approximation is ~0.9), λ is the wavelength of the X-ray used (λ=1.5406Å), β is the full width at half maximum (FWHM) of the diffracted peak (in radians) and θ is the Bragg angle (in degree).

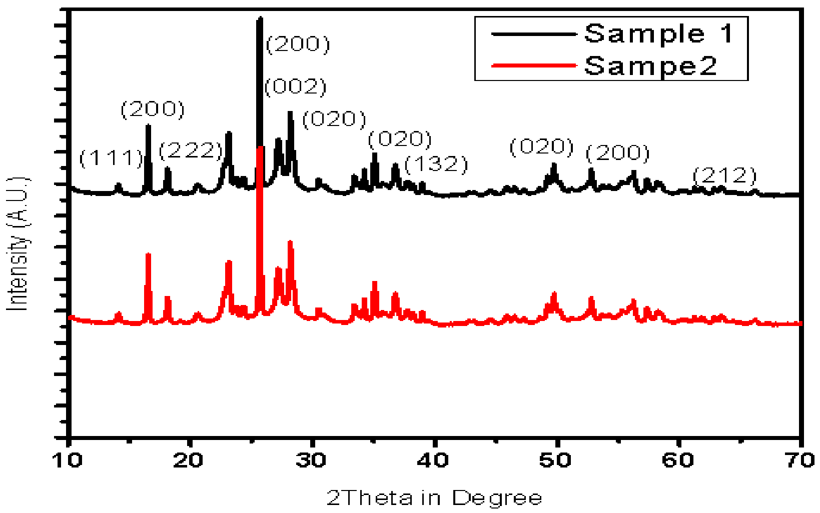


Fig. 1 X-ray diffraction pattern for WO_3 sample 1 and sample 2 at 120^0 C for 12 hours

The X-ray diffraction pattern recorded in the θ-2θ scan mode in fig.1. The WO_3 nanocrystalline particles were studied Sample 1 and sample 2 at 120^0 C for 12 hours respectively in fig. 1 Both sample shows intense at interplanar spacing d = 3.371, 3.100 and 4.088Å and minor intensity peaks at, 5.825, 2.627 Å, indicating monoclinic crystal structure of WO_3 in accordance with JCPDS-ICDD card # 84-1516 shown in fig-1. The above described d lines can be indexed as the (002) and (210) (220) planes respectively.

To calculate the nano crystallite size (t) by

Scherrer Equation, $t = K\lambda/\beta.\cos\theta$,

XRD radiation of wavelength λ (nm), from measuring full width at half maximum of peaks (β) in radian located at any 2θ in the pattern. K can be usually taken as about 0.9

The particle size of WO_3 nanoparticles using results are in good agreement [1][2][3][7][11][24].

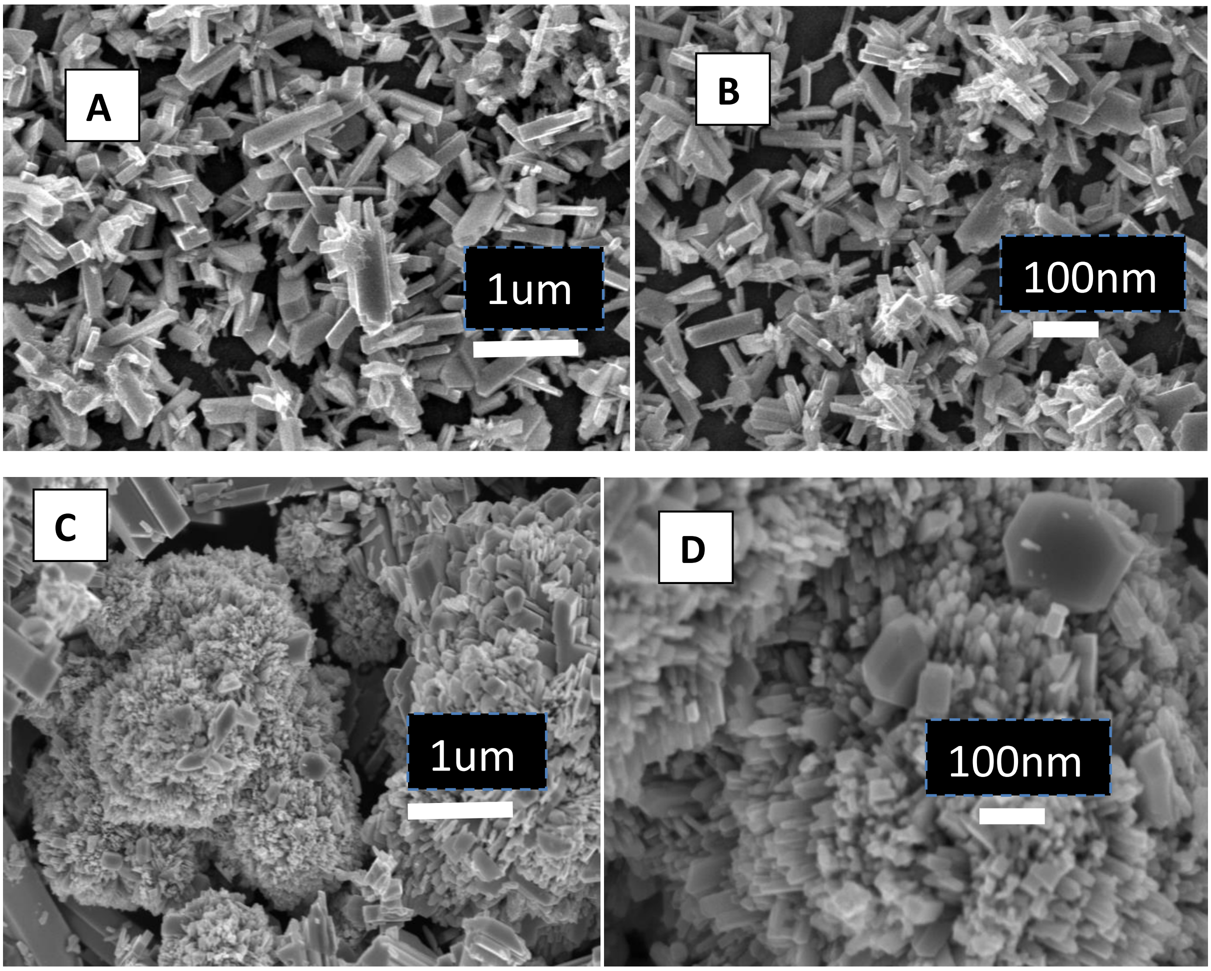
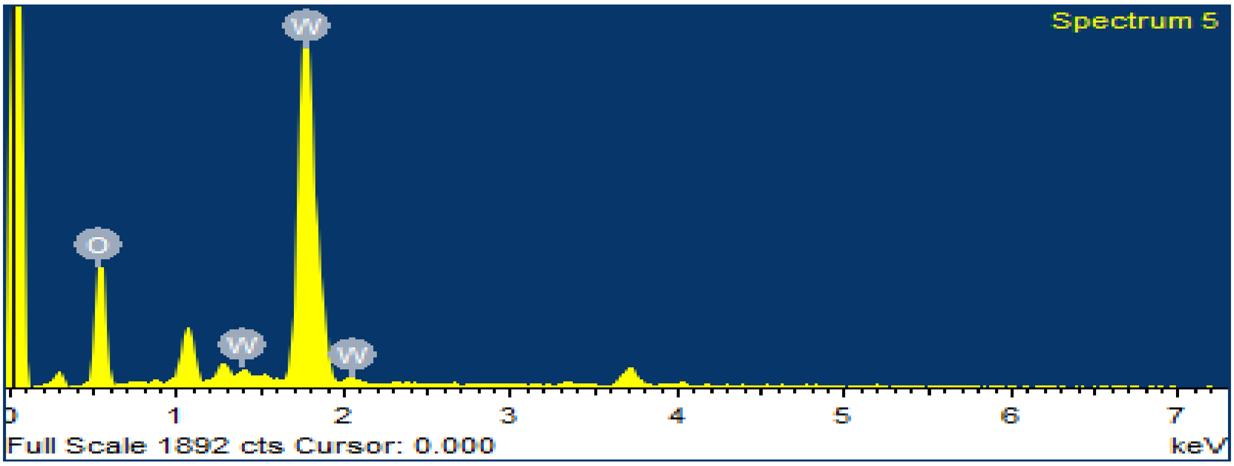


Fig. 2 FESEM image for WO_3 film Sample 1 (A,B) and Sample 2 (C, D)

FESEM: FESEM images of WO nanoparticles at different magnifications are presented in Fig. 2 A, B. The average value of the particle size is 50 nm. Here, sodium ion from the precursor salt i.e. Sodium tungstate dehydrate along with HCl control the phase and morphology. The residual Na+ content ions in the solution decrease with increase in Cl− content due to the electrostatic force of attraction between the ions, results the change in morphology and crystal structure [7].

The morphology of WO_3 nanocrystalline for 12 hours at 120^0 C for sample 1 and sample 2 were examined using FESEM. Figure 2 shows FESEM image for WO_3 film shows nanorod morphology with rod size varying from 50-600nm. In higher magnification for sample 1 shown in fig b clearly shows nanrod forming and self assembled in star flower like structures[4][7]. If dil HCl used this rods forming cauliflower structure which is depicted in fig for sample 2 (C). In higher magnification images these nanorod structures aligned are seen in fig 2 (D).This structures are very useful for gas sensing super capacitor and photo catalytic activities.

Energy dispersive X-ray (EDX) spectroscopy: The elemental composition of as-synthesized samples was measured using energy dispersive X-ray (EDX) spectroscopy for sample 2 EDX analysis, Fig. 3, the average content of Tungsten (W) and Oxygen (O) is 24.5% (atomic percentage) and 75.5%, which confirms that WO_3 are the major constituents of the tungsten oxide nanoparticles and can be correlated with our XRD data, which showed high intensity diffraction peaks for these compositions.



CONCLUSION

In summary cauliflower nanocrystaline WO_3 nanoparticles are successfully synthesized using one step hydrothermal process using concentrated and diluted hydrochloric acid. XRD pattern indicated that monoclinic crystal structure with particle size 50 nm and FESEM images clearly indicates that tungsten oxide showed nanorod at low magnification and these nanorod assembled star like flower. The cauliflower morphology can be seen for dil HCL at low magnification which is useful for electro chromic, photocatalytic and gas sensor as this morphology gives more surface area which enhanced active surface sides can be used for versatile functionalities.

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