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Structural and Optical Characterization of Tungsten Oxide Nanoparticles by Wet Chemical Technique

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ABSTRACT:

Tungsten oxide (WO_3) nanoparticles were synthesized using Wet chemical technique. The synthesized sample was characterized using X – ray Diffraction (XRD), Field emission Scanning Electron Microscopy (FESEM), Energy Dispersive X-ray Analysis (EDAX), UV – Vis Spectroscopy and Photoluminescence studies. X – ray diffraction study reveals the formation of WO_3 nanoparticles with tetragonal structure. The average crystallite size of the nanoparticles was calculated around 36 nm. FESEM studies reveal that the WO_3 nanoparticles have rod like structure. EDAX confirms the elemental composition of W and O compounds in majority. Optical properties of the prepared nanoparticles were analyzed using UV-Vis spectrometry and photoluminescence studies. Photoluminescence spectra exhibited violet and blue emission which was due to oxygen vacancies and surface defects.

KEY WORDS: Nanoparticles, Tungsten oxide, XRD, FESEM, Photoluminescence.

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INTRODUCTION

Nanostructure metal oxides have attracted significant attention due to their advantages over their bulk counterparts[1]. Nanostructures with high surface to volume ratio and small grain size have attracted more due to their unique physicochemical properties and shows potential applications in nanoscaled device fabrication[2]. Among the existing metal-oxide semiconductors, tungsten oxide (WO_3) is a well-known n-type wide band gap semiconductor, inexpensive, environmentally friendly and chemically stable[3,4,5]. Tungsten oxide has been broadly investigated for photo catalysts due to their outstanding electrochromic, gaschromic and optochromic properties[6]. In addition, its other unique properties have also been explored in flat panel displays[7], optoelectronics[8], energy devices[9] and gas sensors[10].WO_3 nanoparticles or nanocrystallites have been synthesized using various techniques such as pyrolysis, thermal decomposition and wet chemical processes such as sol-gel, colloidal processes and ion – exchange methods[11].

In this paper, we report a simple but effective Wet chemical method to synthesize tetragonal tungsten oxide nanoparticles using Sodium tungstate dihydrate powder ($Na_2WO_4.2H_2O$) as a tungsten source. A detailed crystallographic analysis has been performed to elucidate the various aspects of WO_3.

EXPERIMENTAL DETAILS

All the chemicals were of analytical grade and taken without further purification. Sodium tungstate dihydrate ($Na_2WO_4.2H_2O$) is taken as the starting material. Hydrochloric acid (HCl), oxalic acid ($C_2H_2O_4$) and Cationic Surfactant CTAB ($C_{19}H_{42}BrN$) were the other chemicals used for the growth.

For the preparation of WO_3, sodium tungstate dihydrate was dissolved in double distilled water (DDW) and acidification was done by adding HCl to get a pH of 1. A white precipitate was obtained and it was dissolved by adding oxalic acid. Cationic surfactant CTAB Controls the shape of the synthesized nanoparticles. After complete reaction, the solution was stirred in magnetic stirrer at 80° C for about 3 hours. The final product was filtered out and washed with deionized water several times and then dried in hot air oven at 60° C for 2 hours to remove water. After drying, the products were air annealed at 400° C for 1 h and dried flakes were crushed in a pestle-motor was collected in airtight containers and then used for all measurements. The formation process of the WO_3 nanoparticles can be described by the following reactions[12]

$$Na_2WO_4.\ 2H_2O + 2HCl \rightarrow H_2WO_4 + 2NaCl \longrightarrow (1)$$

$$H_2WO_4 \rightarrow WO_3\ (\text{Nanoparticles}) + H_2O \longrightarrow (2)$$

CHARACTERIZATION TECHNIQUES

Synthesized WO_3 nanoparticles were analyzed by X-ray diffraction method by employing a XPERT-PRO X-ray differactometer with CuKα (λ=1.5406) radiation using a tube voltage and current of 40kv and 30mA respectively. Surface morphology and atomic compositions of the nanoparticles was measured by using Field Emission Scanning Electron Microscope FESEM – (SIGMA HV – Carl Zeiss with Bruker Quantax 200 – Z10 EDS Detector). The UV–Visible spectrum of the synthesized nanoparticles was recorded in the range 200 – 800 nm using a Varian, Cary 5000 with a scanning rate of 600nm/min. The powder sample was subjected to photoluminescence study using Varian Cary Eclipse instrument.

RESULTS AND DISCUSSION

X-ray Diffraction Spectroscopy (XRD)

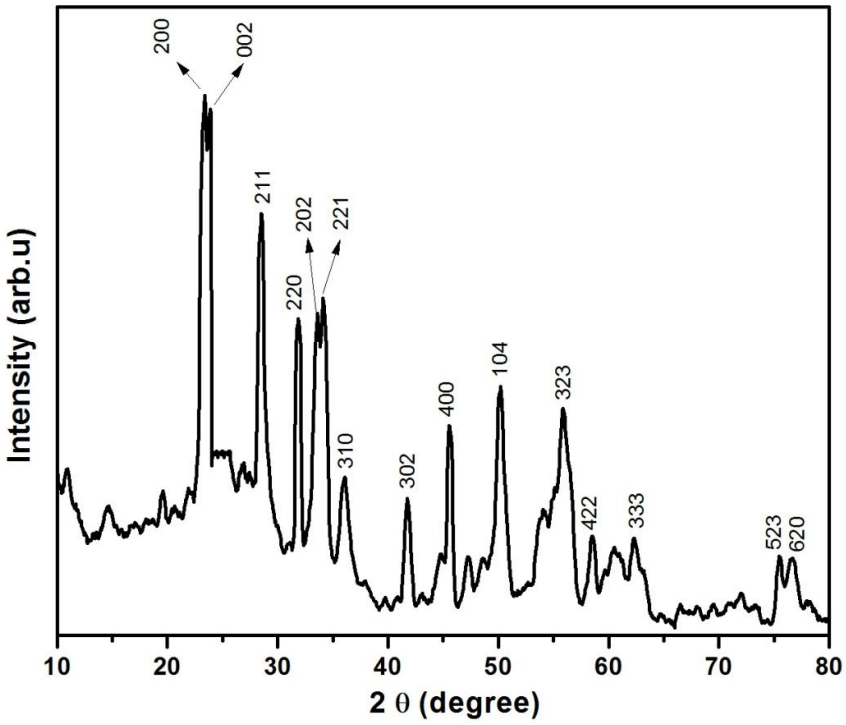

Fig. 1 XRD pattern of WO_3 nanoparticles

Fig. 1 displays the XRD pattern of WO_3 nanoparticles annealed at 400° C and synthesized using wet chemical technique. The diffraction peaks occurring at 2 θ = 23.21°, 23.21°, 23.73°, 28.43°, 33.43°, 34.27°, 36.09°, 41.72°, 45.60°, 50.07°, 55.89°, 58.49°, 62.33°, 75.39°, 76.7003 have been assigned to the lattice planes (200), (002), (211), (220), (202), (221), (310), (302), (400), (104), (323), (422), (333), (523) and (620) respectively. The result shows all the diffraction peaks indexed to tetragonal phase of WO_3 as per the JCPDS data card (ICSD 089092, JCPDS 89-8764; with space group P4/nmm). The calculated lattice parameters of the tetragonal WO_3 phase are a = b = 7.806 Å and c = 7.4373 Å; α = β = γ = 90° which agrees well with reported values. No peaks of any other phase or impurities were observed from the XRD patterns. Strong and sharp diffraction peaks also indicate a good crystallinity of the sample.

Table No. 1: "Average crystallite size calculation from FWHM"

Pos. [°2Th.]	FWHM [°2Th.]	d-spacing [Å]		hkl	Grain size (D) nm	Average Grain size (D) nm
		Standard (JCPDS)	Observed			
23.2176	0.1968	3.9300	3.8311	200	41. 23	
23.7329	0.2952	3.7450	3.7491	002	27.51	
28.4340	0.1968	3.1821	3.1390	211	41.66	
31.8732	0.1476	2.7789	2.8077	220	56.00	
33.4346	0.1476	2.7111	2.6801	202	56.22	
34.2726	0.1968	2.6053	2.6164	221	42.26	
36.0979	0.6888	2.4855	2.4882	310	12.13	
41.7203	0.4920	2.1467	2.1650	302	17.28	36
45.6031	0.1968	1.9850	1.9893	400	43.80	
50.0774	0.1968	1.8215	1.8215	104	44.57	
55.8935	0.2952	1.6421	1.6450	323	38.47	
58.4940	0.2460	1.5910	1.5779	422	37.02	
62.3389	0.5904	1.4877	1.4895	333	15.73	
75.3994	0.1476	1.2600	1.2606	523	68.04	
76.7003	0.5904	1.2427	1.2425	620	17.16	

The average crystallite sizes of the samples were estimated from Debye-Scherrer's equation.

$$D = K\lambda / \beta \cos \theta$$

Where K is the shape factor of the average crystallite (expected shape factor is 0.94), λ is the wavelength in nanometer, β is the full width at half maximum in radians and θ is the peak position. Average grain size of the WO_3 sample calculated from Debye–Scherrer's equation equals to about 36 nm is illustrated in the Table 1.

Field Emission Scanning Electron Microscopy (FESEM)

FESEM is a useful technique to determine the morphology and particle size of the samples. Fig. 2 shows FESEM image of pure WO_3 nanoparticles. It is clearly observed that sample shows rod like structure.

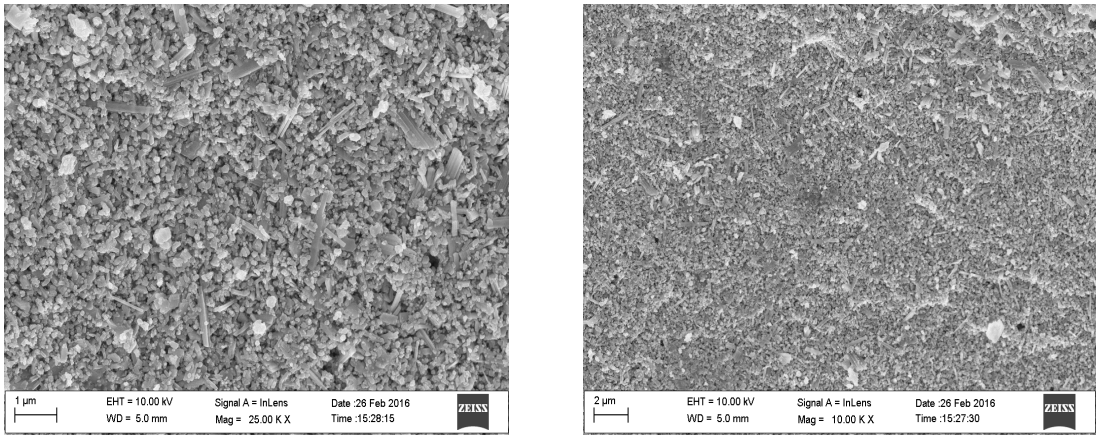

Fig. 2 FESEM images of WO_3 nanoparticles

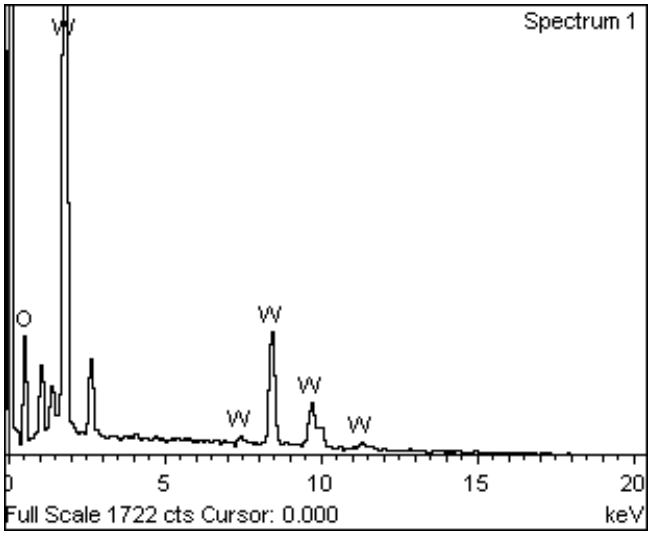

Fig. 3 EDX Spectrum of WO_3 nanoparticles

The chemical composition of WO_3 nanorods were determined by EDAX analysis. Fig. 3 shows the EDAX spectra for pure WO_3. No other element except W and O has been detected which shows that final products are free of impurities.

UV – Visible studies

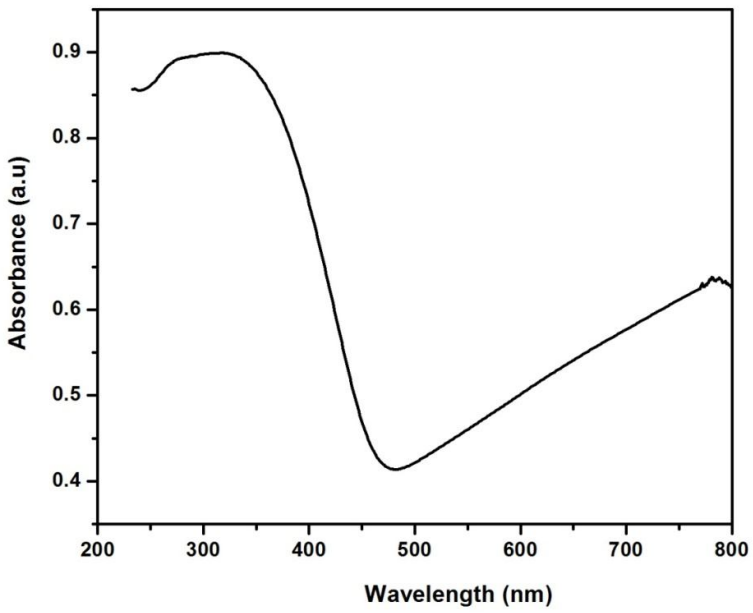

Fig. 4 UV – Visible spectrum of WO_3 nanoparticles

The optical measurement of the prepared sample was carried out at room temperature by using UV–visible absorbance spectrophotometer. The recorded absorbance spectra of WO_3 nanoparticles are shown in Fig. 4. As it can be seen, all samples exhibit a clear absorption edge in the UV-Vis region, which correspond to the fundamental absorption of WO_3 semiconductor. The absorbance generally depends on several factors, such as optical band gap and impurity centers[13] The samples optical band gap can be calculated by using Tauc's equation which Shows a relationship between incident photon energy of semiconductors and the absorption coefficient[14]:

$$\alpha h\nu = B\,(h\nu - Eg)^n$$

Where, B is a constant, the exponential factor n is taken as 1/2 for direct band gap semiconductor and Eg is an optical band gap of the material.

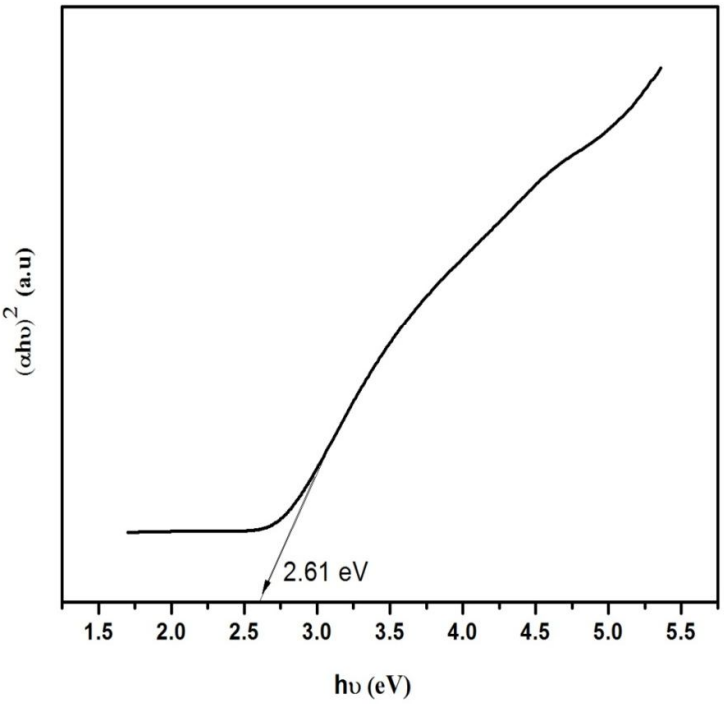

Fig. 5 Bandgap energy of WO_3 nanoparticles

The energy bandgap (Eg) of sample can be found by plotting $(\alpha h\nu)^2$ versus hν and extrapolating the linear portion of the absorption edge as shown in Fig.5. It gives the straight-line plot, the intercept of the tangent to the x-axis will give a good calculation of the band gap, so the expected band gap of WO_3 nanoparticles is 2.61 eV [15].

Photoluminescence studies

The PL spectroscopy is a valuable study to measure the energy distribution of emitted photons after optical excitation and to know the electron hole pair in the semiconducting oxide materials[16]. The oxygen vacancy and lattice distortion of pure tungsten oxide samples were analyzed using photoluminescence spectra and it is shown in the Fig. 6. Dominant peaks are observed at (i) a high intensity peak centered at 362 nm, 383 nm are corresponding to ultraviolet (UV) band (ii) a sharp peak centered at 412 nm related to violet band (iii) a sharp and low intensity peak centered at 492 nm related to blue band (iv) a low intensity and broad peak centered at 520 nm related to green band. UV emissions at 362, 383 and 412 nm is attributed due to the transition to valence band from the high lying defect state in the conduction band due to oxygen vacancies[17]. Blue emission at 492nm and green emission at 520 nm occurred due to surface defects[18]

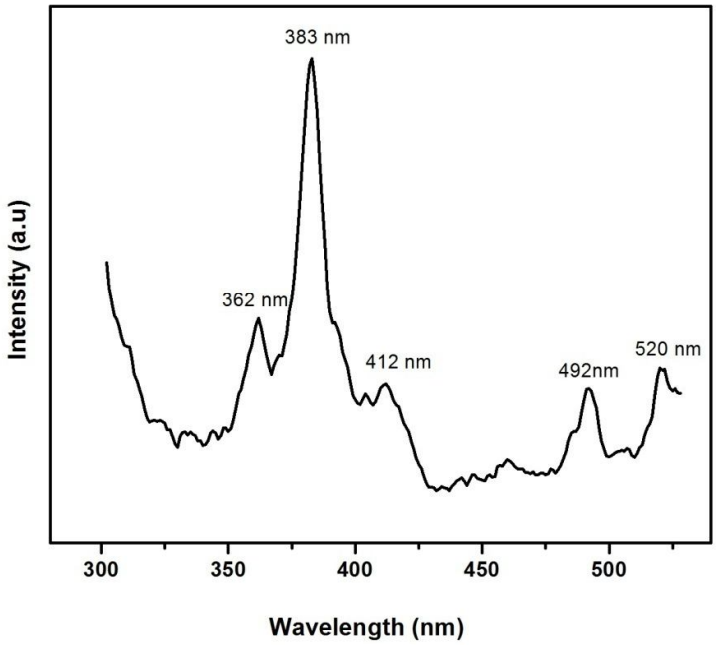

Fig. 6 Photoluminescence spectra of WO_3 nanoparticles

CONCLUSION

In summary, tetragonal WO_3 nanoparticles with high crystallinity have been synthesized by Wet chemical method from sodium tungstate dihydrate and hydrochloric acid. Average crystallite size of the synthesized nanoparticles calculated from Debye – Scherrer equation was around 36 nm. Field Emission Scanning Electron Microscopy confirms the rod like morphology. Optical bandgap was found to be 2.61 eV confirmed from UV – Vis studies. From PL spectroscopy the energy distribution of emitted photons were measured.

REFERENCES

1. Santos, L. *et al.* Synthesis of WO_3 nanoparticles for biosensing applications. *Sensors Actuators, B Chem.* 2016; **223:** 186–194.
2. Patil, V. B., Adhyapak, P. V., Suryavanshi, S. S. & Mulla, I. S. Oxalic acid induced hydrothermal synthesis of single crystalline tungsten oxide nanorods. *J. Alloys Compd.* 2014; **590:** 283–288.
3. Wang, Z., Hu, M. & Qin, Y. Solvothermal synthesis of WO 3 nanocrystals with nanosheet and nanorod morphologies and the gas-sensing properties. *Mater. Lett.* 2016; **171:** 146–149.
4. Kamali, E. & Ehsan, H. Nanocasting Synthesis of Ultrafine WO_3 Nanoparticles for Gas Sensing Applications. 2010; 370–373. doi:10.1007/s11671-009-9490-8

5. Yan, W., Hu, M., Zeng, P., Ma, S. & Li, M. Room temperature NO2-sensing properties of WO_3 nanoparticles/porous silicon. *Appl. Surf. Sci.* 2014; **292:** 551–555.
6. Sun, S., Chang, X. & Li, Z. Growth study and photocatalytic properties of Co-doped tungsten oxide mesocrystals. *Mater. Charact.* 2012; **73:** 130–136.
7. Boukriba, M., Sediri, F. & Gharbi, N. Hydrothermal synthesis of WO_3 Á 1 / 3H_2O nanorods and study of their electrical properties. *Polyhedron* 2010; **29:** 2070–2074.
8. Omri, K., Bettaibi, A., Khirouni, K. & Mir, L. El. The optoelectronic properties and role of Cu concentration on the structural and electrical properties of Cu doped ZnO nanoparticles. *Phys. B Phys. Condens. Matter* 2018. doi:10.1016/j.physb.2018.02.025
9. Wang, X., Zhang, H., Liu, L., Li, W. & Cao, P. Controlled morphologies and growth direction of WO_3 nanostructures hydrothermally synthesized with citric acid. *Mater. Lett.* 2014;**130:** 248–251.
10. Upadhyay, S. B., Mishra, R. K. & Sahay, P. P. Sensors and Actuators B : Chemical Structural and alcohol response characteristics of Sn-doped WO_3 nanosheets. *Sensors Actuators B. Chem.* 2014; **193** 19–27.
11. Wasmi, B. A., Al-amiery, A. A., Kadhum, A. A. H. & Mohamad, A. B. Novel Approach : Tungsten Oxide Nanoparticle as a Catalyst for Malonic Acid Ester Synthesis via Ozonolysis. **2014**.
12. Mehmood, F. *et al.* Effect of Sn doping on the structural, optical, electrical and anticancer properties of WO_3 nanoplates. *Ceram. Int.* 2016. doi:10.1016/j.ceramint.2016.04.010
13. Benzitouni, S. *et al.* Morphology and photocatalytic activity of porous (In, Mg) co-doped ZnO nanoparticles. *Opt. - Int. J. Light Electron Opt.* 2017. doi:10.1016/j.ijleo.2017.12.039
14. Mohammadi, S., Sohrabi, M., Golikand, A. N. & Fakhri, A. Preparation and characterization of zinc and copper co-doped WO_3 nanoparticles: Application in photocatalysis and photobiology. *J. Photochem. Photobiol. B Biol.* 2016; **161:** 217–221.
15. Kalantar-zadeh, K. *et al.* Synthesis of Atomically Thin WO_3 Sheets from Hydrated Tungsten Trioxide. 2010; 5660–5666. doi:10.1021/cm1019603
16. Sayed Abhudhahir, M. H. & Kandasamy, J. Synthesis and characterization of Manganese doped Tungsten oxide by Microwave irradiation method. *Mater. Sci. Semicond. Process.* 2015; **40:** 695–700.
17. Access, O. Studies on the uv- visible and photoluminescent emission in nanocrystalline tungsten oxide Studies on the uv- visible and photoluminescent emission in nanocrystalline tungsten oxide. 2015. doi:10.1088/1757-899X/73/1/012119
18. Solarska, R., Alexander, B. D. & Augustynski, J. Electrochromic and photoelectrochemical characteristics of nanostructured WO_3 films prepared by a sol – gel method. 2006; **9:** 301–306.