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Preparation and Characterizations of Copper doped WO_3 Nanoparticles Prepared by Solvo Thermal cum Chemical method

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Abstract: The copper (Cu) doped tungsten oxide (WO_3) nanoparticles were prepared by solvo thermal cum chemical method. By using tungsten chloride in a cyclohexanol as a solvent. The nanoparticles are synthesized at different temperatures. The formation of Cu doped WO_3 nanoparticles were confirmed by powder x-ray diffraction technique. The surface properties of the nanoparticles were investigated by Scanning Electron Microscope images. The micro structures of the nanoparticles were studied by the EDX spectrometry. The results show that the temperature used to synthesize nano particle is a key factor to get definite Cu doped WO_3 nanoparticles.
Keywords : Copper, tungsten oxide, nano particles and chemical synthesis.

1. Introduction and Experimental

Transition – metal oxide nano materials, such as WO_3, ZnO, TiO_2 and SnO_2 have attracted extensive research interests owing to their unique physical and chemical properties and diverse potential applications in optical and electronic fields [1]. Also it exhibits numerous exciting properties in the area of superconductivity, colossal magneto resistance effect, piezoelectricity, microelectronics, photonics, and photo catalysis and so on [2]. Typically, WO_3 is a technologically important wide band gap (approximately 2·8 eV) metal oxide semiconductor [3]. Recently, many efforts have been devoted to the investigation of tungsten oxide nano materials [4]. The preparation technique and its conditions play important role in tailoring the properties of the materials. Among them, the thermal evaporation technique [5-7], sol–gel method [8], sputtering [9], spray deposition [10], and chemical vapor deposition approach [11, 12] all involve harsh growth conditions.

Many physical properties of WO_3, such as piezoelectricity, electrical conductivity and defect structures, are greatly influenced 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_3 based nano powders. In recent years, Copper (Cu) doped WO_3 has attracted a great deal of attention because it shows a relatively stronger oxidative power under exposure to visible light (>400 nm) [13]. Doping copper with WO_3 has more applications like solid state memory [14], Programmable metallization cell (PMC) [15], Gas sensors [16] are available.

The present investigations are aimed at the characterization of Cu doped WO_3 nano particles synthesized by solvo thermal cum chemical method. The Cu doped WO_3 is prepared at different temperature

like room temperature, 100°C and 400°C respectively. Structural and morphological characterization of the samples is performed using powder X- ray diffraction (XRD), Scanning Electron Microscopy (SEM) and Energy Dispersive X- ray Analysis (EDS) respectively.

Tungsten chloride (Sigma Aldrich 99.99%) and Cyclohexanol were used as a precursor. 30 mg of Tungsten chloride was slowly dissolved in 10 ml of Cyclohexanol to obtain a uniform 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_3 nanoparticles. To prepare copper (Cu) doped WO_3 nanoparticles, we used the paste preparation method. In paste preparation method, the paste was produced by mixing of 2.0 g of Cu anatase powders and 5 g of WO_3 nanoparticles with a mixture consisting of 10.0 g of α-terpineol, 1 g of cellulose, and 25 ml of ethanol, which was solicited for 48 hrs at 1200 Wcm^{-2}. By using the prepared paste thin films were prepared by coating the paste on a FTO conducting glass plate (Hartford FTO, ~30Ω cm^{-2}, 80% transmittance in visible region) using the doctor blade technique. The Cu doped WO_3 is prepared at different temperature like room temperature, 100°C and 400°C respectively.

X-ray diffraction method using CuKα radiation has been used to study the structure of the synthesized nanoparticles. This study was carried out by employing a Brukker Axs D8 Advance X-ray differactometer with CuKα (λ=1.5406) radiation using a tube voltage and current of 40kv and 30mA respectively. The sample was scanned from 15°-80°in 2θ with step size of 0.5° 2θ and scan speed of 0.5°2θ per second. Surface morphology of the synthesized nanoparticles was studied using scanning electron microscopy (SEM; Philips XL40), and the atomic compositions of the nanoparticles was measured by energy dispersive X-ray analyses (EDXA; Inca, oxford instruments) operated at 120 kV.

2. Results and Discussion

2.1 X-ray diffraction analysis

X-ray diffraction pattern has been used to investigate the phase of the synthesized Cu doped WO_3 nanoparticles. The X-ray diffraction pattern of Cu doped WO_3 nanoparticles prepared at 100°C is shown in Fig. 1.

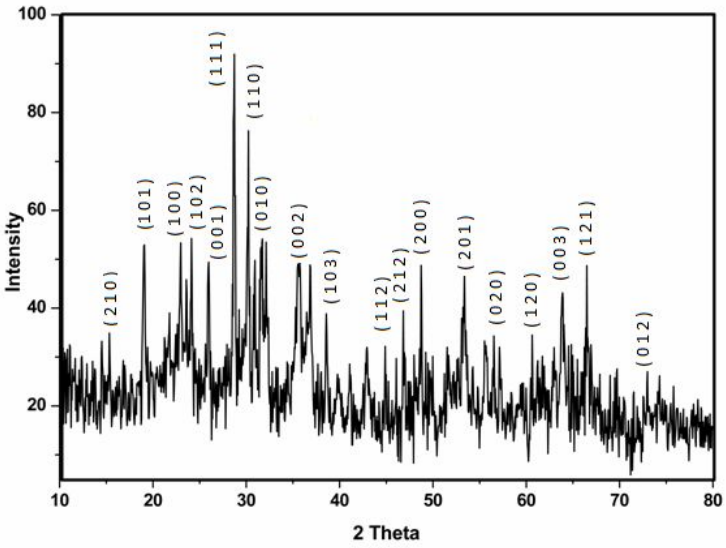

Fig. 1 X-ray diffraction pattern of Cu doped WO_3 at 100°C

Fig. 1 shows the XRD diffraction patterns of Cu doped WO_3 nanoparticles at 100°C temperature. Cu doped WO_3 nanoparticles were annealed at 100°C in muffle furnace for the formation of different nano crystalline phases. The diffraction patterns of nanoparticles can be indexed to the spherical structure of WO_3. No other peaks corresponding to Cu related secondary or impurity phase was found in copper doped sample, which may be attributed to the incorporation of Cu ion into the W lattice site rather than interstitial ones. The mean crystalline size was calculated from the full-width at half-maximum (FWHM) of XRD lines by using the Debye-Scherrer formula:

$$Dh,k,l = 0.9\lambda / (\beta h,k,l\cos\theta)$$

where D is the average crystalline diameter, λ is the wave-length in angstrom, β is the line width at half – maximum and θ is the Bragg angle. We used the most intense peak (111) in the XRD-patterns to calculate the average crystalline size. It can be seen that the average size of nanoparticles decreased as the doping percentage of copper metal is increased. The particles size are in the range of 49 to 39 nm at 100°C corresponding to the Cu doped WO_3 nanoparticles respectively. This observation reveals that in the process of nanostructure formation, definite planes of the growth are affected by adding copper. The reduction of particle size (not shown) was also observed from XRD pattern for Cu doped WO_3 nanoparticles with the incorporation of Cu dopants in the WO_3 lattice. This may be explained by the reduction of sintering rate due to incorporation of dopant atoms into the WO_3 lattice.

2.2 SEM and EDS analysis

The scanning electron microscope images of the WO_3 nanoparticles are shown in Fig.2.

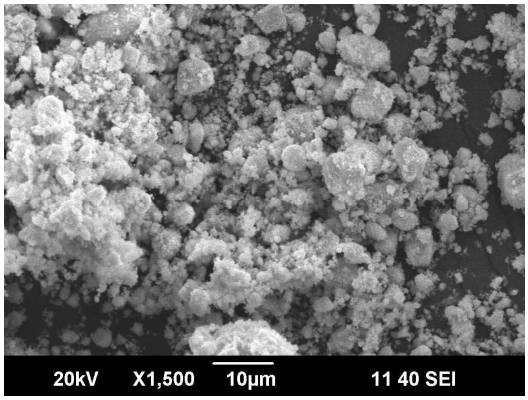

Fig. 2 SEM images of Cu doped WO_3 nanoparticles at 100°C

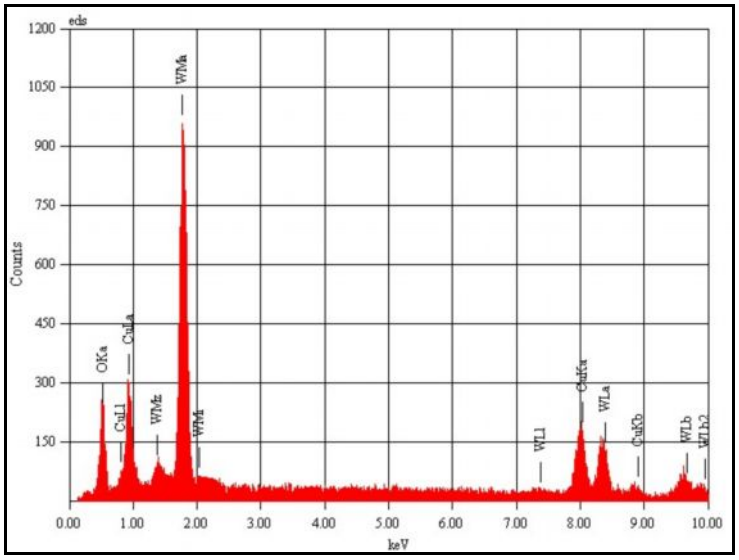

Fig. 3 Energy dispersive x-ray analysis (EDS) pattern of the Cu doped WO_3 nanoparticles at 100°C.

Fig. 2 shows the SEM images of WO_3 nanoparticles prepared at 100°C. The nanoparticles annealed at 100°C were homogeneous and agglomerated with a grain size of 40 nm.The increasing calcinations temperature leads to the trend of decreasing grain size which is believed to be affected by the promotion of crystalline phase in the nanoparticles. The grain size of crystallites in WO_3 nanoparticles annealed at 100°C was observed to be more than 100 nm. The grain sizes as measured by XRD and SEM were quite different. In SEM, the grain size was measured by the difference between the visible grain boundaries whereas in XRD, the measurement was extended to the crystalline region that diffracted X-rays coherently. Therefore, the XRD measurements led to smaller size. The SEM images of doped samples indicate that the samples were homogeneous with dopant (Cu) substituting W sites in WO_3 compound and do not contain any other dopant dominating phases. Fig. 3 Show the

EDS spectra for the annealed Cu doped WO_3 nano particles. It shows that the spherical like shape and morphology of the nano particles were obtained after annealing. Only tungsten (W), Oxygen (O), Copper (Cu) elements were found. All the carbon had been removed during the sintering process. The tungsten element is identified in large that are consistent with the concentration of XRD patterns and SEM micrographs.

Conclusion

Cu doped WO_3 nanoparticles were synthesized with different temperatures by using solvo thermal cum chemical method and its structural and surface properties were studied. We have synthesized Cu doped WO_3 nanoparticles with different temperatures and obtained spherical shape WO_3 nanoparticles. From the XRD analysis we confirmed the formation of Cu doped WO_3 nanoparticles. SEM and EDS reveal that the surface morphology of the synthesized material and composition of Cu doped WO_3 nanoparticles. It can be seen that the average size of nanoparticles decreased as the doping percentage of copper metal is increased. In general the results obtained give a global perspective about the strongly promising structures based on Cu–WO3 for further studies.

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