Preparation and characterization of doped WO_3 photocatalyst powders

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WO_3 semiconductor particles, useful in solar energy conversion processes, were doped with transition metal ions, Ti(III), V(IV), Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and Ru(III) by a high-temperature sintering technique. The method of preparation of these photocatalysts is described in detail. The structural changes effected during sintering were investigated by X-ray powder diffraction (XRD) and scanning electron microscopy (SEM). The XRD analysis indicated that the monoclinic crystal structure of WO_3 was not altered during sintering. SEM studies showed that the sizes of the particles ranged from 1 to 10 μm and the crystallinity was increased due to doping. The dopants were found to be mostly distributed on the surface of WO_3 particles.

1. Introduction

WO_3 semiconductor powders have been used for solar energy conversion processes by many researchers. Oxygen generation [1, 2] from water, synthesis of amino acid [3, 4] and water photolysis into hydrogen and oxygen [5] are some of the works reported using this semiconductor. The absorbance in the visible region [6] and photocatalytic activities [7] of WO_3 powders were found to be increased by doping with transition metal ions. Doping is usually done by sintering at high temperatures. Photosynthetic deposition of copper on TiO_2 and WO_3 powders was carried out by Reiche *et al.* [8] and photoelectrolytic deposition of platinum was reported by Curran *et al.* [9]. Photo-assisted platinum deposition using platinum complexes was done by Hermann *et al.* [10]. Physical characterizations of the semiconductor materials are usually determined by diffuse reflectance measurements [6], X-ray diffraction (XRD) [11] and scanning electron microscopy (SEM) [12].

In this paper, we report for the first time, the preparation and characterization of doped WO_3 powders. Doping with transition metal ions was done by sintering at high temperature. The photocatalysts prepared were characterized using powder X-ray diffraction and scanning electron microscopy. This study was carried out to determine (i) the change in the crystal structure, (ii) the surface modifications, (iii) the change in the particle sizes, and (iv) the change in the surface area, effected due to doping by a high-temperature sintering technique, because these properties play very important roles in the photocatalytic efficiencies of these semiconductor powders towards solar energy conversion.

2. Experimental procedure

2.1. Preparation of the photocatalysts

WO_3 used was obtained from Fluka (Fluka, Switzerland) (> 99.99%) and the other chemicals used for doping were of research grade and were used either as chlorides ($TiCl_3$, $CrCl_3$, $MnCl_2$, $FeCl_3$, $RuCl_3$) or sulphates ($VOSO_4$, $CoSO_4$, $NiSO_4$, $CuSO_4$). Calculated amounts of transition metal compounds (containing ~ 4.0 at % metal ions) were mixed with weighed amounts of WO_3 to which 50 ml doubly distilled water was added and the contents were magnetically stirred for about 2 h to distribute the metal ions throughout the WO_3 particles. Then the water was evaporated by keeping the contents in an oven. The dried sample was ground to a powder, loaded into a silica boat and introduced into a tubular furnace. The temperature of the furnace was slowly raised to 800° C in an argon atmosphere and maintained at 800° C for 1 h. Then the temperature was maintained at 850° C for 2 h and 900° C for 1 h with stepwise increase in temperature. After sintering, the sample was cooled to room temperature and ground to powder.

2.2. Characterization techniques

X-ray diffraction measurements for the powders were taken with computer-controlled XRD units (X-ray generator PW 1130, Vertical Diffractometer PW 1050, Diffractometer Control Unit PW 1710; Philips, Holland). A copper target with a nickel filter was used (Cu$K\alpha$ radiation; $\lambda = 0.154\,18$ nm).

Scanning electron micrographs of the photocatalysts were taken using a Jeol JSM-35 CF Model with × 5000 magnification. The surface areas of these photocatalysts were determined by the BET method.

3. Results and discussion

3.1. XRD

X-ray powder diffraction measurements were taken with $2\theta = 10°$ to 90° for undoped and Cu(II)-doped WO_3 powders. The 2θ values and the corresponding intensities of the peaks are shown in the spectra. The d-spacings and the corresponding I/I_0 values are given in Table I. Figs 1a and b show the XRD spectral

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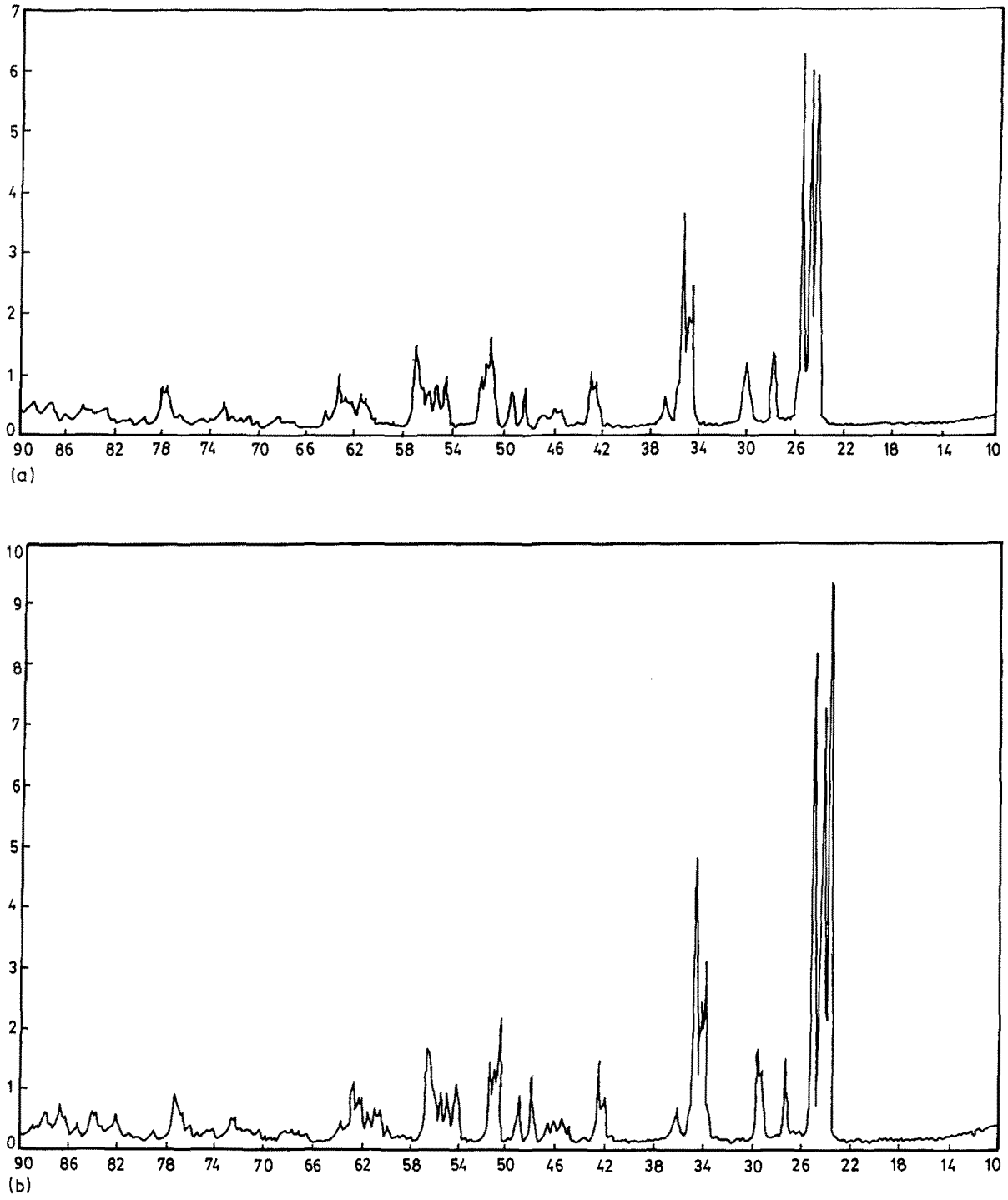

Figure 1 XRD spectrum of (a) undoped WO_3 powders, (b) Cu(II)-doped WO_3 powders (at % Cu $\simeq$ 4.0).

observations for undoped and Cu(II)-doped WO_3 powders, respectively. The 2θ values at which the major peaks appear are found to be almost the same for both the undoped and doped samples.

The observed differences in the intensities of the peaks may be due to the alteration of crystallinity on sintering. At the same time, sintering does not alter the crystal structure, which is proved by the *d*-spacing values observed. It is very interesting to note that the crystallinity of WO_3 powders is increased due to doping as is evidenced from the observed more intense peaks in the spectrum (Fig. 1b) of the Cu(II)-doped WO_3 sample. In Table I the *d*-spacings corresponding to the 2θ and I/I_0 were given for undoped and Cu(II)-doped WO_3 along with the ASTM reported values for WO_3 [13].

Comparing the observed *d*-spacings with those of ASTM, it is clear that they are almost the same in both cases. Hence, it is concluded that the crystal structure is not altered due to doping by the sintering technique. It is known that WO_3 at room temperature has a monoclinic crystal structure [14]. Considering the above observations and discussions, the monoclinic crystal structure (end-centred) of WO_3 is schematically shown in Fig. 2, where the corners have been occupied by oxygen atoms. The end faces of the crystal units (see Fig. 2) are occupied by tungsten and oxygen atoms, alternatively. It is also known that WO_3 has a

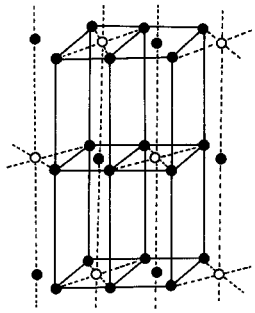

Figure 2 End-centred monoclinic crystal structure of WO_3. (○) W, (●) O. Each tungsten atom is surrounded by 6 oxygen atoms in a distorted "Oh" symmetry.

distorted octahedral ("Oh") symmetry [14]. This is also shown in Fig. 2, where each tungsten atom is surrounded by six oxygen atoms in a distorted "Oh" symmetry.

However, it should be noted that the characteristic peaks of the dopant ions are not observed in the XRD spectrum (Fig. 1b) of $Cu(II)/WO_3$, i.e. there is no new d-value observed in the spectrum of the doped WO_3 (Table I). This is due to the fact that a minimum of 10% concentration of the impurity ions is needed to effect their characteristic XRD peaks. However, only ~4% concentrations were used here. It is also not clear whether the dopants are present as ions or oxides within the WO_3 lattices. XRD study clearly illustrated that there is no change in the crystal structure of WO_3 due to doping and proved that WO_3 is present only as a trioxide and not as mixed oxides of tungsten.

Similar results reported on anatase by St John *et al.* [15], that the anatase structure was maintained even after reduction, support our observations on WO_3.

TABLE I XRD data

Reported, WO_3		Observed			
d (nm)	I/I_0	WO_3 (Fluka)		WO_3 (doped)	
		d (nm)	I/I_0	d (nm)	I/I_0
0.3835	100	0.380 70	99	0.382 47	100
0.3762	95	0.372 99	100	0.374 72	78
0.3642	100	0.362 03	82	0.363 67	73
0.3342	50	0.332 01	21	0.333 30	15
0.3076	50	0.307 76	15	0.308 40	13
0.2684	75	0.266 82	36	0.268 27	28
0.2617	90	0.260 80	53	0.261 70	50
0.2149	60	0.215 96	10	0.215 15	14
0.1917	50	0.191 45	13	0.191 86	12
0.1879	50	0.187 51	10	0.188 03	10
0.1820	75	0.181 77	25	0.182 32	23
0.1793	50	0.179 30	12	0.179 53	11
0.1707	60	0.170 70	15	0.170 99	11
0.1687	55	0.168 61	11	0.168 94	9
0.1670	50	0.166 74	9	0.167 23	9
0.1638	65	0.163 95	19	0.164 14	15
0.1486	60	0.148 62	14	0.148 92	9
0.1242	20	0.124 02	9	0.124 06	9

3.2. SEM

Scanning electron micrographs were taken for all the photocatalysts prepared. Figs 3a to n show the photographs of these powders. The particle structures are found to be quite irregular. Most of the particles have monoclinic appearance. The irregularities in the particle structures might have occurred during grinding the samples at the time of preparation. Figs 3l, m and n are found to be useful in understanding the monoclinic crystal structure. The dopant ions are seen on the surfaces of the WO_3 particles as minute white dots.

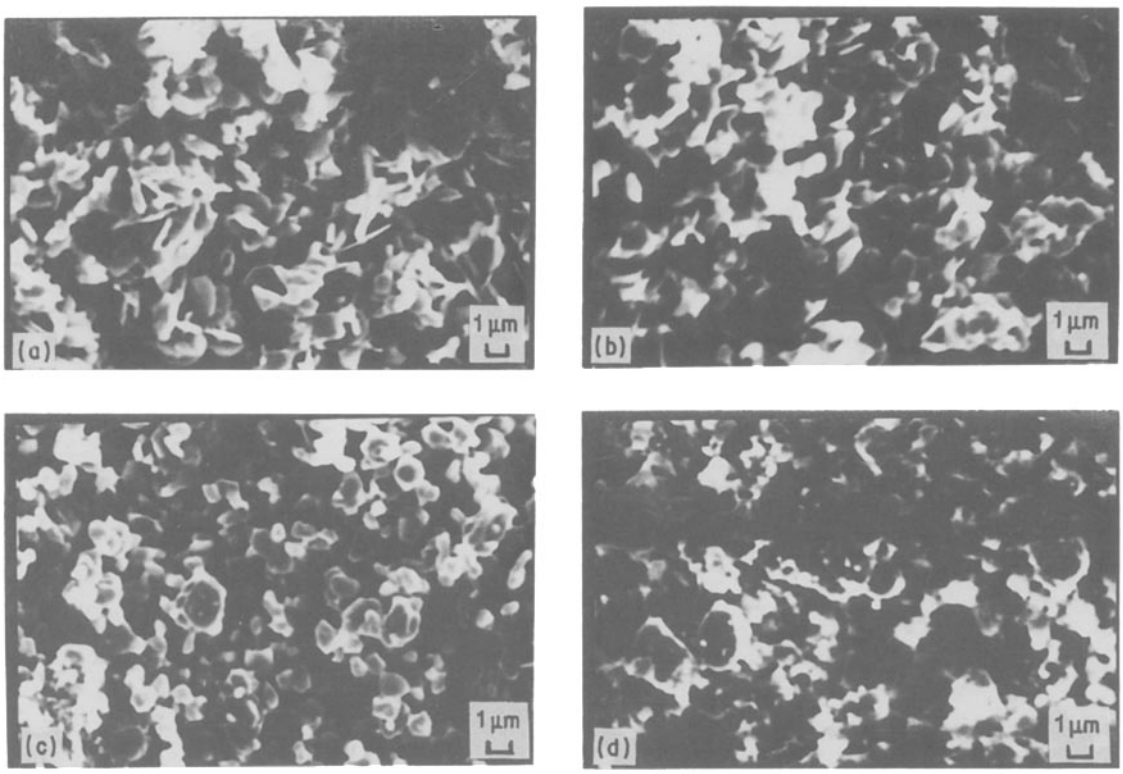

Figure 3 Scanning electron micrographs of: (a) WO_3, unprocessed; (b) WO_3, processed; (c) $Ti(III)/WO_3$; (d) $V(IV)/WO_3$; (e) V_2O_5/WO_3; (f) $Cr(III)/WO_3$; (g) $Mn(II)/WO_3$; (h) $Fe(III)/WO_3$; (i) $Co(II)/WO_3$; (j) $Ni(II)/WO_3$; (k) $Cu(II)/WO_3$; (l) $Zn(II)/WO_3$; (m) RuO_2 (2.5%)/WO_3; (n) RuO_2 (7.5%)/WO_3.

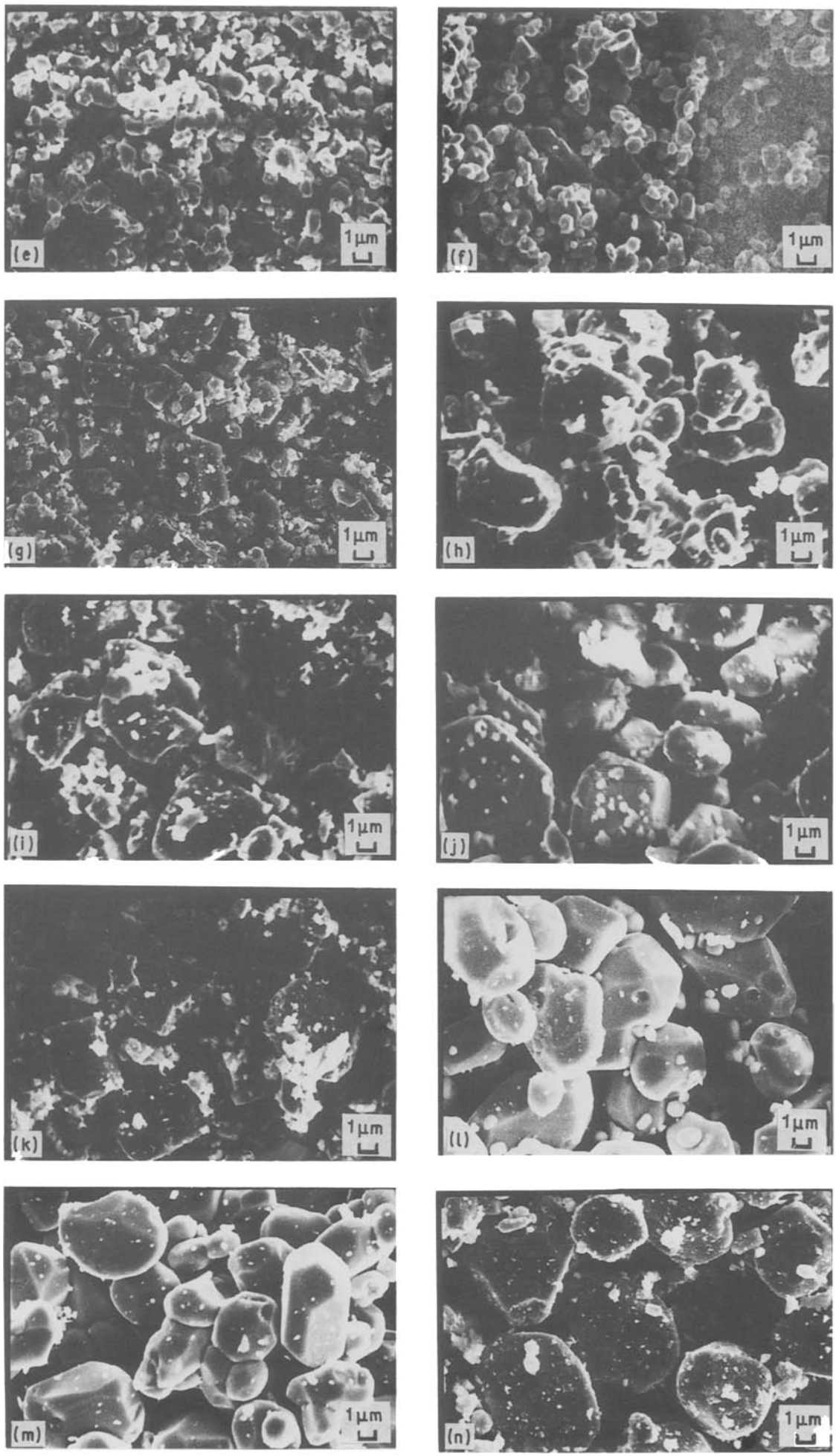

Figure 3 Continued.

However, there is every possibility for these dopants to occupy the interstitial positions, i.e. inside the unit lattices of WO_3 particles. Moreover, it is also very clear from Figs 3g to n that the crystallinity is increased due to doping, which is indicated by the increase in particle (crystal) sizes with well-developed faces. The XRD spectra (Figs 1a and b), where we observe more intense and more sharp peaks in the case of doped sample (Fig. 1b), also support this.

The SEM particles also indicated that the particle sizes range from 1 to 10 μm. In Fig. 3a, because the particle sizes are very small, we observe more void spaces; whereas in the doped samples we observe larger particles with fewer void spaces. Austin Suthanthiraraj *et al.* [16] reported that as the grain sizes increase, which will result in a decrease in the number of void spaces, the conductivity of the material will be increased. Thus, due to sintering, the conductivity of the WO_3 semiconductors could have been increased. The surface area of the undoped WO_3 powders determined by the BET method is found to be $\sim 1.5\,m^2\,g^{-1}$. The surface areas of doped samples are in the range 1.0 to $1.5\,m^2\,g^{-1}$. The increase in the particles sizes are evinced from the micrographs has resulted in a decrease of the surface area of some of the doped samples from the values of the undoped ones. As the dopant concentration is increased from 2.5% (Fig. 1m) to 7.5% (Fig. 1n), the white dots appeared more densely in the micrograph picture (Fig. 1n), which illustrates that the dopants are mostly deposited on the surfaces.

4. Conclusion

The WO_3 semiconductor powders which are used for solar energy conversion processes were photosensitized by doping with transition metal ions. XRD and SEM techniques were used to characterize these materials. The dopants were found to be mostly distributed on the surface of WO_3 particles. The surface areas of the doped WO_3 are found to be less than those of the undoped WO_3 with a consequent increase in the particle size of the former.

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