

SYNTHESIS AND OPTICAL CHARACTERIZATION OF ZINC OXIDE AEROGEL NANO - MODIFIED SOL-GEL METHOD

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Abstract: ZnO aerogel is an artificial nanomaterial having low density, high specific surface consisting of nanoparticles building blocks networked together to form an open and highly porous structure. ZnO aerogel nano powder has been synthesized by a modified sol-gel process using zinc acetate ethanolic solution. FTIR, UV-visible absorption techniques have been used to characterize the as-prepared and the annealed ZnO aerogel powders. The Functional groups are confirmed from FT-IR spectrum. UV-visible results show an increase of the ZnO aerogel optical band gap from those of bulk. XRD is used for the structural characterization of ZnO aerogel nanoparticles. SEM analysis the morphological changes of ZnO obtain by sol-gel process. EDAX shows that the above route produced highly pure ZnO nanostructure.

Keywords: ZnO, Aerogel, Sol-gel, UV, FTIR, SEM, EDAX, X-RD

Introduction

ZnO is one of the extensively investigated semiconducting materials of the II-VI group. Nano-structured ZnO is becoming increasingly important in the present times because of its distinguished properties such as electrical, optical, thermal and magnetic finding potential application as sensors, transducers and catalyst. Compared to other semiconductors, ZnO has wide band gap of 3.37 eV and other large excitation binding energy, which makes excitation stable even at room temperature. ZnO aerogel is an artificial nanomaterial having low density, high specific surface consisting of nanoparticles building blocks networked together to form an open and highly porous structure[1]. The sol-gel process has been used to prepare various ZnO nanostructured morphologies. Different ZnO nanostructures have been synthesized using various techniques and methods [2-4]. In the modified sol gel process, the aerogel powders are prepared under supercritical drying conditions in an organic solvent[5].

In the present work, we synthesized ZnO aerogel powder by modified sol-gel under drying at ethanol at non supercritical conditions followed by annealing process. It was

found the ZnO aerogel nanoparticles can be prepared under non supercritical drying.

2. Materials and Methods

ZnO aerogel was synthesized by dissolving 4g of zinc acetate dehydrate $[(Zn(COOCH_3)_2)]$ in 37ml of ethanol (CH_3OH). The solution was kept under continuous magnetic stirring at room temperature for 20 min. A few drop of monoethanolamine (MEA) were added to this solution. The obtained transparent solution was placed in a one-liter capacity autoclave for 1 hour. A Volume of 89 mL of ethanol was added and the resultant solution was kept under continuous stirring at 100C. After cooling down to surrounding temperature, a white powder was obtained. This powder was annealed at 500°C for 1h.

The synthesized samples were characterized for their structure by x-ray diffraction XPERT-PRO with Cu K α radiation & the surface morphology of the fine powders was examined using a scanning electron microscope. The elemental compositions of the ZnO nanoparticles were determined by using Energy Dispersive X-ray spectra (EDAX). Optical absorption spectrum is taken with SHIMA DZU UV-310PC, UV scanning spectrophotometer.

3. Results and Discussion

The x-ray diffraction pattern of the synthesized ZnO fine powders are shown in **Figure 1**. the size of the particles is calculated by Debye Scherrer's formula. The average crystal size is calculated by the formula

$$D = 0.9\lambda/\beta\cos\Theta \quad (1)$$

K is a constant equal to 0.89, λ the X-ray wave length (0.154095nm) and β the full wavelength at half maximum and Θ the half diffraction angle .the crystal size of the ZnO Nanoparticles calculated from FWHM was tabulated in table 1.

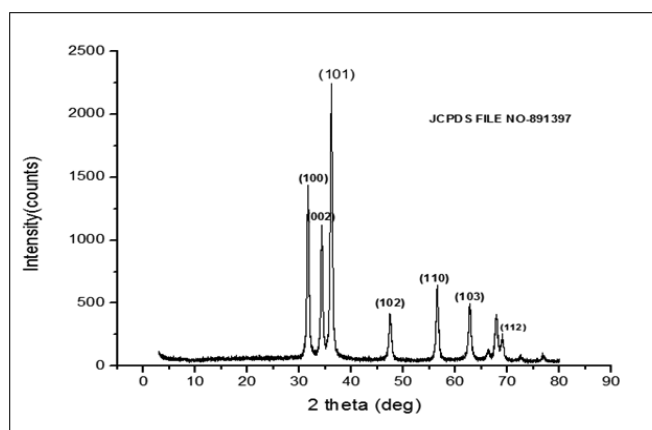


Figure 1 . X-Ray Diffraction of Aerogel Nanoparticles

The sharp intense peaks of ZnO confirms the good crystalline nature of ZnO and the peaks originated from (1 0 0),(0 0 2),(1 0 1),(1 0 2),(1 1 0),(1 0 3),(2 0 0),(1 1 2),(2 0 1),(0 0 4) and (2 0 2) reflections of Hexagonal ZnO with cell parameters $a=b=3.253$, $c=5.213$ (JCPDS Card no #891397) and the average particle size calculated is 17nm.

Table 1

2 θ (deg)	FWHM (deg)	d-spacing (nm)	h k l	Particle Size (nm)
31.613	0.540	2.8279	1 0 0	17
34.300	0.52	2.6123	0 0 2	17
36.104	0.464	2.4858	1 0 1	18
47.396	0.536	1.9165	1 0 2	16
56.459	0.483	1.6285	1 1 0	18
62.669	0.575	1.4812	1 0 3	16
66.272	0.490	1.4092	2 0 0	19
67.837	0.611	1.380	1 1 2	15
68.949	0.61	1.3609	2 0 1	15
72.540	0.54	1.3021	0 0 4	18
76.812	0.49	1.2400	2 0 2	20

Quantitative information concerning the preferential crystal-lites orientation was obtained from the texture coefficient $TC_{(hkl)}$ [6]:

$$TC_{(hkl)} = (I_{m(hkl)}/I_{O(hkl)})/[1/N(I_{m(hkl)}/I_{O(hkl)})]$$

The texture coefficients (TC) are calculated using JCPDS FILE NO-36-1451.the relatively intensity of the 7 most intense peaks and the calculated $TC_{(hkl)}$ values are given in TABLE2. Therefore for an extremely textured aerogel, one of the $TC_{(hkl)}$ would be equal to 7 while the others would be equal to 0; inversely, $TC_{(hkl)}=1$ for all the peaks in a fully randomly oriented aerogel. The peaks in low diffraction angles, $TC_{(hkl)}$ are being under 1, while for the peaks in the high diffraction angles, $TC_{(hkl)}$ are greater than 1. After annealing, $TC_{(100)}$, $TC_{(002)}$, $TC_{(101)}$, $TC_{(102)}$, $TC_{(110)}$, $TC_{(103)}$ and $TC_{(112)}$ intensities increase or decrease towards 1 [7]. This behavior indicates that annealing to improve orientation of the aerogel.

The surface morphology of the synthesized Zinc oxide aerogel Nanoparticles was examined by SEM micrographs. Figure 2 & 3 exhibits a honeycomb porous structure with fine particulate morphology. This result indicates that supercritical drying in methanol leads to produce ZnO particles with less agglomeration yield (low density) with high porosity. Figure 5.4 confirm a spongy structure of the prepared sample. The EDAX spectrum of the prepared ZnO aerogel shows (Figure 4) only Zn (45.36%) and O (54.64%) atoms. The obtained powder is found to be slightly rich on oxygen atoms which indicate the presence of more oxygen atoms at the surface of the synthesized ZnO crystallites.

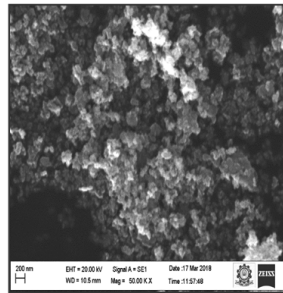


Figure 2

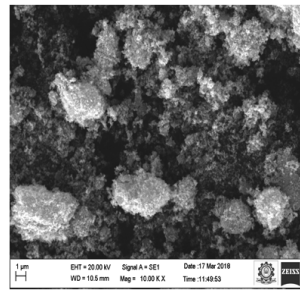


Figure 3

Table-2

h k l	JCPDS FILE NO36-1451($I_{0(hkl)}$)	Annealed aerogel($I_{m(hkl)}$)	Annealed aerogel($TC_{(hkl)}$)
100	57	61	1.2095
002	42	46	1.2378
101	100	100	1.1301
102	21	16	0.8611
110	31	29	1.0572
103	27	20	0.8371
112	22	13	0.6678

The optical absorption spectrum (**Figure.5.**)of ZnO aerogel nanoparticles prepared in modified sol-gel process. The UV visible spectra for ZnO aerogel nanoparticles is high absorption peak of 288nm which implies the lower particle size ZnO. The band gap calculated from UV cut-off is found to be 4.315eV ZnO aerogel nanoparticles. These bandgap values blue shifted relative to the bulk zinc oxide 3.37eV[8].

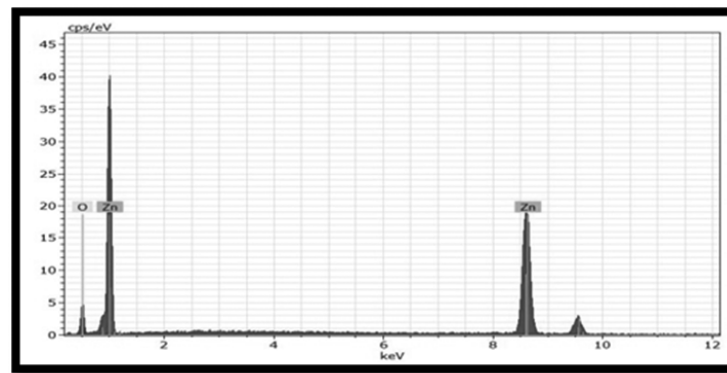


Figure 4 EDAX analysis of prepared ZnO aerogel nanoparticles

El AN Series	unnorm. C	norm. C	Atom. C	Error [wt.%]	[wt.%]	[at.%]	[wt.%]			
O	8K-series	21.12	22.77	54.64	4.38	Zn	30 K-series	71.66	77.23	45.36
1.89										
Total:		92.78	100.00	100.00						

FTIR Spectroscopy uses the infrared region of the electromagnetic spectrum to identify the chemical bonding present within material, whether organic or inorganic. The FTIR spectra (Figure.6.) were recorded in the range of 400-4000 cm^{-1} . FTIR was used to analyze the functional group present in the synthesized ZnO aerogel nanoparticles. The IR absorption bands at 3420, 2905, 2361, 1603, 1360 and 1030 are attributed to O-H, C-H, O-H, C=O, N-O and C-O vibrations (Table 2)

The band observed at 500cm^{-1} is correlated to the metal oxide [8]. FTIR spectra confirm the observed annealing effect by the apparition of the shift of the strong ZnO absorption band to the lower wave number region, indicating an increase in the Zn-O bond length [9,10].

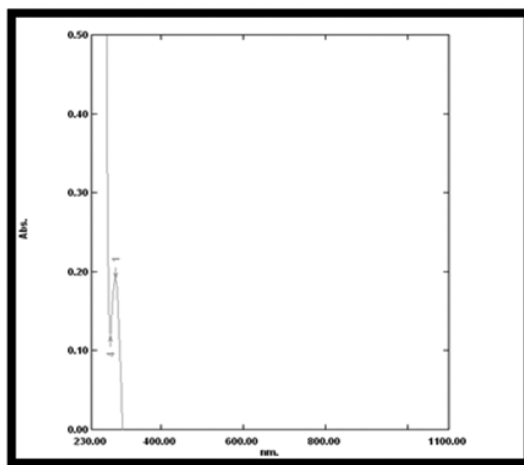


Figure.5. UV Spectra of ZnO aerogel nanoparticles

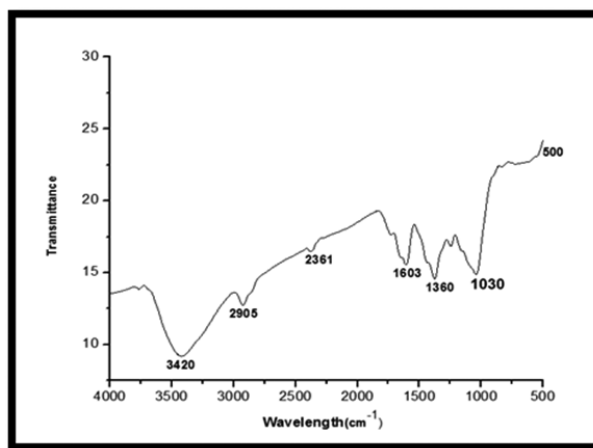


Figure.6. FTIR Spectra of ZnO Aerogel nanoparticles

Table-2

S.No	Wave number	Molecular motion	Functional group
1	3420	O-H Stretch	Amine
2	2905	C-H Stretch	Alkyl
3	2361	O-H Stretch	Carboxylic Acid
4	1603	C=O Stretch	Amide
5	1360	N-O Stretch	Nitro compounds
6	1030	C-O Stretch	Alcohols

Conclusion

ZnO aerogel nanoparticles have been obtained by dissolving zinc acetate dehydrate in ethanol by drying under non critical condition followed by annealing process. The synthesized aerogel has a well-defined ZnO polycrystalline hexagonal wurtzite structure. FTIR spectra confirm the observed annealing effect by the shift of the strong ZnO absorption band to the lower wave number region, indicating an increase in the Zn-O bond length. The UV-Visible absorption analysis indicates the blue shifts and increase in absorbance in the UV wave length. The XRD study reveals that the prepared ZnO aerogel is a hexagonal wurtzite structure. The EDAX spectrum shows the absence of C atoms in the prepared ZnO aerogel nanopowder and confirms the formation of pure ZnO. The EDAX spectrum shows the absence of C atoms in the as-prepared ZnO powder and confirms the formation of pure ZnO. The crystallites surface contains more O atoms than Zn ones. The prepared ZnO aerogel nanopowder consists of nanoparticles building blocks networked together to form an open and highly porous structure. Therefore the prepared ZnO aerogel nanopowder can serve as an excellent material in rubber additives, gas and chemical sensors and photocatalysis applications. Thus the aerogel nanoparticle can be prepared under non-critical conditions which yields same results as samples prepared under supercritical conditions.

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