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SYNTHESIS OF ZINC OXIDE AND ITS MEASUREMENT OF BAND GAP ENERGY USING DIFFUSE REFLECTANCE SPECTRA

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Abstract

Nanostructured Zinc Oxide has been synthesized by employing sol-gel method process using Zinc acetate as the metal precursor and Triethanolamine as a sol stabilizer. The synthesized material has been characterized by XRD, TEM and FTIR. The average particle size of ZnO was 23nm. The XRD analysis of the sample shows formation of nanocrystaline material with Wurtzite ZnO structure. UV visible spectra show maximum absorbance at 360 nm showing $\pi \rightarrow \pi^*$ transition of ZnO molecule. The band gap energy is calculated by DRIFTS which shows 3.26 eV.

Keywords- Nanomaterials, ZnO, Wurtzite phase, band gap energy

1. INTRODUCTION

Now-a-days, efforts have been concentrated on the preparation of metal oxide nanomaterial due to its various physio-chemical properties as compared to bulk materials. The properties of nanomaterials are different from bulk one is due to its nature in the interfacial regions of the nanoparticle. Reduction in the nano size of the semiconducting metals can enhances the structural, electrical and chemical morphologies properties of metal oxide nanoparticles. Zinc oxide which is n-type semiconductor material, band gap group II-VI has received great deal of attention in research and various fields1. Due to its high optoelectronics efficiencies relative to indirect band gap group IV, its wide band gap (3.37 eV), high exciton binding energy (E60 MeV) and high dielectric constant, ZnO considered to be an important semiconductor material for variety of applications in the visible and near ultraviolet region [2-3]. ZnO nanoparticles have received great attention because of their unique catalytic, electrical, gas sensing, optical properties, their non-toxicity, good electrical, optical, and piezoelectric behavior and other advantages such as their low cost and extensive applications in diverse areas.

The determination of band gap in nanomaterial is important in order to elucidate the basic solid state. Band gap indicates the difference in energy between the valence band filled with electrons and the conduction band empty of electrons. The band gap is related to the electric conductivity of the materials. There is value in insulators is known to be large, and that in generally no band gap in metals, but the band gap semiconductors are typically intermediate between these two. The most accepted method used for determination of band gap energy is the Tauc plot where Kubelka-Munk (KM) factor was plotted as a function of energy. The energy corresponding to any wavelength can be determined using the formula given in equation-1, 2 and 3. Equation-2 defines the KM function.

$$E = h\upsilon \qquad (1)$$

$$E = \frac{hc}{\lambda}$$

$$E = \frac{1239.7}{\lambda\,(nm)} \qquad (2)$$

$$F\,(R\infty) = \frac{(1 - R\infty)^2}{2R\infty} \qquad (3)$$

where R∞ is the limiting reflectance

The most linear part of energy vs. K-M function curve was fitted and the intercept on X-axis provided the value of optical band gap. The band gap of nano size materials is mainly associated with two factors as quantum confinement and surface-interface effects4. The quantum size effect leads to the blue shift or increase in Eg (band gap) with decrease in particle size while the surface and interface effects induces the red shift or decrease in energy gap[5] on decreasing the particle size.

With a wide band gap of 3.4 eV and a large exciton binding energy of 60 meV at room temperature, ZnO holds excellent promise for blue and ultra-violet optical devices. UV photoconductivity of ZnO is governed by surface-related and bulk-related processes. The surface-related process is primarily governed by the adsorption and desorption of the chemisorbed oxygen at the surface of the ZnO, which is exploited for gas sensing applications[6].

2. METHODOLOGY

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2.1 Materials:

Zinc acetate used is of AR grade purchased from Merck, INDIA. Other reagents as sodium carbonate and triethanolamine were of GR grade from S-D fine Chem lab.

2.2 Preparation of ZnO nanoparticle

The zinc oxide nanoparticles were synthesized by precipitation the surfactant solution containing triethanolamine and zinc acetate with sodium carbonate. Triethanolamine used as a stabilizer and 50ml of 1M zinc acetate was stirred for 30 minutes. To that solution 0.1M of sodium carbonate was added. The solution turns milky white in colour after addition of sodium carbonate. After the reaction, the suspension was kept under stirring for 5 hours at room temperature, precipitate was filtered and washed with double distilled water and absolute ethanol several times, dried under vacuum for 12 hours. Then zinc oxide nanoparticles were obtained.

The practice of fuel adulteration is not rare. Illegitimate practices while trading is a universal occurrence. Adulteration is significant along with less distribution of fuel to clienteles. These manipulations result in damaged engines and aggravating air quality along with escaping fuel taxes, sinking government income. Under-distribution supplies to buyers contribute to customer losses. Mixing kerosene with gasoline may have damaging deposits in engines. In India; it is mainly due to the substantial price variance amongst products, and also various products of analogous properties have diverse prices or common people don't have any effective tool to distinguish between clean fuel and adulterated, devious operatives will constantly try to feat the condition for monitory gains.

India consumed 4,443,000 barrels of fuel per day in 2016. Given this level of fuel consumption size, analyzing the level of adulteration and shading light on what is at stake will be of significant interest. Even then the data comprising of the harmful effects of fuel adulteration is unavailable. In India, Gasoline contributes as a main automotive fuel. Mixing of kerosene with the same at the point of purchase, during conveyance, and by the end-user such as drivers of Intermediate public transport (Auto Rickshaws), which function on the Indian streets in great records, has developed a critical problem across the country. We don't see the above problem in the economies which allow the capability of fuel manufacturers to update or keep pricing, built on market demand. In the current paper, we investigate the settled techniques for gasoline adulteration with kerosene causing deviations in the qualities of gasoline.

$$Zn(CH_3COO)_2 + Na_2CO_3 \rightarrow ZnO + 2\,CH_3COONa + CO_2$$

2.3 Characterization

The crystallization behavior of the ZnO nanostructure material was analyzed by an X-ray diffractometer (XRD, Model Bruker AXS Kappa APEX). The absorption spectra of the ZnO nanostructure material were obtained by using Uv-Visible Spectrophotometer (Varian Carry5000).

3. RESULT AND DISCUSSION

3.1 XRD Results

Figure 1 shows the XRD patterns of ZnO nanocrystalline powder. All the diffraction peaks are assigned to well indexed to the crystalline hexagonal phase of the ZnO nanomaterial, with lattice constants of a=1.8144Å, d=1.283Å.The XRD peaks of ZnO is found to be (101), (102), (110) and (200) at a diffracting planes at 2θ = 35.88°, 47.28°, 56.28°, and 62.53° respectively indicating the formation of phase pure wurtzite structure of ZnO (JCPDF 79-0208).X-ray diffraction studies confirmed that the synthesized materials were ZnO with wurtzite phase and all the diffraction peaks agreed with the reported JCPDF data.

A definite line broadening of the diffraction peaks is an indication that the synthesized materials are in nanometer range. The grain size was found to be in the range of 9.92 nm depending on the growth condition. The lattice parameters calculated were also in agreement with the reported values.

Table 1 XRD results

Sr. No.	Nanomaterial	2 θ	hkl	Lattice constant 'A°'	X-ray density g/cc	Crystallite size 'nm'
1	ZnO	35.88	101	1.8144	1.817 X 10-22	10
		47.28	102			
		56.28	110			
		62.53	200			
		17.33	200			

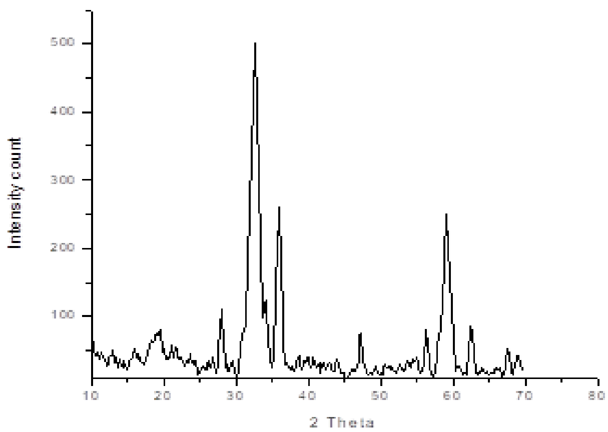

Figure 1 XRD pattern for ZnO nanoparticle

3.2 TEM Result

Fig. 2a shows the TEM image of synthesized ZnO nanoparticles. The ZnO particles are nearly spherical in shape with more agglomeration. The ZnO prepared by this method are rather well separated with an average size of approximately 10-15 nm which is in good agreement with the grain size calculated by Debye-Scherer formula. The specific surface area for NiO nanoparticle was calculated to be 22.01 m2/g.

Fig. 2b shows the corresponding diffraction pattern of ZnO nanoparticles. The Selected Area Electron Diffraction (SAED) pattern also confirms the cubic phase structure of the sample. The image shows the ring pattern of the ZnO which indicates the peak positions obtained in the X-rays diffraction pattern. Also, from the diffraction patterns, the particles give clear diffraction circle those are typical for random oriented and well-defined polycrystalline particles. ZnO nanomaterial with average size of 10nm which has also been confirmed by Jayaraj et al [7].

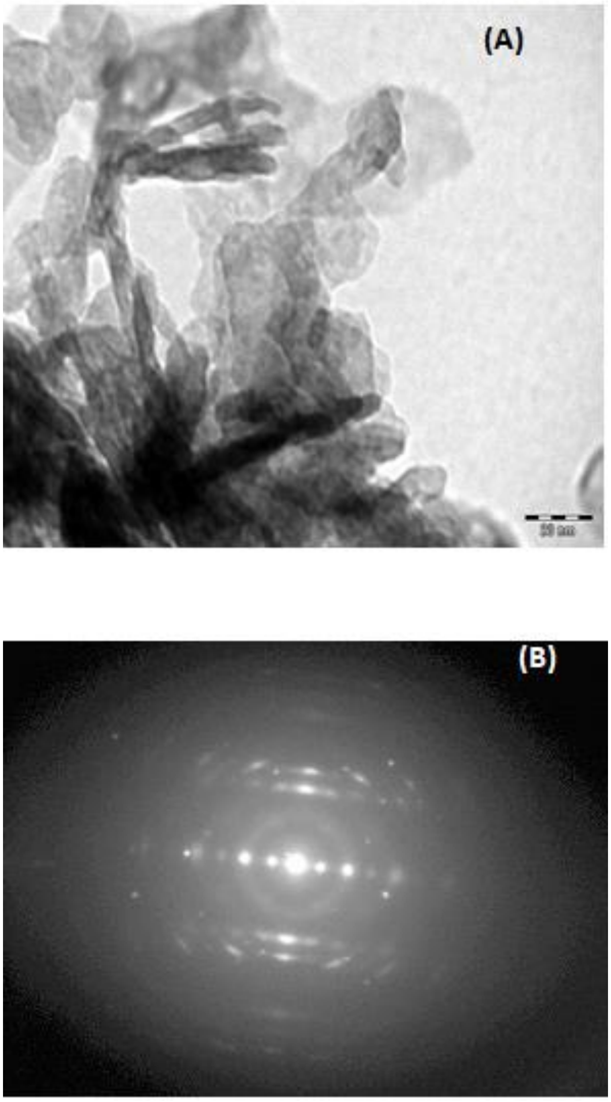

Figure 2 (a)TEM image of ZnO nanoparticle, (b) SAED pattern for ZnO nanoparticle

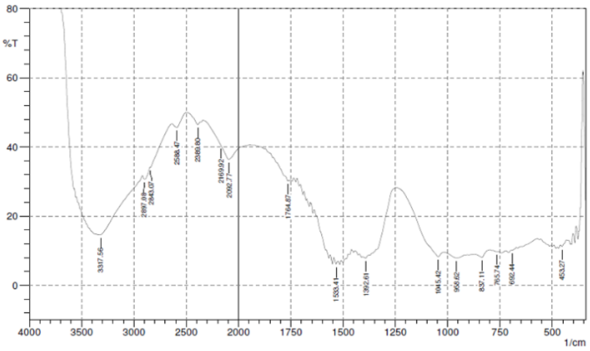

Figure 3 FTIR spectra for ZnO nanoparticles

3.3 FTIR

Fig.3 shows the IR spectra for the sample ZnO nanoparticle. IR spectra shows characteristic absorption peaks at 3317 cm^{-1} and 2897 cm^{-1} which are attributed to the δ(H-O-H) stretching vibrations of water absorbed from the surrounding. The two bands at 1533 and 1392 cm^{-1} can be assigned to asymmetric [υa(C=O)] and symmetric vibrations [υs(C=O)] of carboxyl group respectively [8]. However, the strong peaks at υ(ZnO) = 453 cm^{-1} is due to the stretching vibrations of Zn-O bonds [9] which confirms the formation of nanoparticle.

3.4 Diffuse Reflectance Spectroscopy

UV– visible absorption study is useful in calculation of band gap energy and also for the study of optical properties of the semiconductor nanocrystals [10]. The optical spectra of zinc oxide show a wide absorption peak centered at 380 nm as shown in Fig. 4a. The absorption peak of the ZnO nanoparticles have been shows a red shift due to the decrease in the band gap energy of the particle. The band gap energy was calculated to be 3.26 eV. The observed band gap compression from 3.37 eV of bulk ZnO to lower values may be ascribed due to quantum confinement and surface effects [11].

The spectrum of the metal oxide nanoparticles exhibit absorption bands at a characteristics peak which is due to the first optically allowed transition between the electronic state in the conduction band and the holes state of the valence band. The position of the absorption edge in the spectra of the sample can be shifted to higher energies or lower energies indicating the great influence of quantum confinement as consequence of the small size and large size of the metal oxide nanoparticles.

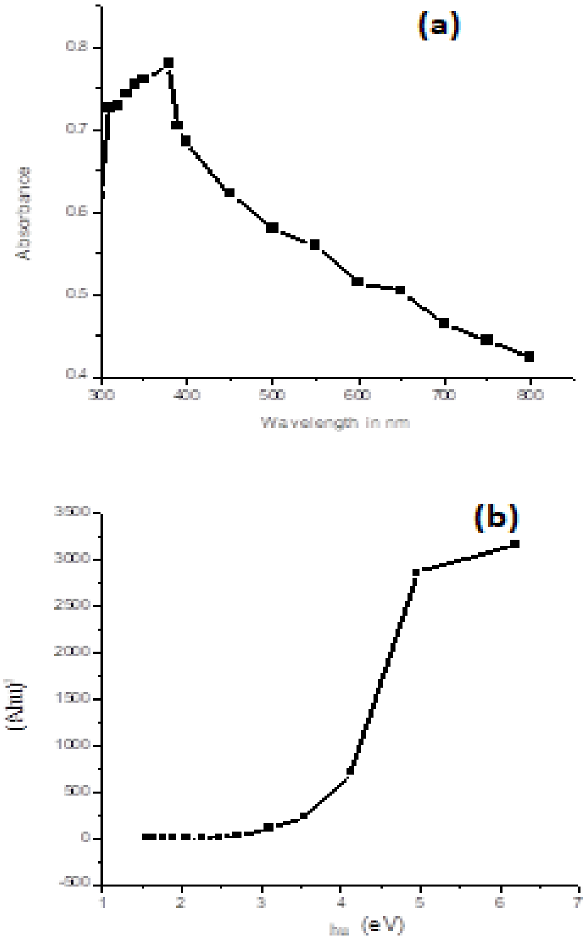

Figure 4 (a) UV-Vis absorption spectrum of ZnO nanoparticles, (b) (Ahυ)n versus (hυ) spectra of synthesized ZnO nanoparticles

4. CONCLUSION

ZnO nanoparticles has been synthesized by precipitation method using very easy, cheap and convenient process. The XRD study has shown the formation of hexagonal crystal structure. FTIR and UV-Visible spectroscopy shows the existence of ZnO nanoparticles. From diffuse reflectance spectra the band gap energy was found to be 3.26eV showing effects of quantum confinement due to small particle size of metal oxide nanoparticles.

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