Journal Of Harmonized Research (JOHR)

Journal Of Harmonized Research in Applied Sciences
3(2), 2015, 87-92

ISSN 2321 – 7456

Original Research Article

SYNTHESIS OF ZINC OXIDE QUANTUM DOT, ANTIMICROBIAL ACTIVITY AND APPLICATION FOR WATER TREATMENT

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Abstract: In the present study we report the synthesis of zinc oxide quantum dot by a chemical route. The obtained nanoparticles were characterized by X-ray diffraction (XRD), FTIR and UV–VIS absorption. Transmission electron microscopic image as well as XRD studies confirmed the nanometer size particles formation within the polymer matrix. The average particle size was found to lie in the range of 3.7–6.9 nm. A UV-VIS optical spectroscopy study was carried out to determine the band gap of the nanocrystalline ZnS thin film and it showed a blue shift with respect to the bulk value. The synthesized nanoparticles showed tremendous antimicrobial activity and can be used for water purification.

Introduction: Zinc oxide nanoparticles have received much attention for their implications in water treatment. Nanotechnology enables us to manipulate materials at nanoscale level (1–100 nm) and control their physicochemical properties. Nano-sized semiconducting materials have generated much interest in recent years owing to their structural, chemical and physical properties which are different from those of the bulk materials (Challa S.S.R. Kumar (2010); Ying Wang *et al.* (1991); Jia Grace Lu *et al.* (2006). Inorganic NPs, including metal oxides, are important materials for applications in medicine, such as biosensing, cell imaging, drug delivery, cancer therapy etc [1–3]. According to the Project on Emerging Nanotechnologies (PEN), Zn rank fifth among the most prevalent nanomaterials in consumer products [4]. Zinc oxide NPs are characterized by their photocatalytic and photo-oxidizing ability against chemical and biological species.

Conventional waste water treatment technologies and methods for disinfection of drinking water like chlorination, ozonation, UV treatment etc demand high capital investment and operation & maintenance cost, and large area. Application of nanotechnology which results in improved water treatment options might help us in removing the finest contaminants from water and with induced specificity to a certain pollutant that destroy or immobilize toxic compounds and pathogens. Heterogeneous photocatalysis is currently being

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Received on: February 2015
Accepted after revision: April 2015
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considered as a promising technique for water purification in comparison to other conventional methods [5, 6] Nanomaterials have been gaining increasing interest in the area of environmental remediation mainly due to their enhanced surface and also other specific changes in their physical, chemical and biological properties that develop due to size effects. Nanotechnology offers lot of promise in the area of water purification owing to large surface to volume ratios offered by nanostructures [7] and the possibility of preparing photocatalytic membranes by growing semiconducting nanostructures on conventional membranes [8, 9]. Research is underway to use advance nanotechnology for purification of drinking water.

In the present study we have synthesized ZnO nanoparticles by chemical method and investigated the structural and optical properties using UV-VIS spectroscopy, TEM and XRD. The purpose of the work is to analyse the antimicrobial activity of synthesized quantum dot.

Experimental

All the chemicals were of analytical grade and used without further purification. In all the experiments, deionized water was used as a solvent. Different sized ZnS nanoparticles have been prepared by chemical co-precipitation method at room temperature [13]. ZnS nanoparticles have been prepared with different molar concentration using zinc sulphate ($ZnSO_4.5H_2O$), and sodium sulphide ($Na_2S.7H_2O$) and without using any capping ligand. For synthesis, the Zinc sulphate and sodium sulphide were taken in different molar concentration. Zinc sulphate (1.0M) and sodium sulphide (1.0M) were dissolved in 100 ml double distilled water separately and the obtained molar solutions were stirred continuously for 20 minutes. While stirring Zinc sulphate 1.0M solution of 100 ml was mixed drop by drop in 100 ml 1.0 M solution of Zinc sulphate. White precipitates of the ZnO nanoparticles were formed slowly in the solution. The obtained precipitate was then filtered washed and dried at room temperature. After drying, the precipitate was crushed to fine powder with the help of mortar and pestle. For thin film form the ZnO samples was stirred with polymer matrix in three hours so that adhesion takes place on glass substrate.

Antimicrobial activity - Well diffusion assay

The Mueller Hinton agar was poured on to sterile Petri plates and plates were inoculated with 2.0 ml of inoculum by spreading the swab over the plate. Cultures of *Escherichia coli*, *Staphylococcus aureus* were swabbed on to the agar plates. With the help of sterile borer, wells of 8mm diameter were cut on the agar plates and loaded with 30µl of ZnO nanoparticle solution and a standard antibiotic (chloramphenicol). Sterile distilled water and 1mM silver nitrate (ZnO) were used as a control. To study the synergistic effect of Zn nanoparticles and antibiotics, the mixture of 15µl of respective concentrations of ZnO nanoparticles and 15µl of antibiotics were added into respective wells. All plates were incubated at 37^0C for 24 hrs. After incubation period, the inhibition diameters were measured with Hi-Media scale. The experiments were performed in triplicate.

Results and Discussion

a) Optical absorption

UV-Visible absorption spectroscopy is very efficient technique to monitor the optical properties of nano sized particles. The UV-VIS absorption spectra of ZnO nanocrystalline are shown in Fig.1 at different condition. The graph A is the condition of irradiation at room temperature and B represent under UV treatment and C represent UV treatment in 12hours. The reduction of pure Zn ions was observed by measuring the UV-Vis spectrum of the reaction using UV- Vis spectrophotometer119 (Systronics) after different time intervals (0h, 24h, 48h, 72h) taking 1ml of the diluted sample, compared with 1 ml of distilled water used as blank. UV-Vis spectral analysis has been done by using spectrophotometer at a resolution of 1 nm from wave length 250to 800 nm. A control reaction mixture was also maintained.

The fundamental absorption, which corresponds to electron excitation from the valence band to conduction band, can be used to determine the

nature and value of the band gap of ZnO particle. The relation between the absorption coefficient (α) and the incident photon energy (hν) can be written as

$$(\alpha\, h\nu)^{1/n} = A(h\nu - E_g) \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

The absorption coefficient α can be calculated from the absorbance (A) or transmittance (T) and the sample thickness (t) using the relatio

$$\alpha = 2.3026\ (A/t) \text{ -------- } 2$$

The band gap energy of the film at wavelength range 250 to 800nm has been calculated using the equation

$$\alpha^2 = C\ (h\nu — E_g) \text{ -------- } 3$$

Where C is a constant related to the effective masses associated with the bands, hν is the photon energy and E_g the band gap energy. The band gap energy is measured by a graph of α^2versus hν data resulting from absorption spectra. The extrapolation of the straight line to $\alpha^2=0$ give the value of band gap energy. From fig2 the band gap values thus obtained are in the range of 2.98-4.2 eV. The absorption spectra also reveal that the excitonic absorption peaks for all these samples are blue shifted compared to the bulk indicating strong confinement. Size quantization of carriers in a small volume crystallite is well known to cause the blue shift. The shift of band gap can be utilized in determining the crystal radius (r) using the effective mass approximation relation [14-15].

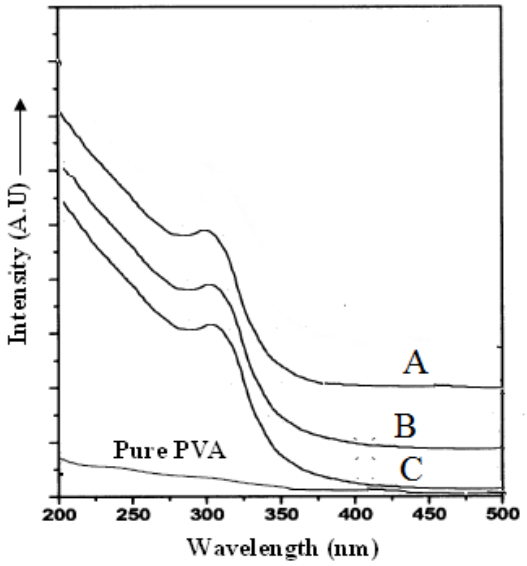

Fig1. Optical absorption of ZnO quantum dot.

$$\Delta E_g = E_g(\text{Film}) - E_g(\text{bulk})$$
$$= [h^2/8\mu r^2] - 1.8e^2/\epsilon_0\epsilon_r r \quad \ldots\ldots (4)$$

Where $1/\mu = 1/m^*_e + 1/m^*_h$, μ is the reduced mass of electron and hole effective masses, $m^*_e=0.34m_0$ and $m^*_h=0.23m_0$ and $\epsilon_r=8.76$ is the permittivity of the sample. The values of band gap and particle size calculated from EMA model for different condition. It is clear that band gap increases with increase of expose of sunlight and the particle size decreases with increase of expose time. The average particle size obtained 4.3 to 6.5 nm.

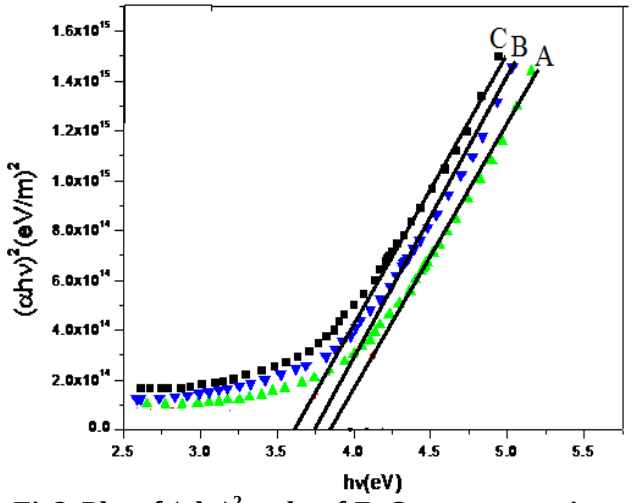

Fig2. Plot of $(\alpha h\nu)^2$ vs hν of ZnO nanocomposite

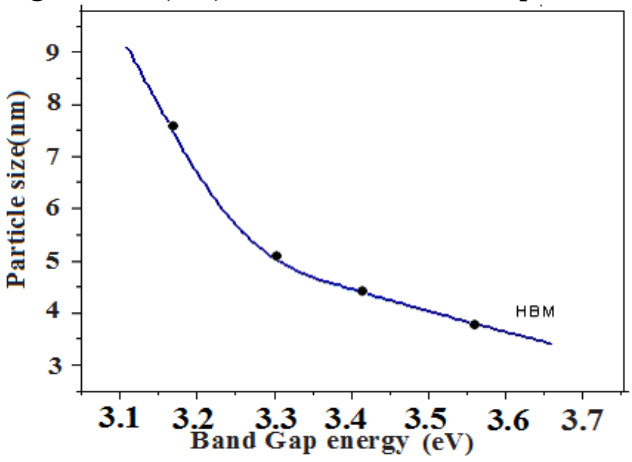

Fig3. Band Gap vs particle size.

b) XRD Analysis: X-ray diffraction (XRD) analysis of drop-coated films of ZnO nanoparticles was prepared for the determination of the formation of ZnO nanoparticle by an X-ray diffractometer operated at a voltage of 40kv and a current of 30mA with Cu Kα radiation.

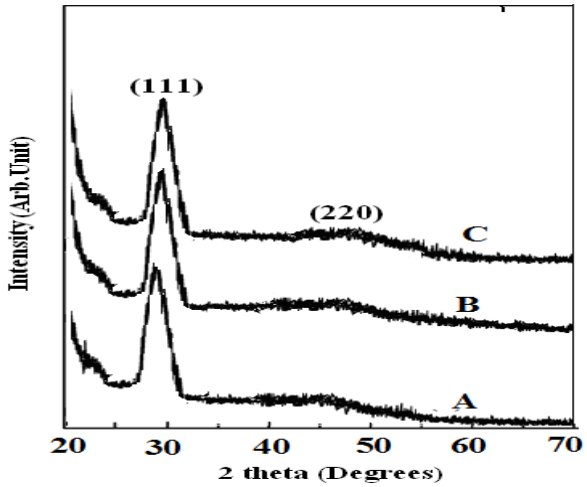

Fig4. XRD patterns of ZnO films deposited on glass substrates for different expose condition

Fig.4 shows XRD patterns of PVA-capped ZnO nanocrystalline films deposited on glass substrate for different different conditions like sunlight irradiation, UV irradiation and room temperature.. The diffraction peaks at angles near $2\theta = 29.2^0$ and $2\theta = 45.15^0$ corresponds to (111) and (220) planes of the mix cubic phase of ZnO. X-Ray peak intensities are weak and broad compared to bulk counterpart suggesting small crystallite size. The X-ray peaks are also found to shift to higher diffraction angle when sample irradiate with room temperature to uv trteatment. The graph A is the condition of irradiation at room temperature and B represent under UV treatment and C represent treatment with long time uv treatment. The lattice contraction is expected to occur because of higher surface to volume ratio with decreasing crystallite size and increase in strain. The shifting of peak position to higher diffraction angle due to strain was confirmed by calibrating the XRD prior to each observation using standard silicon sample [16, 17]. The size of the nanocrystal was determined using Scherer formula [18].

$$D = \frac{kl}{Vw_{2q}\cos q_B} \quad \text{---------- (4)}$$

Where q_B is the Bragg angle and K=0.9 for spherical shape (from TEM not shown here).The obtained values of crystalline sizes are summarized. From the calculation it is seen with long time expose of sunlight average particle size also decrease from 4.5 to 6.8 nm.

C) Antimicrobial activity

Antibacterial activity of the synthesized silver nanoparticles was studied for pathogenic bacterial species like - *Staphylococcus aureus* (gram positive bacteria*)* and *Escherichia coli* (gram negative bacteria). The antimicrobial activity was determined in-vitro by measuring zone of inhibition in mm by using well size of 8mm diameter and 50µl of sample. Ampicillin of 10mg/l, concentration was used as a control antimicrobial agent. The ZnO nanoparticles synthesized showed inhibition zone against the studied bacterial species. The results are shown in the table below. The results depict that silver nanoparticles are efficient giving a zone of inhibition. Thus, the ZnO nanoparticles synthesized significantly inhibit the pathogens.

The antibacterial efficacy of the biological ZnO nanoparticles reported the present study may be ascribed by the mechanism of anchoring or penetrating the bacterial cell wall, and modulating cellular signaling by dephosphorylating putative key peptide substrates on tyrosine residues [19]

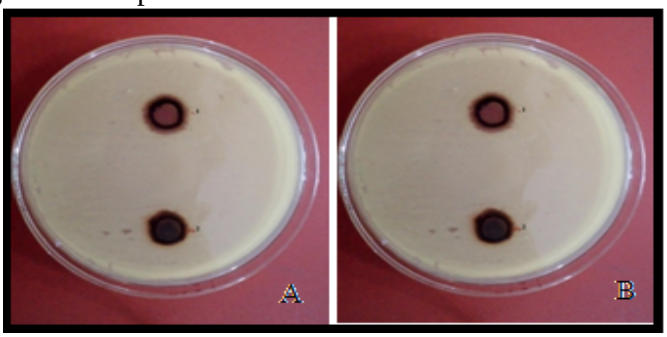

Fig 5. Antibacterial activity of silver nanoparticles against pathogenic bacteria (A)Staphylococcus aureus (B) Escherichia coli

d) FTIR analysis:

The sample was mixed with KCl procured from Sigma. Thin sample disc was prepared by pressing with the disc preparing machine and placed in Fourier Transform InfraRed [FTIR] for the analysis of the nanoparticles The FTIR analysis of silver nanoparticles were recorded at room temperature .FTIR spectra of ZnO nanostructures for different growth condition. For alcohols the most useful absorption is that due to the stretching of the O-H bond. In the free or unassociated state, it appears as a weak but sharp bond at about 2078.11 cm^{-1}.

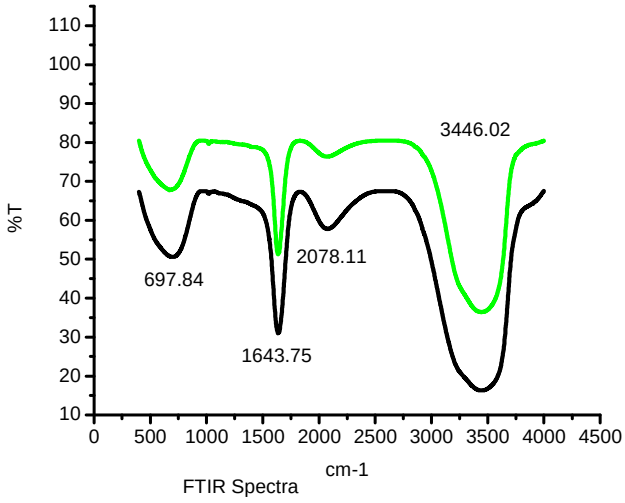

Fig 6. FTIR spectra of mix ZnO nanoparticles.

Conclusion

The synthesized ZnO nanoparticles were characterized by UV-Vis spectrophotometer and XRD measurements and FTIR. The results showed that formation of ZnO nanoparticles and band Gap has been calculated. The band gap of nanocrystalline ZnO increases to higher value as observed from optical absorption data. Moreover, the synthesized ZnO nanoparticles shows antibacterial activity on both gram positive and gram negative bacteria. From the present study, it is clear that the ZnO nanoparticles synthesized can be used effectively in treating bacterial diseases. Control over the shape and size of nanoparticles seems to be very easy with this method.

Acknowledgement

The authors would like to acknowledge IITG for providing XRD facilities. We would also like to acknowledge UGC for providing financial support through major project and Department of Biotechnology (DBT), Ministry of Science & Technology, Government of India is duly acknowledged for financial assistance.

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