African Journal of Basic & Applied Sciences 2 (5-6): 161-166, 2010
ISSN 2079-2034

Photocatalytic Activity of ZnO Nanopowders Synthesized by DC Thermal Plasma

[1]M. Nirmala, [1]Manjula G. Nair, [1]K. Rekha, [1]A. Anukaliani,
[2]S.K. Samdarshi and [2]Ranjith G. Nair

[1]PG and Research Department of Physics, Kongunadu Arts and Science College,
Coimbatore - 641 029, Tamil Nadu, India
[2]Department of energy, Tezpur University, Assam, India

Abstract: Nanosized zinc oxide (ZnO) powders were prepared via DC thermal plasma process from microsized zinc powder while air was employed as a reaction gas. The ZnO nanopowders were characterized by X-ray diffraction, UV-Visible spectrometry, scanning electron microscope and energy dispersive X-ray analysis. The X-ray diffraction analysis of the sample showed the formation of nanopowder with wurtzite ZnO structure. The photocatalytic activities of ZnO powders were evaluated by measuring the degradation of Methylene Blue (MB) in water under the UV region. ZnO nanopowder resisted the growth of tested bacterias.

Key words: Antimicrobial · Methylene blue · Photocatalysis · DC thermal plasma

INTRODUCTION

Semiconductor materials, especially II – VI semiconductors have attracted great interest due to their unique properties and potential applications. ZnO is a semiconductor with wide band gap (3.3 eV), large exciton binding energy (60 MeV), abundant in nature, natural n-type conductivity and environmentally friendly[1]. The most effective functional materials for photocatalytic applications are nanosized semiconductor oxides. ZnO offer low cost, mild reaction conditions, high photochemical reactivity, while affording the use of sun light.

ZnO can absorb UV light with the wavelength equal (or) less than 385 nm, However, for higher photocatalytic efficiency and many practical applications, it is desirable that photocatalyst such as ZnO should absorb not only UV but also visible light due to the fact that visible light accounts for 45% of energy in the solar radiation while UV light less than 10%. In order to absorb visible light, band gap of ZnO has to be narrowed or split into several subgaps, which can be achieved by implanting transition metal ions or by doping nitrogen [2,3].

EXPERIMENT

Thermal plasma technology is being increasingly used in material processing applications. Besides being a source of high temperature and high enthalpy, thermal plasma is a convenient medium to realize many reaction of importance in the metallurgical and chemical industry. Plasma technology is being extensively used in developing surface coatings for a variety of engineering applications, for synthesis of advanced ceramics, production of nanocrystalline materials and for metallurgical treatment of ores and minerals to yield value-added materials. Several methods are difficult to produce relatively large quantity of nanoparticles at a low cost. Recently, DC thermal plasma technique has been developed for synthesizing various oxide nanoparticles at low cost and a high yield rate [4].

DC plasma apparatus consists of a DC generator, a plasma torch, a reaction tube, a chamber, a powder feeder and an injection block was used to synthesize ZnO nanopowder. Atmospheric air was employed as the plasma gas. When the atmospheric air was introduced into the reaction tube with a flow rate in the range of 15 *l*/min, an oxidation reaction took place in the flame of the plasma. Commercially available Zn metal powder with average particle size at 10-15 µm was injected into the plasma region through the powder feeder. The powder was readily evaporated and oxidized by the high temperature of the plasma flame, followed by the rapid condensation in the reaction tube wall. The prepared powder was collected from the Hood and chamber part.

Corresponding Author: A. Anukaliani, PG and Research Department of Physics, Kongunadu Arts and Science College, Coimbatore - 641 029, Tamil Nadu, India, Mob: +09842263940.

Experimental Conditions for the Preparation of ZnO Nanopowder:

Plasma Power	:	7 KW
Open Circuit Voltage (OCV)	:	369V
Type of gas	:	Atmospheric air
Flow rate of the gas	:	15 *l*/minutes
Feeding rate of the material	:	Zn metal powder, 20gram
Reaction time	:	5 minutes

Vapour phase synthesis of carbides, nitrides, borides and oxides have been successfully carried out in RF and DC plasma torch based reactors. Application of thermal plasma in powder synthesis has certain specific advantages over other competitive techniques.

Temperature and enthalpy available in thermal plasmas are very high (typically 10,000-15,000K) to vaporize any material. The process is characterized by high quench rate (10^6-10^8 K/second) favoring homogenous nucleation leading to nanosized particles. Processing time is relatively fast. Any reactive atmosphere can be superimposed over the plasma medium to produce nanosized powder of any desired material. Wide choice of precursors – solid, liquid and gas can be used.Above all, the technique is highly versatile since it can be applied to any material.

RESULTS AND DISCUSSION

The crystal structure and orientation of ZnO nanoparticles have been investigated by X-ray diffraction (XRD) method. The sharp and intense peaks from Figure 1 indicate that the samples are highly crystalline and ZnO nanoparticles have polycrystalline structure [5]. The XRD peaks for (100), (002) and (101) planes indicates the formation of phase pure wurtzite structure of ZnO. The ZnO nanoparticles have a preferred growth orientation along 101 direction. No peaks were observed due to impurities, indicating high purity of the ZnO nanopowders obtained by dc thermal plasma synthesis. The values of a and c for ZnO calculated using the formula, $\frac{1}{d^2} = \frac{4}{3}\left\{\frac{h^2+hk+k^2}{a^2}\right\} + \frac{l^2}{c^2}$

was found to be a = 3.232 Å and c = 5.177 Å. The lattice constants for hexagonal ZnO nanoparticles reported in Joint Committee on Powder Diffraction Standards (JCPDS) matches with the calculated one [6]. The crystalline size of ZnO can be calculated using Scherrar's formula,

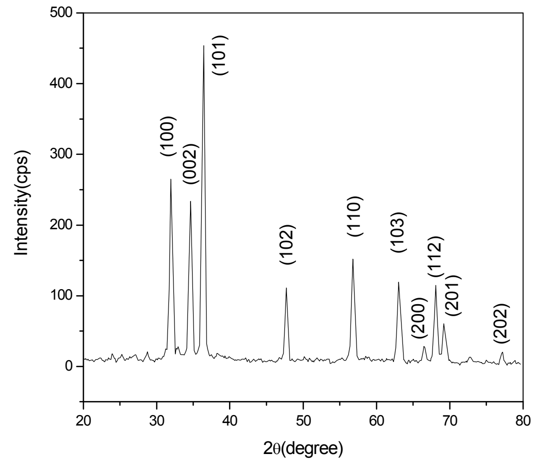

Fig. 1: XRD Pattern of ZnO

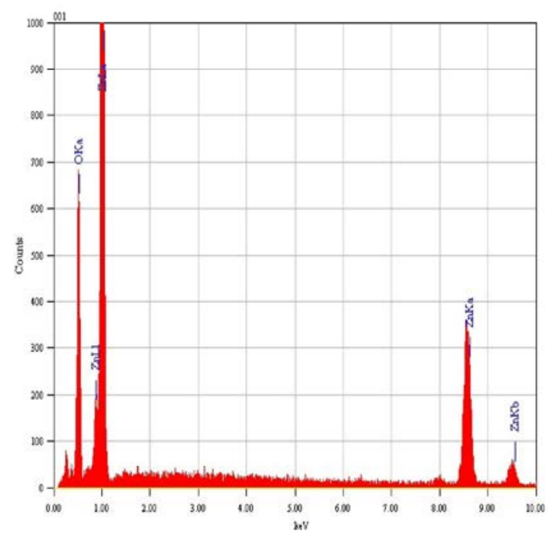

Fig. 2: EDX Spectrum of ZnO

$$D = \frac{0.9\lambda}{\beta\cos\theta}$$

'λ' The wavelength of X-rays (1.5406 for Cuk_{α})
θ Is the Bragg's angle
β Is the full width at half maximum

The average crystalline size is found to be 28 nm. Table 1 shows the XRD parameters of ZnO nanopowders. Figure [2] shows the EDX spectrum of ZnO nanopowders and Table 2 shows the ratio of ZnO elemental composition. EDX spectrum shows four peaks which are identified as zinc and oxygen. Hence, it can be seen that pure ZnO nano powders can be prepared using DC thermal plasma. Formation of a dominant rod like crystal

Table 1: XRD parameters of ZnO

	2θ (Degree)		Interplanar distance (d) (Å)		
hkl	observed	JCPDS	observed	JCPDS	Crystalline size (nm)
100	31.94	31.77	2.80	2.81	27.58
002	34.62	34.42	2.59	2.60	30.00
101	36.43	36.23	2.46	2.48	26.80
102	47.71	47.53	1.90	1.91	26.85
110	56.76	56.60	1.62	1.62	26.80
103	63.02	62.86	1.47	1.48	27.97

Table 2: Compositional analysis of ZnO

Elements	Experimental Results (Atomic %)
Zn	23.14
O	76.86

Table 3: Degradation Rate Constant

S.No.	Sample	Degradation rate constant (exposure to Solar light) (min^{-1})
1.	MB	0.032
2.	ZnO	0.119

(a) (b)

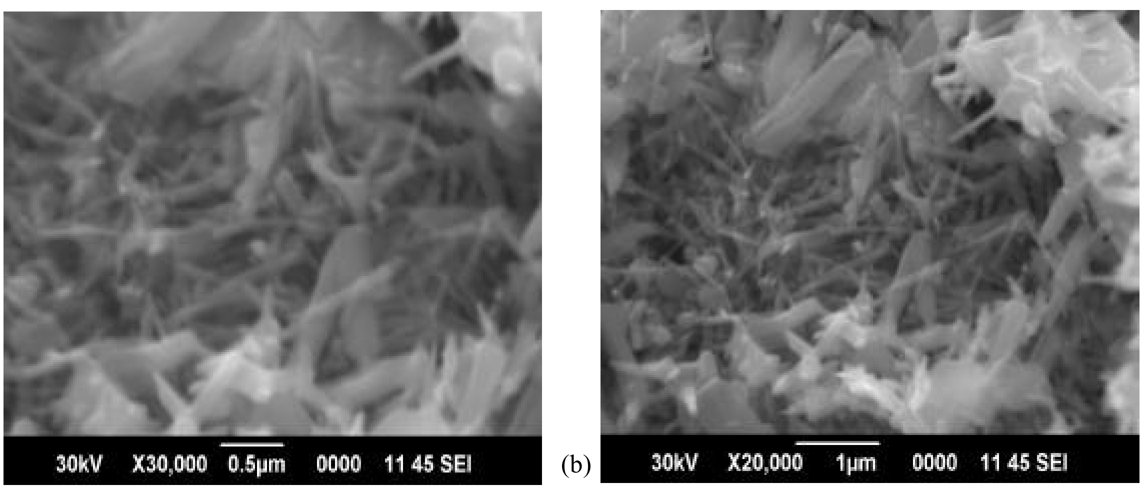

Fig. 3(a,b): a) SEM Image of ZnO
b) SEM Image of ZnO

population has been observed from the SEM analysis of ZnO nanopowders which is shown in the Figure 3. The average crystalline particle size is approximately 65 nm. The same structure was reported by So-Jung Kim *et al*. by thermal plasma method [3].

The UV-vis absorption spectrum of ZnO is shown in Figure 4. The absorption edge takes the value at 284 nm from the absorption curve. This indicates a blue shift in the spectrum. Kumbhakar, has reported that the excitonic absorption peak observed at 262 nm due to ZnO nanoparticles lies much below the band gap wave length of bulk ZnO (388 nm) and the sharpness of the peak indicates monodispersed nature of nanoparticle distribution. In the spectrum, [Fig. 4] the absorption of peak of ZnO at 284 nm may be due to the monodispersion of nanoparticles [7].

The photocatalytic study was performed by the degradation of aqueous methylene blue dye solution.

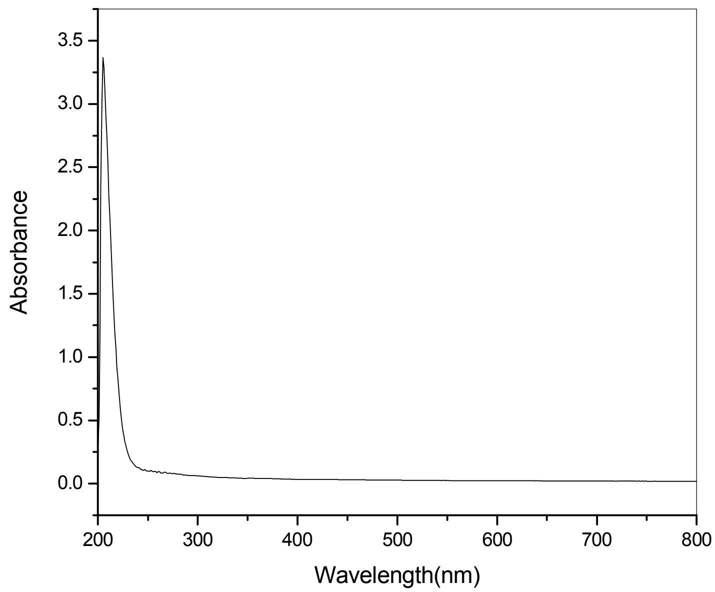

Fig. 4: Absorption Spectrum of ZnO

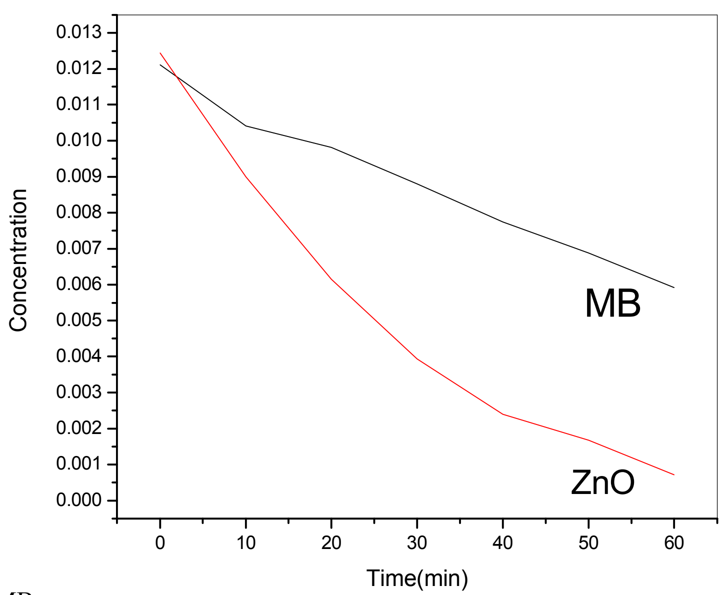

Fig. 5: Degradation of MB

Here, the synthesized ZnO nanopowders where employed as a photocatalyst for the degradation of Methylene Blue (M.B). Time Vs concentration graph Figure 5 was plotted, combining MB and ZnO. It is observed that the degradation of MB is high in the case of ZnO. A graph was drawn between Time Vs ln C/C_0 and the degradation rate constants were calculated from Figure 6 and equation $-\ln\left(\frac{c}{c_0}\right) = kt$.

The values are given in the Table 3.

Lingling zhang [8], reported the antibacterial activity of ZnO against (Escherichia coli, Slamonella typhi, Bacillus subtilis and Staphylococcus aureus). Nagarajan padmavathi and Rajagopalan Vijaya-raghavan [9] reported the antibacterial activity of ZnO against E. coli. Tam [10], investigated antibacterial activity of ZnO against E-coli and B. atrophaeus.

The antibacterial activity of ZnO was performed according to the disc diffusion method using Muller Hinton agar. In this work bacterial strains of Escherichia coli and Klebsiella pneumoniae, were employed.

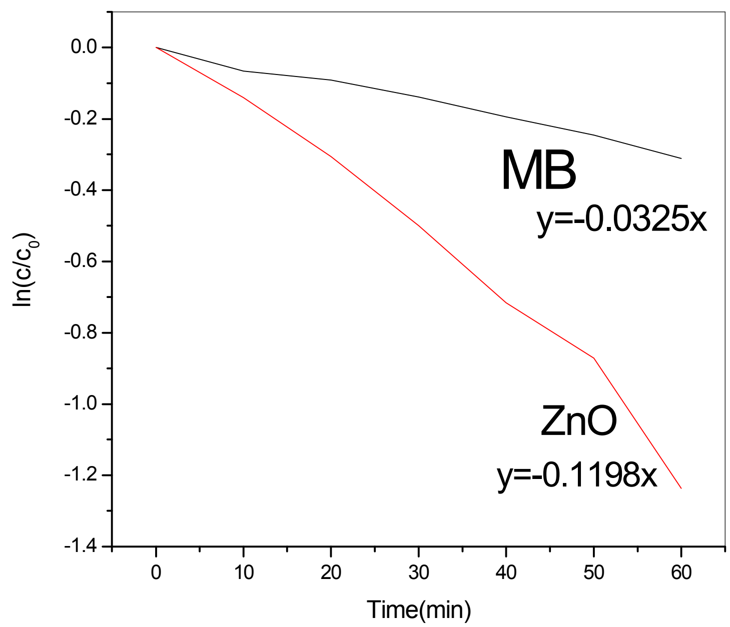

Fig. 6: Degradation Rate Constant

The above mentioned bacterias were grown individually on watt man No.1 filter discs at 37°C for 24 hrs. ZnO exhibited remarkable antibacterial activity against all tested bacterial strains.

CONCLUSION

ZnO nanoparticles have been synthesized by DC thermal plasma. The X-ray diffraction studies indicated the formation of phase pure polycrystalline ZnO. The synthesized ZnO nanopowders resembled a rod like morphology. The Blue shift was observed in the absorption spectra. Photocatalytic study revealed that ZnO decomposes Methylene Blue. In order to enhance the photocatalytic activity of ZnO in visible region it has to be doped / or implanted with suitable metals. The antibacterial test proved that the prepared ZnO can resist the growth of tested bacterias. All the studies reported above leads to the promising applications of the ZnO in reducing the environmental toxicity and can be employed in biomedical applications.

REFERENCES

1. Li, J.H., D.Z. Shen, J.Y. Zhang, D.X. ZhaO, B.S. Li, Y.C. Liu and X.W. Fan, 2007. The effect of Mn2+ doping on strcuture and photoluminescence of ZnO nanofilms synthesized by sol–gel method. J. Luminescence, 122: 352-354.
2. Hsiu-Fen Lin, Shih-Chieh Liao and Chen-Ti Hu, 2009. A new approach to synthesize ZnO tetrapod-like nanoparticles with DC thermal plasma technique J. Crystal Growth, 311(5): 1378-1384.
3. So-Jung Kim and Dong-Wha Park, 2009. Preparation of ZnO nanopowders by thermal plasma and characterization of photo-catalytic property. Applied Surface Sci., 255: 5363-5367.
4. Ko, T.S., S. Yang, H.C. Hsu, C.P. Chu, H.F. Lin, S.C. Liao, T.C. Lu, H.C. Kuo, W.F. Hsieh and S.C. Wang, 2006. ZnO nanopowders synyhesized bydc thermal plasma synthesis. Materials Science and Engineering, B134: 54-58.
5. Pivin, J.C., G. Socol, I. Mihailescu, P. Berther, F. Singh, M.K. Patel and L. Vincent, 2008. Structure and magnetic properties of ZnO films doped with Co, Ni or Mn synthesized by pulsed laser deposition under low and high oxygen partial pressures Thin Solid films, 517: 916-922.
6. Powder diffraction file 36 – 1451 for hexagonal ZnO (1997 JCPDS – International centre for diffraction data).
7. Kumbhakar, P., D. Singh, C.S. Tiwary and A.K. Mitra, 2008. Chemical synthesis and visible photolumiesence emission from monodispersed ZnO nanoparticles. Chalcogenide Letters, 5: 387-394.

8. Lingling Zhang, Yulong Ding, Malcolm povey, David York, 2008. Antimicrobial behaviour of suspensions of ZnO nanoparticles towards *E. coli* Progress in Natural Sci., 18: 939-944.
9. Nagarajan Padmavathy and Rajagopalan Vijaya-Raghavan, 2008. Enhanced bioactivity of ZnO nanoparticles-an antimicrobial study. Sci. Technol. Adv. Matter., 9: 035004-035010.
10. Tam, K.H., A.B. Djurisic, C.M.N. Chan, Y.Y. Xi, C.W. Tse, Y.H. Leung, W.K. Chan, F.C.C. Leung and D.W.T. Au, 2008. Antibacterialactivity of ZnO nanorods prepared by a hydrothermal method. Thin solid films, 516: 6167-6174.