International Journal of Engineering, Science and Mathematics
Vol. 6 Issue 5, September 2017,
ISSN: 2320-0294 Impact Factor: 6.765
Journal Homepage: http://www.ijesm.co.in, Email: ijesmj@gmail.com Double-Blind
Peer Reviewed Refereed Open Access International Journal - Included in the International Serial Directories Indexed & Listed at: Ulrich's Periodicals Directory ©, U.S.A., Open J-Gage as well as in Cabell's Directories of Publishing Opportunities, U.S.A

Green synthesis, Characterization and Cyclic voltammetric studies of nano Zinc oxide

Dr.Chithra P G[1] & Dr.Vijayalekshmi V[2] S N College for Women Kollam.

Abstract- The present study focus on the green chemistry in the synthesis of Zinc Oxide nanoparticles by Zinc nitrate and Allium sativum extract. The Zinc Oxide nanoparticles are known to be one of the multifunctional inorganic nanoparticles and Zinc Oxide crystallites have been synthesized by simple ecofriendly method. Nanoparticles produced by plants are more stable, and the rate of synthesis is faster than that in the case of other organisms.The particle size and morphology of the synthesized nanoparticles is characterized by using X-ray Diffraction(XRD), Scanning Electron Microscope(SEM), Transmission electron microscopy (TEM) and UV-Vis Spectrophotometry. The XRD analysis shows that the synthesized nanoparticles have been indexed as hexagonal system with primitive lattice.

Keywords: Zinc oxide nanoparticles, Green synthesis, X-ray Diffraction, Scanning Electron microscopy

Introduction

Nanotechnology is one of the rapidly growing field with its application in science and technology for manufacturing new materials at the nano scale level (MA. Albrecht et al, 2006)[1]. Nano materials are called "a wonder of modern medicine". (Sangeetha gunalan et al, 2012)[2]. The interaction of Nanoparticles with biological materials established a series of nanoparticle / biological interfaces that depend on colloidal forces as well as dynamic biophysicochemical interactions. These interactions lead to the formation of new nanomaterial with control size shape,surface chemistry, roughness and surface coatings (Nel et al 2009). The use of plants for the synthesis of nanoparticles is a novel method and it provides a cost-effective and environment friendly alternative to chemical and physical synthesis.

Metal oxides play an important role in many areas of chemistry, physics and materials science [3]. The metal elements are able to form a large diversity of oxide compounds [4]. These can adopt a vast number of structural geometries with electronic structures that can exhibit metallic, semiconductor or insulator character. In technological applications, oxides are used in the fabrication of sensors, fuel cells and as catalysts. In the emerging field of nanotechnology, our goal is to make nano structures with special properties with respect to those of bulk [5].

The present study deals with the synthesis of ZnO nanoparticles via Green method. Nanomaterials have attracted interest for their novel optical properties, which differ remarkably from bulk materials. In the present study, we report the synthesis and characterization of ZnO nanoparticles using Allium sativum (garlic), Allium cepa var. aggregatum (shallot) and both respectively. The morphology, structure and stability of the synthesized nanoparticles were studied using Scanning electron microscope(SEM),Tunneling electron microscope(TEM), UV-Vis spectrophotometer, Fourier transform infrared spectroscopy(FT-IR), XRD and its electrochemical studies by Cyclic voltammetry.

Experimental

Materials

The zinc nitrate used for the synthesis of ZnO nanoparticles were of A R grade and used without further purification and the solution was made up with distilled water.

Synthesis

For the synthesis of nanoparticles the Allium sativum, Allium cepa, mixture of Allium sativum and Allium cepa extract was taken in a 250 ml glass beaker along with 4 g of zinc nitrate and the solution was stirred at 70-80℃ using a magnetic stirrer heater for 2 hours until it is reduced to a deep yellow coloured paste. This paste was then collected in a ceramic crucible and heated in a muffle furnace at 400℃ for 2 hours. A light yellow colored powder was obtained and this was carefully collected and packed for characterization purposes. The material was mashed in a mortar-pestle so as to get a finer powder for characterization.

To identify the crystal phase and crystallite sizes of the synthesized nanocrystals X-ray diffraction (XRD) studies were carried out using Shimadzu**,** XRD-6000 diffractometer at room temperature. The morphology was analyzed using scanning electron microscope.

Electrochemical measurements of Cyclic voltammetric studies were conducted using CHI 604D electrochemical workstation with conventional three electrode cell at room temperature. Modified Zinc oxide-glassy carbon electrode or GCE for comparison, was employed as the working electrode. A silver/silver chloride (Ag/AgCl) electrode acted as the reference electrode and a platinum wire as the counter electrode. The supporting electrolyte was 0.1 M KCl. Potassium ferrocyanide was the analyte used.

Result and Discussion

Fig.I: XRD image of ZnO.g NPs

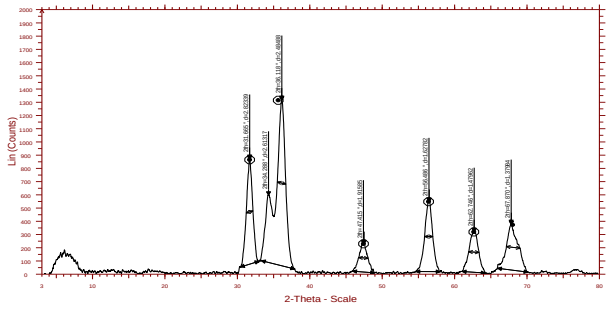


Fig.II: XRD image of ZnO.g+o NPs

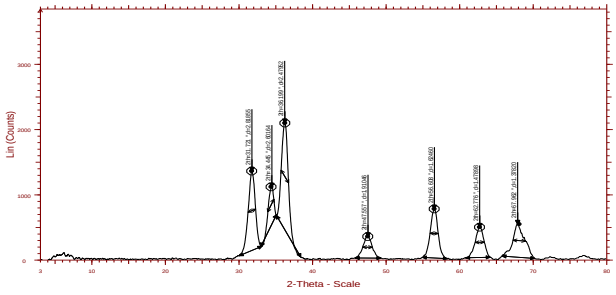


Fig.III: XRD image of ZnO.o NPs

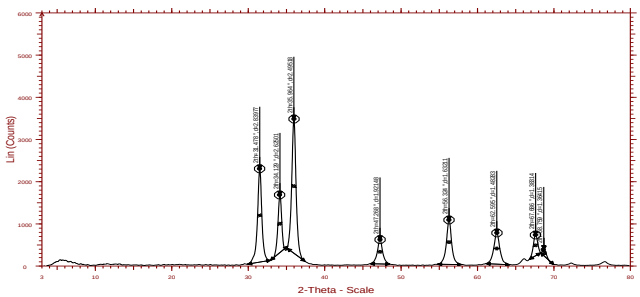
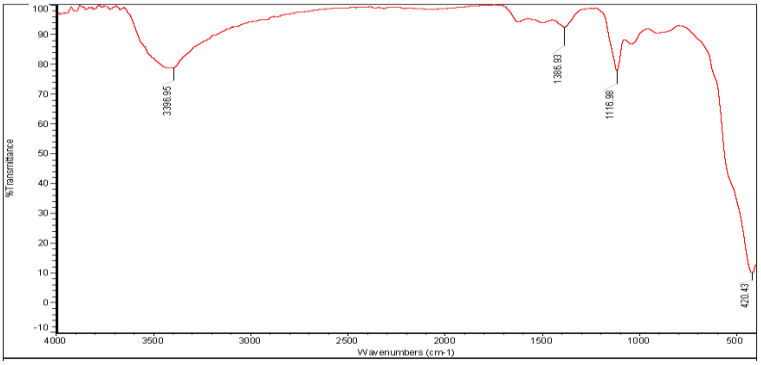


Figure I, II and III represents the X-ray diffraction patterns of ZnO nanopowder in *Allium sativum*, mixture of *Allium sativum and Allium cepa and Allium cepa*. A definite line broadening of the XRD peaks indicates that the prepared material consist of particles in nanoscale range. The diffraction peaks of sample I located at 31.7°, 36.1°, 47.5°, 56.5°, 62.7°, and 67.8° has been keenly indexed as hexagonal system with primitive lattice of ZnO with lattice constants a=3.253 nm and c=5.213 nm (JCPDS card number: 89-1397) and further it also confirms that the synthesized nanopowder was free of impurities as it does not contain any characteristic XRD peaks other than ZnO peaks. The samples II and III have also been indexed as hexagonal system with primitive lattice.

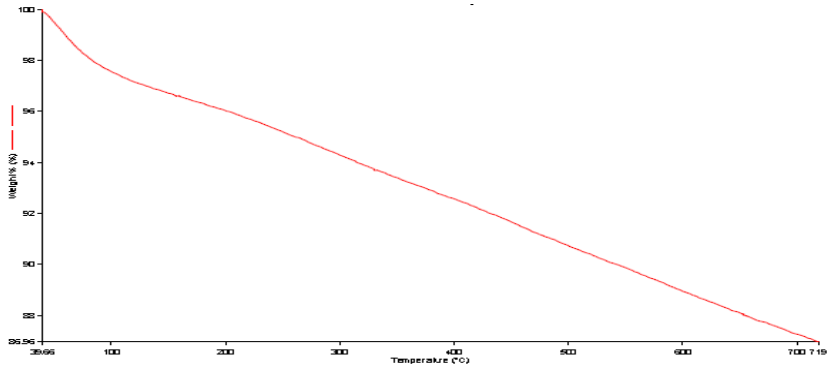
The synthesized ZnO nanoparticle's diameter was calculated using Debye-Scherer formula d=0.89$\lambda/\beta\cos\theta$, where 0.89 is Scherer's constant, λ is the wavelength of X-rays, θ is the Bragg diffraction angle, and β is the full width at half-maximum (FWHM) of the diffraction peak corresponding to plane(101). The average particle size of the samples were found to be 7.011 nm, 7.649 nm and 13.925nm which is derived from the FWHM of intense peaks corresponding to 101, 100,102,110,103 and 112 plane located at 36.1°, 31.7^0, 47.5^o, 56.5^o, 62.7^o and 67.8^o using Scherer's formula. Since the particle size of sample I (ZnO.g) is smaller we select that sample for further characterization.

Fig.IV: FT-IR spectrum of ZnO.g NPs



The band centered at 3360 cm^{-1} corresponds to O-H stretching and bending frequencies of water, indicating the existence of water occluded in the surface of nano particles. The band at 1386 cm^{-1} can be attributed to the presence of carbonaceous material. The band at 420 cm^{-1} is assigned to the stretching vibrations of Zn-O. The stretching frequency of bulk ZnO is 424 cm^{-1}. The peak at 1116 cm^{-1} may be due to CO stretching or CH bending vibrations of Allium sativum extract.

Fig.V: TGA spectrum of ZnO.g NPs



TGA/DTA transition shows a loss of 8 % up to 430^0 C [Fig.V]. 14% weight loss is observed up to 700^0 C. It simply indicates that ZnO is stable above 430^0 C also.

Fig.VI: SEM image of ZnO.g NPs

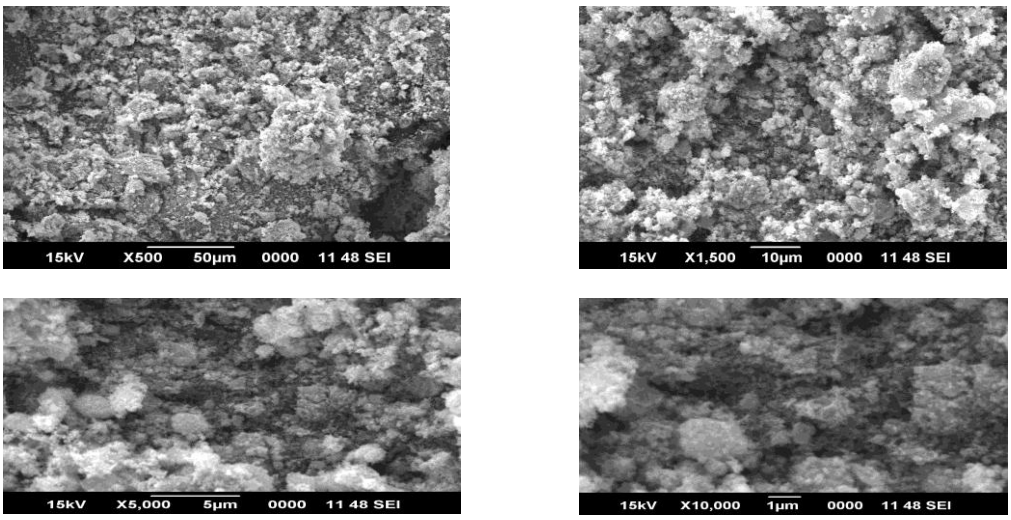
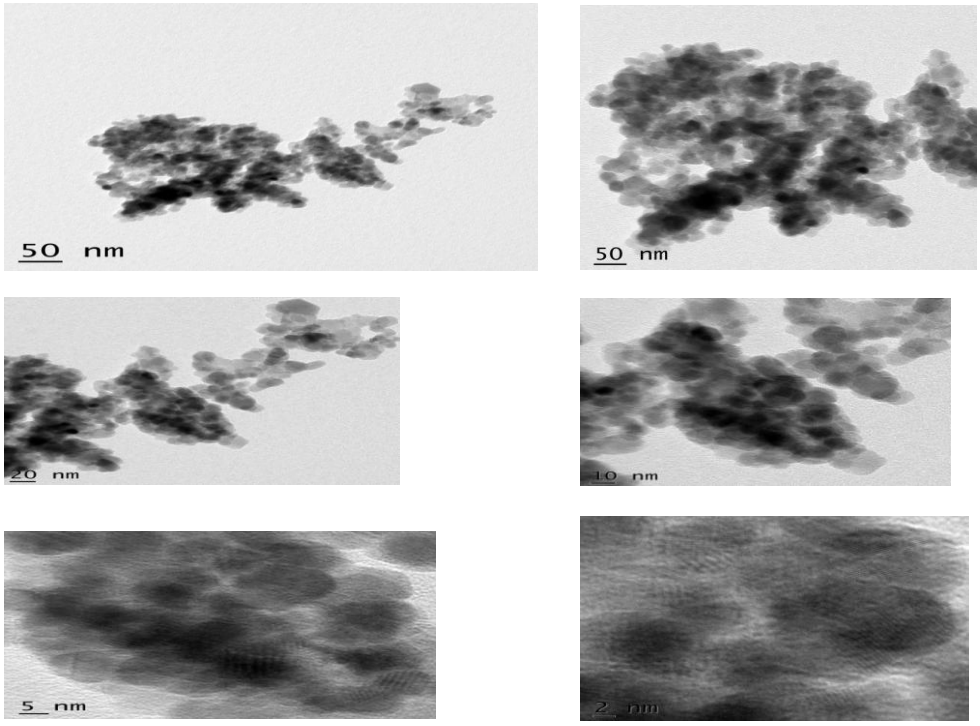
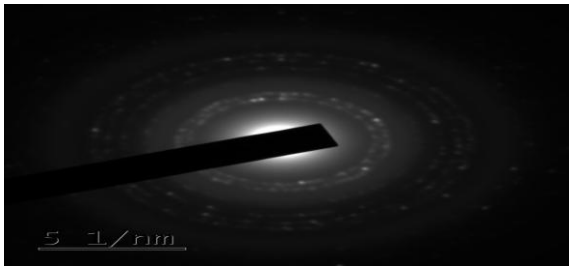


Fig.VI represents the SEM images of the sample under high and low resolution. The surface morphology indicates that nano Zinc oxide exist as clusters. The irregular shape of nanoparticles form a porous surface.

Fig.VII: TEM images of ZnO.g NPs



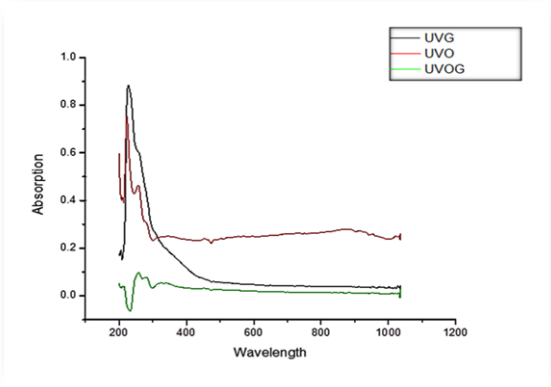
SAED Image



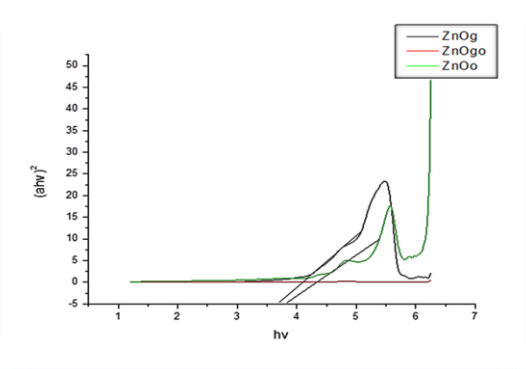
The Zinc oxide nanoparticles obtained through the green synthesis are shown in fig VII as transmission electron microscopy micrographs. TEM analysis was carried out to confirm the actual size of the particles, their growth pattern and the distribution of crystallites. The low resolution TEM micrograph exhibits spherical nanoparticles with diameters of 2-10 nm in size. In our previous study, X-ray powder diffraction was done to obtain the particle size of the prepared metal oxides. The average particle size is 7.011 nm. The particle size calculated from TEM measurement was in good agreement with the particle size calculated from the Debye-Scherrer formula.

The selected area electron diffraction (SAED) pattern in Figure VII shows distinct bright rings which confirm the preferential orientation of nanocrystals instead of irregular. The narrow ring of SAED pattern confirm the nanocrystalline nature of the sample.

Fig.VIII: UV-Vis spectra of NPs



Tauc Plot



UV-Vis absorption spectroscopy is widely being used to examine the optical properties of nano sized particles. The spectra was recorded in the wavelength range 200-1000 nm. The absorption spectra for ZnO.g and ZnO.o exhibit sharp excitonic absorption bands at 229.78 nm and 225.89 nm due to ZnO nanoparticle formation. Sharp absorption of ZnO indicates the mono dispersed nature of the nanoparticle distribution.

Optical energy gap is obtained by extrapolating the linear portion of the absorption spectrum to αhv =0. The energy band gap for ZnO in different mediums are calculated as 3.7 ev and 3.8 ev respectively. Here the band gap is found to be greater than bulk material due to the more quantum confinement and small size. The quantum confinement effect is expected for semiconductor nanoparticles and the absorption edge will be shifted to high energy with decrease in particle size. This is one of the wide band gap material. Wide band gap materials are often utilized in applications in which high temperature operation is important.

Fig.IXa: CV OF ZnO.o, ZnO.g+o and ZnO.g NPs in 1M $K_4Fe(CN)_6$ at a scan rate of 0.05 V/sec

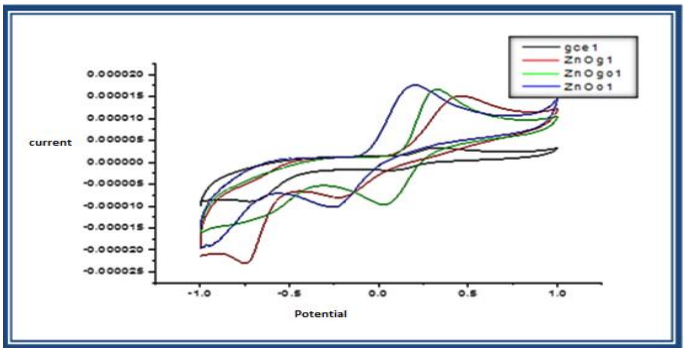


Fig.IXb: CV of ZnO.o NPs in 0.1M, 0.2M, 0.3M and 0.4M $K_4Fe(CN)_6$ at a scan rate of 0.05V/sec

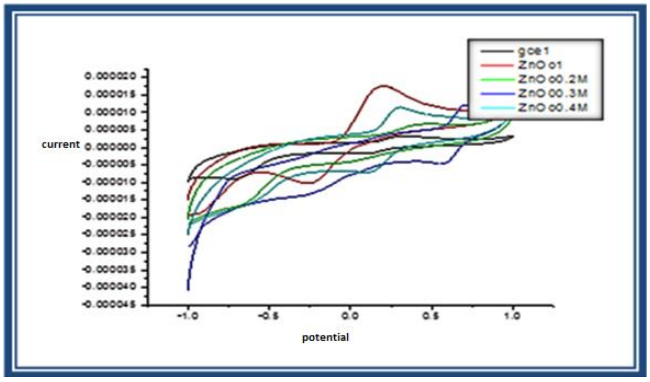
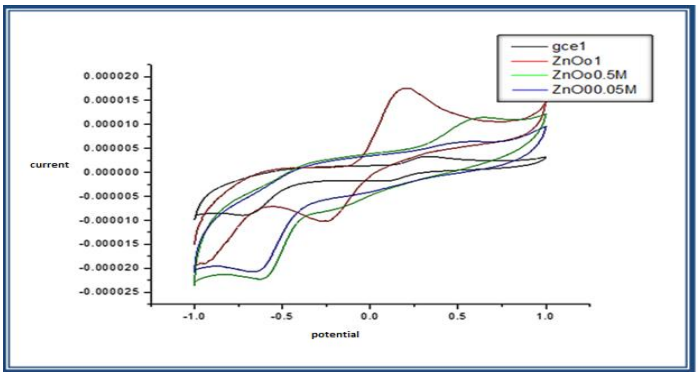


Fig.IXc: CV of ZnO.o NPs in 0.5M and 0.05M $K_4Fe(CN)_6$

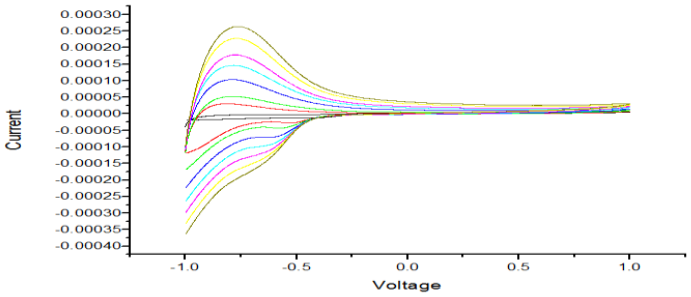


Cyclic voltammetry is one of the most versatile electroanalytical techniques for the study of redox behavior of electroactive species. Electrochemical measurements of Cyclic voltammetric studies were conducted using a CHI 604D electrochemical workstation with conventional three electrode cell at room temperature. Modified Zinc oxide-glassy carbon electrode or GCE for comparison, was employed as the working electrode. A silver/silver chloride (Ag/AgCl) electrode acted as the reference electrode and a platinum wire as the counter electrode. The supporting electrolyte was 0.1 M KCl. Potassium ferrocyanide was the analyte used.

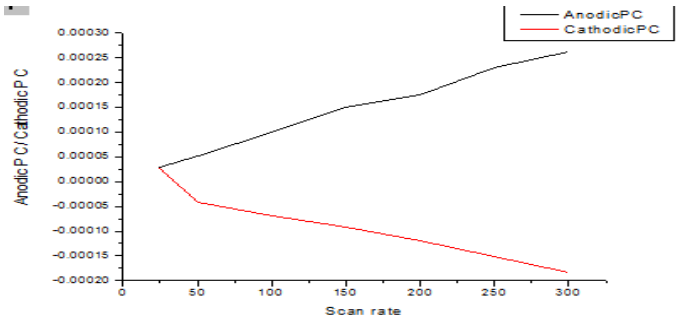
To investigate the electrochemical performance of zinc oxide modified glassy carbon electrode, cyclic voltammetry (CV) was employed over a potential range from +1 to -1 volt. Figure IXa shows CVs of bare glassy carbon electrode, ZnO.o, ZnO.g+o, ZnO.g at a potential scan rate of 0.05V/sec. Cyclic voltammetric behavior of ZnO.o showed one oxidation peak at 0.1972 V and one reduction peak at -0.2601 V. ZnO.g+o showed one oxidation peak at 0.3187V and one reduction peak at 0.03811V. ZnO.g showed one oxidation peak at 0.4490V and one reduction peak at -0.2325V. The CV loops result due to the reaction between ZnO and electrolyte, which is mainly

governed by the intercalation and deintercalation of K^+ from electrolyte into ZnO. The shape of the CV loop of the sample indicate that good charge propagation takes place at the electrode surface. GCEs modified by ZnO were found to perform better in comparison to bare GCE. This suggest that the presence of ZnO could improve the relative electron transfer. All prepared nanomaterials show enhanced peak current than the bare GCE which indicated that the modified electrode can be further used in the application of electrochemical sensors. On increasing the concentration of analyte there is enhancement in peak current in almost all cases.

Figure.Xa: Cyclic voltammetric studies of ZnO.g at differtent scan rates

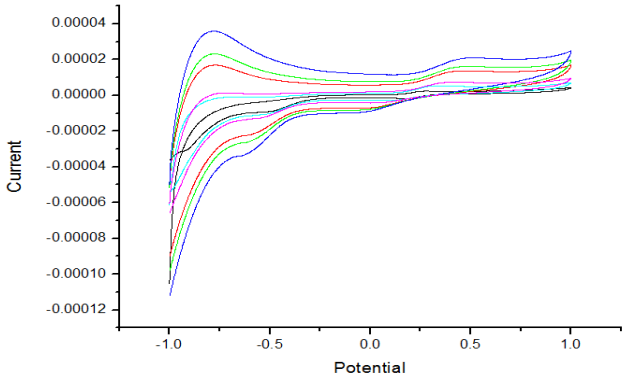


Scan rates used were 25mv, 50mv, 100mv, 150mv, 200mv, 250mv and 300mv

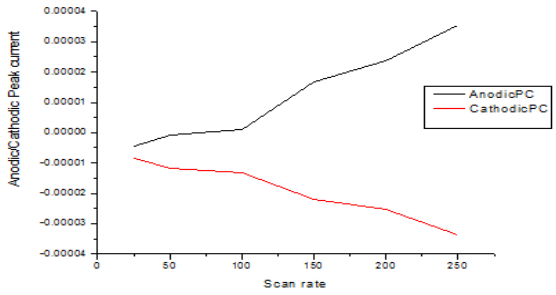


Anodic / Cathodic Peak current at different scan rates in case of ZnO.g NP

Figure.Xb: Cyclic voltammetric studies of ZnO.o at differtent scan rates

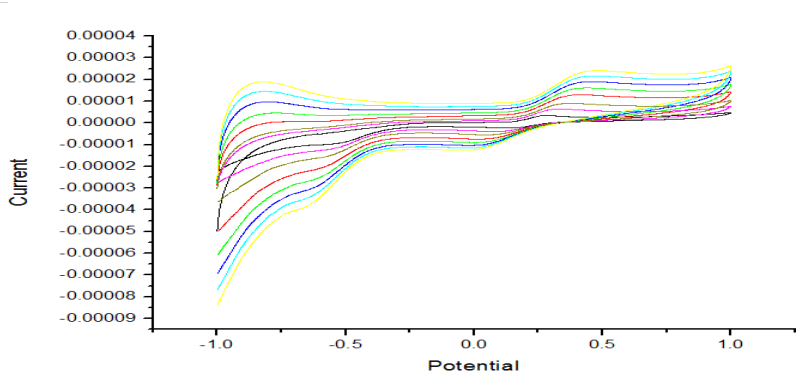


Scan rates used were 25mv, 50mv, 100mv, 150mv, 200mv and 250 mv.

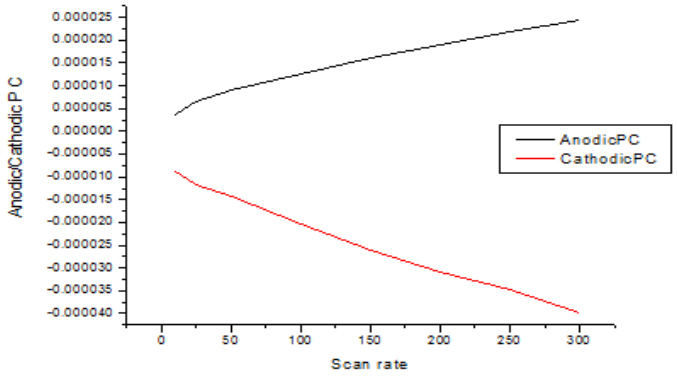


Anodic / Cathodic Peak current at different scan rates in case of ZnO.o NP

Figure.Xc: Cyclic voltammetric studies of ZnO.g+o at differtent scan rates



Scan rates used were 10mv, 25mv, 50mv, 100mv, 150mv, 200mv, 250mv and 300mv



Anodic / Cathodic Peak current at different scan rates in case of ZnO.g+o NP

Figure. X represents the Cyclic Voltammograms at different scan rates between-1.0 to +1.0V. In this case the anodic peak current increases with increasing scan rate but peak potential remains almost constant. In ZnO.g NP the anodic peak current is linearly proportional to scan rate from 25mv to 150mv. The Cathodic peak current is proportional to scan rate from 50mv to 300mv. In ZnO.o NP both the anodic and cathodic peak current is linearly proportional to scan rate from 100 to 150 mv. In ZnO g+o the anodic and cathodic peak current is linearly proportional to scan rate from 50 to 300 mv. The ratio of Anodic to Cathodic peak current remains almost unity. In this case a redox potential shift is observed with an increment in scan rate, implying the redox potential to be diffusion controlled. So the rate of reaction is determined by the diffusion of analyte to the surface of electrode.

CONCLUSION

Nano ZnO is synthesized by Green method. The metal oxide nanoparticle is characterized by XRD, UV, SEM, TEM and Cyclic Voltammetry. A definite line broadening of the XRD peaks indicate that the prepared material consist of particles in nanoscale range. The band gap is found to be greater than bulk material due to the more quantum confinement and small size. This is one of the wide band gap material. Wide band gap materials are often utilized in applications in which high temperature operation is important.

The surface morphology indicate that nano Zinc oxide exist as clusters. The irregular shape of nanoparticles form a porous surface. The particle size calculated from TEM measurement was in good agreement with the particle size calculated from the Debye-Scherrer formula.

The selected area electron diffraction (SAED) pattern in Figure IV shows distinct bright rings which confirm the preferential orientation of nanocrystals instead of irregular. The narrow ring of SAED pattern confirm the nanocrystalline nature of the sample.

From cyclic voltammetric studies the metal oxide nanoparticles exhibited good electrocatalytic activity and the rate of reaction is determined by the diffusion of analyte to the surface of electrode are diffusion controlled. From this investigation the metal oxide can be used as a potential, electrode material for further electronic applications.

References

[1] MA Albrecht, CW Evan, CL Raston, (2006), Green chemistry and the health implications of nanoparticles. Green chemistry, Vol.3, No.8, pp.417-432.
[2] Sangeetha Gunalan, Sivaraj Rajeswari, Rajendran Venckatesh (2012), Green synthesized ZnO nanoparticles against bacterial and fungal pathogens. Progress in Natural science: Materials International.2012;22(6): 693-700
[3] C.Noguera, *Physics and Chemistry at Oxide Surfaces*; Cambridge University Press:Cambridge, UK, (1996).