Available online at www.sciencedirect.com

ScienceDirect

Materials Today: Proceedings 4 (2017) 660–667

materialstoday: PROCEEDINGS

www.materialstoday.com/proceedings

5th International Conference of Materials Processing and Characterization (ICMPC 2016)

Green Synthesis of Zinc Oxide Nanoparticle Using Green Tea Leaf Extract for Supercapacitor Application

[a]A. Clara Dhanemozhi, [b]V. Rajeswari , ,[c]S. Sathyajothi

[a]*Associate professor, Jayaraj Annapackiam College for Women, Periyakulam, Tamilnadu*

[b]*Assistant professor, Thiravium college of Arts and Science, Periyakulam*

[c]*Assstant professor, Jayaraj Annapackiam College for Women, Periyakulam, Tamilnadu.*

Abstract

The advancement of green chemistry in the synthesis of nanoparticles with the use of plants and its parts has become a great attention today. The nanoparticles of metals and metal oxides with green synthesis have reputation on recent developments. Products from nature or that resultant from natural products, such as extracts of various parts of plants have been used as reductions and as ceiling agents during synthesis. In our work, we have chosen green tea leaves(*Camellia sinensis*) for the Green synthesis of Zinc oxide nanoparticles (ZnO Nps). The formation of nanoparticles was observed by visualizing color changes and it was confirmed by Scanning Electron Microscope (SEM), UV-Vis spectrophotometer and Fourier Transform Infra-Red (FT-IR) spectrophotometer. The results of various techniques confirmed the presence of Zinc oxide nanoparticles. The UV-Vis spectrum was recorded to observe the absorption spectra, which exhibited a blue shift absorption peak at 338 nm. The XRD pattern revealed well-defined peaks appearing at 2θ positions corresponding to the hexagonal wurtzite structure of ZnO nanoparticles. The average size of the nanoparticles calculated using XRD data was 54.84 nm, the band gap energy was 3.40eV. FT-IR spectra were recorded for the as prepared nanoparticle to identify the biomolecules involved in the synthesis process. The higher percentage of phenolic compounds, with antioxidant potential, acts as the reducing agent on the metal oxides and significantly present amino acid, protein and lipids helped to control the growth of the nanoparticles. CV study shows an excellent capacitance behaviour, low equivalent series resistance (ESR) and fast diffusion of electrolyte ions into the composite. This confirms that the as-prepared ZnO material is the best suitable material for supercapacitor applications.

Selection and peer-review under responsibility of Conference Committee Members of 5th International Conference of Materials Processing and Characterization (ICMPC 2016).

Keywords: Nanoparticles;Green tea;zinc oxide; conductivity

E-mail address: jdhanemozhi@gmail.com

2214-7853 ©2017 Elsevier Ltd. All rights reserved.
Selection and peer-review under responsibility of Conference Committee Members of 5th International Conference of Materials Processing and Characterization (ICMPC 2016).

1. INTRODUCTION:

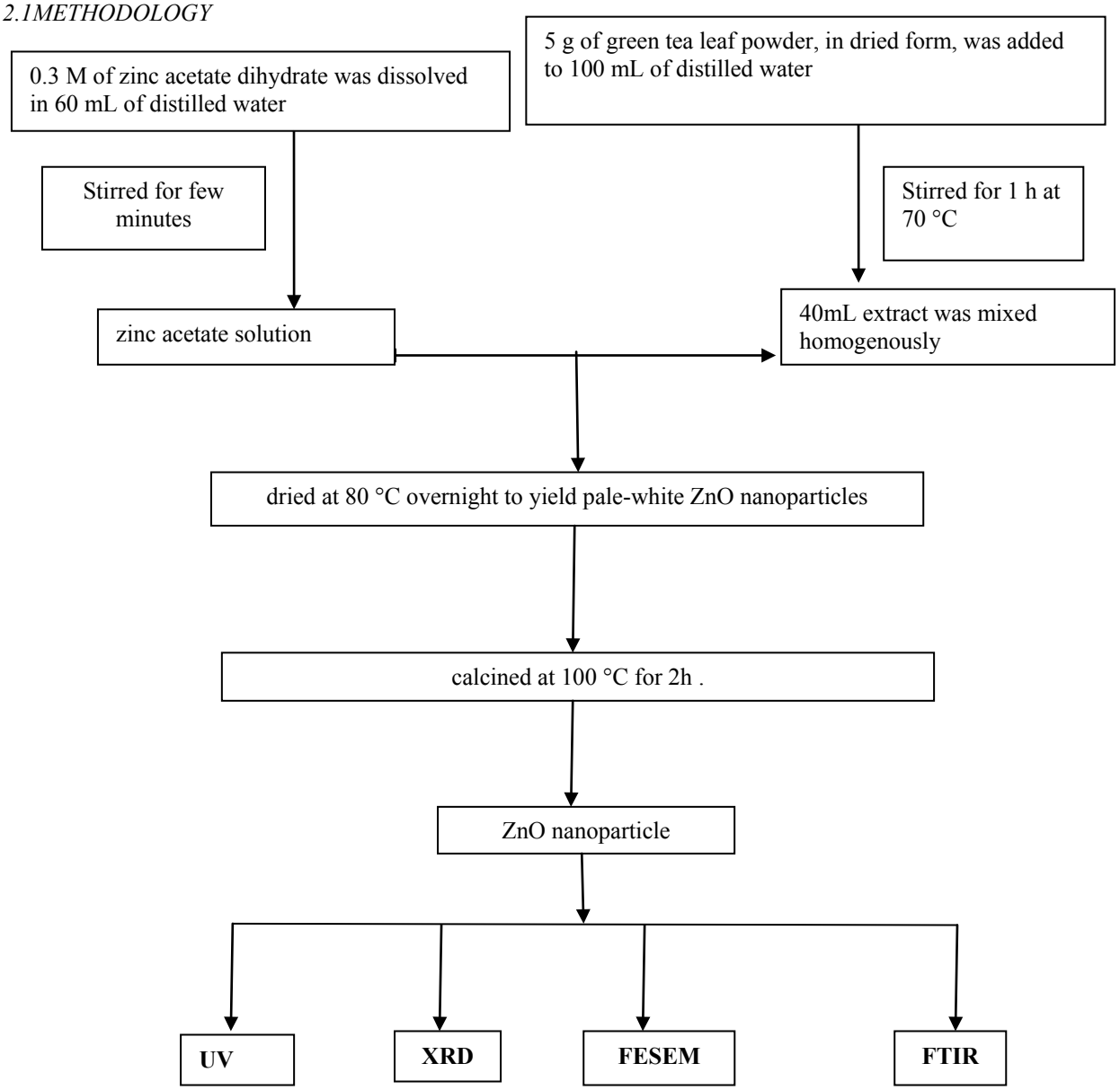
The study of nanomaterials is one of the most and fast developing area in the field of material science. Nanomaterials, controlled to nano crystalline size (less than 100 nm), can show atom-like behaviors which result from higher surface energy due to their large surface area and wider band gap between valence and conduction band when they are divided to near atomic size [1]. Transition metal oxides with nanostructure and semiconductors with dimensions in the nanometer empire have attracted considerable interest in many areas of chemistry, physics, material science, biotechnology, information technology and environmental technology as next generation technologies [2–4]. In recent years, zinc oxide (ZnO), is an important semiconductor with tremendous scientific and technological interest, and increasing awareness towards green chemistry and other biological processes. This led to the development of an eco-friendly approach for the synthesis of nanoparticles. Green synthesis techniques make use of natural products to synthesis nanomaterials. Green synthesis seeks to reduce pollution at source[5-6]. ZnO has proved to be a boon for material and medical science as it has got a combination of unique properties like UV absorption, deodorizing, antimicrobial, antifungal, anticancer and antiviral properties and steady thermal and optical properties causing no threat to the environment. Thus it has got a wide range of applications. Green synthesis of ZnO nanoparticles were agreed out using green tea leaf extract for the eco-friendly development of novel technologies. We have used an eco-friendly method for the synthesis of zinc oxide nanoparticles using aqueous leaf extract of green tea with zinc acetate dihydrate as precursor. ZnO nanoparticles as prepared can have tremendous applications in biomolecular detection, diagnostics, and micro electronics.

Green tea reduces cholesterol and hence preventing cardiovascular disease. Green tea has been the focus of exciting new studies indicating its effectiveness in raising metabolism for weight loss and preventing from cancerous cells and other diseases with its rich content of super antioxidants. It has a long list of potential health benefits and is used to regulate blood sugar and blood pressure, boost the immune system, prevent ulcers, control inflammation, viral colds and flu, prevents gum disease, cavities, and bad breath. Green synthesis procedures have several merits such as, simple, inexpensive, good stability of nanoparticles, less time consumption, non-toxic byproducts and large-scale synthesis. Fresh tea leaf is rich in the flavonol group of polyphenols known as catechins (approximately 30% of the dry leaf weight). Other polyphenols present are flavonoids and their glycosides, chlorogenic acid, gallic acid, coumarylquinic acid and theogallin. Green tea is usually prepared without fermentation so as to prevent the oxidation of green leaf polyphenols. Green tea chemical composition is very similar to that of fresh leaf except for a few enzymatically catalyzed changes which occur with extreme rapidity following plucking. Some new volatile substances are produced during drying. The commonly measured approximate compositions of green tea leaf are: i) phenolic compounds (30%), ii) proteins (15%), iii) amino acids (4%), iv) carbohydrates (7%), v) lipids (7%) and vi) vitamins C and E[7,8]. Phenolic compounds exhibit higher antioxidant potential and antioxidants, which are very good reducers of metal ions, thus supporting the green synthesis of nanoparticles. Further higher contents of proteins, lipids and amino acids help to stabilize the growth of nanoparticles and inhibit particle agglomeration. The present work was aimed at the synthesis of ZnO nanoparticles in the green synthesis process with green tea leaves and to evaluate their capacitance behavior for supercapacitor applications.

2. MATERIALS AND METHODS

Zinc acetate dihydrate with 98.9% purity purchased from Sigma-Aldrich chemicals were used as the precursors. 0.3 M of zinc acetate dihydrate was dissolved in 60 mL of distilled water and stirred for few minutes with stirrer. Fresh leaves of green tea were washed thoroughly with double distilled water, dried and grinded to powder. 5 g of green tea leaf powder was added to 100 mL of distilled water and magnetically stirred for 1 h at 70°C. After cooling to room temperature and filtered through Whatman No. 1 filter paper, 40 mL of this green tea extract was mixed homogenously with the already prepared zinc acetate solution. The reacted solution was dried at 80°C overnight to yield pale-white ZnO nanoparticles, which were finally calcined at 100°C for 2h and preserved for further studies.

2.1METHODOLOGY



3. RESULTS AND DISCUSSION

3.1 XRD studies

Fig.1 shows the XRD spectra of the calcined ZnO nanoparticles at 100°C.. The prominent peaks corresponding to the diffraction planes (100), (002), (101), (102) agree well with the JCPDS Card No. 36-1451, confirming the hexagonal wurtzite structure of the ZnO nanoparticles. The intensity of the peak is very high for 2θ angle value of 33°.The average particle size (D) of synthesized nanoparticles was calculated using the Debye-Scherrer formula

$$D = 0.9\,\lambda / \beta \cos\theta \quad \text{---------- (1)}$$

where λ is the wavelength of X-ray source (CuK_{α} line – 0.1541 nm), β is the full width at half maximum (FWHM) in radians and θ is Bragg's diffraction angle. The calculated value of D was found to be 54.84 nm.

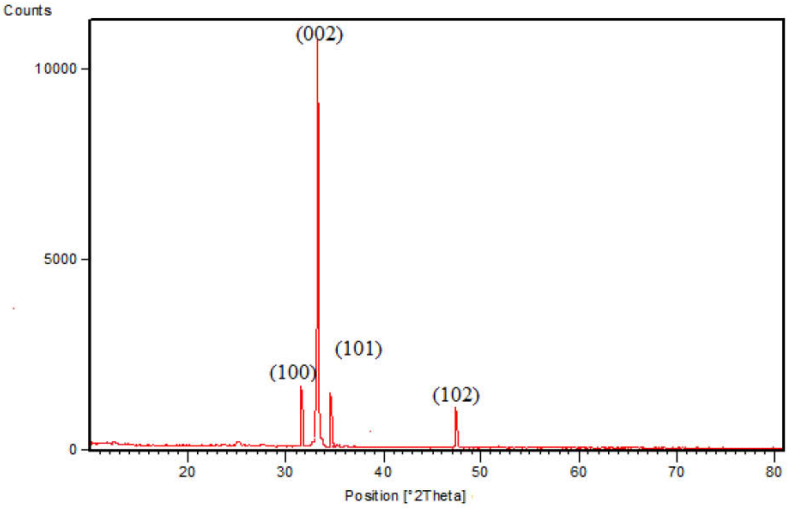


Fig.1. XRD pattern of ZnO Nanoparticles

3.2 Scanning Electron Microscope (SEM) studies

The surface morphology was observed by the field emission scanning electron microscope (FESEM). Fig.2 shows the SEM images of the as synthesized zinc oxide nanoparticle. It is seen that when the calcination temperature is increased further, better surface morphology could be detected.

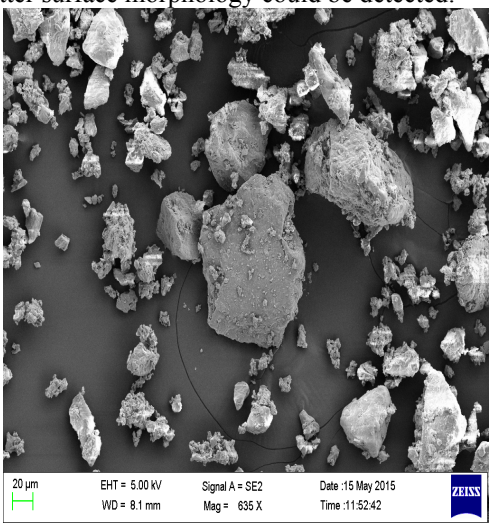


Fig.2. SEM image of ZnO Nanoparticles

3.3 UV-Vis spectrum studies

Electromagnetic radiation such as visible light is commonly treated as a wave phenomenon, characterized by a wavelength or frequency. Fig.3 shows the UV-Vis spectrum of the as synthesized nanoparticle and from the graph, it is seen that the absorption maximum occurred at 338nm. It indicates that it shifts towards the blue line of the spectrum.

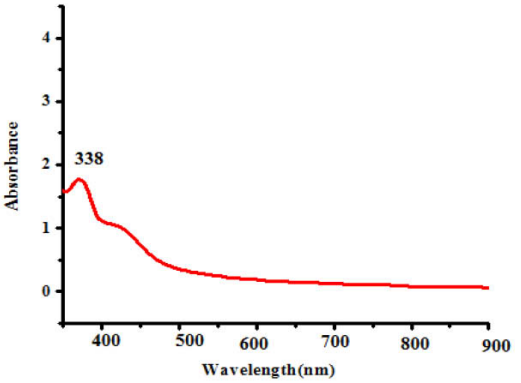


Fig.3. UV pattern of ZnO Nanoparticles

3.4 Band gap

Energy band gap is calculated using Tauc's plot. Tauc's equation is given by

$$\alpha h\nu = A(h\nu - Eg)^{n} \quad \text{——————————} \quad (2)$$

Where α is the absorption coefficient, $h\nu$ is the photon energy, A is theconstant, Eg is the energy bandgap. The value of n is 1/2 or 2 depending upon whether the transition from valence band to conduction band is direct or indirect. The value is 1/2 in case of direct transition and 2in case of indirect transition. Since ZnO is a has a direct band structure, the value of n is 1/2. So, the equation takes the form

$$(\alpha h\nu)^2 = B(h\nu - Eg) \quad \text{——————————} \quad (3)$$

where, B is a constant related to effective masses of charge carriers associated with valence and conduction bands. Intersection of the slope of $(\alpha h\nu)^2$ vs hν curve provides bandgap energy of the samples. According to the experimentally calculated bandgap, the synthesized ZnO nanoparticles should absorb light below 383 nm and absorbance graph is in good agreement with this. The optical direct band gap calculated is 3.40 eV.

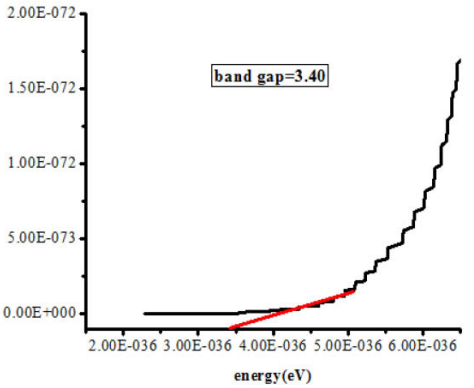


Fig.4 $(\alpha h\nu)^2$ vs hν curve

3.5 FT-IR analysis

FT-IR spectroscopy study was done for the as prepared nanomaterial. The analysis of the IR spectrum involves the relationship of the absorption bands (vibrational bands) with the chemical compounds in the sample. the biomolecules present in plant extracts that are responsible for the reduction and stabilization processes of the green synthesis of nanoparticles can be identified with this study. The FT-IR spectrum of the synthesized ZnO NPs are shown in Fig(5).

in the IR spectrum of ZnO NPs, the absorption bands occur at 3450.65 cm^{-1}, 1556.55 cm^{-1},1429.25 cm^{-1} and at 1072.42 cm^{-1}. The occurrence of band at 3450.65 cm^{-1} is due to stretching vibrations of O–H groups in water, alcohol and phenols and N–H stretching in amines. The strong band at 1556.55 cm^{-1} is due to the C=C stretch in aromatic ring and C=O stretch in polyphenols. The C–N stretch of amide-I in protein gives the band at 1429.25 cm^{-1}. The C–O stretching in amino acid causes a band at 1072.42 cm^{-1}. The involvements of these biomolecules in the reduction and stabilization actions are clearly identified from the IR spectrum of the synthesized ZnO NPs. The additional two peaks appearing at 613.36 and 459 cm^{-1} in the IR spectrum of the ZnO NPs are the characteristic peaks of ZnO molecules. It is found that the presence of higher percentage of phenolic group of molecules is responsible for the reduction process and the amino acids and amide linkages in protein are responsible for the stabilization of the ZnO nanoparticles.

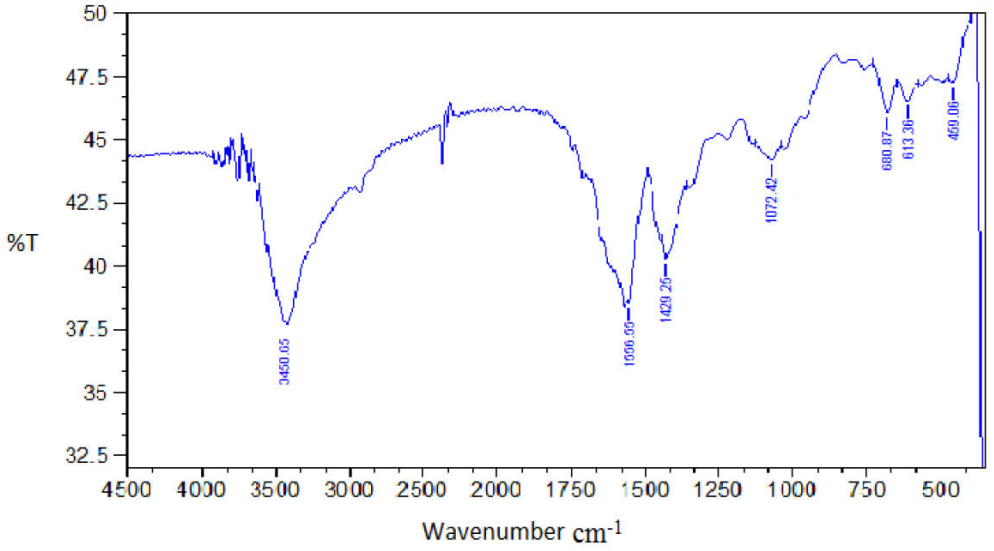


Fig.5 FTIR pattern of as-synthesised ZnO nanoparticles.

3.6 ELECTROCHEMICAL PROPERTIES FOR SUPERCAPACITOR APPLICATIONS

Electrochemical properties of the electro-active material were tested by cyclic volttametry (CV), and electrochemical impedance spectroscopy (EIS).

3.7 CYCLIC VOLTAMETERY

The electrochemical properties of as-prepared Zinc oxide, were investigated by Cyclic Voltammetery. It is worth nothing that the introduction of zinc oxide would enhance the specific capacitance and electrochemical stability of metal oxides in many reports. In our method of CV described by the different sweep rate of ZnO, Fig. (6) shows the CV curves over a voltage ranging from 0.0 to 0.6V vs. Ag/AgCl for ZnO at a scan rate of 100 mV/s, and observed as the potential scan rate is increased. CV curve is quasi-rectangular in a shape along the current-potential axis without obvious redox peaks, that all the samples have ideal capacitive behavior with the scan rate from 5mV/S to 100 mV/s.The Faradic peak of ZnO has nearly a symmetric profile and a small peak separation, indicating a good reversibility and a fast charge transfer process in the surface.

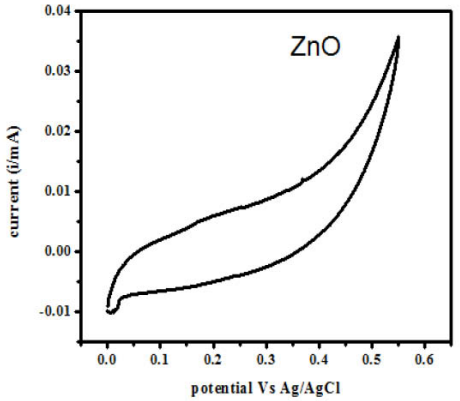


Figure 6 Cyclic voltammetery analysis of Zinc oxide (ZnO)

3.8 ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

Electrochemical impedance spectroscopy (ESI) analysis is the method for examining the fundamental behavior of electrode materials for supercapacitors. Fig.7 shows the electrochemical impedance spectrum of ZnO. The high–frequency is corresponding to the charge transfer limiting process and is ascribed to the pseudo–capacitance at the contact interface between electrode and electrolyte solution. The straight line in the low frequency range is related to the diffusive resistance (Warburg resistance) of the electrolyte into the interior of the electrode and ion diffusion/transport into the electrode surface. The equivalent series resistance (ESR) can be obtained from X-axis intercepts of the electrochemical impedance spectrum, which includes of including the resistance of KOH aqueous solution, the intrinsic resistance of the electro-active material and the contact resistance at the interface between the electrode and current collector. The ESR value of ZnO electrode materials is found to be 28.3 □.

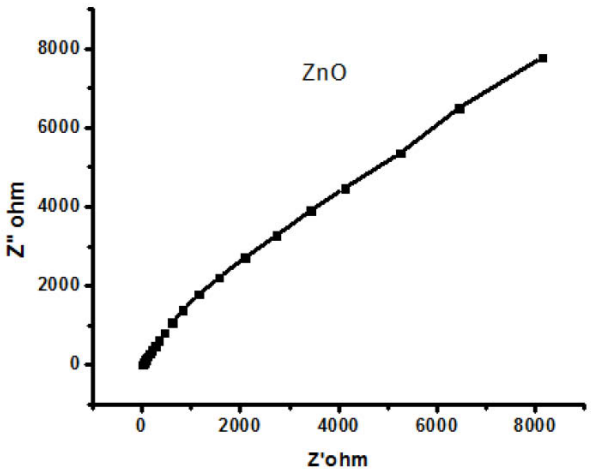


Fig. 7 Electrochemical impedance spectroscopy analysis of ZnO

4.CONCLUSION

ZnO nanoparticles were successfully synthesised by the green tea leaves extract assisted synthesis. The average size of the particles was 54 nm as obtained from XRD data. The band gap of ZnO is 3.40eV. The FT-IR studies clearly indicated that the presence of higher percentage of phenolic group of molecules present in the green

tea is responsible for the reduction process and the amino acids and amide linkages in protein are responsible for the stabilization of the ZnO nanoparticles. CV curve indicated an excellent capacitance behaviour, low equivalent series resistance (ESR) and hence fast diffusion of electrolyte ions into the composite. This confirms that the as-prepared ZnO materials are the best suitable material for supercapacitor applications.

References

[1]. A.V. Dijken, E.A. Meulenkamp, D. Vanmaekelbergh, A. Meijerink, J. Luminescence 90 (2000) 123.
[2]. Z.L.Z.L. Wang, Annu. Rev. Phys. Chem. 55 (2004) 159.
[3] Y.J. Kwon, K.H. Kim, C.S. Lim, K.B. Shim, J. Ceramic Proc. Res. 3 (3) (2002) 146.
[4]. P.M. Aneesh, K.A. Vanaja, M.K. Jayaraj, Proc. of SPIE, vol. 6639, 2007, p. 1.[5]. Tundo P. and Anastas P._. Eds, Green Chemistry: Challenging Perspectives. Oxford University Press, Oxford, UK, (2000)
[5]. Reed S.M. and Hutchison J.E., Green Chemistry in the organic teaching laboratory: an environmentally benign synthesis of adipic acid, J Chem Educ 77, 1627-1628 (2000)
[6]. Cabrera C, Artacho R, Giménez R. Beneficial effects of green tea--a review. Journal of the American College of Nutrition 2006;25(2):79-99.
[7]. Lin Y-S, Tsai Y-J, Tsay J-S, Lin J-K. Factors affecting the levels of tea polyphenols and caffeine in tea leaves. Journal of agricultural and food chemistry 2003;51(7):1864-73.
[8]. S.R.Senthilkumar, T.Sivakumar. Green Tea (Camellia Sinensis) Mediated Synthesis Of Zinc Oxide (Zno) Nanoparticles And Studies On Their Antimicrobial Activities.International Journal of Pharmacy and Pharmaceutical Sciences ISSN- 0975-1491 Vol 6, Issue 6, 2014.