Synthesis and Electrochemical Characterization of Nickel Oxide Nanoparticles Prepared Using Leavening Agent for Supercapacitor Application

A.Nirmalesh Naveen*, Subramanian Selladurai

Ionics lab, Department of Physics, Anna University, Chennai, Tamil Nadu, India 600025.
* email: nirmalesh.naveen@gmail.com

Abstract— **Using leavening agent porous nickel oxide of nanocrystallite was prepared as an electrode material for supercapacitor application. Sodium bicarbonate ($NaHCO_3$) is commonly used as a leavening agent to make breads and cakes spongy by the evolution of carbon dioxide. Here, the same principle was used to prepare nanoparticle of high porosity which is the most essential property for highly efficient electrode materials. Prepared materials were characterized using XRD, FTIR and SEM. Phase purity and high crystalline nature of prepared nickel oxide nanoparticle was revealed from X-ray study. Crystallite size of ca. 4 nm was calculated for the prepared material using Scherrer formula. FTIR study further confirms the formation of nickel oxide and provides details about the functional groups attached to the compound. FESEM images displays the porous nature and nearly spherical particles formed on the evolution of CO_2. Electrochemical features of the material were characterized using Cyclic Voltammetry (CV), Chronopotentiometry and Electrochemical impedance spectroscopy (EIS) in 1 M KOH electrolyte solution. Pseudocapacitive nature expected for metal oxide nanoparticles can be seen from the CV curve showing pair of redox peaks corresponding to $Ni^{2+} \leftrightarrow Ni^{3+}$ transition. High reversibility of the transition can be understood from the nearly symmetrical nature of the CV curve. Maximum capacitance of $342Fg^{-1}$ was observed for a scan rate of 5 mV/s within the potential window -0.15 – 0.55 V. Charge-discharge studies further confirms the pseudocapacitive nature observed and also from the CV studies. Low resistance offered by NiO electrode material was seen from the Nyquist plot.**

Keywords- Porosity; cyclic voltammetry; supercapcitors; Nyquist plot; pseudocapacitance

I. INTRODUCTION

In recent years, research on electrode materials for supercapcitor applications has gained greater pace. Supercapacitor or electrochemical capacitor is an electrochemical energy storage device superior to its conventional dielectric counter parts in many aspects [1-3]. While conventional dielectric capacitors can store energy at few 10's of farad per gram, supercapacitors can store 100 -1000's of farad per gram. They have higher energy density than ordinary capacitors and high power density than batteries. Owing to their fast charge/discharge characteristics, flexibility and long lifespan, they have attracted wide applications such as auxiliary power source in hybrid vehicles, portable mobile devices, ignition systems, micro-electronics, rockets etc. [4, 5]. Based on the type of charge, storage mechanism electrode materials for supercapcitors can be classified into two type's (i) carbonaceous materials that store energy by charge separation at the electrode-electrolyte interface and (ii) metal oxides and conducting polymers with multiple oxidation states that stores energy by faradaic redox process. Metal oxides dominate all these materials as a potential candidate for electrode material due to its large specific capacitance, long cycle life and better conductivity. RuO_2 and IrO_2 show ideal electrochemical performance in acid and basic electrolytes, but their applicability was hindered by cost effectiveness and toxicity of the materials. Other metal oxides were preferred over these noble metal oxides such as Co_3O_4 [6], NiO [7], MnO_2 [8], Fe_2O_3 [9] etc. Among this nickel oxide has attained great interest due to its ability for fast reversible oxidation/reduction reaction between its divalent (Ni^{2+}) and tetravalent state (Ni^{3+}). Previously, porous NiO had been prepared by several methods like electro-deposition [10], precipitation [11], hydrothermal [12], chemical bath deposition [13] etc. But they are not cost effective and involve longer time and multiple steps. Hierarchical porous materials, which contain interconnected macro/meso/micropores, have enhanced performance for catalysis, separation and energy storage due to the increased mass transport through macropores and mesopores and maintenance of a specific surface area on the level of micropore systems [14]. Hence it is essential to prepare highly porous nanomaterials in a cost effective and time saving manner.

Here we have developed a new chemical method to synthesis porous nickel oxide with very small crystallite size. Leavening effect commonly used by bakers to make breads and cakes porous and spongy was utilized here for the nanomaterial preparation. NiO nanomaterial prepared by this method has very small crystallite size, determined from XRD studies. FESEM images reveal the spherical nature of the particles with intermittent pores formed under the influence of the leavening agent. Electrochemical tests were carried to evaluate the electrodes performance.

II. EXPERIMENTAL

All the chemicals used were of analytical grade. Initially, 0.1 M of starch was added to 100 mL of deionized water and then kept under stirring at 60 ˚C. 0.1 M of nickel nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$) dissolved separately in deionized water was added to the starch solution slowly. To the above mixture, 0.5 M of sodium bicarbonate ($NaHCO_3$) or baking soda was added partially. Brisk effervescence was observed due to the release of tremendous amount of CO_2 during the reaction with sodium bicarbonate. Finally 0.5 M of sodium hydroxide (NaOH) was added to boost the hydrolysis by releasing OH^- ions. Remaining sodium bicarbonate was added in frequent time intervals. Carbon-dioxide evolution during the synthesis had hindered the crystallite growth and aided rapid nucleation growth of nickel hydroxides. Obtained green precipitate was washed repeatedly using de-ionized water, ethanol and acetone to remove all the unreacted components. Fine particles of NiO were obtained by calcining the sample at 300 ˚C for 3 h.

III. RESULTS & DISCUSSION

A. X-ray studies

X-ray diffraction (XRD) pattern of the prepared compound reveals the crystalline nature, phase purity and structure details. Figure 1 shows the powder XRD pattern recorded for as prepared nickel oxide. Five diffraction peaks (111), (200), (220), (311) and (222) were observed, not only their peak position but their intensity also matches the standard pattern of FCC type NiO with a space group of Fm3m(225) (Joint Committee on Powder Diffraction Standards (JCPDS) file no. 04-0835) [15].

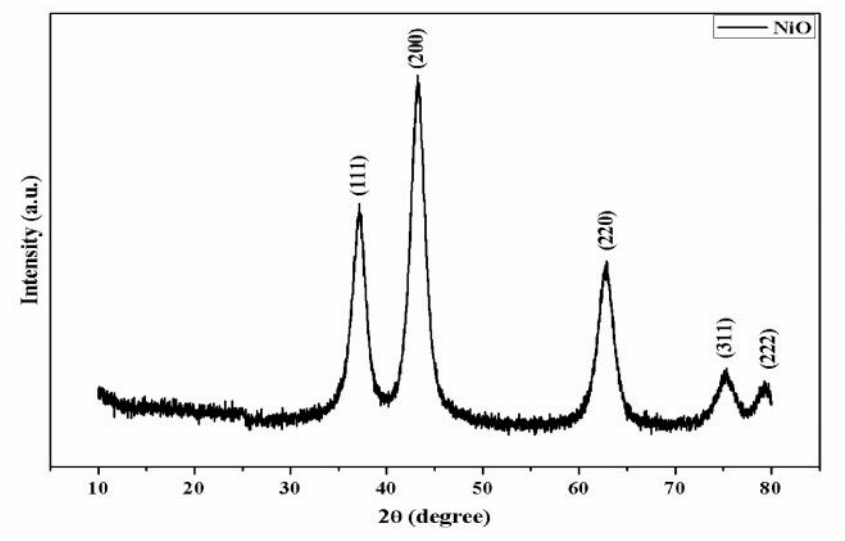

Figure 1. Powder X-ray diffraction pattern of as prepared nickel oxide nanoparticle indexed to JCPDS 04-0835.

Absence of secondary peaks in the XRD pattern illustrates the stoichiometric purity of the NiO samples. The broadness and intensity of the respective peaks of NiO samples were attributed to their crystallinity and crystallite size. Average crystallite size of the prepared materials was calculated using Scherrer equation given below

$$d = 0.9*\lambda / \beta*\cos\theta \qquad (1)$$

Where d is the crystallite size, λ is the X-ray wavelength (1.542 Å), θ is the Bragg diffraction angle and β is the full width at the half maximum (FWHM) of the diffraction peak [16]. 4.6 nm of average crystallite size was calculated from the XRD pattern. Use of leavening agent has hindered the crystallite growth and led to the formation of small size nanoparticles.

B. Fourier Transform Infra-red studies (FTIR)

FTIR spectrum recorded between 500 cm^{-1} to 4000 cm^{-1} is displayed in figure 2. Absorption band in the region of 600-700 cm^{-1} was assigned to Ni-O stretching vibration mode. A wide band at 3415 cm^{-1} and weak band at 1631 cm^{-1} was attributed to the OH stretching vibrations arising from the hydroxyl group attached to the metal oxide and H-O-H bending vibration mode respectively [17]. Physiadsorped and structurally bonded water that remains after low temperature calcination was visible from the broad absorption bands.

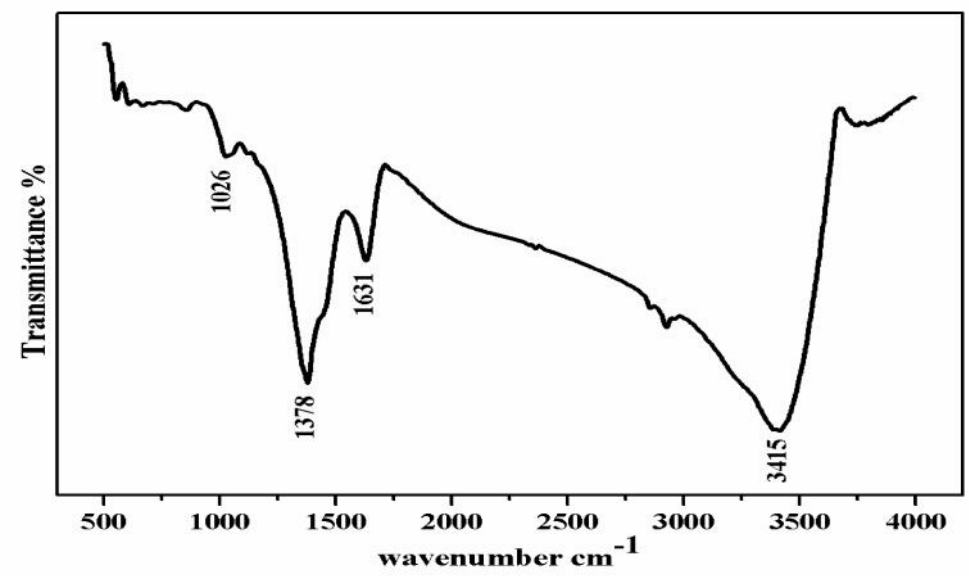

Figure 2. Shows the FTIR spectrum recorded between 500 cm^{-1} – 4000 cm^{-1}

Doublet peak observed at 1378 cm^{-1} was attributed to the C-H bending vibrations (methyl group) of residue starch present in the NiO. Band at 1026 cm^{-1} was an evidence of C-O vibrations originating from carbonate residues of sodium bicarbonate used in compound preparation [18].

C. Morphological Studies

Field emission scanning electron (FESEM) microscopy imaging technique was utilized to acquire information about the particle morphology on the nanoscale. Figure 3 (a) & (b) shows the low and high magnification images of NiO. Images reveal the spherical nature of the particles formed with intermittent pores that allow facile diffusion of electrolyte ions. Particles remained to be in the nano regime, use of leavening agent has predominant role in hindering the particle growth and spherical shape formation of the particles with sufficient pores. Carbon dioxide released during the reaction had prevented the particles from aggregating. Such surface morphology can be highly advantageous for supercapacitor application.

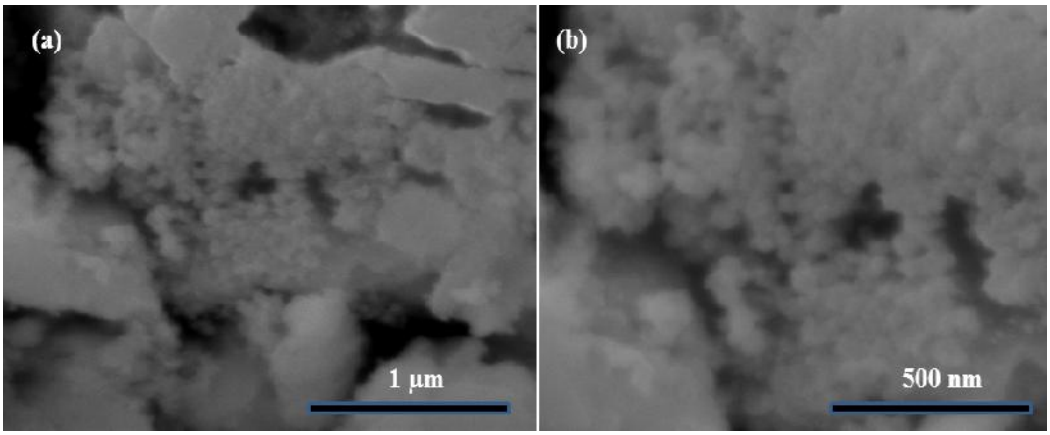

Figure 3. (a) &(b) shows the low and high magnification images of spherical shape NiO nanoparticles with intermittent pores created by CO_2 evolution

D. Electrochemical Characterizations

Cyclic Voltammetry (CV) is a predominant technique widely used to determine the capacitive behavior of the electrode material. Figure 4 (a) shows the typical CV curve of nickel oxide recorded at various scan rates in 1 M KOH electrolyte between -0.15 – 0.55 V potential window. Large potential window (0.7 V) means high energy density, materials with high energy density is technologically important. A pair of redox peaks was observed for all the scan rates which indicate that the major type of charge storage was pseudocapacitive in nature. The redox couple of nickel oxide in alkaline solution can be expressed as follows [10]

$$NiO + OH^- \leftrightarrow NiOOH + e^- \quad (2)$$

Redox process was highly fast and reversible seen from the nearly symmetrical current response even at high scan rates. Current response increases linearly with the increase in scan rate which is suitable for power applications. Pores created by CO_2 evolution during material synthesis can act as ion buffering reservoirs which sustain the supply of OH^- ions at high scan rates [19]. With increase in scan rate there is no much shift in the peak positions exhibiting lower polarization effect in the electrode material and reason for better reversibility. Specific capacitance of the material is calculated from the equation given below

$$SC = 1/(v \times m\ (Va-Vc))\ {}_{(Va)}{}^{(Vc)} \int IV\ dV \quad (3)$$

The SC values were calculated graphically by integrating the area under the I-V curves and then dividing by the sweep rate v ($V\ s^{-1}$), the mass of the material (m), and the potential window (Va to Vc) [15].

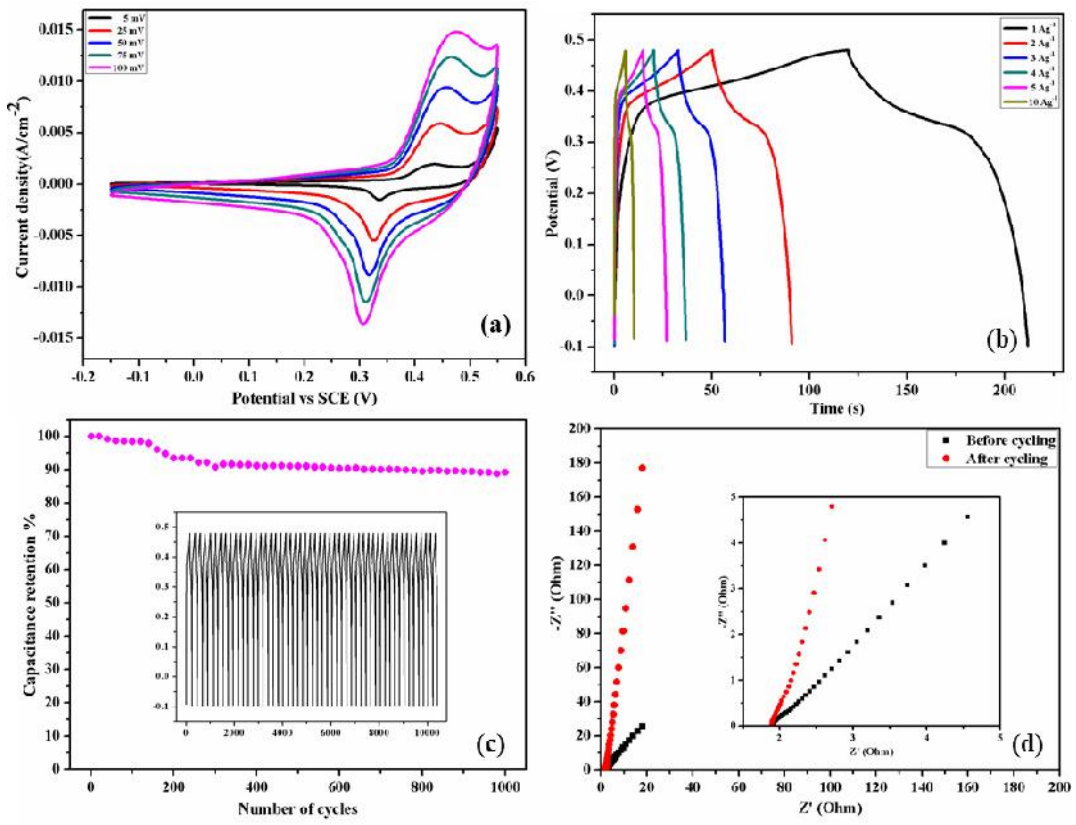

Figure 4. (a) exhibits the cyclic voltammetry recorded for various scan rates, (b) charge-discharge profile of NiO in KOH, (c) long cycling studies to detrmine compound stability & (d) Nyquist plot depicting the low resitance offered by the porous electrode.

A maximum specific capacitance of 342 F/g was calculated for 5 mVs^{-1} scan rate. Figure 4 (b) displays the charge – discharge profile of the electrode material using chronopotentiometry (CP). Deviation from ideal triangular charge/discharge curve depicts the pseudocapacitive behavior complimenting the results obtained from CV studies. Reversibility of the material was once again cognizant from the nearly equal charge/ discharge time. Specific capacitance of 320 F/g was calculated at 1 A/g current density from CP measurements which is close to the value obtained from CV studies. Long cycling measurement was carried for 1000 cycles to determine the materials ability to retain its capacitance after long charge-discharge process. Graph between number of cycles and capacitance retention % is shown in figure 4 (c), after 1000 cycles NiO retains 89 % of its original capacitance. Outstanding electrode stability observed from the indistinguishable CV shapes at different scan rates and long cycling study depicts the material ability to be commercialized. Nyquist plot drawn between real part Z' and imaginary part –Z'' of the complex impedance spectroscopy recorded between 1 Hz – 1 MHz is shown in figure 4 (d) [20]. Near absence of semicircle at the high frequency region depicts the high conductive nature of the material. The point at x-axis where the imaginary part meets gives the solution resistance or equivalent series resistance [21] of the material, a very low ESR value of 1.9 Ω was observed for NiO which remains to be the same even after 1000 cycles. Slope of the line at mid and low frequencies gives an estimate of the diffusion resistance or Warburg impedance of the system. The line becomes almost parallel to the imaginary axis over cycling, as the immersion time increase electrolyte ions diffuse well into the pores created by the leavening effect and thereby inheriting lower diffusion resistance.

IV. CONCLUSION

Nickel oxide nanoparticles of very small crystallite size with high crystallinity and purity were prepared using leavening agent. FTIR spectrum provides the details of the functional groups attached to the metal oxide. Influence of leavening agent on the formation of spherical particle with intermittent pores was observed from FESEM images. Electrochemical tests reveal the pseudocapacitive behavior of the material with excellent integrity over cycling. Redox process was highly fast and reversible, which are essential qualities of an efficient electrode material for supercapacitor applications.

ACKNOWLEDGMENT

Authors would like to appreciate the financial assistance provided by Anna University by providing Anna Centenary Research Fellowship (ACRF) for A. Nirmalesh Naveen (Lr.No.CR/ACRF/2013/37).

REFERENCES

[1] Lei Yang, Shuang Cheng, Yong Ding, Xingbao Zhu, Zhong Lin Wang, and Meilin Liu, "Hierarchical Network Architectures of Carbon Fiber Paper Supported Cobalt Oxide Nanonet for High-Capacity Pseudocapacitors," Nano Lett., vol. 12, pp. 321−325, 2012.

[2] Weiwei Zhou, Jinping Liu, Tao Chen, Kim Seng Tan, Xingtao Jia, Zhiqiang Luo, Chunxiao Cong, Huanping Yang, Chang Ming Li and Ting Yu," Fabrication of Co_3O_4-reduced graphene oxide scrolls for high-performance supercapacitor electrodes," Phys. Chem. Chem. Phys.,vol. 13, pp.14462–14465, 2011.

[3] Hao Jiang, Ting Zhao, Chaoyi Yan, Jan Ma and Chunzhong Li," Hydrothermal synthesis of novel Mn_3O_4 nano-octahedrons with enhanced supercapacitors performances," Nanoscale, vol. 2, pp. 2195–2198, 2010.

[4] A. Nirmalesh Naveen∗, Subramanian Selladurai, Electrochimica Acta," Investigation on physiochemical properties of Mn substituted spinel cobalt oxide for supercapacitor applications," vol. 125, pp. 404–414, 2014.

[5] Jing-Jing Deng, Jian-Cheng Deng, Zi-Ling Liu, Hui-Ren Deng, Bo Liu, "Influence of addition of cobalt oxide on microstructure and electrochemical capacitive performance of nickel oxide," J Solid State Electrochem, vol. 13, pp. 1387–1394, 2009.

[6] Yanhua Li, Kelong Huang, Suqin Liu, Zufu Yao," Meso-macroporous Co_3O_4 electrode prepared by polystyrene spheres and carbowax templates for supercapacitors," J Solid State Electrochem, vol. 15, pp. 587–592, 2011.

[7] Yan-zhen Zheng, Hai-yang Ding, Mi-lin Zhang, "Preparation and electrochemical properties of nickel oxide as a supercapacitor electrode material," Materials Research Bulletin, vol. 44, pp. 403–407, 2009.

[8] Min-Sun Song, Kyung Min Lee, Yu Ri Lee, In Young Kim, Tae Woo Kim, Jayavant Laxman Gunjakar, and Seong-Ju Hwang," Porously Assembled 2D Nanosheets of Alkali Metal Manganese Oxides with Highly Reversible Pseudocapacitance Behaviors," J. Phys. Chem. C,vol. 114, pp. 22134–22140, 2010.

[9] Maiyong Zhu, Ying Wang, Dehai Meng, Xingzhang Qin, and Guowang Diao, "Hydrothermal Synthesis of Hematite Nanoparticles and Their Electrochemical Properties," J. Phys. Chem. C,vol. 116, pp. 16276−16285, 2012.

[10] Mao-Sung Wu and Min-Jyle Wang, "Nickel oxide film with open macropores fabricated by surfactant-assisted anodic deposition for high capacitance supercapacitors," Chem. Commun., vol. 46,pp. 6968–6970, 2010.

[11] Jun-Wei Lang, Ling-Bin Kong, Wei-Jin Wu, Yong-Chun Luo and Long Kang," Facile approach to prepare loose-packed NiO nano-flakes materials for supercapacitors," Chem. Commun.,pp. 4213–4215, 2008.

[12] Hao Jiang, Ting Zhao, Chunzhong Li and Jan Ma," Hierarchical self-assembly of ultrathin nickel hydroxide nanoflakes for high-performance supercapacitors," J. Mater. Chem.,vol. 21,pp. 3818, 2011.

[13] A.I. Inamdara, YoungSam Kima, S.M. Pawarb, J.H. Kimb, Hyunsik Ima, Hyungsang Kim, "Chemically grown, porous, nickel oxide thin-film for electrochemical supercapacitors," Journal of Power Sources, vol. 196,pp. 2393–2397, 2011.

[14] Da-WeiWang, Feng Li, Hui-Ming Cheng, "Hierarchical porous nickel oxide and carbon as electrode materials for asymmetric supercapacitor," Journal of Power Sources, vol. 185,pp. 1563–1568, 2008.

[15] Sumanta Kumar Meher, P. Justin, and G. Ranga Rao, "Microwave-Mediated Synthesis for Improved Morphology and Pseudocapacitance Performance of Nickel Oxide," ACS Appl. Mater. Interfaces,vol. 3, pp. 2063–2073, 2011.

[16] A. Nirmalesh Naveen and S. Selladurai, "Novel synthesis of highly porous spinel cobaltite ($NiCo_2O_4$) electrode material for supercapacitor applications," AIP Conference Proceedings,vol. 246, pp. 1591, 2014.

[17] Sharanabasava V.Ganachari, Ravishankar Bhat, Raghunandan Deshpande and Venkataraman A, "Synthesis and characterization of nickel oxide nanoparticles by self-propagating low temperature combustion method ,"Recent Research in Science and Technology, vol. 4(4), pp. 50-53, 2012.

[18] K. Anandan and V. Rajendran, "Structural, optical and magnetic properties of well-dispersed NiO nanoparticles synthesized by CTAB assisted solvothermal process," Nanoscience and Nanotechnology: An International Journal,vol. 2(4), pp. 24-29, 2012.

[19] Xiaojun Zhang, Wenhui Shi, Jixin Zhu, Weiyun Zhao, Jan Ma, Subodh Mhaisalkar, Tuti Lim Maria, Yanhui Yang, Hua Zhang, Huey Hoon Hng, and Qingyu Yan, "Synthesis of Porous NiO Nanocrystals with Controllable Surface Area and Their Application as Supercapacitor Electrodes," Nano Res., vol. 3(9), pp. 643–652, 2010.

[20] Sumanta Kumar Meher, P. Justin, G. Ranga Rao, "Pine-cone morphology and pseudocapacitive behavior of nanoporous nickel oxide," Electrochimica Acta, vol. 55, pp. 8388–8396, (2010).

[21] Subbukalai Vijayakumar, Sadayappan Nagamuthu, and Gopalan Muralidharan," Supercapacitor Studies on NiO Nanoflakes Synthesized Through a Microwave Route," ACS Appl. Mater. Interfaces,vol. 5, pp. 2188−2196, 2013.