

Analysis of Structural, Morphological and Electrochemical on Ni (OH)₂ Coated Carbon Sphere by Hydrothermal Method

R. Ranjithkumar, C. Sambathkumar, N.Nallamuthu, M. Krishna kumar, P. Devendran

Abstract: Nickel hydroxide Ni (OH)₂ nanoparticles (Nps) effectively embedded on carbon sphere (Ni(OH)₂@CS) by facile hydrothermal method. The prepared sample was characterized through powder XRD analysis which clearly shows the crystalline structure of the Ni(OH)₂@CS. FTIR spectra gave the functional group in the carbon sphere Ni(OH)₂@CS Ni-O, C-O, C-C, C=C, and OH vibration on the Ni(OH)₂@CS. The scanning electron microscope (SEM) shows the surface morphology of the sample. Energy dispersive analysis shows the elemental conformation of the prepared sample. The electrochemical performance analysis shows the Galvanostatic charge-discharge, cyclic voltammetry analysis gives the specific capacitance of the prepared sample. The impedance analysis shows the electrode-electrolyte interface on the electrode material.

Keywords : Ni(OH)₂, carbon sphere, chemical reflux method, cyclic voltammetry, charge-discharge analysis.

I. INTRODUCTION

The modern development of society depended with vitality and predominant widespread electric-vehicle, electronic gadgets and well known hybrid electric vehicle demand for energy source can be supplied using an unavoidable source such as electrochemical energy storage and sources[1-2]. The emergency need for effective energy storage devices was lead to in a prevalent and high concerned research exertion into the electrochemical energy storage devices too named as supercapacitors, ultracapacitors and Electrochemical double layer capacitor (EDLC) [3]. Carbon-based supercapacitors, additionally called EDLC, have pulled in extensive research interest as revolutionary control type vitality storage gadgets in the outlook of their remarkable properties, includ high-power densities, long cycle life and fast charging/releasing rate just as high safely[3-8].

The carbon-based materials with the permeable structure are one of the passionately debated issues in the region of materials science. The high explicit surface zone, enormous pore volume, well-requested and controllable permeable

structure, unique morphologies of carbons and their outstanding chemical, mechanical and warm dependability make them fascinating for remarkable applications including catalysis, energy storage and change, water purification and sensing.[9-18] Variety of carbon material having excellent capacitance behaviour like carbon onion[19], carbide-derived carbon[20], carbon aerogels [21], carbon nanotube[22] outstanding retentivity of the electrode material[23]. Carbon sphere contains more advantages compare to exhausting material like spherical geometry, good liquidness, controllable porosity and ultra-tuneable size. Among, these innovative materials outstanding property and extraordinary application like catalysis, water purification as well as air purifications energy conversion and storage[10-14]. The synthesis strategies method of carbon spheres have been developing from multicomponent exclusively templating[24-27], hydrothermal carbonization (HyTC) [27], emulsion polymerization[28], self-assembly [29] and Stober method [30-33].

The electrochemical performance essential for electrode material like the metal oxides, hydroxide, nitrides and carbides and well-known electrode material for redox reactions. Closely, transitions metal oxides and hydroxides their electrochemical reactions in electrode material occurred extensively like Co(OH)₂ Fe₃O₄, MnO₂, V₂O₅, NiCo₂O₄, ZnO and Ni(OH)₂ enabling high reversible redox reaction from the electrode surface[34-36]. Moreover, The transition metal oxides (TMOxs) exhibit the good specific capacitance because the reason they possess many redox states as well as it contains a variety of hierarchical structure and pores nature of the material. Among, the hierarchical structure play a un avoids role in enhancing the energy density [37-38] The combines of metal hydroxides materials with carbon-based composite provide high perform of electrode material.

In present work, we coated the Nickel hydroxides to the carbon sphere surface. We found the electrochemical analysis of the prepared electrode material. The cyclic voltammetry analysis gives information about the oxidation and reduction reaction of the Ni(OH)₂ coated carbon sphere. The galvanostatic charge- discharge analysis gives the performance of the electrode material.

Revised Manuscript Received on December 16, 2019.

* Correspondence Author

P. Devendran^{*}, ^aDepartment of Physics, International Research Centre, Kalasalingam Academy of Research and Education, Krishnankoil – 626126. Tamil Nadu, India. p.devendran@klu.ac.in

P. Lakshmanan, ^bDepartment of chemistry, International Research Centre, Kalasalingam Academy of Research and Education, Krishnankoil – 626126. Tamil Nadu, India.

II. MATERIAL SYNTHESIS

A. Materials

All the chemical reagents and were of AR grade and used without further purification. Nickel (II) nitrate hexahydrate Ni(NO₃)₂·6H₂O and Glucose were acquired from Sigma Aldrich.

B. Carbon sphere synthesis method

In a typical synthesis of the carbon sphere from 1M glucose were added in 120ml deionized water Stirred in 10mins. The solution was transferred into the Teflon-lined autoclave (stainless steel) kept at 180 °C for 10hrs. Further, the product was collected by beaker kept in ultrasonic treatment for 10min to form the uniform sphere dispersion. Moreover, the products were centrifuged at 6000rpm and washed several times with deionized water and ethanol. Finally, the sample was dried at 80 °C for 12hrs in a vacuum oven.

C. Ni(OH)₂ coated on Carbon sphere

Separately, Nickel(II) nitrate hexahydrate Ni(NO₃)₂·6H₂O was added 0.1M in 110ml deionized water. The solution was stirred in 20 min to make a light green solution. Further, the NaOH pellets 0.3g were added 15ml deionized water. The NaOH solution was added to Nickel nitrate solution into drop by dropwise then get precipitate. Moreover, added 0.5g carbon sphere in the nickel hydroxide solution stirred at 3hrs. That stirred solution was transferred to a Teflon lined autoclave (stainless steel) and kept at 100 °C for 10 hrs. Moreover, the products were centrifuged at 6000rpm and washed several times with deionized water and ethanol. Finally, the sample was dried at 80 °C for 12hrs in a vacuum oven.

III. RESULTS AND DISCUSSION

A. Structural characterization

The observed XRD pattern recorded at the 2θ range of 10 to 70. The crystalline peaks show the phase and hexagonal structure of Ni(OH)₂.

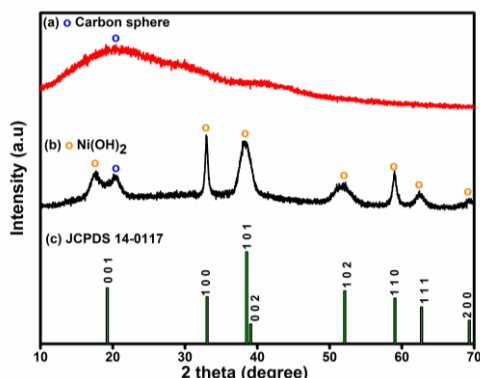


Fig. 1. XRD analysis of (a) carbon sphere and (b) NiOH₂ coated carbon sphere

Fig. 1(a) shows the XRD pattern of the carbon sphere and the broad peak appeared at 22°. The XRD pattern shows perfectly matched with the previous literature [39]. The Fig.1 (b) shows the crystalline peaks of Ni(OH)₂ coated on the carbon sphere exactly matched with JCPDS card No.

14-0117. The sharp peaks observed a range of 32.9°, 38.3°, 58.9°. The crystallite size was estimated theoretically by using Debye–Scherrer formula,

$$D = k\lambda/\beta\cos\theta \dots \dots \dots (1)$$

The calculated average crystallite size was 30 nm.

B. FTIR analysis

The FTIR spectrum recorded at in the range of 400cm⁻¹ to 4000cm⁻¹. The FTIR spectrum shows the vibrations of intermolecular interactions of carbon sphere and NiOH₂ coated carbon sphere.

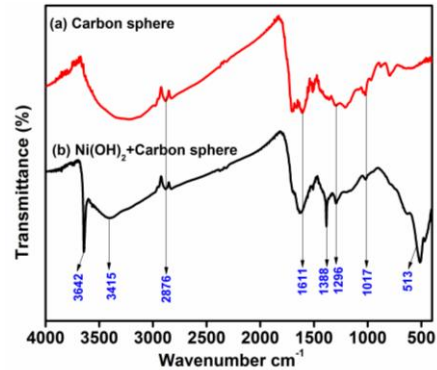


Fig. 2. FTIR spectrum of (a) carbon sphere and (b) NiOH₂ coated carbon sphere

Fig. 2(a) shows the spectrum of the carbon sphere. They observed some vibrations in the range at 3612cm⁻¹, 3415cm⁻¹ O-H vibrations[40]. The vibrations in the present peak at –C=O in 1611cm⁻¹, 1388cm⁻¹ [41-42]. stretching C-C vibrations. Fig. 2(b) shows the spectrum of NiOH₂ coated carbon sphere. The Vibration observed at the range in nearly 513cm⁻¹ it's closely matched with the Ni-O stretching lattice vibration[43].

C. Surface and Elemental analysis

SEM images of NiOH₂ coated carbon sphere shown in Fig. 3 and the Elemental all are confirmed to EDXS analysis. The SEM images have different magnifications scanned of NiOH₂ coated carbon sphere. The Fig. 3(a) shows the images of NiOH₂ coated carbon sphere in the range of 20µm and as well as fig. 3(b) shows the same at the range of 1µm. The SEM images clearly reveal that the NiOH₂ was fully coated on the surface uniformly of carbon sphere.

The Fig. 3(d) shows the elementals are conforming through EDXS pattern analysis. The pattern of elementals is a presence in the Ni(OH)₂ coated carbon sphere. The percentage of elements also measured the carbon contains in the sharp peak of 38.1%. The oxygen contains 33.5% and also Ni contains 28.4%.

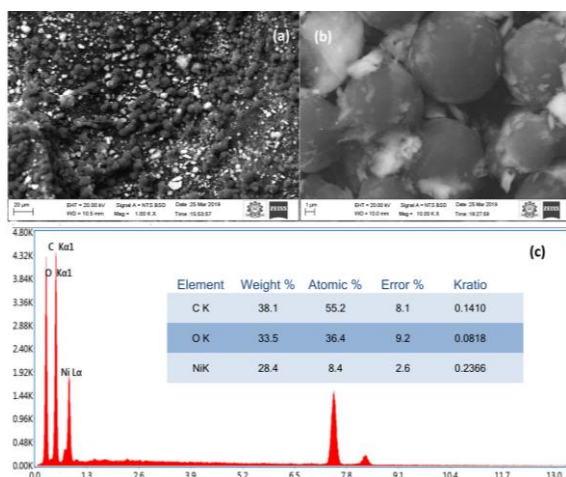


Fig. 3. Surface morphology of NiOH₂ coated carbon sphere with different magnifications

The fig 3(c) shows that the elemental composition of the prepared composite. The carbon contains the peak at the K α radiation characteristic x-ray emits at the range of 0.277keV and the intensity was high. It shows the moreover the percentage of carbon was very high from the EDAX graph 38.1%. The Oxygen exhibits the range of radiation characteristic x-ray K α 0.525keV and the oxygen contain 33.5%. Finally, the Ni peak contains in the range of 7.47keV in 28.4%.

D. Electrochemical analysis

1) Cyclic voltammetry

The electrochemical analysis of the prepared electrode material was observed from the range of 0 to 0.6V. The Electrochemical results show the oxidation and reduction states of the NiOH₂ coated carbon sphere. The oxidation takes place between the 0.33V and the reduction takes place the nearly 0.58V. The oxidation current occurs at the negative current then the reduction current observed at the positive range.

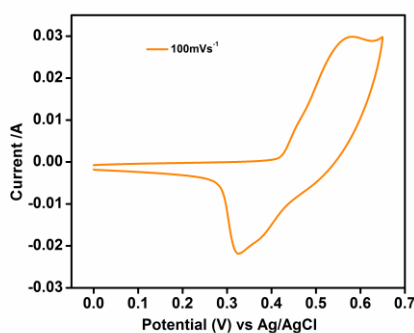


Fig. 4. Cyclic voltammetry curve of NiOH₂ coated carbon sphere working electrode

2) Galvanostatic charge-discharge

In Fig.5 shows the charge-discharge of the prepared NiOH₂ coated carbon sphere of the sample. The Charge-discharge curve gives information about the Internal resistance of the NiOH₂ coated electrode material and the specific capacitance of the prepared sample. In the fig shows the 1mA scan rate at the potential windows from the 0 to 0.55V. They have long charged and also discharge time.

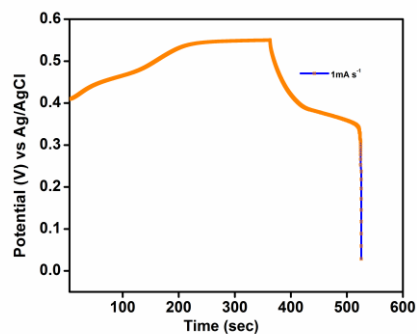


Fig. 5. The charge-discharge curve of NiOH₂ coated carbon sphere

IV. CONCLUSION

In conclusion, we prepare the NiOH₂ coated carbon sphere via the hydrothermal method. The crystalline structure was characterized through powder x-ray analysis. The presenting morphology was finder by the SEM images. The prepared elementals are predicted from the elemental analysis. The functional group vibrations are observed from the FTIR analysis. Here, we find the electrochemical studies showed that the material composite becomes a good material for electrochemical applications.

ACKNOWLEDGMENT

Author R.Ranjithkumar gratefully thanks to Kalasalingam Academy of Research and Education [KARE] to provide University Research Fellowship (URF) scheme and also thankful IRC provide characterisation facilities.

REFERENCES

- Zhu, T.Liu, F. Qian,T.Y. JinHan,E.B. Duoss, J.D.Kuntz, C.M.Spadaccini, M.A.Worsely, Y.Li, Supercapacitors based on three-dimensional hierarchical graphene aerogels with periodic macropores. *NanoLett. Vol.16*, (2016) pp.3448–3456.
- Z.Chen, M.Zhao,L. Lv, K.Zhou,X. Jiang,X.Ren,X. Mei, Fast ion transport through ultrathin shells of metal sulfide hollow nanocolloids used for high-performance energy storage, *Sci. Rep.* 8 vol.30 (2018) pp.18504-18506.
- Zhong, C.; Deng, Y.; Hu, W.; Qiao, J.; Zhang, L.; Zhang, J., A Review of Electrolyte Materials and Compositions for Electrochemical Supercapacitors. *Chem. Soc. Rev.* 2015, 44,pp. 7484–7539.
- Yang, Z.; Jing, R.; Zhang, Z.; Chen, X.; Guan, G.; Qiu, L.; Ye, Z.; Peng, H., Recent Advancement of Nanostructured Carbon for Energy Applications. *Chem. Rev.* 2015, 115,pp. 5159–5342.
- Zhu, Y.; Li, N.; Lv, T.; Yao, Y.; Peng, H.; Shi, J.; Cao, S.; Chen, T., Ag-Doped PEDOT:PSS/CNT Composites for Thin-Film All-Solid-State Supercapacitors with a Stretchability of 480%. *J. Mater. Chem. A* 2018, 6, pp.941–947.
- Chen, Z.; Xie, H. Q.; Hu, L. F.; Chen, M.; Wu, L. M., Fabrication of Novel Lamellar Alternating Nitrogenoped Microporous Carbon Nanofilm/MoS₂ Composites with High Electrochemical Properties. *J. Mater. Chem. A* 2017, 5, pp.22726–22734.
- Lv, T.; Liu, M.; Zhu, D.; Gan, L.; Chen, T., Nanocarbon-Based Materials for Flexible All-Solid-State Supercapacitors. *Adv. Mater.* 2018, 10, 1705489.
- Wang, Y.; Tao, L.; Xiao, Z.; Chen, R.; Jiang, Z.; Wang, S., 3D Carbon Electrocatalysts in Situ Constructed by Defect-Rich Nanosheets and Polyhedrons from NaCl-Sealed Zeolitic Imidazolate Frameworks. *Adv. Funct. Mater.* 2018, 28, 1705356.

9. Benzigar, M. R., Talapaneni, N., Joseph, S., Ramadass, K., Singh, G., Scaranto, J., & Ravon, U. Recent advances in functionalized micro and mesoporous carbon materials : synthesis and applications. *Chemical Society Reviews*. (2018).
10. B. Hu, K. Wang, L. Wu, S. H. Yu, M. Antonietti and M. M. Titirici, Engineering Carbon Materials from the Hydrothermal Carbonization Process of Biomass. *Adv. Mater.*, 2010, 22, 813–828.
11. A. A. Deshmukh, S. D. Mhlanga and N. J. Coville, Carbon spheres. *Mater. Sci.Eng.*, R, 2010, 70, 1–28.
12. M.-M. Titirici and M. Antonietti, Chemistry and materials options of sustainable carbon materials made by hydrothermal carbonization. *Chem. Soc. Rev.*, 2010, 39, 103–116.
13. J. Lee, J. Kim and T. Hyeon, Recent Progress in the Synthesis of Porous Carbon Materials. *Adv. Mater.*, 2006, 18, 2073–2094.
14. B. Hu, S.-H. Yu, K. Wang, L. Liu and X.-W. Xu, Functional carbonaceous materials from hydrothermal carbonization of biomass: an effective chemical process. *Dalton Trans.*, 2008, 5414–5423.
15. Pang, J.; Zhang, W.; Zhang, H.; Zhang, J.; Zhang, H.; Cao, G.; Han, M.; Yang, Y., Sustainable Nitrogen-Containing Hierarchical Porous Carbon Spheres Derived from Sodium Lignosulfonate for High-Performance Supercapacitors. *Carbon* 2018, 132, 280–293.
16. Xiong, S, Fan, J, Wang, Y, Zhu, J, Yu, J, Hu, Z., A Facile Template Approach to NitrogenDoped Hierarchical Porous Carbon Nanospheres from Polydopamine for High-Performance Supercapacitors. *J. Mater. Chem. A* 2017, 5, 18242–18252.
17. Hao, J, Wang, J, Qin, S.; Liu, D, Li, Y, Lei, W., B/N Co-Doped Carbon Nanosphere Frameworks as High-Performance Electrodes for Supercapacitors. *J. Mater. Chem. A* 2018, 6, 8053–8058.
18. Liu, Z.; Zhou, Z.; Xiong, W.; Zhang, Q., Controlled Synthesis of Carbon Nanospheres via the Modulation of the Hydrophilic Length of the Assembled Surfactant Micelles. *Langmuir* 2018, 34, 10389–10396.
19. Shaibani, M.; Smith, S. J. D.; Banerjee, P. C.; Konstas, K.; Zafari, A.; Lobo, D. E.; Nazari, M.; Hollenkamp, A. F.; Hill, M. R.; Majumder, M., Framework-Mediated Synthesis of Highly Microporous Onion-Like Carbon: Energy Enhancement in Supercapacitors without Compromising Power. *J. Mater. Chem. A* 2017, 5, 2519–2529
20. Yair, K.; Marcus, R.; Emanuel, K.; Lars, B.; Alexander, K.; Stefan, K.; Gleb, Y., High-Rate Electrochemical Capacitors Based on Ordered Mesoporous Silicon Carbide-Derived Carbon. *ACS Nano* 2010, 4, 1337–1344.
21. Zhang, Y.; Zhao, C.; Ong, W. K.; Lu, X., Ultrafast-Freezing-Assisted Mild Preparation of Biomass-Derived, Hierarchically Porous, Activated Carbon Aerogels for High-Performance Supercapacitors. *ACS Sustain. Chem. Eng.* 2018, 7, 403–411.
22. R. Ranjithkumar, S. Ezhil Arasi, S. Sudhahar, N. Nallamuthu, P. Devendran, P. Lakshmanan, M. Krishna Kumar, Enhanced electrochemical studies of ZnO–CNT nanocomposite for supercapacitor devices, *Physica B* Vol.568 (2019) pp.51-59.
23. Xue, D., Zhu, D., Xiong, W., Cao, T., Wang, Z., Lv, Y., ... Gan, L. (2019). Template-Free, Self-Doped Approach to Porous Carbon Spheres with High N/O Contents for High-Performance Supercapacitors. *ACS Sustainable Chemistry and Engineering*, 7(7), 7024–7034
24. M. T. Gokmen and F. E. Du Prez, Prog. Porous polymer particles: a comprehensive guide to synthesis, characterization, functionalization and applications. *Polym. Sci.*, 2012, 37, 365–405.
25. H. Gröger, C. Kind, P. Leidinger, M. Roming and C. Feldmann, Nanoscale Hollow Spheres: Microemulsion-Based Synthesis, Structural Characterization and Container-Type Functionality. *Materials*, 2010, 3, 4355–4386.
26. J. Hu, M. Chen, X. Fang and L. Wu, Fabrication and application of inorganic hollow spheres. *Chem. Soc. Rev.*, 2011, 40, 5472–5491.
27. X. Lai, J. E. Halpert and D. Wang, Recent advances in micro-/nano-structured hollow spheres for energy applications: From simple to complex systems. *Energy Environ. Sci.*, 2012, 5, 5604–5618.
28. Y. Li and J. Shi, Hollow - Structured Mesoporous Materials: Chemical Synthesis, Functionalization and Applications. *Adv. Mater* 2014, 26, 3176–3205.
29. Y. Shi, Y. Wan and D. Zhao, Ordered mesoporous non-oxide materials *Chem. Soc. Rev.*, 2011, 40, 3854–3878.
30. Y. Xia, B. Gates, Y. Yin and Y. Lu, Monodispersed Colloidal Spheres: Old Materials with New Applications. *Adv. Mater.*, 2000, 12, 693–713.
31. S. Kubo, R. Demir-Cakan, L. Zhao, R. J. White and M. M. Titirici, Porous Carbohydrate - Based Materials via Hard Templating. *ChemSusChem*, 2010, 3, 188–194.
32. Y. Xia and R. Mokaya, Synthesis of Ordered Mesoporous Carbon and Nitrogen - Doped Carbon Materials with Graphitic Pore Walls via a Simple Chemical Vapor Deposition Method. *Adv. Mater.*, 2004, 16, 1553–1558.
33. Y. Xia, Z. Yang and R. Mokaya, Mesostructured Hollow Spheres of Graphitic N-Doped Carbon Nanocast from Spherical Mesoporous Silica. *J. Phys. Chem. B*, 2004, 108,19293–19298
34. J. R. Miller and P. Simon, Electrochemical capacitors for energy management. *Science*, 2008, 321, 651–652.
35. K. Wang, H. P. Wu, Y. N. Meng, Z. X. Wei, Conducting polymer nanowire arrays for high performance supercapacitors. *Small*, 2014, vol. 10, pp.14-31.
36. Sivaganesh, D., Saravanakumar, S., Sivakumar, K. S. Syed Ali Esther, AkapoEzra Alemayehu, R. Rajajeyaganthan, R. Saravanan. *J Mater Sci: Mater Electron* (2019) 30: 2966.
37. L.L. Fan, X.F. Li, Recent advances in effective protection of sodium metal anode, *Nano Energy* 53 (2018) 630-642.
38. D.B. Xiong, X.F. Li, Z.M. Bai, S.G. Lu, Recent advances in layered Ti3C2Tx MXene for electrochemical energy storage, *Small* 14 (2018) 1703419.
39. Zhang, X., Ma, J., Yang, W., Gao, Z., Wang, J., Liu, Q., ... Jing, X. (2014). Manganese dioxide core-shell nanowires in situ grown on carbon spheres for supercapacitor application. *CrystEngComm*, 16(19), 4016–4022.
40. M. Sevilla and A. B. Fuertes, Chemical and structural properties of carbonaceous products obtained by hydrothermal carbonization of saccharides. *Chem.–Eur. J.*, 2009, 15, 4195–4203.
41. S. X. Liu, J. Sun and Z. Huang, Carbon spheres/activated carbon composite materials with high Cr (VI) adsorption capacity prepared by a hydrothermal method. *J. Hazard. Mater.*, 2010, 173, 377–383.
42. X. M. Sun and Y. D. Li, Ag@ C core/shell structured nanoparticles: controlled synthesis, characterization, and assembly. *Langmuir*, 2005, 21, 6019–6024.
43. M A.. Elshahawy, K. H. Ho, Y. Hu, Z. Fan, Y. Wei Benedict Hsu, C. Guan, Q. Ke, J. Wanga. Microwave – assisted hydrothermal synthesis of Nanocrystal β-Ni(OH)₂ for supercapacitor application. *CrystEngComm*, 2016,18, 3256-3264