

Preparation and Structural Characterization of $\text{Ni}_3\text{V}_2\text{O}_8$ Nanoparticles for Supercapacitor Applications

N. Nallamuthu, K. Ramesh, Ramesh Chandra Mallik

Abstract: Energy perception and Energy consumption are major consideration in daytoday life in every place in world. Electrochemical energy storage devices are best remedies to fulfill the energy consumption and also serve as a alternate energy source of renewable energy devices. Here, $\text{Ni}_3\text{V}_2\text{O}_8$ is developed by hydrothermal process. The crystalline phase, size and structural properties are identified using X- ray Diffraction techniques. The functional group and molecular bond formations are analysed using Fourier transform Infrared spectroscopy. The prepared $\text{Ni}_3\text{V}_2\text{O}_8$ nanoparticles are most applied for electrode of supercapacitor applications.

Keywords: $\text{Ni}_3\text{V}_2\text{O}_8$, Hydrothermal method, supercapacitors, XRD, FTIR, SEM.

I. INTRODUCTION

Nowadays, Supercapacitors have been more specific attention to researchers due to their lower maintenance, greater cyclic stability and high power density and it is distinguishes as environmental free green energy storage system [1-3]. Supercapacitors are broadly used in several electronic items such as digital cameras, interruptible power supply, pulse laser techniques, electric vehicles, electric consumable devices, etc. [4]. Generally, Supercapacitors have very lower energy density, compared with solid state batteries. Hence, the extensive research work has been implemented to enhancement and retain in value of energy density [5,6]. Due to charge transfer and storage phenomena, Supercapacitors are formed as two different kind of parts such as i) pseudocapacitors (in which fast surface charge transfer or faradiac transfer of charges) ii) Electric double layer capacitors (in which charges are accumulated through the way of non-faradiac functions) [7]. Due to the lower energy density formed on electric double layer capacitor, its applicability is limited as a supercapacitor device. Currently, metal oxides; particularly transition elements based metal oxides are providing excellent performance in fast charge transfer reaction and revise faradiac process with higher energy density values. Higher energy density measurements

are evaluated through the identified specific capacitance of the materials. Ruthenium oxide is one of the best transition metal oxide which provide better performance of specific capacity as 720 Fg^{-1} [8]. Moreover, it has certain sensible limitations of toxic in nature, highly expensive and lower abundance. Hence, the scientific interest of this metal oxide has reduced for supercapacitor applications. To overcome these higher obstacles, several kinds of single transition metal oxides, double (metal) oxides has been evaluated as electrode component of supercapacitor. In past years, lower cost transition metal oxides of NiO , MnO_2 , V_2O_5 , Co_3O_4 , CoO and WO_3 have been revealed to enhance the electrochemical performance with higher energy density by different scientific researchers. [9,10] Due to availability of different existing oxidation states in transition metal oxides, it response the enhance redox reaction by faradiac transfer which is granted the better quality of specific capacitance. [11] Furthermore, some variety of transition binary metal oxides of ABO_4 , AB_2O_4 , $\text{A}_2\text{B}_2\text{O}_7$, $\text{A}_3\text{B}_2\text{O}_8$, etc. (where A and B are Transition metals with different oxidation states) are also examined to improve the specific capacitance. This representation results aggravated us to develop $\text{A}_3\text{B}_2\text{O}_8$ based metal oxide where the enormous amount of A has best electrochemical performance and B is taken as pentavalent element. Vanadium is assigned as a pentavalent B ion in $\text{A}_3\text{B}_2\text{O}_8$ type metal oxide and Ni is allocated as A element in this type. Superior electrochemical and catalytic performance of elements A and B are responsible to formation of superlative structural characteristics [12-18]. Wang et. al have revealed the prepared $\text{Ni}_3\text{V}_2\text{O}_8$ for lithium batteries and reported the specific capacitance as 500 Fg^{-1} . [19] B. Prusty et. al have also investigated vanadium nickel oxide with specific capacitance of 412 Fg^{-1} [20]. Liu et al. also examined nickel vanadium oxide and cobalt vanadium oxide for supercapacitor applications [21]. Here, we have planned to develop the lower cost with high electrochemical performance electrode material of $\text{A}_3\text{B}_2\text{O}_8$ material as $\text{Ni}_3\text{V}_2\text{O}_8$. Due to multitalented properties and various device applications, several methods has been investigated to development of nanoparticle including thermal oxidation, microwave, ultrasonic spray pyrolysis, pulsed laser deposition, sputtering, electro deposition, combustion, pechni process, sol-gel, surfactant templating method, etc. Due to some inconvenience and difficulties of the above methods, such as complicated experimental procedure, necessity of sophisticated instruments, high processing temperature, time consumption,

Revised Manuscript Received on December 15, 2019.

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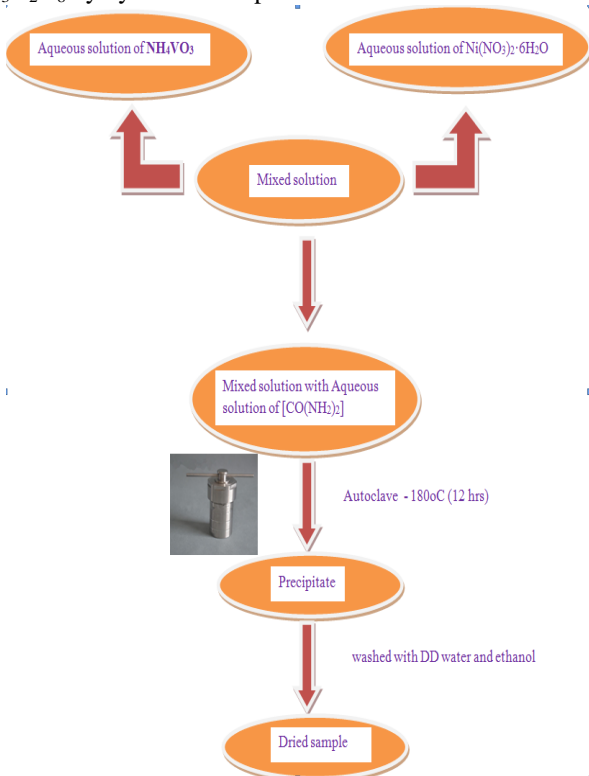
multi-step reaction and limitation for large scale applications. Hence, developing easy and simple, lower expensive and robust approach to preparation of Ni₃V₂O₈ by hydrothermal process is highly desired for supercapacitor device applications.

II. EXPERIMENTAL SECTION

A. Preparation of Ni₃V₂O₈ by hydrothermal process

The starting materials purchased as analytical grade chemicals of Ni(NO₃)₂·6H₂O (Nickel nitrate hexa hydrate) and NH₄VO₃ (Ammonium meta vanadate) from Merck scientific chemicals, India, are used to prepare the Ni₃V₂O₈ nanomaterials. Urea is used as chelating agent in hydrothermal process. All aqueous solutions of chemicals are made using double distilled (DD) water.

The aqueous solution of ammonium metavanadate and the aqueous solution of nickel nitrate hexa hydrate are mixed based on stoichiometric ratio. 2ml of HNO₃ is mixed to prohibit the precipitation of ammonium meta vanadate. The solutions are stirred constantly to make it as clear transparent solution. Urea is formed as aqueous solution and also mixed with the previous transparent solution. After one hour, the resultant solution is filled as 150 ml in Teflon-lined autoclave setup. It is allocated in muffle furnace for heat treatment of 180°C for 12 hours. After cooling to room temperature, the obtained precipitates are collected and washed with distilled water for three times and also with ethanol once. Thus, it is dried to 70°C for 6 hrs. The dried precipitates with heat treatment are characterised for various techniques such as XRD and FTIR. Scheme 1. represent the preparation of Ni₃V₂O₈ by hydrothermal process.



Scheme.1. Preparation of Ni₃V₂O₈ by hydrothermal process

III. RESULTS AND DISCUSSION

A. Powder X-Ray Diffraction Analysis

Diffracted X-ray pattern is collected for synthesized ZnO nanoparticles by using D8 advance ECO XRD instrument of SSD160 1D X-ray detector with Cu-K α (1.5406 Å). Powder sample of Ni₃V₂O₈ is scanned from 10° to 80° with a scanning rate of 0.02° per sec. X – Ray diffractogram for Ni₃V₂O₈ is displayed in Fig. 1. Fig.1 shows X – Ray diffractogram of the prepared sample, every part of the characteristic diffraction peaks could be matched to orthorhombic Ni₃V₂O₈. It is verified by XRD peaks appeared in JCPDS data (Ref. NO. 98-000-1545). At 600o C, the intensity of XRD peaks increased which means increase size of the crystallites. X- ray Diffraction peaks belonging to impurities could not be found, indicating that the precursor was completely transformed into Ni₃V₂O₈ metal oxides. The size of the crystallite is estimated by Scherrer's equation.

$$D = 0.9\lambda/\beta\cos\theta$$

Where, β is full width and Half maximum of X-ray diffracted crystalline peaks and λ is indicated as wavelength of X-ray [22]. The estimated average crystallite size is obtained about ~25 nm.

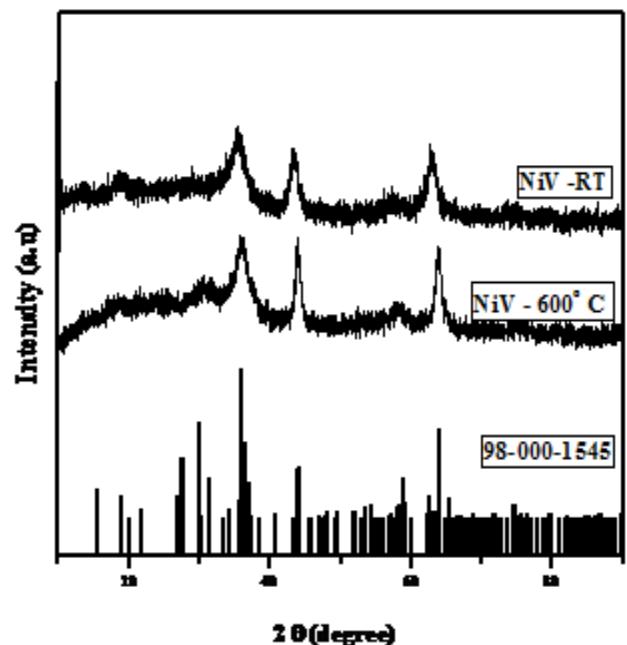


Fig. 1.PXRD pattern of Ni₃V₂O₈, heat treated at various temperatures

B. FTIR

Shimadzu IR Trace-100 spectrometer instrument is used to record the FTIR spectra by the KBr pellet technique. The 400-4000cm⁻¹ range is recorded as shown in Fig.2

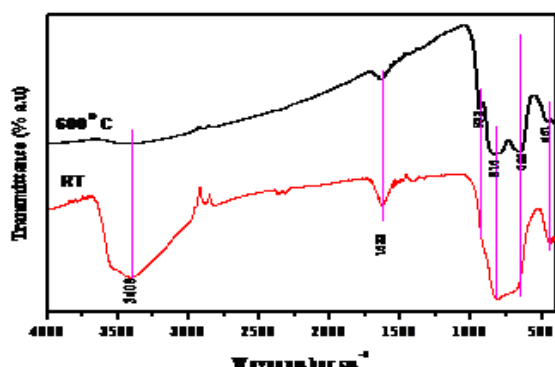


Fig. 2. FTIR spectrum of $\text{Ni}_3\text{V}_2\text{O}_8$, heat treated at various temperatures

The Fig.2, described FTIR spectra of $\text{Ni}_3\text{V}_2\text{O}_8$ nanocomposites at ambient temperature and heat treated for 4h at 600°C . Several IR bands are found to be observed at 3408 cm^{-1} , 1622 cm^{-1} , 932 cm^{-1} , 816 cm^{-1} , 655 cm^{-1} and 461 cm^{-1} [23]. A broad band around 3408 cm^{-1} attributes the stretching mode of OH group which is contributed by adsorbed water molecules. Band formed at 1622 cm^{-1} can be contributed due to OH group in the sample. IR peak at 932 cm^{-1} is obtained corresponds to V-O bond in stretching mode. The band at 816 cm^{-1} and 655 cm^{-1} are ascribed due to symmetric and asymmetric stretching of V-O-V formation. IR band at 461 cm^{-1} is observed indexing the confirmation of the occurrence of crystalline Ni –O bond formation. [22]

IV. CONCLUSION

$\text{Ni}_3\text{V}_2\text{O}_8$ nanoparticle has been successfully synthesized by hydrothermal process. The XRD revealed the orthorhombic phase of $\text{Ni}_3\text{V}_2\text{O}_8$ nanomaterials and verified by JCPDS data. The average crystallite size is calculated as 25nm. No diffraction peaks belonging to impurities could be found, indicating that the precursor was completely transformed into $\text{Ni}_3\text{V}_2\text{O}_8$ metal oxides. The FTIR spectrum confirmed the formation pure metal oxides $\text{Ni}_3\text{V}_2\text{O}_8$.

V. ACKNOWLEDGMENT

The author NNM would like to gratefully acknowledge KARE for constant supporting to this research work. Also, financial assistance from DST-SERB(TARE), India through the Research Project (TAR/2018/001323) is gratefully acknowledged by N. Nallamuthu.

REFERENCES

1. Wang YG, Xia YY, "Electrochemical capacitance characterization of NiO with ordered mesoporous structure synthesized by template SBA-15", *Electrochim Acta*, vol. 51, (2006) pp. 3223–3227.
2. Zhao DD, MW X, Zhou WJ, Zhang J, Li HL "Preparation of ordered mesoporous nickel oxide film electrodes via lyotropic liquid crystal templated electrodeposition route", *Electrochim Acta* vol. 53 (2008) pp. 2699–2705.
3. Xiong SL, Yuan CZ, Zhang XG, Xi BJ, Qian YT "Controllable synthesis of mesoporous Co_3O_4 nanostructures with tunable morphology for application in supercapacitors", *J Chem Eur*, vol. 15 (2009) pp. 5320–5326.
4. Pang H, Yan Z, Wang W, Chen J, Zhang JS, Zheng HH "Facile fabrication of $\text{NH}_4\text{CoPO}_4 \cdot \text{H}_2\text{O}$ nano/microstructures and their

5. primarily application as electrochemical supercapacitor", *Nano* vol. 4 (2012) pp. 5946–5953.
6. Pang H, Liu YY, Li J, Ma YH, Li GC, Ai YN, Chen J, Zhang JS, Zheng HH, "Cobalt phosphite micro architectures assembled by ultra long nano ribbons and their application as effective electrochemical capacitor electrode materials", *Nano*, vol. 5 (2013) pp. 503–507.
7. Pang H, Yan Z, Ma Y, Li G, Chen J, Zhang J, Du W, Li S, "Cobalt pyrophosphate nano/microstructures as promising electrode materials of supercapacitor", *J Solid State Electrochem* vol.17 (2013) pp.1383–1391.
8. Theerthagiri J, Thiagarajan K, Senthikumar B, Khan Z, Senthil RA, Arunachalam P, Madhavan J, Ashokkumar M "Synthesis of hierarchical cobalt phosphate nanoflakes and their enhanced electrochemical performances for supercapacitor applications", *Chem Select*, vol. 2 (2017) pp.201–210.
9. Trasatti S, Kurzweil R "Electrochemical supercapacitors as versatile energy stores", *Platin Met Rev* vol. 38 (1994) pp. 46.
10. ZY L, Yang Q, Zhu W, Chang Z, Liu JF, Sun XM, Evans DG, Duan X "Hierarchical Co_3O_4 @Ni-Co-O supercapacitor electrodes with ultrahigh specific capacitance per area", *Nano Res*, vol. 5 (2012) pp. 369–378.
11. Wang GX, Cai J, HF X, Lu L, Zhao H, "Enhanced capacitance of a NiO electrode prepared in the magnetic field", *J Appl Electrochem* vol. 44 (2014) pp. 391–398.
12. Xu H, Zhuang JX, Li JL, Zhang JL, HL L "Liquid precipitation synthesis of Co_3O_4 for high performance electrochemical capacitors" *Ionics*, vol. 20 (2014) pp. 489–494.
13. Lawes G, Harris AB, Kimura T, Rogado N, Cava RJ, Aharony A, Wohlman OE, Yildirim T, Kenzelmann M, Broholm C, Ramirez AP "Magnetically driven ferroelectric order in $\text{Ni}_3\text{V}_2\text{O}_8$ ", *Phys Rev Lett* vol. 95 (2005) pp. 087205.
14. Wang DF, Tang JW, Zou ZG, Ye J, "Photophysical and photocatalytic properties of a new series of visible-light-driven photocatalysts $\text{M}_3\text{V}_2\text{O}_8$ (M = Mg, Ni, Zn)", *Chem Mater* vol. 17 (2005) pp.5177–5182.
15. He ZZ, Yamaura J, Ueda Y, "Morphologies of $\text{Ni}_3\text{V}_2\text{O}_8$ single crystals", *Cryst Growth Des*, vol. 8 (2008) pp.799–801.
16. Zhaorigetu B, Li WZ, Kieffer R, Xu HY, "Synergetic effect between NiO and $\text{Ni}_3\text{V}_2\text{O}_8$ in propane oxidative dehydrogenation", *React Kinet Catal Lett*, vol. 75 (2002) pp. 275–287.
17. Zheng S, ZS W, Wang S, Xiao H, Zhou F, Sun C, Bao X, Cheng HM "Graphene based materials for high-voltage and high- energy asymmetric supercapacitors", *Energy Storage Mater*, vol. 6 pp. (2017)70–97.
18. Das AK, Sahoo S, Arunachalam P, Zhang S, Shim JJ, "Facile synthesis of Fe_3O_4 nanorod decorated reduced graphene oxide (RGO) for supercapacitor application", *RSC Adv*, vol. 6 (2016) pp. 107057–107064.
19. Justin P, Meher SK, Raob GR, "Tuning of capacitance behavior of NiO using anionic, cationic and nonionic surfactants by hydrothermal synthesis", *J Phy Chem*, vol. 114 (2010) pp.5203–5210.
20. Wang C, Fang D, Wang H, Cao Y, Xu W, Liu X, Luo Z, Li G, Jiang M, Xiong C, "Uniform nickel vanadate ($\text{Ni}_3\text{V}_2\text{O}_8$) nanowire arrays organized by ultrathin nanosheets with enhanced lithium storage properties", *Sci. Rep.*, vol. 6 (2016) p. 20826.
21. Prusty B, Adhikary MC, Das CK "Supercapacitor electrode material based on nickel vanadiumoxide", *JA Chem Sci* vol. 6 (2015) pp. 91–95.
22. Liu MC, Kong LB, Kang L, Li X, Walsh FC, Xing M, Lu C, Maa XJ, Luob YC "Synthesis and characterization of $\text{M}_3\text{V}_2\text{O}_8$ (M= Ni or Co) based nanostructures: a new family of high performance pseudocapacitive materials. *J Mater Chem A* vol. 2 (2014) pp. 4829–5150.
23. A. Shameem, P. Devendran, V. Siva, R. Packiaraj, N. Nallamuthu, S. Asath Bahadur, "Electrochemical performance and optimization of $\alpha\text{-NiMoO}_4$ by different facile synthetic approach for supercapacitor application", *Journal of Materials Science: Materials in Electronics* vol. 30 (2019) pp. 3305–3315.
24. C. O'Dwyer, V. Lavayen, S. B. Newcom, M. A. Santa Ana, E. Benavente, G. González, C. M. Sotomayor Torres, "Vanadate Conformation Variations in Vanadium Pentoxide Nanostructures", *Journal of the Electrochemical Society*, vol. 154 (2007) pp. 1029-1035.