K.L.E Society's

S.NIJALINGAPPA COLLEGE

Re-accredited by NAAC at 'A+' grade with 3.53 CGPA

College with UGC-STRIDE Component-I

II Block, Rajajinagar, Bengaluru. Karnataka-560010. INDIA

Proceedings

IQAC Initiated UGC- STRIDE Sponsored

UGC
University Grants Commission

STRIDE
SCHEME FOR TRANS DISCIPLINARY RESEARCH FOR INDIA'S DEVELOPING ECONOMY

TWO DAY INTERNATIONAL e - CONFERENCE

on

"APPLIED MATERIALS AND TECHNOLOGY - 2020"

held on 9th & 10th October 2020

An Approach to Trans-Disciplinary Research

Organised By

Department of Physics

ISBN: 978-93-5437-097-7

website: www.klesnc.org

E-mail: phyconference@klesnc.org

Author Index

ISBN: 978-93-5437-097-7

KLE Society's
S. Nijalingappa College
II[nd] Block, Rajajinagar, Bengaluru-560010
Re-accredited by NAAC at 'A' grade with 3.53 CGPA
College with UGC STRIDE Component -I

Title:

Proceedings of IQAC Initiated UGC-STRIDE Sponsored Two Days International e-Conference on "Applied Materials & Technology – 2020" An approach to Trans-disciplinary Research

Author's Name: Dr. Arunkumar B. Sonappanavar

Editorial Committee Details:

Sl.No.	Author Details	Designation	Contributor Details
1	Dr. Arunkumar B. Sonappanavar	Principal	Scientific Editor
2	Prof. K. Nagi Reddy	Associate Professor	Associate Editor
3	Dr. Shivananda C S	Assistant Professor	Associate Editor
4	Mrs. Saroja R. Savadatti	Assistant Professor	Member
5	Dr. Indudhar P. Vali	Assistant Professor	Member
6	Mrs. Shreeshmal Bhavya	Assistant Professor	Member
7	Mr. Parameshwar G Gouda	Assistant Professor	Member
8	Mr. Vishal S V	Assistant Professor	Member
9	Ms. Meghana H N	Assistant Professor	Member
10	Mr. Santhosh Kumar M	Assistant Professor	Member

Published By: Self Published

Publisher's Address,

Dr. Arunkumar B. Sonappanavar, Principal, K.L.E. Society's S. Nijalingappa College, 2[nd] Block, Rajajinagar, Bengaluru, Karnataka -560010.

Email: klesncphysics@gmail.com Website: http://www.klesnc.org Tel: 080 2352 6055

Publisher's Details,

Dr. Arunkumar B. Sonappanavar, Principal, K.L.E. Society's S. Nijalingappa College, 2[nd] Block, Rajajinagar, Bengaluru, Karnataka -560010.

Email: klesncphysics@gmail.com Mobile: +919483946362

Printer's Details,

Principal, K.L.E. Society's S. Nijalingappa College, 2[nd] Block, Rajajinagar, Bengaluru, Karnataka -560010.

Edition Details: 1 (First Edition), 2020

ISBN: 978-93-5437-097-7

PRINCIPAL
Sri Jagadguru Renukacharya College
of Science, Arts & Commerce
Bengaluru-560 009.

Reduced graphene oxide Nano sheet Decorated Nb_2O_5 composite for Advanced Energy Storage Material

R. Sandhya[1], M. Mylarappa*[2], S. Kantharaju[2], Rajaiah B[1], Deepushree S.R[1]

[1]*Department of Chemistry, KLE Society's S.Nijalingappa College, Bengaluru-560010.*

[2]*Department of chemistry, Sri Jagadguru Renukacharya College of Science, Arts and Commerce, Bengaluru-560009.*

*Corresponding author: *E-mail address*: mylu4mkallihattu@gmail.com

Abstract

Facile synthesis of rGO-Nb_2O_5 composite for energy storage studies has been reported. Graphene oxide (rGO) was prepared by the modified Hummer's method. The metal oxide (Nb_2O_5) was introduced to the rGO to form the composite by the hydrothermal method. The prepared samples were characterized by X-ray diffraction, scanning electron microscopy, Fourier transform infrared spectroscopy and UV-Visible spectroscopy. The CV measurements reveal a significant enhancement in electrochemical reversibility and the specific capacitance of rGO and Nb_2O_5/rGO were found to be 45 Fg^{-1} and 110 Fg^{-1} respectively. These results indicates that capacitive behaviour and electron transfer of Nb_2O_5/rGO nano composite was predominantly more compared to rGO. The charge-discharge curves display well-symmetry and linear deviations with change of the time indicating superior capacitance. This is mainly because of the electrode reversible reaction and also revealed that as a kind of super capacitor electrode materials. The obtained electrode materials showing the highest specific capacitance with excellent rate capability.

Keywords: rGO, Nb_2O_5/rGO composite, characterization, energy storage studies.

1. Introduction

Industry and research centres around the globe are coping to address the world-wide energy demand and are competing with all available alternative technologies. Super capacitors signify an attractive alternative for portable electronics and automotive applications due to their high specific power and extended life. In fact, the growing demand of portable systems and hybrid electric vehicles, memory protection in complementary metal-oxide-semiconductor (CMOs), logic circuit, vapour-compression refrigeration system (VCRs), CD players, PC's and UPS in security alarm systems, remote sensing, smoke detectors etc. require high power in short-term pulses [1].

Reduced graphene oxide (rGO) - metal oxide nanocomposite is the trending field, with applications in batteries, supercapacitors, tracing and absorption of heavy and toxic elements, photocatalytic dye degradation, fire fighting coatings, biosensors and electroctalysts in oxide fuel cells [2-9]. Many studies have observed rGO nano composite materials decorated with metal and reported that the resulting materials have enhanced properties that are absent in their individual components [10].

The functionalization of metal oxide nanocomposite on the graphene matrix improves the performance of metal oxide nanocomposite, which exhibit properties like agglomeration and Ostwald ripening. The composite of graphene with metal oxides like SnO_2, MnO_2, Co_3O_4, Nb_2O_5, V_2O_5, Fe_2O_3 and RuO_2 have proved the enhancement of electrochemical and psuedocapacitance behaviour by overcoming the limitations such as reduced electrical conductivity, poor electrochemical cycling ability and low specific capacitance. A hybrid system consisting of graphite cathode and Nb_2O_5 anode has been tested for suitability as a hybrid supercapacitor [11-16].

Synthesis of reduced graphene oxide-Nb_2O_5 nanocomposite and its structural, optical and electrochemical properties have been reported. Shishan Qi et al. studied the photocatalytic applications of graphene nanocluster decorated niobium oxide nanofibers [17]. [Nb_2O_5/graphene based pseudo capacitive electrode for asymmetric supercapacitor has been reported by Kong et al. with a specific capacitance value of 80 Fg^{-1} at 0.2 Ag^{-1} [18]. Wang et al. reported the fabrication of hybrid electrochemical capacitor with binder-free Nb_2O_5 graphene and studied the electrochemical characteristics with the discharge specific capacity of 58 Fg^{-1} at 0.1 Ag^{-1} [19]. Nb_2O_5 anchored graphene nanosheets organic hybrid have been

synthesized with low amount of graphene content with the capacitance value of 34 Fg^{-1} at 0.05 Ag^{-1} [20].

In the present investigation, the synthesis of rGO-Nb_2O_5 nanocomposites by hydrothermal method has been presented. This method resulted in the formation of homogeneous composite with uniform distribution of Nb_2O_5 on the graphene surface. The structural, optical and electrochemical properties of the rGO-Nb_2O_5 nanocomposites were systematically studied and the results were compared with pure graphene and Nb_2O_5 nanoparticles.

2.1 Materials and Method

2.1.1 Materials

The materials used for the entire work with all the specifications, purity, grades, structural and chemical formulas with suppher names are mentioned in the Table 1.

Table 1. Details about the chemicals used

Materials	Formula	Specifications	Suppliers
Sodium Nitrate	$NaNO_3$	Molar mass: 84.9g/mol	Merck, Bangalore
Sulphuric acid	H_2SO_4	Molar mass: 39.9 g/mol	Sigma Aldrich
Hydrogen peroxide	H_2O_2	Molar mass: 34.01 g/mol	Merck, Bangalore
Potassium permanganate	$KMnO_4$	Molar mass: 158.0 g/mol	Merck,Bangalore
Niobium chloride	$NbCl_5$	Molar mass: 270.17g/mol	Sigma Aldrich
Tri-Sodium citrate	$Na_3C_6H_5O_7$	molar mass:294.10 g/mol	Merck
Sodium Sulphite	Na_2SO_3	molar mass: 126.0 g/mol	Merck, Mumbai

2.2 Experimental

2.2.1 Synthesis of Graphene Oxide (GO)

Graphene oxide (GO) was prepared by 1g $NaNO_3$ and 2g of graphite powder was added to 1000ml beaker which was placed in ice bath and temperature was maintained from 0-6°C.

Then 98% H_2SO_4 was added to it slowly. The reaction mixture with ice bath was kept on magnetic stirrer with constant stirring. Accurately 6g of $KMnO_4$ was added very slowly in instalments with duration of 3 hours. While adding $KMnO_4$ the mixture starts to spill and effervescence is observed therefore caution must be taken to avoid explosion. After 2 hours the beaker was removed from ice bath and was placed on a hot plate with magnetic stirrer and temperature was maintained at 30 C. The colour slowly changes to brownish black and the temperature was increased every half an hour. After 2 hours add 100 ml of H_2O with constant stirring and by turning off heat. Then 80 ml H_2O_2 was added to terminate the reaction and to remove excess $KMnO_4$. When ppt. settles down yellow colour solution is obtained. The obtained solution was filtered using Buckner funnel and then placed in hot air oven at less than 90°c overnight.

2.2.2 Preparation of Nb_2O_5/rGO nanocomposites

In a typical synthesis process, 0.3 g of the reduced graphene oxide was dispersed in distilled water and sonicated for 3 h. Then 0.1 g of $NbCl_5$ was added and stirred using a magnetic stirrer. After 1 h, 1% sodium citrate was boiled for 55 minutes and 100 mg of sodium sulphite in 5 ml of distilled water were added to the solution and stirred for 3 hours, cooled to the room temperature.The solution was filtered using a Wattman filter paper and the product washed with distilled water and ethanol for several times. The prepared composite solution was dried in vacuum at 333K for 24 h to obtain the rGO-Nb_2O_5 nanocomposite.

3. Result and Discussion

3.1. X-Ray Diffraction Studies

The phase composition and the crystallinity of the powder was detected by X-ray diffractometer using the Shimadzu-7000 X-ray diffract meter with monochromatized Cu Ka radiation. The XRD of rGO, Nb_2O_5 and Nb_2O_5/rGO were shown in Fig. 4.1 a) to Fig. 4.3 c). The average crystallite sizes of particles were assessed in agreement with Scherer's equation using full width at half maximum (FWHM) evidence.

$$D = \frac{0.9\,\lambda}{\beta \cos\theta} \ldots\ldots (1)$$

where K: constant depends on the grain shape (about 0.90), λ: the X- ray wavelength (0.15418 nm), β: the full width at half maximum (FWHM) of the diffraction line and θ: the diffraction angle.

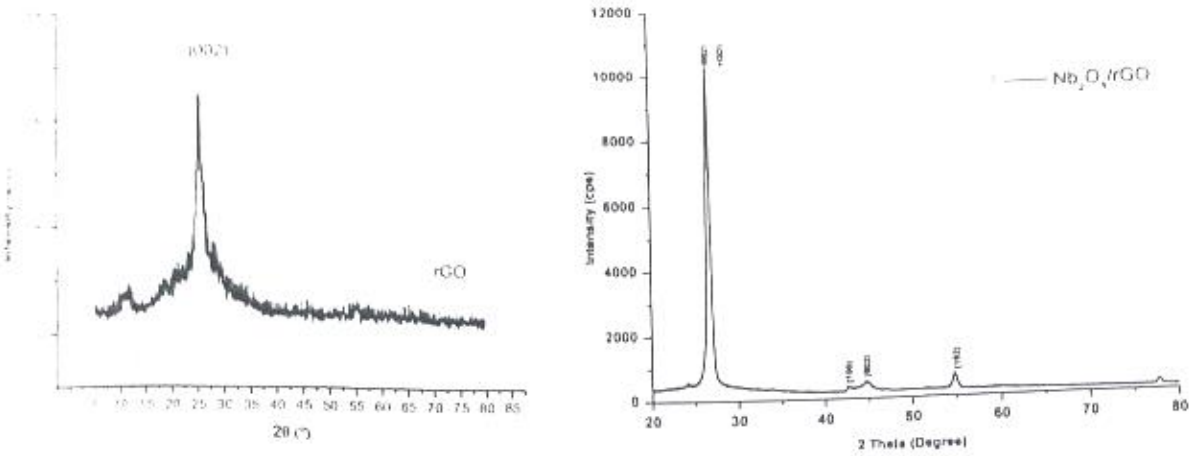

Fig 1 XRD spectrum of a) graphene oxide b) Nb_2O_5/rGO.

The calculated mean crystallite size of the rGO, Nb_2O_5 and Nb_2O_5/rGO were found to be 14, and 9.8 nm. The peaks shown in the XRD pattern of Nb_2O_5/rGO are intense and sharp, presenting good crystallinity of the prepared sample. No evidence of impurity peaks was noted, which indicated that high pureness. The strong and narrow peak signifies that the product has well crystalline nature of particles. The Scherer's equation and Williamson and Hall (W-H) method were used to calculate the total crystalline sizes of rGO, Nb_2O_5 and Nb_2O_5/rGO. The W-H method recommended that when the domain effect and lattice micro strain effect were together concurrently working, their mutual effects gives the final line broadening FWHM which was the sum of grain size and lattice distortion.

$$\beta\cos\theta = \varepsilon(4\sin\theta) + \frac{\lambda}{D} \qquad (2)$$

The equation (2) indicates a straight line between 4sinθ and βcosθ whereε; the strain associated with the nano composites. The intercept (0.90λ/D) of the line gives crystallite size (D) and slope of line gives the strain (ε). The values obtained from above equation were analogous with the crystallite size calculated from Scherer's equation. The other structural

parameters such as dislocation density (δ), strain (ε) and stacking fault (SF) were controlled by the accompanying connection. The dislocation density and stacking fault were estimated by using the following relations.

$$\delta = \frac{1}{D^2} \quad (3)$$

$$\varepsilon = \frac{\beta \cos\theta}{4} \quad (4)$$

$$SF = \frac{2\pi^2}{45\sqrt{3}\tan\theta} \quad (5)$$

3.2 Field Emission Scanning Electron Microscopy and EDS Studies

The energy-dispersive X-ray (EDX) analyses were obtained for as prepared materials to confirm the existence of Niobium, Oxygen and Carbon as the elementary components in the morphology of the prepared composites was studied by Field emission scanning electron microscope (FE-SEM) and the images are shown in Fig.2. The morphology of Nb_2O_5/rGO composite contains graphene sheets and it is observed that Nb_2O_5 is intercalated between the graphene sheets as shown in Fig.2. Higher magnification image confirms the paper like structure of graphene with Nb_2O_5 attached on the surface. The increase in the graphene weight percent causes the aggregation of Nb_2O_5 with graphene and hence graphene structure becomes irregular flake-like morphology as shown in the magnified image.

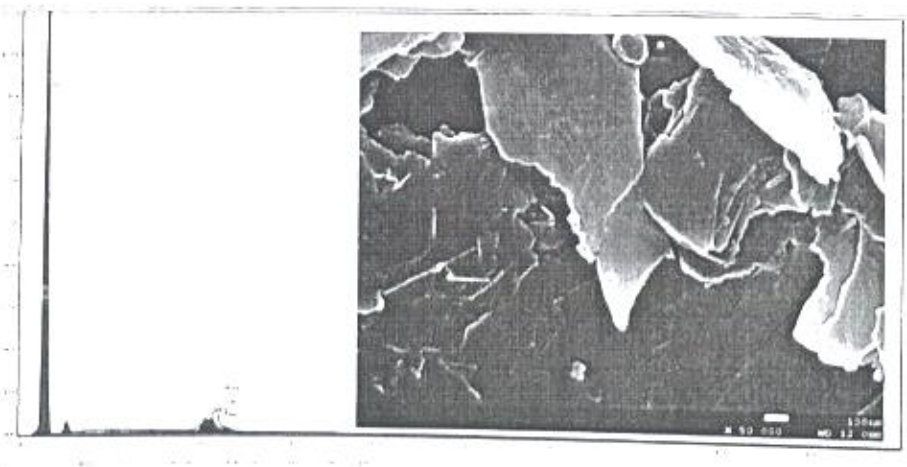

Fig 2 EDAX/FESEM micrographs of Nb_2O_5/rGO nano composite

3.3 Fourier transforms infrared spectrometer studies

FT-IR measurements was carried out to obtain further insights on Nb_2O_5/rGO nanocomposites as shown in Fig.3. The broad band observed at ~3430 cm^{-1} for the as-synthesized samples corresponds to the O–H stretching vibration of physically adsorbed water and or intercalated water molecules in the GO and rGO nanocomposites. Other FT-IR peaks at 1724 cm^{-1} (C=O stretching vibration of –COOH group), 1624 cm^{-1} (C=C stretching vibration), 1231 cm^{-1} (C–O stretching vibrations in epoxide), 1084 cm^{-1} (C–OH stretching vibration in alkoxy group). The FT-IR spectrum of Nb_2O_5 shows a band at 510 cm^{-1} attributed to the Nb-O vibration of the Nb_2O_5 crystal.

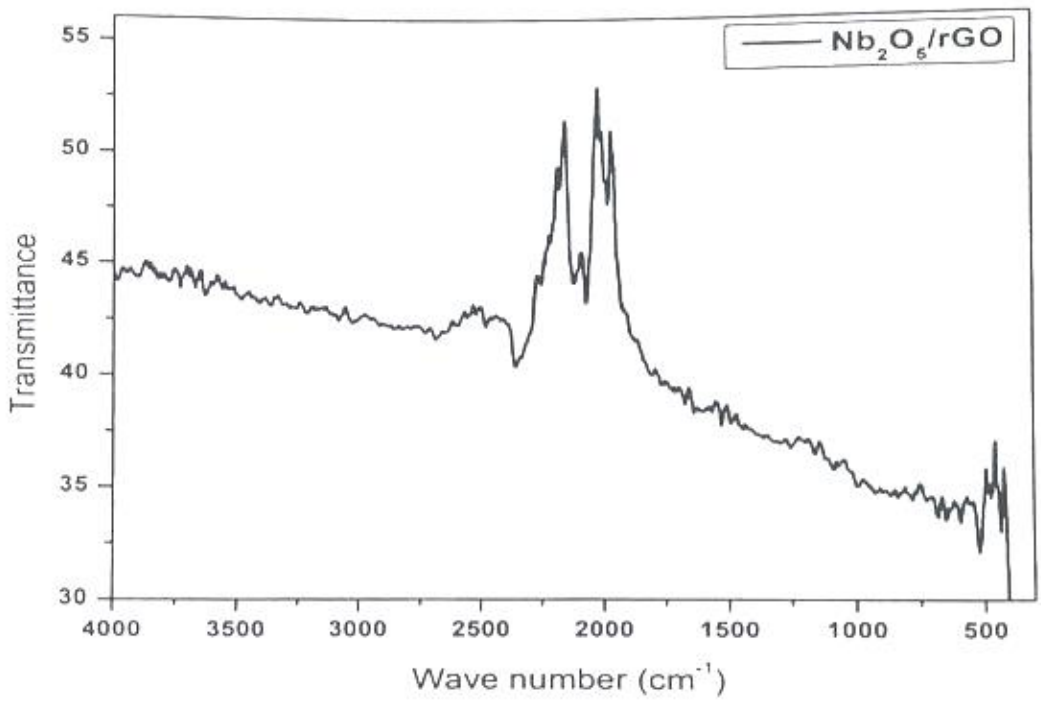

Fig 3 EDAX/FESEM micrographs of Nb_2O_5/rGO nano composite

3.4 Band gap analysis

In the present case optical studies of the unirradiated and electron irradiated films were carried out in the wavelength range 190-700 nm. Here for any set of measurements, first the wavelength scan is performed without the sample as reference in the beam path and then the samples are placed within the sample holder having a hole of 2 mm diameter and kept in the

4. Electrochemical Studies

4.1. Cyclic Voltammetry studies

In the CV analysis, the working electrode (Nb_2O_5/rGO) was prepared by mixing 0.025 g of active material + 0.475 g of graphite + 3-5 drops of polytetrafluoroethylene (PTFE) solution which was added as a binder and blended by hand mixing with a mortar and pestle for about 30 minutes until a uniform thin sheet achieved. The obtained thin sheet was pressed on nickel mesh (area about 1 cm^2) to create a good conductivity with the Ni mesh and active material. The obtained electrode was dried at 50° C for 48 hours and the prepared electrodes were kept for 20 days electrode setting because for stability of the electrode as shown in Fig.5.

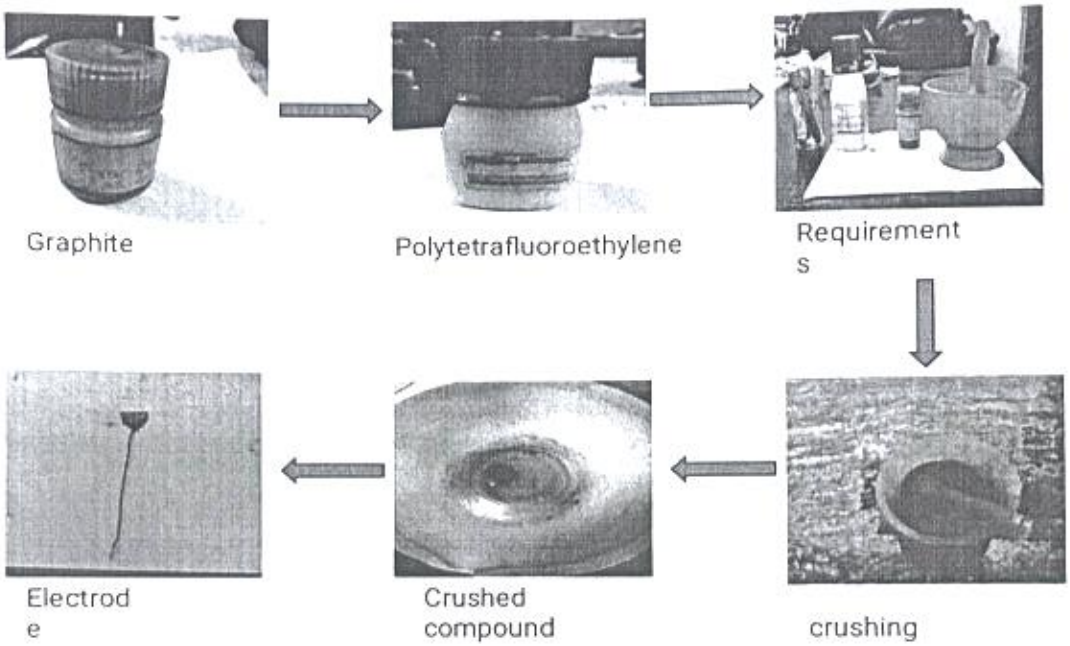

Fig 5 Method of Preparation of working electrode using graphite and binder.

An electrochemical measurement comprises three electrode system having active material, Ag AgCl electrode and a platinum as counter electrode. CV measurements were applied in the potential range -0.6 to 0.02 V using 3M KOH as shown in the Fig.6 a) and Fig.6 b). In Fig.6 a) and Fig.6 b). the electrochemical reversibility was calculated by seeing of the difference between the E_O and E_R at 0.01 V/s scan rate. The results revealed that the electrode

reversibility reaction of Nb_2O_5 rGO (Table 2) was decreased as compared to that of rGO and CV curves displays a quasi-reversible electron transfer process representing that capacitive behaviour was predominantly based on the redox mechanism. According to the Randles-Sevcik equation for reversible process, the height current is denoted by the equation.

$$Ip = 2.69 \times 10^5 \times n^{3/2} \times A \times D^{1/2} \times C_0 \times v^{1/2}$$

where n is the number of electron transferred in the reaction, the active surface area (A), diffusion co-efficient (D), scanning rate (v) and initial concentration of the chemical (C_0) respectively. The greater linear association involving in peak current (ip) and number of electron transferred ($n^{3/2}$) confirm that the electrode reaction of rGO and Nb_2O_5/rGO was measured by hydrogen diffusion co-efficient (D). The increased D values of Nb2O5/rGO revealed that electrochemical activity are more effective compared to that of rGO respectively.

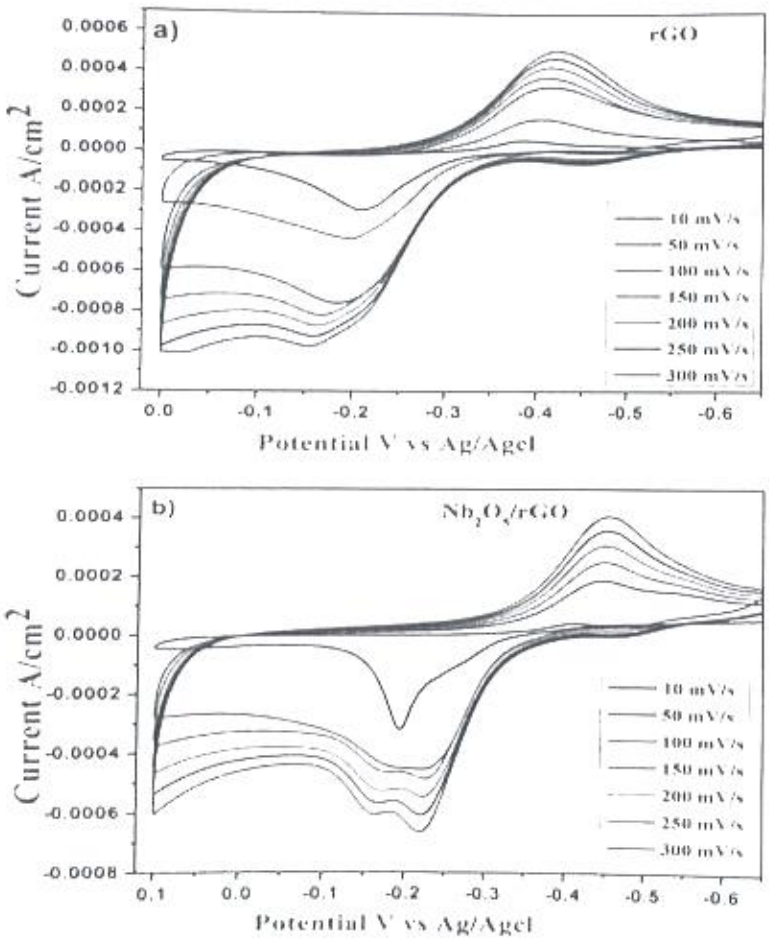

Fig.6. CV curves of a) rGO b) Nb_2O_5/rGO

$$\int_{V1}^{V2} I\,(V)dV = \int_{V1}^{V2} (Cp \times m \times k)dV$$

If we look above equation integrate the left side

$\int_{V1}^{V2} I\,(V)dV$ = Area represents the area of the CV at the centre

I (V) × dV = Y × X Area

∴ the equation (4) becomes

Area = $\int_{V1}^{V2}(Cp \times m \times k)dV$ – (5) for specific material the Cp, m,k constant

∴ the integral equation (5) becomes solved as

Area = (V_2-V_1) Cp × m × k

During the charging of capacitor then the Area A and the equation becomes

$A_1 = (V_2-V_1)$ Cp × m × k

Simillarly, during discharging capacitor the area A and the equation becomes

$A_2 = (V_2-V_1)$ Cp × m × k

From the calculations of area A inside the CV curve we have to susbtitute equation (3.9) from equation (3.10)

$A = A_1-A_2 = [(V_2-V_1)$ Cp × m × k $] - [(V_1-V_2)$ Cp × m × k $]$

$A = 2\,(V_2-V_1)$ Cp × m × k]

$\frac{A}{2} = (V_2-V_1)$ Cp × m × k

$\frac{A}{2\,(V2-V1)\,m \times k} = Cp$ Or $Cp = \frac{A}{2\,m\,k(V2-V1)}$

where Cp = Specific capacitance F g⁻¹, A = Area inside the CV curve unit AV

PRINCIPAL
Sri Jagadguru Renukacharya College
of Science, Arts & Commerce
Bengaluru-560 009.

m = mass of active, k = scan rate of material CV (total range) is the potential difference window of CV (total voltage range) we will have equation can be used. In Fig 6 a)-b), the specific capacitance values of rGO and Nb_2O_5-rGO were calculated and found to be 45 Fg^{-1} and 110 Fg^{-1} respectively.

5. Conclusion

rGO-Nb_2O_5 nanocomposite was successfully prepared by hydrothermal method. The morphology and structure of the composite were studied by XRD, FESEM-EDS and CV analyses. From electrochemical studies, the specific capacitance values of rGO and Nb_2O_5-rGO was found to be 45 Fg^{-1} and 110 Fg^{-1} respectively.

Acknowledgment

The authors' thanks to the Sri Jagadguru Renukacharya Education Society (SJRES) and Principal of SJRC for their encouragement in extending the lab facilities for completion of the research work.

References

[1] Humberto Gómeza, Manoj K. Ramb, Farah. Alvia, P. Villalba, Elias (Lee) Stefanakosc, Ashok Kumara, J. Power Sources. 196 (2011) 4108.
[2] X. Zhu, Y. Zhu, M. Shanthi, M.D. Stoller, S. Rodney J. Ruoff, Power Sources. 196 (2011) 6473. .
[3] I.T. Kim, A. Magasinski, K. Jacob, G. Yushin, R. Tannenbaum, Carbon. 52 (2013) 56.
[4] H. Yang, J. Jiang, W. Zhou, L. Lai, L. Xi, Y. M. Lam, Z. Shen, B. Khezri, T. Yu, Nanoscale Res. Let. 6 (2011) 1.
[5] A.K. Mishra, S. Ramaprabhu, J. App. Phy.112 (2012) 104315.
[6] B.P. Sahoo, S. Sahoo, A.K. Satpati, D. Li, D. Bahadur, Biosensors and Bioelectronics. 43 (2013) 293.
[7] S. Guo, G. Zhang, Y. Guo, J.C. Yu, Carbon. 60 (2013) 437.
[8] C. Bao, L. Song, C.A. Wilkie, B. Yuan, Y. Guo, Y. Hu, and X. Gong, J. Mat. Chem. 22 (2012) 16399.
[9] W. Hong, H. Bai, Y. Xu, Z. Yao, Z. Gu, G. Shi, J. Phys. Chem. C. 114 (2010) 1822.
[10] V. Goyal, A.A. Balandin, Appl. Phys. Lett. 100 (2012) 073113-1.
[11] F. Li, J. Song, H. Yang, S. Gan, Q. Zhang, D. Han, A. Ivaska, L. Niu, Nanotech. 20 (2009) 455602. [21] S. Chen, J. Zhu, X. Wu, Q. Han, X. Wang, ACS. Nano. 5 (2010) 2822.
[12] K. SengáTan, C. MingáLi, Phy. Chem. Phy.13 (2011) 14462.

[13] R. Thangappan, S. Kalaiselvam, A. Elayaperumal, R. Jayavel, Solid State Ionics, 5 (2014) 15321.
[14] K.K. Lee, S. Deng, H.M. Fan, S. Mhaisalkar, H.R. Tan, E.S. Tok, K.P. Loh, W.S. Chin, C.H. Sow, Nanoscale 4 (2012) 2958.
[15] Minoh Lee1, Suresh Kannan Balasingam, Hu Young Jeong, Won G. Hong, Han-Bo-Ram Lee,Byung Hoon Kim & Yongseok Jun. 5 (2015) 8151.
[16] Gum-Jae Park, D. Kalpana, AK. Thapa, H. Nakamura, Y.S Lee, M.Yoshio, Bull. Korean Chem. Soc. 30 (2009) 817.
[17] S. Qi, L. Fei, R. Zuo, Y. Wang, Y. Wua., J. Mater. Chem. A, 2 (2014) 8190.
[18] L. Kong, C. Zhang, S. Zhang, J. Wang, R. Cai, C. Lv, W. Qiao, L. Linga D. Long, J. Mater. Chem. A. 2 (2014) 17962.
[19] L.P. Wang, L. Yu, R. Satish, J. Zhu, Q. Yan, M. Srinivasan, Z. Xu, RSC Adv. 4 (2014) 37394.
[20] P. Arunkumar, A.G. Ashish, B. Babu, S. Sarang, A.Suresh, C.H. Sharma, M. Thalakulama, M. M. Shaijumon, RSC Advances. 5 (2014) 59997.