

Synthesis and Characterization of rGnO/Ni(OH)₂ and rGnO/NiO Nano Composites

H.S.I. Feranando^{1,2}, N.D.Bandara², D.D.N.B Daya², M.T.V.P. Jayaweera¹, and
I.R.M. Kottegoda¹

¹*Materials Technology Section, Industrial Technology Institute, Colombo 07, Sri Lanka*

²*Department of Physics, University of Colombo, Colombo 03, Sri Lanka.*

ABSTRACT

Reduced graphene oxide (rGnO) is a nano material which has exerted interest in many researches due to its unique properties such as high surface area, stability, conductivity and flexibility. Recently much attention has been paid on preparation of nanocomposites using rGnO with a view to enhance properties in various applications. Combination of rGnO with other materials such as Ni(OH)₂ and NiO results in the formation of nanocomposites which may improve the properties of individual rGnO, Ni(OH)₂ and NiO. A novel, easy, time and cost efficient synthesis methods for rGn/Ni(OH)₂ and rGnO/NiO is presented here which can also be used in bulk production. The composites were characterized using X-Ray Diffraction Spectroscopy (XRD), Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR). The broad peaks of the XRD analysis suggests that the Ni(OH)₂ and NiO particles with smaller size are formed and the FTIR confirms the formation of rGnO. The SEM images show the morphology of rGnO. The composites contains a minority of functional groups such as OH, NH and C=O in small quantities.

1. INTRODUCTION

The world is in an extensive demand for energy thus efficient energy control should be accomplished via improved methods. Nanotechnology has conglomerated with the industries by providing novel material with exciting properties to address the above requirement and other properties which had not been exploited so far are being identified in the effort.

Graphene is one such recently identified nanomaterial that is utilized and can be utilized in a diversified product portfolio due to its high conductivity and ultrahigh specific surface area, as well as excellent mechanical properties [1]. It is demonstrated that Graphene is a one-atom-thick sheet of sp²-bonded carbon atoms in a honeycomb crystal lattice. It is the thinnest known material in the world and conceptually a basic building block for constructing many other carbon materials [2].

Ni(OH)₂ and NiO are two crystalline structures that are subjected to research for ages with interest. Ni(OH)₂ is an important material for its wide applications in batteries, fuel cells, electrochemical supercapacitors, electrolyzers, solar cells and electronic devices. NiO has attracted increasing attention owing to potential use in a variety of applications such as catalysis, battery cathodes, gas sensors, electromagnetic filters and magnetic material[3]. Most attracting features of NiO are its excellent durability and electrochemical stability, low material cost, promising ion storage material in terms of cyclic stability, large span optical density and possibility of manufacturing by variety of techniques[4]. Because of the volume effect, the quantum size effect, the surface effect

and the macroscopic quantum tunnel effect, nanocrystalline NiO is expected to possess many better properties than those of micro-metre sized NiO particles [5].

Graphene can improve the fast electron transfer to a great extent especially as a conductive additive into the Ni(OH)₂ electrode [6]. Graphene is an excellent 2D support to load polymers and other nano particles [7].

The present work provides a novel, simple, cost efficient, time preserving one pot method of synthesis of rGnO/Ni(OH)₂ and reduced rGnO/NiO composites.

2. EXPERIMENTAL

2.1 Synthesis of Reduced Graphene Oxide

Graphite used was in powder form (~38 μm) obtained from Kahatagaha graphite mine, Sri Lanka. The reagents and chemicals H₂SO₄, H₃PO₄, HCl, KMnO₄, H₂O₂, absolute ethanol and ether were of analytical grade and were produced by Sigma-Aldrich Co., USA and Superchem Products Ltd, England.

First, graphite oxide (GO) was obtained from natural graphite following the improved method obtained by Marcano et al in 2010 [8].

3 g of Graphite were dissolved in 360 ml of 37% sulphuric acid (H₂SO₄) and 40 ml of phosphoric acid (H₃PO₄). Then 18 g of potassium permanganate (KMnO₄) was added at 40°C while the solution was stirred using a magnetic stirrer. It was stirred for 28 hrs at 50°C temperature. Then the solution was allowed sufficient time to acquire room temperature after which ice made of 500 ml of distilled water and 50 ml of 30% hydrogen peroxide (H₂O₂) were added to the solution and stirred for 18 hrs. Then the mixture was centrifuged at 3900 rpm for 5 mins and the precipitate was washed with distilled water, hydrochloric acid (HCl) and ethanol respectively. Finally it was washed with ether until the supernatant became a flocculent precipitate and was vacuum dried at 60°C overnight to obtain GO. The obtained GO was heated to 400°C in Argon to obtain rGnO.

2.2 Synthesis of rGn/Ni(OH)₂ Composite

The chemicals NiCl₂.6H₂O (98%) and ammonia solution were produced by Sigma Aldrich Co., USA. rGnO was prepared as described in section 2.1.

268 mg of NiCl₂ and 200 mg of rGnO were dissolved in 350 ml of distilled water. The mixture was sonicated for 15 min. Then ammonia solution was added drop wise for about 1 1/2 hr while stirring rigorously with a magnetic stirrer at the temperature 55°C – 60°C until the pH of the mixture reached the value 9. The solution was further stirred for 30 min. Next, the supernatant was decanted away and the precipitate was washed three times with distilled water and twice with ethanol. The precipitate was oven dried for 3 hr at 90°C. (Sample 1).

2.3 Synthesis of rGn/NiO Composite

The above synthesized rGn/Ni(OH)₂ was Argon purged at 550°C for 1 hr at a flow rate of 0.5 l min⁻¹ (Sample 2).



Figure 1: The main conversions at the synthesis process of sample 1

2.4 Characterization

The composites were subjected to X-ray diffraction (XRD) characterization with Regaku ultima VI, X-ray Diffractometer to identify the crystalline phase contained in the composite. $\text{Cu K}\alpha$ ($\lambda=1542 \text{ \AA}$) radiation was incident on the sample and the crystallographic information were obtained as per the Inorganic Crystal Structure Database(ICSD). Scanning Electron Microscopic (SEM) test was used to obtain the surface morphology information of the samples and SEM were obtained using a LEO 1420 vp Scanning Electron Microscope. The scanning was undertaken to the limit of the maximum available resolution of the instrument. The Fourier Transform Infrared spectroscopy (FTIR) was carried out using a Bruker Tensor 27 to determine type of the atomic bonding in composites.

3. RESULTS AND DISCUSSION

3.1 X-Ray Diffraction Pattern Analysis (XRD)

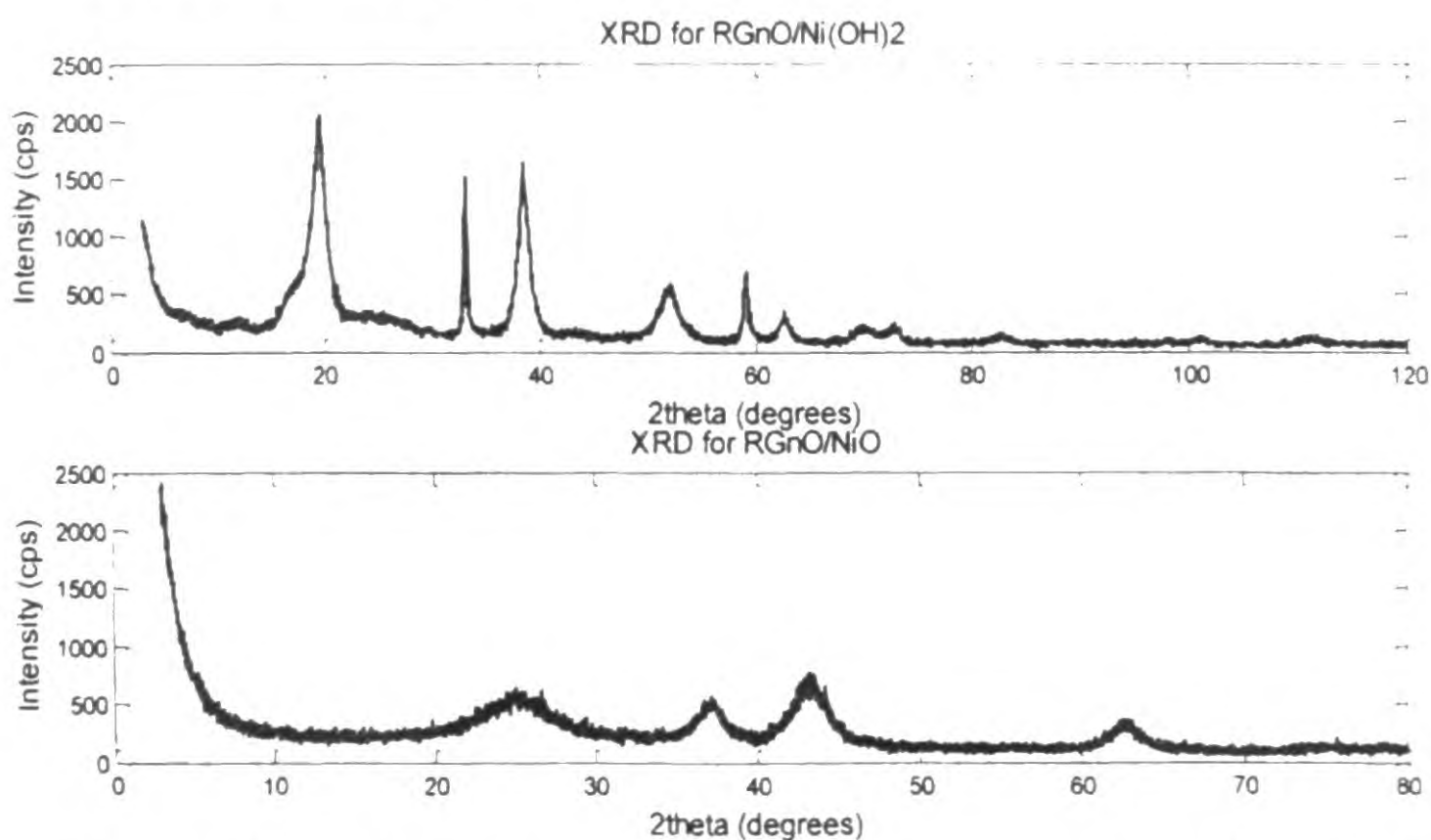


Figure 2: The X-Ray diffraction pattern corresponding to rGnO/Ni(OH)_2 and rGnO/NiO composites

The XRD can be used to identify the formation of composites with rGnO. Figure 2 represents the XRD pattern corresponding to rGnO/Ni(OH)₂ and rGnO/NiO nanocomposites. The peak at $2\theta = 26^\circ$ obtained for rGnO/NiO sample corresponds to rGnO which suggested that rGnO had not been subjected to any deformations as a result of the synthesis process of the composite and hence it can be further justified that reduced graphene oxide is stable. However the peak at $2\theta = 26^\circ$ is not visible for rGnO/Ni(OH)₂ presumably due to overlapping of the peak corresponds to Ni(OH)₂. The peaks corresponding to $2\theta = 19.23^\circ, 33.03^\circ, 38.50^\circ, 52.03^\circ, 58.98^\circ, 62.65^\circ$ attributable to the miller indices (0 1 1), (1 0 0), (0 1 1), (0 1 2), (1 1 0), (1 1 1) respectively of sample 1 suggest the existence of Ni(OH)₂ and the peaks at $2\theta = 37.20^\circ, 43.20^\circ, 62.87^\circ$ attributable to miller indices (1 1 1), (2 0 0), (2 2 0) respectively in sample 2 confirms the existence of NiO. The broad diffraction peaks suggest that the crystallites are smaller in size as per the Scherrer Equation published by Paul Scherrer in 1918 in which the intensity is inversely proportional to crystal size[9]. The nonexistence of NiCl₂ and Ni peaks confirms that the synthesis method is complete and controlled properly.

3.2 Scanning Electron Microscopy(SEM)

The morphology of the nanocomposites was viewed through SEM and it clearly demonstrates the ripples of reduced graphene oxide. Ni(OH)₂ particles were not clearly visible even though the maximum possible magnification was exercised. This could have been due to the minority of Ni(OH)₂ particles present with respect to rGnO and/or due to the nano scale particle formation.

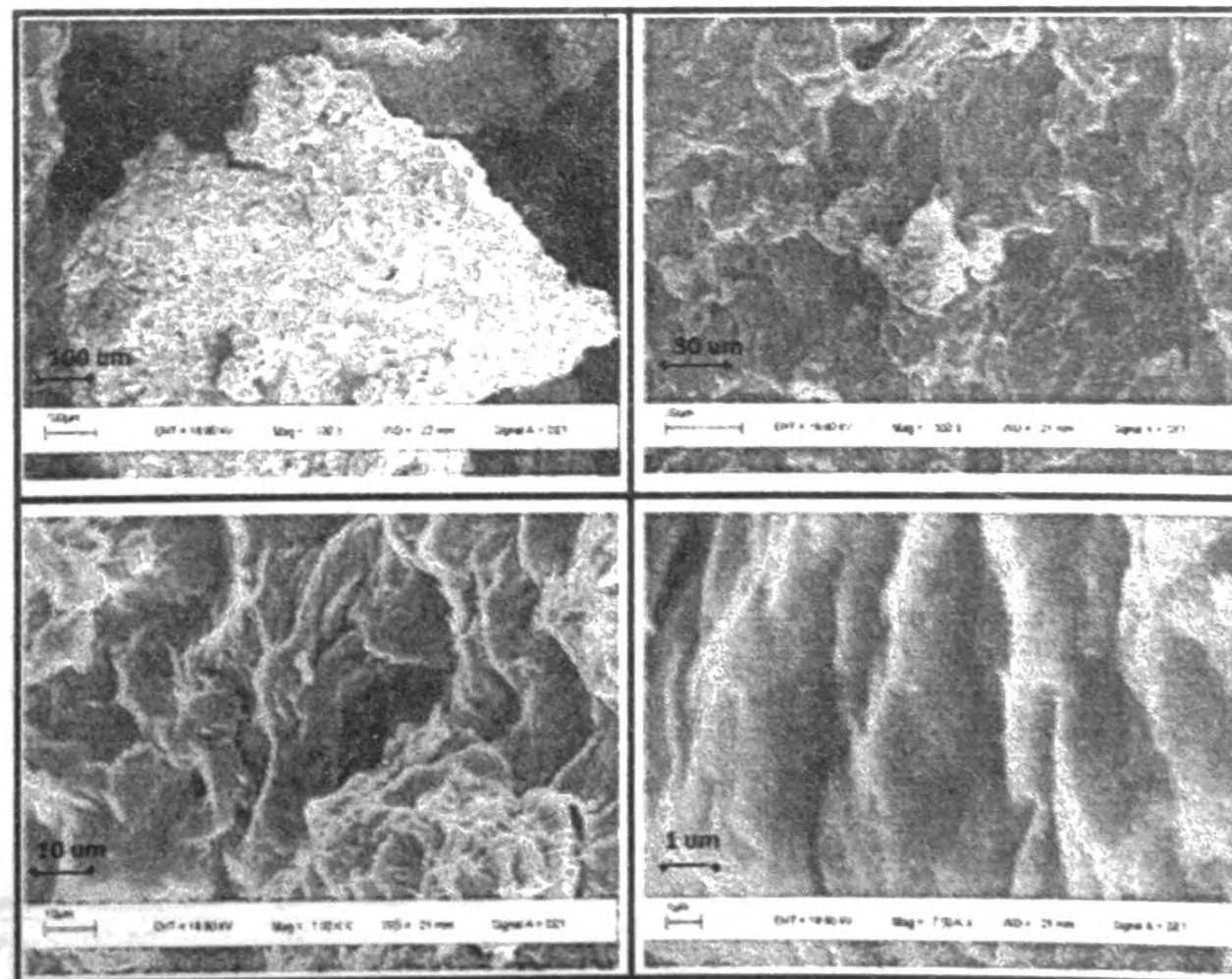


Figure 3: The SEM observations for rGnO/Ni(OH)₂ at different magnifications

3.3 FOURIER TRANSFORM INFRARED SPECTROSCOPY(FTIR)

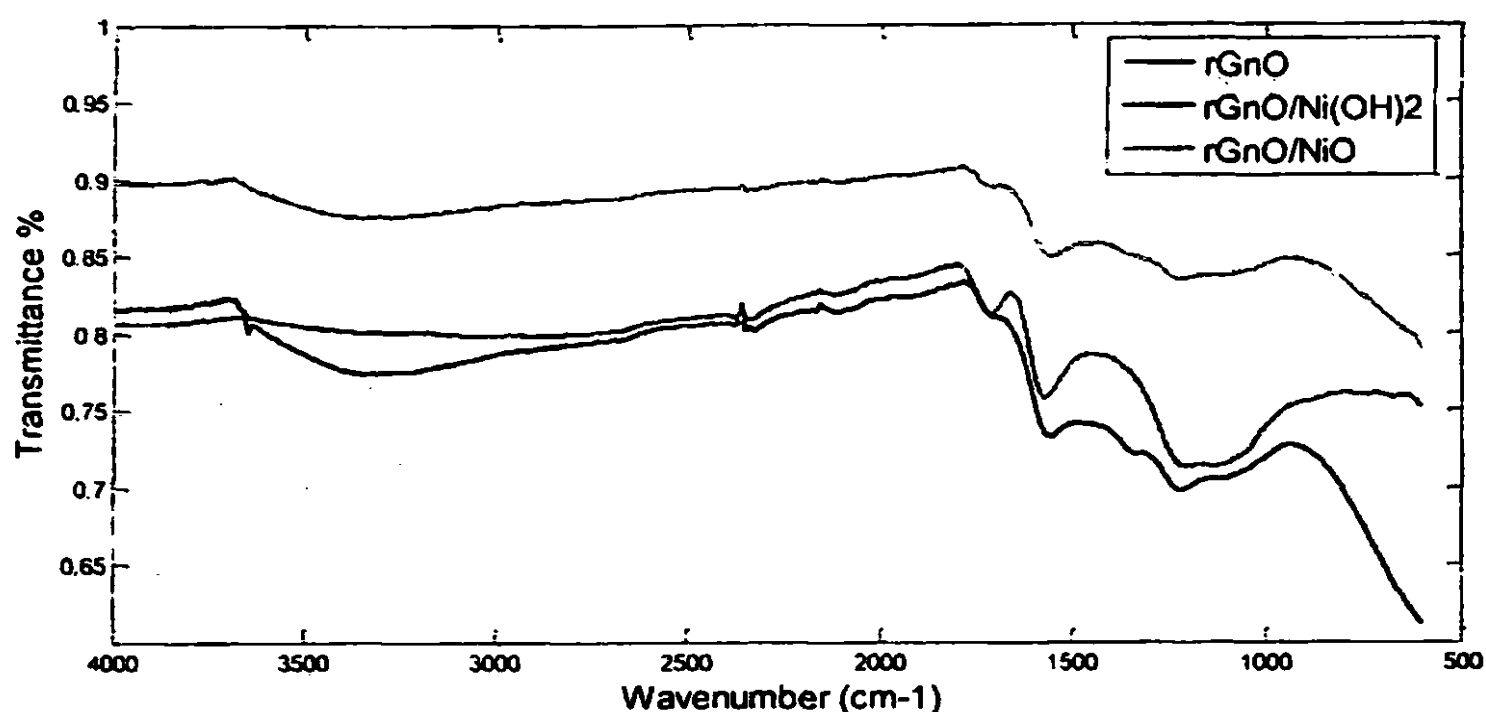


Figure 4: The Fourier Transform Infrared Spectroscopy for rGnO, rGnO/Ni(OH)₂ and rGnO/NiO

FTIR Spectroscopy was used to identify the formation of the nanocomposites and the presence of the functional groups [10]. The broad peak ranging from 3800–2200 cm^{-1} is attributable to O–H stretching vibrations of absorbed water molecules and structural OH groups indicating high inclusion and/or attachment of water. The peak in the low frequency region close to 1610 is attributable to O–H vibrations of water. The peaks for the functional groups, such as C=O (1714 cm^{-1}), C–OH (1368 cm^{-1}), and C–O (1060 cm^{-1}), were observed in all samples with different intensities, demonstrating that those functional groups have been reduced completely. The band ranging from 3800–2200 cm^{-1} (O–H stretching vibration) is reduced in rGnO and rGnO/NiO samples but not reduced in rGnO/Ni(OH)₂, probably due to the vibrations of OH groups in rGnO/Ni(OH)₂. The peak at about 1574 cm^{-1} in all samples reflects the skeletal vibration of (C–C), suggesting that reduced graphene oxide is formed in all samples.

The peaks corresponding to Ni(OH)₂ and NiO are at $\sim 500 \text{ cm}^{-1}$ which is a range beyond the capacity of the instrument. The introduction of a peak near the above value in the composites vis a vis to rGnO sample provides a possibility of such existence [11]. However, the presence of NiO and Ni(OH)₂ was clearly verified by XRD.

4. CONCLUSION

The composites rGnO/Ni(OH)₂ and rGnO/NiO synthesized using the exclusive method discussed above, satisfy the expected composite formation and hence have the major advantage of demonstrating high performance in various applications. The method is time preserving and cost efficient hence suitable for bulk production as well. These composites may be suitable for various applications such as in batteries, electrolyzers and solar cells. Efforts are being made in using for applications such as in supercapacitors which is still in progress.

ACKNOWLEDGEMENT

The authors are grateful for the financial support and other facilities provided by the University of Colombo, Sri Lanka and the Industrial Technology Institute, Sri Lanka.

REFERECES

- [1] L. Niu, J. Wang, W. Hong, J. Sun, Z. Fan, X. Ye, H. Wang and S. Yang, *Solvothermal Synthesis of Ni/Reduce Grappene Oxide Composites as Electrode Materials for Supercapacitors*, *Electrochimica Acta*, 123 (2014) 560-568.
- [2] Zhong-Shuai Wua,b,1, Guangmin Zhoua,1, Li-Chang Yi, *SciVerse ScienceDirect*, Graphene/metal oxide composite electrode materials for energy storage, 1 (2011) 107-131.
- [3] M. El-Kemary, N. Nagy and I. El-Mehasseb, *Materials Science in Semiconductor Processing*, NiO nanoparticles: synthesis and spectral studies of interactions with glucose, 16 (2013) 1747-1752.
- [4] P. Patil and L. Kadam, *Applied Surface Science*, Preparation and characterization of spray pyrolyzed nickel oxide (NiO) thin films, 199 (2002) 211-221,.
- [5] X. Deng and Z. Chen, *Materials letters*, Preparation of nano-NiO by ammonia precipitation and reaction in solution and competitive balance, 58 (2003) 276-280.
- [6] S. Min, C. Zhao, G. Chen and X. Qian, *One-pot hydrothermal synthesis of reduced graphene oxide/Ni(OH)₂ films on nickel foam for high performance supercapacitors*, *Electrochimica Acta* 115, 115 (2014) 155-164.
- [7] S.J.Li, J.Z.He, M.J.Zhang, R. Zhang, X. Lv, S.H.Li and H.Pang, *Electrochimica Acta*, Electromechanical description of dopamine using water soluble sulfonated graphene, 102 (2013) 58-65.
- [8] D.C. Marcano, *Improved Synthesis of Graphene Oxide*, *ACS Nano*, 4 (2010) 4806-4814.
- [9] S. A. Speakman, *Estimating Crystallite Size Using XRD*, MIT Center for Materials Science and Engineering , 2010.
- [10] I. R. Kottegoda , X. Gao, D. N. Liyanage , C. H. Manorathne, J. Wang, J.-Z. Wang, H.-K. Liu and Y. Gofer, *Comparison of Few-layer Graphene Prepared from Natural Graphite through Fast Synthesis Approach*, *Journal of Materials Science & Technology*, 31 (2015) 907-912,.
- [11] J. Coates, *Interpretation of Infrared Spectra*, A Practical Approach, John Wiley & Sons Ltd, Chichester, (2000).