ISSN: 0976-3031

Available Online at http://www.recentscientific.com

CODEN: IJRSFP (USA)

International Journal of Recent Scientific Research
Vol. 8, Issue, 8, pp. 19049-19053, August, 2017

International Journal of Recent Scientific Research

DOI: 10.24327/IJRSR

Research Article

GREEN SYNTHESIS OF N-GRAPHENE BY HYDROTHERMAL-MICROWAVE IRRADIATION FOR ALKALINE FUEL CELL APPLICATION

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DOI: http://dx.doi.org/10.24327/ijrsr.2017.0808.0619

ARTICLE INFO

Article History:

Received 17th May, 2017
Received in revised form 21th June, 2017
Accepted 28th July, 2017
Published online 28th August, 2017

Key Words:

Graphene, nitrogen-doped, microwave synthesis, oxygen reduction reaction, electrocatalytic measurement

ABSTRACT

We demonstrate the synthesis of N-graphene *via* efficient hydrothermal-microwave irradiation method for oxygen reduction reaction (ORR). The high energetic uniform heating of microwave irradiation produces highly exfoliated nitrogen-doped graphene layers in shortest time. Notably, the nitrogen content of doped graphene has been evaluated ~6.86 at%. The synthesized N-graphene characterized by Fourier-transform infrared spectroscopy, scanning electron microscopy, transmission electron microscopy, powder X-ray diffraction and Raman spectroscopy. The electrochemical measurements of the catalysts were demonstrated excellent electrocatalytic activity for ORR in alkaline medium *via* 4-electron processes.

INTRODUCTION

The oxygen reduction reaction (ORR) is an imperative electrolytic reaction in energy conversion systems such as Li-ion batteries, fuel cells, and other industrial electrocatalytic processes (Novoselov *et al.*, 2005). In the fuel cells, the cathodic ORR plays a vital role in electricity generation. Platinum and platinum based catalysts have been extensively studied as an out-performing catalyst for ORR reaction (Wu *et al.*, 2008; Kumar *et al.*, 2016). However, the Pt-based catalysts are expensive and also it becomes sluggish in nature with time, which results in the search for an alternate catalyst such as graphene-based materials (Qu *et al.*, 2010). Graphene is a new two-dimensional (2D) low-cost carbon material with great interest and unique properties of strength, durability, high surface area, exceptional high electron mobility, and conductivity (Lu *et al.*, 2013). Hence, it has wide application potential in various fields such as energy storage materials, biosensors, nanoscale-electronics and transistors (Shuangxi *et al.*, 2015). However, graphene has been a hurdle to be used in-spite-of its unique properties because of the lack of electronic mobility (Luca *et al.*, 2015). To address the constraints in electronic properties of graphene, chemical doping has been considered as a promising approach. Nitrogen and boron are wide-ranging candidates for chemical doping in graphene (carbon-based material) because of similarity in atomic size, available valence electrons for stable covalent bonding with adjacent carbon atoms and easy substitution of carbon atom in graphene (Xin *et al.*, 2011). The C-N bond configuration is very much responsible to enhance the catalytic activity. N-graphene has been described extensively and explored for its higher electrocatalytic activity for the ORR and for the better performance in alkaline fuel cell applications (Lee *et al.*, 2014).

Interestingly, the incorporation of different types of nitrogen provides N-doping along with more functionality into the carbon network of graphene for property design. There are various techniques for synthesizing N-doped graphene such as chemical vapor deposition, thermal annealing, arc-discharge method, nitrogen plasma process *etc.* (Wang *et al.*, 2009; Sridhar *et al.*, 2010). However, most of the techniques exhibit unavoidable shortcomings e.g. low yield, long duration of synthesis, the complex procedure for N-doping in graphene. The microwave irradiation for chemical reactions extended

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popularity due to great advantages of convenient solvent superheating, precise control of the reaction and accelerating reactions. Microwave irradiation acts as high-frequency electric fields and offers selective dielectric heating due to differences between dielectric constants of solvent and reactant which accelerate reactions (Lee *et al.*, 2014, Sridhar *et al.*, 2010). Additionally, the microwave irradiation is an exceptional technique for producing scaled-up processes without fluctuating thermal gradient effects in the advancement of industrial or large scale synthesis of nanomaterial. The microwave application has been initiated for the synthesis of graphene oxide (GO), graphene and exfoliation of graphitic compounds. In this paper, we demonstrated the rapid synthesis of N-doped graphene from graphite *via* the green route of microwave irradiation. Nitrogen was doped successfully into the graphene by the hydrothermal-microwave irradiated reaction. The electrochemical properties of N-graphene were examined towards the oxygen reduction reaction.

Experimental Section

Materials

Graphite flakes and Nafion solution (~5%) were purchased from Sigma-Aldrich. Sulphuric acid, potassium hydroxide, and Liq. NH_3 bought from HiMedia chemicals. Pt/C commercial standard catalyst (40 wt% Pt on Vulcan XC-72 R carbon), absolute ethanol and 30% HCl were procured from Alfa Aesar. Millipore water was used for all synthesis and electrochemical studies.

Synthesis of GO and N-graphene

The graphene oxide (GO) was prepared from graphite flakes *via* modified Hummers process (Shahriary *et al.*, 2014). The synthesized GO were dispersed in H_2O (2 mg/ml), which gives the appearance of the brown colloidal solution. N-graphene were synthesized by hydrothermal-microwave reduction of GO with liquid ammonia. About 20 ml of GO dispersed in water and 14 ml of liquid NH_3 as a nitrogen source were mixed and sealed in a Teflon-lined autoclave (100 ml capacity) and the temperature maintained at 170°C for 3 h for the reaction. After cooling to room temperature, the solution was transferred and sealed into microwave reactor vial. The reaction condition in a microwave reactor (Anton Paar, Monowave - 300) was controlled at temperature 180°C for 2 min at the frequency of 2.45 GHz. The resultant products were thoroughly washed with Millipore H_2O and ethanol. The samples were dried at 80°C in a vacuum oven.

Characterization

The synthesized catalysts were analyzed by Fourier transform infrared spectroscopy (Thermo Nicolet Corporation) to observe the functional groups in the samples. Morphological studies were carried out by using scanning electron microscopy (SEM-HITACHI Model: S-3400N) and transmission electron microscopy (JEM-200CX at 200 kV). Powder X-ray diffraction (ULTIMA IV, RIGAKU, Japan, Cu Kα radiation) for determination of phase purity and crystallization degree. Raman spectroscopy (Great Lake, Renishaw, UK) of powdered samples were analyzed in the range of 100-3200 cm^{-1} by an excitation wavelength of 514 nm by semiconductor diode laser of 0.5% power at room temperature.

Electrochemical tests

The rotating disk-electrode (RDE) instrument (Biologic instruments, VSP/VMP 3B-20) was used to perform electrochemical tests on synthesized catalyst samples at 25°C. The substrate of glassy carbon disc electrode was used with geometric area 0.071 cm^2. The catalyst (4 mg) added into Millipore H_2O (1 ml) and ultrasonicated for 45 min to prepare the catalyst suspension. The aliquot of 20 µl dispersed suspension of N-graphene was loaded onto glassy carbon disk. The Nafion solution (0.5 wt %) was dropped on the prepared catalyst and dried it well. The counter electrode and reference electrode were Pt-wire and saturated calomel electrode, respectively.

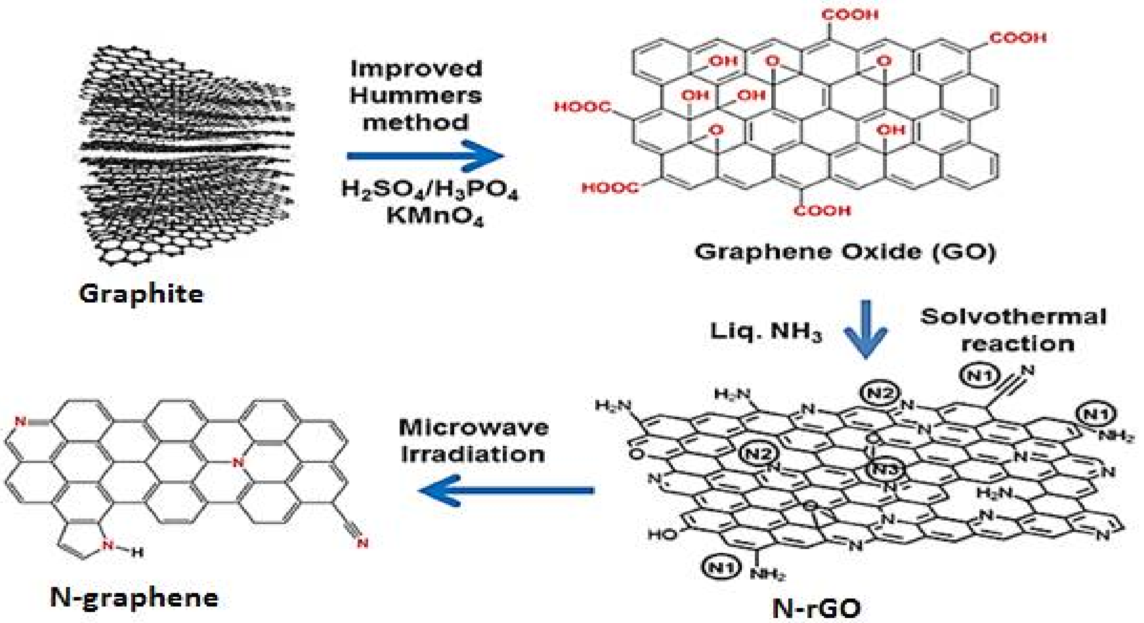

Figure 1 Scheme representing the preparation of GO, N-rGO, N-graphene catalysts

Linear sweep voltammetry (LSV) was demonstrated by using RDE for ORR activity measurement in aq. KOH (0.1 M) saturated with O_2 at 5mVs^{-1} scan rate with different rotation speeds.

RESULT AND DISCUSSION

N-graphene was synthesized *via* a facile hydrothermal-microwave technique as represented schematically in Figure 1. FT-IR spectra of graphite flakes, graphene oxide, N-rGO and N-graphene are shown in Figure 2. The synthesized GO from graphite flakes consists of various oxygen functional groups and attributed to the O-H stretching vibrations at 3400 cm^{-1} and C=O stretching vibrations at 1720 cm^{-1}. The vibrations at 1600 cm^{-1} refer to the skeletal vibrations of un-oxidized graphite. The vibrations at 1220 cm^{-1} confer to the stretching vibrations of -OH and at 1060 cm^{-1} stretching vibrations of C-O (Bag *et al.*, 2016). After the reaction of GO with the nitrogen source, the N-rGO formed and the OH stretch being reduced and C-N stretch is found between 1430 cm^{-1} to 1480 cm^{-1}

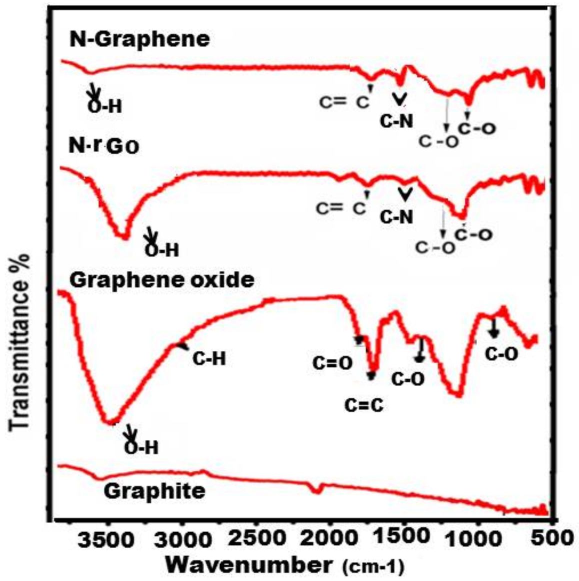

Figure 2 FTIR spectra of graphite, graphene oxide, and N-graphene

The band (3400 cm-1) O-H stretching vibration peaks was reduced to a greater extent for the N-graphene. The epoxy and hydroxyl groups were considerably reduced due to the deoxygenation whereas the main peak (C-N stretch) was detected between 1430 cm^{-1} to 1480 cm^{-1}. The SEM and TEM images of N-graphene with typical graphene sheet like structure are shown in Figure 3. Microwave irradiated uniform heating treatment resulted in a fine sheet and layered structures. The GO nanosheets also showed crumple and ripple structures, which describes the appearance of these features might be due to the deformation of the graphite oxide layers that occurred during the exfoliation and restacking processes (Lee *et al.*, 2014). Furthermore, the formation of oxygen functional group in the graphene oxide layers also contributes to its thermal instability at high temperature (Fu *et al.*, 2013).

Figure 4 shows the XRD patterns for graphite, GO, N-rGO and N-graphene. The main diffraction peaks at 26.8°, 9.5°, 25.9° and 26.3° were indexed to the (002) planes of the above samples. The XRD analysis of N-rGO revealed a slight broad peak centered at 25.9°, which confirms the recovery of the graphitic crystal structure and the shoulder peak refers to the exfoliation of the graphene oxide sheets.

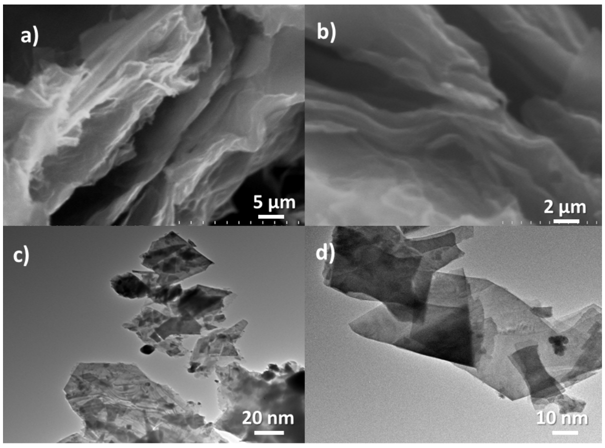

Figure 3 SEM micrograph of N-graphene; a) and b). TEM images of N-graphene; c) and d).

Further, the N-rGO under microwave heating resulted in the formation of N-graphene. The peak position of N-graphene was not altered in compare to N-rGO, but the sharp peak reveals the number of stacked layers.

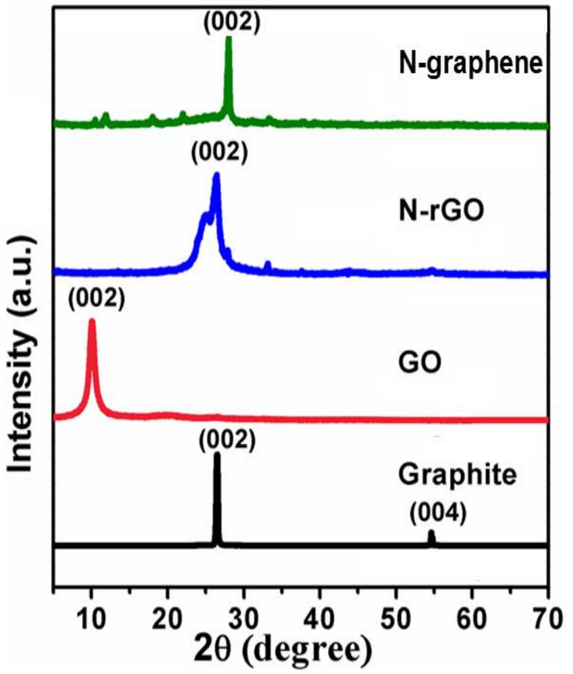

Figure 4 XRD patterns of graphite, GO, N-rGO, and N-graphene

The Raman spectra of the prepared catalyst shown in Figure 5. The prepared N-graphene exhibited two pinpointing peaks at 1595.7 cm^{-1} of the G band with E_{2g} symmetry attributes to ordered sp^2 array and at 1351.5 cm^{-1} of the D band with A_{1g} symmetry, which inclined to the various defects including sp^3 bonded carbon, vacancies, topological defects and dangling bonds. The G and D bands shifted slightly negative in N-graphene compare to N-rGO. In the samples (Graphite, GO, N-rGO and N-graphene), the D band peak and the G band peak showed slightly broad conferring few-layers of graphene with defects. The peak intensities of N-graphene slightly decreases, which implies nitrogen doping in the graphene structure.

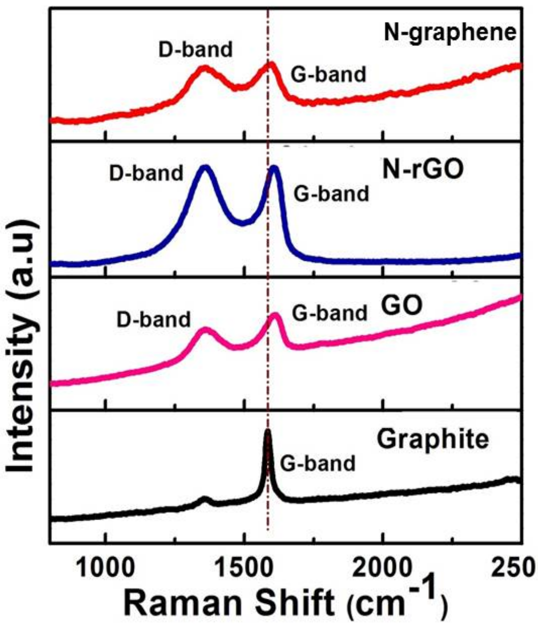

Figure 5 Raman spectra of the graphite, GO, N-rGO and N-graphene

Figure 6 (a) and (b) shows the electrochemical activity of N-graphene as well as N-rGO in N_2 and O_2 saturated aq. KOH (0.1 M) electrolytic solution was studied at a scan rate of 50mVs^{-1} with the help of cyclic voltammetry (CV). In the N_2-saturated solution, CV curves were obtained between the potential -1.0 to +0.2 V without observing reduction peak for N-rGO and N-graphene.

On the other hand, in the O_2 saturated electrolyte, a notable reduction peak (E peak) was noticed at -0.36 V for N-rGO electrode, displaying a considerable reduction method, which is a promising result for the graphene-based catalyst. The catalytic activity was further improved for N-graphene which revealed more positive ORR peak potentials at -0.3V and higher currents density. Therefore, the peak current of the N-graphene reveals that it is significant and well-defined diffusion limiting currents, representing the enhanced electrocatalytic activity of N-graphene toward ORR over the N-rGO.

To further glean into the ORR activity, LSV measurements were conducted to study the ORR activity of N-rGO, N-graphene and Pt/C catalysts in a 0.1 M KOH O_2-saturated solution with a scanning rate 10mVs^{-1}. Figure 7 displays the ORR polarization curves of the N-rGO, N-graphene, and Pt/C catalysts at 1600 rpm. Interestingly, the E onset of N-rGO has been initiated at –0.22 V and the N-graphene (N-G) catalyst was observed at – 0.18 V, which is close competition for the standard Pt/C catalyst whose onset is experimentally found to be -0.05 V. The number of electrons (n) transferred per O_2 in the ORR activity was estimated to 3.8 e which is ~4 e by the Koutecky-Levich (K–L) Eqn. $1/J=1/B\omega^{1/2} + 1/J_K$ (Liu *et al.*, 2013).

The N-doping not only alters the graphene surface by developing the nitrogen functional groups with the help of Liq. ammonia but also it changes its electronic structures. In addition, N-doping into the graphene sheets increases the electrocatalytic activity *via* an increase in the number of active centers during the process of decrease in defects but the identity and role of active centers were still in controversial. The N-graphene has resulted in increased electrocatalytic activity than that of N-rGO catalyst because of rapid reaction kinetics with the superior movement of an electron per oxygen molecule at N-graphene (Zheng *et al.*, 2013). The N-doping induces the active sites of graphene and improves the properties to enhance the electron transfer efficiency in the graphene structure. In this work, N-graphene accounts higher activity than N-rGO as thus improve the graphene surface and enhancing the ORR activity in the alkaline medium.

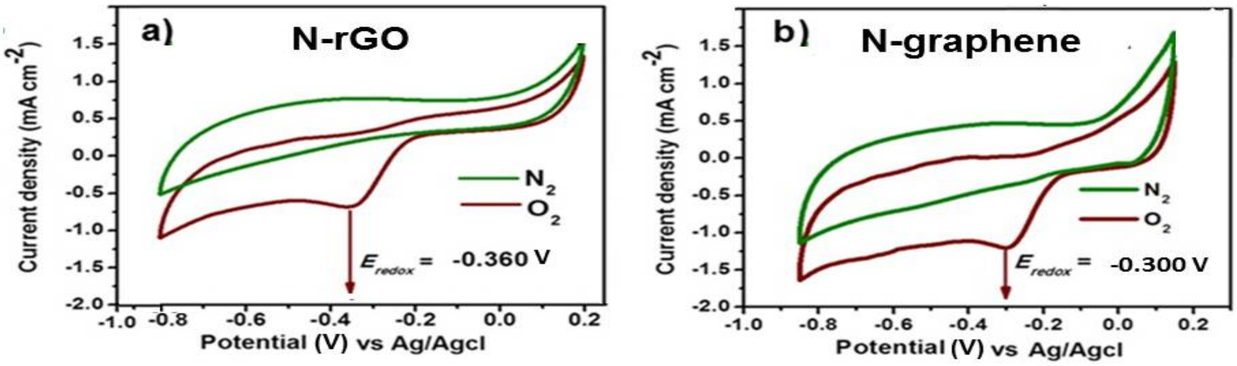

Figure 6 Cyclic voltammograms of (a) N-rGO (b) N-graphene in N_2 and O_2 saturated 0.1 M KOH at scan rate 50 mVs^{-1}

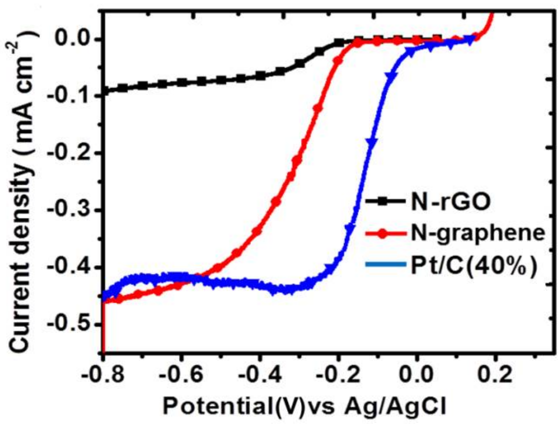

Figure 7 Linear sweep voltammograms of N-rGO, N-graphene and Pt/C at 1600 rpm in O_2-saturated aqueous 0.1 M KOH solution at scan rate 5mVs^{-1}

CONCLUSION

We report the synthesis of N-doped graphene by energy efficient green microwave irradiation techniques. The synthesis of high nitrogen contenting N-graphene has been demonstrated at low-temperature *via* hydrothermal-microwave heating of reduced graphene oxide with liquid ammonia. The doping efficiency of nitrogen concentration was estimated ~6.8 at %. The diffusion kinetics of N-doped graphene was significantly high due to doped-N and shown high activity at par with Pt/C commercial catalyst. The E onset reaches up to -0.22 V for N-rGO and the N-graphene catalyst was found to be at -0.18 V which is very close competitive compared to commercial Pt/C catalyst whose onset is -0.05 V. Moreover, the N-graphene revealed higher catalytic activity and enhanced operation stability under fuel cell condition. Hence, N-graphene is an encouraging electrocatalyst for advancing the fuel cell applications.

Acknowledgments

We express our sincere thanks to Central Instrumentation Facility, Pondicherry University, and CSIR-Central Electrochemical Research Institute, Chennai for providing necessary facilities. We are indebted to Dr. A. K. Sahu (Scientist) CSIR-CERI, Chennai for his kind help and motivation.

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How to cite this article:

Sudhakar S *et al.*2017, Green Synthesis of N-Graphene By Hydrothermal-Microwave Irradiation For Alkaline Fuel Cell Application. *Int J Recent Sci Res.* 8(8), pp. 19049-19053. DOI: http://dx.doi.org/10.24327/ijrsr.2017.0808.0619

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