

SYNTHESIS AND CHARACTERIZATION OF IODINE DOPED GRAPHENE BY AN UNCATALYZED REACTION

Adriana Marinoiu* , Elena Carcadea, Irina Petreanu, Elena Marin, Bianca Sucea, Amalia Soare

National Research and Development Institute for Cryogenics and Isotopic Technologies - ICSI Rm. Valcea, Uzinei Street no. 4, P.O. Box Râureni 7, 240050, Râmnicu Vâlcea, Romania

ABSTRACT

An iodine substituted graphene was synthesised by physic-chemical techniques (oxidation-delaminating-reduction) in order to obtain a metal free catalyst for the oxygen reduction reaction (ORR). The doping with iodine takes place in the reduction step by a simple route, without a specific catalyst. The final product obtained as a black powder was characterised by wavelength dispersive X-ray fluorescence (WDXRF) spectroscopy, Scanning Electron Microscopy coupled with Energy Dispersive X-Ray Spectroscopy (SEM-EDX), surface area estimated from BET method, thermal gravimetric analysis. The presence of iodine is evidenced mainly by EDX spectra and WDXRF spectroscopy.

Keywords: iodine, doped graphene, fuel cell.

1. INTRODUCTION

Graphene, an atomically thin material with theoretical surface area of $2600\text{m}^2/\text{g}^1$, has a great potential in the field of catalysis, separation and storage area if properly assembled into functional 3 D materials at large scale.

There is an important trend to replace the Pt-based oxygen reduction reaction (ORR) electrocatalysts with metal-free electrocatalysts having high catalytic activity and long-term operation stability in attempt to reduce the cost of fuel cell and make this technology accessible for commercialization. Since Jasinski first reported a non-noble metal catalyst for ORR in 1964 (Li X. L. et al., 2008), lots of research have been conducted in this filed and a group of non-noble metal catalysts have been developed and recognized as FeNC catalyst (Wang Z. et al., 2013). Recently, carbon-based materials doped with heteroatom, such as boron (B), halogen (Cl, Br, I), nitrogen (N), phosphorus (P), sulphur (S), and their mixtures, have attracted attentions as metal-free ORR eletrocatalysts. The difference in electronegativity between the heteroatom dopants (B=2.04, I=2.66, N=3.04, P=2.19 and S=2.58) and carbon atom (2.55) in covalently doped graphitic carbon

*Corresponding author: Adriana Marinoiu, E-mail: adriana.marinoiu@icsi.ro, phone: 0250 732744, fax: 0250 732746

SYNTHESIS AND CHARACTERIZATION OF IODINE DOPED GRAPHENE BY AN UNCATALYZED REACTION

frameworks can polarize adjacent carbon atoms (Wang Z. et al., 2013). As a new and efficient member of carbon family, graphene becomes a promising choice of material for ORR catalyst owing to its superior electrochemical and mechanical performance with lower price compared to Pt-based catalysts. Both experimental and theoretical results have demonstrated that the introduction of hetero-atoms N, B, P, S, Se, H and I into graphene networks will bring interesting ORR activity (Kalita G. et al., 2011). Iodine-doped graphene shows metallic behaviour, as evidenced by transport measurements at temperatures ranging from 300 K to 2 K and magnetic fields from 0 to 8 T. At room temperature, the resistance at zero gate voltage is reduced by 97% upon iodine doping, showing that the iodine doped graphene has promising potential as catalysts and also for optoelectronic applications (Kraszkiewicz L. et al., 2006; Poh H. L. et al., 2013; Chu S. W. et al., 2012). Recently, the research on transport properties of monolayer graphene doped with iodine molecules indicated that the charge neutrality points shifts to the hole carrier regime, indicating p-type doping (Tristant et al., 2015).

Furthermore, the physio-chemical properties of iodine doped graphene such as its chemical state, thermal stability and work function conditions have not been intensively investigated even they are critical parameters for a successful obtaining of graphene based electrodes in industrial applications and particularly for fuel cell domain.

This work presents a method for synthesis of the iodine doped graphene starting from graphite through an uncatalytic reaction. The doping process takes place in the reduction step of chemical synthesis of graphene and potassium iodide serves as dopant. This process involves the formation of mainly covalent bonds with iodine atoms. A part of iodine atoms do not participate at this process and form as molecular iodine I_2 . This by-product is removed through an iterative process of extraction (Ghosh S. et al., 2012; Chenyang L. et al., 2014; Luo X. et al., 2013; Zhao Y. et al., 2011).

We prepared doped graphene materials in order to study the possibility of their use as ORR catalyst in PEMFC due to their unique structural and electrical properties and to other prominent characteristics, such as high specific surface area, relatively uniform pore size distribution and ordered pore structure.

2. EXPERIMENTAL

2.1. Materials and Methods

All chemicals were of analytical grade and used as received. The following materials were used in this experimental study: Purified natural graphite (PMM7) was purchased from KOH-I-NOR Graphite SRO Czech Republic and has the following characteristics: concentration = < 99.5 %wt., ash = max. 0.5 %wt., specific surface = $9 \text{ m}^2\text{g}^{-1}$ (BET). All other reagents and chemicals were procured from: Merck (H_2SO_4 95-97 %wt. for analysis, P_2O_5 < 98 %wt. for analysis, $NaBH_4$ < 98 %wt. for synthesis), Fluka ($KMnO_4$ < 99 %wt. for analysis; $K_2S_2O_8$ min. 99 %wt for analysis), Chimopar Bucharest (Na_2CO_3 < 99.8 %wt. for analysis; $NaCl$ < 99.5 %wt. for analysis; ethanol < 96 %wt. for analysis) and OLTCHIM SA (H_2O_2 ~35 %wt. technical grade; HCl pharmaceutical grade < 32 %wt).

a. Graphene material synthesis

Graphene (Gr) was prepared in four steps, according to our earlier report, namely: pre-oxidation, oxidation, exfoliation, reduction (Marinoiu et al., 2015). Graphite oxide (GO) was prepared by Tour method, including the pre-oxidation treatment (Marcano et al., 2010). In the pre-oxidation stage the H_2SO_4 was intercalated into graphite, in respect to a better access of the reactants in the oxidation step. Summarily, graphite was added into a reaction mixture containing concentrated H_2SO_4 , $\text{K}_2\text{S}_2\text{O}_8$, and P_2O_5 , under stirring in an oil bath. The reaction mixture were heated under continuous stirring until $80\text{ }^\circ\text{C}$, maintained at this temperature for 4 hours and cooled at the room temperature. The obtained GO was washed with distilled/deionized water, filtered with a G3 fritted funnel, washed again with in order to obtain pH 6 and dried 24 h at about $50\text{ }^\circ\text{C}$. Pre-oxidized graphite was obtained. Concentrated H_2SO_4 , P_2O_5 and g pre-oxidized graphite were added slowly, under continuous stirring in a glass reactor thermostated in an ice bath. After the suspension temperature was stabilized below $10\text{ }^\circ\text{C}$, KMnO_4 were added slowly, maintaining the temperature below $10\text{ }^\circ\text{C}$. After one hour, the reaction mass was gradually heated to $50\text{ }^\circ\text{C}$ and stirred 24 h at this temperature. The reaction mass was introduced slowly under stirring in cold water and 35 %wt. H_2O_2 was carefully added until the colour turned to bright yellow. The resulted suspension was separated by decantation and centrifugation (15 min/10000 RPM). The obtained solid is redispersed in HCl 10 wt%, and then separated by centrifugation. The obtained gel is dried by freeze drying technique as lyophilization method.

Few layer graphene were synthesized by exfoliating of GO under specific conditions. GO exfoliation was performed in an ultrasonic bath for 2 hours to 110 W / 40 kHz at $30\text{-}40\text{ }^\circ\text{C}$. A colloidal solution of graphene oxide (GrO) $\sim 1\text{ g/l}$ concentration was obtained.

In order to reduce GrO to the graphene, a fresh 5 wt. % NaBH_4 solution was added to the colloidal solution of GrO at $80\text{ }^\circ\text{C}$ and dosed under stirring in $\sim 2\text{ h}$. The reaction mass was maintained at $90\text{ }^\circ\text{C}$ for 4 hours, cooled to room temperature. The separated solid was dried, re-dispersed by sonication in concentrated H_2SO_4 and mechanically stirred for 12 hours at $120\text{ }^\circ\text{C}$. After cooling, the reaction mass was washed with distilled water until free of SO_4^{2-} , filtered, washed with water and ethanol and dried at $80\text{ }^\circ\text{C}$.

b. Doped graphene synthesis

A novel approach was used for their synthesis: the reduction of graphite with HI via non-catalyzed reaction. The obtained sample was labeled GrI. The general synthesis includes the following steps: pre-oxidation, oxidation, exfoliation and reduction. A detailed description of the synthesis process regarding the first three stages has been reported previously. Regarding the reduction step, in order to reduce the GrO to graphene and to its doping with iodine, the following procedure was performed. In a 2 liter 4-neck flask placed in a glycerol thermostatic bath and equipped with mechanical stirring, thermometer, reflux condenser and addition funnel was introduced GrO. $\sim 145\text{ g}$ HI 55% wt. (equivalent to 80 g HI) is added in 3 h at $80\text{-}85\text{ }^\circ\text{C}$. The reaction time is established at 24 hours at this temperature. The reaction mass was cooled and separated by centrifugation, which is the only applicable separation method. The separated solid was washed three times by redispersion in 1500 ml water and centrifugation. After the third wash test, the

SYNTHESIS AND CHARACTERIZATION OF IODINE DOPED GRAPHENE BY AN UNCATALYZED REACTION

solution is still acidic pH (~ 3.0) and the test for X⁻ is positive due to the HI presence. The weaker H⁺...I⁻ interaction in HI facilitates the dissociation of the proton from the anion and is the reason why HI is the strongest acid of the hydrohalides (pK_a about 10). Thus, small amounts of HI dissolved into solution will result in acid pH values. The separated solid was brought to constant weight at 50°C in a vacuum desiccator placed in an oven (~ 7 hours).

According to the information from literature, the elemental iodine is separated by repeated extraction with acetone. For this purpose, the solid product obtained in previous stage was placed in a cartridge paper and was extracted in a Soxhlet extractor with acetone until extract is colorless. After drying to constant weight (loss mass is $\sim 31\%$) at 50°C, the GrI sample was obtained.

2.2. Characterization methods for prepared samples

The elemental analysis of the samples was determined by wavelength dispersive X-ray fluorescence (WDXRF) spectroscopy method. The Rigaku ZSX Primus II spectrometer is equipped with an X-ray tube with Rh anode, 4.0 kW power, with front Be window of 30 μm thickness. The measurements were performed onto pressed pellets under vacuum. The XRF data were analyzed using EZ-scan combined with Rigaku's SQX fundamental parameters software which is capable of automatically correcting for all matrix effects, including line overlaps.

Quantachrome Autosorb-IQ instrument was used to obtain N₂ isotherms at 77 K, from which the surface area based on Brunauer-Emmet-Teller (BET) theory and pore size distribution were estimated. Generally the BET surface areas were calculated from N₂ adsorption isotherm relative pressure ranging from 0.05 to 0.30, if nearly perfect linear BET correlation was observed. The BET surface area was recorded when linear correlation factor at least R² = 0.9998 was achieved. Morphology was studied using scanning electron microscopy (SEM).

3. RESULTS AND DISCUSSION

Thicker multilayer composite is clearly visible from the SEM images in Figure 1. The graphene sheets are highly disordered as large chunks and contain large amount of waves or wrinkles on their surface.

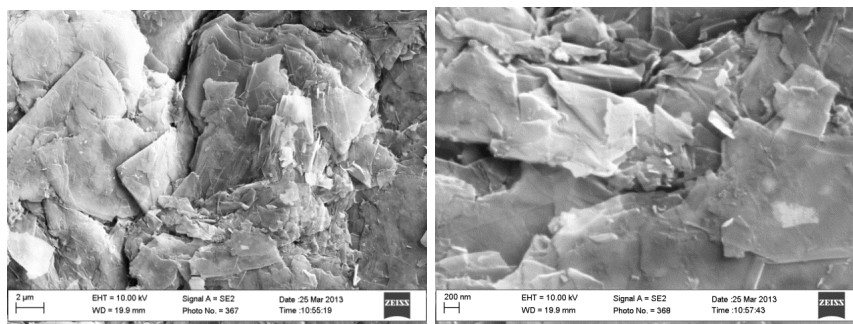


Figure 1. SEM analysis of the prepared iodine doped graphene

Figure 1 shows the surface morphology of iodine doped graphene (GrI) sample at two scanning resolution. The low resolution image shows a quite uniform

surface morphology. In the high resolution we can notice the stacked and tightly packed layers of HI reduced graphene nanoplatelets.

The energy dispersive spectroscopy was used for elemental composition of doped graphene. A set of several determinations for every scanning resolution was performed in order to obtain the accurate estimation about elemental composition, table 1. However, a high dispersion among the data could be observed, indicating the fact that this is not a precise method. It is known the fact that the iodination reaction or physical sorption took place in the whole bulk of the graphenes and not only on the edges of graphene flakes (Simek et al., 2014). Therefore other analytical techniques were used in order to estimate the elemental content.

Table 1. Statistical processing of EDX dates for GrI samples

EDX analysis	Resolution (μm)	C (wt. %)	O (wt. %)	I (wt. %)
Spots	70	78.01	20.80	1.19
		90.63	4.11	5.27
	10	79.89	19.41	0.71
		81.98	17.23	0.79
		83.33	15.90	0.78
		82.54	16.79	0.67
	7	82.53	17.00	0.47
		84.28	14.95	0.76
	6	80.26	19.23	0.51
	Averages		82.40	16.86
Surface	70	78.63	20.27	1.10
		78.09	20.70	1.22
	10	79.93	19.62	0.44
		81.50	17.83	0.67
	7	79.91	19.60	0.49
	6	81.60	17.79	0.61
		81.89	17.41	0.70
	Averages		81.66	17.68

The elemental analysis of the samples was determined by a more adequate method, namely the wavelength dispersive X-ray fluorescence (WDXRF). Elemental composition, including carbon, oxygen and iodine is presented in table 2.

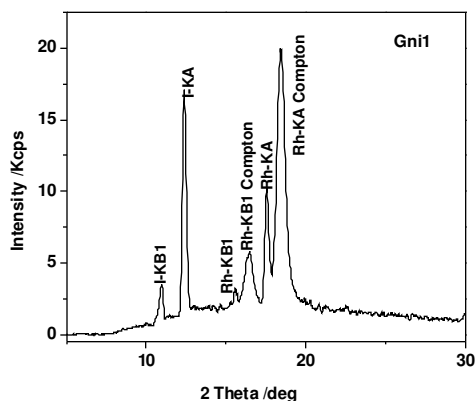


Figure 2. Iodine XRF spectrum of GrI sample

SYNTHESIS AND CHARACTERIZATION OF IODINE DOPED
GRAPHENE BY AN UNCATALYZED REACTION

Table 2. The elemental analysis by X-ray fluorescence spectroscopy for iodine-doped graphene

Element	Result (mass%)	Det. Limit	El. Line	Intensity
C	74.5415	0.30351	C -KA	14.4556
O	24.2411	1.39174	O -KA	0.3569
I	0.3308	0.00691	I -KA	15.3304

The iodine concentration obtained by XRF were not in agreement with EDS analysis. This fact can be explained by the high surface sensitivity of XRF, where the amounts of C, O, H and I can be different compared to the bulk.

The high BET surface area of synthesized graphene-based materials indicated a significant extent of delamination. The estimated surface area were: 670 m²/g for graphene material and 335 m²/g for iodine doped graphene. The decreasing of GrI surface area sustains the doping of graphene as result of pores coverage. The BET surface area was obtained from the nitrogen adsorption–desorption isotherms shown in Figure 3. The isotherms were similar exhibiting a typical type-IV curve at low relative pressure and a hysteresis loop at relative pressure from 0.4, indicating the presence of microporosity, mesoporosity, and some macroporosity.

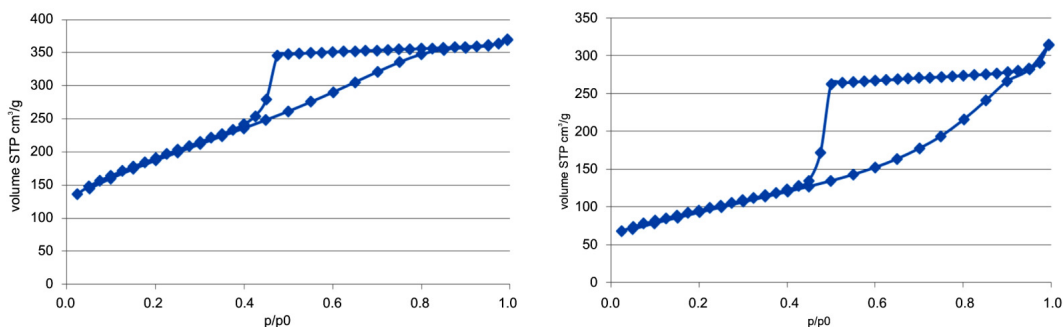


Figure 3. The adsorption–desorption isotherms for graphene (left) and iodine doped graphene (right)

The corresponding graphene sheet numbers per stack were calculated using these BET surface areas based on the following simple geometric law:

$$N = 2600 / A_{\text{BET}}$$

where N is number of sheets in a stack, 2600 is the theoretical surface area of monolayer graphene in m²g⁻¹, and A_{BET} is the measured BET surface area of the sample in m²g⁻¹. This law is derived by assuming insignificant edge contribution to surface area (valid for very high aspect-ratio materials), non-porous flakes, and sufficient irregularity (including imperfections) in the plate surface or packing arrangements to prevent atomically-perfect face-to-face adhesion that would lead the creation of new bonds and surface area loss.

Thermogravimetric analysis of the graphite oxide is presented in the Figure 4 and interpreted in the table 3. The value for iodine loss is essentially higher than that observed in XRF measurements, due to the different method.

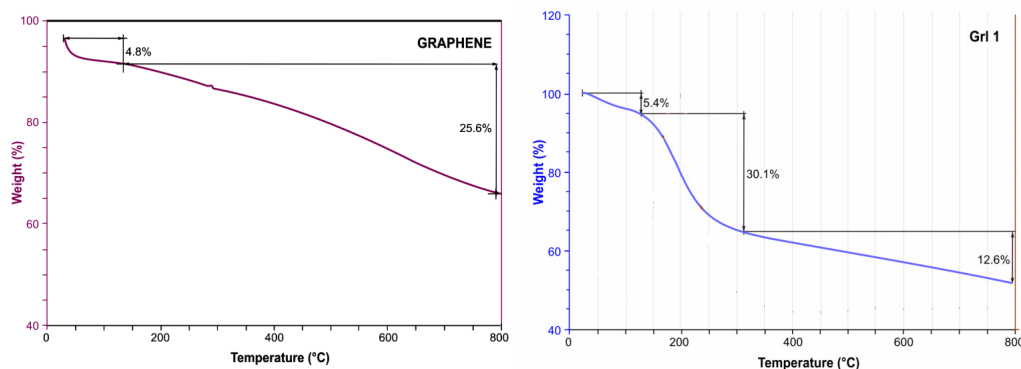


Figure 4. Thermogravimetric analysis for graphene and iodine doped graphene

Table 3. The interpretation of thermogravimetric analysis

Range temperature (°C)	Mass loss (% wt.)		Assignment
	Gr	GrI	
20-127	4.8	5.4	Evaporation + water desorption
127-313	5.5	30.1	Iodine elimination + elimination of organic groups
313-790	20.1	12.6	Elimination of organic groups with C, O, H, N, S
20-790	30.4	48.1	-

4. CONCLUSIONS

In this paper, we demonstrated an easy and verifiable process in order to obtain iodine doped-graphene materials, using as route the reduction with HI as non-catalyzed reaction starting from commercial graphite. The decreasing of GrI surface area from 670 (corresponding to graphene) to 335m²/g, sustains the doping of graphene as result of pores coverage. SEM image illustrates a very rough surface structure as thicker multilayer composite. The wavelength dispersive X-ray fluorescence method confirms the presence of 0.33%wt iodine in prepared graphene composite. The results suggest new insights and practical method for designing a high performance metal-free ORR catalyst by a scalable technique.

Acknowledgment. This work is supported by the National Agency of Scientific Research from Romania by the National Plan of R & D, Project No. PN. 16 36 01 02.

REFERENCES

Chenyang L., Feng H., Xiaochong Z., Qiangeng Z., Sonping L., Hong L., 2014, *Low temperature reduction of free-standing graphene oxide papers*

SYNTHESIS AND CHARACTERIZATION OF IODINE DOPED
GRAPHENE BY AN UNCATALYZED REACTION

with metal iodides for ultrahigh bulk conductivity, Scientific Reports, 4:3965.

- Chu S.W., Baek S. J., Kim D. C., Seo S., Kim J. S., Park Y. W., 2012, *Charge transport in graphene doped with diatomic halogen molecules (I_2 , Br_2) near Dirac point*, Synth. Met., 162:1689-1693.
- Ghosh S., Yamijala S. S., Pati S. K., Rao C., 2012, *The interaction of halogen molecules with SWNTs and graphene*, RSC Adv., 2:1181-1188.
- Kalita G., Wakita K., Takahashi M., Umeno M., 2011, *Iodine doping in solid precursor-based CVD growth graphene film*, J. Mater. Chem., 2011; 21:15209-15213.
- Kraszkievicz L., Sosnowski M., Lech Skulski, 2006, *Oxidative Iodination of Deactivated Arenes in Concentrated Sulfuric Acid with $I_2/NaIO_4$ and $KI/NaIO_4$ Iodinating Systems*, SYNTHESIS 2006; 7: 1195-1199.
- Li X. L., Wang X. R., Zhang L., Lee S. W., Dai H.J., 2008; Science 319:1229.
- Luo X., Fang C., Li X., Lai W., Liang T., 2013, *Adsorption behaviors of cesium and iodine atoms on the graphite surface by the first principles*, J. Nucl. Mater, 441:113-118.
- Marcano D., Kosynkin D., Berlin J., Sinitskii A., Sun Z., Slesarev A., Alemany L., Lu W., Tour J., *Improved Synthesis of Graphene Oxide*, ACS NANO, 2010, 4 (8):4806
- Marinoiu A., Teodorescu C., Carcadea E., Raceanu M., Varlam M., Cobzaru C., Stefanescu I., *Graphene-based Materials Used as the Catalyst Support for PEMFC Applications*, Materials Today: Proceedings, 2(6), 2015, Pg. 3797-3805, The Selected Papers of 10th International Conference on Physics of Advanced Materials, ICPAM-10. doi:10.1016/j.matpr.2015.08.013
- Poh H. L., Šimek P., Sofer Z., Pumera M., 2013, *Halogenation of Graphene with Chlorine, Bromine, or Iodine in a Halogen Atmosphere* Chem-Eur J., 19:2655-2662.
- Simek P., Sedmidubsky D., Klimova K., Sofer Z., *Towards graphene iodide: Iodination of graphite oxide*, 2014, Nanoscale, DOI: 10.1039/c4nr05219f
- Tristant D., Puech P., Gerber I.C., *Theoretical Study of Graphene Doping Mechanism by Iodine Molecules*, J. Phys. Chem. C, 2015, 119 (21), pp: 12071-12078
- Wang Z., Wang W., Wang M., Meng X., Li J., 2013, *P-type reduced graphene oxide membranes induced by iodine doping*, J. Mater Sci., 48:2284-2289.
- Zhao Y., Wei J., Vajtai R., Ajayan P. M., Barrera E. V., 2011, *Iodine doped carbon nanotube cables exceeding specific electrical conductivity of metals*, Sci. Rep., 2011; 1-5.