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PII: S0167-577X(19)30067-9
DOI: https://doi.org/10.1016/j.matlet.2019.01.035
Reference: MLBLUE 25580

To appear in: *Materials Letters*

Received Date: 4 January 2019
Accepted Date: 5 January 2019

Please cite this article as: A. Devadoss, R. Subramaniyan, K. Asokan, B. Kim, S. Pitchaimuthu, Enhanced Water Oxidation Catalytic Performance of Graphene Oxide by Gamma Ray Irradiation Post-Treatment, *Materials Letters* (2019), doi: https://doi.org/10.1016/j.matlet.2019.01.035

# Enhanced Water Oxidation Catalytic Performance of Graphene Oxide by Gamma Ray Irradiation Post-Treatment

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Keywords: Carbon materials, Radiation damage, Gamma ray irradiation, Water oxidation, Surface modification, Catalysis.

**Abstract**

Herein, we report the influence of γ-ray irradiation process on the physicochemical properties of partially reduced graphene oxide (PRGO) thin films. It is found that γ-ray irradiation at 25KGy alters the surface, chemical environment, and wettability properties of PRGO *via* inducing edge sites and oxygen moieties, resulting in increased water oxidation performance.

**Introduction**

Graphene nanostructures with high surface area can serve as platform for catalysts, sensors, adsorbents, radical scavengers and cross-linking generators [1]. In particular, graphene oxide (GO) - an oxidized graphene sheet chemically exfoliated from graphite, has been widely applied as low-cost, electron-transport scaffold in composite based water oxidation/reduction [2, 3]. Here, the catalytic activity of GO composite greatly depends on the number of edge sites at GO and thus, the development of production-friendly surface treatment and/or chemical functionalization process are critical. In this line, gamma (γ) irradiation is a well-established and environmentally benign non-contact civil nuclear technique [4] used in various applications. In particular, the chemical-free nature and short process duration fosters γ-irradiation process very attractive towards large-scale, manufacture-friendly process developments. In general, γ-irradiation in liquid medium was utilised for conductivity restoration in GO *via* inducing chemical changes on GO surfaces. It is reported that the electrons generated *via* γ-irradiation in liquid medium can be utilised for the simultaneous reduction of GO and silver ion to form the graphene-silver nanoparticles hybrids [5].

Recently, it's been reported that γ-irradiation process can be utilised to engineer the interfacial interaction between polymer-carbon materials including carbon nanotubes [4, 5] and graphene [1, 6]. Anson-Casaos *et al*. studied the effect of γ-irradiation on the few layered GO powder, chemically reduced GO, and graphene nanoribbons. Small changes were found in the graphene sheets stacking and chemical composition, while significant increase in the defects were found due to the displacement of carbon atoms in graphene lattice [6]. On the other hand, solid phase modifications would be much more beneficial due to the negligible utilization of chemical reagents or gas molecules, validating an environmentally cleaner

process. Here, the energy of γ-rays dictates the interaction with matter either through Compton scattering, the photoelectric effect or pair production [7]. For instance, processes involving low-energy γ-irradiation (<1.022MeV) would follow the Compton and/or photoelectric effects, whereas, the higher energy γ-ray irradiation (>1.022MeV) is expected to induce ionization in the material *via* capturing the negatively charged electrons or positively charged holes, which might knock the atoms out of their lattice sites [8]. This process may generate additional defect sites and dislocations.

This report explores the influence of electrolyte-free, γ-irradiation on the physiochemical properties of partially reduced GO (PRGO) thin films. The effect of γ-irradiation on surface, chemical environment, and wettability property of PRGO were studied in detail. To the best of our knowledge, for the first time, we demonstrate the improved catalytic performance of the high energy γ-irradiated PRGO films towards water oxidation.

**Experimental**

The PRGO films were prepared using as-synthesized GO solution by spin coating technique. The experimental details of PRGO films preparation and characterisation techniques were explained in the supporting information (S1).

*Preparation of γ-irradiated PRGO:* The γ-irradiation experiments were performed at Inter University Accelerator Centre, New Delhi, India. The PRGO films were loaded into irradiation chamber (model GC-1200 made by BRIT, Mumbai). The samples were irradiated with the γ-rays generated from a Cobalt-60 source (1.33 MeV) for different dose (10 and 25KGy). The γ-ray irradiated samples were coined as 10KGy-GO and 25KGy-GO.

**Results and Discussion**

The schematic illustration of surface modification of PRGO thin films into RGO by γ-irradiation is shown in Fig. 1a. It is anticipated that γ-irradiation results in the formation of RGO films with higher density of edges, which is confirmed by the subsequent surface analysis. The surface morphology of the untreated and γ-irradiated PRGO films at 10 kGy

and 25 kGy were studied using AFM (Fig. 1b). It is found that the γ-irradiation induces significant surface changes on PRGO films like inducing exfoliation and defect sites on the surface, resulting in a significant decrease in the surface roughness. To fully understand the effect of γ-irradiation on PRGO films, the wettability nature of PRGO films was studied using contact angle measurement (Fig. 1c). As anticipated, the water contact angle changes from 91° (PRGO) to 76° (10 KGy-GO) and 50° (25 KGy-GO), upon γ-irradiation, which is ascribed to the formation of higher density of edge sites resulting in large number of hydrophilic groups. Fig. 1d-i shows the HRTEM images and SAED patterns of untreated and γ-irradiated PRGO films, respectively. The HRTEM images of PRGO (Fig. 1d-e) shows smooth layers of PRGO films. Conversely, Fig. 1g-h shows that the γ-irradiation induces additional exfoliation and wrinkled structures creating edge sites on PRGO films. Thus, it is evident that the process of γ-irradiation can be utilised to induce additional edge sites in GO.

The chemical environment of γ-irradiated PRGO films was analysed using XPS. Fig. 2 shows the de-convoluted C1s (2a-c) and O1s (2d-f) spectra of PRGO, 10 kGy-GO and 25 kGy-GO, respectively. The qualitative analysis of XPS peaks are explained in supporting information S2. The atomic ratio of C, O and N in all films were estimated from Fig. 2 (a)-(f) and enlisted in table S1 (supporting information). From table S1, atomic percentage of lattice oxygen (532.2 eV) has been markedly increased from 9.7% to 18.5% by 25KGy γ-irradiation. Also, atmospheric oxygen (534.1 eV) quantity of γ-irradiated GO is increased from 0.5 to 1.59 which is responsible for hydrophilic nature exists in this sample (Fig. 1c). Furthermore, nitrogen quantity is significantly reduced from 1.36 to 0.53 after γ-irradiation. This clearly endorse that γ-irradiation modify the chemical environment of PRGO. The Raman spectra for untreated and γ-irradiated PRGO films shows the D and G-bands at 1346 $cm^{-1}$ and 1593 $cm^{-1}$, respectively (Fig. 2g). It is known that the ratio of I(D)/I(G) is a clear indicator of the defect

density [9]. It is found that the I(D)/I(G) ratio of PRGO reduced from 1.1 to 1.0 upon γ-irradiation at 25 kGy attesting the additional defect sites.

We examine the influence of γ-irradiation on electrocataltic activity of γ-irradiated PRGO films through testing as anode in water splitting reaction under 1M NaOH electrolyte using conventional three-electrode system. The JV results of untreated and γ-irradiated PRGO electrodes are presented in Fig. 3a. The current generation at positive potential indicates the water oxidation reaction at anode surface and water reduction reaction at platinum cathode surface. This can be explained as follows:

$4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$ (Pt cathode)

$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$ (GO anode)

From Fig. 3a, the 25 KGy-GO electrode showed approximately 6 times greater performance than untreated PRGO at 1.0 V vs Ag/AgCl. The enhanced water oxidation performance might be attributed to the oxygen species doping, and hydrophilic property. To understand the origin of enhanced catalytic activity, ultraviolet photoelectron spectroscopy (UPS) analysis were performed (Fig.3b) [10]. The work function results imply that fermi level of PRGO is modulated from 6.5 eV to 7.8 eV under 25 KGy γ-irradiation. As discussed above (Fig. 2d-f) the oxygen species doping at GO lattice increases hole concertation at Fermi level. This might lead to Fermi level shift towards positive potential which is favourable for water oxidation reaction at p-type PRGO anode. Furthermore, the hydrophilic property of 25 KGy γ-irradiated PRGO surface enhances hydroxide (OH-) adsorption and $O_2$ desorption, which is key for water oxidation reaction. The enhanced water oxidation catalytic performance of PRGO can be applied in other electrochemical applications including sensors, batteries, and water treatment.

**Conclusion**

For the first time, we validate the γ-irradiation process towards enhancing the catalytic activity of PRGO films towards water oxidation. The γ-irradiation process induces edge sites and oxygen moieties at PRGO surface and thus, modulates the Fermi level position for enhanced water oxidation performance.

**Acknowledgement**

AD and SP acknowledges the joint-financial support from Welsh Government and European Commission under European Regional Development Funds (ERDF) through Ser Cymru II MSCA COFUND Fellowship and Ser Cymru II Rising star fellowship. B. Kim and S. Ramasundaram acknowledge Korea Ministry of Education, Science and Technology for their partial financial support via National Research Foundation for the priority Research Centers Program (NRF-2018R1A6A1A03025526).

**Figure legends**

**Figure 1**. (a) Schematic illustration of surface modification of PRGO layer to RGO by γ-irradiation; (b) AFM images, and (c) water contact angle photographs of untreated and gamma ray irradiated PRGO thin films; HRTEM images of (d) untreated and (g) γ-ray irradiated PRGO at 200 nm scale (inset shows the low magnification HRTEM images at 500 nm scale); High magnification HRTEM images of (e) untreated and (h) treated PRGO at 20 nm scale (note that Figure 1(f,) and 1(i) shows respective SAED patterns).

**Figure 2**. C1s core spectra of (a) untreated PRGO, (b) 10KGy and (c) 25KGy γ-irradiated PRGO; O1s core spectra of (d) untreated PRGO, (e) 10KGy and (f) 25KGy γ-irradiated PRGO, and (g) Raman spectra of untreated and γ-irradiated PRGO films.

**Figure 3**. (a) J-V results of PRGO of untreated and gamma ray irradiation treated PRGO anodes in water oxidation reaction (note that 1 M NaOH is used as electrolyte); and (b) UPS results.

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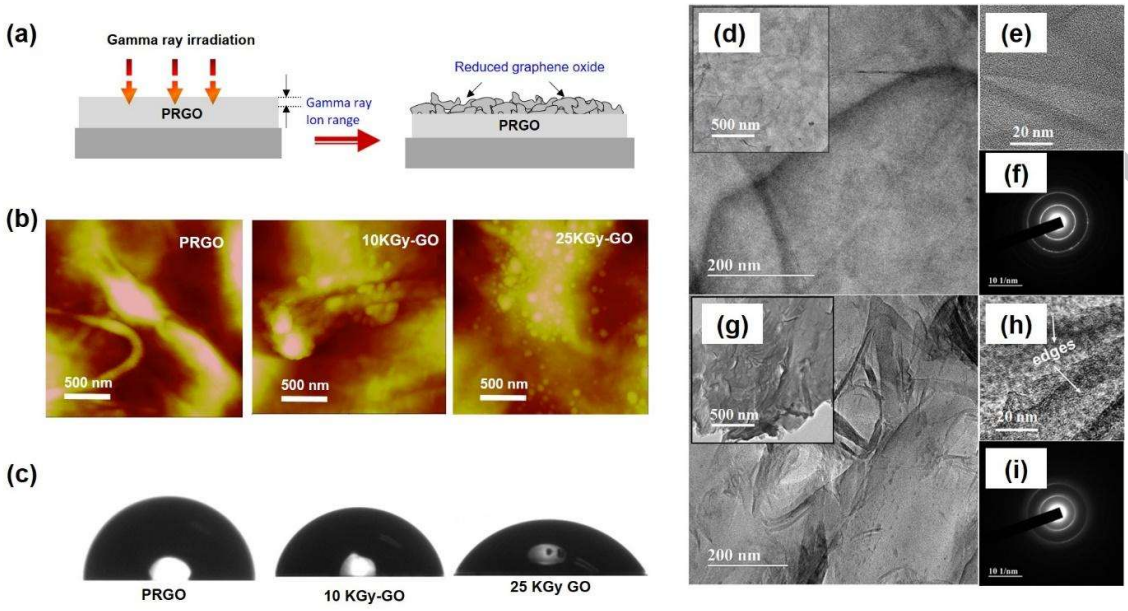


**Figure 1**

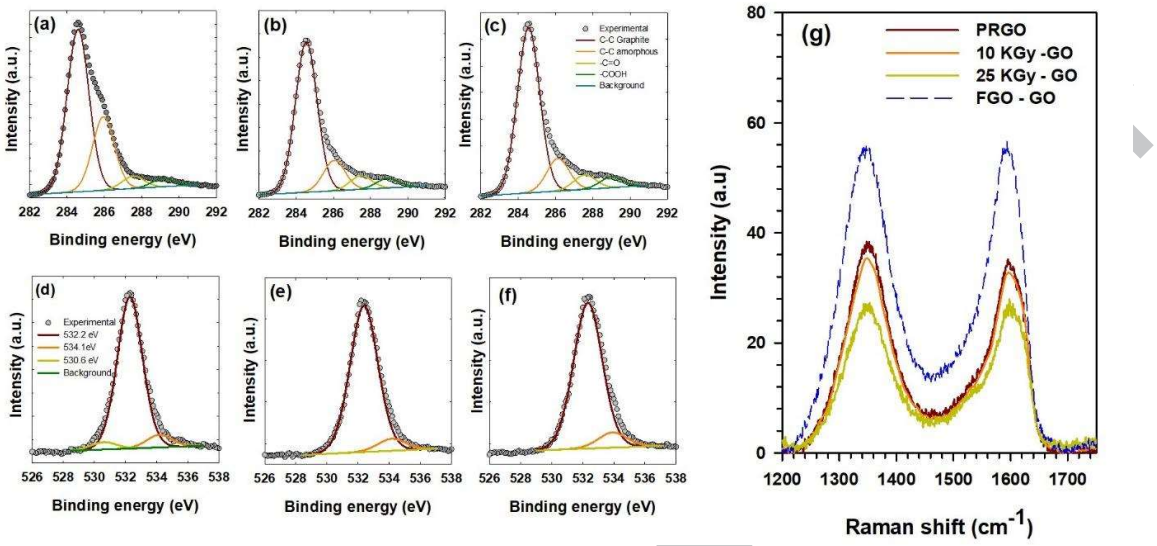


**Figure 2**

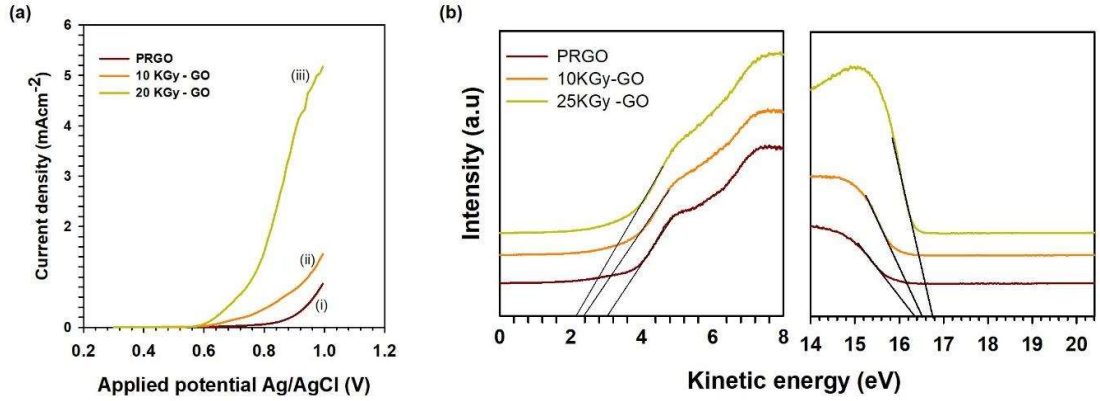


**Figure 3**

**Declaration of interest statement**

All authors confirm that this manuscript has not been published elsewhere and is not under consideration by another journal. All authors have approved the manuscript and agree with submission to *Materials Letters*.

**Conflict of interest statement**

The authors have no conflicts of interest to declare.

**Highlights**

- Exploring the effect of γ-irradiation on partially reduced graphene oxide films
- γ-irradiation induces edge sites and oxygen moieties at graphene oxide lattice
- Improving the hydrophilic nature via γ-irradiation
- High water oxidation catalytic activity achieved at 25 KGy γ-irradiated graphene oxide