

Photoluminescence of Reduced Graphene Oxide Prepared from Old Coconut Shell with Carbonization Process at Varying Temperatures

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Abstract. Reduced graphene oxide (rGO) powder has been prepared from coconut shells by carbonization process at 400°C, 600°C, 800°C and 1000°C for 5 hours at ambient air. In this study the exfoliation rGO was added into distilled water with variation of concentration solution using the sonication process for 3 hours and centrifugation at 4000 rpm for 20 minutes. The characterization were performed by using XRD and photoluminescence (PL) spectroscopy. The photoluminescence or rGO showed the peak of excitation and emission at wavelengths ranging from 340 nm to 800 nm. The PL emission spectra are at wavelength ranging from UV to visible region approaching red. Observation showed that the photoluminescence intensity was significantly increased by the increasing content of rGO in the solution. The influence of the varying temperature on the PL spectra will also be discussed in this study.

1. Introduction

Graphite is an allotrope of carbon that consists of thin sheets of bonds between carbon atoms in hexagonal structure. Graphene, a two-dimensional (2D) building block for other sp^2 carbon allotropes with other dimensionality, is a single layer sheet of carbon atoms arranged as a hexagonal honey-comb lattice structure. It has unique properties which are promising for application in various fields such as supercapasitor, solar cell, sensors and optoelectronic materials [1]. Ideal graphene is a zero bandgap semiconductor that contains sp^2 clusters which are not favorable for luminescence application [2]. Like graphene, graphene oxide (GO) is formed by the oxidation of graphite, with still sp^2 carbon atoms in its structure [3]. Meanwhile, reduced graphene oxide (rGO) is the loss of oxygen and hydrogen atoms in the structures that resemble graphene. The GO and rGO are still hot topics in the research and development of graphene.

The materials that can be used in producing the carbon compounds is coconut shell, which is promising, low-cost, simple, and environmental-friendly. Based on the previous research [4], the old coconut shell heated at 400°C and 600°C has produced rGO phase having diffraction peak of XRD at $2\theta = 24^\circ$ and 43° in all variation of the atmosphere. Further development of the rGO is the process in order to obtain a thinner sheet size, even a single layer of rGO, by means of exfoliation process. Exfoliation process consisting of the sonication and centrifugation in water is the most common. There are various approaches used for GO to synthesize of rGO, such as chemical vapor deposition (CVD), chemical method, mechanical exfoliation and cleavage, and thermal annealing [5]. The reduction of



GO is definitely a key topic, and different reduction processes results in different properties that in turn affect the final performance of materials or devices composed of rGO [6].

Previous studies have established that rGO films exhibited decreased photoluminescence (PL) spectra and were blue-shifted as compared to GO films, resulting from the newly formed small sp^2 clusters after reduction [2]. Red-to-near-infrared PL emitted from chemically-reduced GO has been reported, consistent with increasing disorder length scale with reduction [7]. The rGO has been widely applied in energy storage devices, photovoltaics devices, corrosion protection, and lubricants [8]. In this study, we are investigating the optical properties of rGO prepared from old coconut shell using photoluminescence (PL) spectroscopy.

2. Experiment

The main materials used in this study are old coconut shell and distilled water. The equipment used in this study are furnace (as main heating treatment), ultrasonic washer (as dissolving the sample) and centrifuge (as precipitation to produce the solution). The first step was the process of burning coconut shell to produce charcoal, and then it was crushed into powder. Subsequently, it was heated at a temperature 400°C, 600°C, 800°C and 1000°C for 5 hours at ambient air. Subsequently, the resulted powder was added into distilled water with various solution concentrations of 0.001 mg/ml, 0.002 mg/ml and 0.003 mg/ml. Exfoliation was achieved by ultrasonic washer of the dispersion for 3 hours. Finally, the sample was collected by centrifugation (4000 rpm) for 20 minutes to remove any unexfoliated graphite [9]. Characterization were performed by using XRD (*Philips X'pert*) to identify the existence of rGO phase in the resulted powder after heated at varying temperatures and photoluminescence (PL) spectroscopy (*Perkin Elmer LS-55*) to determine the optical properties of the sample.

3. Results and Discussion

The following is one of the X-Ray Diffraction (XRD) pattern for coconut shell charcoal sample heated at 400°C shown in Figure 1. A further analysis by comparing with reference [10] confirmed that the sample has the similar wide peaks with rGO phase at $2\theta \sim 23^\circ$ and 43° . The peak width indicates the small crystal size of rGO and its structure of layer arranged in short range of the layer stack. The XRD result is related to the processes of removing intercalated water molecules and the oxide groups. The bond between carbon and oxygen in the form reduced graphene oxide phase decreases with increasing temperatures.

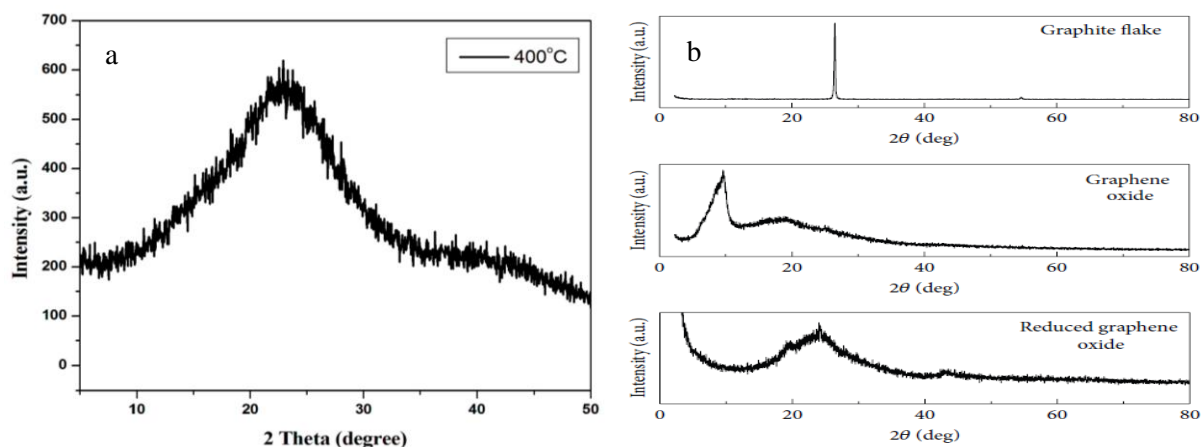


Figure 1. XRD pattern of (a) coconut shell charcoal sample in heating temperatures 400°C, (b) Graphite flake, GO, and rGO [10]

In order to investigate the optical properties of rGO, a photoluminescence study was carried out. Figure 2 (a,b,c) shows one of the results of PL emission spectra with different excitation wavelengths (λ_{ex}) at 800°C in all concentrations solution. With the increasing excitation wavelength from 296 to 352 nm, the emission peak has been red-shift with a gradual decrease in intensity. Almost at every temperature produces the same excitation wavelengths, but at temperatures of 800°C, the resulting emission spectra are more stable than others. Figure 2 (d) shows the PL spectra of rGO at 800°C in all concentrations of solution with $\lambda_{ex} = 343$ nm, it can be seen that the PL intensity tends to increase with increasing concentration of the solution.

Figure 3 represents the PL spectra at $\lambda_{ex} = 343$ nm of rGO with each temperatures prepared by exfoliation process at three different content of solutions. The higher temperature in each of concentration solution has led to an increased emission peak (red-shifted). It is supported by the results of XRD, that the higher temperatures, the reduction graphene oxide phases tends to decrease. Otherwise, the decrease of temperatures leads to a decrease in the emission peak (approaching blue-shifted). The rGO sheets exhibiting quenching in PL emission spectra are blue-shifted due to increased sp^2 clusters after reduction [3]. In the room temperature PL spectra, the defect peak is suppressed in the sample reduced at higher temperature [3].

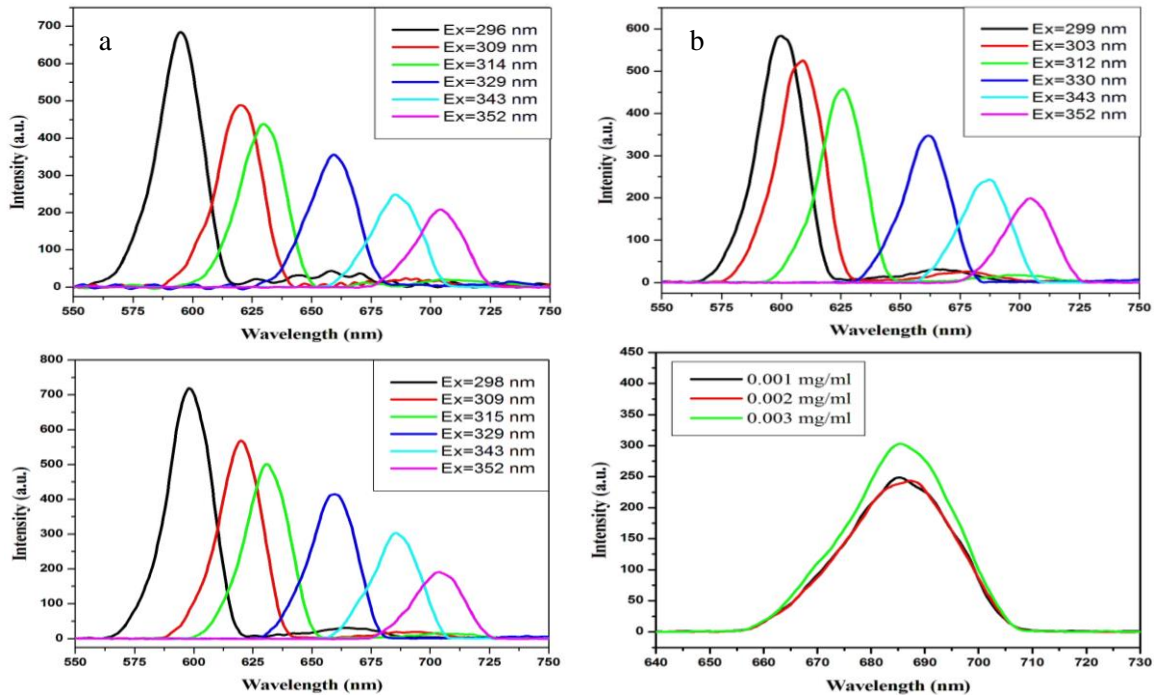


Figure 2. PL spectra of rGO at 800°C with concentration of solution: (a) 0.001 mg/ml, (b) 0.002 mg/ml, and 0.003 mg/ml. (d) PL spectra of rGO at 800°C in all concentrations of solution with $\lambda_{ex} = 343$ nm

The optical properties of sp^2/sp^3 combined materials can be influenced by the size and fraction of the chains and clusters [11]. PL in amorphous carbon originates from the radiative recombination of electrons and holes in the band-tail states created by sp^2 clusters. The photoluminescence of rGO due to the disappearance of functional oxygens which is due to the restoration of more number of sp^2 clusters, the newly formed sp^2 clusters in rGO can provide percolation pathways between sp^2 clusters already present [3]. Therefore, the electron-hole recombination of these sp^2 states improves blue fluorescence.

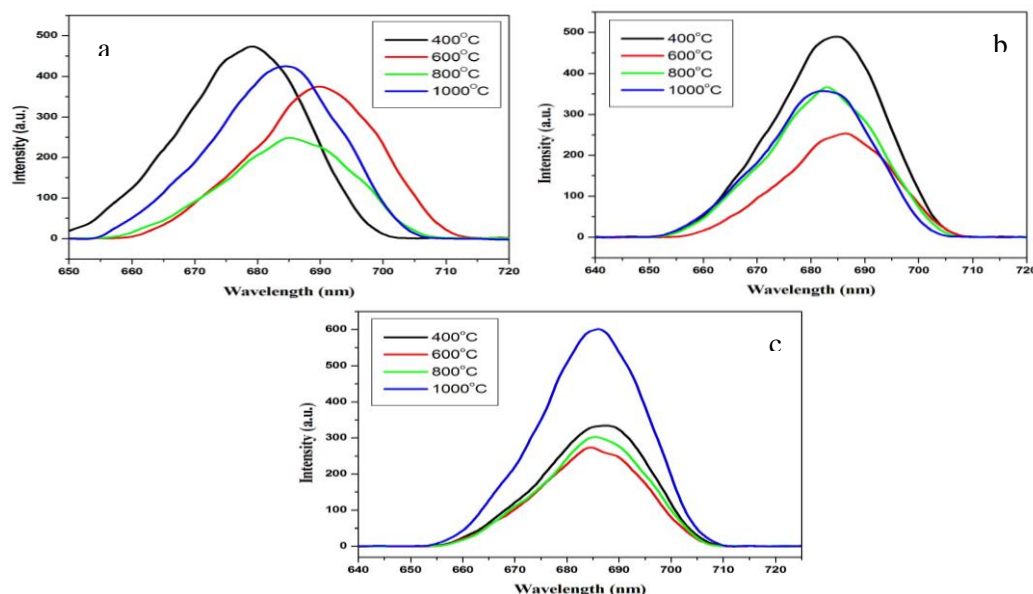


Figure 3. PL spectra of rGO at $\lambda_{\text{ex}} = 343$ nm with concentration of solution: (a) 0.001 mg/ml. (b) 0.002 mg/ml. and 0.003 mg/ml

4. Conclusion

In conclusion, we have prepared the rGO from coconut shell charcoal at three different concentration solutions with varying heating temperatures. In addition, PL spectra of rGO exhibits that the lower temperatures carbonization will produce the decrease of emission peak (approaching blue-shifted). The photoluminescence intensity was significantly increased by the increasing content of rGO in the solution.

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