SYNTHESIS AND CHARACTERIZATION OF REDUCED GRAPHENE OXIDE BY CHEMICAL REDUCING METHOD

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Abstract

Graphene oxide (GO) and reduced graphene oxide (rGO) were successfully synthesized by modified Hummer's method and chemical reduction method. The essential parameters including oxidation and reduction process were confirmed by both visualization and by using characterization tools. Ultraviolet-visible(UV-vis), Fourier transform infrared (FT-IR) and X-ray diffraction (XRD) were conducted for the formation of targeted product, compound identification and crystal structures of synthesized materials. It was found out that the chemical reduction method could successfully reduce GO to rGO without using high energy consumption. Finally, this method results in high reduction degree of GO and large amount of rGO.

.   **Keywords**: graphene oxide, reduced graphene oxide, chemical reduction

Introduction

The conversion of light energy changes directly into electricity by solar cell devices represents one of the most promised for highly remarkable and renewable power. Many different types of solar cells including Si-based, thin film, organic and polymer solar cell and perovskite solar cells have been studied and produced. Among them, perovskite solar cells are the rapidly emerging as the photovoltaic (PV) technology since it has high mobility and fast respond to light, highly efficient and friendly to environment. Perovskites possess properties similar to inorganic semiconductors and the power conversion efficiency of these has improved from 3.8 % to 22.1 % within 7 years (Johan *et al.*, 2017). Recently, graphene-based materials have been used as promising candidates for electron buffer layers for organic electronic applications.

Many believe that perovskites are the future of solar power and researchers are discovering how to combine graphene with perovskites to create even more efficient PV. Recently, planar perovskite solar cells with reduced graphene oxide nanosheets as the hole transport layer was fabricated (Yeo *et al.*, 2014).This perovskite layer is not only highly efficient but also has device stability. Its distinctive structure makes them perfect for enabling low-cost, high efficiency, thin, lightweight and flexible panels. The aim of this research is to synthesize the reduced graphene oxide (rGO) nanoparticles in order to use it as a hole transport layer of perovskite solar cells.

Graphite oxide was firstly produced from pristine graphite by using strong oxidizing agents. However, graphite oxide and GO can be produced by similar in chemical process but different in their structure (Dreyer *et al.*, 2010). Graphite oxide is a bulk solid and itcan be changed into few layer GO by using thermal or mechanical process. Especially, the ultrasonic exfoliation of graphite oxide (sonication method) was an effective way to obtain a single or few layers of GO. GO is the oxide form of graphene, where a large number of oxygen-containing functional groups are bonded with carbon atoms. The presence of oxygen functional groups makes the inter layer spacing of GO larger than graphite. Therefore, GO has high specific surface

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area, high mesopore volume, and certain level of electrical conductivity(Hsu *et al.*,2018). In contrast, rGO contains fewer amounts of oxygen functionalized groups as compared to GO which can be synthesized in chemical reagent and thermal reduction and multistep reduction. The reduction of GO is not only for removing the oxygen functional group but also for recovering the conjugated network of the graphitic lattice. These structure changes obtained the more electrical conductivity and other properties of grapheme (Wang *et al.*,2008).

On the other hand, high reduction temperature and strong reducing agents are required for the complete conversion of GO to rGO. High-temperature reduction processes require excessive energy consumption and get wrinkly amount of rGO sheet. Strong reduction agent can be realized GO interacts with chemical reagent and it can produce a large amount of rGO and can exhibit excellent electrical conductivity. There are plenty of reducing agents such as phenyl hydrazine, hydrazine hydrate, sodium borohydride, ascorbic acid, amino acids and strongly alkaline solutions were used in the past and recently work. In this work, the reduced graphene oxide (rGO) was prepared by using strong reducing reagent sodium borohydride ($NaBH_4$) in order to get mass production and more efficient in conductivity. And also, calcium chloride ($CaCl_2$)was used as catalyst to improve the reduction ability of $NaBH_4$.This method is a cheaper and easily available way for the mass production of rGO compared with thermal reduction.

Materials and Methods

Synthesis of Graphite Oxide

In this synthesis, Graphite powder, sulfuric acid(H_2SO_4,98%) and potassium permanganate($KMnO_4$) were used as a graphite oxide source, solvent and oxidizing agent according to the modified Hummers method (Zaaba *et al.*,2017). Typically, graphite powder (1 g) was dissolved in concentrated H_2SO_4 (50 ml) and phosphoric acidH_3PO_4 (5.5 ml) volume ratio (9:1) with stirring and then $KMnO_4$ (3 g) was slowly added to the mixture. The reaction mixture was then heated to 40^0C for 6 h. After that, 100 ml of deionized water (DI) was slowly added to the reaction mixture in order to fully stop the oxidation process. Then, the slurry was quenched inside the ice bath. Hydrogen peroxide (H_2O_2) (30 wt%, 10 ml) was slowly added to remove the excess $KMnO_4$. The resultant suspension of graphite oxide was separated by centrifugation and then the remaining solid was thoroughly washed with 1 Mhydrochloric acid(HCl) followed by DI water and acetone to remove the sulfate and contaminations. The gel-like graphite oxide was dried at only room temperature.

Synthesis of Graphene Oxide (GO)

Subsequently, previous synthesized graphite oxide was filtered and washed with DI water, 1 M HCl and acetone. The filtered paste was dissolved in 100 ml of DI water. And then, the solution was sonicated for 2 h to exfoliate the layers and centrifuged for 20 mins each at 4000 rpm for several times. Finally, GO flake was thus obtained and dried only at room temperature.

Synthesis of Reduced Graphene Oxide (rGO)

For synthesis of rGO, chemical reducing method was used. GO paste, $NaBH_4$, $CaCl_2$and DI water were used as an rGO source and reducing agents and solvent. Firstly, as-prepared GO paste was diluted in DI water to form a suspension of 30 ml, 3 mg/ml. Secondly, $NaBH_4$ (0.342 g) and 50 mM of $CaCl_2$ (0.15 g) then were added to a 30 ml of GO suspension. The

mixture was kept stirring at room temperature until complete reduction. The final mixture was centrifuged for 20 minsat 4000 rpm to remove aggregated rGO particles. Finally, the obtained black rGO powder was dried only at room temperature for 24 hours for further characterization.Figure 1 illustrates the experiment procures of reduced graphene oxide (rGO).
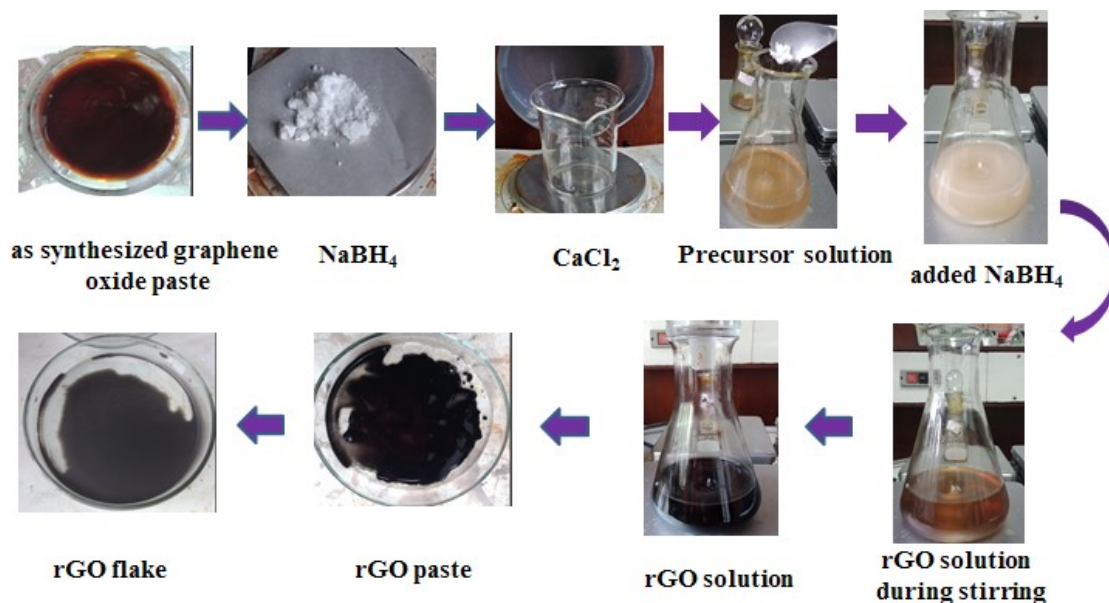

Figure 1 Experimental procedures for synthesis of reduced graphene oxide (rGO)

Characterization

Graphite, as- prepared graphite oxide, GO and rGO were analyzed by using several techniques. The absorbance of GO and rGO solutions were detected by EVOLUTION220 UV-Visible Spectrophotometer. FTIR NICOLET iS5 spectrophotometer was used to characterize the presence of functional groups in as-prepared samples. X-ray diffraction (XRD) patterns of graphite, graphite oxide and graphene oxide and reduced graphene oxide were recorded by RIGAKU-RINT 2000 XRD machine to identify the crystal structure of synthesized samples.

Results and Discussion

Figure 2 shows the colloidal graphite oxide, GO, and rGO in water. Graphite oxide synthesized by modified Hummer's method results in a yellow is haqueous suspension when dispersed in water as shown in Figure 2(a). Figure 2(b) is confirmed that the exfoliation of previous graphite oxide by sonication results in a brown color and semitransparency of GO. Hydrophilic properties of GO was due to their negative surface charge induced the electrostatic repulsion among them and making it strongly hydrophilic(Park *et al.*,2009). In contrast, blackprecipitates are formed when the GO was reduced by chemical reduction method, as shown in Figure 2(c). This is a hydrophobic characteristic of rGO orgraphene sheets with less polar functionality on the surface of the sheets, compared to that of GO (Stankovich S *et al.*,2007).

Visualization

Figure 2 (a) Graphite oxide (b) Graphene oxide(GO) (c) Reduced Graphene oxide(rGO)

UV-Vis result

From Figure 3, the strong absorption peak of GO at 230 nm and it is quite similar with the work reported by (Li*et.,al.,* 2008)where the absorption peak was at 231nm.Then, the peak was red-shifted to 297 nm after reduction using $NaBH_4$and $CaCl_2$, respectively. The absorption of rGO peak red shifted to 297nm suggests that the electronic conjugation within graphene sheets was restored (increased electron concentration after the reduction).
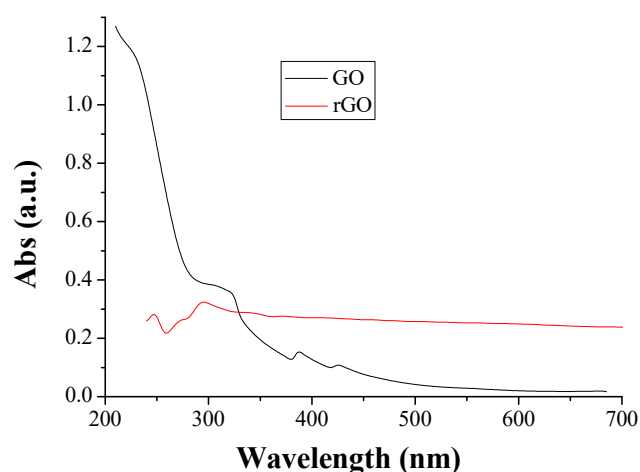
Figure 3 UV-VIS spectrum of graphene oxide and reduced graphene oxide

FT-IR result

The presence of different types of oxygen functional groups in GO and rGO were confirmed by their FT-IR spectra as shown in Figure 4.The broad peaks observed around 3300 cm^{-1}were due to stretching vibration of O-H groups. Besides, the various oxygen functional groups such as alkoxy stretching peak (1030 cm^{-1}), epoxy stretching vibration peak (1152 cm^{-1}) and   -C = O stretching vibration peak (1734 cm^{-1}) can be seen in the FT-IR spectra(Zhang *et al.,*2010).The rGO peak at (1617 cm^{-1}) was due to stretching vibration of C=C (Marcano *et al.,*2010).By matching GO and rGO peaks, the rGO peak dramatically reduced after reduction using $NaBH_4$ and $CaCl_2$ where the carbonyl group can be reduced effectively according to Figure 4. The remaining distant peaks for rGO appearing at(1560 cm^{-1}), (1373cm^{-1}), (900 cm^{-1})were assigned to aromatic C=C,O-H in-plane bending and O-H out of plane bendingre spectively(Yang

et al., 2015).Thus, some oxygen containing functional group of GO were eliminated by using $NaBH_4$as a reducing agent and $CaCl_2$as a catalysis.
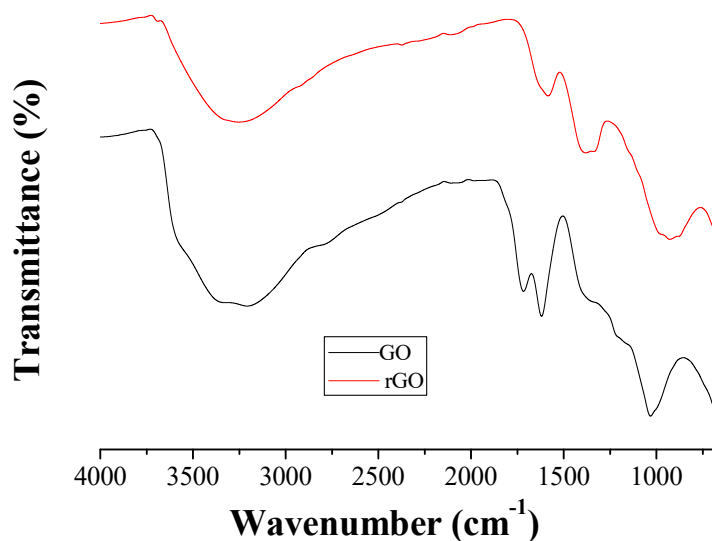

Figure 4 FT-IR spectra of GO and rGO

XRD Result

In this analysis, XRD was used to determine the crystal structure and match the interlayer spacing of graphite, graphite oxide, GO and rGO. The interlayer spacing of obtained samples can be calculated according to the bragg's law (Li *et al.,*2015) .

$$n \lambda = 2d\sin\theta$$

where, n is the diffraction series , λ is the X-ray wavelength(λ = 1.54 A$^\circ$),d is interlayer spacing and θ is the angle between the wave vector of the incident plane wave.The 2θ peak of graphite powder was at26°, indicating that the interlayer distance of graphite powder was 3.42Å. After chemical oxidation, the 2θ peak shifted to10°, which indicates that the graphite was fully oxidized into graphite oxide with an interlayer distance of 8.83 Å. After sonication, 2θ peak of graphene oxide was also 11°which is similar to graphite oxide's peak and its interlayer distance was 8.03 Å. After reduction, a narrow 2θ peak was found out to be at 25° suggesting that the rGO was almost fully reduced. The interlayer distance of rGO is 3.56 Å which is fairly close to that of graphite powder (3.42 Å). This condition can be obviously seen in Figure 5and Figure 6.
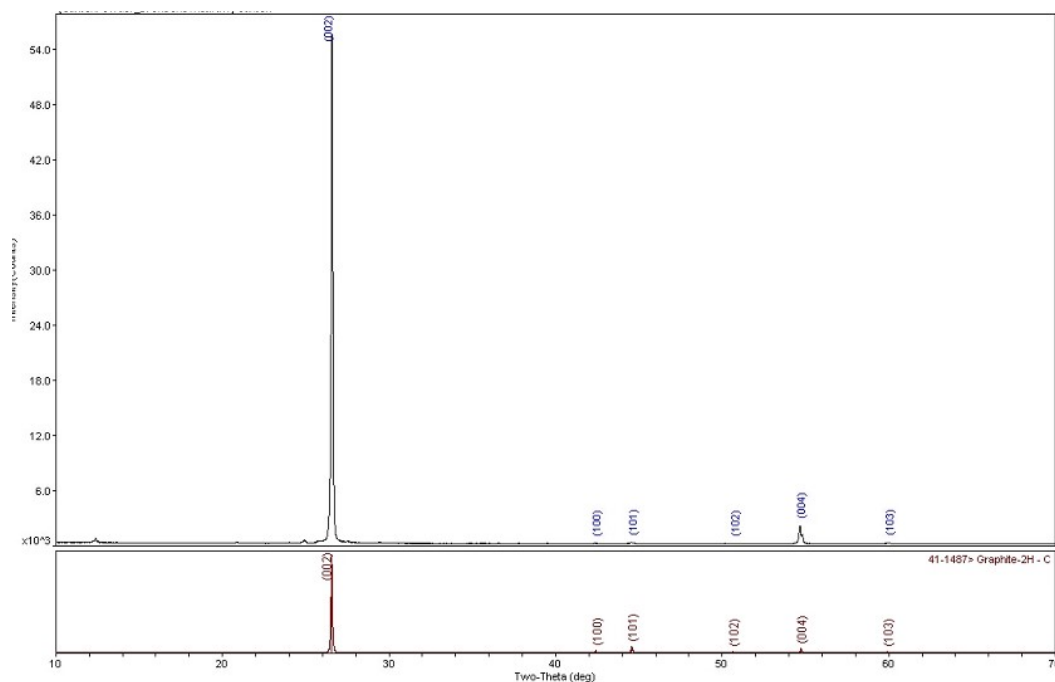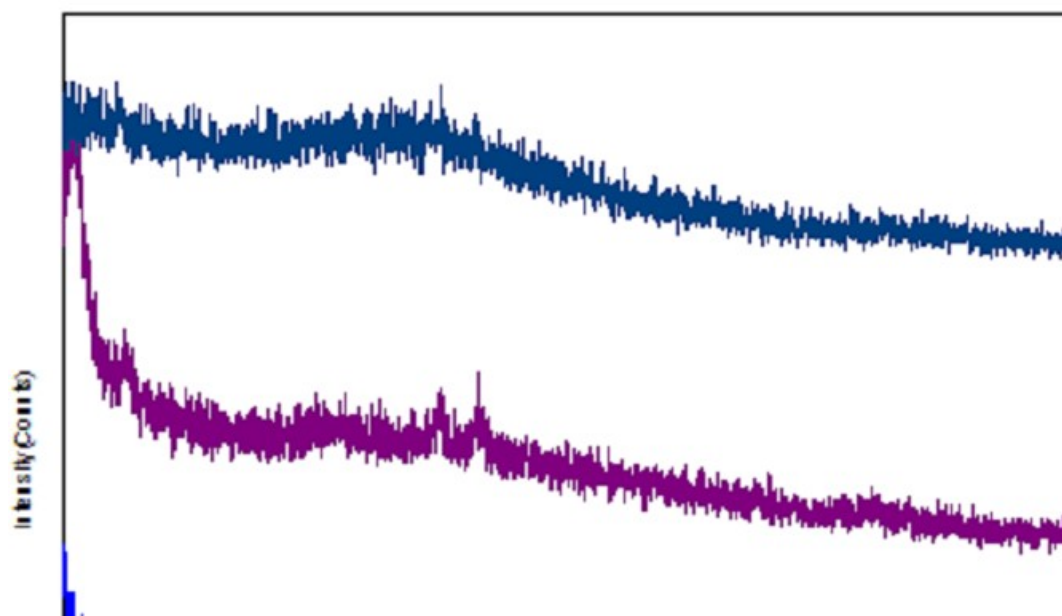
Figure 5 XRD spectrum of Graphite powder

Figure 6 XRD spectra of graphite oxide, graphene oxide and reduced graphene oxide

Conclusion

In this research, graphite to graphite oxide was synthesized by modified Hummer's method by systematically varying the experimental parameters including temperature, reaction time and concentration of $KMnO_4$. Graphene oxide (GO) was successively prepared by sonication process. Reduced graphene oxide (rGO) was effectively synthesized by chemical reduction method using strong chemical reducing agents, $NaBH_4$ together with $CaCl_2$at room temperature. The formation of targeted products including graphite oxide, GO and rGO were completed by observing the color changing throughout the process. Visualized results were

additionally confirmed by characterization tools such as UV-vis , FT-IR and XRD.UV-Vis result suggested that maximum absorption wavelength occurred at 230 nm and 297 nm of the synthesized samples were GO and rGO. By FT-IR results, some oxygen containing functional group of GO were successfully eliminated by using strong reducing agentNaBH$_4$ and CaCl$_2$ and this tended to successful formation of rGO. Therefore, it is obviously that NaBH$_4$ and CaCl$_2$are most effective at reducing -C = Ospecies. Finally, the formation of GO and rGO by interlayer distance of XRD results confirmed that the final product was reduced graphene oxide.

Acknowledgements

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