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SYNTHESIS AND CHARACTERIZATION OF GRAPHENE OXIDE-BASED NANOMATERIALS USING OIL PALM LEAVES AND TEA LEAVES WASTES

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Chair : Assoc. Prof Che Azurahanim Che Abdullah, PhD
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Graphene, which is considered as a unique material due to having an excellent electron conductivity and having the potential as coupling agent with photocatalyst. Despite of that, the challenges came in when consider the cost to mass produce as it will be expensive. Besides, there is a rising concern for the environment when it comes to converting GO to RGO as a cheap alternative to pristine graphene. This is because of the harmful chemicals is conventionally used to reduced GO into RGO. Hence, the objective of the first part of this research was to synthesized graphene oxide (GO) from tea waste as a replacement for commercially available graphite. Then, RGO/TiO_2 was synthesized and the rate of degradation for methyl orange (MO) was observed as the ratio between GO and TiO_2 change. The conversion of tea waste biomass was carried via carbonization at high temperature and further used as starting material to produce graphene oxide (GO). The oxidation and exfoliation of graphitized carbon was successfully achieved using modified Hummer's method. The as synthesized GO was loaded with titanium dioxide nanoparticles (TiO_2) using hydrothermal method to produce RGO/TiO_2. The prepared nanocomposites were characterized by means of XRD, FTIR, Raman and FESEM analysis. The evaluation for RGO/TIO_2 nanocomposite photocatalytic activity was carried out based on degradation of methyl orange (MO) under the ultraviolet (UV) light irradiation. Results obtained using FTIR results revealed the successful oxidation of graphitized carbon with the presence of carboxyl and hydroxyl group. FESEM images suggested the changes of surface morphology from graphite flakes structure into few layers of graphene sheets. Therefore, it can be indicated that graphitized tea waste has the potential to be an alternative replacement for commercial graphite as a precursor to synthesis the GO. Moreover, GO obtained has immense potential for degradation of various water pollutants when combined with TiO_2. Photocatalytic activity experiment inferred that the importance of optimum ratio between GO to TiO_2 which can resulted in difference in the degradation efficiency; RGO/TiO_2 1:8 > RGO/TiO_2 1:4 > TiO_2 > RGO/TiO_2 1:6 > RGO/TiO_2 1:10. In the second part of the project, graphite was used as starting material and was oxidized using modified Hummer's method. The oil palm leaves extract was utilized as an alternative reducing agent to produce reduced graphene oxide. This is due to a rising concern on the usage of conventional reducing agent which is harmful towards the environment. The oil palm leaves extract with the mixture of graphene oxide (GO) solution was refluxed to produce reduced graphene oxide (RGO). The as-synthesized green approach RGO material were then characterized using X-ray diffraction (XRD), UV visible spectroscopy (UV-Vis), energy dispersive X-ray (EDX), transmission electron microscopy (TEM), and Raman spectroscopy. The results revealed that the interspace distance between plane increased proportionally as graphite was oxidized, increasing from 0.33 nm to 0.84 nm. The reduction process of GO using oil palm leave extract showed the success in removing the hydroxyl group and amorphization of sp^2 carbon structures. The reduction process resulted in increase of C/O ratios from 1:1 to 3:1. Raman spectroscopy revealed that the G band position was restored comparable to graphite as the reduction process successful achieved. TEM images and selected area electron diffraction (SAED) patterns illustrated the confirmation of the successfully synthesized of the monolayer of graphene sheet. Electrochemical studies carried out for both GO and RGO have positively differentiated and concluded a better voltage-current response of RGO in comparison to GO. The as synthesized RGO in the current project holds various potential for further investigation and industrial applications not limited to just supercapacitor and photocatalyst.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

SINTESIS DAN PENCIRIAN BAHAN NANO GRAFIN OKSIDA MENGGUNAKAN DAUN KELAPA SAWIT DAN SISA DAUN TEH

Oleh

MUHAMMAD AMIR FAIZ BIN MOHD SHAIFUDDIN

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Grafin dianggap sebagai bahan yang unik kerana mempunyai sifat sebagai konduktor elektron yang sangat baik dan berpotensi sebagai bahan gandingan dengan fotomangkin. Walaupun begitu, ia menjadi satu cabaran apabila kos untuk pengeluaran secara besar besaran dipertimbangkan kerana ianya akan menjadi mahal. Selain itu, terdapat kebimbangan yang semakin meningkat terhadap alam sekitar apabila cuba untuk menukar GO kepada RGO sebagai alternatif murah kepada grafin yang tulen. Ini kerana bahan kimia yang konvensional biasanya digunakan sebagai bahan penurun GO menjadi RGO. Oleh yang demikian, objektif yang pertama bagi kajian ini ialah penghasilan grafin oksida (GO) daripada daun teh sebagai pengganti grafit yang tersedia secara komersial. Selepas itu, komposit RGO/TiO_2 telah dihasilkan dan kadar degradasi metil oren (MO) diuji apabila nisbah antara GO dan TiO_2 juga berubah. Penukaran biojisim sisa teh dilakukan melalui pengkarbonan pada suhu tinggi dan seterusnya digunakan sebagai bahan pemula untuk menghasilkan grafin oksida (GO). Pengoksidaan dan pengelupasan karbon grafit berjaya dicapai dengan menggunakan kaedah Hummer yang diubahsuai. GO yang disintesis dimuat dengan zarah nano titanium dioksida (TiO_2) menggunakan kaedah hidroterma untuk menghasilkan nanokomposit RGO / TiO_2. Nanokomposit yang dihasilkan dicirikan dengan kaedah analisis XRD, FTIR, Raman dan FESEM. Penilaian untuk aktiviti fotokatalitik nanokomposit RGO / TiO_2 dilakukan berdasarkan kadar degradasi metil oren (MO) di bawah penyinaran sinar ultraviolet (UV). Keputusan analisis FTIR menunjukkan kejayaan pengoksidaan karbon grafit dengan kehadiran kumpulan karboksil dan hidroksil. Imej FESEM mencadangkan perubahan morfologi permukaan dari struktur kepingan grafit menjadi beberapa lapisan kepingan grafit. Oleh itu, boleh ditunjukkan bahawa sisa teh bergrafit berpotensi menjadi pengganti alternatif kepada grafit komersial sebagai bahan pemula untuk mensintesis GO. Selain itu, GO yang diperolehi mempunyai potensi besar untuk degradasi pelbagai bahan pencemar air apabila digabungkan dengan TiO_2. Eksperimen aktiviti fotokatalitik menyimpulkan bahawa pentingnya nisbah optimum antara bahan GO ke TiO_2 yang boleh menyebabkan perbezaan kecekapan degradasi; RGO / TiO_2 1: 8> RGO / TiO_2 1: 4> TiO_2> RGO / TiO_2 1: 6> RGO / TiO_2 1:10. Dalam bahagian kedua projek, grafit digunakan sebagai bahan permulaan dan dioksidakan menggunakan kaedah Hummer yang diubahsuai. Ekstrak daun kelapa sawit dengan campuran larutan grafin oksida (GO) direfluks untuk menghasilkan grafin oksida (RGO) terturun. Bahan RGO yang disintesis melalui pendekatan hijau kemudian dicirikan menggunakan difraksi sinar-X (XRD), spektroskopi optik UV (UV-Vis), serakan sinar-X (EDX), mikroskop elektron transmisi (TEM), dan spektrum Raman. Hasil kajian menunjukkan bahawa jarak antara ruang antara satah meningkat secara berkadar ketika grafit teroksidasi, meningkat dari 0.33 nm menjadi 0.84 nm. Bahagian kedua kajian ini tertumpu kepada penggunaan ekstrak daun kelapa sawit sebagai ejen penurunan. Hal ini berikutan kerisauan yang meningkat akibat daripada penggunaan bahan kimia berbahaya sebagai ejen penurun kepada alam sekitar. Proses penurunan GO menggunakan ekstrak daun kelapa sawit menunjukkan kejayaan menyingkirkan kumpulan hidroksil dan amorfus struktur karbon sp^2. Proses penurunan didapati meningkatkan nisbah C / O dari 1:1 hingga 3:1. Spektrum Raman menunjukkan bahawa kedudukan jalur G dipulihkan setanding dengan grafit selepas proses penurunan berjaya dipulihkan Imej TEM dan corak difraksi elektron di kawasan terpilih (SAED) menggambarkan pengesahan monolayer lembaran grafin yang berjaya disintesis. Kajian elektrokimia yang dilakukan untuk GO dan RGO berjaya membezakan dan menyimpulkan tindak balas voltan-arus RGO yang lebih baik berbanding dengan GO. RGO yang disintesis dalam projek ini mempunyai potensi untuk penyelidikan lebih lanjut dan aplikasi industri yang tidak terhad hanya pada superkapasitor dan fotomangkin.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

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LIST OF ABBREVIATIONS

AC	Activated Carbon
CNT	Carbon Nanotube
CRGO	Chemically Reduced Graphene Oxide
CV	Cyclic Voltammetry
CVD	Chemical Vapor Deposition
EDX	Energy Dispersive X-Ray
ERGO	Electrically Reduced Graphene Oxide
FESEM	Field Emission Scanning Electron Microscope
FTIR	Fourier Transform Infrared
GO	Graphene Oxide
MO	Methyl Orange
MWNT	Multi-Walled Nanotube
PET	Polyethyleneterephthalate
RGO	Reduced Graphene Oxide
SWNT	Single-Walled Nanotube
SCCM	Standard Cubic Centimeters Per Minute
TEM	Transmission Electron Microscope
UV	Ultraviolet
UV-Vis	Ultraviolet-Visible
XRD	X-Ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 Research Background

Nanomaterials are materials with nanometer-scale dimensions ranging from one to one hundred nanometer. These nanomaterial's physical and chemical properties were exploited to their full potential, depending on the desired behavior needed for their application. Structures made of nanomaterials come in a variety of shapes and sizes. For example, nanotubes, nanocrystals, quantum dots, and graphene are from the same carbon nanomaterial family but with different physical structure. The unique properties of nanomaterials are becoming important as technology advances. Nanomaterials used in the nanotechnology show significant differences from atomic-molecular or bulk materials. Furthermore, the tunable properties of nanomaterials play an important role. Their synergistic effect and physical properties were easily modifiable using various methods (Gogotsi 2006). Hence, the development of new technologies and devices benefited from their tunable features. The nanotechnology field has grown rapidly in the last few decades. This is because of the availability of powerful tools for characterizing nanomaterials. Characterization tools such as electron microscopy and spectroscopy can reveal a wealth of information about the synthesized nanomaterials (Gábor 2006; Joseph et al. 2017). This resulted in a steady increase in the number of reported methods for synthesis of nanomaterials. A lot of research has also reported a better understanding of the size, morphology, and optical dependence of materials for their application. Graphene is a nanomaterial that has gained popularity in the last decade. Geim and Novoselov (2009) were the first to introduce it, and it has been extensively researched since then. It has become the center of attention in nanotechnology application.

Graphene is made from numbers of carbon atoms that was arranged hexagonally. Additionally, it is referred to as a single layer of graphite. Categorization of graphene-based nanostructures is possible based on their oxygen content, layer count, and surface modifications. The most frequently used classifications of carbon materials are graphite, graphene, and reduced graphene oxide (RGO) (Kumar et al., 2019). It is composed of sp^2 hybridized carbon, with each carbon atom connected by a covalent bond in the same planar. The van der Waals force connected the graphene monolayer. The properties of graphene have increased interest in graphene development in a variety of fields. Li et al., (2018) demonstrated the superiority of graphene electrochemical performance. Graphene is mechanically strong as well, with a high Young's modulus of 1.0 TPa. In theory, graphene has a large surface area (2630 m^2g^{-1}) and a 40-fold higher rate of adsorption than activated carbon (Aunkor et al., 2016; Zhao et al., 2015).

Graphene can be synthesized as a layer of hexagonally arranged carbon atoms through vapor deposition or layer separation from bulk graphite. The formation of the graphene layer from bulk graphite is ideal for graphene mass production. Graphite will be oxidized and exfoliated into GO during this process. Currently, there is a lot of interest in using biomass products as a precursor to synthesize graphene. Agricultural waste biomass, for example, has gradually gained global attention as a low-cost resource for nanomaterial synthesis. Several studies have reported the possibility of synthesizing GO from biomass and waste. Some researchers reported using biomass to synthesize GO, such as cow bone, soot, sugarcane bagasse, chitosan, polyethyleneterephthalate (PET) bottle, and camphor (Kalita et al. 2010; El Essawy et al. 2017; Somanathan et al. 2015; Lavorato et al. 2014; Akhavan et al. 2014).

These straightforward methods mentioned above is considered have a room for improvement considering the GO produced still has an abundance of oxygen functional groups left. Hence, the next step reduction of GO is required for the reconstruction of the lattice. Several methods for reducing GO and forming RGO have been demonstrated. However, concerns about mankind and the environment also have grown gradually. This is because the use of harmful and highly toxic reducing agents in many of the methods. Green synthesis, which is safer to practice, is now the focus of researchers. Several plant-derived green reducing agents have been demonstrated. These findings could pave the way for fewer pollutions caused by modern technology. The RGO produced using green reducing agents may be useful for other applications and perform similarly to pristine graphene.

For instance, the use of graphene in photocatalytic studies has garnered considerable interest. Due to graphene's superior structural and electronic properties, numerous efforts have been made to utilize it as a coupling material with semiconductor material in photocatalytic activity. Titanium Dioxide (TiO_2) nanoparticles have been used as a photocatalyst for degrading dye pollutants for a long period of time. However, TiO_2's potential in visible light is limited by the high rate of electron and hole recombination. Since then, research has focused on graphene oxide (GO) and reduced graphene oxide (RGO) as TiO_2 coupling agents. Numerous fabrication methods for graphene-TiO_2 nanocomposites have been described in recent years. Additionally, the optimal ratio of these materials has been investigated. During the photochemical reaction of graphene-TiO_2 nanocomposite, TiO_2 nanoparticles were irradiated with an energy source greater than their bandgap energy (3.2 eV). The generation of electrons in the conduction band (e^-) and holes in the valence band (h^+) (Zhang et al., 2010). The 0 eV bandgap of graphene is regarded as an ideal electron transfer bridge (Leary and Westwood 2011).

1.2 Problem Statement

Considering the potential of graphene nanomaterials in various field of applications, there is still a gap on more economical and sustainable approach to mass produce graphene. One of the challenges is to tackle the increasing agricultural waste that has been generated. Utilizing agricultural waste to produce valuable nanomaterials seems like a more economical approach that can do cost-saving in industry. Following that, numerous methods for synthesizing graphene oxide (GO) and reduced graphene oxide (RGO) have been demonstrated. Using the agricultural waste, there is a challenge to produce a high-quality nanomaterials product and making it possible for mass produce.

The as-synthesized GO using a modified Hummer's method may address the issue of mass production. However, researchers are still racing to develop a method for producing high-quality RGO that is environmentally friendly. In the chemical method, a hazardous chemical such as hydrazine remains the most efficient reductant. The majority of other green reducing agents reported are either inefficient or impractical in Malaysia due to their scarcity.

1.3 Objectives

The purpose of this research is to synthesize GO and RGO from agriculture waste. Additionally, the photocatalytic activity of GO/TiO_2 was observed. Additionally, this research also carried out the chemical reduction of GO using oil palm leaves extract to produce RGO.

The following are the work's specific objectives:

1 To convert tea waste into graphitic carbon and synthesis GO using modified Hummer's method
2 To evaluate the RGO/TiO_2 nanocomposite photocatalytic activity using methyl orange
3 To characterize the structural and chemical properties by means using XRD, FTIR, FESEM, TEM, Raman, and UV-Vis.
4 To synthesize RGO by utilizing oil palm leaves as an alternative reducing agent and evaluate structural and chemical properties.

1.4 Scope of study

The scope of the works was divided into two parts. The first part focuses on the preparation and characterization of GO using a modified Hummer's method. TiO_2 nanoparticles, a well-known photocatalyst, were used as a coupling agent with GO. The second part of this study examined the potential of oil palm leaves as a reducing agent for GO. We characterized and compared the structural properties and performance of GO and RGO.

In the first part, this manuscript will discuss the synthesis and characterization of GO from tea waste. Tea waste was chosen as a precursor to commercial graphite. Additionally, the prepared GO will be coupled with TiO_2 nanoparticles using hydrothermal method to synthesis a nanocomposite GO/TiO_2. Photodegradation of MO under UV light condition using GO/TiO_2 also will be observed in this work's first project.

The second part of this work is to produce reduced graphene oxide (RGO) using oil palm leaves extract. This section characterized the structural properties, as well as voltage-current response of GO and RGO to determine the potential for further application of the RGO synthesized from green reductant.

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