HYDROXYL FUNCTIONALIZED GRAPHENE AS A SUPERIOR ANODE MATERIAL FOR ELECTROCHEMICAL OXIDATION OF METHYLENE BLUE

Yusbarina Yusbarina^{1,3}, Roto Roto^{1,✉} and Kuwat Triyana²

¹Department of Chemistry, Gadjah Mada University, Sekip Utara Yogyakarta, 55281, Indonesia

²Department of Physics, Gadjah Mada University, Sekip Utara Yogyakarta, 55281, Indonesia

³Department of Chemistry Education, State Islamic University of Sultan Syarif Kasim Riau, Pekanbaru, 28293, Indonesia

✉Corresponding Author: roto05@ugm.ac.id

ABSTRACT

Graphene and its derivatives are among the emerging materials to be studied extensively for many electrochemical applications. The work's objective is to learn the hydroxyl functionalized graphene-modified electrode in the electrochemical oxidation of methylene blue, which is known as a significant industrial dye. Hydroxyl functionalized graphene (G-OH) has been synthesized using graphite as a precursor by a combination of electrochemical exfoliation and sonication methods. Graphite was electrochemically exfoliated in 1.0 M Li₂SO₄ solution for 2 h to produce oxidized graphene flakes. The oxidized graphene flakes were sonicated in 75% acetone for 2 h to yield G-OH. The product crystal structure and elemental composition were checked with XRD and SEM-EDX. The produced G-OH has an atomic content of C 77.98% and O 22.02%. We also confirmed the product by UV-Vis, FTIR, and Raman spectrometries. The G-OH was deposited on the stainless-steel electrode (SS) and tested in the electrochemical oxidation of methylene blue (MB). The cyclic voltammogram of the bare SS electrode and SS/G-OH modified electrode gives oxidation current peak detected at -0.61 V by 0.47 mA and 5.58 mA, respectively. It suggested a high electrocatalytic ability of the SS/G-OH electrode for the electrochemical oxidation reaction. The electrochemical process by the electrode could degrade >92% of the initial MB within 5 min and >99% within 30 min. The GC data suggested that MB mainly degraded to CO₂ and H₂O. This graphene-based electrode could be a potential for the electrochemical oxidation of many organic pollutants to yield environmentally friendly products.

Keywords: Hydroxyl Functionalized Graphene, Exfoliation, Sonication, Electrochemical Degradation, Methylene Blue

RASAYAN J. Chem., Vol. 14, No.2, 2021

INTRODUCTION

Azo dyes are extensively used in textile and cosmetic industries, usually discharged majority during the dyeing process into the effluents.¹ The toxic and carcinogenic properties of these wastewaters cause health problems in aquatic living.² Azo dyes are non-biodegradable dyes, so that they must be treated before discharging into the environment. Electrochemical oxidation is an effective waste treatment method widely used to degrade dyes,³ such as methylene blue. Electrochemical oxidation's advantages are mild and straightforward operating conditions under ambient temperature and pressure and the potential to produce CO₂ and H₂O as final products.⁴

The efficiency of the electrochemical oxidation reaction depends highly on the nature of the electrode material and the operational conditions.⁵ Many electrodes have been used, such as boron-doped diamond,⁶ IrO₂-SnO₂-Sb₂O₅⁷ with a diverse target of dyes. The electrodes are so expensive that they are less applicable for wastewater treatment.⁸ In most electrochemical degradation trials, efficiency usually remains to be the main issue.

Carbon-based materials are suitable electrodes for wastewater treatment because of their high conductivity, availability, and non-toxicity. Based on previous studies, graphene-based materials can be applied as electrode material in the electrochemical oxidation process.⁹⁻¹¹ Graphene is a 2D thin sheet of carbon network with sp² hybridization. It has excellent mechanical strength, outstanding catalytic

properties, and corrosion resistance.¹² The functionalization of graphene with an oxygen-containing functional group presented high electrocatalytic performance for the degradation of dyes.^{13,14} The functionalization of graphene with hydroxyl functional group creates hydroxyl functionalized graphene (G-OH). G-OH contains a lot of hydroxyl groups on its structure that determine its reactivity in the electrochemical oxidation of the dyes. The production processes for G-OH are simple with two-step synthesis in a relatively short time at room temperature, with no need for complex equipment, and without the use of hazardous chemicals.

The objective of the work is to investigate the hydroxyl functionalized graphene-modified electrode in the electrochemical oxidation of methylene blue, one of the industrial azo-dyes. In this work, the synthesis of oxidized graphene was carried out by electrochemical exfoliation. The sonication process was applied to give G-OH. The SS/G-OH modified electrode was prepared by anodic electrodeposition. The modified G-OH electrode was confirmed first by cyclic voltammetry before electrochemical oxidation of MB in the NaCl solution. The progress of the electrochemical oxidation reaction was monitored by UV-Vis spectrophotometry. The product of the electrolysis was analyzed using GC-MS.

EXPERIMENTAL

Materials

Graphite rod with 99.99% purity was acquired from Walfont, China. Lithium sulfate, acetone, sodium chloride, hydrochloric acid, and methylene blue (MB) were purchased from Merck, Germany.

Instrumentation

We used a Thermo Scientific UV-Vis spectrophotometer to record UV-Vis spectra and a Shimadzu Prestige 21 to acquire FTIR spectra. A Rigaku Miniflex600 XRD with CuK α radiation was applied to obtain XRD patterns. A Hitachi Scanning Electron Microscope SU3500 was used to record SEM-EDX data. The Raman spectra were recorded by Horiba Scientific's Raman spectrometer equipped with LabSpec 6 software. An industrial DC power supply of Sanfix SP-305E was used to perform electrochemical exfoliation of graphene as well as electrochemical oxidation. The cyclic voltammetry was performed on an eDAQ Potentiostat controlled with Echem v2.1.0 software. The product of electrochemical degradation of MB was identified by using a Shimadzu QP-2010S GC-MS.

Synthesis of G-OH

The electrochemical exfoliation process was carried out in the electrochemical cell, which consists of both cathode and anode of graphite rods with a diameter of 10 mm. The electrolyte was 1,0 M lithium sulfate. Both electrodes were parallel arranged in such a way with a distance of 1 cm. The electrodes were connected to an industrial DC power supply with an applied voltage of 8,0 V for 120 min. The exfoliated product of electrolysis was filtered and washed with distilled water. 0,2 g of the solid was dispersed in 100 mL of 75% (v/v) acetone solution and sonicated for 120 min to obtain G-OH dispersion. The hydroxyl functionalized graphene was dried at 80 °C for 2 h before further characterization with SEM-EDX, XRD, UV-Vis, FTIR, and Raman spectrometries.

Preparation of SS/G-OH electrode

The preparation of the SS/G-OH electrode was carried out by using an anodic electrodeposition method using a DC power supply. The 316L stainless steel (SS) electrode with dimensions of 5,0-cmx3,0-cm was wet sand-papered with emery paper, degreased using detergent, and then sequentially sonicated in acetone, anhydrous ethanol, and double-distilled water. The bare electrode was immersed in the 2 g/L G-OH dispersion to deposit the G-OH¹⁵ and supplied with a voltage of 30 V for 3 min with 316L stainless steel as an anode and cathode. The cyclic voltammetry (CV) of the obtained SS/G-OH working electrode was recorded using eDAQ Potentiostat. Pt electrodes as cathodes and Ag/AgCl electrodes as reference electrodes. The CV was measured in the supporting electrolyte of 0,1 M NaCl.

Electrochemical Oxidation of MB Using SS/G-OH Electrode

Electrochemical oxidation of 20 mg/L MB with 0,05 M NaCl electrolyte solution was carried out in batch type electrolysis cell of 100 mL volume using an industrial DC power supply with the prepared SS/G-OH electrode as anode and SS cathode. The electrochemical oxidation study was carried out using the current

density 20 mA/cm², the solution initial pH 3, and various electrolysis times of 5, 15, 30, and 60 min. The electrolysis progress was monitored by using a UV-Vis spectrophotometer. The product of the electrolysis was analyzed using GC-MS.

RESULTS AND DISCUSSION

Synthesis of G-OH

The synthesis of G-OH was done according to the reactions (1). Synthesis of graphene and its derivatives by the electrochemical exfoliation has advantages including ease to operate, operating at ambient temperature, and environmentally friendly.¹⁶ Factors affecting the thickness and oxygen content of graphene flakes are the type and concentration of electrolytes and the operational conditions of electrolysis.¹⁷ Since 1 M lithium sulfate was used as an electrolyte, SO₄²⁻ is attracted to the anode and intercalated into the inter-graphite layer, causing an increase in the distance between the layers.¹⁸ Besides sulfate ions, OH⁻ produced from water oxidation also undergoes intercalation into the graphite layer.¹⁹ These intercalation processes cause exfoliation of the graphite layer into thinner layers of graphene flakes. During exfoliation, graphene could partially oxidize to yield oxidized graphene, as shown in reaction (1). Ultrasonication improves the exfoliation of graphite by providing additional energy to break the van der Waals bond.²⁰ Ultrasonication provides the necessary activation energy for electronic transfer to form G-OH²¹. Also, hydrogen atoms and hydroxyl radicals are generated by transient cavitation in aqueous solutions, which may react with solutes in the bulk of the solution.^{22,23} The hydroxyl radical causes oxidized graphene to be oxidized to yield more hydroxyl in the graphene structure.

Reaction-1: Synthesis of hydroxyl functionalized Graphene

Characterization of G-OH

The FTIR data is shown in Fig.-1. The strong peak at 3425 cm⁻¹ is indicative of the O-H stretching vibration mode. The G-OH has a much stronger peak at 3425 cm⁻¹ than that of oxidized graphene. The peak at 1620 cm⁻¹ is indicative of the O-H bending vibration mode. The C-O vibration mode of G-OH is viewed at a peak at 1126 cm⁻¹. The peak at 1720 cm⁻¹ is absent, meaning that there is no C=O bond in the structure of G-OH. A peak near 2924 cm⁻¹ is due to the presence of C_{sp3}-H stretching vibration mode. All of the indicative FTIR peaks confirm the previous reports.²⁴

Figure-2 shows the UV-Vis spectrum of G-OH. A single peak at 266 nm is observed. It could be assigned as a C=C bond of the graphene hexagonal structure. It is believed to be due to the excitation of the C=C framework of graphene.²⁵ The XRD pattern of G-OH shows a decrease in peak intensity at 26.7°. Typical (002) peak of graphene was observed at 2θ of ~26° (JCPDS Number 01.0646).²⁶ Many small peaks could be due to the diffraction of graphite, which was not converted into graphene.

The I_D/I_G ratio obtained from the Raman spectrum is commonly used to evaluate the defect in graphene and other carbonaceous materials.²⁰ The I_D/I_G of oxidized graphene flakes and G-OH are 1,03 and 1,26, respectively. The increase of the I_D/I_G ratio in the G-OH (Fig.-4) suggests that the graphene flakes have been functionalized with hydroxyl groups. The hydroxyl groups present in the graphene edges cause an increase in the amount of carbon sp³, thereby increasing the degree of carbon defects. The same results were obtained in the report earlier.²⁴

The SEM-EDX results show that multilayer graphene with a composition of 83,75% C and 16,25% O was formed in the electrochemical exfoliation step. The sonication process causes the addition of hydroxyl groups in graphene to form G-OH with a chemical composition of 77,98% C and 22,02% O. It

gives a measured O/C atomic ratio of 1:4. The reported work showed that graphene oxide has about 40% C_{sp3} bonding with a measured O/C atomic ratio of 1:5.²⁷

Fig.-1: FTIR Spectra of (a) Graphite, (b) Oxidized Graphene, and (c) G-OH.

Fig.-2: UV-Vis Spectra (a) Graphite, (b) Oxidized Graphene, and (c) G-OH.

Fig.-3: XRD Pattern of G-OH, insert: XRD Pattern of Graphite

Fig.4: Raman Spectra of (a) Graphite, (b) Oxidized Graphene, and (c) G-OH

Cyclic Voltammetry of G-OH

Instead of using glassy carbon to limit the interference of another carbonaceous surface, we use a stainless-steel electrode. The cyclic voltammogram of the SS/G-OH electrode was recorded to understand the redox process of the modified electrode. Figure-6 shows the produced CV. The G-OH was deposited on the SS electrode by the electrochemical reaction. The bare SS electrode shows redox peak currents centered at -0,61 V with the cathodic and anodic peak currents of about 0,47 mA. It could be attributed to the redox of proton/hydrogen.²⁸

The SS/oxidized graphene (SS/G) and SS/G-OH modified electrode give oxidation current peak detected at -0,61 V by 3,94 mA and 5,58 mA, respectively. The oxidation of Cl⁻ to Cl₂ and the ease of reducing Cl₂ to Cl⁻ occurs at the SS/G-OH electrodes during the oxidation and reduction scan, respectively. The performance of the electrode could be due to the successful functionalization of the graphene to hydroxyl groups. According to the previous works, the reactions (2), (3), (4), and (5) could occur.²⁹

Modification of the electrodes and the electrocatalytic reaction of species in the solution have been extensively studied.³⁰⁻³³ The same results occur for the CV of the Ti/TiO₂-NiO₂ electrode in the blank electrolyte. Ti electrode surface that does not contain redox-active species produces a smaller peak current than that of the Ti/TiO₂-NiO₂ electrode.³⁴

Indirect electrolysis of organic compounds relies on the oxidation of pollutants by oxidizing species produced in situ on the electrode surface.⁵ One of the potent oxidizing agents is the hydroxyl radical (•OH). It is very reactive with organic compounds.³⁵ Hydroxyl functionalized graphene (G-OH) contains a

lot of hydroxyl groups on its structure that determine its reactivity in the electrochemical degradation of the organic compounds. The use of G-OH as an electrode coating material could provide excessive hydroxyl radicals ($\cdot\text{OH}$), which will act as a strong oxidizing agent according to the reactions (2) and (3). The $\cdot\text{OH}$ radical could react readily with species available in the solution. Also, if NaCl solution is used as a supporting electrolyte, the G-OH could further oxidize Cl^- to Cl_2 which is also known as a potent oxidizing agent according to the reactions (4) and (5). It will increase the electrocatalytic performance of the G-OH as an electrode modifier in the electrochemical degradation of organic compounds.

Fig.-5: SEM and EDX Results of (a) Graphite, (b) Oxidized Graphene, and (c) G-OH.

Fig.-6: Cyclic Voltammogram of (a) G-OH modified electrode, (b) Oxidized Graphene-modified Electrode, and (c) Blank Electrode in 0.10 M NaCl with a Scan Rate of 50 mV/s. The right is the modified electrode.

Electrochemical Oxidation of MB

In this work, we used MB as a model for the azo dye, which has an aromatic group with the formula of $\text{C}_{16}\text{H}_{18}\text{N}_3\text{SCl}$ and is one of the cationic dyes with strong adsorption power. It has three absorbance peaks in the UV-Vis region at 246, 292, and 664 nm, respectively. The decrease in the absorbance in the UV-Vis region indicates degradation. A decrease absorbance intensity at the peak of 664 nm mainly suggests the deterioration of the MB structure. In comparison, the absorbance intensity decrease in the UV region at 292 and 246 nm indicates that the benzene ring structure and the conjugation system of the phenothiazine species have been decomposed.³⁶

Based on Fig.-7, after 5 min of electrolysis, the peak at 664 nm decreased by 92%, at 292 nm by 87%, and at 246 nm by 74%. The peak at 664 nm reduced entirely after 30 min of electrolysis. Since the peak at 246 nm also disappears, the benzene ring seems to break down.

As indicated by the UV-Vis spectrum, the degradation product of MB was supported by the GC-MS data. Figure-8(a) show the gas chromatograms of the product after 5 min of electrolysis. The mass spectrometry results show that the main intermediate products of electrochemical oxidation of MB are organic acids. It confirms the proposed pathway of degradation methylene reported before.³⁷

As suggested by GC-MS results in Fig.-8, based on the m/z value of the main products of peak #6 and peak #9 detected at the retention time of 34,4 min and 37,9 min are decanoic and 11-octadecenoic acids, respectively. According to the m/z value, a smaller peak than the previous ones at a retention time of 45,8 min (peak #12) is believed to be benzene-1,2-dicarboxylic or phthalic acid. A single benzene ring's appearance suggests that MB was degraded to a single ring structure before degrading further to give small molecules, mainly CO_2 and H_2O .

Fig.-7: UV-Vis Spectra of 20 ppm MB with a variation of electrolysis times, the initial current density was set at 20 mA/cm^2 , solution initial pH 3, the distance between the electrodes of 1.0 cm

Fig.-8: Gas Chromatograms of the MB electrolysis product using SS/G-OH modified electrode, (a) after electrolysis for 5 min and (b) for 30 min, at a current density of 20 mA/cm^2 .

Fig.-9: Proposed Reaction Mechanism of MB degradation by electrochemical degradation by using SS/G-OH electrode.

Figure-8(b) shows the gas chromatogram of the electrolysis product for 30 min. The mass spectra were not shown since there is no appreciable gas chromatogram was observed. The gas chromatograph peak is small, which indicates that the intermediate product has been degraded to CO_2 , H_2O , and small organic species. However, it might contain water-soluble species. The proposed reaction pathway is indicated in Fig.-9.

The appearance of intermediate products indicates that the electrochemical oxidation of MB using SS/G-OH electrodes occurs in two steps. First, the MB molecules react with the surface $\bullet\text{OH}$ radicals and soluble oxidizing agents, presumably Cl_2 and HOCl , to yield smaller linear molecules. Second, these small molecules further degraded to produce CO_2 and H_2O .

Consistent with the UV-Vis and GC data of the electrolysis product, it suggests that the SS/G-OH electrode catalyzes MB's electrochemical degradation reaction to produce environmentally friendly compounds that are CO_2 and H_2O . Thus, the SS/G-OH electrode may potentially find application in the electrochemical degradation of other pollutants.

CONCLUSION

We applied a combination of electrochemical exfoliation and sonication to produce multilayer hydroxyl functionalized graphene. The product had an elemental composition of 77,98% C and 22,02% O. The

electrochemical oxidation of MB using SS/G-OH electrode in NaCl electrolyte showed that the MB concentration decreased by > 99% after 30 min of electrolysis. The analysis results by GC-MS suggest that MB degraded to CO₂, H₂O, and other water-soluble species. It indicates that hydroxyl functionalized graphene can be extended as anode material for different industrial azo dyes' electrochemical oxidation.

ACKNOWLEDGMENT

We thank the Ministry of Religion of the Republic of Indonesia for the 5000 Doctoral Scholarships Program, the Ministry of Research, Technology, and Higher Education of the Republic of Indonesia for *Penelitian Disertasi Doktor* (PDD) grant (grant number 3070/UNI.DITLIT/DIT-LIT/PT/2020), and the Ministry of Education and Culture of the Republic of Indonesia for *Riset Kolaborasi Indonesia* (RKI) grant (grant number 812/UN1/DITLIT/DIT-LIT/PT/2020).

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[RJC-6180/2020]