BUKTI KORESPONDENSI

Judul Atikel	: Performance Of The Composite Electrode Of Reduced Graphene Oxide Palm Oil Shell-Zinc Oxide (rGOCKS-ZnO)
Vol./No./Tahun/.Hal	: 12/2/2023/
Link Artikel	: doi:10.22487/j24775185.2022.v11.i2.pp111-116
Link view artikel	: https://jurnal.fkip.untad.ac.id/index.php/jppmt/issue/view/165
Nama Jurnal	: Jurnal Akademika Kimia
Link Jurnal	: http://jurnal.fkip.untad.ac.id/index.php/jak/
Link Sinta	: **SINTA-Science and Technology Index** (kemdikbud.go.id)
Penulis	: *Thamrin Azis, Muhammad Zakir Muzakkari[1], Muh Nurdin[1], Maulidiyah[1], Wa Ode Muslia[1], C Bijang[2]. Tahril[3]
Status Penulis	: Penulis korespondensi
Institusi Penulis	: Jurusan Kimia FMIPA Universitas Halu Oleo
Bidang Keahlian	: Kimia Lingkungan

HISTORI PROSES

Nama Operator	Status	Waktu	Cara korespondensi	Deskripsi
Penulis	Submission	29 May 2023, Jam 08.25 AM	Author's Email	A New manuscript has been successfully submission: 1 Aticle
Jurnal Akademika Kimia(JKA)	Initial check of the menuscript	29 May 2023, Jam 08.25 AM	Author's Email	Need to improve the description of pictures 2, 5 and 9 as well as references
Penulis	Resubmit revised manuscript Revisi 1	01 Juni 2023, Jam 10.30 AM dan 07 juni 2023 Jam 06.07	Author's massage	Revised manuscript Artikel perbaikan
Jurnal AkademikaKimia (JKA)	Revision required	12 Juni 2023, Jam 10.56 AM	Author's Email	Need provided references and citationseviewers
Penulis	Resubmit revised manuscript Revisi 2	14 Juni 2023, Jam 01.15 AM	Author's massage	Revised manuscript Artikel perbaikan
Jurnal AkademikaKimia (JKA)	Accepted	25 May 2023, Jam 11.46 AM	Author's massage	The paper has been accepted
Jurnal AkademikaKimia (JKA)	Published	30 May 2023	Author's massage	The paper has been Published

1.Bukti konfirmasi submit manuscript(Authour)
29 May 2023
Bukti konfirmasi pemeriksaan awal (Reviwier)
29 May 2023

JurnalAkademika Kimia2(1): 1-7, February 2023
ISSN (online) 2477-5185 | ISSN (print) 2302-6030
http://jurnal.untad.ac.id/jurnal/index.php/JAK/index

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Performance Of The Composite Electrode Of Reduced Graphene Oxide Palm Oil Shell-Zinc Oxide (rGOCKS-ZnO) As A Chemical Oxygen Demand (COD) Sensor By Photoelectrocatalysis

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Received 03 December 2019, Revised 08 January 2019, Accepted 14 February 2019
doi: 10.22487/j24775185.2023.v3.i4.pp

Abstract

Preparation of reduced graphene oxide composite electrodes from palm shells (rGOCKS-ZnO) as a chemical oxygen demand (COD) sensor by photoelectrocatalysis has been successfully carried out. The preparation of rGOPS-ZnO electrodes by thermal reduction method and modified Hummer. The XRD results showed several peaks of rGOCKS-ZnO namely 23.287°, 26.781°, 29.889°, 32.468°, 35.109°, 37.14°, 39.822°, 43.559°, 47.927°, and 48.537°. SEM-EDX analysis reveals the surface of graphene sheets containing aggregates in shape small particles attached to graphene sheets. The results of the EDX analysis consisted of C 67.82%, O. 19.2%, Zn. 7.85% and 5.13% impurity. The CV and LSV tests showed that the rGOAK-ZnO electrode with a variation of 1gram: 0.3 gram had a good response to the oxidation process under visible light. The profile tests of these organic dyes (methylene blue) in concentrations of 0,5 ppm, 1.0 ppm, 2.0 ppm, and 3,0 ppm were applied by Multi Pulse Amperometry (MPA). The performance of the rGOPS-ZnO electrode electrode has been in determining the value of COD by photoelectrocatalytic good sensitivity, linearity, limit of detection, repeatability and service life. The COD value was determined using the rGOPS-ZnO electrode and obtained 2.97897 mg/LO2 close to the theoretical value.

Keywords:*Cocoa shell charcoal, reduced graphene oxide (rGO), zinc oxide (ZnO), COD sensor, photoelectrocatalysis*

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JurnalAkademika Kimia2(1): 1-7, February 2023
ISSN (online) 2477-5185 | ISSN (print) 2302-6030
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Introduction

The palm oil industry produces large amounts of industrial waste as a by-product in the form of palm shell (OPS) which contains cellulose (26.27%), hemicellulose (12.61%) and lignin (42.96%). To day, palm shells are getting a lot of attention because they can be used as a basic ingredient for making Reduced graphene oxide (rGO) Zakir et al, 2019. Reduced graphene oxide (rGO) is a derivative of graphene (Abakumovi, O et al., 2021) which has been developed by various researchers because it has good electrical conductivity, thermal conductivity, mechanical properties, and a large surface area.

Graphene and its derivatives (rGO) can be applied in electrochemical sensors because it can increase the density of the analyte molecules attached so that it can increase the selectivity, sensitivity, and device miniaturization in electrochemical sensors (Guler,M. et al., 2018). One application of the sensor is a photoelectrocatalytic based sensor. The advantages of this method are that it is not harmful to the environment, low cost and chemically stable (Riyani, K. et al., 2012). Reduced graphene oxide (rGO) can be applied to electrochemical sensors (photoelectrocatalytic) in developing ZnO as an agent for decomposing organic matter and Chemical Oxygen Demand (COD) sensors (Azis et al., 2021).

Methods for determining COD can be classified into two categories, simple(conventional) and electrochemically using Ag_2 and CuO composite working electrodes. However, the measurement results provide a smaller COD value when compared to the standard method, because only a small fraction of organic matter can be mineralized by electrochemical oxidation systems (Nurdin, M. et al., 2021).

Zinc oxide (ZnO) is a semiconductor that can be used as a photocatalyst in photocatalytic reactions, especially waste treatment(Nurdiansah et al., 2020). The advantages of the ZnO catalyst are non-corrosive, environmentally friendly, high dielectric constant, relatively abundant, stable, non-toxic, bandgap energy of 3.37 eV and excitation energy of 60 meV. The large band gap energy makes ZnO only active by exposure to UV light thereby limiting its performance. The limitations of the ZnO photocatalyst can be overcome by modifying (doping) the ZnO material using reduced graphene oxide (rGO).Based on this background, a research was conducted on the performance of reduced graphene oxide composite electrode palm oilshell zinc oxide(rGOAK-ZnO) as a chemical oxygen demand (COD) sensor by photoelectrocatalysi.

Method

Instruments and materials

Method

The tools in this research are X-Ray Diffraction (Shimadzu 6000), Fourier Transform Infra Red (FTIR), (Shimadzu 8400), Scanning Electron Microscope Energy Dispersive X-Ray (SEM-EDX) (HITACHI SU 3500), UV-Vis spectrophotometer (UVD-2950,Labimed, INC). The materials used are potassium permanganate (KMnO4) (*Merck*), sulfuric acid (H2SO4) (*Merck*), hydrogen peroxide (H_2O_2) (*Merck*), hydrochloric acid (HCl) (*Merck*), Methylene Blue, Whatman filter paper, aluminum foil, liquid pa.

Synthesis of graphite oxide

The method used to oxidize graphite to graphite oxide in this study is the modification of the Hummer's Method.Synthesis begins with stirring 2 grams of palm shell graphite, 4 grams $NaNO_3$graphite with 98 ml of 98 % H_2SO_4 for 4 hours in an ice bath at temperature of around 5 °C. After that, 8 grams of $KMnO_4$ were added gradually for one hour. The solution was removed from the ice bath and stirred at 25 °C for 20 hours. After that, the addition of 200 ml of distilled water is was carried out in stages.After 1 hour of stirring, 30 % H_2O_2 was added to the solution. The addition of H_2O_2 aims to stop the oxidation process and cause the color of the solution to turn yellow. The solution is was left in a stirring condition for 30 minutes, then the solution is was centrifuged to separate the precipitate. After that, 15 mL of 37 % HCl was added to remove the remaining metal ion. Then it periodically washed untilneutral pH is was obtained.During the washing process, the color of the solution would turn darker due to peeling of graphite to graphite oxide. The neutral solution was then dried at 105 °C for 12 hours to obtain graphite oxide sheet.

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Preparation of rGOAK-ZnOelectrodes

The rGOAK-ZnO powder with mass variations of 0.1 grams, 0.2 grams, and 0.3 grams of ZnO was crushed and put into a watch glass containing paraffin. Then, heated in paraffin temperature 80ºC. The mixture is stirred and inserted into the electrode body while being pressed so that it solidifies. The composite material was characterized using SEM-EDX, XRD and FTIR.

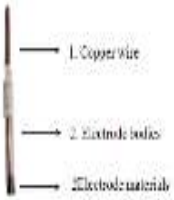


Figure 1. The working electrode components

Characterization of rGOAK-ZnO composites

To assess the characteristics of ZnO/rGO/TiO_2 composite. To determine the crystal structure. Analysis using XRD was carried out to determine the crystal structure of graphene which had been synthesized at an angle of $2\theta^0$ = 20-80^0 and λ Cu-Kα=1.54060 Å.Fourier Transform Infrared Spectroscopy (FTIR) (Scientific Nicolet iS10) test was done to determine the functional groups of the composite at wavenumber range 4000-400cm^{-1}.

Measurement of chemical oxygen demand (COD)

Measurement of COD using photoelectrocatalysis is based on the photocatalytic reaction that occurs on the surface of ZnO. Photoelectrocatalysis with e^-/h^+photogeneration pairs play a role in the reduction-oxidation reactions of organic compounds in solution. When the electrode is irradiated with UV light, the decomposed substance will release electrons. Then transferred to the working electrode. The electrons produced in the form of a light current are used as an amperometric analytical signal.The light current will decrease until the rate of oxidation is equal to the rate of diffusion, so that the current value is zero when the light is turned off. The COD value is determined by the following equation.

$$[COD]_{teoritik} = \frac{Q}{4FV} \times 32000 \quad (1)$$

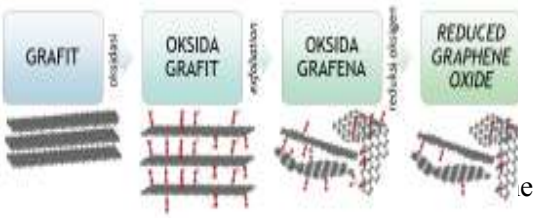
$$[COD]_{teoritik} = \frac{8000nC}{} \quad (2)$$

Where
Q = the charge (Coulomb)
I = light current
A = the number of electrons transferred
F = Faraday constant
V = The sample volume
C = the concentration (Molar)

Results and Discussion

Synthesis of reduced graphite oxide of palm shells

Graphite palm shell charcoal is oxidized to graphite oxide using $NaNO_3$ catalyst, H_2SO_4 solvent and $KMnO_4$ oxide.In the synthesis process, Oxidation using $KMnO_4$ aims to weaken the distance between the layers so as to facilitate the exfoliation process of graphite oxide into graphene oxide (ElFaham et al., 2021; Jain, 2022). Furthermore, the graphene oxide (GO) solution was heated using a hydrothermal apparatus to form a more stable GO structure.From this reduction process *reduced graphene oxide*(rGO)material will be formed (Rattan et al., 2020;Jose at al., 2018), as shown in **Figure 2.**



e

oxide(rGO)

Characterization of fourier transform infrared (FTIR)

The characterization results of GO, rGOand rGO_ZnO with Fourier Transform Infrared(FTIR) can be shown in **Figure 3**

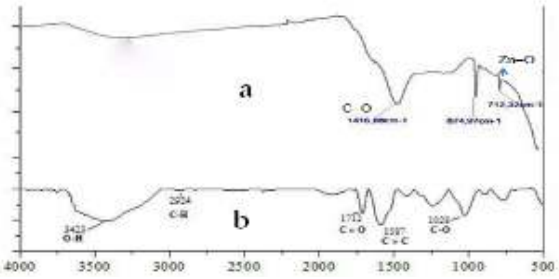


Figure 3. FTIR spectra of the GO, rGO_{PS}, and ZnO-rGO_{PS}composites.

In the FTIR spectrum for GO, the broad peak centered at 3423 cm is attributed to the O-H (Sujiono, E H et al.,2020 and Monteserín C et al.,2017) stretching vibrations, and the peaks at 2924 cm^{-1}, 1712 cm^{-1}, 1589 cm^{-1},1028 cm^{-1} and 1587 cm^{-1} are assigned to the C–H, C=O sp^2 -hybridized C=C group and C–O (Sujiono, E H et al.,2020 and Selim Md et al.,2012) stretching, respectively. In contrast, the peaks at 2924 cm^{-1}, 1712 cm^{-1}, 1589 cm^{-1}, and 1028 cm^{-1} cm are missing from the FTIR spectra of the ZnO-rGO_{PS}composites.In addition, the ZnO-rGOPS FTIR spectra showed a peak at 712 cm^{-1} where ZnO bonds identified ZnO compounds.

X-Ray difraction (XRD)

Characterization was performed using XRD to determine the crystal structure of the rGO-ZnO composite electrode(Mursalim., et al 2017). The x-ray diffraction pattern shows specific peaks which are characteristic of rGO_{PS}-ZnO. The XRD patterns of the obtained products are shown in Figure 4.

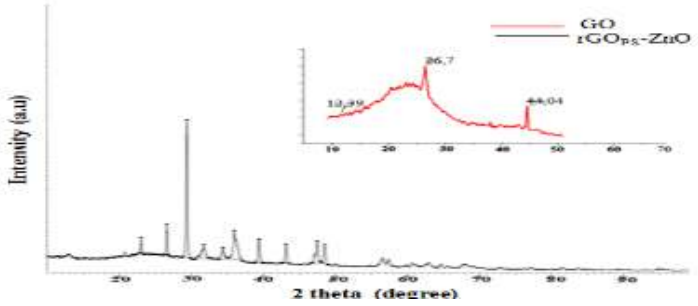


Figure 4. XRD patterns of GO and rGO_{PS}-ZnO

Figure 4 showed the results of the graphene oxide (GO) rGOPS-ZnO pattern. Based on the results, it can be ractogram for peaks of 2θ = 12.39º (d-spacing=7.138Å), 26.7º(d-spacing=7.138Å), and 44.04º(d-spacing =3.350Å). The characteristic feature of GO crystals is that they have 2θ bands at 25° and 45° (Putri, et al., 2019; Robaiah et al., 2019). The observed peak confirms that the graphene oxide sheet peels off from the graphite flakes. In addition, the rGO-ZnO diffraction pattern indicated several peaks at an angle of 2θ, namely 23.287º(d-spacing = 3.350Å), 26.781° (d-spacing =3.34976Å), 29.889°(d-spacing = 3.03552Å), 32,468° (d-spacing = 2,8181Å) 32,468° (d-spacing = 2,6038Å), 35,109 ° (d-spacing = 2,49305Å), 37,14° (d-spacing = 2,28422 Å), 39.822° (d-spacing = 2.09428 Å), 43.559°(d-spacing =2.09428 Å), 47.927°(d-spacing=1.91183Å) and 48.537 d-spacing=1.87479Å) (Liu et al., 2018).

From the data, showing doped rGO_{PS} in ZnO, it is proven that there are peaks of rGOPS and ZnO crystals in the obtained XRD diffractogram pattern. Based on standard joint committee powder of diffraction ZnO (JCPDS 36-1451), The results of the XRD characterization show that ZnO has a distinctive peak at an angle of 2θ = 35.109°, 37.14° (100), 39.822° (101); 47.927° and 48.537° (102).

SEM and EDX

The morphology of the rGO-ZnO sample at the x5000 and x 10000 magnification is shown Figure 5.

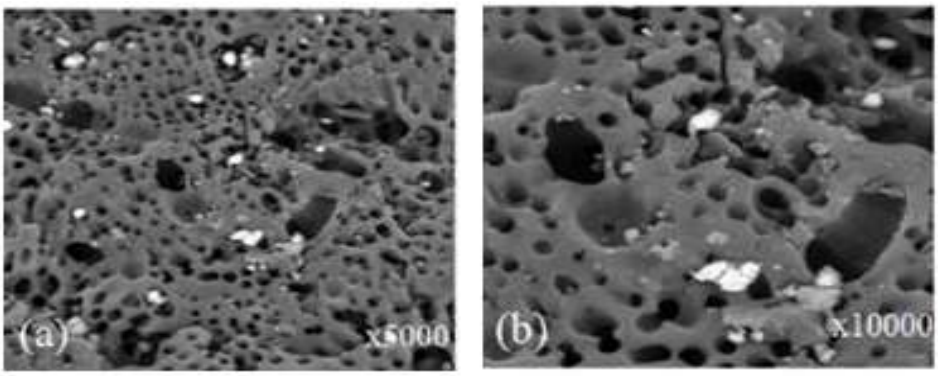


Figure 5. Morphology of rGO_{PS}-ZnO (a) Magnification x 5,000 and (b) x 10,000

Figure 5. the result of SEM characterization of the rGOPS-ZnO composite, showingThe morphology of the porous surface contains bright black and white particles identifying the presence of rGOCKS and ZnOparticles.The EDX analysis results are shown in **Figure 6.** Showed the presence of carbon (C), oxygen (O), and zinc (Zn) elements to identify the success of doping rGOCKS on ZnO.

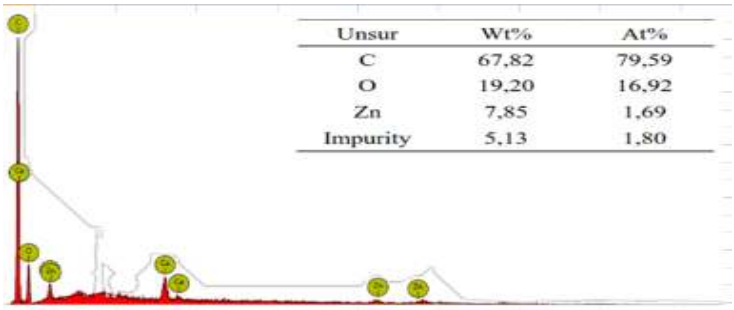


Figure 6. EDX result of ZnO

Activity test of rGO_{PS}-ZnO electrode using LSV and CV

The electrochemical test has applied using three electrodesvariation namely rGO- ZnO,platinum (Pt) electrode, and Ag/AgCl electrode. The electrolyte was used at 0.01 $MK_3[Fe(CN)6]$ to observe the reduction- oxidation (redox) peaks and also the rate of electron transfer (Momeni, M.M, et al.,2019)

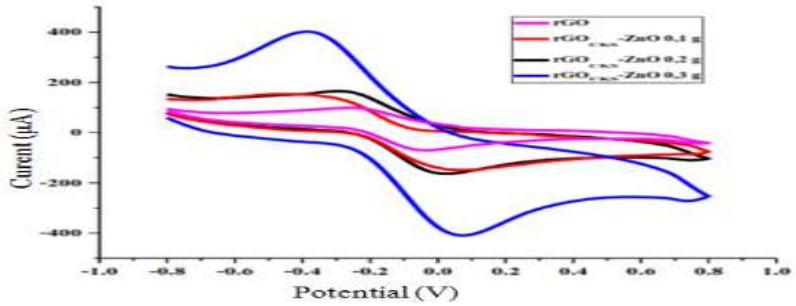


Figure 7. The CV graph by comparing the four working electrodes using $K_3[Fe(CN)6]$ as the electrolyte solution.

Figure 7 shows the voltammogram curve of $K_3[Fe(CN)6]$ electrolyte using a scan rate of 1,0 Vs^{-1}in the potential range from electrodes were measured regardingredox peaks (Ipa = oxidation current; Ipc = reduction current; Epa = oxidation potential;Epc = reduction potential), it can be seen in Table 1.

Tabel 1. The three working electrodes performance regarding oxidation–reduction peak (refers to Figure 4)

Electrode	*Ipa(μA)*	*Ipc(μA)*	*Epa(V)*	*Epc(V)*
rGO	49	-19	-0,24	-0,04
rGOCKS- ZnO 0,1 g	95	-30	-0,29	0,01
rGOCKS- ZnO 0,2 g	102	-48	-0,36	0,02
rGOCKS- ZnO 0,3 g	226	-92	-0,39	0,06

Based on **Figure 7** and **Table 1.** shows the measurements using the four electrodes under $K_3[Fe(CN)6]$ electrolyte solution have produced the redox peaks with a scan rate of 1,0 Vs^{-1}. The 0.3 g rGO-ZnO electrode gave a higher peak current response (266 μA) compared to other electrodes. This is due to an increase in the number of electron transfers from the analytes produced from doping. The Linear Sweep Voltametry (LSV) method is a micro-scale electroanalytic method that

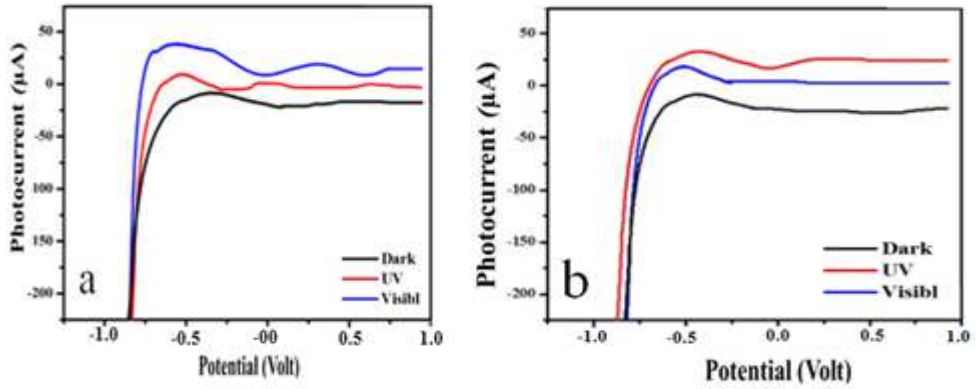


Figure 8. Test of electrode activities by the process of LSV (a) ZnO and(b). rGO-ZnO.

The light current response of the electrode that is not illuminated by UV light (dark) does not indicate a light current. This is because electrons and holes are not formed as the initiator of oxidation andreduction reactions. When the UV illumination of ZnO and (b). rGO_{PS}-ZnO electrodes shows a highincrease in light current, this indicates photocatalytic activity

Figure 8a.shows that when hitUV light irradiation, ZnO electrode performance is higher. This is consistent with the theory that TiO2 is active with an energy gap of 3.2 eV only in the UV regionwith a wavelength of around 388 nm (Maulidiyah, et al., 2017). **Figure 8b** shows the effect of UV light irradiation, visible light and is not irradiation (dark) on the rGO-ZnO working electrode. When the rGO-ZnO electrode is irradiated with visible light, it shows an increase in the light current. This is because rGO doping has decreased ZnO bandgap energy and serves as an electron acceptor to increase the electrons and holes that enter the ZnO surface . On the other hand, the addition of rGO dopant to ZnO can reduce the energy gap of ZnO, so that the electrodes can absorb light at a fairly large wavelength with les energy (Basavarajappa P S, et al., 2020 &Patil S B, et al., 2019).

Photocurrent response of the methylene blue

Photocurrent response measurement of ZnO electrodes and rGO_{PS}-ZnO electrodes to Methylene Bluewas carried out using the Multi Pulse. Amperometry (MPA) method. The test was carriedout on the test solution with a respective concentration of 0.5, 1, 2, and 3 ppm. The amperogram of rGO-ZnO electrode agains Methylene Blue are shown in Figure 9.

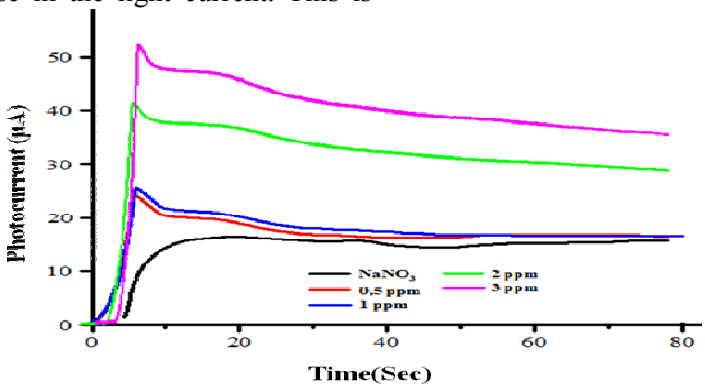


Figure 9. The photocurrent response of methylene blue, amperomogram of rGO-ZnO electrode.

Figure 9. shows the photocurrent produced by methylene blue (MB) is greater than that of the electrolyte solution. The resulting light current is the sum of the oxidation currents of methylene blue (MB) andthe oxidation currents of electrolyte solutions. The photocurrent produced by methylene blue (MB) is greater than that of the electrolyte solution. The decrease in photocurrent occurs because the methylene blue (MB) compound decreases in solution due to photocatalytic degradation. The greater the concentration of organic compounds,

The higher the photocurrent response produced. The performance of the rGO-ZnO electrode is known by observing the proximity of the generated charge value to the theoretically generated charge value. **Figure 10** shows Qnett's relationship with methylene blue (MB)compounds.

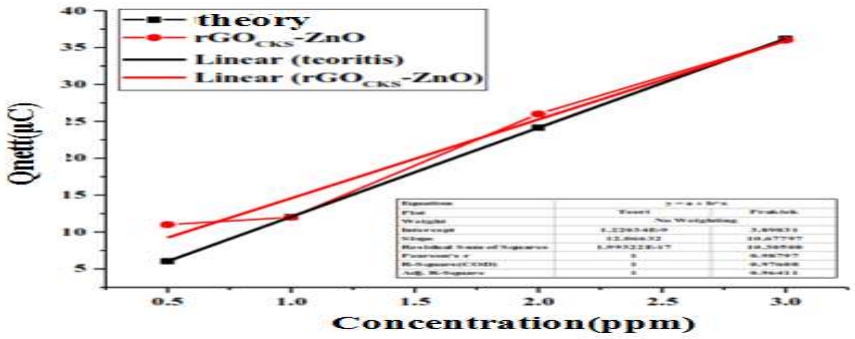


Figure 10. The relation between Qnett and concentration of methylene blue (MB) compound.

Based on **Figure 10**. The performance of the rGO-ZnO electrode shows the highest level of accuracy in methylene blue (MB). This is due to the molecular structure of methylene blue (MB) which makes it easy to mineralize.In addition, the resulting charge is directly related to the concentration of the test compound. This is in line with the law of Faraday, which states that the greater the solution concentration, the greater the charge received. This is due to the interactionof the analyte molecule and the surface of the electrode.The strong interaction with the surface of thecatalyst causes an increase in the rate of oxidation of organic compounds so that the resulting load is greater.

Determination of chemical oxygen demand (COD) value

Figure 11 represents the linearity of the measurement data for COD values on methylene blue (MB) using the rGO-ZnO electrode to see the theoretical COD value with a photo electrocatalytic approa

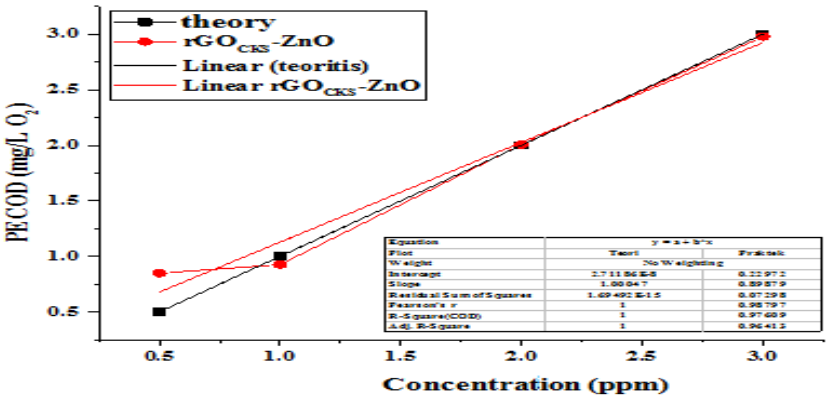


Figure 11. compares theoretical COD values and CODPEC values as the methylene

Figure 11 compares theoretical COD values and COD PEC values as the methylene blue (MB) concentration increases from 0,5 ppm to 3,0 ppm. The data show that increasing the concentration of methylene blue (MB) makes the COD PEC value close to linearity to the theoretical COD value, so that the probability of linearity is observed at methylene blue (MB) concentrations from 0.5 ppm to 3.0 ppm, as shown in table 2.

Table 2. Methylene blue (MB)COD using rGO-ZnO electrode

Concentration (ppm)	COD (mg/L O2) Theoretical	COD (mg/L O2) Photoelectrocatalytic (COD PEC)
0,5	0.5002345	0.84907
1,0	1.000469	0.92626
2,0	2.0009379	2.00689
3,0	3.0014069	2.97877

Determination of Linearity, Detection Limit and sensitivity

The linear regression equation applied to the results must have intercept values not significantly different from zero. If the non-zero significant intercept is obtained, it must be proved that this has no effect on the accuracy of the method (Veerasamy R, et al,. 2011)

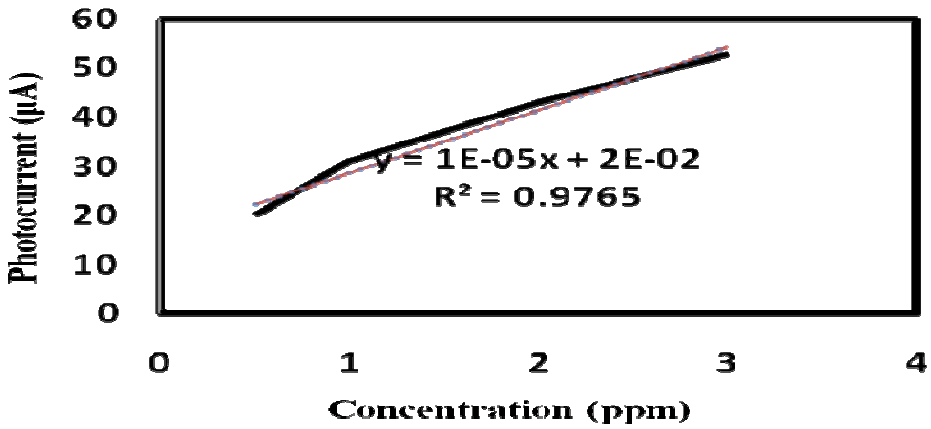


Figure 12. Linear graph of methylene blue test compound

The linearity can be found from the coefficient slope based on methylene blue concentration toward oxidation peak (Ipavalue) which showed in Fig. 8. We obtain the linearity equation is $y = 10^{-5} x + 0,02$ with an intercept value of 0,02 and a slope of 10^{-5}. It aims to determine the range area that occurs in measuring the methylene blue compound by R2 = 0,9765 or close to 1. According to Nurdin et al (2009), at low concentration the photodegradation process is only influenced by photo hole capture process on catalyst surface while at high concentration compound structures affect the photodegradation process of the compounds(Muzakkar et al., 2021). Determination of the detection limit was carried out to find out the smallest concentration of methylene blue in the sample that can still be detected by the rGO-ZnO sensor and still provide a significant response. Detection limit shows the levelthe sensitivity of the electrode, the lower the detection limit, the betterits sensitivity to the sample (Lukmana, K. M, et al., 2018).). Then, the LoD has been obtained from calculation results is 0,06 ppm which shows that rGOC-ZnO composite is able to detect methylene blue compound up to a concentration of 0.06 ppm. The rGO-ZnO electrode has the capability of detecting methylene blue with high sensitivity.This can be seen from the greater slope and higher sensitivity.

Electrode repeat test

The repeatability test was conducted to exhibit the working electrode performance against the consistency of measurement. This treatment therGOAK-ZnO composites has been tested by using methylene blue. **Figure 13** depicts the results of repeatability working electrode that the high-performance.

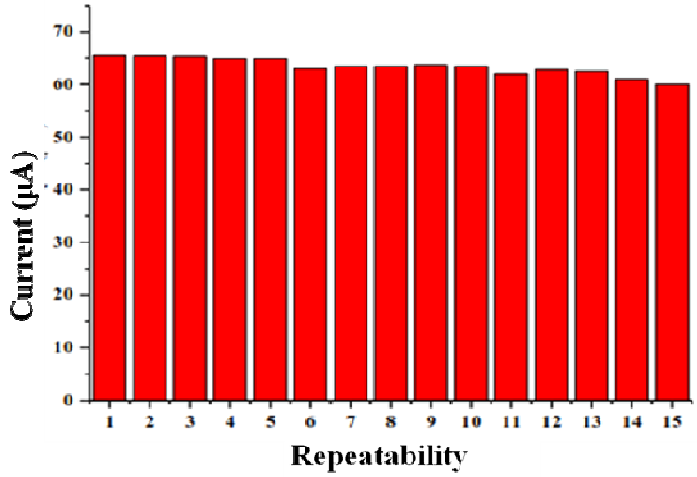


Figure 13. The histogram of oxidation current versus the repeating measurement.

Figure 13 depicts the results of repeatability working electrode that the high-performanceof rGO_{PS}-ZnO stability for 15 times tested.Based on this study (**Figure 10**), we obtain calcuating the standard of deviation (SD) of 1,57 and Relative Standard Deviation(RSD) is 2,48%. We declare that the rGO-ZnO composites has stabilized due to the Horwitz value is obtained less than 2% (1,24 %)

Electrode lifetime determination

Especially, we explore a lifetime of rGO-ZnO to obtain the high-performance electrode for 14 days. The lifetime test performance has been carried out by using the same solution on the repeatability test Extension life time electrode enforced for clarifying Extension life time electrode enforced for clarifying rGO-ZnOto sensitivity against fipronil. to sensitivity against methylene blue. Mean while, if it is to be increased, the rGO-ZnO composite must remove organic compounds on the surface of the electrode.

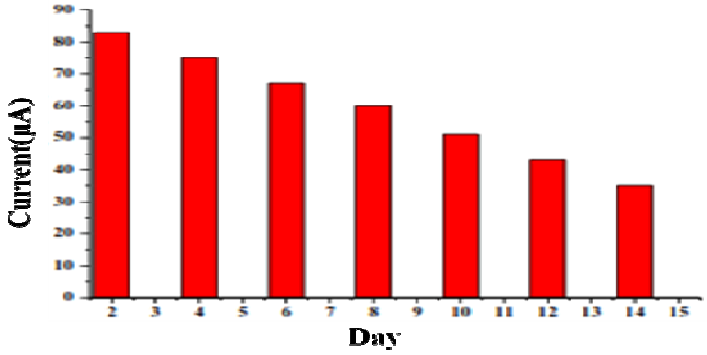


Figure 14. life time test of rGO-ZnO composites.

Fig. 14 exhibits that the optimum performance electrode from 1 until 8 days relatively stable, while the 9 until 14 days the low-performance electrode. This condition that the longer electrode used causes thickening diffusion on the electron transfer system and limiting peak current

Conclusion

Electrodes of rGO-ZnOhave been successfully. Then the rGO-ZnO electrodes were characterized using FTIR, XRD and SEM-EDX. FTIR results show absorption at wavenumbersof 1416 $cm^{-1}$and 712 cm^{-1}, indicated as C-O and Zn-O bonds. The XRD results of rGO-ZnO show. peaks at an angle of 2θ, namely 23.287º, 26.781°, 29.889°, 32.468°, 35.109°, 37.14°, 39.822°, 43.559°,47.927°, and 48.537. SEM-EDX analysis revealed a porous graphene sheet surface, black and white colored particles identified the presence of rGO and ZnO. The results of the EDX analysis consisted of C 67.82%, O. 19.20%, Zn. 7.85% and 5.13%

impurity. The detection limit obtained was 0,06 ppm. and the repeatability was indicated by a Horwitz Ratio (HorRat) value of 1,24%. The optimum measurement stability in analyzing methylene blue is 14 days. The COD value is close to the theoretical concentration of 3 ppm (2.97897mg/LO_2).

Acknowledgments

The authors would like to thank the Physical Chemistry Laboratory and the Inorganic Laboratory of the Faculty of Mathematics and Natural Sciences, Halu Oleo University, which have assisted in completing this research.

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Bukti konfirmasi resubmit artikel revisi
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JurnalAkademika Kimia2(1): 1-7, February 2023
ISSN (online) 2477-5185 | ISSN (print) 2302-6030
http://jurnal.untad.ac.id/jurnal/index.php/JAK/index
OPEN ACCESS

Performance Of The Composite Electrode Of Reduced Graphene Oxide Palm Oil Shell-Zinc Oxide (rGOCKS-ZnO) As A Chemical Oxygen Demand (COD) Sensor By Photoelectrocatalysis

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Received 03 December 2019, Revised 08 January 2019, Accepted 14 February 2019
doi: 10.22487/j24775185.2023.v3.i4.pp

Abstract

Preparation of reduced graphene oxide composite electrodes from palm shells (rGOCKS-ZnO) as a chemical oxygen demand (COD) sensor by photoelectrocatalysis has been successfully carried out. The preparation of rGOPS-ZnO electrodes by thermal reduction method and modified Hummer. The XRD results showed several peaks of rGOCKS-ZnO namely 23.287°, 26.781°, 29.889°, 32.468°, 35.109°, 37.14°, 39.822°, 43.559°, 47.927°, and 48.537°. SEM-EDX analysis reveals the surface of graphene sheets containing aggregates in shape small particles attached to graphene sheets. The results of the EDX analysis consisted of C 67.82%, O. 19.2%, Zn. 7.85% and 5.13% impurity. The CV and LSV tests showed that the rGOAK-ZnO electrode with a variation of 1gram: 0.3 gram had a good response to the oxidation process under visible light. The profile tests of these organic dyes (methylene blue) in concentrations of 0,5 ppm, 1.0 ppm, 2.0 ppm, and 3,0 ppm were applied by Multi Pulse Amperometry (MPA). The performance of the rGOPS-ZnO electrode electrode has been in determining the value of COD by photoelectrocatalytic good sensitivity, linearity, limit of detection, repeatability and service life. The COD value was determined using the rGOPS-ZnO electrode and obtained 2.97897 mg/LO2 close to the theoretical value.

Keywords:*Cocoa shell charcoal, reduced graphene oxide (rGO), zinc oxide (ZnO), COD sensor, photoelectrocatalysis*

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JurnalAkademika Kimia2(1): 1-7, February 2023
ISSN (online) 2477-5185 | ISSN (print) 2302-6030
http://jurnal.untad.ac.id/jurnal/index.php/JAK/index

Introduction

The palm oil industry produces large amounts of industrial waste as a by-product in the form of palm shell (OPS) which contains cellulose (26.27%), hemicellulose (12.61%) and lignin (42.96%). To day, palm shells are getting a lot of attention because they can be used as a basic ingredient for making Reduced graphene oxide (rGO) Zakir et al., 2019. Reduced graphene oxide (rGO) is a derivative of graphene (Abakumovi et al., 2021) which has been developed by various researchers because it has good electrical conductivity, thermal conductivity, mechanical properties, and a large surface area.

Graphene and its derivatives (rGO) can be applied in electrochemical sensors because it can increase the density of the analyte molecules attached so that it can increase the selectivity, sensitivity, and device miniaturization in electrochemical sensors (Guler,M. et al., 2018). One application of the sensor is a photoelectrocatalytic based sensor. The advantages of this method are that it is not harmful to the environment, low cost and chemically stable (Riyani, K. et al., 2012). Reduced graphene oxide (rGO) can be applied to electrochemical sensors (photoelectrocatalytic) in developing ZnO as an agent for decomposing organic matter and Chemical Oxygen Demand (COD) sensors (Azis et al., 2021).

Methods for determining COD can be classified into two categories, simple(conventional) and electrochemically using Ag_2 and CuO composite working electrodes. However, the measurement results provide a smaller COD value when compared to the standard method, because only a small fraction of organic matter can be mineralized by electrochemical oxidation systems (Nurdin, M. et al., 2021)..

Zinc oxide (ZnO) is a semiconductor that can be used as a photocatalyst in photocatalytic reactions, especially waste treatment (Nurdiansah et al., 2020). The advantages of the ZnO catalyst are non-corrosive, environmentally friendly, high dielectric constant, relatively abundant, stable, non-toxic, bandgap energy of 3.37 eV and excitation energy of 60 meV. The large band gap energy makes ZnO only active by exposure to UV light thereby limiting its performance. The limitations of the ZnO photocatalyst can be overcome by modifying (doping) the ZnO material using reduced graphene oxide (rGO).Based on this background, a research was conducted on the performance of reduced graphene oxide composite electrode palm oilshell zinc oxide(rGOAK-ZnO) as a chemical oxygen demand (COD) sensor by photoelectrocatalysis.

Method

The tools in this research are X-Ray Diffraction (Shimadzu 6000), Fourier Transform Infra Red(FTIR), (Shimadzu 8400), Scanning Electron Microscope-Energy Dispersive X-Ray (SEM-EDX) (HITACHI SU 3500), UV-Vis spectrophotometer (UVD-2950,Labimed, INC). The materials used are potassium permanganate (KMnO4) (*Merck*), sulfuric acid (H2SO4)(*Merck*), hydrogen peroxide (H_2O_2)(*Merck*), hydrochloric acid (HCl) (*Merck*), Methylene Blue,Whatman filter paper, aluminum foil, liquid paraffin, sodium nitrate ($NaNO_3$), and ZnO powder.

Synthesis of graphite oxide

The method used to oxidize graphite to graphite oxide(Zhu et al.,2010) in this study is the modification of the Hummer's Method (Chen, et al., 2013). Synthesis begins with stirring 2 grams of palm shell graphite, 4 grams $NaNO_3$ graphite with 98 ml of 98 % H_2SO_4 for 4 hours in an ice bath at temperature of around 5 °C. After that, 8 grams of $KMnO_4$ were added gradually for one hour. The solution was removed from the ice bath and stirred at 25 °C for 20 hours. After that, the addition of 200 ml of distilled water is was carried out in stages.After 1 hour of stirring, 30 % H_2O_2 was added to the solution. The addition of H_2O_2 aims to stop the oxidation process and cause the color of the solution to turn yellow. The solution is was left in a stirring condition for 30 minutes,

then the solution is was centrifuged to separate the precipitate.After that, 15 mL of 37 % HCl was added to remove the remaining metal ion. Then it periodically washed untilneutral pH is was obtained.During the washing process, the color of the solution would turn darker due to peeling of graphite to graphite oxide. The neutral solution was then dried at 105 °C for 12 hours to obtain graphite oxide sheet.

Preparation of rGO-ZnOelectrodes

The rGO-ZnO powder with mass variations of 0.1 grams, 0.2 grams, and 0.3 grams of ZnO was crushed and put into a watch glass containing paraffin.Then, heated in paraffin temperature 80ºC. The mixture is stirred and inserted into the electrode body while being pressed so that it solidifies. The composite material was characterized using SEM-EDX, XRD and FTIR.

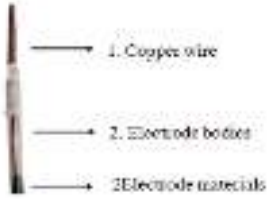

Figure 1. The working electrode components

Characterization of rGO-ZnO composites X-ray diffraction

To assess the characteristics of ZnO/rGO/TiO_2 composite. To determine the crystal structure. Analysis using XRD was carried out to determine the crystal structure of graphene which had been synthesized at an angle of $2\theta^0$ = 20-80^0 and λ Cu-Kα = 1.54060 Å.Fourier Transform Infrared Spectroscopy (FTIR) (Scientific Nicolet iS10) test was done to determine the functional groups of the composite at wavenumber range 4000-400 cm^{-1}.

Measurement of chemical oxygen demand (COD)

Measurement of COD using photoelectrocatalysis is based on the photocatalytic reaction that occurs on the surface of ZnO.Photoelectrocatalysis with e^-/h^+ photogeneration pairs play a role in the reduction-oxidation reactions of organic compounds in solution. When the electrode is irradiated with UV light, the decomposed substance will release electrons. Then transferred to the working electrode.The electrons produced in the form of a light current are used as an amperometric analytical signal.The light current will decrease until the rate of oxidation is equal to the rate of diffusion, so that the current value is zero when the light is turned off. The COD value is determined by the following equation.

$$[COD]_{teoritik} = \frac{Q}{4FV} \times 32000 \quad (1)$$

$$[COD]_{teoritik} = \frac{8000nC}{} \quad (2)$$

Where
Q = the charge (Coulomb)
I = light current
A = the number of electrons transferred
F = Faraday constant
V = The sample volume
C = the concentration (Molar)

Results and Discussion

Synthesis of reduced graphite oxide of palm shells

Graphite palm shell charcoal is oxidized to graphite oxide using $NaNO_3$ catalyst, H_2SO_4 solvent and $KMnO_4$ oxide.In the synthesis process, Oxidation using $KMnO_4$ aims to weaken the distance between the layers so as to facilitate the exfoliation process of graphite oxide into graphene oxide (ElFaham et al., 2021; Jain, 2022). Furthermore, the graphene oxide (GO) solution was heated using a hydrothermal apparatus to form a more stable GO structure.From this reduction process *reduced graphene oxide*(rGO)material will be formed (Rattan et al., 2020;Jose at al., 2018), as shown in **Figure 2.**

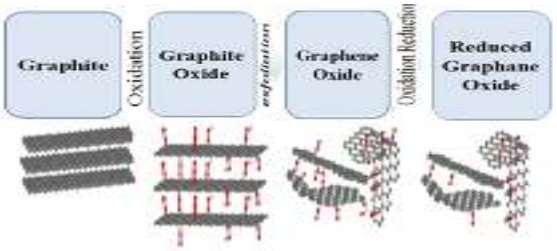

Figure 2. Preparation of reduced graphene oxide(rGO)

Characterization of fourier transform infrared (FTIR)

The characterization results of GO_{PS}, rGO and rGO_ZnO with Fourier Transform Infrared (FTIR) can be shown in **Figure 3.**

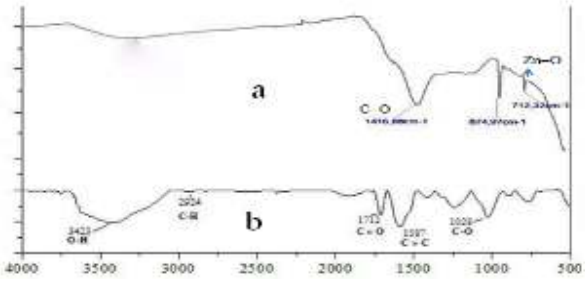

Figure 3. FTIR spectra of the GO, rGO, and ZnO-rGO composites

Figure 3. shows the FTIR spectra of the GO, and rGO-ZnO composites. In the FTIR spectrum for GO, the broad peak centered at 3423 cm is attributed to the O-H (Sujiono et al.,2020; Monteserín et al.,2017) stretching vibrations, and the peaks at 2924cm^{-1}, 1712cm^{-1}, 1589cm^{-1},1028cm^{-1} and 1587$cm^{-1}$are assigned to the C–H, C=O sp^2 -hybridized C=C group and C–O (Sujiono et al.,2020 Selim Md et al.,2012) stretching, respectively. In contrast, the peaks at 2924 cm^{-1}, 1712 cm^{-1}, 1589 cm^{-1}, and 1028 cm^{-1} cm are missing from the FTIR spectra of the ZnO-rGO composites.In addition, the ZnO-rGO FTIR spectra showed a peak at 712 cm^{-1} where ZnO bonds identified ZnO compounds.

X-Ray difraction (XRD)

Characterization was performed using XRD to determine the crystal structure of the rGO-ZnO composite electrode(Mursalim et al., 2017). The x-ray diffraction pattern shows specific peaks which are characteristic of rGO-ZnO. The XRD patterns of the obtained products are shown in **Figure 4.**

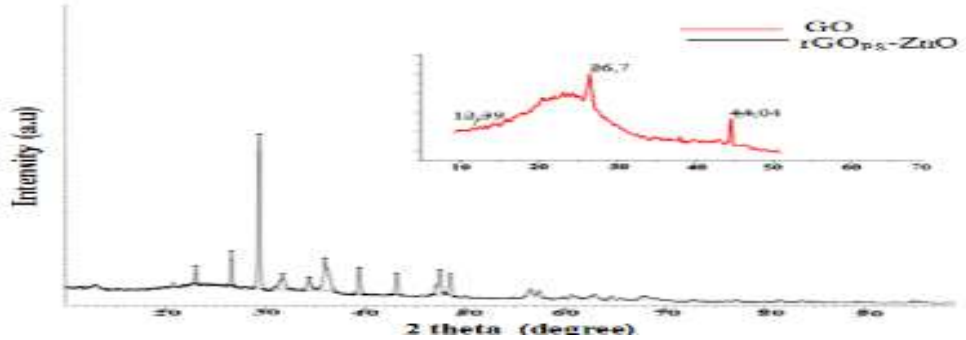

Figure 4. XRD patterns of GO and rGO-ZnO

Figure 4 showed the results of the grapheme oxide (GO) rGO-ZnO pattern. Based on the results, it can be ractogram for peaks of 2θ = 12.39º(d-spacing=7.138Å), 26.7º(d-spacing=7.138Å), and 44.04º(d-spacing =3.350Å). The characteristic feature of GO crystals is that they have 2θ bands at 25° and 45° (Putri, et al., 2019; Robaiah et al., 2019). The observed peak confirms that the graphene oxide sheet peels off from the graphite flakes.In addition, the rGO-ZnO diffraction pattern indicated several peaks at an angle of 2θ, namely 23.287º(d-spacing =3.350Å), 26.781° (d-spacing = 3.34976Å), 29.889°(d-spacing =3.03552Å), 32,468° (d-spacing =2,8181Å), 32,468° (d-spacing = 2,6038Å), 35,109° (d-spacing = 2,49305Å), 37,14° (d-spacing = 2, 28422 Å),

SEM and EDX

The morphology of the rGO-ZnO sample at the x5000 and x 10000 magnification is shown **Figure 5**

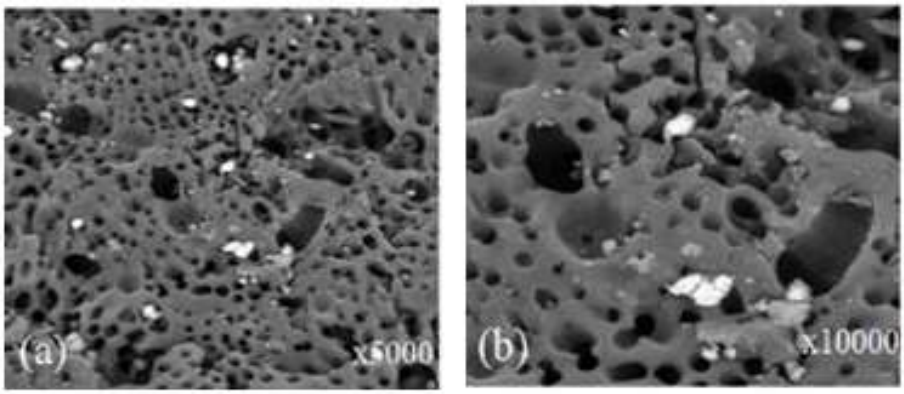

Figure 5. Morphology of rGO-ZnO (a) Magnification x 5,000 and (b) x 10,000

Figure 5. the result of SEM characterization of the rGO-ZnO composite, showingThe morphology of the porous surface contains bright black and white particles identifying the presence of rGO and ZnO particles.

The EDX analysis results are shown in **Figure 6.** Showed the presence of carbon (C), oxygen (O), and zinc (Zn) elements to identify the success of doping rGO on ZnO.

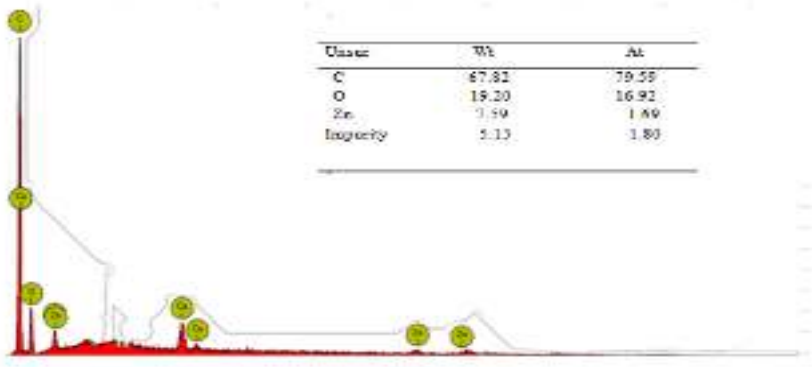

Figure 6. EDX result of ZnO

Activity test of rGO$_{PS}$-ZnO electrode using LSV and CV

The electrochemical test has applied using three electrodes variation namely rGO-ZnO, platinum (Pt) electrode, and Ag/AgCl electrode. The electrolyte was used at 0.01MK_3[Fe(CN)6] to observe the reduction–oxidation (redox) peaks and also the rate of electron transfer (Momeni, M.M, et al.,2019)

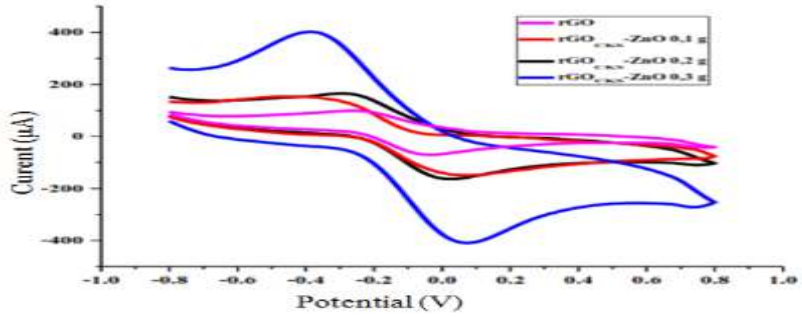

Figure 7. The CV graph by comparing the four working electrodes using K_3[Fe(CN)6] as the electrolyte solution

Figure 7 shows the voltammogram curve of $K_3[Fe(CN)6]$ electrolyte using a scan rate of 1,0 Vs^{-1}in the potential range from − 0.8 to 0.8 Vs^{-1} . The high intensity of current peak from the four electrodes were measured regardingredox peaks(Ipa = oxidation current; Ipc = reduction current; Epa = oxidation potential;Epc = reduction potential), it can be seen in **Table 1.**

Tabel 1. The three working electrodes performance regarding oxidation–reduction peak (refers to **Figure 7**)

Electrode	*Ipa(μA)*	*Ipc(μA)*	*Epa(V)*	*Epc(V)*
rGO_{PS}	49	-19	-0,24	-0,04
rGOCKS- ZnO 0,1 g	95	-30	-0,29	0,01
rGOCKS- ZnO 0,2 g	102	-48	-0,36	0,02
rGOCKS- ZnO 0,3 g	226	-92	-0,39	0,06

Based on **Figure 7.** and **Table 1.** shows the measurements using the four electrodes under $K_3[Fe(CN)6]$ electrolyte solution have produced the redox peaks with a scan rate of 1,0 Vs^{-1}.The 0.3 g rGOCKS-ZnO electrode gave a higher peak current response (266 μA) compared to other electrodes.This is due to an increase in the number of electron transfers from the analytes producedfrom doping.

The Linear Sweep Voltametry (LSV) method is a micro-scale electroanalytic method that examinesinformation about the analyte based on the measurement of current (I) as a function of potential (V) using 0.1M $K_3[Fe(CN)6]$electrolyte solution connected to the Portable Pontensiostat (Azis T et al., 2021). measurement of the response of the photocurrent (light current) which is the current that can be observed when the electrode is irradiated with UV and Visible ligh

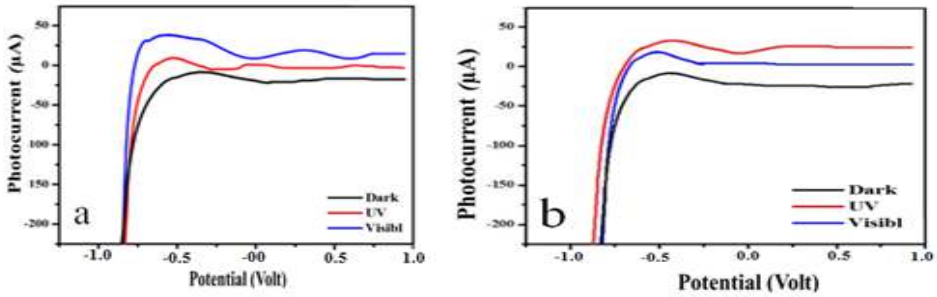

Figure 8. Test of electrode activities by the process of LSV (a) ZnO and (b). rGO-ZnO.

The light current response of the electrode that is not illuminated by UV light (dark) does not indicate a light current. This is because electrons and holes are not formed as the initiator of oxidation andreduction reactions. When the UV illumination of ZnO and (b). rGO-ZnO electrodes shows a highincrease in light current, this indicates photocatalytic activity.

Figure 8a.shows that when hit UV light irradiation, ZnO electrode performance is higher. This is consistent with the theory that TiO_2 is active with an energy gap of 3.2 eV only in the UV region with a wave length of around 388 nm (Maulidiyah, et al., 2017). **Figure 8b** shows the effect of UV light irradiation, visible light and is not irradiation (dark) on the rGO-ZnO working electrode. When the rGO-ZnO electrode is irradiated with visible light, it shows an increase in the light current. This is because rGO doping has Decreased ZnO band gap energy and serves as an electron acceptor to increase the electrons and holes that enter the ZnO surface. On the other hand, the addition of rGO dopant to ZnO can reduce the energy gap of ZnO, so that the electrodes can absorb light at a fairly large wavelength with less energy (Basavarajappa P S, et al., 2020 &Patil S B, et al., 2019).

Photocurrent response of the methylene blue

Photocurrent response measurement of ZnO electrodes and rGO-ZnO electrodes to Methylene Blue was carried out using the Multi Pulse Amperometry (MPA) method. The test was carried out on the test solution with a respective concentration of 0.5, 1, 2, and 3 ppm. The amperogram of rGO-ZnO electrode againsMethylene Blue are shown in **Figure 9**

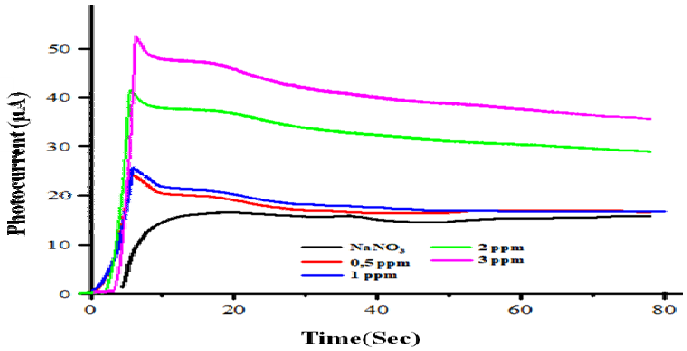

Figure 9. The photocurrent response of methylene blue, amperomogram of rGO-ZnO electrode.

Figure 9. shows the photocurrent produced by methylene blue (MB) is greater than that of the electrolyte solution.The resulting light current is the sum of the oxidation currents of methylene blue (MB) andthe oxidation currents of electrolyte solutions. The photocurrent produced by methylene blue (MB) is greater than that of the electrolyte solution. The decrease in photocurrent occurs because the methylene blue (MB) compound. decreases in solution due to photocatalytic degradation. The greater the concentration of organic compounds, the higher the photocurrent response produced. The performance of the rGO-ZnO electrode is known by observing the proximity of the generated charge value to the theoretically generated charge value. **Figure 10** shows Qnett's relation ship with methylene blue (MB) compounds.

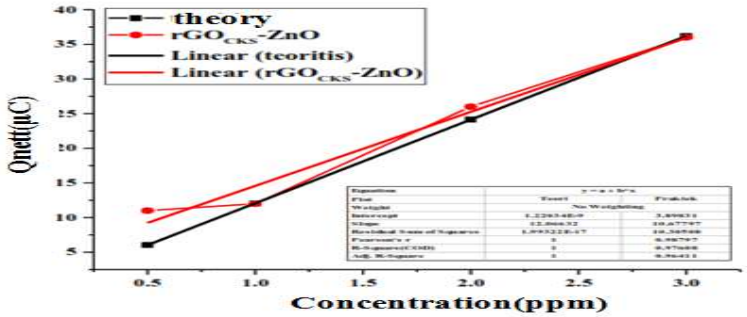

Figure 10. The relation between Qnett and concentration of methylene blue (MB) compound.

Based on **Figure 10**. The performance of the rGO_{PS}-ZnO electrode shows the highest level of accuracy in methylene blue (MB). This is due to the molecular structure of methylene blue (MB) which makes it easy to mineralize.In addition, the resulting charge is directly related to the concentration of the test compound.This is in line with the law of Faraday, which states that the greater the solution concentration, the greater the charge received.This is due to the interactionof the analyte molecule and the surface of the electrode.The strong interaction with the surface of thecatalyst causes an increase in the rate of oxidation of organic compounds so that the resulting load is greater.

Determination of chemical oxygen demand (COD) value

Figure 11 represents the linearity of the measurement data for COD values on methylene blue (MB) using the rGO-ZnO electrode to see the theoretical COD value with a photoelectrocatalytic approach.

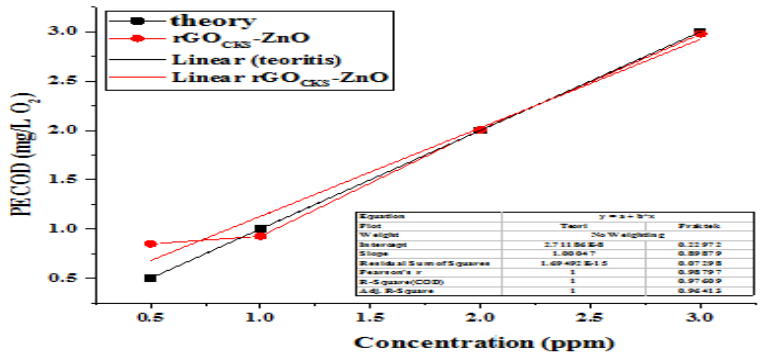

Figure 11. Relationship of the concentration of the test compound to PECOD

Figure 11 compares theoretical COD values and COD PEC values as the methylene blue (MB) concentration increases from 0,5 ppm to 3,0 ppm.The data show that increasing the concentration of methylene blue (MB) makes the COD PEC value close to linearity to the theoretical COD value, so that the probability of linearity is observed at methylene blue (MB) concentrations from 0.5 ppm to 3.0 ppm, as shown in table 2

Table 2. Methylene blue (MB) COD using rGOPS-ZnO electrode

COD (mg / L O_2)		
Conceration (ppm)	**Theoretical**	**Photoelectrocatalytic (COD PEC)**
0,5	0.5002345	0.84907
1,0	1.000469	0.92626
2,0	2.0009379	2.00689
3,0	3.0014069	2.97877

Determination of linearity, detection limit and sensitivity

The linear regression equation applied to the results must have intercept values not significantly different from zero.If the non-zero significant intercept is obtained, it must be proved that this has noeffect on the accuracy of the method (Veerasamy et al.,2011).

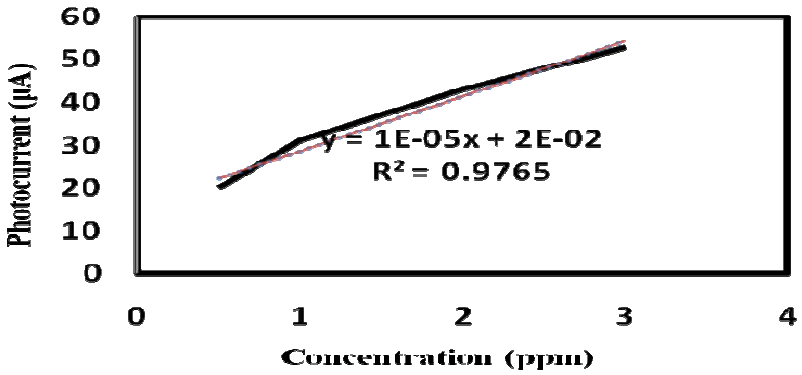

Figure 12.. Linear graph of methylene blue test compound.

JurnalAkademika Kimia2(1): 1-7, February 2023
ISSN (online) 2477-5185 | ISSN (print) 2302-6030
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The linearity can be found from the coefficient slope based on methylene blue concentration toward oxidation peak (Ipavalue) which showed in **Figure 13.** We obtain the linearity equation is $y = 10^{-5}x + 0,02$ with an intercept value of 0,02 and a slope of 10^{-5}. It aims to determine the range area that occurs in measuring the methylene blue compound by R2 = 0,9765 or close to 1. According to Nurdin et al (2009), at low concentration the photodegradation process is only influenced by photo hole capture process on catalyst surface while at high concentration compound structures affect the photodegradation process of the compounds(Muzakkar et al., 2021).

Determination of the detection limit was carried out to find out the smallest concentration of methylene blue in the sample that can still be detected by the rGOAK-ZnO sensor and still provide a significant response. Detection limit shows the levelthe sensitivity of the electrode, the lower the detection limit, the betterits sensitivity to the sample (Lukmana, K. M, et al., 2018). Then, the LoD has been obtained from calculation results is 0,06 ppm which shows that $rGOC_{PS}$-ZnO composite is able to detect methylene blue compound up to a concentration of 0.06ppm. The rGOAK-ZnO electrode has the capability of detecting methylene blue with high sensitivity.This can be seen from the greater slope and higher sensitivity.

Electrode repeat test

The repeatability test was conducted to exhibit the working electrode performance against the consistency of measurement. This treatment therGOAK-ZnO composites has been tested by using methylene blue. **Figure 14** depicts the results of repeatability working electrode that the high-performance.

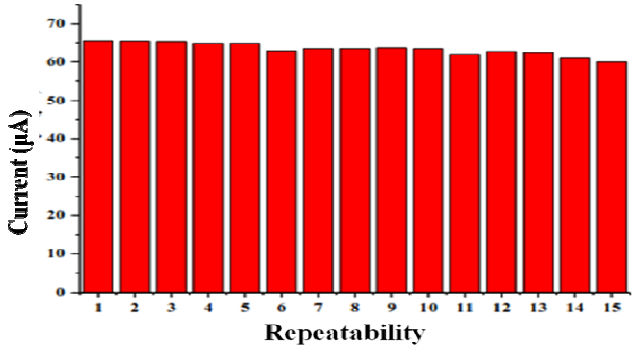

Figure 13. The histogram of oxidation current versus the repeating measurement.

Figure 13 depicts the results of repeatability working electrode that the high-performanceof rGO_{PS}-ZnO stability for 15 times tested.Based on this study (**Figure 13**), we obtain calcuating the standard of deviation (SD) of 1,57 and Relative Standard Deviation(RSD) is 2,48%. We declarethat the rGOPS-ZnO composites has stabilized due to the Horwitz value is obtainedless than 2% (1,24 %).

Electrode lifetime determination

Especially, we explore a lifetime of rGO-ZnO to obtain the high-performance electrode for 14 days. The lifetime test performance has been

carried out by using the same solution on the repeatability testExtension lifetime electrode enforced forclarifying Extension lifetime electrodeenforced for clarifying rGO-ZnO to sensitivity against fipronil. to sensitivity against methylene blue. Meanwhile, if it is to be increased, the rGO-ZnO composite must remove organic compounds on the surface of the electrode

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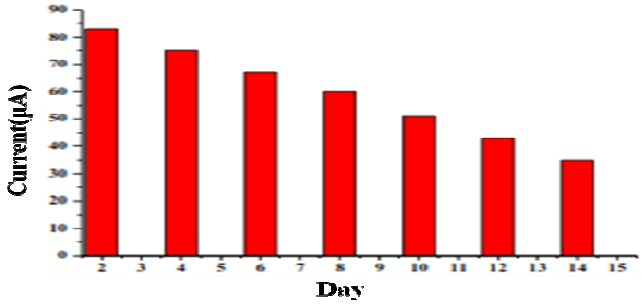

15. lifetime test of rGO-ZnOcomposites.

Figure 15. exhibits that the optimum performance electrode from 1 until 8 days relatively stable, while the 9 until 14 days the low-performance electrode.This condition that the longer electrode used causes thickening diffusion on the electron

Conclusion

Electrodes of rGOPS-ZnO have been successfully. Then the rGOPS-ZnO electrodes were characterized using FTIR, XRD and SEM-EDX. FTIR results show absorption at wavenumbers of 1416 cm^{-1} and 712 cm^{-1}, indicated as C-O and Zn-O bonds. The XRD results of rGO-ZnO show peaks at an angle of 2θ, namely 23.287º, 26.781°, 29.889°, 32.468°, 35.109°, 37.14°, 39.822°, 43.559°,47.927°, and 48.537. SEM-EDX analysis revealed a porous graphene sheet surface, black and white colored particles identified the presence of rGO and ZnO.The results of the EDX analysis consisted of C 67.82%, O. 19.20%, Zn. 7.85% and 5.13% impurity. The detection limit obtained was 0,06 ppm. and the repeatability was indicated by a Horwitz Ratio (HorRat) value of 1,24%. The optimum measurement stability in analyzing methylene blue is 14 days. The COD value is close to the theoretical concentration of 3 ppm (2.97897mg/LO_2).

Acknowledgments

The authors would like to thank the Physical Chemistry Laboratory and the Inorganic Laboratory of the Faculty of Mathematics and Natural Sciences, Halu Oleo University, whichhave assisted in completing this research.

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Bukti konfirmasi accepted
(25 May 2023)

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25 May 2023

ACCEPTANCE LETTER

Dear Author(s),

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Article Title	:	Performance of The Composite Electrode of Reduced Graphene Oxide Palm OilShell - Zinc Oxide (rGOCKS - ZnO) as a Chemical Oxygen Demand (COD) Sensor by Photoelectrocatalysis
Institutions	:	[1]Department of Chemistry, Faculty of Mathematics and Natural Sciences,University of Halu Oleo, Kendari – Indonesia, 93232 [2]Chemistry Department, Faculty of Mathematics and Natural Sciences, Universityof Pattimura, Maluku – Indonesia, 97233 [3]Chemistry Education Study Program/ Department of Mathematics and NaturalScience Education, Faculty of Teacher Training and Education – Tadulako University, Palu – Indonesia 94119

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