Preparation of rGO/MnO₂ Composites through Simultaneous Graphene Oxide Reduction by Electrophoretic Deposition

Hariyati Purwaningsih, Ni Made Intan Putri Suari, Widiyastuti Widiyastuti, and Heru Setyawan*

ABSTRACT: We report the preparation of manganese dioxide (MnO₂) nanoparticles and graphene oxide (GO) composites reduced by an electrophoretic deposition (EPD) process. The MnO₂ nanoparticles were prepared by the electrolysis of an acidic KMnO₄ solution using an alternating monopolar arrangement of a multiple-electrode system. The particles produced were γ-MnO₂ with a rod-like morphology and a surface area of approximately 647.2 m²/g. The GO particles were produced by the oxidation of activated coconut shell charcoal using a modified Hummers method. The surface area of the GO produced was very high, with a value of approximately 2525.9 m²/g. Fourier transform infrared spectra indicate that a significant portion of the oxygen-containing functional groups was removed from the GO by electrochemical reduction during the EPD process after sufficient time following deposition of the GO. The composite obtained by the EPD process was composed of reduced graphene oxide (rGO) and γ-MnO₂ and exhibited excellent electrocatalytic activity toward the oxygen reduction reaction following a two-electron transfer mechanism. This approach opens the possibility for assembling rGO composites in an efficient and effective manner for electrocatalysis.

1. INTRODUCTION

Manganese dioxide (MnO₂) has been reported to be an excellent electrocatalysis of the oxygen reduction reaction (ORR) in alkaline media.¹⁻³ The sluggish ORR kinetics represent a bottleneck for the development of certain electrochemical storage and conversion energy technologies, such as polymer membrane fuel cells and metal–air batteries. Among the different crystal structures of MnO₂, α- and γ-MnO₂ structures are promising electrocatalysis because they contain one-dimensional (1D) channels, which are considered to be relatively more accessible and the most active among the various MnO₂ crystal structures.⁴ However, the practical application of MnO₂ is limited by its instability owing to structural degradation during long-term cycling⁵ and low electrical conductivity, which hinders electron transport.⁶

To overcome the poor conductivity of MnO₂ and enhance electron transport, a high-conductivity material such as carbon is usually added. Recently, hard disordered carbons that can be produced by the carbonization of biomass such as cellulose and coconut shells have attracted considerable attention for use as electrode materials.⁷,⁸ The surface area of the carbonized biomass can be increased significantly by oxidation in a harsh environment using a modified Hummer method to form graphene oxide (GO). To restore the structure and properties of graphene, GO can be partly reduced to graphene-like sheets by removing oxygen-containing groups.⁹ Several methods have been used for GO reduction including thermal reduction,¹⁰,¹¹ reduction using chemical reagents,¹² and hydrothermal¹³ and electrochemical reduction.¹⁴⁻¹⁷ Among these, electrochemical reduction offers many advantages for the reduction of GO to remove oxygen-containing groups.⁹ Electrochemical reduction mainly occurs by electron transfer on the electrode surface; therefore, this method usually requires no special chemical agent. It can be performed through either direct electrochemical reduction of GO in suspension onto the substrate electrode or pre-deposition of GO onto the substrate electrode prior to the electrochemical reduction process.¹⁸ An et al. reported the fabrication of a thin film and simultaneous GO reduction on the anode surface during electrophoretic deposition (EPD).¹⁹ The EPD method has several advantages for the preparation of thin films, such as a high deposition rate, good uniformity, and ease of scale-up. It was assumed that this method could be a promising environmentally friendly synthetic route for producing reduced graphene oxide (rGO)-containing composites.
Here, we report the preparation of an rGO/MnO₂ composite using the EPD method. The GO used in this study was synthesized from activated coconut shell charcoal using the modified Hummers method. The γ-MnO₂ nanoparticles were prepared by the electrolysis of an acidic KMnO₄ solution in an alternating monopolar arrangement of a multiple-electrode system. The effects of the EPD time and voltage on the composite properties were investigated. The prepared composites were then evaluated for use as electrocatalysts for the ORR.

2. RESULTS AND DISCUSSION

2.1. Characteristics of the Composites. Figure 1 shows the change in X-ray diffraction (XRD) pattern after coconut shell charcoal was activated, treated with the modified Hummer method, and electrochemically reduced during EPD.

![XRD pattern](image)

**Figure 1.** Change in the XRD pattern of (a) coconut shell charcoal (b) after being activated, (c) treated with the modified Hummers method, and (d) electrochemically reduced during EPD.

The increase in the interlayer spacing may be caused by the decrease in the band intensities related to oxygen functionality groups and the increase in intensity of the C–C band indicate that GO was successfully reduced to rGO.

Figure 2. FTIR spectra of different phases of carbon originating from (a) coconut shell charcoal, (b) GO, and (c) rGO.

OH/H₂O bands. The carbonyl functional groups (C=O) are indicated by the bands located at 1694 cm⁻¹; the epoxy (C–O–C) stretching appears at 1067 cm⁻¹. The bands at 1574 cm⁻¹ can be attributed to C–C vibrations of the graphene skeleton. The band corresponding to C=O vibrations does not appear in the spectrum of coconut shell charcoal, as shown in Figure 2a.

The diffraction peaks of GO shifted slightly to the right at 24.1° (002), and an additional weaker peak appeared at 43.5° (Figure 1d). The peaks can be assigned to rGO with an interlayer distance of 3.705 Å, which is smaller than that of GO. FTIR analysis was performed to further confirm this. As shown in Figure 2c, the band at 1694 cm⁻¹ corresponding to carbonyl (C=O) that disappeared and the intensity of the band corresponding to epoxy (C–O–C) groups became weaker after EPD. By contrast, the band intensity at 1574 cm⁻¹, which corresponds to C–C bonding, was stronger. The decrease in the band intensities related to oxygen functionality groups and the increase in intensity of the C–C band indicate that GO was successfully reduced to rGO.

Figure 3 shows the XRD patterns of the rGO/MnO₂ composites prepared using EPD at different times, including the as-prepared MnO₂ particles obtained from the electrolysis of the KMnO₄ solution. All the diffraction peaks in the XRD pattern of Figure 3a can be indexed to γ-MnO₂ (ICDD 00-004-0779, a = 6.36 Å, b = 10.15 Å, c = 4.09 Å). Although prepared at the same pH, the structural phase of MnO₂ produced using the multiple-electrode system is different from that produced using the one-pair electrode system. In the one-pair electrode system, the structural phase of the particles produced was α-MnO₂. However, both phases contain one-dimensional (1D) channels, which is advantageous because the surface is easily accessible by molecules or ions involved in a surface reaction. The composites prepared using EPD, as shown in Figure 3b–e, show no changes in the characteristic peaks, that is, the structural phase, for both γ-MnO₂ and rGO. The FTIR spectra of the composites, as shown in Figure 4, also show that GO was reduced to rGO after EPD. The intensity of the bands related to oxygen functional groups decreased, and the
intensity related to C–C increased. In addition, a band at 691 cm$^{-1}$ that appears in the MnO$_2$ sample also appears in the composite. This band can be attributed to Mn–O vibrations.

Figure 5 presents the Raman spectra of the composite prepared using EPD compared with the spectra of GO and rGO. There are two intense peaks in the Raman spectra of the three samples at approximately 1359 cm$^{-1}$ (D-band) and 1605 cm$^{-1}$ (G-band) and one weak peak at approximately 2226 cm$^{-1}$ (2D-band). The D-band is an irregular band originating from defects in graphitic materials. By contrast, the G-band deals with the movement of stretching fields between sp$^2$ atoms. The ratio of $I_D/I_G$ is approximately 0.91 for GO, and it is relatively constant after electrochemical reduction during EPD. However, the $I_D/I_G$ ratio increased significantly for the rGO/MnO$_2$ composite to 1.07, which is not low when compared to that of pure graphene. The increase in the $I_D/I_G$ ratio indicates that there are more defects and disorders in the carbon structure, which may be due to carbon exfoliation. The low, nearly constant $I_D/I_G$ ratio of rGO indicates that the first 10 min of GO deposition is not sufficient to significantly reduce the GO deposited on the nickel electrode. An additional time of 10 min during electrophoretic deposition of MnO$_2$ provides more time to further reduce GO to rGO. The lower 2D-band intensity than that of its counterpart G-band and the wide broad peak of its 2D-band indicate the formation of a multilayer graphene material.

The crystallite size, $L_a$, in disordered carbon materials can be estimated from the $I_D/I_G$ ratio using the equation

$$L_a \text{ (nm)} = (2.4 \times 10^{-10}) \lambda_i^4 (I_D/I_G)^{-1} \tag{1}$$

where $\lambda_i$ is the wavelength of the laser source (nm). The crystallite sizes of GO and rGO estimated using this equation are approximately 40.2 and 36.1 nm, respectively. The values agree well with the crystallite size estimated from the XRD pattern using the Scherrer equation, which produces values of approximately 44.1 nm for GO and 42.0 nm for rGO.

Figure 6 shows transmission electron microscopy (TEM) images of the as-prepared GO obtained by the modified Hummers method and the corresponding rGO obtained after EPD for 10 min at a voltage of 4 V. It can be observed that the GO has a thick cloud-like morphology, and after being electrodeposited, a few layered sheets appeared inside the cloud. These observations confirm the formation of layered sheets in the GO from the activated coconut shell carbon and in the rGO obtained by EPD from GO. However, the selected-area electron diffraction (SAED) patterns of GO and rGO are quite different. The SAED pattern of GO exhibits blurred bright rings, indicating that the particles are amorphous or poorly crystalline. Conversely, the SAED pattern of rGO has broad diffraction rings, indicating that the materials are not amorphous but are at least partially ordered at the nanometric scale. These SAED results corroborate the XRD results.

Figure 7a shows TEM images of $\gamma$-MnO$_2$ particles prepared by the electrolysis of KMnO$_4$ in an acid solution using an alternating monopolar configuration of the multi-electrode. The particles have a rod-like morphology with a diameter of approximately 10 nm. The broad diffraction rings in the SAED pattern of the particles (right side of Figure 7a) indicate that the particles are not amorphous but are at least partially ordered at the nanometric scale. The $d$-spacing calculated from the fringe distance from the center of the SAED pattern ranges from 1.63 to 6.89 Å, which matches the $d$-spacing of the $\gamma$-MnO$_2$ phase based on the XRD standard, confirming the XRD patterns of (a) MnO$_2$, (b) GO, and composites prepared at different EPD times: (c) 2 min, (d) 5 min, (e) 10 min, and (f) 15 min.

Figure 4. FTIR spectra of composites prepared at different EPD times: (a) 2 min, (b) 5 min, (c) 10 min, and (d) 15 min.
results. Figure 7b shows TEM images of the MnO2/rGO composite obtained after 10 min of EPD at a voltage of 4 V. The particles with a rod-like morphology are likely MnO2 and are similar to the morphology observed for MnO2 particles obtained in the electrochemical system at a low pH. The broad diffraction rings with a clear image of points form a specific pattern belonging to rGO, as the points do not appear in the SAED pattern of rGO. The specific surface area of the original MnO2 was approximately 647.2 m²/g (Table 1). A high surface area is expected for particles with a rod-like nanomorphology.

The specific surface area of the original coconut shell charcoal was approximately 856.8 m²/g. The surface area increased significantly to 1742.2 m²/g when the charcoal was activated with KOH at 800 °C; it increased further to 2525.9 m²/g after the activated carbon was treated with the modified Hummers method. The considerable increase in the surface area of the carbon after the Hummers process indicates that the modified Hummers method can effectively exfoliate the carbon layers in the activated carbon. When a composite was formed with rGO and MnO2, the surface area decreased slightly. This was probably caused by the insertion of MnO2 nanoparticles into the gaps between carbon sheets.

2.2. Electrocatalytic Activity toward ORR. Figure 8a shows cyclic voltammetry (CV) curves of the rGO/MnO2 composites prepared at different EPD times in an O2-saturated 0.1 M KOH solution. A reduction peak appears in the CV curves of all the rGO/MnO2 composites prepared at different EPD times. Notably, the reduction peaks of the rGO/MnO2 composites become more positive as the EPD time increases, indicating that the catalytic activity improved. Among them, the rGO/MnO2 composite prepared at an EPD time of 10 min exhibits higher catalytic activity than the other composites. The limiting current density of the rGO/MnO2 composite prepared at an EPD time of 10 min is 0.84 mA/cm² (at ∼0.30 V), which is nearly the same as that of the composite prepared at an EPD time of 5 min and is higher than that of the composites prepared at EPD times of 2 and 15 min (Figure 8b). It is apparent that the rGO/MnO2 composites can serve as an active electrocatalyst for the ORR.

Figure 9 shows typical LSV curves for the rGO/MnO2 composites prepared at different rotation speeds and prepared at an EPD time of 10 min in an O2-saturated 0.1 M KOH solution. The kinetic current density and the number of electrons transferred per oxygen molecule were evaluated using the Koutecky−Levich (K−L) equation:

\[
\frac{1}{i} = \frac{1}{B\omega^{1/2}} + \frac{1}{i_k}
\]

(2)

\[
B = 0.201nFC_{O_2}D^{2/3} \nu^{-1/6}
\]

(3)

In eqs 2 and 3, \(i\) is the measured current density, \(\omega\) is the angular velocity, \(i_k\) is the kinetic current density, \(n\) is the number of electrons involved in the ORR, \(F\) is the Faraday
constant, $D_{O_2}$ is the diffusion coefficient of $O_2$ in KOH solution, and $\nu$ is the kinematic viscosity. The oxygen concentration in the KOH solution was calculated from

$$\log C_{O_2} = \log 1.26 \times 10^{-3} - 0.1746C_{KOH}$$  \hspace{1cm} (4)

The number of electrons and the kinetic current density are obtained from the slope and intercept of eq 1 by plotting $i^{-1}$ versus $\omega^{-1}$. The results are presented in Table 2 for the

| samples                  | surface area (m²/g) |
|--------------------------|---------------------|
| MnO₂                     | 647.2               |
| charcoal                 | 856.8               |
| activated carbon         | 1742.2              |
| GO                       | 2525.9              |
| rGO/MnO₂ composite       | 1965.6              |

Figure 7. (a) TEM images of MnO₂ prepared by the electrolysis of KMnO₄ in acidic solution using an alternating monopolar configuration of multi-electrode and its corresponding SAED pattern. (b) TEM images of the MnO₂/rGO composite deposited using EPD for 10 min at a voltage of 4 V and its corresponding SAED pattern.

Figure 8. (a) CV curves of the rGO/MnO₂ composites prepared at different EPD times in an O₂-saturated 0.1 M KOH solution. (b) LSV curves of the rGO/MnO₂ composites prepared at different EPD times with a rotating speed of 1600 rpm in an O₂-saturated 0.1 M KOH solution.
different rGO/MnO2 composites. The kinetic current density of the rGO/MnO2 composites prepared at an EPD time of 2 min was approximately 0.9 mA/cm². It increased to a nearly constant value of approximately 1.1 mA/cm² when the composites were prepared at EPD times of 5 and 10 min and then dropped to 0.6 mA/cm² when the EPD time was prolonged to 15 min. The decrease in the kinetic current with a prolonged deposition time may be caused by the increase in the amount of low-conductivity MnO2 particles in the composite. Conversely, the number of electrons transferred during ORR is relatively constant, with a value of approximately 2. The electron number of approximately 2 suggests that the ORR mechanism on the rGO/MnO2 composites in alkaline media follows the reactions above.

4. EXPERIMENTAL SECTION

4.1. Materials. Coconut shell charcoal (CSC) was collected from a local market in Surabaya, Jawa Timur, Indonesia. Sulfuric acid (H2SO4; 98.0 wt %; reagent grade), hydrochloric acid (HCl; 37.0 wt %; reagent grade), potassium hydroxide (KOH; reagent grade), and hydrogen peroxide (H2O2; 30.0 wt %) were purchased from Merck. Sodium nitrate (NaNO3; reagent grade), polyvinylidene difluoride (PVdF; reagent grade), and 1-methyl-2-pyrrolidone (NMP; reagent grade) were purchased from Sigma-Aldrich. Potassium permanganate (KMnO4; reagent grade) was supplied by Uni-Chem, Indonesia. Nickel foam was purchased from KGS Scientific. All chemicals were used as received, without further purification.

4.2. Preparation of Graphene Oxide. Graphene oxide (GO) was prepared from coconut shell, a renewable biomass that is abundantly available. The γ-MnO2 was synthesized electrochemically using an alternating monopolar arrangement of a multi-electrode system. This method can efficiently produce rod-like γ-MnO2 nanoparticles. Both the GO and the γ-MnO2 particles have very high surface areas: 2525.9 m²/g for GO and 647.2 m²/g for γ-MnO2. The EPD process maintained the high surface area of the rGO/γ-MnO2 composite. It exhibited excellent performance toward the ORR following a two-electron transfer mechanism. The EPD approach appears to be promising for assembling an electrode composed of rGO on complex surfaces and shapes.

Table 2. Number of Electrons and Kinetic Current Density of rGO/MnO2 Composites Prepared at Different EPD Times Evaluated Using the K−L Equation

| samples     | n (−) | i_k (mA/cm²) |
|-------------|-------|--------------|
| rGO/MnO2 2 min | 1.6   | 0.9          |
| rGO/MnO2 5 min | 1.9   | 1.2          |
| rGO/MnO2 10 min | 2.4   | 1.1          |
| rGO/MnO2 15 min | 1.7   | 0.6          |

Equation 5 represents the reduction of oxygen to hydrogen peroxide via a two-electron pathway, which is further reduced to hydroxide, as shown in eq 6. The two-electron pathway has also been demonstrated previously for the electrocatalytic reaction of oxygen reduction on manganese dioxide. These results suggest that the rGO/MnO2 composites prepared using electrophoretic deposition are promising for use as active electrocatalysts for the ORR.

3. CONCLUSIONS

It has been demonstrated that GO can be reduced electrochemically during the preparation of composites composed of rGO and γ-MnO2 using the EPD process. The content of oxygen-containing groups was significantly reduced, and the as-deposited rGO/γ-MnO2 showed a very high surface area. The rGO was prepared from coconut shell, a renewable biomass that is abundantly available.
dark green, which typically took about 1 h, and the stirring was continued for another 1 h. The mixture was placed in a 40 °C water bath and stirred for 20 h. The stirring was continued in an ice bath for 20 h while slowly adding 80 mL of water, and then stirring was continued for another 1 h. The mixture was moved to an 80 °C water bath, and after the temperature became constant, 200 mL of water was added slowly. Then, the mixture was immediately immersed in an ice bath for 1 h. Then, 20 mL of H$_2$O$_2$ solution was added slowly until no more bubbles were observed. The solids were separated, washed with HCl solution and demineralized water, and dried under vacuum at 120 °C for 12 h.

### 4.3. Preparation of Manganese Dioxide Nanoparticles

Manganese dioxide nanoparticles were prepared by electrolysis of KMnO$_4$ under acidic conditions following our method,$^1$ except that the electrodes consisted of eight carbon plates arranged in an alternating monopolar configuration.$^{20,21}$ The electrodes had dimensions of 3.0 cm × 11.0 cm × 1.0 cm. They were arranged into four rows, each of which consisted of two electrodes separated by a distance of 2 cm. The electrolyte was 0.5 M KMnO$_4$ solution, and the pH was adjusted to 0.2 by adding H$_2$SO$_4$ solution. The electrolysis was performed under stirring at a voltage of 3 V and a temperature of 60 °C for 3 h. The precipitate was separated and dried in an oven at 150 °C for 4 h.

### 4.4. Preparation of Composites

The rGO/MnO$_2$ nanocomposite was prepared by electrophoretic deposition (EPD) of the particles on nickel foam. The dimensions of the nickel foam were 20 mm × 70 mm × 5 mm. The EPD was carried out by immersing the nickel foam first in the GO suspension and subsequently in the MnO$_2$ suspension. The solid concentration for each suspension was 1.5 g/L. The nickel foam was connected to the positive terminal of the DC power supply, and carbon, as the counter electrode, was connected to the negative terminal. The voltage was varied from 2 to 4 V for both GO and MnO$_2$. The electrophoretic deposition of GO was varied from 2 to 15 min and was fixed at 10 min for MnO$_2$. During the EPD, the GO that had been deposited on the Ni foam was simultaneously reduced electrochemically to rGO. This method has the advantage of avoiding the use of dangerous reductants such as hydrazine and has no byproducts.

### 4.5. Characterization

The morphology of the samples was observed using a transmission electron microscope (Jeol JEL-1400). Infrared (IR) spectra were recorded using a Fourier transform infrared spectrophotometer (Nicolet iS10; Thermo Scientific) over a wave number range of 500–4000 cm$^{-1}$. Raman spectra were measured using a Raman spectrophotometer (Micro Confocal XploraPlus; Horiba) with an ion laser excitation wavelength of 532 nm. The crystalline phase was identified using X-ray diffraction (XRD; PANalytical X’Pert Pro). The specific surface area was quantitatively determined by N$_2$ adsorption–desorption at 77 K (NOVA 1200; Quantachrome). The samples were degassed at 300 °C for 3 h prior to analysis. The surface area was calculated using the Brunauer–Emmett–Teller method.

The electrocatalytic activity of the rGO/MnO$_2$ composite toward the ORR was evaluated using a rotating disk electrode (RDE) with a three-electrode setup, in which the composite acted as the working electrode. It was prepared by mixing the rGO/MnO$_2$ composite with 1-methyl-2-pyrrolidinone (NMP; Sigma-Aldrich) as the solvent and poly(vinylidene fluoride) (PVDF; Sigma-Aldrich) as the binder at a mass ratio of 4:1:1. The dispersion was transferred onto a platinum disk and dried in an oven at 45 °C for 2 h to form a thin composite layer. Platinum foil and a Ag/AgCl electrode were used as the counter and reference electrodes, respectively. The electrolyte was an oxygen-saturated 0.1 M KOH solution, which was maintained under an oxygen atmosphere during the electrocatalytic test. The three electrodes were connected to a potentiostat/galvanostat instrument (PGSTAT 302N; Metrohm).

Linear polarization was performed by scanning the potential between −1.2 and +1.2 V with a scan rate of 100 mV/s. Cyclic voltammetry (CV) was performed by scanning the potential between −0.8 and +0.8 V (vs Ag/AgCl) at a scan rate of 100 mV/s. Linear sweep voltammetry (LSV) was performed by varying the rotation speed from 400 to 2000 rpm. The potential was scanned from −0.8 to +0.5 V (vs Ag/AgCl) at a scan rate of 5 mV/s. The number of transferred electrons and the kinetics of current density were predicted using the Koutecky–Levich (K–L) equation.

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