A Green Method to Prepare Composite of Graphene Oxide-Manganese Oxide using a Modified Hummer’s Method

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Abstract. A composite graphene oxide-manganese oxide (GO-MnO$_x$) was facilely fabricated in one-step preparation by modified Hummer’s method. The Hummer’s method for graphene oxide preparation produced manganese residue as byproduct, therefore, we modified the Hummers method to convert the manganese residue into value-added materials with aqueous sodium hydroxide (NaOH). The number of Mn on composite and surface chemistry was investigated. GO-MnO$_x$ was characterized by atomic absorption spectroscopy (AAS), UV-Visible spectrometer, fourier transform infrared (FT-IR), X-ray diffraction (XRD), and transmission electron microscopy (TEM). Quantitative measurements showed that GO-MnO$_x$ 1 and 2 have the number of Mn of 1.4231 and 2.0958 µg/g, respectively. FTIR showed the presence of functional groups such as hydroxyl, epoxy, carboxyl, carbonyl and manganese oxide. XRD confirmed the interlayer spacing of GO-MnO$_x$ synthesized by our techniques is lower than GO-MnO$_x$ produced by other processes. TEM showed that GO-MnO$_x$ is single layer yet and Mn species was not homogeneously distributed on composite.

1. Introduction
Manganese oxide (MnO$_x$), a transition metal oxide, has attracted the attention of researcher due to less toxicity, large natural abundance of manganese element, cheaper, environmentally-friendly and high redox potential [1,2]. Up to now, MnO$_x$ has been applied in many fields such as catalyst, supercapacitor, adsorbent [3–5], etc. However, the bulk of MnO$_x$ has low thermal and chemical stability, difficulties in separation from aquatic solution, and low surface area [6] which seriously limit their application. Therefore, MnO$_x$ was added on supporting materials as well as zeolite [7], silica nanoparticles [8], and carbon-based materials (e.g. graphite oxide) [9] to increase the physicochemical properties such as preventing the aggregation and increasing the stability and catalytic activity [10]. Graphene oxide (GO) is a more promising material for preparation GO-MnO$_x$ composite than carbon black and carbon nanotube (CNT). The presence of functional groups (hydroxyl, carboxyl, epoxy groups) on GO provides hydrophilic character and chemical reactivity which cause GO easily to bind with other composites [11,12]. Moreover, GO has superior physical and chemical properties such as high specific surface area, good mechanic and thermal properties, eco-friendly and biodegradable [13–15]. On the other hand, the segregation and agglomeration of GO caused by Van der Waals interactions can be prevented by addition of manganese oxide on GO [16]. Other studies have also proven that GO-MnO$_x$ composite has high conductivity and the surface area can be easily separated from aquatic solution which is beneficial for the oxidation of organic molecules [6,17,18].
GO is synthesized from natural graphite or other carbon-based materials with various methods such as Hummers method [19], epitaxial growth [20] and chemical vapor deposition (CVD) [21]. However, the epitaxial growth and CVD needed high temperature reaction condition up to 1000°C and low yield [22]. Hummers method has also limitations in practical use such as the hazardous reagents are involved in the reactions (e.g., sodium nitrate or potassium chlorate) [23]. For this reasons, Hummers method with modification has been investigated and could be a promising method for the preparation of GO-MnO$_x$ composite due to its simple, safe, and efficient reaction process, high oxidation level of graphite and less expensive [24]. Previous researches have reported the synthesis of GO-MnO$_x$ with a modification of Hummers method. Nevertheless, a few of process required additional amount of potassium permanganate (KMnO$_4$) after the sonication of graphite oxide [10,25–27]. Recently, Suzuki and Nishina reported one-step preparation of graphite oxide-manganese oxide composite with a modification of Hummers method which used potassium hydroxide (KOH) to precipitate the residual Mn on graphite oxide without an excessively addition of KMnO$_4$[9]. This method converted residual Mn which is a byproduct into a value material. Nevertheless, graphite oxide was not exfoliated with sonication process affecting the properties of surface chemistry.

In this work, one-step synthesis of GO-MnO$_x$ was investigated using the modification of Hummers method with a ratio of KMnO$_4$:H$_2$SO$_4$ as oxidant and the sodium hydroxide (NaOH) to precipitate the residual Mn. The route of synthesis GO-MnOx can be divided into three stages. Firstly, natural graphite was oxidized by KMnO$_4$ and strong acid was added to improve the solubility of inorganic carbon in solution. Basically, inorganic carbon is inert at room temperature [28]. Secondly, the mixture was diluted with water solution and then graphite oxide was centrifuged and added NaOH to precipitate Mn salt on GO. Thirdly, the graphite oxide was exfoliated by sonicator to produce mono/bilayer graphene oxide. The composite was then characterized by atomic absorption spectroscopy (AAS), UV-Visible (UV-Vis) spectrophotometer, fourier transform infrared (FT-IR), X-ray diffraction (XRD), and transmission electron microscopy (TEM).

2. Experimental Section

2.1. Materials and Instruments

In this work, natural graphite powder was purchased from CV. Pratama. The high purity chemicals include 95% H$_2$SO$_4$ from Smart Lab Indonesia, KMnO4 and NaOH from Merck. The instrumentation used to analyse are the UV-Visible spectrophotometer (UV-1600 series), atomic absorption spectroscopy (Thermo Scientific, ICE 300 series), fourier transform infrared (Shimadzu, 8400S), X-ray diffraction (PANalytical XPert-3), and transmission electron microscopy (JEOL JEM-1400 and HITACHI H-9500).

2.2. Synthesis of GO-MnO$_x$ Composite

Natural graphite was used as the starting material to prepare GO-MnO$_x$ by the modified Hummers method [19]. Three gram of graphite powder was added to a 95% (50 mL) H$_2$SO$_4$ and stirred for 15 min. KMnO$_4$ was slowly added to the mixture in an ice bath (<10°C) and stirred for 2 h at 35°C. The resulting mixture was added with DI water (150 mL) dropwise, while the temperature was maintained at 90°C. Under vigorous stirring the mixture was cooled down so that the temperature did not exceed 50°C. After 30 min, the suspension was added with DI water (20 mL) and centrifuged at 4000 rpm for 20 minutes. The supernatant was removed, and the suspension was added with DI water (150 mL). A solution of NaOH (3 M, 30 mL) was added slowly into the suspension in an ice bath at <5°C, and then the suspension was stirred for 15 min at room temperature. The suspension was filtered and washed with a sufficient amount of DI water, sequentially. The product was dried at an oven (<40°C) and fully dispersed in the DI water (300 mL). The resulting mixture was sonicated in a water bath sonicator operating at 100 W for 30 min. Then, the filtering and drying (<40°C) were carried out to collect the composite.
2.3. Designation of the prepared samples
GO-MnO₃ 1 and GO-MnO₃ 2 were synthesized by taking the same amount of sulfuric acid and potassium permanganate, as well as the concentration of NaOH. However, the sequence of centrifugation step between GO-MnO₃ 1 and GO-MnO₃ 2 was different. On the preparation of GO-MnO₃ 2, the mixture firstly was cooled down in an ice bath (<5°C) after oxidized with KMnO₄ and diluted with water, and added slowly with NaOH, and then the final mixture was centrifuged.

Table 1. Synthesis parameters (the ratio of mass KMnO₄ and volume H₂SO₄ as well as the concentration of NaOH) and designations of the prepared samples.

| Sample   | Graphite (g) | KMnO₄ (g) | 95% H₂SO₄ (mL) | 30 mL NaOH (M) |
|----------|--------------|-----------|----------------|----------------|
| GO-MnO₃ 1 | 3            | 6         | 50             | 3              |
| GO-MnO₃ 2 | 3            | 6         | 50             | 3              |

3. Results & Discussion

3.1. Synthesis of GO-MnO₃ Composite
The modification of surface and lateral dimension is profitable strategy to improve the physicochemical properties of GO-MnO₃ materials. In this research, we prepared GO-MnO₃ composite via Hummers method [19] with modification, as illustrated in Figure 1 and showed in Figure 2. By permanganate and strong acid, graphite was oxidized and several graphitic structures are broken up into smaller fragments [29,30]. The specific oxidizing agent species attacking graphene layers is not studied systematically. Several researches reported that the green-colored dimanganese hepatoxide (Mn₂O₇) was oxidizing agent which can be isolated from KMnO₄/H₂SO₄ solution [12]. Manganese salts and the highly reactive dimanganese hepatoxide can be reduced with the centrifugation process [31]. This step also was carried out to acquire GO with high purity. In contrast, our process intended to convert the residual Mn into value-added materials. Here, our method investigated the effect of the addition of NaOH before and after the centrifugation step toward the number of Mn on GO-MnO₃ composite. As seen in Table 2, GO-MnO₃ 1 has lower concentration of Mn than GO-MnO₃ 2, although on same condition (see experimental section). In GO-MnO₃ 1, the residual Mn without oxidation has been reduced with supernatant caused by centrifugation process. Therefore, the number of Mn precipitated by NaOH was diminished. The number of Mn on composite can be seen in Table 2.

Figure 1. Schematic of synthesis of GO-MnO₃ by means of the modified Hummers method (A: structur of graphite, B: predicted structure of graphite oxide containing oxygen functional groups, C: the graphite oxide exfoliates into graphene oxide).
Figure 2. The image of graphite as starting material (A) and GO-MnOx as the product (B) in this research. The two materials have no difference significantly.

Table 2. The concentration of Mn on GO-MnOx analyzed by AAS.

| Sample Code | Mass of Sample (g) | Concentration of Mn (µg/g) |
|-------------|--------------------|---------------------------|
| GO-MnOx 1   | 0.50001            | 1.4231                    |
| GO-MnOx 2   | 0.50003            | 2.0958                    |

The reduction of lateral size of graphite oxide sheets to graphene oxide (several layers) could be attained via sonication process because the surface chemical properties of GO sheets changed can be negligible [32]. During sonication, the exfoliation process is occurred repeatedly [33]. As seen in XRD pattern (Figure 5), the low intensity of GO-MnOx showed that graphite was exfoliated to form GO-MnOx with slightly layers. The formation and propagation of cracks which are catalysed by the presence of sp$^3$ defects in the basal of graphene lattice during sonication induced the physical breakdown of GO sheets [34]. As demonstrated in the following sections, the effect of sonication resulted in the acquisition of GO-MnOx, which differed by their surface chemical properties and crystal structure (as seen in the next section).

3.2. Characterization of GO-MnOx composite

The FTIR spectra of graphite and GO-MnOx are given in Figure 3. IR spectra of graphite is similar to IR spectra of graphite in the reference [35]. The IR spectrum of GO-MnOx showed characteristic peaks at ~1050, ~1200, ~1380, ~1700, and ~3400 cm$^{-1}$, ascribed to C–O–C (alkoxy), O=C–O (epoxy), C–OH (carboxyl), C=O (carbonyl), O–H (hydroxyl) stretching vibrations, respectively [36,37]. The peak at ~1570 cm$^{-1}$ corresponded to C=C skeletal vibrations from unoxidized graphitic domains. Moreover, % transmittance of FTIR spectra shows the number of functional group vibrations. The presence of peak at ~500-700 cm$^{-1}$ might be interpreted as Mn–O–C vibration [26,38]. These peaks (GO-MnOx, 1 and 2) were similar to each other. However, the intensity of peaks was different and even disappeared in some cases. The low intensity of the peaks around ~1050, ~1380, ~1700, and ~500-700 cm$^{-1}$ suggest that GO-MnOx 1 and 2 might have a slightly low abundance of alkoxy, carboxyl, hydroxyl and manganese oxide, respectively. This means that composite has minor differences in changes in the chemical environment although have been added with oxidized agent or base concentration.

UV-Vis spectra for graphite and GO-MnOx in the range 200–800 nm is investigated in water solution, as seen in Figure 4. The maximum absorbance of GO-MnOx at $\lambda = 230$ nm is assigned to $\pi \rightarrow \pi^*$ transitions in conjugated systems [39,40]. A shoulder at $\lambda = 290$ nm often attributed to the $n \rightarrow \pi^*$ transition of carbonyl group on GO-MnOx disappears [28], which might be due to a less numbers of conjugated systems with carbonyl. In contrast, the maximum absorbance for graphite was not detected probably due to the absence of the oxygen groups.

In the XRD pattern of graphite (Figure 5) it was clear that graphite showed a peak at about $2\theta = 26^\circ$ with interlayer distance of $d = 0.34$ nm which was similar to graphite in the reference [41]. The XRD analysis of GO-MnOx (1 and 2) showed the shifting of interlayer distance ($d = 0.37$ nm) at about $2\theta =
24.5° which is still slightly bigger than interlayer distance of graphite. Comparing with the literature, this peaks were corresponded to the reduction of graphene oxide peaks with the fewer oxygen containing groups, whilst the peak of GO generally appeared at $2\theta = 10-15^\circ$ with interlayer distance about 0.8 nm [42]. This suggests that the functional oxygen groups on GO-MnO$_x$ not fully reduced into graphene. Moreover, due to the low amounts of MnO$_x$ in the composite, there are no signals ascribed to MnO$_x$ species. However, the presence of MnO$_x$ can be confirmed by FTIR. Furthermore, the broader peak of XRD with lower intensity indicated the low crystallinity (amorphous phase) of GO-MnO$_x$ compared with graphite [43].

![FTIR spectra of graphite and GO-MnO$_x$ (1 and 2).](image1)

**Figure 3.** FTIR spectra of graphite and GO-MnO$_x$ (1 and 2).

![UV-Vis spectra of graphite and GO-MnO$_x$ (1 and 2).](image2)

**Figure 4.** UV-Vis spectra of graphite and GO-MnO$_x$ (1 and 2).

The morphology GO-MnO$_x$ was characterized by TEM and presented in Figure 6. TEM images showed that GO-MnO$_x$ has been exfoliated into a thin layer but not to a single layer. The images of composite showed to be crumpled, overlapped, and folded which clearly appeared in the edges might due to aggregation, as displayed in Figure 6. Moreover, due to little Mn eluted into graphene oxide,
The TEM images were not confirmed the MnO$_x$ crystal growth on the GO surface even on higher magnified of TEM image, in agreement with the obtained XRD pattern (Figure 5).

![Graphite and GO-MnO$_x$ XRD patterns](image)

**Figure 5.** XRD patterns of graphite and GO-MnO$_x$.

![GO-MnO$_x$ TEM images](image)

**Figure 6.** TEM images with magnification 20000x of GO-MnO$_x$ 2 (a) GO with crystals suspected of manganese oxide (b), respectively.

**4. Conclusions**

In summary, the composites were successfully synthesized by modified of Hummer's technique. This is supported by AAS data which shows the slight number of Mn on GO-MnO$_x$. Moreover, XRD analysis shows the lower intensity of GO-MnO$_x$ comparing with graphite which indicated that the several layers of graphite have been exfoliated into slight layers by sonication process.
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