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Preliminary study of exfoliated graphite (EG) produced by electrochemical exfoliation and EG-TiO₂ composite

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Abstract. In this research, Exfoliated Graphite (EG) materials have been synthesized using the electrochemical exfoliation method. The starting materials are graphite sheets, before the exfoliation process, a simple pre-treatment was carried out, by immersing the graphite sheet in a mixture solution of sulfuric acid (H₂SO₄) and hydrogen peroxide (H₂O₂) with a ratio of 95:5 to widen the interlayer distance in graphite sheets for the optimum electrochemical exfoliation process. This study used ammonium sulfate solution (NH₄)₂SO₄ as an electrolyte with a concentration 0.25 M. The obtained EG materials are then composited with TiO₂ to increase the resulting energy density of the materials. The in-situ sol-gel method was used to synthesize the EG-TiO₂ composite assisted by microwave irradiation. The resulting materials were characterized using X-ray diffraction (XRD), Fourier Transform infrared (FTIR), and LCR meter. Based on the XRD results, the EG-TiO₂ composite showed an amorphous structure with an average crystallite size of 24.9 - 49.9 nm. It also shows that the XRD pattern of the EG-TiO₂ composite has a lower peak intensity than the EG material. The FTIR result shows that the functional group of the rGO-TiO₂ composite has a combination of Ti-O-Ti and Ti-O-C vibrations, which indicates the chemical interaction of TiO₂ with EGs.

Keywords: composite, electrochemical exfoliation, exfoliated graphite, titanium dioxide.

1. Introduction

Over the past few decades, research on renewable energy sources such as solar energy, geothermal energy, wind energy, and biofuels has experienced a significant increase. Likewise, electrochemical energy storage devices such as supercapacitors and rechargeable batteries have attracted the attention of researchers and industry [1]. Supercapacitors have advantages such as high-power density, relatively long service life, fast charge-discharge process, and simple operation [2]. To improve supercapacitor performance, the choice of electrode material is of key importance. Materials such as graphene and Exfoliated Graphite (EG) have attracted attention due to their large surface area, excellent electrical conductivity, and fast electronic mobility [3]. EG synthesis using the Electrochemical Exfoliation method has succeeded in producing material with high specific capacitance. The influence of pre-treatment on the exfoliation process can control the amount of EG material produced. The results show that the H₂SO₄:H₂O₂ solution with a volume fraction of 95:5 has the most optimal degree of exfoliation, this sample also shows excellent electrochemical properties, and has a specific capacitance of 71.95 F g⁻¹ [3].



However, to improve the performance of supercapacitors, combining EG with other materials such as transition metal oxides, such as titanium oxide (TiO_2), or conductive polymers has become a promising strategy. TiO_2 is considered a promising electrode material due to its pseudocapacitive behavior, chemical stability, and environmental friendliness [4]. Among transition metal oxides, titanium oxide is considered a promising electrode material for supercapacitor applications. However, titanium oxide, like other metal oxides, has poor electronic conductivity which limits its use in some applications. Therefore, incorporating titanium oxide into EG will overcome the deficiencies in the conductivity and cycle stability of the electrode material [2].

Based on the background above, this research will focus on mixing EG material produced via the electrochemical exfoliation method with TiO_2 which is composited using the sol-gel method assisted by microwave radiation. The resulting composite material will be characterized to identify its properties including crystal size, band gap and electrical conductivity. Thus, this research aims to develop environmentally friendly carbon-based materials that have wide use, especially as a substitute for non-renewable fossil energy sources.

2. Experimental Method

2.1. Pre-Treatment Graphite Sheet

The graphite sheet was cut into rectangles measuring approximately 5.5 cm x 2.5 cm. Prepare the mixture solution of sulfuric acid (H_2SO_4 98%) and hydrogen peroxide (H_2O_2 50%) with a volume fraction of $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2$ is 95:5. The graphite sheet was immersed in $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ solution for 6 minutes and leaving about 1.5 cm of the part not submerged for the alligator clamp.

2.2. Electrochemical Exfoliation Graphite Sheet

In the electrochemical exfoliation process, 100 ml of ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) with a concentration of 0.25 M was used as the electrolyte solution. The graphite sheet that has been pre-treated is connected to the positive pole, and the carbon electrode to the negative pole of the DC power supply. The two electrodes are placed in ammonium sulfate solution ($(\text{NH}_4)_2\text{SO}_4$) and ensure that they are not completely immersed. Then the DC power supply is connected to the electricity source. The electrode was subjected to a constant potential bias of 10 V for 3.5 hours. The exfoliation results were then washed repeatedly using distilled water until neutral. Then the samples were dried in an oven at 60° C for 6 hours. Further, the obtained sample was dispersed in DI water and sonicated for two hours. Next, the sample was centrifuged for 15 minutes at 1000 rpm to separate large particles from the dispersion. Then the samples were dried using the oven at 80° C for 18 hours.

2.3. Synthesis of EG-TiO₂ Composite

In this process, 40 mg EG powder was dispersed into 20 ml DI water and sonicated for 1 hour. Then, 0.4 ml TTIP and 10 ml ethanol were stirred for 1 hour at room temperature. Next, 8 ml of TTIP solution was added to EG solution followed by microwave irradiation for 10 minutes. The obtained sample then filtered and washed using ethanol and water several times, then dried in an oven at 60°C for 12 hours.

3. Result and Discussion

Figure 1. shows the illustration mechanism of the electrochemical exfoliation process on a graphite sheet. An electric field causes the anode to expand concurrently with gas generation as the anion in the electrolyte travels into the graphite layer to increase the interlayer distance. Graphene is produced by reducing and peeling off the interlayer van der Waals force. During anode exfoliation, the graphite foil's edges and grain boundaries are attacked by the hydroxyl radicals ($\cdot\text{OH}$) produced by the electrolyzed water. The graphite layer depolarizes and expands as a result of further oxidation at grain boundaries and edge sites, which encourages the insertion of sulphate ions (SO_4^{2-}) into the graphite layer. Ultimately, gaseous species like SO_2 and O_2 are produced by the reduction of SO_4^{2-} anions and the self-oxidation of water in the graphite interlayer. The gas in the graphite interlayer acts as a driving factor

for the effective exfoliation of graphene (Fig. 1). Despite the high peeling effectiveness of anode electrochemical exfoliation, the resulting graphene has structural flaws and an oxygen-containing functional group as a result of the anode graphite's oxidation reaction [9].

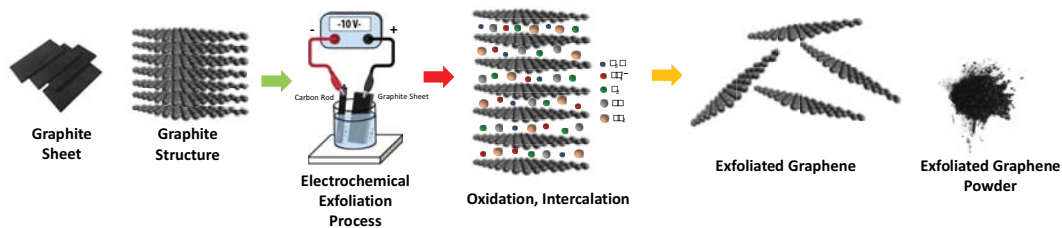


Figure 1. Schematic illustration of the electrochemical exfoliation on graphite sheet

Functional groups in pure graphite, exfoliated graphite and EG-TiO₂ composites were identified using FTIR. The resulting wave number shows the vibration of the chemical structure contained in the sample. Transmittance shows a linear correlation with sample variation [5]. As seen in Figure 2, the entire spectrum shows an absorption band at around 555 which shows the O-H functional group where the peak is related to the oxygen functional group originating from alcohol and water, at wave number 568 there are Ti-O-Ti and Ti-O-H compound bonds. This indicates that TiO₂ has been successfully added to exfoliated graphite. According to [6] a strong transmission peak occurs in the wave number range 850-500 cm⁻¹ which is due to the influence of oxygen in the air which is adsorbed on the TiO₂ surface during the synthesis process. 1637 shows the presence of aromatic ring vibrations (C=C) [7], 2346 contains CO₂ compounds [8]. The shift in the wave number peaks of the hydroxyl and carbon groups, in pure and composite EG materials, indicates that TiO₂ material has been deposited on the EG surface to form an EG-TiO₂ composite.

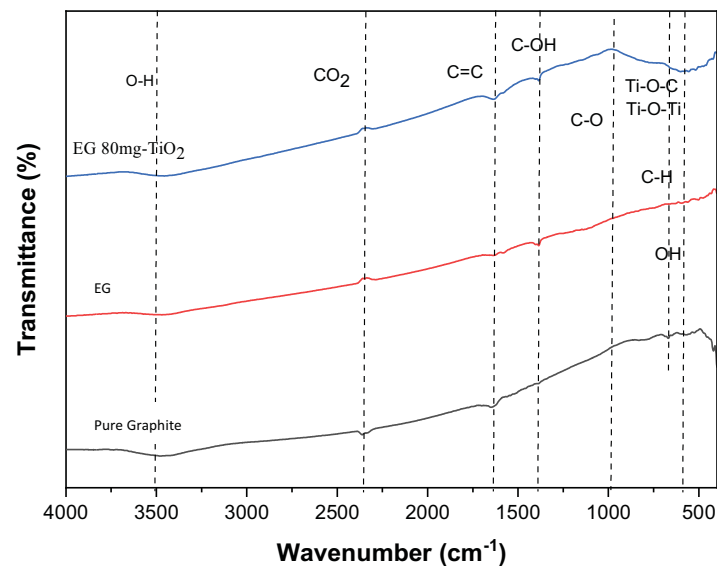


Figure 2. The IR spectrum of pure graphite, EG and EG-TiO₂ composite

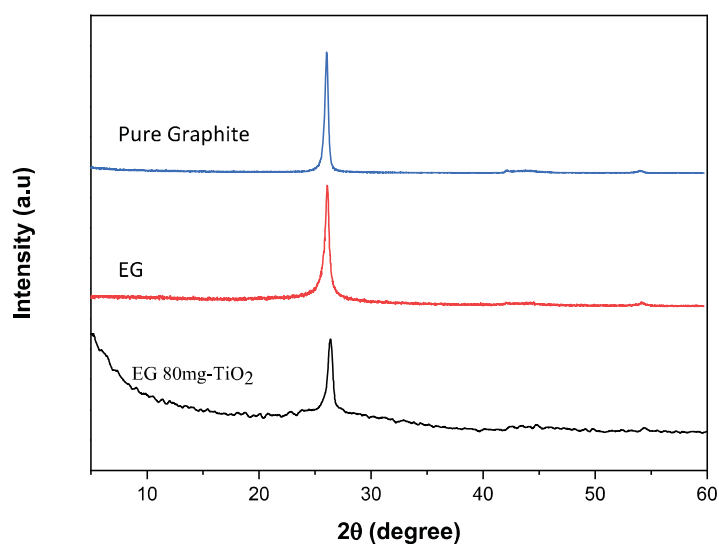


Figure 3. Diffraction patterns of pure graphite, Exfoliated Graphite (EG), and EG 80mg-TiO₂ composite

Figure 3. shows the X-ray diffraction pattern of pure graphite, EG and EG-TiO₂ composite. All the samples have almost identical peaks at $2\theta \sim 26^\circ$ in their diffraction patterns, which were enlarged along 2θ from 25° to 28° [10]. It can be seen that in the (002) plane, the peaks of graphite 2θ are relatively identical. Each sample experienced a minor shift at an angle of 26.27° to 26.34° , for pure graphite and EG respectively. This shift is also known as a sign of changes in the distance between graphite layers (d-spacing). The sharp peaks in the sample indicate that the EG obtained has good crystallinity because the sample is oxidized during the electrochemical exfoliation process [12]. The EG-TiO₂ composite sample using microwave assistance with a medium duty cycle shows a peak at $2\theta = 26.45^\circ$ with a smaller peak intensity than pure graphite and EG. Analysis of test results using XRD in terms of crystal size and distance between layers are shown in Table 1. The samples with large crystal sizes exhibit lower conductivity due to reduced ion mobility, and the greater the d-spacing value, the higher the capacitance [3]. The shift of the peak plane to a lower 2 theta is another indication of interlayer distance expansion in graphite [11].

Table 1. Crystal size and distance between lattices in pure graphite, exfoliated graphite and EG-TiO₂ composites

Sample	Peak Position (deg)	FWHM (rad)	D (nm)	d-spacing (Å)
Pure Graphite	26.27	0.4180	19.487	3.38
Exfoliated Graphite (EG)	26.34	0.2175	37.512	3.383
EG 80mg-TiO ₂	26.45	0.3264	25.002	3.366

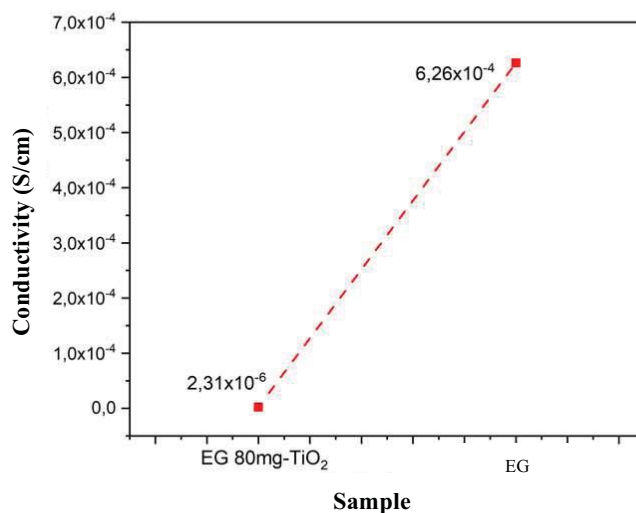


Figure 4. Electrical conductivity of EG and EG 80mg-TiO₂ composite

The electrical conductivity of the samples is depicted in Figure 4. The electrical conductivity values of the EG and Composite EG-TiO₂ samples are 6.26×10^{-4} S/cm and 2.31×10^{-6} S/cm respectively. The LCR meter result shows that EG has a higher electrical conductivity than the EG-TiO₂ composite. This is due to the low conductivity value of TiO₂, which means that when EG is combined with TiO₂, the combined conductivity value is less than the electrical conductivity of the individual EG.

4. Conclusion

Exfoliated graphite was successfully synthesized using the electrochemical exfoliation method with the pre-treatment process using H₂SO₄/H₂O₂ solution. The EG-TiO₂ composite has been successfully synthesized using the in-situ sol-gel method assisted by microwave irradiation. The X-ray diffraction pattern of the pure graphite, Exfoliated Graphite (EG) and EG-TiO₂ have identical peaks at $2\theta \sim 26^\circ$ which is a characteristic of exfoliated graphite materials. The electrical conductivity of EG is greater than the EG-TiO₂ composite, which has a conductivity value of 6.26×10^{-4} S/cm and 2.31×10^{-6} S/cm for EG and EG-TiO₂ respectively.

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