Graphene/SiO₂ Nanocomposite From Natural Material

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Abstract. This work, reports on the results of research, fabrication of natural-based Graphene/SiO2 nanocomposites; graphene (GO) was prepared from coconut shells using the Hamers method and silica nanoparticles (SiO2) derived from Tetraethyl-orthosilicate precursors. Graphene/SiO2 nanocomposite fabrication using the one-pot process. The Crystal structure was analyzed using XRD, functional groups with FTIR and D-band and G-band that identified sp2 orbitals with Raman Spectroscopy. The analysis of adsorption properties of methylene blue dyes dissolved in water studied by UV-Vis spectroscopy. Graphene/SiO2 characteristics are obtained both in terms of structure and adsorption power of colours in the water, which is characterized by a trend of decreasing adsorption intensity on the UV-Vis curve.

Keywords: Nanocomposite, Graphene, Graphene/SiO2

1   Introduction

Traditionally, Graphite is known to have a high level of hardness and is resistant to abrasion, has a high porosity, so that its absorption power is very good; and very suitable for use as a filter media in the water treatment process. Activated carbon can be obtained from basic ingredients of coconut shell [1],[2]. In previous studies, it was informed that from old coconut shells which had undergone a carbonization process at 400ºC had the main molecular bonds of graphene (C=C and C-C and impurity bonds such as C-H, C-O, C=O and O=H) [2]. Graphene is a new type of material consisting of carbon atoms in a flat lattice configuration form. This configuration resembles a honeycomb structure with atomic order thickness. So thin is this graphene layer that it is one example of a two-dimensional (2D) material.

In general, rGO synthesis is produced using the Hummer's method [1],[2]. Hummer's method is a chemical method that can be used to produce graphite oxide by adding potassium permanganate to a solution of graphite, sodium nitrate, and sulfuric acid. In this method, there are stages of the ultrasonification process and the hydrothermal process resistance so that graphene results that have electrical conductivity, and good working performance [2-4].

Silica is one of the layered poly-silicate crystals whose layers consist of tetrahedral SiO4. Silica is a natural silicate crystal although it can also come from the synthesis of quartz sand [4],[5], and also in various other organic materials, such as baggase-ash [4], rice husk [4]. Also in the market there are very many product variants in the form of powder, granul, gel, and aerogel [5],[6]. Some chemicals which are precursors such as sodium silicate, and TEOS

(tetraethyl orthosilicate) [1],[7]. Silica particle (SiO_2), graphene is a material that has a trend as the best candidate for filter media.

The prospect of application of SiO2 and rGO nanoparticles is very broad, the latest is found that rGO nets in sheet form (membrane technology) can separate NaCl molecules from seawater, and this is the beginning of a technological revolution in the provision of clean water for consumption from seawater, from technology desalination process into a nanotechnology based graphene filter [1],[2],[5]. In the initial stages, of course the question is how the characteristics of graphene if combined with SiO_2 nano particles; this is very interesting, both SiO_2 and graphene are inert, porous and some other superior properties. Various methods can be used for fabrication of nanoparticle composites, such as In-situ, co-precipitation, sol-gel and other chemical processes [8]. The fabrication method that has been widely used is the sol-gel process with one-pot reaction techniques; which is effective for producing rGO/SiO_2 material.

In the following discussion, we will discuss the characterization of Graphene/SiO_2 composites based on natural materials. RGO particles were obtained from coconut shells and SiO_2 from the TEOS precursor. Furthermore, an analysis of the characteristics of the Graphene/SiO_2 composite and the effect of calcination temperatures up to 800°C, and how the transformation of the SiO2 phase in the composite system. Several tests for characterization, including XRD, Raman Spectroscopy, FTIR, UV-VIS and SEM.

2 Materials and Method

2.1 Material and Methode

The ingredients that must be prepared are coconut shell as the main ingredient for the production of graphene, Tetraethyl orthosilicate (TEOS) as a precursor of SiO2, ethanol, hydrochloric acid (HCl), Pro Analysis (37%), Sodium hydroxide (NaOH), Ammonium hydroxide solution (NH4OH) , and DI-water.

2.2 Synthesis and Characterisation

The formation of rGO uses the Hummer method from coconut shell material. Coconut shell is cleaned and dried, then crushed, followed by the combustion process at a temperature of 400oC for 5 hours. Graphene (GO) is smoothed and sieved with a size of 200 mesh to be homogeneous and facilitate the reaction process. The final stage is added distilled water and HCl solution for ultrasonication for 2 hours. The precipitate yields were then filtered and dried at 60oC, obtained with rGO powder [1],[2]. Fabrication of Graphene/SiO_2 nanocomposites using the one-pot process method; TEOS solution as amorphous SiO2 precursor. In this study, RGO mass was made into three variations, namely S#1 (1 gram) sample, S#2 (1.5 gram) sample and S#3 (2.5 gram) sample. The rGO powder was put into DI-water, then TEOS solution and Ethanol solution were added, stirring for 1 hour at a temperature of 110oC, the sauce was constantly dripping with HCl. The final product of the Graphene/SiO_2 composite, dried at 60oC for 24 hours. Composite is calcined at 800oC. Characterization of samples using X-Ray Diffraction (XRD), Fourier Transform Infra-Red (FTIR) which showed that the functional groups formed, absorption power using UV-Vis, and morphology with SEM analysis.

3 Result and Discussion

3.1 X-Ray Diffraction Analysis

The XRD test results show that the Graphen/SiO2 composite diffraction pattern shows that the peak diffraction of SiO2 nanoparticles with angular positions of 2θ~20o-35o precisely at 21.9o the SiO2 phase is amorphous and the diffraction peaks of GO graphene are at 24.9o and 43.0o for the crystal fields respectively (002) and (100). The XRD diffraction pattern of the Graphen/SiO2 composite sample shows that there are rGO peaks and SiO2 peaks. In sample S#2 the diffraction peaks appear for the graphene to start to form the crystalline phase, but in general amorphous dominance. Follow at **Figure 1**.
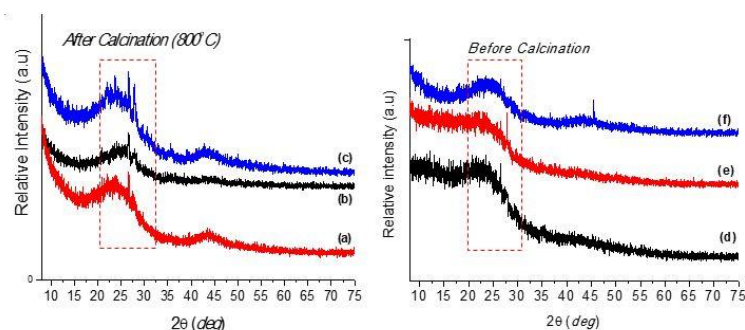

Fig. 1. Pattern X-ray diffraction of SiO2, rGO, and Graphene@SiO2 samples.

Details of diffraction peak positions in Graphene/SiO2 samples are presented in Table 1, for S#1, S#2, and S#3 samples have similarities with previous studies [1,3,4]. The Graphene/SiO2 nanocomposite has formed; in the range of 2θ ~ 20-30° there is a hump as shown by the rGO and SiO2 samples; and in the range of 2θ~ 42-46° there is a peak which marks the graphene phase, from the rGO sample. X-ray diffraction data and analysis with High-score plus, obtained information on the peak and the crystal field as presented in **Table 1**. And at an angle of 2θ~ 26° identified the crystal field (002), and at an angle of 2θ ~ 43° Crystal fields were identified (100) [5],[10],[11].

Table 1. Peak position (2θ) of Graphene@SiO2 samples and reference.

Peak	1	2	Notes
	26,35º	42,59º	S#1 Sample
	27,01º	42,55º	S#2 Sample
2θ(deg)	26,41º	44,0º	S#3 Sample
	26,37º	-	[5]
	24,9º	43,0º	[3,5,10]
(hkl)	(002)	(100)	

Based on the XRD results **Figure 2** for the Graphen/SiO2 composite sample after calcining (at 800oC) shows that there is a difference with the Graphen/SiO2 composite before calcining

where **Figure 1**, in this diffraction pattern there is a crystal phase that appears at 2 angles (2θ) different. The crystalline phases that emerge are the crystalline phase. In this result varies with different masses and the presence of the cristobalite crystalline phase. As the calcination temperature increases followed by changes in the structure of the amorphous SiO2 leading to polycrystalline, crystalline phase is formed.
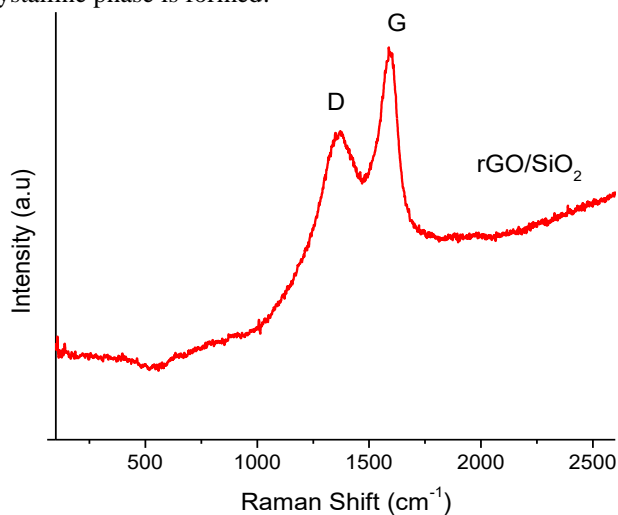

Fig. 2. Raman spectroscopy of Graphene/SiO2 sample.

In **Figure 2**, a Graphene/SiO2 sample of Raman Spectroscopy graphs, identified the presence of D-band and G-band peaks. Raman spectroscopy is one of the most sensitive techniques for characterizing disturbance in carbon sp2. The D-Mode is caused by irregular graphene structures. The presence of interference in the sp2 hybridization carbon system results in a resonant Raman spectral. The G-band mode arises from stretching the C-C bond in graphene material, and is generally applicable to all sp2 carbon systems. In **Figure 2**, it appears that the intensity of ID (D-peak) is lower than IG (G-peak), meaning that the stretching of C-C is more dominant than the level of interference in sp2 orbitals. All types of sp2 carbon material show strong peaks in the range of 2500-2800 cm-1 in the Raman spectrum.

3.2 Fourier-transform Infrared Spectroscopy Analysis

Based on the results of the FTIR test shows that the wave number 3454 cm-1 there is an O-H bond vibration which is characteristic of the SiO_2 peak. At the top of the rGO shows that the wave numbers 1150 cm^{-1} and 1630 cm^{-1} are vibrations of the bond of the graphen function group, namely C-O and C=C, respectively. And at wave number 1732 cm-1 is stretching C = O bond. For the FTIR results, the characteristics of the Graphene/SiO2 composite showed similarities to the functional groups of the rGO and SiO_2 surfaces. If observed, there appears to be a decrease in the infra red wave absorption peak (range of wave numbers 1450-1750 cm^{-1}) for samples S #1, S#2 and S#3 respectively; this indicates that the greater the composition of the graphen mass added, the freedom of movement of the Si-O function group is increasingly limited [1],[4,[12], seen at **Figure 3**.
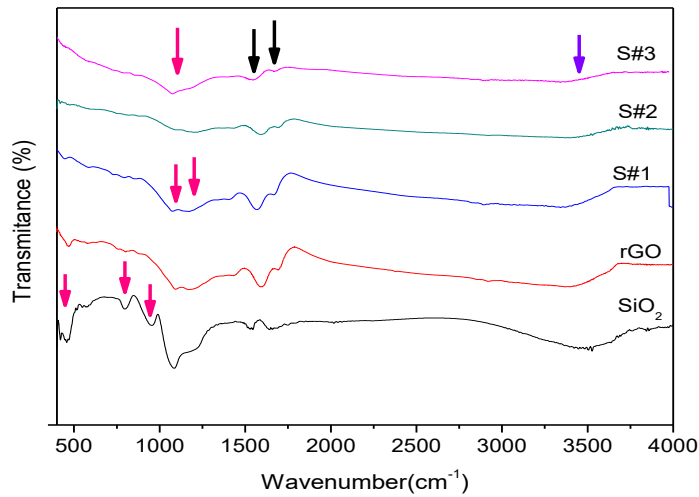
Fig. 3. FTIR spectra of rGO/SiO2 composite before calcination (S#1, S#2 dan S#3).

The same trend also occurs in Graphene/SiO$_2$ composite samples after calcination, showing the difference in rGO/SiO2 composites, the greater the mass composition of rGO. added (S #1, S#2, and S#3) the infrared vibration peak peaks also decreased. However, because the crystalline phase has begun to form both RGO and SiO2 in its composite system, the red wave absorption is lower than when before calcining. The difference is seen in each sample where in sample S#1, the peak contribution of SiO$_2$ and rGO can still be clearly observed, but in sample S#2 and sample S#3 this is only visible rGO particles only. So if the greater the mass fraction of RGO is added, the contribution functional group of SiO$_2$ particles will be less visible when calcined at high temperatures **Figure 4**.

3.3 Ultra Violet-Visible (UV-Vis) Test Results

As shown in Figure 5, the spectroscopic UV-Vis graph for samples S # 1, S # 2 and S # 3 before calcination is treated **Figure 5** (a) and after calcination treatment **Figure 5** (b) there appears to be a trend decreased adsorption intensity for each sample. While for each sample (S # 1, S # 2, and S # 3) an increase in the intensity of adsorption occurs with an increase in the amount of mass RGO, for both types of samples (before and after calcination). The effect of the addition of rGO mass fraction is to reduce the absorption ability [3],[10].
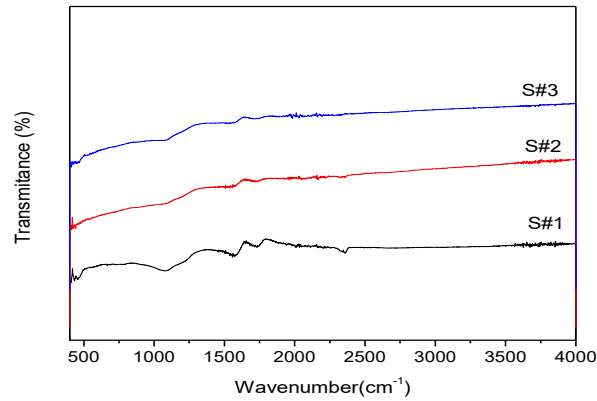
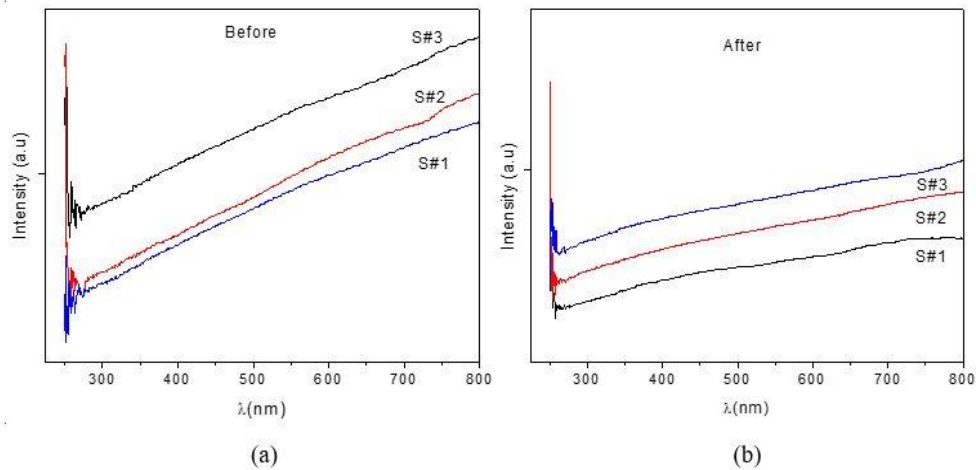**Fig. 4.** FTIR spectra of rGO/SiO2 composite after calcination (S#1, S#2 dan S#3).

Fig. 5. Uji UV-Vis spectral of rGO@SiO$_2$: (a) Before, and (b) After Calcined (800°).

3.4 Morphology of rGO/SiO$_2$ Composite

It can be seen in **Figure 7**, the morphology of the rGO/SiO2 composite sample particles for the conditions before and after the calcination process at 800°C. The particle size of RGO and SiO2 particles grow in size after calcination, while there are small pores on the large particle.

Analysis with EDX obtained atomic data elemental Si, C, O as the main constituent of the rGO/SiO2 composite, as in the graph **Figure 6** below. That the atomic element C is the atomic percentage (~ 75.16%) or the percentage weight (~ 67.65%), while for the Si element (atomic % ~1.27 and weight % ~ 2.68). The presence of element C is more dominant, and this indicates the composition of graphene in the composite rGO/SiO2 is more dominant, and tends to be the matrix [1],[2,[10].
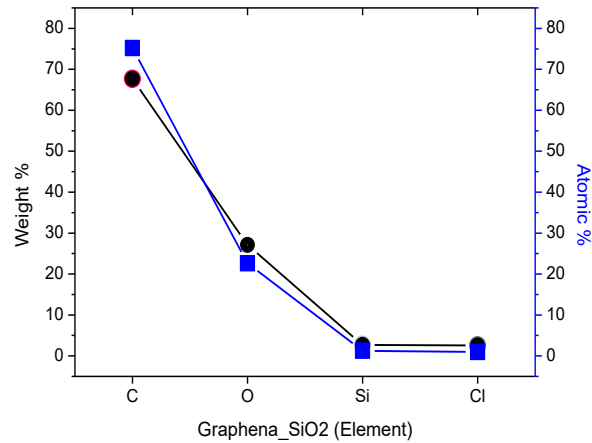
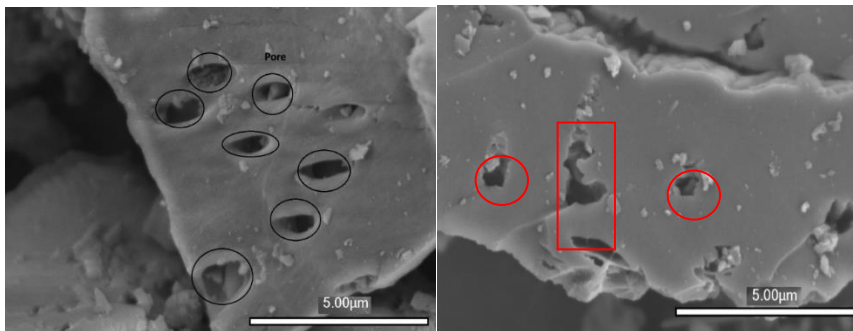**Fig. 6**. EDX of SiO2@rGO composite: element of C,Si,O and others.

Fig.7. Image of SiO2/rGO composite: (a) before, and (b)after of calcination (800°C).

4 Conclusion

The graphene/SiO2 composites successfully synthesized by one-pot processing method, characterized by X-ray diffraction profiles, EDX and D-band and G-band, which are typical properties of graphene that has sp2 orbitals. rGO nanoparticles were prepared using the Hamers method from natural ingredients, coconut shells. There is a transformation of the crystalline phase of graphene/SiO2 composite samples (temperature of 800°C), from amorphous to cristobalite phase. The RGO mass fraction decreases the absorption of UV-Vis waves. The existence of rGO acts as a matrix; particle morphology, there are micro-pore and voids scattered in various positions; this situation affects the absorption power.

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