Effect of Reaction Time on the rGO-CoS Composite Structural Properties

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Abstract. In this research, the rGO-CoS composites were successfully synthesized from GO and the Cobalt and Sulfur precursors via solvothermal reaction. The GO material was obtained by Hummer method reaction synthesis. In term of rGO synthesis, reaction time is one of important factors that determine the reduction process and the resulting material properties. Therefore, we studied the influence of reaction time to the chemical properties of the obtained composites by varying i.e 12, 24, 36 and 48 hours of reaction time. The characterizations were carried out using Scanning Electron Microscope (SEM), X-Ray Diffraction (XRD), and Fourier Transform Infra-Red (FTIR). Morphological observation of rGo-CoS shows that rGO-CoS are has many thin layers, rougher, and wider surface. From the XRD result, GO shows shift of peak diffractogram to 2θ 9.56° with interplanar space 9.24 Å and rGO-CoS 36 shows several peaks at 2θ 30.84, 35.47, 47.54, 54.94°. The GO spectrum pattern shows specific functional group, OH groups (hydroxyl), carboxyl stretching vibration C=O (-COOH), C=C of unoxidized graphite consisting aromatic rings, and epoxy group vibration C-O(,) while rGO and rGO-CoS shows decrease in intensity of these bands. It concluded that the rGO-CoS 36 (hours) is considered as the most optimum reduction reaction time.

1. Introduction
Graphene is a material that has attracted the attention of many researchers because it has good chemical, electronic, mechanical, and physical properties so that this material has the potential to be applied as an electronic component. Graphene oxide (GO) is a derivative of graphene that has also received a lot of attention because it is cheap and easy to synthesize [1].
GO can be synthesized using the Hummers method. The advantage of this method is that it will not produce toxic gases such as NO₂, N₂O₄, or ClO₂ in the reaction, so this method is environmentally friendly [2].

rGO (Reduced Graphene Oxide) can be synthesized from GO by the hydrothermal method. The GO reduction process is carried out by thermal reduction with the temperature above 180 °C or 200 °C [3] and the addition of a reducing agent which aims to remove the oxygen functional groups present in the GO structure. The advantages of this method are that it is scalable and simple, environmentally friendly, and industrially compatible [4]. rGO is alternate material as counter electrode Pt free in DSSC with comparable efficiency because of rGO’s high conductivity and catalytic activity [5].

First transition metal also potential to replace Pt as a counter electrode because of its abundance and low-cost material. Among them are the VIII group the fourth period, such as Ferrum (Fe), Cobalt (Co), and Nickel (Ni), was used as power and environmental catalyst in many important reaction catalytic industry [6]. Especially Co because of its great electrical conductivity and catalytic activity [7]. But, the first transition metal including Co has relatively low-efficiency electron transport between particle and unstable compared to Pt, makes electrocatalytic properties in DSSC is limited. In order to improve electrocatalytic performance, CoS is grafted on the surface of rGO become rGO-CoS composite.

Hydrothermal reaction time for rGO synthesis is one of the important factors that determine the reduction process and the resulting material properties. The longer the reaction time, the better the reduction process and the resulting material properties. However, there is a time limit where if the reaction is carried out longer, the reaction becomes inefficient [8]. Therefore, in this research, we’re not only synthesize the rGO-CoS composites but also study about the influence of reaction time to the chemical properties of obtained materials, in this case is rGO-CoS composites.

2. Experiment

2.1 Materials and characterization

The material was used in this study is graphite (Alfa Aesar), KMnO₄ (Merck), NaNO₃ (Merck), H₂SO₄ (Merck), H₂O₂ (Merck), HCl (Merck), Co(NO₃)₂·6H₂O (Merck), thiourea (Merck), ethylenediamine (Merck), ethanol (Merck). Material characterizations were performed using X-Ray Diffraction (Rigaku Miniflex 600, Cu Kα radiation, λ=1.5406 Å, 40 kV, 15 mA, 2θ from 10-90°), Fourier Transform Infra-Red (FTIR) spectroscopy (FTIR Prestige-21 Shimadzu type 8201PC, KBr pellet wavenumber 4000-500 cm⁻¹), Scanning Electron Microscope (SEM) (FEI Inspect S50, high voltage 15 kV).

2.2 Synthesis of Graphene Oxide (GO)

Synthesis of graphene oxide was conducted using the Hummer’s method. At maintained temperature in range 0-20 °C, 2 grams of graphite are dissolved in 98 mL of H₂SO₄ and stirred. After 1 hour of stirring, 4 grams of KMnO₄ were added. The stirring process is carried out for 4 hours and the mixture turns blackish green. The stirring process was continued at 35 °C for 20 hours. Then 200 mL of distilled water were added and stirred for 1 hour. The solution is added with 20 mL 30% H₂O₂ dropwise. The mixture obtained was centrifuged and washed with 0.15 M HCl and distilled water until the pH was neutral. Then the mixture was heated for 12 hours at temperature 110 °C.

2.3 Synthesis of Reduced Graphene Oxide (RGO)

28 mg GO products from Hummer’s method was added into 40 ml deionized water and then sonicated for 60 minutes. 4 mmol thiourea was added to the solution and mixed for 60 minutes. 2 ml ethylenediamine was added to the mixture and transferred to Teflon-lined autoclave, the solvothermal process was maintained under temperature 200 °C for 24 hours. Mixture products were centrifuged and rinsed several times with ethanol and deionized water. And then the products were dried with freeze-drying for 12 hours.
2.4 Synthesis of Reduced Graphene Oxide-Cobalt Sulfide (RGO-CoS)

28 mg GO was dissolved in 40 mL of destilled water and sonicated for 60 minutes, then added 1 mmol of Co(NO$_3$)$_2$.6H$_2$O and 4 mmol thiourea was added and stirred for 60 minutes. 2 mL of ethylenediamine was added and put into the Teflon-lined autoclave for the hydrothermal process at 200 °C with a variation time of 12, 24, 36, and 48 hours. The resulting mixture was centrifuged and washed with ethanol and deionized water several times, then dried by freeze-drying for 12 hours.

3. Results and Discussion

3.1 Scanning Electron Microscope (SEM)

Figure 1. Shows the images of Co(NO$_3$)$_2$.6H$_2$O, GO, and rGO-CoS. Co(NO$_3$)$_2$.6H$_2$O and GO as starting material were compared with rGO-CoS as the product of synthesis by solvothermal reaction. The morphology of Co(NO$_3$)$_2$.6H$_2$O are small agglomerates formed the group in an irregular position. Compared to GO, it has wider and flatter surface area [9], which looks sticks to one and another. If Co(NO$_3$)$_2$.6H$_2$O has a small agglomerates, while GO has a big agglomerates, plain and relatively smooth at surface. While in the rGO-CoS morphology, it has a wide surface area but also consist of many thin layers with the surface is rougher than in GO. Cobalt precursor and thiourea were formed became CoS then grafted on to the GO surface and its vicinity during the solvothermal reaction. In this reaction also occurred the reduction reaction and exfoliation process of GO material transforming to rGO. These reaction process together leading to the rGO-CoS formation.

![Figure 1](image_url)

Figure 1. Morphology of a) Co(NO$_3$)$_2$.6H$_2$O, b) GO, and c) rGO-CoS 36.
3.2 X-Ray Diffraction

Figure 2 shows diffractograms of graphite, synthesized products of GO, rGO and rGO-CoS 36. Although graphite, GO, rGO, and rGO-CoS are carbon-based, all of them shows different diffractograms pattern, due to the difference in arrangement and atom addition. Graphite as starting material shows diffractograms that it has one sharp peak at 2θ 26.32° with orientation direction (200) and interlayer spacing 3.38 Å. GO that was synthesized by the Hummer method shows shifting of peak diffractogram to 2θ 9.56° with interplanar space 9.24 Å. The increased in interplanar space indicate that the oxygen atoms was added because of oxidation reaction and it means the GO material was successfully formed. After the reduction process, GO transforms to rGO that showed from the diffractogram in peak at 2θ 24.83° with interlayer space 3.58 Å. Interlaminar spacing reduced between GO and rGO, from 9.24 Å to 3.58 Å as shown in Table 1, meaning that the distance between layers is closer one to another and indicates the removal of some oxygen functional group during the reduction process. The shifting peak from 9.56° to 24.83° can be concluded that rGO has been successfully synthesized. The diffractogram of rGO-CoS 36 shows several peaks at 2θ 30.84, 35.47, 47.54, 54.94° which can be assigned to the plane (100); (002); (102); and (110). This peak pattern is similar to JCPDS No. 75-0605 which corresponds to CoS. The crystal parameters of materials can be seen in Table 1.

**Table 1.** Crystal parameters of Graphite, GO, and rGO.

| Sample     | 2θ   | Height (cts) | FWHM | d-spacing (Å) | Rel. Int (%) |
|------------|------|--------------|------|---------------|--------------|
| Graphite   | 26.32| 10246.26     | 0.20 | 3.38          | 100.00       |
| GO         | 9.56 | 560.77       | 0.26 | 9.24          | 81.72        |
| rGO        | 24.83| 52.86        | 0.09 | 3.58          | 100.00       |

![Diffractograms of graphite, GO, rGO, and rGO-CoS 36.](image)

Figure 2. Diffractograms of graphite, GO, rGO, and rGO-CoS 36.

Hydrothermal time reaction to synthesize rGO material is one of the important factors that affect the reduction process and material properties that produced [8]. rGO-CoS also rGO based material, which means time reaction also affects the produced rGO-CoS material properties. Figure 3 shows similarity in all diffractograms, four major peaks formed indicate that synthesized rGO-CoS was
successfully formed. All of the diffractogram patterns show low material crystallinity because of rGO in amorphous condition. There is almost no sharp peak in each variation time, but the intensity of the peak in each diffractogram is different.

![Diffractogram of rGO-CoS variation hydrothermal reaction time 12, 24, 36, and 48 hours.](image)

**Figure 3.** Diffractogram of rGO-CoS variation hydrothermal reaction time 12, 24, 36, and 48 hours.

### 3.3 Fourier Transform Infra Red (FTIR) Spectroscopy

This instrument is used to characterize the difference of a functional group of material, in this case, oxygen based functional group in GO and rGO. Figure 4 shows spectrum pattern comparison of GO, rGO, and rGO-CoS. GO spectrum pattern shows specific functional group, broad-spectrum around 3000-3672 cm\(^{-1}\) correlates to OH groups (hydroxyl), band at 1722 cm\(^{-1}\) correlates to carboxyl stretching vibration C=O (-COOH), at 1621 cm\(^{-1}\) demonstrates vibration C=C of unoxidized graphite consisting aromatic rings, and band at 1053 cm\(^{-1}\) represents to epoxy group vibration C-O (-C). After hydrothermal reaction of GO to rGO, it has a less broad hydroxyl group (OH) and other bands were reduced significantly, this indicates rGO was successfully synthesized. Spectrum rGO-CoS shows almost no band, because GO has been reduced significantly, not only by thiourea but also CoS that was grafted on the rGO, because CoS also has reduction properties.
Figure 4. FTIR spectrum of GO, rGO, and rGO-CoS 36.

Figure 5 shows spectrum of synthesized material by variation hydrothermal reaction time. It can be seen from the pattern, it seems similar but the transmittance (%) intensity of oxygen correlated functional groups are decreased as increasing reaction time. It shows in the peak that correlates to OH group, broad-spectrum around 3000-3672 cm\(^{-1}\) and peak that correlates C-O at 1053 cm\(^{-1}\). It is because of more functional group reducted along with reaction time [10]. The time reaction of rGO-CoS 36 with 36 hours hydrothermal reaction time can be considered as a threshold which the further treatment becomes inefficient because rGO-CoS 48 shows peaks with bigger intensity transmittance than rGO-CoS 36.
Figure 5. FTIR spectrum of rGO-CoS variation of reaction time 12, 24, 36, and 48 hours.

4. Conclusions
Material GO, rGO, and rGO-CoS were successfully synthesized by the hydrothermal method. It concluded from the material characterization results i.e XRD, FTIR, and SEM. XRD shows all of the synthesized material is in amorphous phase, because the GO as starting material was in amorphous condition, then CoS were grafted to GO. FTIR shows the reduction of oxygen containing functional group. Lastly, SEM shows the morphology of synthesized rGO-CoS as a combination of specific morphology from Co(NO$_3$)$_2.6$H$_2$O and GO. And the hydrothermal reaction time affect to the peak intensity peak in diffractogram and transmittances of band functional group. The results of the characterization shows rGO-CoS 36 composites with 36 hours hydrothermal reaction time is the optimum reduction time.

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