Preliminary Study of Reduced Graphene Oxide Cobalt Sulfide Synthesis

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Abstract. Graphene is a material that has amazing electrical and optical properties. This research will discuss the effect of adding Cobalt Sulfide (CoS) on the reduction of graphene oxide (RGO) by using variations in the CoS ratio to improve the electrochemical properties of RGO. Graphene oxide (GO) is reduced by adding (Co(NO₃)₂.6H₂O, thiourea (CH₄NS) and added with ethylenediamine, then all materials reacted via solvothermal process. RGO that has been successfully synthesized will be characterized to determine the structural and chemical characteristics of the synthetic material by using X-Ray Diffraction (XRD), Fourier Transform Infra-Red Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), and Spectrophotometer UV-Vis. According to the results characterizations there are many differences on the optical characteristic and morphology on each phase of GO, RGO and RGO CoS.

1. Introduction

Graphene is the basic atomic structure in carbon nanomaterial, which has a two-dimensional allotrope of carbon at sp² in the form of a planar monolayer [1]. Graphene is the strongest material ever measured, and show that atomically perfect Nano scale materials can be mechanically tested to deformations well beyond the linear regime [2]. Compared to other nanomaterial, one-atom-thick graphene sheets with a two-dimensional planar geometry can enhance electron transport for more effective devices in energy applications [3]. Graphene has a transparent level and low resistance value which is the best material that can be used on electrodes to improve photovoltaic (PV) performance. Besides being a combination of resistance and transmittance values, graphene has a high conductivity value so that graphene can be used as the best base material in electronic equipment [4].

GO was produced using the Hummers method invented by Hummers and Offeman in 1958 [5]. This process begins by reacting the stirred graphite together with the concentration of sulphuric acid, sodium nitrate and potassium permanganate at temperatures below 20° [6].
It is possible to produce a material with properties close to graphene, but it must be able to remove the oxygen group function in GO [7, 8]. RGO is a material that is similar to graphene which is synthesized in stages through GO synthesis and then the material is reduced. Electrochemical reduction is possible by changing the oxygen functional group CO and CO gas at a certain temperature. GO reduction can be achieved through chemical reduction methods via solvothermal to reducing compounds [9].

Carbon-based nanocomposite materials have high specific surface area and good electrical conductivity. Due to these properties, it is a promising electrode material for supercapacitor applications. Graphene-based metal oxide and polymer composites have been shown to be effective for enhancing the specific capacitance than their individual performance in supercapacitor because of the synergistic effect between the composite materials. RGO that have been added by precursor metal oxide (Cobalt Sulfide) can improve the catalysis process and conductivity performance [10]. The presence of CoS nanoparticles hindered the position/stack of the N-RGO layer and increases the space between the layers, which effectively improved the electrochemical performance of the catalysts [11].

This research will discuss the effect of adding Cobalt Sulphide (CoS) on the reduction of graphene oxide (RGO) and using variations in the CoS ratio to improve the electrochemical or electrical properties of RGO.

2. Experimental
2.1 Materials and characterization
The materials were used in this paper including graphene oxide (GO), Cobalt nitrate hexahydrate (Co(NO$_3$)$_2$.6H$_2$O, AR), Ethanol (Merck), distilled water, thiourea (Merck), ethylenediamine (Merck). Materials characterizations were performed using X-Ray Diffraction (Rigaku Miniflex 600, Cu Kα radiation, λ=1.5406 Å, 40 kV, 15 mA, 2θ from 5-80°), Fourier Transform Infra-Red (FTIR) spectroscopy (FTIR Prestige-21 Shimadzu type 8201PC, KBr pellet wavenumber 4000-500 cm$^{-1}$), Scanning Electron Microscope (SEM) (FEI InspectS50, high voltage 15 kV) and Spectrophotometer UV-Vis (Hitachi, 200-600 nm).

2.2 Preparation Reduction Graphene Oxide
Graphene oxide (GO) powder as much as 28 mg was dispersed into 40 mL distilled water by sonication for 60 minutes. After that, it has been stirred for 60 minutes, after finishing stirring, drop with 2 mL ethylenediamine. After that the mixed solution was transferred to an autoclave to carry out the solvothermal process at 200°C for 24 hours. Subsequently, the solution is washed with a mixture of ethanol and distilled water until the smell disappears then the RGO solution is dried in freeze drying for 12 hours to get RGO powder.

2.3 Reduction Graphene Oxide Cobalt Sulfide
Graphene Oxide (GO) powder as much as 28 mg was dispersed into 40 ml distilled water by sonication for 60 minutes. Furthermore, (Co(NO$_3$)$_2$.6H$_2$O, AR) with mass variations of 145.52 mg (0.5 mmol), 291.04 mg (1mmol) and 582.08 mg (2mmol) then mixed with thiourea with 152 mass variations, (2mmol), 304.8 mg (4mmol) and 609.6 mg (8mmol) are then stirred for 60 minutes, after finishing stirring, drop with 2 mL ethylenediamine. After that the mixed solution was transferred to the autoclave to carry out the solvothermal process at 200°C for 24 hours. Then the solution is washed with a mixture of ethanol and distilled water until the smell disappears then the RGO-CoS solution is dried in freeze drying for 12 hours to get RGO-CoS powder. Figure 1 is illustration of the all steps for preparation RGO-CoS. In this paper want to discuss three variation of RGO that using variation ratio between GO and Cobalt-Sulfide, there are RGO-CoS 1(1:5), RGO-CoS 2 (1:10), RGO-CoS 3(1:20).
3. Result and Discussion

3.1 X-ray diffraction (XRD)

The XRD patterns for synthesized CoS composite materials with different molarity ratios are shown in Figure 2. The peaks identical to GO do not appear in the RGO-CoS pattern indicating that GO has been successfully reduced. All the existing patterns show the type of material that tends to be amorphous. In materials with a composite RGO-CoS 1 and RGO-CoS 2, there is a peak that located at 2θ similar with the typical RGO peak area. As shown in figure 1, the characterization peaks observed in the range 2θ=0°-90° were identified and can be exclusively indexed to the (100), (101), (102), (110) diffraction orientation of CoS (JCPDS, No 75-0605).

All diffraction patterns show a low crystallinity of the material which may be due to the amorphous conditions of the RGO material [12]. As the mole increases its intensity is getting longer. It can be seen that the diffraction pattern in the material RGO-CoS 1 tends to be low and decreasing. Materials RGO-CoS 3 also showed the peak with the highest intensity compared to the other variations.

Figure 2. XRD all variation RGO-CoS, (a) reduction graphene oxide (RGO) (b) graphene oxide, (c) RGO-CoS 1 (d) RGO-CoS 3 (e) RGO-CoS 2
3.2 Fourier Transform Infra-Red (FTIR) spectroscopy

The Figure 3a and 3b shows FTIR spectra of GO and RGO. It is clear that there are some reduction intensity of peaks in RGO compare to spectrum of GO, this is due to the extensive oxygen containing functional group reduction. GO has strong and broad bonds in the O-H chain which vibrate in the value range of 3300cm\(^{-1}\), the carboxyl functional group (C = O) at 1710 cm\(^{-1}\) and skeletal vibration (C = C) at 1620 and vibrational epoxy (C-O) at 1050 cm\(^{-1}\). After the GO material is formed, a further process is carried out through a solvothermal method which shows a lower wide peak of –OH than the peak of GO and the intensity of all of the absorbance on each peaks decreased. This indicates the reduction in functional groups that occurred during the thermal reduction process which means to indicate the successful transformation to be RGO material [13, 14].

The graph in figure 3b shows the variations in the addition of CoS into RGO composites, in these three variations there are three important peaks, namely at 1640 cm\(^{-1}\), 1100 cm\(^{-1}\), and 3300 cm\(^{-1}\). After being identified in each spectrum in the image above, especially at the peak 1100 cm\(^{-1}\) and 1640 cm\(^{-1}\), they show the bending vibration of sulfonated groups and bending vibration of absorbed H\(_2\)O on CoS [15] satisha while the peak of 3300 cm\(^{-1}\) shows the OH hydroxyl group which is still very high in the three variations [16].

3.3 Scanning Electron Microscope (SEM)

Figure 4 shows the pictures of all material show the unevenly distributed morphology. The image of RGO tends to have morphology in the form of flat sheet and with big size. The material of synthesized RGO-CoS shows the uneven/ rough surface as if there are agglomerations of small particles (CoS) which surround the surface of RGO material.
3.4 Spectrophotometer UV-Vis

The optical absorption spectra of the GO, RGO and RGO-CoS materials are shown in Figure 5. The graphite oxide material having peak of absorption in 232 nm with energy band gap of 5.39 eV. This GO absorption value is almost the same as the GO synthesized by previous researchers which showed a peak at 230 nm [17]. However, after being reduced to RGO the peak absorption was shifted to 258 nm with energy band gap of 4.81 eV. This value is almost the same as previous researchers who showed the RGO peak at a wavelength of 263 nm [18]. While the RGO-CoS composite shows a peak at 510 nm with energy band gap of 2.43 eV in the variations of RGO-CoS 1, RGO-CoS 2, RGO-CoS 3 showing absorption peaks at the same wavelength with having value is almost same as previous research who shown the CoS peaks 511 nm with band gap energy of 2.43eV[18].

4. Conclusion
In conclusion, all of RGO-CoS in three variations ratios were successfully synthesize. The RGO-CoS was prepared using solvothermal method. The comparison results of XRD, SEM and FTIR results of these materials: GO, RGO-CoS1, RGO-CoS2 and RGO-CoS3 indicated that they were successfully synthesized. According to the result of characterizations, there is some difference among the three ratio variations. However the difference is not really significant, since it doesn’t affect the value of band gap. However each phase of GO, RGO –CoS have differences on its optical characteristic and morphology. On
the phase RGO-CoS has the lowest value of band gap and the visible surface on SEM is unevenly distributed compared with its surface on GO.

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