

## Synthesis of Zinc Selenide/Graphene Oxide Composite via Direct and Indirect Hydrothermal Method

(Sintesis Komposit Zink Selenida/Grafin Oksida melalui Kaedah Hidroterma Langsung dan tidak Langsung)

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### ABSTRACT

*Zinc selenide/graphene oxide (ZnSe/GO) composite is synthesized using hydrothermal method. Two different methods such as direct and indirect route have been investigated to form the ZnSe/GO composite. In this research, the graphene oxide used was in sheet and liquid form. The synthesized composite was then characterized using X-ray diffraction (XRD) for phase identification, field emission scanning electron microscopy (FESEM) for morphology analysis and ultraviolet-visible spectroscopy (UV-Vis) for optical properties. ZnSe/GO composite showed absorption peak ranging from 460 to 480 nm with the optical band gap obtained through Tauc equation. The optical band gap of the ZnSe/GO composite has been tuned down to a smaller value as compared to the bulk ZnSe compound. The optical band gap has been reduced to around 2.53 eV when liquid graphene oxide was used while around 2.23 to 2.32 eV when graphene oxide sheet was used. The purity of ZnSe/GO composite synthesis via indirect hydrothermal method is higher than those synthesized via direct hydrothermal method. The type of graphene oxide will affect the morphology of the composite where the ZnSe compound was either wrapped by tiny thorn-like substance or graphene oxide layer.*

*Keywords: Band gap tuning; morphology; UV-vis spectroscopy; x-ray diffraction*

### ABSTRAK

*Komposit zink selenida/grafin oksida (ZnSe/GO) telah dihasilkan menggunakan kaedah hidroterma. Dua kaedah berlainan iaitu secara langsung dan tidak langsung telah dikaji untuk menghasilkan komposit ZnSe/GO. Dalam kajian ini, grafin oksida yang digunakan adalah dalam bentuk lembaran dan cecair. Komposit yang dihasilkan ini kemudian dicirikan dengan menggunakan instrumen pembelauan sinar-X (XRD) untuk mengenal pasti fasa sampel, mikroskopi medan pancaran pengimbasan elektron (FESEM) untuk analisis morfologi dan spektroskopi ultraungul/boleh nampak (UV-Vis) untuk mengenal pasti sifat optiknya. Komposit ZnSe/GO menunjukkan puncak penyerapan dalam lingkungan 460 hingga 480 nm dengan jurang jalur optik diperolehi melalui persamaan Tauc. Jurang jalur optik ZnSe/GO komposit telah dikurangkan ke nilai yang lebih kecil berbanding dengan sebatian ZnSe. Jurang jalur optik telah dikurangkan ke 2.53 eV apabila cecair grafin oksida digunakan manakala antara 2.23 hingga 2.32 eV apabila lembaran grafin oksida digunakan. Ketulenan komposit ZnSe/GO yang dihasilkan melalui kaedah hidroterma secara tidak langsung adalah lebih tinggi berbanding dengan komposit yang dihasilkan melalui kaedah hidroterma secara langsung. Jenis grafin oksida akan memberi kesan terhadap morfologi komposit dengan sebatian ZnSe sama ada dibalut oleh bahan duri kecil atau lapisan grafin oksida.*

*Kata kunci: Morfologi; pembelauan sinar-X; penalaan jurang jalur; spektroskopi UV-Vis*

### INTRODUCTION

Zinc selenide is one type of II-VI semiconductor which is yellow in colour with bulk energy band gap of 2.7 eV. Zinc selenide existed in cubic structure at low temperature and wurzite structure at high temperature. Zinc selenide mainly used in the application of infrared devices, light emitting diode, laser diode and other optothermal devices (Bhaskar et al. 1999). Zinc selenide can be synthesis by sol-gel method, wet chemical method, spray pyrolysis and solvothermal method (Patel et al. 2014). Previous studies have showed that a blue shift with the wavelength around 355 to 455 nm when the particle size of zinc selenide

become smaller (Zhu et al. 2000). Thus, the size of particle would affect the optical properties of a material.

Nowadays, researchers are interested and incorporated intercalated, exfoliated or expanded graphite platelets into materials to synthesis nanocomposites (Syuhada et al. 2014). Graphene is made up of carbon atoms in hexagonal shape and it is in atomic layer thick because it consists of carbon atom with sp<sup>2</sup>-hybridization which arranged in two-dimensional sheet. It has been reported that graphene is unique due to its properties such as high electric conductivity (Wu et al. 2012), strong mechanical properties (Li et al. 2009) and high chemical stability

(Muller et al. 2009). Composite is a type of material which consists of two or more materials that combined. The properties of the composite will become better as compare to the single material. The properties can be strengthen in term of optical, physical, mechanical, thermal and electrical properties (Askeland et al. 2011).

In the present work, we synthesized ZnSe/GO composite via direct and indirect hydrothermal method using graphene oxide sheet and liquid graphene oxide. The optical properties of the composites were further investigated and discussed.

## EXPERIMENTAL DETAILS

### CHEMICALS

The chemicals used were zinc acetate ( $\text{Zn}(\text{CH}_3\text{COO})_2$ ) (HmbG Chemical  $\geq 99\%$ ), selenium (Se) (HmbG Chemical  $\geq 99\%$ ), ethylene diamine tetraacetic acid (EDTA) (HmbG Chemical  $\geq 99\%$ ) and sodium hydroxide (NaOH) (Fisher Scientific  $\geq 99\%$ ). Graphene oxide (GO) used were in sheet and liquid form (16 mg/mL) obtained from Low Dimensional Materials Research Centre, Universiti of Malaya.

### SAMPLE PREPARATION

There are two types of hydrothermal technique, direct and indirect, which is implemented in this study to synthesis the ZnSe/GO composite. For direct hydrothermal method, 1.32 g of zinc acetate dihydrate and 3.2 g of sodium hydroxide is dissolved in 20 mL of distilled water and stirred for 50 min, which will be solution X. Solution Y was prepared by dissolving 0.5 g of selenium powder with 3.2 g of sodium hydroxide in 20 mL of distilled water and stirred for 50 min. Solution Y is then poured into solution X where graphene oxide sheet and 1.75 g of EDTA are added into the mixture and stirred for another 15 min. The mixed solution is then transferred into a 50 mL Teflon-lined autoclave and heated for 24 h at 190°C. The resultant product is then centrifuged with ethanol and dried at 50°C for 24 h (Han et al. 2014). The sample produced was labelled as Sample A. The procedures were then repeated by replacing graphene oxide sheet with liquid graphene oxide and labelled as Sample B.

For indirect hydrothermal technique, solutions X and Y was prepared as mentioned before. Solution Y was then poured into solution X and 1.75 g of EDTA was added into the mixture and stirred for another 15 min. The mixture was then transferred into a 50 mL Teflon-lined autoclave and heated for 36 h at 180°C. The yellow powder (zinc selenide) formed was then washed with ethanol and dried at 50°C for 24 h. The zinc selenide powder formed and 6.4 g of sodium hydroxide were dissolved in 40 mL of distilled water and graphene oxide sheet was added into the mixture in stirring condition. The mixture was then transferred into 50 mL Teflon-lined autoclave and

heated for 24 h at 190°C. The resultant product was then centrifuged with ethanol and dried at 50°C for 24 h. The sample produced was labelled as Sample C. The procedures were then repeated by replacing graphene oxide sheet with liquid graphene oxide and labelled as Sample D.

## CHARACTERIZATION

PANalytical X'pert Pro PW3040 MPD X-Ray Diffractometer (XRD) using copper  $\text{CuK}\alpha$  radiation ( $\lambda=0.15406$  nm) in the range of 20° to 80° is used to characterize the structural properties of the sample formed. The sample was scanned using field emission scanning electron microscope (FESEM); Hitachi SU8000; for morphological study and the optical measurement of the samples was carried out using near infrared ultraviolet-visible spectroscopy (Shimadzu UV-3600).

## RESULTS AND DISCUSSION

### XRD ANALYSIS

Figure 1 shows the XRD spectrum for zinc selenide and zinc selenide/graphene oxide composite synthesized through hydrothermal techniques. The composite was in cubic structure and with 5 sharp and narrow peaks at 27.27°, 45.23°, 53.60°, 66.07° and 72.67°. The phases were (111), (022), (113), (004) and (133) which were similar to zinc selenide structure. The XRD spectrum showed the purity of zinc selenide/graphene oxide composite synthesized through indirect hydrothermal method was higher as compared to those synthesized via direct hydrothermal method where additional phases has been observed on the sample synthesized via direct hydrothermal method. For Sample A (refer to Table 1), peaks detected at 31.62°, 34.41° and 38.51° with the phases of (11), (004) and (01) match well with the disodium oxalate with monoclinic structure. For Sample B, the result obtained contains zinc oxide in hexagonal structure with peaks at 31.77°, 34.42° and 36.25° and the phases at (010), (002) and (011). The purity of the composite was higher via indirect hydrothermal synthesis since the pure zinc selenide was formed during the first stage before it reacts with graphene oxide in order to form the composite. Meanwhile for direct hydrothermal synthesis, since all the materials were added into the medium of reaction at one time, the chances to form zinc oxide and disodium oxalate will be higher once the heat energy was applied. At a high temperature, zinc ions tend to react with oxygen easier, where the oxygen atoms came from the atmosphere, water and precursors. The compound synthesized is comparable to the results obtained by Kumaresan et al. (2002) who synthesized zinc selenide thin films via photochemical deposition and Lokhande et al. (1998) who synthesized zinc selenide via chemical bath deposition which contain impurity.

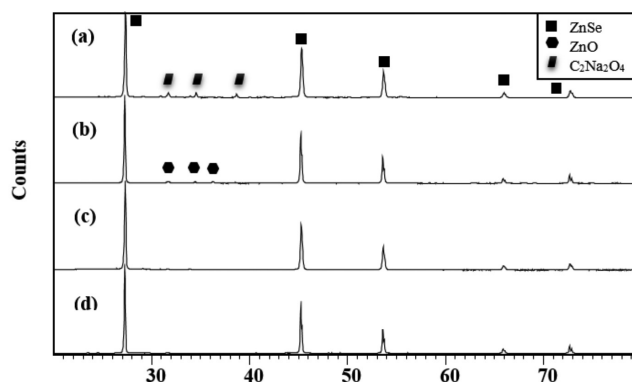


FIGURE 1. XRD spectrum of (a) Sample A, (b) Sample B, (c) Sample C and (d) Sample D

TABLE 1. Type of samples

Sample	Description
A	Direct hydrothermal method using graphene oxide sheet
B	Direct hydrothermal method using liquid graphene oxide
C	Indirect hydrothermal method using graphene oxide sheet
D	Indirect hydrothermal method using liquid graphene oxide

#### MORPHOLOGY ANALYSIS

Figure 2(a) and 2(b) shows the FESEM image of the original graphene oxide and zinc selenide, respectively. Figure 3(a) - 3(d) shows the FESEM image for ZnSe/GO composite through 4 different route in micron-size. The sample component was further confirmed by carried out energy-dispersive x-ray spectroscopy (EDX) as shown in Figure 5 where it consists of carbon, oxygen, zinc and selenide elements. Figure 4 shows the tiny rod like component synthesized via direct hydrothermal method using liquid graphene oxide (Sample B). The tiny rod like component has been proved that it was zinc oxide through EDX results as shown in Figure 6. This result has been further confirmed through XRD spectrum (Figure 1) where it showed the existence of zinc oxide phase. The FESEM images for the composite prepared using graphene oxide sheet shows the zinc selenide is wrapped by little thorn-like substance in Figure 3(a) and 3(c). When the

composite was prepared using graphene oxide in liquid form, the graphene oxide layer tends to wrap the zinc selenide like candy wrapping paper as shown in Figure 3(b) and 3(d). The homogeneity of the composite was higher for composite synthesized via indirect hydrothermal route as compared to the direct synthesis. This was due to the heat energy being absorbed by zinc ions and selenium ions to form zinc selenide and at the same time, the heat was also distributed to graphene oxide to form the composite in the direct synthesis route. Thus, the energy was not sufficient for the reaction to be completed.

#### OPTICAL PROPERTIES

Figure 7 shows the UV-VIS absorption spectrum of the prepared composites. ZnSe/GO composite shows absorption peak in between 460 and 480 nm. However, for direct hydrothermal synthesis using liquid graphene oxide (Sample B), an additional peak at 370 nm has been

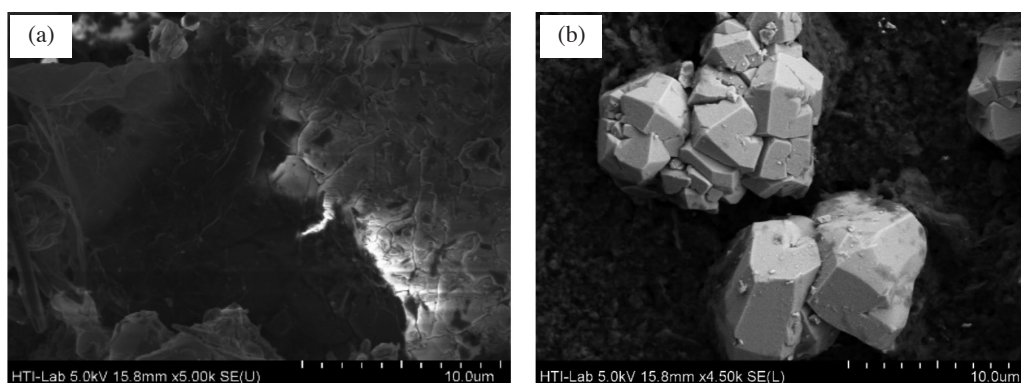


FIGURE 2. FESEM image for (a) graphene oxide and (b) zinc selenide

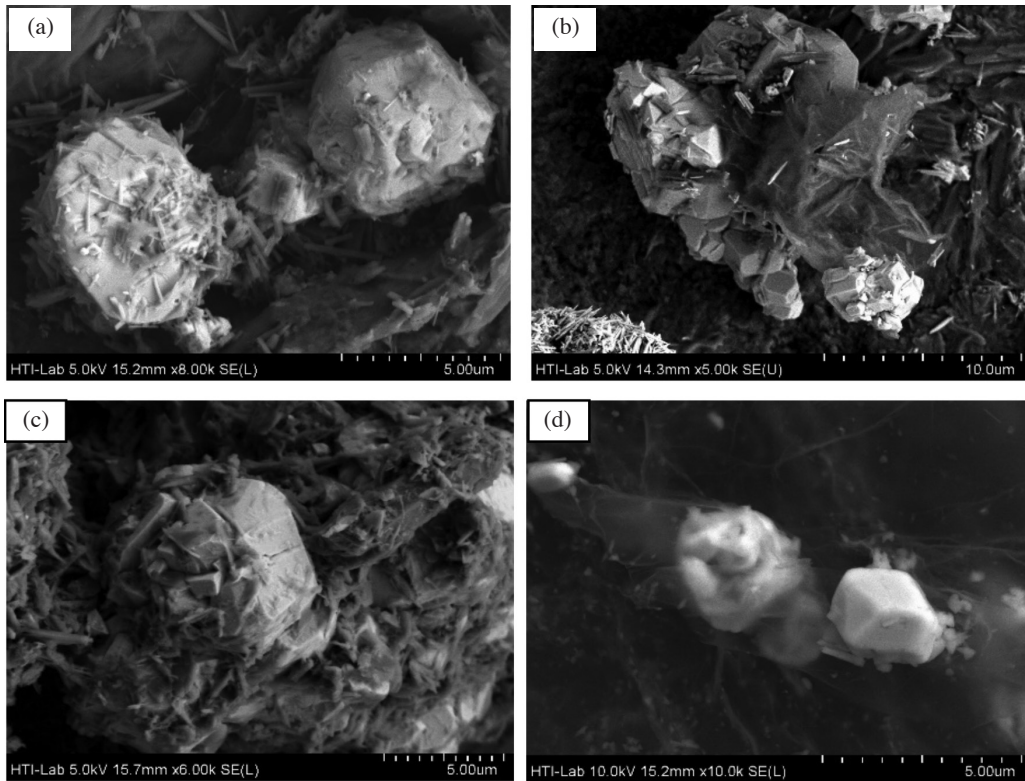


FIGURE 3. FESEM images of (a) Sample A, (b) Sample B, (c) Sample C and (d) Sample D

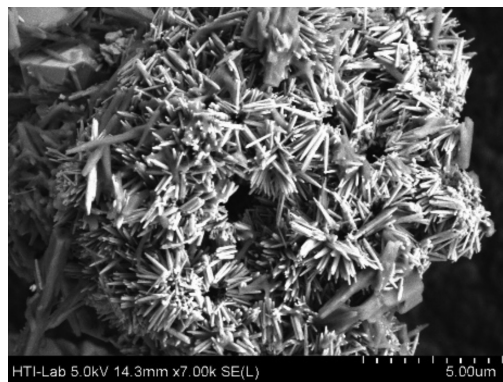


FIGURE 4. FESEM image of zinc oxide in sample B

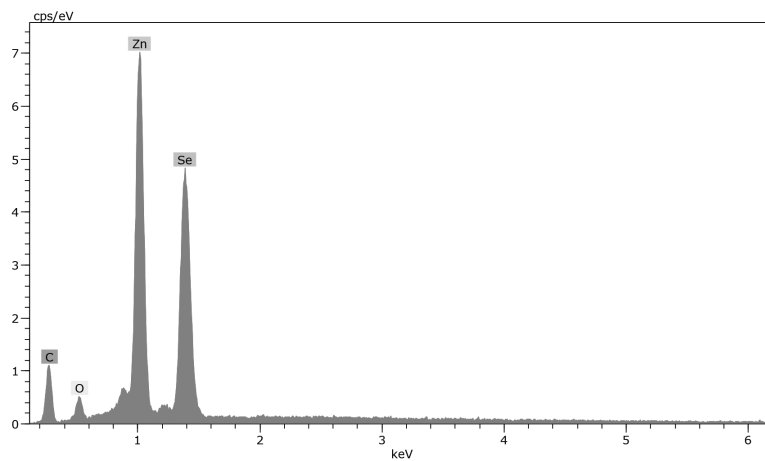


FIGURE 5. EDX spectrum of the ZnSe/GO composite

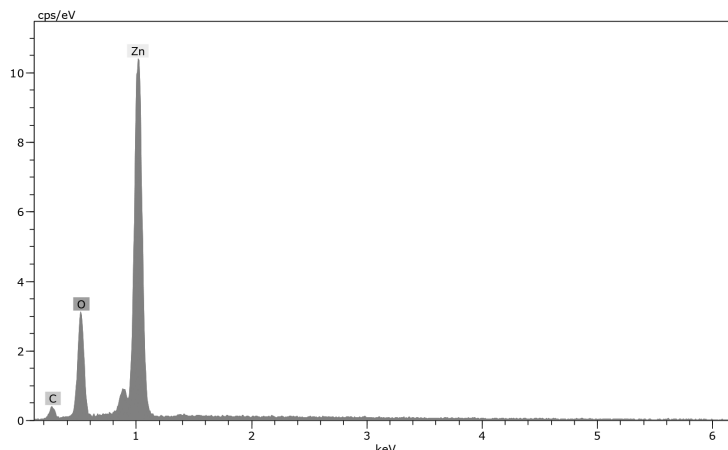


FIGURE 6. EDX spectrum for zinc oxide

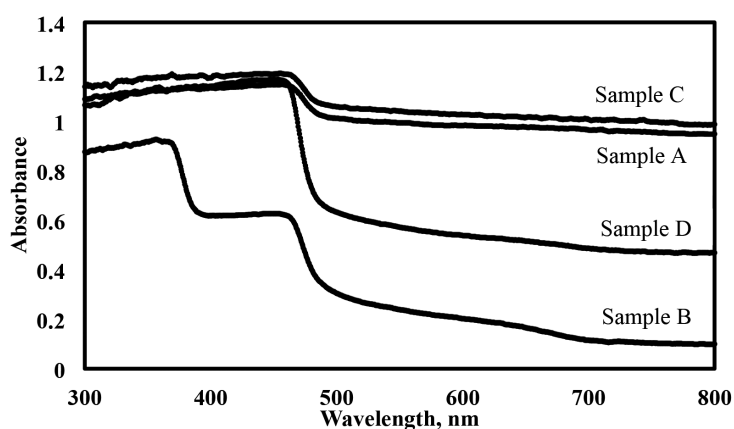


FIGURE 7. UV-Vis absorption spectrum of sample

observed. By extracting the UV-Vis data, optical band gap of the composite can be determined by Tauc equation (Liu et al. 2013):

$$\alpha hv = K (hv - E_g)^n \quad (1)$$

where  $\alpha$  is absorption coefficient;  $h\nu$  is photon energy;  $E_g$  is the band gap energy;  $K$  is a constant; and  $n$  is different possible electronic transitions where the value can be  $\frac{1}{2}$  for direct band gap and 2 for indirect band gap.

The optical band gap of zinc selenide and ZnSe/GO composites obtained is shown in Table 2. The optical band gap for the ZnSe/GO composites was in the range of 2.30 eV to 2.55 eV. There were two optical band gaps which have been observed for Sample B; 2.52 and 3.10 eV. The optical band gap at 2.52 eV belongs to ZnSe/GO composite while the optical band gap at 3.10 eV belongs to zinc oxide where bulk zinc oxide has band gap energy of 3.18 eV (Segovia et al. 2011). On the other hand, the results also showed the optical band gap of ZnSe/GO composites synthesized using liquid form of graphene oxide has higher value as compare to the composites synthesized using graphene oxide sheet.

TABLE 2. Optical band gap value for sample

Sample	Optical band gap energy (eV)
Zinc selenide	2.70
A	2.23
B	2.52 , 3.10
C	2.32
D	2.53

## CONCLUSION

Zinc selenide/graphene oxide composite has been successfully synthesized via direct and indirect hydrothermal method. The purity of the composite was higher when it was synthesized using indirect hydrothermal method. When graphene oxide sheet was used, zinc selenide tends to be wrapped by thorn-like form of substance while when liquid graphene oxide was used, graphene oxide tends to become a candy wrapping paper which wrap the zinc selenide. The band gap energy of the composites ( $\approx 2.53$  eV) was higher when liquid graphene oxide was used as compared to the composites synthesized using graphene oxide sheet ( $\approx 2.23$  eV). The overall band

gap energy of the ZnSe/GO composites were lower as compared to the band gap energy of bulk zinc selenide which means the application can operate much better at lower temperature.

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