

## Effect of Reduced Graphite Oxide as Substrate for Zinc Oxide to Hydrogen Sulfide Adsorption

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### 요 약

ZnO(산화아연)와 rGO(환원 흑연산화물, reduced graphite oxide)로 구성된 복합체를 제조하여 중저온 영역(300-500 °C)에서 H<sub>2</sub>S(황화수소) 흡착실험을 수행하였다. rGO에 붙어있는 수산화기, 에폭시기, 그리고 카르복실기와 같은 산소를 포함하는 관능기들이 H<sub>2</sub>S 흡착에 미치는 영향을 조사하기 위해서 다양한 특성분석(TGA, XRD, FT-IR, SEM, 그리고 XPS)을 실시하였다. GO(흑연산화물, graphite oxide)를 rGO로 환원시키기 위해서 마이크로파 조사법을 사용하였다. 마이크로파 조사법에 의한 환원공정에서는 온화한 환원분위기를 조성하여 rGO 표면에 상당량의 산소 관능기들이 남아있는 것을 확인하였다. 이러한 관능기들은 나노 크기의 ZnO가 2D rGO 표면에 균일하게 부착되도록 유도하여 고온 영역에서도 ZnO의 응집 및 소결이 일어나는 것을 방지하는 효과가 있다. 이로 인해 ZnO/rGO 복합체는 순수한 ZnO와 비교하여 3.5배 정도의 흡착량을 보여주었다.

**주제어** : ZnO/rGO 복합체, H<sub>2</sub>S 흡착, 환원 흑연산화물, 산화아연

**Abstract** : Zinc oxide (ZnO) and reduced graphite oxide (rGO) composites were synthesized and tested as adsorbents for the hydrogen sulfide (H<sub>2</sub>S) adsorption at mid-to-high (300 to 500 °C) temperatures. In order to investigate the critical roles of oxygen containing functional groups, such as hydroxyl, epoxy and carboxyl groups, attached on rGO surface for the H<sub>2</sub>S adsorption, various characterization methods (TGA, XRD, FT-IR, SEM and XPS) were conducted. For the reduction process for graphite oxide (GO) to rGO, a microwave irradiation method was used, and it provided a mild reduction environment which can remain substantial amount of oxygen functional groups on rGO surface. Those functional groups were anchoring and holding nano-sized ZnO onto the 2D rGO surface; and it prevented the aggregation effect on the ZnO particles even at high temperature ranges. Therefore, the H<sub>2</sub>S adsorption capacity had been increased about 3.5 times than the pure ZnO.

**Keywords** : ZnO/rGO composite, H<sub>2</sub>S adsorption, Reduced graphite oxide, Zinc oxide

### 1. Introduction

Hydrogen sulfide (H<sub>2</sub>S) is the most common sulfur component found in natural gas. It is an undesirable component in most industrial applications and is deleterious to the environment. H<sub>2</sub>S is known to be a major contributor to acid rain when oxidized in the atmosphere to SO<sub>2</sub>. In industrial processes, sulfur impurities rapidly deactivate or poison catalysts, which are widely used in the chemical or petrochemical industries[1]. Therefore,

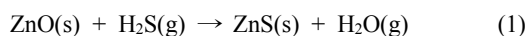
the removal of toxic gases (SO<sub>2</sub>, H<sub>2</sub>S etc.) has become a critical issue. Since the 19<sup>th</sup> century, various approaches to remove H<sub>2</sub>S, such as sorption, catalysis or condensation, have been applied[2]. Among those approaches, different adsorbents, such as activated carbon, zeolites[3,4], modified alumina[5] or metal oxides[6,7], have been investigated for H<sub>2</sub>S removal process. Historically, the high temperature range (500-800 °C) H<sub>2</sub>S sorbents were extensively developed for hot-gas desulfurization (HGD)[2]. Zinc oxide (ZnO) is considered as a very effective sorbent for removal of H<sub>2</sub>S from hot gas streams, from a thermodynamic point of view, with the formation of zinc sulfide (ZnS)[8] (see Eq. (1)). An important drawback when using ZnO for hot-gas H<sub>2</sub>S removal

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process is its thermal instability to volatile metallic zinc[9]. However, for lower temperature applications, thermal stability is no longer an issue and ZnO can be converted to ZnS at ambient condition[10].



Graphene (2 dimensional, mono-atomic thick  $sp^2$ -carbon structure) has recently received increasing attention as a material of interest due to its high electronic conductivity, large surface area and high mechanical strength[11,12]. Because of those benefits, most of graphene-based material studies focused on the electrochemistry field, such as battery[13,14] or super-capacitors[12,15]. More recently, graphite oxide (GO) with metal oxide composites have been extensively studied as adsorbents[16-18]. Graphite oxide-based or graphene-based materials are known to be useful for water purification, toxic gas removal and ammonia adsorption applications[19-21]. Graphite oxide which possesses oxygen functional groups attached on both sides of the surface received attention due to its ability to modify the physical properties and surface chemistry to enhance the interactions with target molecules[22]. The presence of oxygen groups on the surface of GO makes (or anchors) bonds with active metal oxides. Therefore, those oxygen functional groups are able to modify the availability of active sites on the surface of adsorbents depending on the dispersion of those active metal oxides and their chemical heterogeneity with GO[17]. When considering metal oxides for gas-solid adsorption, one of the major issues is to avoid aggregation of nano-sized particles with temperature. Indeed, particle aggregation leads to losses in active surface area, with consequences of lower utilization efficiency of the adsorbent. Based on the above, the objective of the present study is to evaluate zinc oxide with reduced graphite oxide (rGO) composites as adsorbents of  $\text{H}_2\text{S}$  at mid-high temperature. The morphology and surface chemistry changes from those composites are expected to affect the  $\text{H}_2\text{S}$  removal efficiency.

## 2. Experimental

### 2.1. Synthesis of graphite oxide

A modified graphite oxide (GO) synthesis procedure based on our previous work[23], was used in this study. Graphite oxide was synthesized using a mixture of 360 mL of sulfuric acid (Sigma-Aldrich, ACS reagent, 95.0-98.0%) and 40 mL of phosphoric acid (Sigma-Aldrich, ACS reagent,  $\geq 85$  wt% in  $\text{H}_2\text{O}$ ), and 3.0 g of graphite powder (Sigma-Aldrich,  $< 45 \mu\text{m}$ ,  $\geq 99.99\%$ ). This mixture was placed in an ice bath and when the temperature reached below  $5^\circ\text{C}$ , 18.0 g of  $\text{KMnO}_4$  (Samchun Chemical, 99.3%) was added drop-wise. The mixture was stirred for 1 h and

then transferred to a heating mantle to provide isothermal conditions at  $50^\circ\text{C}$ . The oxidation process was conducted for 18 h. The system was then cooled to room temperature naturally, and then placed in an ice bath again. 400 mL of de-ionized water and 15 mL of 30%  $\text{H}_2\text{O}_2$  (OCI Company Ltd, 30 wt% in  $\text{H}_2\text{O}$ ) were added gradually. The mixture turned bright yellow and generated copious bubbles. The mixture was stirred for 1 h and then centrifuged at 3,500 rpm for 3 min. The remaining solid paste was washed with a mixture of 100 mL of de-ionized water and 100 mL of 30%  $\text{HCl}$  (Sigma-Aldrich, ACS reagent, 37%) twice. The product was then rinsed twice again with 200 mL of de-ionized water. After the washing steps, the paste was freeze- and vacuum-dried overnight.

### 2.2. Synthesis of nano-zinc oxide (ZnO)/reduced graphite oxide (rGO) composite

400 mg of GO was dissolved in 200 mL of ethylene glycol (Sigma-Aldrich, Reagent Plus<sup>®</sup>,  $\geq 99\%$ ) and then underwent ultra-sonication for 30 min. 100 mL of 0.1 M aqueous  $\text{NaOH}$  (Sigma-Aldrich, ACS reagent,  $\geq 97.0\%$ ) solution was added, and the mixture was sonicated for an additional 30 min. Then, 100 mL of 0.07 M aqueous zinc acetate (Sigma-Aldrich, ACS reagent,  $\geq 98\%$ ) solution was added into the mixture drop-wise (2.0 mL/min) for 50 min. 300  $\mu\text{L}$  of hydrazine solution (Sigma-Aldrich, 35 wt% in  $\text{H}_2\text{O}$ ) was added before the reduction process. The zinc acetate/GO (ZnAc/GO) mixture was reduced by microwave irradiation for 3 min (1 min irradiation with 1 min break, 3 times). This reduction process produces ZnO/rGO composite. After cooling down, the ZnO/rGO mixture was filtered and washed with de-ionized water three times until the pH reached around 7.0. Finally, the paste was freeze- and vacuum-dried overnight. For reference, ZnO itself powder was also prepared.

### 2.3. $\text{H}_2\text{S}$ adsorption breakthrough tests

Dynamic breakthrough tests were conducted at moderate temperature ( $300^\circ\text{C}$ ).  $0.5 \text{ cm}^3$  of the adsorbents diluted with  $1.0 \text{ cm}^3$  of  $\text{Al}_2\text{O}_3$  (Sigma-Aldrich,  $\sim 150$  mesh) for a total of  $1.5 \text{ cm}^3$  of bed were packed into a quartz tube (internal diameter 10 mm). The mass of the adsorbents were measured around 0.158 g for ZnO/rGO and 0.355 g for ZnO. In a typical test, a flow of  $\text{H}_2\text{S}$  (10.7 mL/min, 3.01 vol% of  $\text{H}_2\text{S}$  balanced with  $\text{N}_2$ ) was mixed with 186.3 mL/min of  $\text{N}_2$  gas before passing through the adsorbent bed. The initial  $\text{H}_2\text{S}$  concentration was 1,638 ppm with a total flow rate of 197.0 mL/min. The product stream was further diluted with 1800.0 mL of  $\text{N}_2$  before injection to the  $\text{H}_2\text{S}$  analyzer due to the limitation of the  $\text{H}_2\text{S}$  analyzer (Fluorescence  $\text{H}_2\text{S}$  Analyzer, Model 101E, Teledyne). The experiments were carried out until the output  $\text{H}_2\text{S}$  concentration reached  $\sim 10$  ppm. The effects of  $\text{CO}_2$  and  $\text{H}_2$  on the  $\text{H}_2\text{S}$  adsorption capacity of the

sorbents were examined. 2.8 vol% of CO<sub>2</sub> or H<sub>2</sub> gases (5.0 mL/min) were mixed with the H<sub>2</sub>S/N<sub>2</sub> stream (total flow rate of 197.0 mL/min) and passed through the adsorbent bed. In order to quantify the reactivity of ZnO with H<sub>2</sub>S, sorbent utilizations were calculated as follows:

$$\text{Sorbent utilization (\%)} = \frac{t}{t^*} \times 100 \quad (2)$$

where  $t$  is the experimental breakthrough time (min/g of ZnO), and  $t^*$  is the theoretical breakthrough time (min/g of ZnO), which can be obtained from Eq. (3).

$$t^* \left( \frac{\text{min}}{\text{g ZnO}} \right) = \frac{1 \text{ mol H}_2\text{S}}{1 \text{ mol ZnO}} \times \frac{1 \text{ mol ZnO}}{81.4 \text{ g ZnO}} \times \frac{22,400 \text{ ml H}_2\text{S}}{1 \text{ mol H}_2\text{S}} \times \frac{1}{V_{\text{H}_2\text{S}} (\text{ml/min})} \quad (3)$$

where  $V_{\text{H}_2\text{S}}$  is 0.32 mL/min here. From Eq. (3), the theoretical breakthrough time ( $t^*$ ) is calculated as 890 min/g ZnO. The experimental breakthrough time is determined when the outlet H<sub>2</sub>S concentration reaches 1ppm.

### 2.3. Characterizations

X-ray diffraction (XRD, Rigaku, 40 kV/100 mA of X-Ray, step size: 0.02°) was used for adsorbent characterization; 5-60° of  $2\theta$  range was measured. Scanning electron microscopy (FE-SEM) images were obtained using a Hitachi S-4700 with an accelerating voltage of 5.0 kV. Thermo-gravity analysis (TGA, TA Instruments, TGA-2050) was used with an air flow of 50 mL/min. Fourier-transform infrared (FT-IR) spectroscopy was carried out using a Nicolet 6,700 (Thermo Scientific) with KBr dilution at 1 : 300 weight ratio. X-ray photoelectron spectroscopy (XPS, AXIS Ultra DLD, KRATOS Inc.) was used with Mono chromatic Al K $\alpha$  (1486.6 eV) for X-ray source, 0.05 eV/step; and no surface treatment were used.

## 3. Results and Discussions

### 3.1. Characterizations of adsorbents

Graphite oxide (GO) is the product of the oxidation of graphite powder. It has been widely known that the  $2\theta$  characteristic peak of the GO is in range of 9-10°[24]. For ZnO/rGO composite in this study, the  $2\theta$  was located at 9.7° which is corresponding to the interlayer spacing of 9.2 Å (Figure 1). It confirms that the interlayer spacing had been increased since it is widely reported that the typical interlayer spacing for graphite is 3.4 Å [25,26]. From previous studies proposed that various hydrophilic oxygenated functional groups such as hydroxyl, carboxyl and epoxy are located between the graphene layers[27,13]. The characteristic

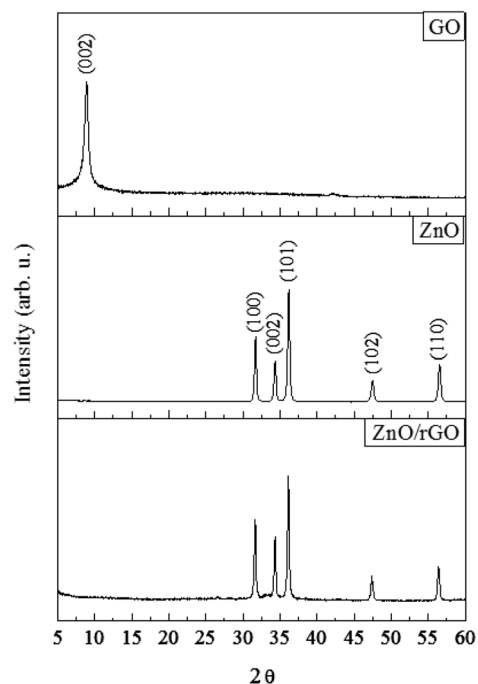


Figure 1. XRD for graphite oxide, zinc oxide and Zinc oxide/rGO.

peaks for zinc oxide (ZnO) were shown at 31.6, 34.4, 36.1, 47.7 and 56.4° and those values are matched with JPCDS 36-1451. For this study, the ZnO/rGO had been prepared. After the microwave-assisted irradiation, the characteristic peak of GO had been collapsed; but ZnO peaks were remained. It implies that the oxygen containing functions groups were removed and graphene layers were detached each other, and turned to 2D layer substrate.

In order to examine the quantity of H<sub>2</sub>S adsorbed on ZnO, thermogravimetric analyzer (TGA) test was conducted (Figure 2). Two main phase changes were observed at 268.9 and 355.6 °C. It could expect that at 268.9 °C, the oxygen functional groups were destroyed; at 355.6 °C, all remained carbon elements were

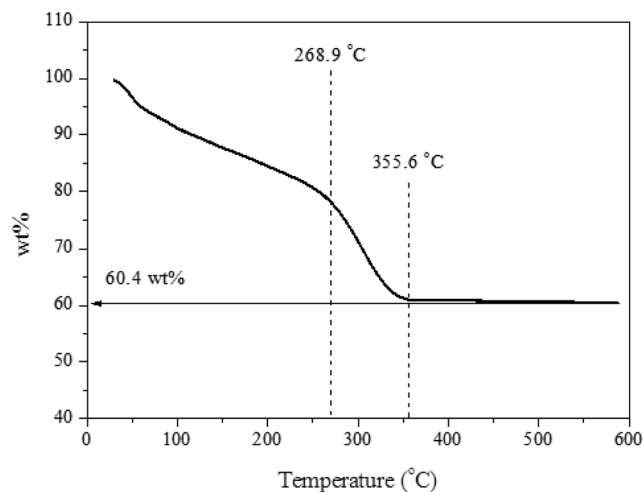
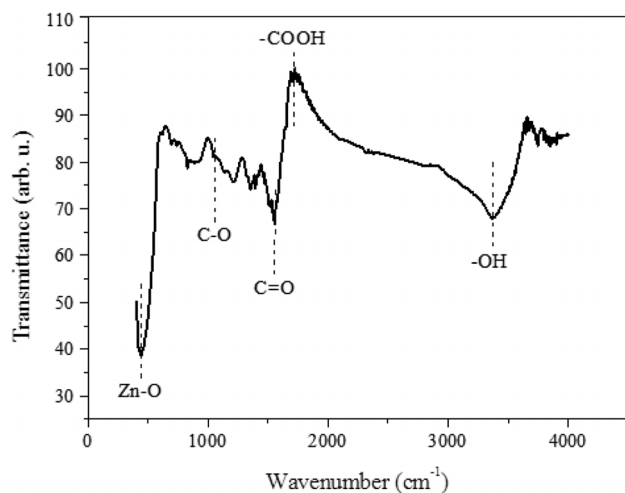


Figure 2. TGA analysis for ZnO/rGO composite.

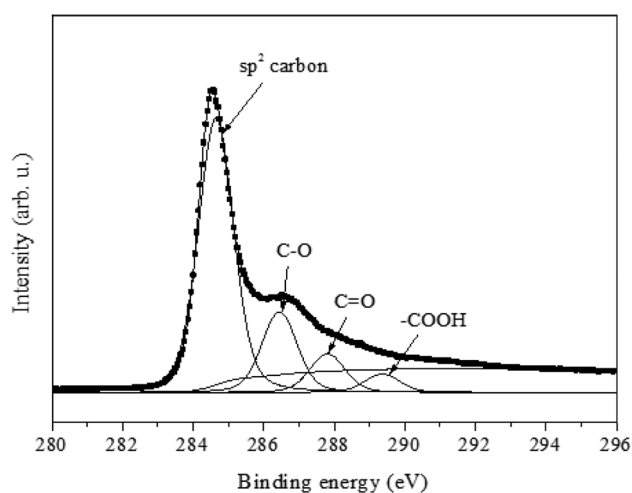


**Figure 3.** FT-IR analysis for ZnO/rGO composite.

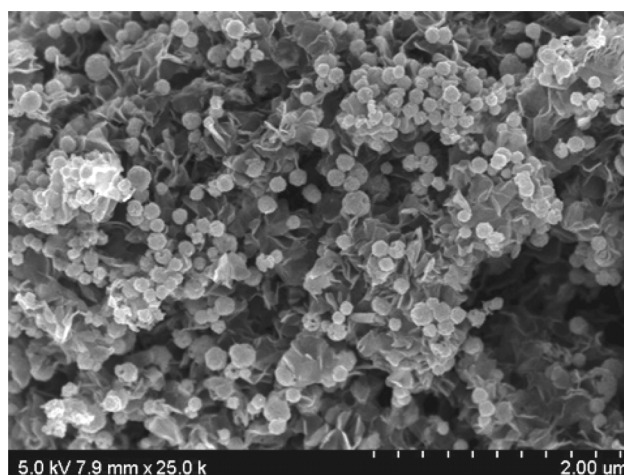
combusted. Then only ZnO had been remained; and no further weight decrease had been observed. It was estimated that 60.4 wt% was associated with ZnO. It could be concluded that the ZnO/rGO composite possesses 60.4 wt% of ZnO and rest of them should be considered as rGO component.

As mentioned above, the 3D GO had been converted to 2D rGO plane by the microwave irradiation while ZnO particles were loaded onto the rGO surface. From FT-IR (Figure 3), it was found that the oxygen functional groups were still remained on the rGO surface. From previous studies, those oxygen functional groups are acting as anchor sites to hold metal ions and promote the metal oxide dispersion[26]. A strong and broad absorption peak is located at  $3,373\text{ cm}^{-1}$  which was assigned to the stretching vibrations of O-H. It implies that the rGO surface contains abundant O-H bonds; and those hydroxyl groups could act as anchor sites to hold ZnO particles. In addition, absorbance peaks at  $1,720\text{ cm}^{-1}$  for carboxyl,  $1,569\text{ cm}^{-1}$  for carbonyl and  $1,052\text{ cm}^{-1}$  for epoxy.

From FT-IR, the oxygen functional groups are identified. In order to get quantitative information, C1s XPS analysis (Figure 4) was conducted. Specifically, the binding energies of 286.5, 287.8 and 289.4 eV could be identified as epoxy (C-O), carbonyl (C=O) and carboxyl (-COOH), respectively; and 284.6 eV represents carbon-carbon  $sp^2$  configuration (Figure 4). By comparing the area ratio of the spectra (carbon-carbon/carbon-oxygen), the quantitative information of oxygen functional groups could be achieved. From previous study[23], the degree of oxygen portion for graphite oxide was 2.69 and 0.15 for graphene. For ZnO/rGO composite, the carbon to oxygen ratio was calculated as 0.39. It indicates that the amount of oxygen in the ZnO/rGO composite is less than GO but larger than graphene. It suggests that the microwave reduction method decreases the oxygen content from GO, but rGO surface contains oxygen functional groups even after the reduction process.



**Figure 4.** C1s XPS analysis for ZnO/rGO composite.



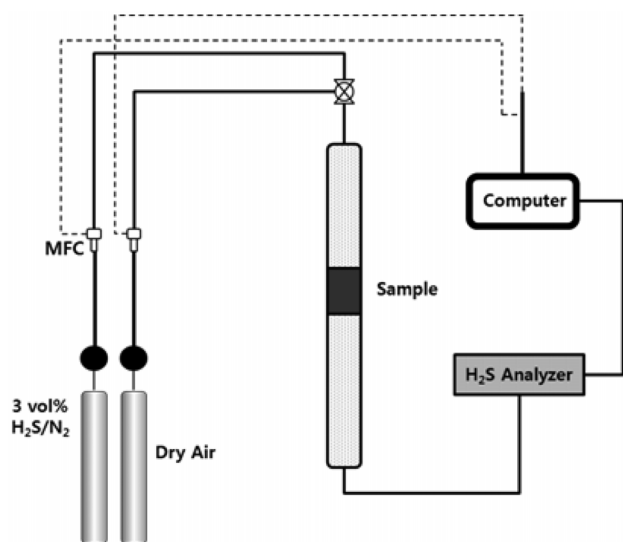
**Figure 5.** SEM image of ZnO/rGO composite.

The direct support for the formation of nano-sized ZnO deposited onto the rGO surface could be achieved from SEM analysis (Figure 5). The average ZnO particle size was calculated as around 150 nm. The shape of ZnO was hexagonal; and it could be supported from the XRD characteristic peaks. The 2D rGO planes help dispersing ZnO particles which could increase the active surface area of ZnO. In addition, the ZnO particles were dispersed between the rGO planes since the metal salt ( $Zn^{2+}$ ) ions were well allocated between the rGO surfaces during the synthesis process[27].

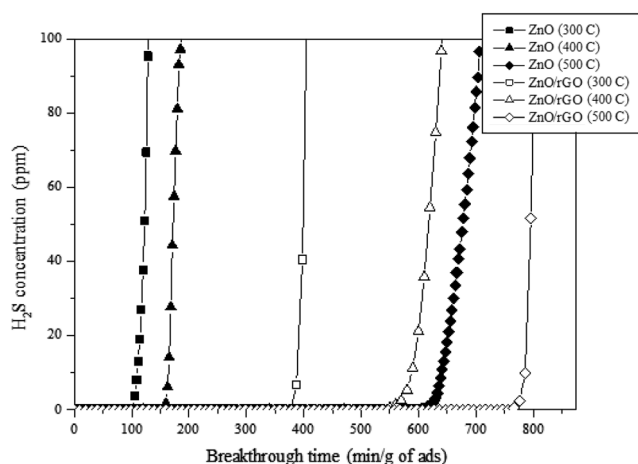
As discussed above, the microwave irradiation process provides a mild reduction environment to GO since oxygen functional groups are still remained on the rGO surface. This was confirmed from the FT-IR and XPS analysis. Due to the oxygen functional groups, the metal salt ions (i.e.  $Zn^{2+}$ ) were anchored with the hydroxyl groups on rGO surface. Then it promotes the dispersion of the metal oxide (i.e. ZnO) through the rGO substrate. Those phenomena lead to increase the active ZnO surface for  $H_2S$  adsorption.

### 3.2. H<sub>2</sub>S adsorption breakthrough tests

The schematic diagram of the H<sub>2</sub>S adsorption test is presented in Figure 6. 3.01 vol% of H<sub>2</sub>S (balanced with N<sub>2</sub>) was flowed through the adsorption bed. The reaction temperature was set to 300-500 °C. From our previous study (data now shown), the graphene-based materials (i.e. GO, rGO and graphene) did not adsorb any H<sub>2</sub>S molecules due to the lack of active sites. Therefore, the H<sub>2</sub>S adsorption capacity shown in Figure 7 indicates that the adsorption capacity comes from ZnO. The average particle sizes of pure ZnO and ZnO in the ZnO/rGO composite were measured as 110 and 95 nm, respectively. Due to the thermodynamic energy, the H<sub>2</sub>S adsorption capacity for ZnO increased as the reaction temperature increased. At 300 °C, the pure ZnO particle showed 105.4 min breakthrough time; at 400 °C, 156.7 min and at 500 °C, 598.3 min (per gram of adsorbent). However,



**Figure 6.** The schematic diagram of H<sub>2</sub>S adsorption experimental setup.



**Figure 7.** H<sub>2</sub>S adsorption breakthrough curves for pure ZnO and ZnO/rGO composite at different temperatures.

when the nano-sized ZnO particles were dispersed on the 2D rGO surface, the H<sub>2</sub>S adsorption capacities at various temperatures had been increased dramatically (i.e. at 300 °C, 387.4 min, at 400 °C, 549.9 min and at 500 °C, 766.1 min/gram of adsorbent). It can be noticed that the ZnO/rGO composite showed the benefits at lower temperature since the ZnO/rGO composite showed about 3.7 times higher adsorption capacity than pure ZnO at 300 °C. At higher temperature (400 °C), the ZnO/rGO composite also showed about 3.5 times higher performance than that of pure ZnO. It indicates that even at low temperatures (i.e. 300 to 400 °C) the well dispersed active ZnO particles exhibit the maximum ZnO utilization efficiency. From previous study, it was confirmed that the rGO substrate prevents the aggregation effect of the nano-sized ZnO at 300 °C[26]. Those benefits preventing the aggregation of ZnO by using 2D rGO surface provide higher active surface area for H<sub>2</sub>S molecules which leads the higher H<sub>2</sub>S adsorption capacity. However, when high thermo energy had been provided (i.e. 500 °C) to ZnO, the H<sub>2</sub>S breakthrough time had been jumped to 598.3 min per gram of adsorbent. The breakthrough time for the ZnO/rGO composite was 766.1 min/gram of adsorbent (about 1.3 times higher than that of pure ZnO). Those phenomena represent that the nano-sized ZnO particles deposited onto the rGO surface showed the benefits at relatively lower temperatures (i.e. 300 to 400 °C) than higher temperature (500 °C).

## 4. Conclusion

It has been studied that the 2D reduced graphite oxide (rGO) substrate plays a critical role in order to disperse the nano-sized (avg. of 95 nm) zinc oxide (ZnO) at mid to high temperature ranges (300 to 500 °C). Due to the oxygen containing functional groups, such as hydroxyl, epoxy and carboxyl groups, the metal ions are able to be anchored onto the rGO substrate; and confirmed by SEM. From FTIR and XPS, those oxygen functional groups attached on rGO surface were identified and quantified. For H<sub>2</sub>S adsorption, even at the mid temperature (300 and 400 °C) the ZnO/rGO composite showed about 3.5 times larger H<sub>2</sub>S adsorption capacity. It confirms the roles of oxygen functional groups holding metal oxide particles and it prevents the aggregation effect on the nano-sized ZnO particles. Therefore, the ZnO/rGO composite provides higher active surface area to the H<sub>2</sub>S molecules than pure ZnO.

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