

## SYNTHESIS OF GRAPHENE ON ZnO SUBSTRATE BY CHEMICAL VAPOR DEPOSITION

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**Abstract:** Graphene was synthesized by chemical vapor deposition (CVD) method on the ZnO catalyst substrate thin plate form at 550°C in the time periods of 5 min; 10 min and 30 min. ZnO substrates were fabricated by hydrothermal method at 125°C in 10 hours. Material structures are characterized by XRD, TEM, SEM and TGA. The obtained ZnO substrate was a thin plate form and uniform. Graphene was grown on ZnO substrate with thicknesses in the range 7-10 nm, number of layers 10-15.

**Keywords:** Nanocomposite, CVD method, Graphene, Absorbance wavelength.

### 1. INTRODUCTION

Graphene is known as a single layer structure  $sp^2$  – bonded carbon atoms arranged in a two dimensional lattice, with outstanding physical and chemical properties. It has great surface area, good thermal conductivity, and high transparent and electron mobility [1]. In recently, graphene has attracted many scientists because of various applications such as transistors, nano-electronic devices and sensors [2, 3]. Additionally, in graphene-based nanocomposites, hybrid of metal oxide ( $MnO_2$ ,  $TiO_2$ ,  $ZnO$ ,...) and graphene are widely investigated, but ZnO combined graphene is the most popular. They have various application in different fields.

Chen *et al.* successfully synthesized of graphene-zinc oxide nano-walls composite by one-step co-electrodeposition, graphene oxide was electrochemically reduced and zinc oxide was electrodeposited simultaneously. The obtained products presented superior electrochemical activity [4]. Zhang *et al.* also prepared composite of graphene – zinc oxide through a spontaneous reduction of graphene oxide via zinc slice in one-spot approach at room temperature, and used to modify glassy carbon electrode for developing of electrode sensor, used to detect ascorbic acid, dopamine and uric acid [5]. Pahari *et al.* studied ZnO coating amorphous graphene with vary thickness, graphene affects the optical and hydrophobic properties of zinc oxide. It is seen that with increase coating optical gap has been decrease [6]. Park *et al.* synthesized ZnO/G from ZnO nanorod and graphene thin layer has high electrical conduction and good optical properties [7]. Fan *et al.* prepared ZnO/G by hydrothermal method, powder GO was added into solution contain ZnO sol. Under UV radiation, composite presented higher effective ability than usual [8].

In this work, we investigated the synthesis process of graphene/ZnO nano-composite by CVD method. This is an effective method for preparing high quality graphene film, large surface area and suitable to industrial scaling at low cost [9]. Owing to method's advantages and exceptional application of ZnO and graphene nano-composite, this work opened new approaches in graphene as well as zinc nano-materials.

### 2. EXPERIMENT

#### 2.1. Chemicals

Chemicals were used in this work such as: Zinc sulfate heptahydrated solid  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ , sodium hydroxide solid NaOH, cyclohexane, and nitrogen.

## 2.2. Synthesis of ZnO substrate

The starting material used was  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  solid available (28.7g). It was dissolved in a 400mL- beaker by deionized water then heat to  $70^\circ\text{C}$  and stir constantly on magnetic stirring machine. Then, gradually add 52ml 0.4M NaOH solution to beaker and remain temperature in 2 hours. After that, place it to deposit and remove water, the remained mixture was transfer to 2 tubes to centrifugate 3 or 4 times. The white solid was obtained having pH medium. The  $\text{Zn}(\text{OH})_2$  were transferred into a Teflon-lined stainless steel autoclave of 60 ml capacity and sealed. The autoclave was maintained at  $125^\circ\text{C}$  for 10h. After cooling down to room temperature naturally, the white product was collected. The product was centrifuged, filtered out and washed with de-ionized water and alcohol for several times, and then dried at  $60^\circ\text{C}$  in air. Finally,  $\text{Zn}(\text{OH})_2$  was dehydrated at  $550^\circ\text{C}$  in 2 hour to transform ZnO.

## 2.3. Synthesis of graphene on ZnO

The CVD system was presented as below

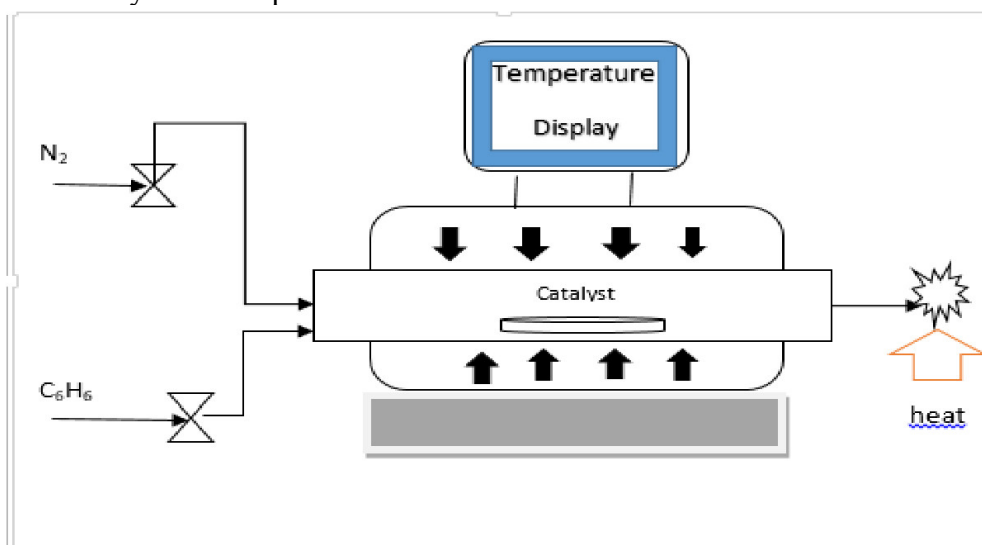


Figure 1. CVD system.

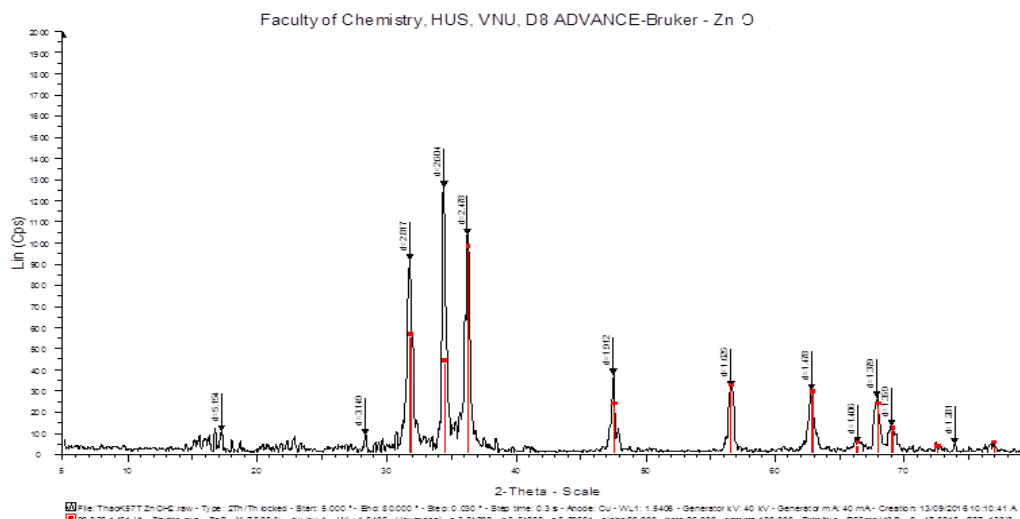
Catalyst ZnO was placed on the silica boat. It was loaded on a substrate holder of CVD system. Then, cyclohexane and  $\text{N}_2$  gases were dried and adjusted (velocity and flow rate) to get the desired graphene before they came into the system. Set up temperature at  $600^\circ\text{C}$  and take reaction in 5, 10, 30 minutes. The excess gases were burned to avoid polluting. After that, cooling the product to room temperature.

## 2.4. Characterization of materials

The morphologies and the microstructure of the synthetic products were analyzed using transmission electron microscope (TEM) technique (Tecnai G2 20 S-TWIN/FEI), Scanning electron microscopy (SEM). X-ray diffraction was used to investigate crystalline structure of ZnO. The thermal analysis method (TGA) indicated the ratio G:ZnO in the sample. The optical absorption properties were investigated using a UV-vis diffuse reflectance spectrophotometer.

### 3. RESULTS AND DISCUSSION

The typical XRD patterns of the ZnO are shown in *Fig. 2* and table 1.



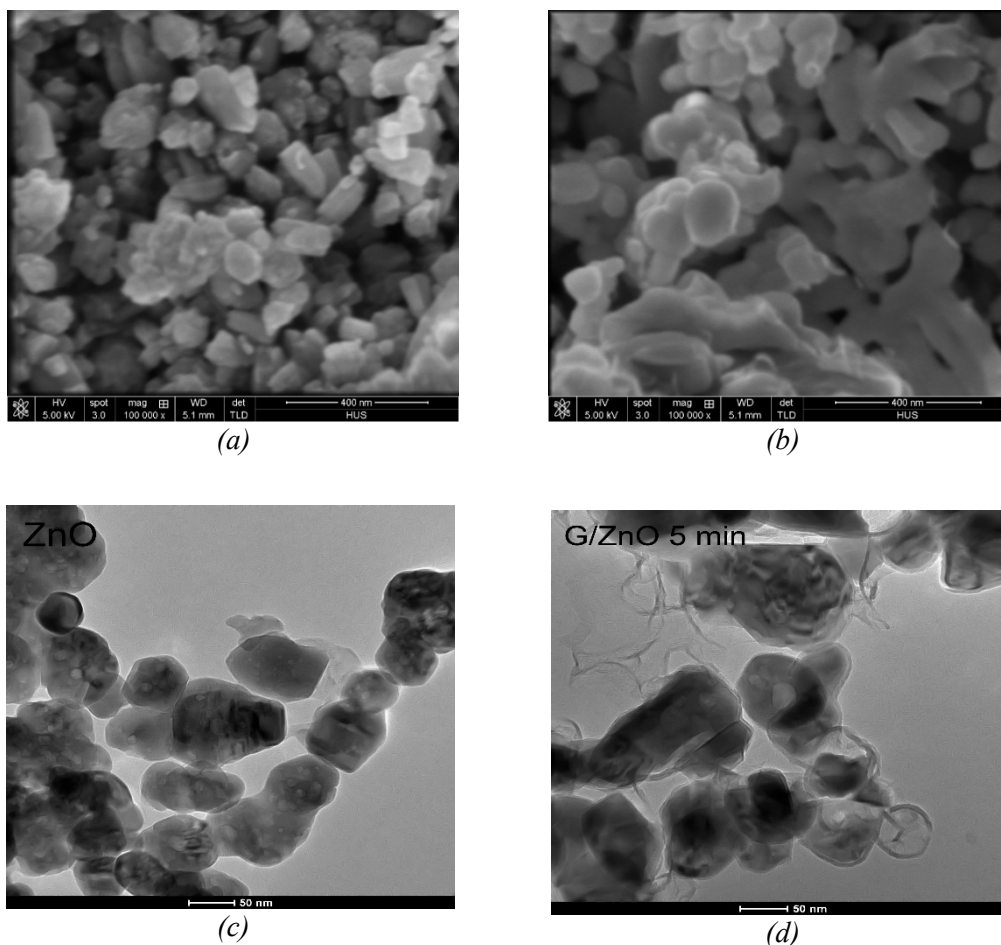
*Figure 2.* XRD pattern of ZnO.

*Table 1.* The peaks  $2\theta$  and crystalline plans of ZnO.

Peaks $2\theta$	31.7	34.4	36.2	47.5	56.6	62.9	66.3	67.9	69.2	77.0
Crystalline planes	(1 0 0)	(0 0 2)	(1 0 1)	(1 0 2)	(1 1 0)	(1 0 3)	(2 0 0)	(1 1 2)	(2 0 1)	(2 0 2)

It shows that there are ten main peaks at  $2\theta$  which correspond to the crystalline planes of ZnO, respectively, with an average size of 35 nm according to Scherer's formula.

*Fig.3a and 3b* show SEM of ZnO and G/ZnO 5min. It has seen that ZnO particles quite distributed equally. By comparing figure a and b, clearly that graphene was grown on the surface of zinc oxide. The formation is uniform and smooth.

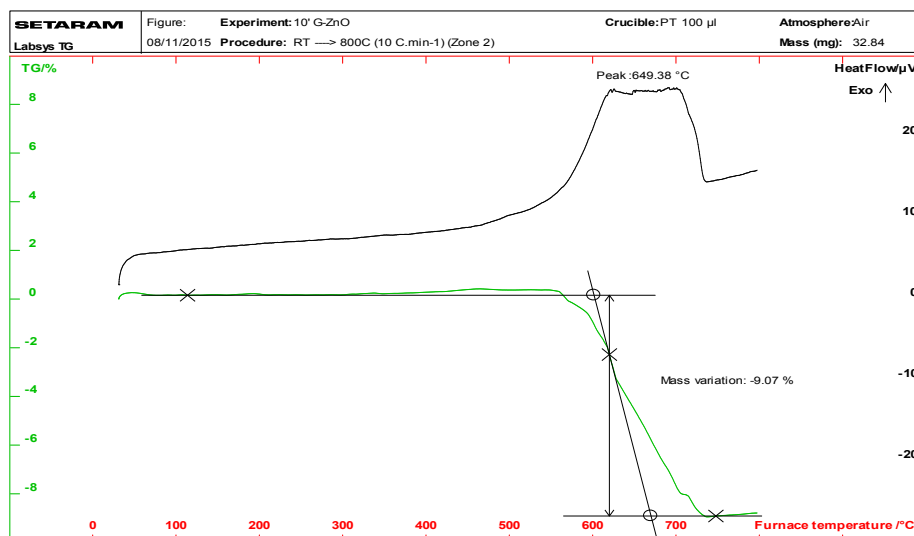


**Figure 3.** Representative SEM images of ZnO (a) substrates and G/ZnO 5 min (b); TEM images of ZnO (c) and G/ZnO 5min (d).

TEM images (Fig. 3c and d) show clearly that graphene were grown on ZnO substrate, but the formation is not uniform on all ZnO particles. Graphene also has sheet plate forms with 7-10 nm in thickness, and 10 -15 layers. The ratio of carbon in materials increase with more time interval of ZnO in CVD system (Table 2). This ratio was determined by Thermal gravity analysis method. The mass loss around 600°C is the percentage of carbon in material.

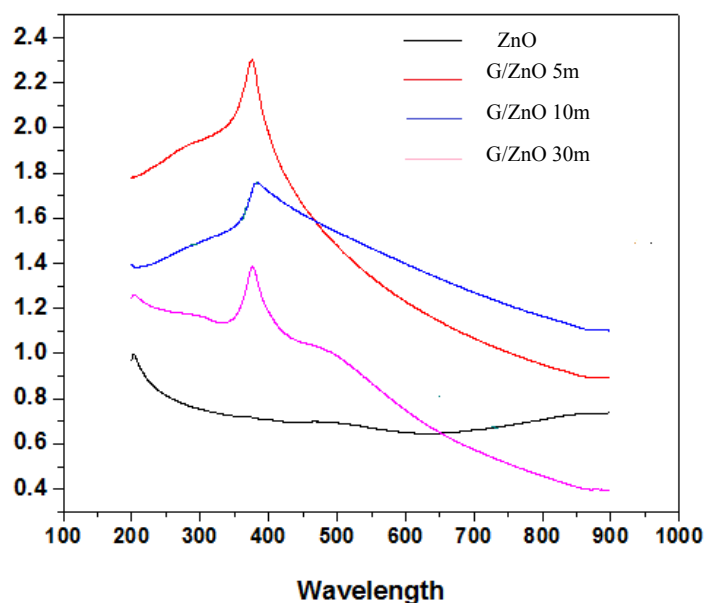
**Table 2.** Percentage of carbon in sample vs. time.

Reaction time (min)	5	10	30
G (%)	4.8	9.7	15



**Figure 4.** Thermal analysis of G/ZnO 10 min.

UV-vis spectroscopy was used to evaluate the absorbance wavelength of materials.



**Figure 5.** UV-vis spectroscopy (quality and unit in vertical axis).

The UV-vis spectroscopy (Fig.5) show that the presence as well as ratio of graphene affects significantly to the absorbance wavelength of Zinc oxide. Graphene coated on zinc oxide decrease the band gap of ZnO semiconductor and enhance the absorbance intensity of materials

#### 4. CONCLUSION

Graphene on ZnO substrate was successfully synthesize by chemical vapor deposition method from cyclohexane as a starting material. The SEM and TEM images proved the formation of graphene on the surface of zinc oxide with 7-10 nm thickness, number of

layers 10 -15. The ratio of graphene in composite depends on reaction time in CVD system. Since the band gap of obtained materials are narrower than ZnO pure, it has potential application for photocatalysis.

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## TÓM TẮT

### NGHIÊN CỨU TỔNG HỢP GRAPHENEN BẰNG PHƯƠNG PHÁP CVD TRÊN XÚC TÁC ZnO

Graphen hình thành trên xúc tác ZnO dạng phiến mỏng ở 550°C trong các khoảng thời gian 5, 10 và 30 phút. ZnO được điều chế bằng phương pháp thủy nhiệt ở 125°C trong 10 giờ. Cấu trúc và tính chất của vật liệu được xác định bằng các phương pháp XRD, TEM, SEM và TGA. ZnO tổng hợp được có cấu trúc phiến mỏng, đồng đều. Graphen trên nền ZnO có chiều dày trong khoảng 7 - 10 nm và có số lớp từ 10 -15 tùy thuộc vào thời gian phản ứng.

**Từ khóa:** Vật liệu xúc tác quang, Hiệu suất xử lý, G/ZnO, CVD.

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