# SYNTHESIS OF $TiO_2$ - GRAPHENE NANOPLATELETs ($TiO_2$/GNPs) COMPOSITE FROM ILMENITE AND NATURAL GRAPHITE FOR PHOTOCATALYSIS IN ENVIROMENTAL TREATMENT

Truong Ngoc Tuan*, Nguyen Thi Hoai Phuong, Tran Van Chinh

***Abstract:*** *In the present study, titanium dioxide/graphene nanoplatelets ($TiO_2$/GNPs) composites have been synthesized from precursors of ilmenite and natural graphite flakes with difference in pH of medium. As-prepared composite materials were characterized by XRD, SEM, TEM, EDX and BET techniques, UV-VIS diffuse reflectance.*

**Keywords:** Graphene nanoplatelets (GNPs); $TiO_2$/GNPs composites; Ilmenite; Photocatalysis; Graphite flakes.

## 1. INTRODUCTION

Environmental pollution has attracted much attention these decades. Millions of tons of wastewater are generated every day and discharged to the rivers and oceans. Under most circumstances, it contains both inorganic and organic pollutants [1]. Since wastewater contains both inorganic and organic pollutants, it is ideal if they can be removed through a single process. Photocatalysis is famous AOP which is one of the most economical and facile approaches to treat both inorganic and organic contaminants in the water [2]. Titanium dioxide, one of the most widely used photo-catalysts, has the ability to reduce heavy metal ions has higher valance to which has lower valance under UV radiation. Beside $TiO_2$ also can help degrade many kinds of organics under UV light [3]. Moreover, $TiO_2$ is desirable because of its high efficiency, low cost, nontoxicity, and high stability.

Graphene is composed of $sp^2$-hybridized carbon atoms. Graphene has gained significant attention due to its incredibly high specific surface area (theoretical value: 2620 $m^2/g$), high thermal conductivity, and outstanding electrical conductivity [4]. Moreover, graphene also is supporting material for enhancement of the photoactive properties of photocatalysis due to its large surface area, high conductivity, ionic mobility, and superior mechanical flexibility. Degradation reaction would happen after pollutants are adsorbed on graphene if $TiO_2$ is attached on graphene [5]. In addition to serving as a platform to help collect pollutants, graphene can improve electron transfer rate and thus expedite the degradation process.

To achieve this goal, herein we designed a nanocomposite, graphene nanoplatelets attached with $TiO_2$ ($TiO_2$/GNPs) via a simple one-pot hydrothermal method. Ilmenite ore ($FeTiO_3$) in Viet Nam has abundant reserves (about 35 million tons) which is a popullar precusor in order to synthesis $TiO_2$. Titanium slag 85% is a by-product of manufacture of $TiO_2$ 92%. Thus, indirect synthetic $TiO_2$/GNPs will improve commercial efficiency.

## 2. EXPERIMENTAL

### 2.1. Materials and equipments

Materials: Titanium slag 85% (by-product of titanium 92% manufacture from Binh Dinh Ilmenite,) $C_2H_5OH$ 96% (PA- Duc Giang), acetone, $H_2SO_4$, $KHSO_4$, $K_2S_2O_8$, natural graphite flake (China, <180 micrometer).

Equipments: Autoclave reactor; ultrasonic device (China, 20 kHz); heating oven (30-300°C) (China); hot plate magnetic stirrer (China).

## 2.2. Preparation

*2.2.1. Preparation $TiOSO_4$ solution*

Titanium slag 85% was washed with distilled water, dried in heating oven and milled in mill ball machine until particles size was about bellow 0,149 mm (pass through 100 mesh sieve). Mixture of 10 g milled titanium slag (85%) and 70 g $KHSO_4$ was calcined at 600$^o$C in two hours. After the calcination, the slag was leached in distilled water, filter insoluble precipitate and remove remained solution. An then insoluble solids were leached in $H_2SO_4$ 10%. The leaching product solution was obtained.

*2.2.2. Preparation GNPs*

GNPs was synthesized by facile one pot method as described in [10]. Natural graphite flakes were washed with distilled water several times and dispersed 2g graphite flakes in concentrated sulphuric acid (98%). The mixture was stirred on magnetic stirrer and then 10g $K_2S_2O_8$ was added. The reaction mixture was stirred continuously in three hours. After that the residue was filtrated, washed with distilled water several times, finally washed with acetone one time and dried at 90$^o$C in two hours in heating oven.

*2.2.3. Preparation $TiO_2$/GNPs*

* Sample M1

50 ml ethanol and 0.05 g GNP was added to 50 ml $TiOSO_4$ solution. The mixture was then ultrasonicated for 30 minutes at 46$^o$C and stirred for 30 minutes. On the flowing step, 40 ml of a 2 M NaOH solution was slowly added to the reaction mixture under stirring. The stirring was continued for 30 minutes. The resulting mixture was transferred to an autoclave. Set temperature for heating oven at 150$^o$C for 2 hours. The precipitate was washed with distilled water and absolute ethanol then dried at 60$^o$C for 2 hours.

* Sample M2

Sample M2 was prepared via same process performed on Sample M1 except the presence of 2M NaOH solution.

## 2.3. Material characterization

The chemical composition of the material was characterized by Energy-dispersive X-ray (EDX) spectrometry on Hitachi S-4800. The morphology of the material was characterized by scanning electron microscope (SEM; Hitachi S-4600) and transmission electron microscope (TEM; EMLab NIHE). The specific surface areas were measured by nitrogen sorption experiments based on BET equation on equipment TriStar II 3020 Version 3.02. The phase transitions and crystal structure of as-prepared materials were studied by the X-ray diffraction (XRD) method with the X'Pert Pro instrument using Cu Kα-radiation. The tests were conducted by the stepwise method (of 0.5 step degree), X-ray source voltage of 40 kV and electron beam current of 100 mA with scanning angle 2θ from 5 to 90$^o$. Raman scattering measurements were performed at room

temperature on micro-Raman system using Renishaw Invia spectrometer. The Raman spectra were excited with the 633 nm of the He-Ne laser operating at low incident power in order to avoid sample heating. Ultraviolet-visible (UV-vis) spectra of the specimens (Model V-670, Jasco) were obtained using the diffuse reflectance (DR) technique in the range of 200 to 2500 nm using a $BaSO_4$ plate as the reflectance standard.

## 3. RESULTS AND DISCUSSION

The morphology of the $TiO_2$/GNPs material was characterized by scanning electron microscope (SEM) and transmission electron microscope (TEM) with images showed in Figure 1. It can be clearly seen that the obtained GNPs have the multilayers structure with thin overlapping sheets which had a diameter of tens of microns. TEM images also show the uniform nano-sized $TiO_2$ particles were distributed over the surface of GNPs sheets

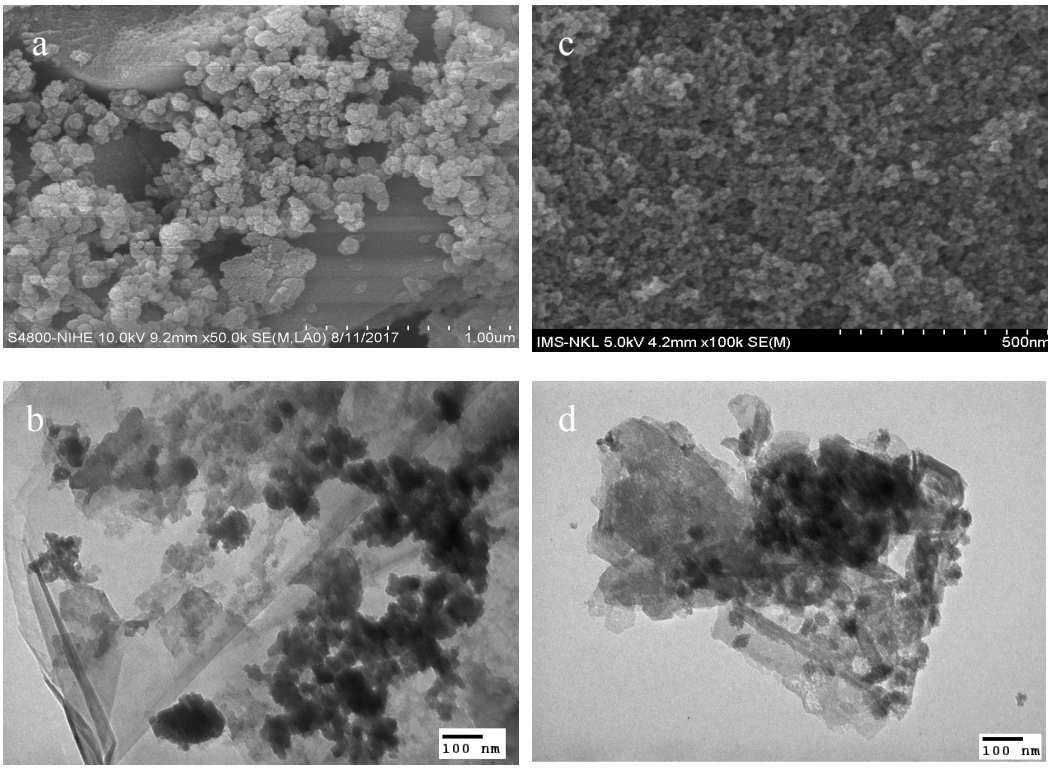


***Figure 1.*** *SEM and TEM images of $TiO_2$/GNPs M1 sample (a, b) and of M2 sample (c, d).*

The chemical composition of the material was characterized by Energy-dispersive X-ray (EDX) spectrometry. The results obtained in Table 1 below show that this material is a combination of narrow multilayer graphene that is represented by the element C in the chemical composition along with the presence of oxygen and titanium elements. The absence of other elments in as-prepared is the result of the removing impurity completely.

***Table 1.*** *Chemical composition of the $TiO_2$/GNPs composite material.*

| Elements | GNPs | | M1 | | M2 | |
|---|---|---|---|---|---|---|
| | Wt% | At% | Wt% | At% | Wt% | At% |
| C | 82.57 | 87.05 | 26.74 | 41.16 | 28.94 | 44.22 |
| O | 15.28 | 12.1 | 39.16 | 45.25 | 36.84 | 42.27 |
| S | 2.15 | 0.85 | 2.22 | 1.28 | 2.11 | 1.21 |
| Ti | | | 31.87 | 12.30 | 32.11 | 12.30 |
| Total | 100 | 100 | 100 | 100 | 100 | 100 |

X-ray diffraction (XRD) measurements were applied to investigate the crystallographic structure of the as prepared materials. The XRD patterns of GNPs and $TiO_2$/GNPs (M1 and M2) are shown in Fig. 2. M2's patterns all exhibit peaks at 25.35°, 38.15°, 47.95° and 54.35°, corresponding to the (101), (004), (200) and (105) planes of the anatase phase. XRD Patterns of GNPs and once of M2 had a peak which ovelap peak at 26,65° of graphite corresponding to (002) plane but intensity of the peak different between the materials. Absence of peaks in M1's patterns that indicated amorphous structure of $TiO_2$/GNPs. And Peak (002) plane of graphitic structure was also disappeared because content of Ti in M1 was higher content of C. Calculated size of $TiO_2$ particles in M2 sample according to the Debye Scherrer equation was about 16,4 nm.

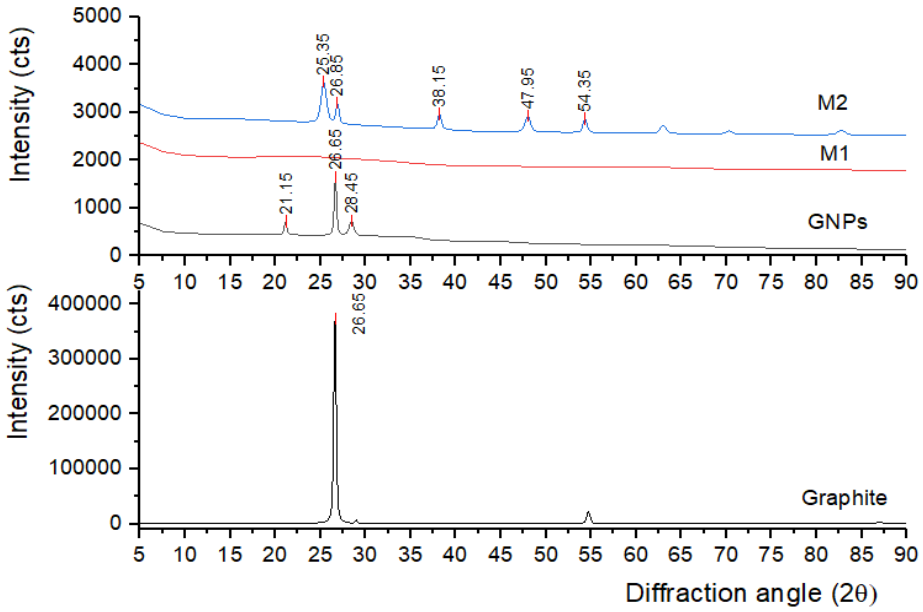


***Figure 2****. The XRD patterns of the Graphite, GNPs and $TiO_2$/GNPs (M1 and M2).*

The surface area of GNPs and $TiO_2$/GNPs materials which was measured by nitrogen sorption experiments in the pressure range of 0.080 to 0.292 at and at 77.3°K based on BET equation was showed in table 2. With these value, we can see that the surface area and the ability to expose to adsorption object of $TiO_2$/GNPs materials increased compared to GNPs and pure $TiO_2$. Thus, the presence of nanoscale $TiO_2$ particles on GNPs surface made the increase of

capability of as-prepared $TiO_2$/GNPs materials. However, surface area of M1 was higher than M2 which could cause the difference on crystallographic structure between M1 and M2.

***Table 2.*** *BET surface area, pore size and pore volume.*

| | BET Surface Area ($m^2/g$) | Pore volume ($cm^3/g$) | Pore size (nm) |
|---|---|---|---|
| GNPs | 119.9 | 0.051 | 2.165 |
| M1 | 198.6 | 0.086 | 2.19 |
| M2 | 160.1 | 0.112 | 2.40 |

Fig. 3 shows the $[F(R)h\nu]^{1/2}$ plot for indirect transition corresponding to anatase structure. The Kubelka-Munk function F(R) is equivalent to absorbance in these UV-Vis DRS spectra and hν is the photon energy, $h\nu = (1239/\lambda)$ eV, where λ is the wavelength in nm. The value of hν extrapolated to $F(R)h\nu = 0$, which gives an absorption energy, corresponds to a band gap $E_{bg}$ [12]. It could see that $E_{bg}$ of M1 (2,85 eV) reduced more than that of M2 (2,95 eV) and energy band gap of two $TiO_2$/GNPs materials was both lower than $TiO_2$. Thus $TiO_2$/GNPs materials could have photo activity in VIS and shift their optical absorption edge from UV into visible light range.

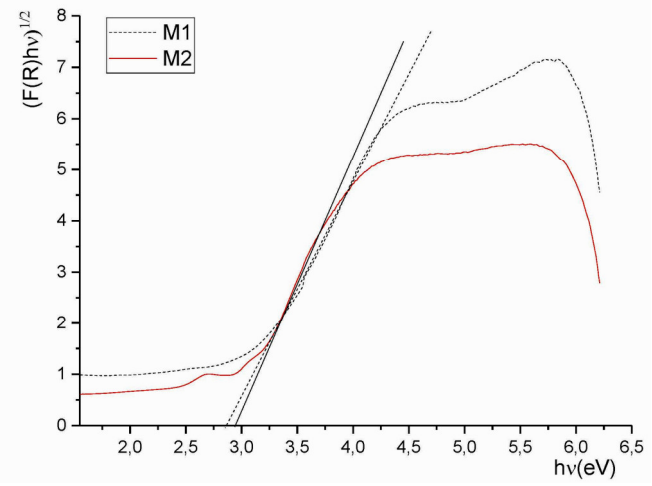


***Figure 3.*** *UV-VIS Diffuse Reflectance of the $TiO_2$/GNPs materials.*

## 4. CONCLUSIONS

The $TiO_2$/GNPs composite was successfully synthesized by hydrothermal method from titanium slag and natural graphite. $TiO_2$ particle with nanoscale size (16 nm with M2) was disturbed uniformity on GNPs surface. The morphology of $TiO_2$ particle, energy band gap, BET surface area of titanium dioxide on the graphene nanoplatelets composite depend on pH value of prepared medium. BET surface area of as-prepared materials were determined to be 198.6 $m^2/g$ (M1) and 160.1 $m^2/g$ (M2) while their $E_{bg}$ were 2,85 ev (M1) and 2,95 eV (M2). the results of this study, this $TiO_2$/GNPs composite is promising in the field of environmental treatment in practice as photo catalyst in VIS.

## REFERENCES


[1]. A.Sayari, S.Hamoudi, Y.Yang. *"Applications of Pore-Expanded Mesoporous Silica. 1. Removal of Heavy Metal Cations and Organic Pollutants from Wastewater, Chemistry of Materials"*, **Vol. 17**, pp. 212. (2005).

[2]. Bailey S. E., Olin T. J., Bricka R. M. & Adrian D. D. "*A review of potentially low-cost sorbents for heavy metals, Water Research"*, **Vol. 33,** p. 2479 (2009).

[3]. Venkata Ramana Posa, Viswadevaryalu Annavarama & Dinarayana Reddy Somala. *"Fabrication of graphene – $TiO_2$ nanocomposite with improved photocatalytic degradation for acid orange 7 dye under solar light irradiation",* **Vol. 39** (3), pp. 759–767 (2016).

[4]. Ferrer P.R., Mace A., Samantha N.T. and Ju-Won Jeon. *"Nanostructured porous graphene and its composites for energy storage applications, Nano Converg"*, **Vol. 4** (29), pp. 1-19 (2017).

[5]. Zhang L. et al. *"Electrospun titania nanofibers segregated by graphene oxide for improved visible light photocatalysis"*, Applied Catalysis B: Environmental, **Vol. 201,** pp. 470–478 (2017).

[6]. Mr. Duong Duc La, Suresh Bhargava and Sheshanath V. Bhosale. *"Improved and A Simple Approach For Mass Production of Graphene Nanoplatelets Material"*, Chemistry Select, **Vol. 5**, pp. 949 – 952 (2016).

[7]. Ibram Ganesh, Polkampally P. Kumar, Abhishek K. Gupta, Panakati S.C. Sekhar, Kalathur Radha, Gadhe Padmanabham, Govindan Sundararajan - *Preparation and characterization of Fe-doped TiO2 powders for solar light response and photocatalytic applications*, Processing and Application of Ceramics, **Vol. 6** (1), pp. 21–36 (2012).


## TÓM TẮT

### TỔNG HỢP VẬT LIÊU TỔ HỢP $TIO_2$ - GRAPHENE NANOPLATELETS ($TIO_2$/GNPs) TỪ ILMENITE VÀ GRAPHIT TỰ NHIÊN LÀM XÚC TÁC QUANG TRONG XỬ LÝ MÔI TRƯỜNG


*Trong nghiên cứu này, vật liệu tổ hợp oxit titan/graphene nanoplatelets ($TiO_2$/GNPs) được tổng hợp từ các tiền chất ilmenite và graphit tự nhiên dạng phiến với sự khác nhau về giá trị độ pH của môi trường tổng hợp. Các vật liệu tổ hợp đã tổng hợp được xác định các đặc trưng thông qua các phương pháp như XRD, SEM, TEM, kỹ thuật BET và phổ UV-VIS phản xạ khuếch tán. Vật liệu tổ hợp $TiO_2$/GNP gồm các hạt có kích thước nano (khoảng 16 nm), có diện tích bề mặt 196,8 $m^2/g$ (M1) và 160,1 $m^2/g$ (M2), có hoạt tính quang trong vùng ánh sáng khả kiến.*



**Từ khóa:** Graphene nanoplatelets (GNPs); Vật liệu tổ hợp $TiO_2$/GNPs; Xúc tác quang; Graphite flakes.

*Received 19th April 2018*
*Revised 22th June 2018*
*Accepted 18th October 2018*



*Author affiliations:* Academy of Military Science and Technology;
*Corresponding author: ngoctuan109@gmail.com.