SYNTHESIS AND CHARACTERIZATION OF GNPs/Ti-Fe BINARY OXIDE COMPOSITE FROM ILMINITE OF CENTRAL VIET NAM USING HYDROTHERMAL METHOD

Truong Ngoc Tuan\textsuperscript{1,*}, Tran Van Chinh \textsuperscript{1}, Nguyen Hoang Tuan\textsuperscript{2}, Nguyen Thi Hoai Phuong\textsuperscript{1}

\textsuperscript{1}Institute of Chemistry and Materials, Academy of Military Science and Technology, 17 Hoang Sam, Ha Noi
\textsuperscript{2}Military Technical Academy, 236 Hoang Quoc Viet, Ha Noi

*Email: ngoctuan109@gmail.com

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ABSTRACT

In the present study, GNPs/Ti-Fe binary oxide composites were synthesized from ilmenite of Central Viet Nam using hydrothermal method. The effect of amount of Fe on the morphology, structure and photocatalytic performance of prepared materials were characterized by scanning electron microscopy, transmission electron microscopy, X-ray diffraction, UV–VIS Diffuse Reflectance spectrophotometer, Energy-dispersive X-ray spectroscopy and BET techniques. The results showed that Ti-Fe binary oxide nanoparticles distribute on GNP sheets, the BET surface area of as-prepared material was 328.6 m\textsuperscript{2}/g and the material exhibited efficient photocatalytic performance in visible light (energy band gap was 1.9 eV).

Keywords: graphene nanoplatelets (GNPs), GNP/Ti-Fe binary oxide composite, photocatalytic material, ilmenite.

1. INTRODUCTION

The development of industries causes a high risk of environment pollution, especially heavy metal contaminant. Some heavy metals as cadmium, chromium, lead, etc are considered carcinogens which can penetrate into water resources, soil, air and biosphere, and destroy habitat and indirectly effect human health. There are several ways for heavy metal removal, including electrochemical treatments (electrocoagulation, elector-floatation, and electrodeposition), physicochemical processes (chemical precipitation, Ion exchange), adsorption (activated carbon, carbon nanotubes, and wood sawdust adsorbents), or current methods (membrane filtration processes, photocatalysis processes, and nanotechnology) \cite{1}.

Photocatalysis is a famous advanced oxidation process (AOP) \cite{2} which uses non-toxic semiconductors that harness light with appropriate wavelength instead of chemical compounds \cite{3}, is suitable for tropical climate of Viet Nam. In addition, the photocatalysis process is also an efficient process because of its simple design, low-cost operation, high stability, and high
removal efficiency [4]. In contrast with other semiconductors, TiO$_2$ is widely used for environmental applications which band gap energy ($E_{bg}$) is 3.2 eV (anatase) or 3.02 eV (rutile) in order to be able to promote photocatalytic reactions [5]. However, the solar energy of about 3.0 eV is less than 5 %, that limits the commercial potential through the low photoreaction rates [6]. Binary oxide Ti and Fe will solve this problem and may effectively enhance photo activity of TiO$_2$ and utilize the visible light [7]. Ilmenite ore (FeTiO$_3$) in Viet Nam has abundant reserves (about 35 million tons) which is a nature composite of Ti and Fe. Thus indirect synthetic binary oxide Ti and Fe could improve commercial efficiency.

Graphene has a honeycomb structure composed of an atomic sheet of sp$^2$-bonded carbon atoms, and has large surface area, high transparency, and high electric charge carrier mobility [8]. These electronic and photonic properties make it an ideal candidate material for enhancement of TiO$_2$ photo reactivity [9]. Graphene nanoplatelets (GNPs) is a multilayer type of graphene with its thickness in nanoscale which can be obtained by exfoliation of natural graphite flakes.

Here in, we describe a synthesis of GNP/Ti-Fe binary oxide composite which include two simple steps with ilmenite ore and graphite flakes used as precursor substances.

2. MATERIALS AND METHODS

2.1. Material

2.1.1. Raw material

Titanium slag 85 % and 52 % (by-product of titanium 92 % manufacture from Binh Dinh Ilmenite,) C$_2$H$_5$OH 96 % (PA- Duc Giang), acetone, H$_2$SO$_4$, KHSO$_4$, K$_2$S$_2$O$_8$, natural graphite flake (China, < 180 µm).

2.1.2. Equipment

Autoclave reactor; ultrasonic device (China, 48 kHz); heating oven (30-300 °C) (China); hot plate magnetic stirrer (China).

2.1.3. Preparation intermediate solution (solution A)

Titanium slag 85 % and 52 % was washed by 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 % or 52 %) and 70 g KHSO$_4$ was calcined at 600 °C in two hours. After the calcination, the slag was leached in solution H$_2$SO$_4$ 10 %. The leaching product solution was obtained.

2.1.4. Preparation of GNPs

GNPs was synthesized by facile one spot method as described in [10]. Natural graphite flakes were washed by distilled water several times and dispersed 2 g graphite flakes in concentrated sulphuric acid (98 %). The mixture was stirred on magnetic stirrer and then 10 g K$_2$S$_2$O$_8$ was added. The reaction mixture was stirred continuously for three hours. After that the
residue was filtrated, washed by distilled water several times, finally washed by acetone one time and dried at 90 °C in two hours in heating oven.

2.1.5. Preparation of GNP/Ti-Fe binary oxide composite

100 ml ethanol and 0.05 g GNP was added to 100 ml solution A. The mixture was then ultrasonicated from 5 to 6 times (5 minutes each time) stirred for 30 minutes. 1 M NaOH solution was slowly added to the reaction mixture under stirring until pH was 6. The stirring was continued for 30 minutes.

The obtained mixture was transferred to an autoclave and the hydrothermal reaction performed at 150 °C for 2 hours. The precipitate was vacuum filtered and washed with distilled water and ethanol. Then residue dried at 60 °C for 2 hours.

2.2. 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°.

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 BaSO4 plate as the reflectance standard.

3. RESULTS AND DISCUSSION

Chemical composition of raw material as GNPs, titanium slag 85 % and 52 %, and product as Ti-Fe binary oxides on GNPs which were synthesized from titanium slag 85 % (TGG85) and titanium slag 52 % (TGG52), as described in Table 1.

The results obtained in Table 1 below showed that the element C in the chemical composition of GNP was major with approximate 83 wt%, beside the presence of oxygen (15 wt%) and sulphur (2 wt%) elements. Silicon was not a desired substance in composition of titanium slag with 2.36 wt% (titanium slag 85 %) and 3.65 wt% (titanium slag 52 %). However, composition of prepared material (TGG85 and TGG52) didn’t exhibit the presence of silicon and the products were almost pure. Ratio of Ti and Fe in as-prepared materials and in precursors of titanium slag were changed of small amount. Fe and Ti ratio in TGG85 was 8.6 % ((in precursor titanium slag 85 % was 7.3 %) and this ratio in TGG52 was 41.89 % (in precursor titanium slag 52 % was 41.05 %). This change showed that synthesis method of TGG had little effect to ratio
of Ti-Fe. Percentage of C in TGG85 and TGG52 was almost equal (35.63 % and 37.13 %) hence GNP's content was equal.

**Table 1.** Chemical composition of Titanium slag (85 % and 52 %), GNP's, TGG85 and TGG52.

| Elements | GNP's | Titanium slag 85% | TGG85 | Titanium slag 52% | TGG52 |
|----------|-------|-------------------|-------|-------------------|-------|
|          | Wt%   | At%              | Wt%   | At%              | Wt%   | At%              | Wt%   | At%              |
| Ti       | 47.72 | 24.68            | 20.10 | 6.98             | 18.8  | 8.21             | 11.95 | 4.10             |
| Fe       | 3.75  | 0.73             | 1.88  | 0.56             | 13.09 | 4.90             | 8.61  | 2.53             |
| O        | 15.28 | 12.1             | 46.17 | 71.49            | 40.62 | 42.21            | 64.46 | 84.18            |
| Si       | 2.36  | 1.2              |       |                  | 3.65  | 2.72             |       |                  |
| C        | 82.57 | 87.06            | 35.63 | 49.33            |       |                  | 37.16 | 50.80            |
| S        | 2.15  | 0.85             | 1.77  | 0.92             |       |                  | 1.61  | 0.82             |
| Total    | 100   | 100              | 100   | 100              | 100   | 100              | 100   | 100              |

**Figure 1.** SEM micrograph of GNP's (a), photograph of GNP's (b), SEM micrograph of TGG85 (c) and TEM micrograph of TGG85 (d).
As showed in Fig. 1a (SEM), GNPs had multilayer structure which composed of several sheets, sized of about 10 ± 20 µm. Figure 1b showed difference between prepared GNPs and graphite flake of the same weight (0.1g), bulk density of GNPs was smaller very much than bulk density of graphite flake. Figures 1c and 1d depict SEM and TEM micrograph of TGG85 which showed that nanoscale Ti-Fe binary oxide particles almost dispersed on GNPs base.

All XRD patterns in Fig. 2 were characterized by a strong and sharp peak at 2θ around 26.65° corresponding to (002) but intensity of the peak is different for various materials. Intensity of the peak in XRD pattern of graphite was highest which was 230 times larger than that of GNPs. This result was explained as on conversion to GNPs, the inter planar carbon bonds of get broken and the crystalline size of graphite is reduced.

XRD pattern of TGG85 showed a peak at 2θ = 38.05 with low intensity, corresponding to (112) lattice plane reflection of structure TiO₂ anatase except a peak corresponding to (002). Peak (101) of structure crystal anatase did not show up because of overlap between this peak with strong peak (002) of GNPs. It could see that content of crystal of TiO₂ was very low and major TiO₂ in TGG materials was of amorphous shape. Peak (112) of structure crystal anatase was disappeared in XRD pattern of TGG52 which was explained as reduction of content of Titanium in TGG52 composition. No diffraction corresponding of iron oxides was observed.

The values of BET surface area, BJH adsorption average pore width and BJH adsorption pore volume of the GNPs, TGG85 and TGG52 were presented in Table 2. Surface area value of
GNPs was 119.9 m²/g, corresponding to approximately 22 layers (surface area of single layer graphene was 2340 m²/g [11]). It could see that BET surface area of TGG85 was the highest. Nanoscale metal oxides were distributed on GNPs causing surface area of TGG materials increased. In addition, surface area of TGG was increased very much as compared with pure nanoscale TiO₂ and FeO₂.

Table 2. BET surface area, pore volume and pore size of as-prepared materials.

|          | BET Surface Area (m²/g) | Pore volume (cm³/g) | Pore size (nm) |
|----------|-------------------------|---------------------|----------------|
| GNP      | 119.9                   | 0.051               | 2.165          |
| TGG85    | 328.6                   | 0.126               | 2.125          |
| TGG52    | 138.0                   | 0.051               | 2.143          |

The FT-IR spectrum of the materials showed various characteristic peaks as seen in Fig 3. In this spectrum, the absorption band at about 3400 cm⁻¹ is related to stretching of O–H, beside carbonyl group and skeletal ring vibrations at 1637 cm⁻¹, and C–O–C groups at about 1100 cm⁻¹. A band between 650 and 800 cm⁻¹ in FT-IR spectrum of TGG85 and TGG52 were seen which was attributed to different vibrational modes of TiO₂. Anatase and rutile phases of TiO₂ exhibited certain strong FT-IR absorption bands in the regions of 850–650 cm⁻¹ and 800–650 cm⁻¹. The broad intense band seen below 1200 cm⁻¹ on TGG85 and TGG52 curves was due to Ti-O-Ti vibrations. The absorption band at about 600 cm⁻¹ on TGG85 and TGG52 curves was corresponded to Fe-O bond vibration of Fe₂O₃. Other characterized absorption bands of Fe₂O₃ did not present as they could be merged with absorption bands of TiO₂ and GNPs.

Figure 3. FT-IR spectrums of GNPs, TGG85 and TGG52.

The Raman spectrum of GNPs (Figure 4) exhibited two in three the characteristic bands of graphene (D, G, 2D) with absence of the D band. The graphene G-band at 1600 cm⁻¹ wavenumber arises from the stretching of the C–C bond in graphitic materials, and was common
to all sp² carbon systems. The G peak corresponds to the E_{2g} phonon at the Brillouin zone centre, its relative intensity increases with the number of layers. The D-band at 1300 cm⁻¹ wavenumber is due to the breathing modes of sp² atoms and requires a defect for its activation. The 2D band at about 2700 cm⁻¹ wavenumber represents the second-order zone-boundary phonons. It is always seen, even when no D peak is present. The shape and position of the 2D peak distinguish single and multilayer samples, and this peak is also sensitive to the doping. Single-layer graphene has a sharp, single 2D peak, in contrast to graphite and multilayers graphene. In addition, single layer graphene can also be identified by analysing the peak intensity ratio of the 2D and G band [13]. The ratio between I_{2D} and I_G of these bands for high quality (defect free) single layer graphene will be seen to be equal to 2. This ratio, lack of a D band and a sharp symmetric 2D is often used as a confirmation for a high quality defect free graphene sample [14]. Shape and position of 2D band of GNPs/s Raman spectrum and ratio I_{2D}/I_G = 0.45 indicated multilayers structure of prepared material.

The presence of Ti and Fe in TGG85 and TGG52 caused the ratio I_{2D}/I_G increased. The increase of content of Fe while total content metal oxides in two prepared materials were approximate which made almost no change of the ratio I_{2D}/I_G (1.05 with TGG85 and 1.01 with TGG52). The result showed similar effect of titanium oxide and iron oxide on the ratio of the 2D and G band.

Figure 4 shows the Raman spectrum of TiO₂ nanocrystals in prepared TGG materials. In the Raman lines of TGG85, the peaks at 191.6; 395.6; 510.8 and 665.4 cm⁻¹ can be assigned as the E_g, B_{1g}, A_{1g} or B_{1g}, and E_g modes of the anatase phase, respectively [12]. The strongest E_g mode at 191.6 cm⁻¹ arising from the external vibration of the anatase structure is well resolved, which indicates that an anatase phase was formed in the as-prepared TGG85. In the Raman lines of TGG52, the characterized peaks of anatase almost disappeared, only the peak at 156.3 remained which was explained as the reduction of content of Ti. The presence of the peak at about 1310 cm⁻¹ in Raman spectrum of TGG85 and TGG52 may be due to the two-magnon
scattering aroused from the interaction of two magnons created on antiparallel close spin sites in $\alpha$-Fe$_2$O$_3$ is visible [12]. The increase of Fe content in TGG materials caused the growth of intensity of the peaks at 1310 cm$^{-1}$.

The UV-Vis diffuse reflectance spectra (DRS) of the as-prepared TGG materials were presented in Fig. 5. The DRS spectra of TGG85 revealed three $\lambda_{\text{max}}$ absorbance peaks at about 290 nm, 455 nm and 625 nm while the DRS spectra of TGG52 also displayed three $\lambda_{\text{max}}$ absorbance peaks at about 345 nm, 455 nm and 720 nm. Thus the doping of Fe ions into TGG materials could shift their optical absorption edge from UV into visible light range (i.e., red shift).

![Graph showing UV-Vis Diffuse Reflectance of TGG85 and TGG52.](image)

*Figure 5. UV-VIS Diffuse Reflectance of TGG85 and TGG52.*

![Graph showing transformed diffuse reflectance spectra of TGG85 and TGG52.](image)

*Figure 6. Transformed diffuse reflectance spectra of TGG85 and TGG52 was showed: a) indirect band gap and b) direct band gap energy values.*
Figure 6a shows the \([F(R)h\nu]^{1/2}\) plot for indirect transition and Fig. 6b shows the \([F(R)h\nu]^2\) for indirect transition. The Kubelka-Munk function \(F(R)\) is equivalent to absorbance in these UV-Vis DRS spectra and \(h\nu\) is the photon energy, \(h\nu = (1239/\lambda)\) eV, where \(\lambda\) is the wavelength in nm. The value of \(h\nu\) 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 TGG materials decreased while content of Fe increased. In case of indirect transition, the calculated values were 2.75 eV and 1.9 eV corresponding to TGG85 and TGG52. In case of direct transition, the values were 3.6 eV and 2.75 eV corresponding to TGG85 and TGG52. Thus TGG85 and TGG52 could shift their optical absorption edge from UV into visible light range.

**4. CONCLUSION**

TGG85 and TGG52 were composite materials of Ti-Fe binary oxides on GNPbase which were prepared from raw materials as titanium slag (by-product of manufacture Titanium 92% from Binh Dinh Ilmenite) and natural graphite flakes. Intermediate product GNP was synthesized via a facile one pot method. GNP had multilayers structure with diameter was 10-20 \(\mu\)m and BET surface area was 119.9 m\(^2\)/g corresponding to 22 layers. The synthesis method used for TGG materials almost removed completely impurity which was in titanium slag precursor. Ti-Fe binary oxides in TGG were nanoscale, amorphous phase and distributed on surface of GNP which increased surface area (max 328.6 m\(^2\)/g with TGG85) and increased energy band gap (max 1.9 eV m\(^2\)/g with TGG85 in case of indirect transition). Influence of content of Fe and Ti on morphology and shape of TGG materials were also investigated in this article.

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