Photoactivity of Reducing Graphene Oxide and Titanium Dioxide Composite for Cinnamic Acid Degradation

Nguyen Phung Anh1,2, Huynh Thi Kim Chi1,2, Nguyen Tri1 and Hoang Thi Kim Dung1,2,*

1Institute of Chemical Technology – VAST, 01 Mac Dinh Chi Str., Dist. 1, Ho Chi Minh City 700000, Vietnam
2Graduate University of Science and Technology, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet Str., Cau Giay Dist., Hanoi 100000, Vietnam

Reducing graphene dioxide (rGO) and titanium dioxide (TiO2) composites with various rGO/TiO2 ratios were prepared by hydrothermal method, in which rGO was synthesized from graphene powder according to modified Hummers method using microwave. Physico-chemical characteristics of the samples were investigated by the methods of N2 adsorption-desorption measurements, X-ray diffraction, Raman, Fourier transform infrared spectroscopy (FT-IR), UV-Vis spectroscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). rGO-TiO2 (1:25) catalyst had smaller particle size and higher surface area than whose of pure TiO2. Moreover, this modification also extended the region of photon absorption of TiO2 towards the visible range of 397-437 nm. The catalytic activity was investigated by photodegradation of cinnamic acid (CA) solution, which have been shown higher activity than that of the pure TiO2 catalyst. The optimum conditions in this study for the degradation of CA were determined as follows: the ratio rGO/TiO2 of 1:25, catalyst concentration of 0.75 g L⁻¹, oxygen supply of 0.5 L min⁻¹, initial pH solution of 3.8 and reaction temperature of 25°C. In this condition, cinnamic acid conversion in the solution reached approximately 90% after 60 minute reaction. [doi:10.2320/matertrans.MD201721]

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1. Introduction

Environmental pollution such as emission of contaminants has been one of the serious problems nowadays. Photocatalysts have been known for treatment in environmental applications. In fact, TiO₂ was the most compatible choice for commercial catalyst due to its biological and chemical inertness, cost-effectiveness and strong oxidizing power of its photogenerated hole. However, the large band gap of TiO₂ (3.2 eV) limited its use to the UV region of the solar spectrum, which accounts for a very small fraction of solar energy (approximately 3–5%); the ability of oxidation is limited by its fast recombination rates that leads to low photoactivity. Graphene-based TiO₂ composites have been proved to be an efficient method to improve the properties and photoactivity of TiO₂ to overcome above disadvantages.

tGO is an allotrope of carbon with two-dimensional crystal structure, which comprises one atom-thick planar sheets of sp² bonded carbon atoms that are densely packed in a honeycomb crystal lattice. The rGO has attracted many scientists in global because of its exceptional physical properties such as high thermal stability, electronic conductivity and mechanical strength. This material has wide promise in many fields as composite materials, biological engineering, optical electronics, ultrafiltration, photovoltaic cells, energy storage, etc.

The common method for producing graphene is reducing graphene oxide from graphite powder. This procedure begins with graphite powder as the carbon source. Graphite oxide (GO) is formed by the powder reacts with a mixture of sodium nitrate, potassium permanganate and sulfuric acid in a process known as Hummer method. However, this graphene derivative has many oxygen-containing functional groups, such as hydroxyl groups, carbonyl and carboxyl groups that disrupt the conjugated π system and prevent them to reach maximum strength and conductivity. These oxygen-containing functional groups are eliminated by reducing the graphene oxide to form rGO, that leads to improving strength and conductivity of the material. The reduction of GO using microwaves was highly efficient and achieved the goal of high-quality graphene with desirable properties.

The authors had reported that the photogenerated electrons in the regions of conductive band may be transferred into rGO and the holes remained on TiO₂, leading to retarding the recombination of electrons and holes. Moreover, rGO may also provide high surface areas or the desired functional groups for the efficient adsorption. The possible formation of Ti–O–C bonds may also affect the performance of rGO-TiO₂ composites in photooxidation. Furthermore, rGO could control the morphology of TiO₂ nanoparticles. Therefore, rGO-TiO₂ samples were investigated for the photodegradation of organic compounds, including pesticide (chlorpyrifos), herbicide (2,4-dichlorophenoxyacetic), dyes (malachite green, rhodamine B and methylene blue).

Cinnamic acid (CA–C₉H₈O₂) – a phenolic compound commonly exists in vegetable oil plants and washing wastewaters. It can cause some serious skin, eye allergies and respiratory irritation, thus affecting human health. In previous studies treatment of CA solutions was investigated by photocatalytic systems TiO₂–UV on pure TiO₂, Fe-TiO₂, Cr-TiO₂ and N-TiO₂ catalysts. The results indicated that the catalysts reached high photoactivity in this reaction.

Therefore, in this study, to determine the properties of synthesized composites by degradation of CA as well as the modification of the conventional method in CA treatment, rGO was synthesized from graphite powder according to
modified Hummers method using microwaves, and then the nanocomposites of reduced graphene oxide and TiO$_2$ (rGO-TiO$_2$) with various rGO/TiO$_2$ ratios were prepared by a simple method (hydrothermal) and compared the photocatalytic performance for degradation of CA solutions.

2. Experimental

2.1 Preparation of rGO-TiO$_2$ nanocomposites

rGO-TiO$_2$ nano-composites with different rGO:TiO$_2$ ratios were prepared two steps as follows:

Step 1: Preparation of rGO from graphite powder according to modified Hummers method by microwave-assisted treatment. Firstly, 3.0 g graphite powder was added to 400 mL of concentrated H$_2$SO$_4$/H$_3$PO$_4$ (9:1) solution and stirred in an ice-water bath. Continuously, 9.0 g KMnO$_4$ was added slowly to keep the temperature lower than 20°C. After that, the reaction system was transferred to the temperature of 35°C and ultrasound within 2 hours. Then, the mixture was sonicated to produce a fine dispersion and heated to 35°C for 4 hours to obtain graphene oxide. Subsequently, the GO solution was mixed and put into the microwave at the power of 350 watts. After reaction in microwave, deionized water was added into the mixture and put into the ultrasonic tank for 4 hours at 30°C. After centrifuging and rinsing to pH 6, the sample was dried to obtain rGO nanosheets. The effect of reaction time in the microwave to obtain the rGO samples was investigated. The obtained rGO samples were denoted as rGO-350-x, where x represents reaction time in the microwave. Here x was chosen as 3, 5 and 7 minutes, respectively.

Step 2: Preparation of rGO-TiO$_2$ composites by hydrothermal method. Firstly, rGO was dispersed in 50 mL ethanol. This mixture was controlled to pH about 3–4 using HNO$_3$, added 15 mL of tetraisopropyl orthotitanate Ti(OC$_3$H$_7$)$_4$ (TTIP), and stirred for 10 minutes. Nextly, the solution was added to deionized water (10 mL) and stirred at room temperature for 2 hours to form a highly viscous solution. Afterwards, the mixture was transferred to a Teflon autoclave, which was heated at 200°C for 10 hours. Then, the sample was washed by distilled water. Finally, the sample was dried in the air, after that, drying in the dryer at 80°C, 100°C and 120°C, respectively, in 2 hours for each of temperature level to obtain rGO-TiO$_2$ nanocomposites. The rGO-TiO$_2$ composites were denoted as rGO-TiO$_2$ (1:y), where 1:y represents the ratio of rGO/TiO$_2$. Here y was chosen as 1, 10, 15, 20, 25, and 30, respectively.

2.2 Physico-chemical characteristics analysis

Physico-chemical characteristics of rGO and rGO-TiO$_2$ samples were investigated by various methods, including BET surface areas (Nova Station B, Quanta chrome Nova Win Instrument), X-ray powder diffraction analysis–PXRD (Bruker D2 Phaser powder diffractometer), Raman spectroscopy (Labram-H, Horiba JobinYvon), scanning electron microscopy–SEM (FE–SEM JEOL 7401), transmission electron microscopy–TEM (JEOL JEM 1400), Fourier transform infrared–FT-IR (Tensor 27-Bruker spectrophotometer), and UV-Vis absorption spectroscopy (UV–1800 model, Shimadzu, Japan).

2.3 Photocatalytic activity

Experiments for photocatalytic degradation of cinnamic acid in the presence of O$_2$ agents was carried out using the batch photocatalytic system. The photocatalytic reactor is an inner quartz double-wall jacket with inlet and outlet for the water circulation to maintain the temperature of reaction mixture. Reactor is designed with the volume of reaction solution of 250 mL and radium halite 9W/78 UVA G23 lamp (36 lamps, $\lambda \approx$ 350–400 nm, capacity 36 LEDs × 0.160 mW = 5.76 W of UV-A). The photo-reactor was isolated by using a thick plastic black cover. In addition, the reaction mixture is mixed by magnetic stirrer. The schematic diagram of the photocatalytic reaction system was described in the previous publications. In all experiments, CA solution volume of 250 mL, CA concentration of 50 mg/L and stirring speed of 250 rpm were fixed. Influences of catalyst concentration and operation parameters (i.e. initial solution pH or flow rate of O$_2$ concentration) on the photocatalytic activity of catalysts were investigated. The catalysts were separated by filtration (syringe filter, pore size of 0.22 µm, sartorius NY) from the aqueous solutions prior to analyzing the CA in the solution were determined by UV-Vis spectrophotometer (UV–1800 model, Shimadzu, Japan) at $\lambda_{\text{max}} = 272$ nm.

3. Results and Discussion

3.1 Physico-chemical characteristics of samples

The result of reduction process of GiO can manifest itself in Raman spectra by the changes in relative intensity of two main peaks: D and G. The D mode is activated by the presence of defects and its intensity is an expression for short range disorder whereas G mode is caused by the first order scattering of E$_{2g}$ mode. According to Fig. 1, the D peak ($v = 1350$ cm$^{-1}$) is more intense than that of G peak ($v = 1630$ cm$^{-1}$) on rGO-350-5 catalyst. The D vibration band of rGO increased mainly because of the orientation of sp$^2$ carbon form. On the other hands, the G vibration band of rGO increased due to the removal of oxygen moieties in rGO’s structure. These results are consistent with previous publication. Comparison to the sample rGO-350-3 and sample rGO-350-7, the rGO-350-5 sample showed higher
intensity of characteristic peaks. It indicated that the removal of oxygen-containing groups on this sample was better than that of others. So, the procedure that put GiO in the microwave at the power of 350 watts for 5 minutes is the optimal process which was chosen to obtain the rGO nanosheets in this study.

The rGO sample was characterized by X-ray diffraction, as shown in Fig. 2. After chemical reduction, the broad diffraction of rGO appeared in the range of 20° to 26°. The broad peak may stem from the partial restacking of exfoliated graphene layers. This shows that the graphite oxide had been effectively reduced to rGO. The characterized peaks were relatively steep and large because the functional groups which attached to the surface and edges have been reduced by heat and microwave. The authors also obtained the same results. In this case, the d-spacing increased from 0.335 nm to 0.703 nm. On XRD spectra of rGO-TiO2 catalyst (Fig. 2), characteristic peaks of TiO2 anatase phase appeared at 2θ of 25.3°, 37.8°, 48.1°, 55.1° and 62.7°, respectively, with the strongest intensity at 2θ of 25.3°. The different peaks of rGO almost disappeared on rGO-TiO2 (ratio of 1:25) probably due to disrupted layer-stacking regularity.

The rGO and rGO-TiO2 samples were investigated by FT-IR spectroscopy (Fig. 3). The FT-IR spectrum of rGO demonstrates the presence of low oxygenated functional groups with absorption peaks of alcoholic –OH bending band (ν = 1410 cm⁻¹), –OH bending band of water or C=O stretching band (ν = 1630 cm⁻¹), carboxylate or ketone C=O stretching band (ν = 1740 cm⁻¹), and the band of –OH groups on the surface (ν = 3420 cm⁻¹). In the case of the rGO-TiO2 catalyst, the oxygen-containing groups demonstrated the low intensity of absorption peak in the range of 1000–2000 cm⁻¹. However, the strong peaks in the range of 400–1000 cm⁻¹ could be attributed to a combination of the Ti–O–Ti and Ti–O–C stretching vibrations. The existence of Ti–O–C bonds in the rGO-TiO2 aerogel implies the chemical bonding between TiO2 and rGO.

SEM images of rGO showed that rGO has a relatively large surface area (Fig. 4(a)). These parameters indicate very good exfoliation of graphite during oxidation process. TiO2 particles tend to accumulate on the surface of the composite. SEM images of rGO-TiO2 also shows the nanostructures of the rGO-TiO2 (Fig. 4(b)), with the effective distribution of TiO2 nanoparticles on the surface to prevent agglomeration of rGO. The authors reported that TiO2 nanoparticles could be attached on rGO nanosheets via physical absorption, electrostatic binding or charge transferring interactions.
TEM image of the rGO nanosheet are shown in Fig. 5(a). The result showed the presence of wrinkles and folds on the sheet which is the characteristic of a few-layered rGO nanosheet. The TEM image of the sample rGO-TiO$_2$ (1:25) showed uniformly the dispersal of spherical morphology of anatase TiO$_2$ nanoparticles on rGO sheets (Fig. 5(b)). The TiO$_2$ nanoparticles are well separated from each other, it shows that aggregation was greatly prevented. The average particle size of the TiO$_2$ nanoparticles was observed by 10 nm. The particle size of rGO-TiO$_2$ catalyst was smaller and more uniform than that of the pure TiO$_2$ (25 nm). The specific surface areas of pure rGO, TiO$_2$, and rGO-TiO$_2$ nanocomposites were 313.2, 43.6 and 135.4 m$^2$·g$^{-1}$, respectively. Because rGO nanosheets were covered on surface of TiO$_2$, the rGO-TiO$_2$ sample showed specific surface area larger than the pure TiO$_2$. Therefore, the surface area of rGO-TiO$_2$ sample increased due to the synergetic effect of rGO. The large surface area leads to more of the pollutant molecules being able to be adsorbed on the large surface area, leading an increased photocatalytic degradation efficiency.

Band gap energy (E$_g$) of semiconductor in general is calculated by popular method based on light velocity c$^{28)}$. The relationship between (K$A\bar{h}$)$^{1/2}$ and (h$\bar{A}$) is built to determine band gap energy E$_g$ where K is reflectance from Kubelka-Munk transformation, it can be determined by the eq. (1) as follows:

$$K' = (1 - R)2/2R$$  

(1)

The Tauc plot of catalysts is showed in Fig. 6, where E$_g$ is determined at the point of intersection of the tangent line and the horizontal axis. Then, light wavelength threshold was calculated by the following equation:

$$E_g = \frac{hc}{\lambda} = \frac{h\bar{A}}{2}$$  

(2)

UV-Vis spectroscopy measurements and Tauc plot (Fig. 6) of catalysts indicated that rGO-TiO$_2$ composite enabled the extension the region of the photon absorption zone of TiO$_2$ towards the visible waves of 394–437 nm as well as reduce its band gap energy from 3.15 eV down to 2.84 eV. This may be due to the absorption contribution of rGO, the enhancement in surface charge of TiO$_2$, and the partial restoration of the π electron conjugation system as a result of the hydrothermal and chemical reduction process. $^{29}$

3.2 Photocatalytic activity of samples
According to previous investigations, the initial conditions of photocatalytic degradation of CA solution with the catalysts were determined as follows: catalyst concentration of 0.75 g·L$^{-1}$, Q$_{air}$ of 0.3 L·min$^{-1}$, initial solution pH of 7 and reaction temperature of 25°C. At these conditions, the CA conversion with rGO-TiO$_2$ nanocomposite catalyst in the different rGO/TiO$_2$ ratios was shown in Fig. 7.

As shown in Fig. 7, the CA concentration by rGO treatment is nearly unchanged after preadsorption of all samples in dark. This demonstrated that the degradation of CA had poor performance in adsorption conditions by using rGO. On rGO-TiO$_2$ catalysts, the more the ratio of rGO/TiO$_2$
increased from 1:10 to 1:25, the more the conversion of CA was. The highest photoactivity was reached at a ratio of 1:25. After 60 minutes, the conversion efficiency of CA (X_{60}) on samples reached 13%, 20%, 30% and 55%, respectively, with the exception of rGO/TiO_2 ratio of 1:30, it reduced to 28%. The rGO-TiO_2 nanocomposite with ratio of 1:25 that favorably worked in an acidic environment and showed higher activity than that of pure TiO_2 (X_{60} = 45%) in our previous work. This could be explained by the moving of photogenerated electrons from the valence band (VB) to the conduction band (CB) of TiO_2 and transported to the rGO nanosheets, leading to increasing superoxide ions formation. Hence, the delocalized electrons from the CB reside in the aromatic structure of rGO, suppressing their recombination with VB holes that led to the higher photocatalytic activity of rGO-TiO_2 composite. The 3D structure of the rGO-TiO_2 can hold the electrons for a longer time, which in turn forms more free radicals, including the OH and O_2^- to promote the degradation of CA solution (eqs. (3)-(6)). Additionally, the rGO can lessen the mass transferring constraint by increasing the availability of CA near the TiO_2 surface. As mentioned in our work, oxygen played an important role in the photocatalytic reaction, it assured the presence of sufficient electron scavengers to trap the excited conduction-band electron from the recombination. However, too much oxygen supply led to appearance of foams that interfered with the absorption of UV light by reaction solution. On the other hand, there was a decrease in the efficiency of CA treatment, a part of catalyst particles moved to the surface of the solution because of the air bubbles which were appeared by the supply of oxygen too much that lead to reducing the amount of catalyst in solution. So, the optimal air flow rate of 0.5 L·min^{-1} supplying for photoreaction was chosen.

The treatment of CA solution at pH 3.8 was higher than that at pH 5 and pH 7 (Fig. 8(b)). It reached 92% of treatment efficiency after 60 minutes of photoreaction. This may be due to the point of zero charge (PZC) of obtained rGO was found about 3.2–3.6. When the solution pH value was compared to PZC value such as solution pH value was approximate PZC value, the catalyst surface is the absence of electrostatic force, therefore the adsorption of the catalyst surface is not too high, so it is favorable for the reaction. At the solution pH value was less than PZC value, the surface of rGO-TiO_2 catalyst became a positive charge (i.e. TiO_2 + H_2O ↔ TiO_2H^+ + OH^-) and gradually exerted a force of electrostatic attraction which attracts the negatively charged compounds which can intensify the adsorption onto the photon activated TiO_2 surface for subsequent photocatalytic reactions. At solution pH value was higher than that of PZC value, the catalyst surface became negatively charged
(i.e. TiOH + OH− ↔ TiO2− + H2O) and repulsed the anionic compounds in water. The difference of pH level will affect the charge density of TiO2 catalyst surface. In addition, the pH 3.8 of solution possesses the quantity of H+ ions more than that of others. H+ ions should be able to combine with O2− radicals to generate HOO− radicals (eq. (7) and (8)) and improve the efficiency of CA degradation.

\[
\text{TiO}_2 (e^-) + O_2 \rightarrow O_2^- + \text{TiO}_2 \\
O_2^- + H^+ \rightarrow \text{HOO}^* 
\]

So, the pH 3.8 of initial solution was consistent for CA photodegradation with rGO-TiO2 (1:25) composite.

The optimal conditions of photocatalytic degradation of CA with rGO-TiO2 composite in the 1:25 ratio are as detailed: reaction temperature of 25°C, catalyst concentration of 0.75 g·L⁻¹, air flow rate of 0.5 L·min⁻¹, the pH of 3.8 initial solution. The treatment efficiency of CA solution reached 92%. In comparison with Fe-TiO2, Cr-TiO2 and N-TiO2, rGO-TiO2 composite showed higher photodegradability. The presence of rGO not only reduced particle size but also increased surface area and retarded the recombination of electrons and holes. Additionally, rGO may also owned functional groups for the efficient adsorption of CA. Therefore, the efficiency of CA conversion of rGO-TiO2 composite was higher than that of others.

The kinetics of CA degradation of the rGO-TiO2 (1:25) catalyst was determined to further demonstrate its photocatalytic activity (Fig. 9). CA concentration at different intervals of time was determined and substituted in the following formula:

\[
\text{−Ln(C}_t/C_0) = k \times t 
\]

where, k signs the apparent reaction rate constant, C₀ signs the initial concentration of CA, Cₜ signs the concentration of CA at the reaction time and t signs the reaction time. The straight line obtained in the kinetic indicate that the degradation of CA applies pseudo first order kinetics. The k values of the synthesized catalyst were calculated using the above formula (0.0424 min⁻¹). The results showed that the degradation rate of CA is quite fast over time on this optimal catalyst. The degradation of methylene orange (MO) and methylene blue (MB) by rGO-TiO2 catalyst in this study was compared to that of CA that was studied by H. Yu, where the apparent conversion rate constant of CA solutions was slower. It can be explained that the positive phenylamine (PhNH₂) molecules were loaded on the rGO-TiO2 surface (PhNH₂/rGO-TiO2) increasing preferential adsorption of targeted MB and MO. The k of CA photocatalytic degradation by rGO-TiO2 catalyst in this work was much higher than that of MB with rGO-CeO₂ catalyst (k = 0.0226 min⁻¹), and that of the pure TiO2 catalyst (k = 0.0115 min⁻¹).

4. Conclusion

rGO-TiO₂ composites were successfully prepared by hydrothermal method, in which rGO was synthesized from graphite powder according to modified Hummers method by using microwaves. The obtained rGO-TiO₂ sample with the rGO/TiO₂ ratio of 1:25 exhibited a mesoporous structure and TiO₂ nanoparticles uniformly anchored onto the rGO nanosheets. The modification of TiO₂ by combination with rGO has significantly reduced the single particle size of catalyst and increased the total surface specific area of catalyst from 43.6 m²·g⁻¹ up to 135.4 m²·g⁻¹ as well as extended the region of the photon absorption of nanocomposites towards the visible waves (394–437 nm). Comparing to the pure TiO₂, rGO-TiO₂ (1:25) nanocomposite did not only improve photocatalytic activity but also reduced initial pH solution from 7 down to 3.8 (not adjust pH of reaction solution) in the photodegradation of CA solution. After 60 minute reaction, the conversion efficiency of cinnamic acid reached approximately 90%. These results contributed to demonstrate that rGO-TiO₂ nanocomposites have greatly potential in the photodegradation of aromatic compounds as well as recalcitrant surfactants.

REFERENCES