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Research Article

Investigating for Photocatalytic Activity of Hybrid TiO_2/Reduced Graphene Oxide and Application in Reducing VOCs

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Abstract

In this study, rGO/TiO_2 hybrid nanostructures (rGO : reduced Graphene Oxide) have been successfully fabricated for the purpose of application in the treatment of volatile organic compound (VOCs) that harmful for the environment through the method of directly measuring the change in concentration of decomposed VOCs in real time under UV-excited conditions using a home-made measuring system. the results showed that hybrids TiO_2 : rGONFs (reduced Graphene Oxide nano flake) samples with the weight ratio between two kind of material are 99%:1% and 98%:2% which reduced VOCs faster than 2 time intrinsic TiO_2. The phenomenon of 2D materials involved in the hybrids lead to the fact that the photocatalytic activity of TiO_2 had been significantly improved, this can be explained as follows: When heterogeneous hybrid was formed, because of the difference in energy levels of conduction band between two materials was negligible, heterojunction barrier is not too high this made the photogenerated electrons from TiO_2 easily move through rGONFs under UV stimulation. This thing has significantly reduced the recombination of the generated carrier in TiO_2 during irradiation, which lead to an increase in the lifetime of the carrier and make photocatalytic reaction of the assembly become more effective.

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Keywords: rGO; TiO2; nanocomposite; photocatalysis; VOCs

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1. Introduction

Along with the development of industry and urban modernization, environmental pollution issues are increasing critically with many different types of pollutants in which volatile organic compounds (VOCs) being a direct cause of harm to human health [1–3], especially cancer. Facing with the above situation, the need for a safe and effective solution that can thoroughly decompose solid and gaseous wastes is extremely urgent. Photocatalytic oxidation (PCO) reaction is considered one of the most effective methods toward decomposing organic wastes under appropriate lighting conditions [4–7].

In recent years, nanostructured metal oxide semiconductors, such as TiO_2, SnO_2, ZnO, WO_3, CuO, have been receiving considerable attention from researchers in applications of habitat improvement [8–10]. In particular, TiO_2 was specific interested by scientists because of its advantages for a photocatalyst such as: high optical efficiency, good chemical stability, low cost and environmental friendliness [11–14]. However, the intrinsic TiO_2 itself still has certain limitations like large band gap (3.2 eV in Anatase phase) [15,16] and high photo-induced charge

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recombination rate [17], which reducing remarkablely the catalytic efficiency of this material. Thus, methods of modifying surface and constructing nano material heterostructure (hybridization) have been developed and reseached as an effective solution to improve the photocatalytic activity of TiO_2 [18–21]. With outstanding physical and chemical properties, the 2D layer material group is promising candidate for combining with TiO_2 to enhance the efficiency of photocatalytic processes.

After Novoselov and Geim discovered the monolayer structure of Carbon atoms by exfoliating Graphite flake in 2004 [22], Graphene materials quickly is attracted the attention of researchers due to its many outstanding advantages such as: large surface area ratio, good carrier transfer ability, high mechanical strength and flexible properties. However, the band gap of Graphene ~ 0 eV [22] that makes the applicability to optical processes of this material become limited. Instead of that, making a hybrid of Graphene with other semiconductors is seen to be a better way to increase the efficiency of the optical activities for host materials because of their superior electrical conductivity of Graphene allows it to efficiently receive and transfer photogenerated carriers.

Graphene oxide (GO) is an oxidized derivative of Graphene with functional groups that make many speciffic physical and chemical properties for this material, these functional groups can be removed by chemicals or heat to create reduced-Graphene Oxide (rGO) a substance that quite similar to Graphene. In many cases, rGO is often seen as an alternative version of Graphene, as this material also has a large surface area similar to Graphene. Beside that, GO and rGO can be easily synthesized and less expensive. The product obtained after the reduction still has a small amount of functional groups on the surface of the material, the results of author group of Wang Yu [23] have shown that these groups make rGO have more advantaged in bonding.

In previous experimental studies, the photocatalytic properties of intrinsic TiO_2 under UV have been reported has showed magnificent results in environmental applications [24]. However, the life time of electrons in this material very short, so reducing the recombination of the charge carriers becomes one of the most important factors to raise the photocatalytic performance. In this work, we focus in investigating the contribution of rGO to photocatalytic efficiency of TiO_2.rGO nano flake and hybrid TiO_2/rGO was synthesised with the different rate of mass in the direction that increasing the concentration of 2D material and reducing with the host. The samples was use in decomposing the taget gas (toluene) determined by a real-time direct measurement.

2. Materials and Method

2.1 Synthesis of Aqueous GO Dispersion

We prepared graphene oxide (GO) solution from the modified Hummers' method. For a detailed description, 0.2 g of Graphite flake (Merck, 98%) were mixed with 46 mL of H_2SO_4 (Merck, 98%), at 0 °C, 0.6 g of $KMnO_4$ (Merck, 93.5%) were added in small amounts. After 2 h of mixing, the solution is stirred at room temperature for 30 min. The mixture was diluted with 92 mL of deionized (DI) water and incubated at 90 °C for half an hour. Finally, 5 mL H_2O_2 (Merck, 30%) was added to this suspension, The solution turned into yellow-brownish that was GO. This solution was continued to be centrifuged at 5,000 rpm for 5 min to separate the solid material at the bottom. Finally, the residual acid in GO was washed by DI water until pH ~ 7. GO product would be dispersed into solvent (aceton/ethanol) to form GO solution with concentration ~ 2 mg/mL. Depending on the intended use, this GO solution can be ultrasonically pulverizated at high power (80 W) for uniform small GO pieces (called nano sheet GO).

2.2 Synthesis of Hybrids TiO_2/rGO

To synthesis the TiO_2/rGO hybrid, we do follow steps: The GO (2.0 mg/mL) and TiO_2 (Merck, 99%) (4.0 mg/mL) solutions were mixed under ultrasonic pulverizated condition for half an hour, the mixture was continuously added 0.15 mL hydrazine monohydrate (Merck, 98%) and stirred in 10 min. After the above stage, the solvent is removed by heat, leaving a gray-white powder. Finally, the powder was subjected to a thermal shock at 350 °C for 5 min, the result was a solid powdered TiO_2/rGO hybrid. For the purpose of investigating the enhanced activity of host materials which hybride with nano sheet rGO, the mass ratio of TiO_2:rGO samples were changed to 99:01 and 98:02, respectively. To simplify, the hybrid samples are abbreviated to TiO_2-rGO (99:1), TiO_2-rGO (98:2) with rGO content of 1% and 2%.

2.3 Material Characterizations and Photocatalysis

The structure and surface morphology of rGO and TiO_2/rGO hybrid materials were described through Raman spectroscopy in region of 1000 – 3000 cm^{-1}, X-ray diffraction (XRD) analysis was carried out using a Bruker D8-Advance diffractometer with 2θ = 20°-80° under Cu-K_α excitation (wavelength, λ = 0.15418 nm, voltage = 40 kV, current = 10 mA) and images from "Tescan VEGA-II LSU" scanning electron microscope (SEM). Meanwhile, the Fourier transform infrared method ("Bruker EQUINOX 55" spectrometer, spectral region from 500–4000 cm^{-1}) allows to determine the composition of substances in the compound of TiO_2/rGO hybrid.

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To facilitate for estimating photocatalic properties of materials, we built a home-made system to detect VOCs and other vapor organic compounds (Figure 1). The system consists of the following main components: Airtight metal chamber (2l) independent of the outside environment, the parameter of temperature T = 40 °C and humidity RH = 60% were maintained stably during the survey. Each of PCO experiment, a fixed amount of Toluene (40 µL) was vaporied and injected into the chamber. This Toluene vapor will be loaded and continuously circulated in the chamber by a flow of Argon gas at the rate of 5 mL/s through a diaphragm pump, the UV light source used is 20 W UV-A (λ_{peak} = 355 nm, 0.8 mW/cm^2),VOCs concentrations were measured and recorded by a gas sensor PQN-3835 (made in Korea).

3. Results and Discussion

3.1 Morphology and Structure of Nano Materials

3.1.1 rGO nano sheet

Raman shift (Figure 2(a)) were used to characterize disordered patterns in the Carbon lattice, in which three major peaks appeared at the positions of 1344 cm^{-1}, 1588 cm^{-1}, and 2655 cm^{-1} corresponds to the D, G, and 2D bands respectively (characteristic band of this material). Besides, the SEM image (Figure 2(b)) also shows in detail the surface morphology of rGO, the pieces are separated from each other with small size of about 10 – 20 nm and relatively uniform that can be called as nano sheet.

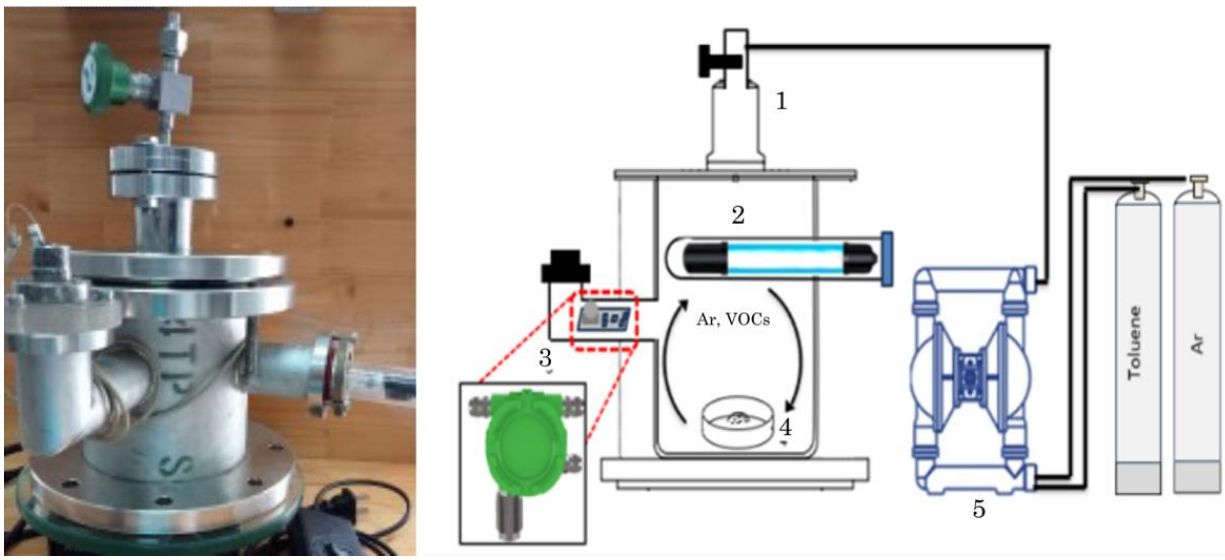

Figure 1. VOCs measurement system: (1) Gas supply valve to the system, (2) UV source, (3) VOCs gas sensor PQN-3835, (4) Sample, (5) Diaphragm pump.

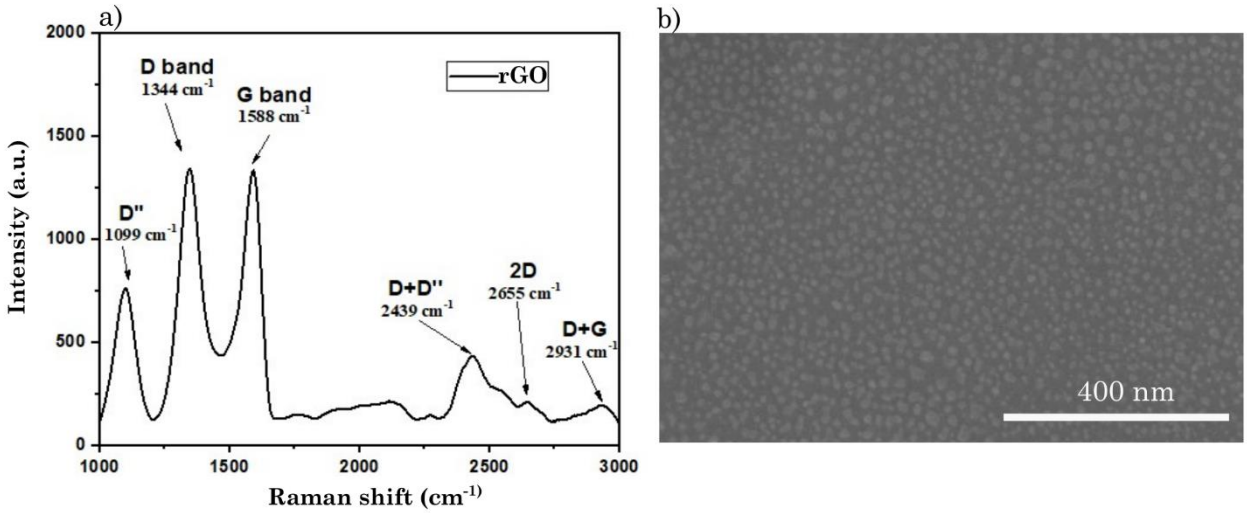

Figure 2. Structural and morphological analysis of rGO (a) Raman spectroscopy, (b) SEM image

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3.1.2 Hybrid rGO/TiO_2

The characteristic structures of pure TiO_2 and TiO_2/rGO hybrid materials were analyzed through XRD patterns. The results shown in Figure 3(a) determining the existence of characteristic diffraction peaks of TiO_2 (anatase phase) at angles 2θ = 25.3, 37.80, 48.1, 53.9, and 55.1 corresponding to the lattice families (101), (004), (200), (105) and (211), respectively. However, the formation of peaks representing rGO material was not detected in the TiO_2/rGO hybrid and the structure of the TiO_2 host material was not affected by high-power ultrasound and thermal annealing processes. Therefore, the FT-IR spectroscopy combined with SEM images are used to determine the components present in the TiO_2/rGO hybrid sample. Specifically, the SEM image shows the formation of small rGO pieces with sizes from 20 nm to 30 nm scattered on the surface of TiO_2 nanoparticles as shown in Figure 3(b). In addition, the results recorded from the infrared spectrum (Figure 3(c)) also show that in addition to the appearance of spectral peaks of TiO_2, in the survey sample, there are also peaks at positions 1066 cm^{-1} and 1461 cm^{-1} which are characteristic for C–O (Epoxy group) and C–C bonds in GO materials, respectively. It is worth noting that the appearance of another peak found at position 745 cm^{-1} representing the Ti–O–C bond, indicates the formation of a stable binding state between TiO_2 and rGO. This result has also been reported in similar studies in which Chen Ying's group is typical [25].

3.2 The Ability to Decompose VOCs of the TiO_2/rGO Hybride

The application of nanostructured materials to decompose volatile organic compounds into substances that are harmless to the environment and human health through photocatalysis is a research trend that has been interested in recent years. In this study, the photocatalytic activity of TiO_2 nanoparticles and TiO_2/rGO hybrid material with Toluene test gas acting as VOCs was determined through real-time direct measurement. Specifically, after the test samples had been exposed to UV light for 4 h, the change in the concentration of VOCs (Δ_{PCO}) was recorded and calculated according to the following formula:

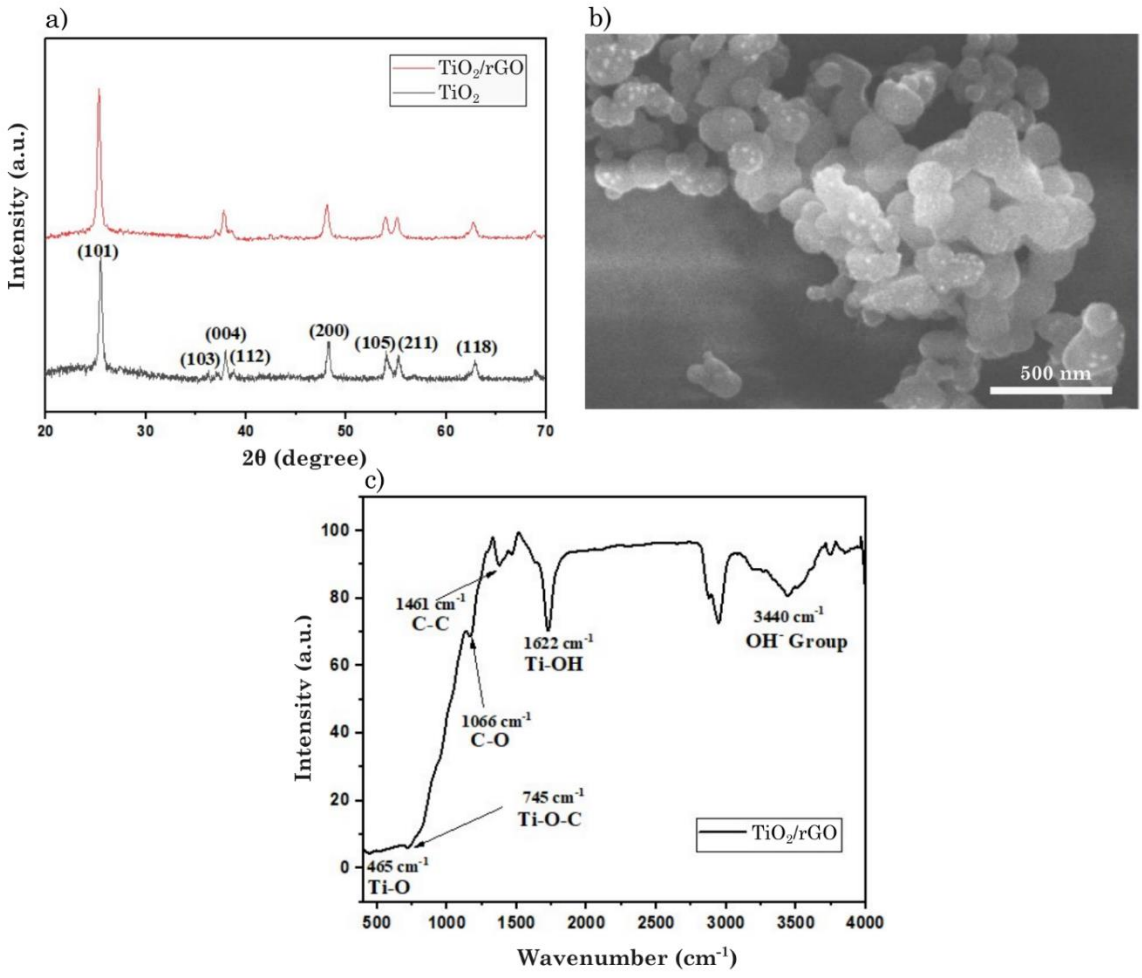

Figure 3. Structural and morphological analysis of TiO_2/rGO: (a) XRD pattern; (b) SEM image; (c) FT-IR spectra.

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$$\Delta_{PCO}(\%) = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

in which, C_0 (ppm) and C_t (ppm) are the concentrations of toluene gas at the start and end time, respectively.

The main purpose of this study is to investigate the enhancement of photocatalytic capabilities of 2D materials rGO on TiO_2 host material. Thereby, measurements of the concentration of VOCs in each respective time point were carried out with 2 types of materials, pure TiO_2 and TiO_2/rGO hybrid. A constant amount of Toluene vapor (40 µL) is injected into the system and continuously circulated in the reaction chamber by a diaphragm pump. Changes in test gas concentration were continuously recorded through the PQN-3835 sensor during the reaction.

Figure 4(a) shows performance of Toluene gas decomposition catalyzed by pure TiO_2 samples with 4 curves corresponding to the test samples with mass of 300 mg, 400 mg, 500 mg, and 600 mg. First, it can be seen that the concentration of Toluene decreases by half in less than the first hour. At subsequent time intervals, the rate of organic gas treatment tends to slow down and gradually approach minimum constant values. Actual data also shows that after 4 h of reaction, the amount of VOCs decomposed Δ_{PCO} in TiO_2 (300 mg), TiO_2 (400 mg), TiO_2 (500 mg), and TiO_2 (600 mg) samples were: 84%, 86%, 91%, and 97%, respectively. Thus, the efficiency of the photocatalysis process increases gradually with the increase of the amount of TiO_2 material.

To investigate the effect of rGO on the photocatalysis of the TiO_2 host material, we selected a 300 mg TiO_2 sample to compare the

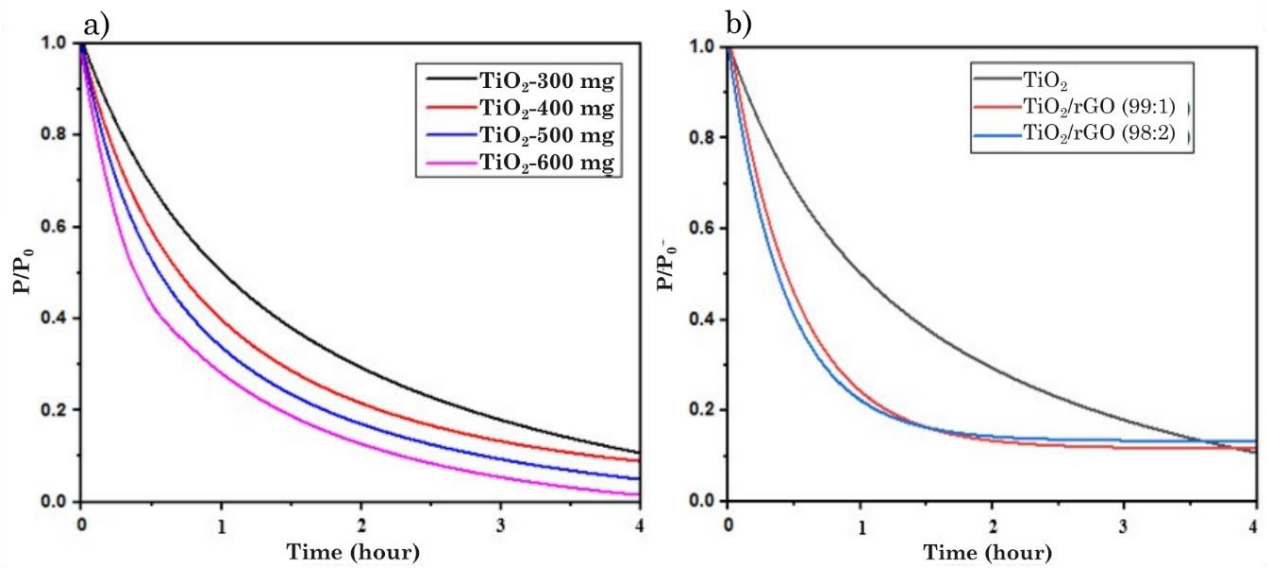

Figure 4. Photocatalytic of: (a) pure TiO_2, (b) TiO_2/rGO.

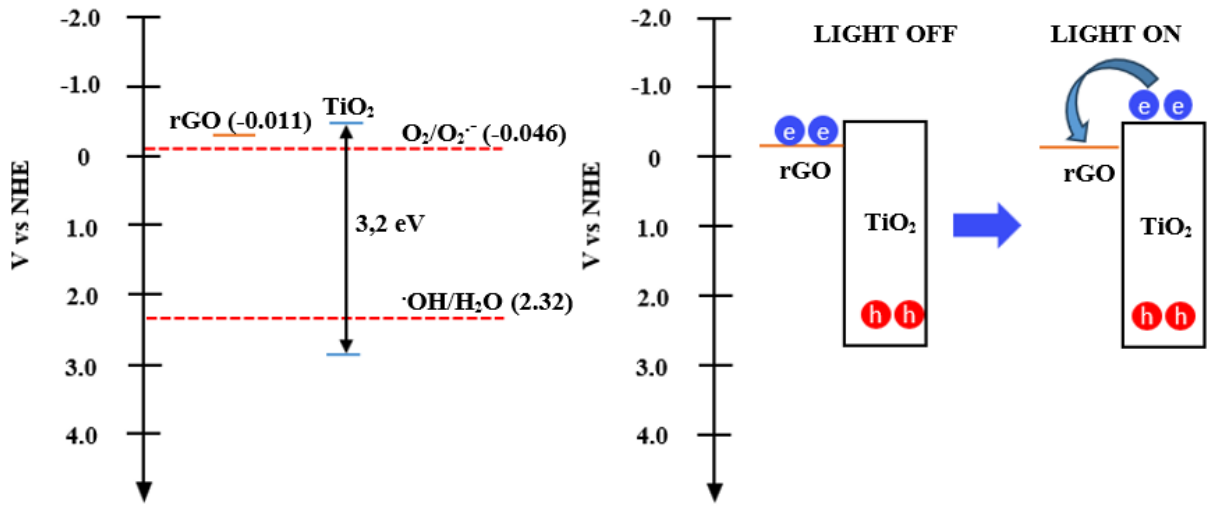

Figure 5. Scheme of energy of TiO_2 and rGO

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catalytic efficiency between pure and hybrid materials. In which, the hybrids samples were prepared according to the mass ratio between TiO_2 and rGO of 99%:1% and 98%:2%, respectively. All measurement parameters and conditions remained the same as the previous experiment. The results shown in Figure 4(b) indicate that although the mass of TiO_2 has decreased, with the participation of rGO, the two hybrids' samples show a superiority in Toluene decomposition compared to the pure TiO_2 sample. Specifically, similar to the pure TiO_2 sample (300 mg), the TiO_2/rGO hybrid samples all degraded ~85% of the original VOCs, however, the organic matter decomposition rate in the hybrid sample was ~4 times faster when after only 1 h the Toluene concentration decreased to a minimum constant value (the 300 mg pure TiO_2 sample needed 4 h to reach this value).

From the above results, we confirmed that rGO material played a key role in promoting the enhancement of the photocatalytic activity of the TiO_2 host material. This can be explained as follows: with the formation of the heterojunction, due to the small difference in energy levels of the two materials, a low potential barrier is formed in the energy band structure of the hybrids (described in detail in Figure 5). The photogenerated electrons in TiO_2 easily moved across this barrier, causing the recombination of the photogenerated carrier in TiO_2 to decrease during irradiation, resulting in an increase in the lifetime of the photogenerated carrier leading to a significant improvement in the photocatalytic efficiency. The study of the author group Ho [2] on the hybridization of Tianium Oxide with another 2D material, Phosphorene, also shows similarity with ours.

4. Conclusions

In summary, we demonstrated that rGO materials and TiO_2/rGO hybrid materials has been successfully synthesized with the desired morphology and material properties. In particular, rGO nanosheets possess large and uniform sheets along with well dispersion. Moreover, the TiO_2/rGO composite material exhibits a good combination in which TiO_2 nanoparticles is well decorated on the surface of rGO. The excellent dispersion and attachment of TiO_2 is originated from Ti-O-C bonding interaction between TiO_2 and rGO which can be confirmed by FTIR spectra. The efficiency of photocatalytic reaction of TiO_2/rGO hybrid materials (with mass ratio 99%:1% and 98%:2%) showed photocatalytic performance of degradation toward toluene gas in comparison with pure sample in which toluene gas decomposition occurs at the rate more than twice as fast. This result leads to, in presence of rGO material that reduced the recombination rate of photogenerated electrons and holes and enhances the charge seperation in TiO_2 materials under irradiation; thus, leading to photocatalytic performance under UV irradiation was significantly improved. This research can provide a new route for designing and developing next generations of TiO_2-based catalyst.

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CRediT Author Statement

Author Contributions: *N.T.P. Thanh, T.Q. Nguyen, and L.T.T. Giang*: Experiments, Methodology, Review and Editing, Investigation; *H.V. Giang*: Data Curation; *N.T. Danh, T.K. Chi*: Data Curation, Investigation, Writing Draft Preparation; *T.Q. Trung*.: Supervision. All authors have read and agreed to the published version of the manuscript.

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