

# Photocatalytic Performance of Graphene-TiO<sub>2</sub> Hybrid Nanomaterials Under Visible Light

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**Abstract:** This study describes the development of graphene-TiO<sub>2</sub> conjugates for the enhancement of the photocatalytic efficiency of TiO<sub>2</sub>. Graphene-based hybrid nanomaterials have attracted considerable attention because of the unique and advantageous properties of graphene. In the proposed hybrid nanomaterial, graphene serves as an electron acceptor to ensure fast charge transfer. Effective charge separation can, therefore, be achieved to slow down electron-hole recombination. This results in an enhancement of the photocatalytic activity of TiO<sub>2</sub>. In addition, increased adsorption and interactions with the adsorbed reagents also lead to an improvement in the photocatalytic activity of graphene-TiO<sub>2</sub> hybrid nanomaterials. The acquired result is encouraging in that the photocatalytic activity of TiO<sub>2</sub> was initiated using visible light (630 nm) instead of the typical UV light.

**Keywords:** Graphene, TiO<sub>2</sub>, Photocatalyst, Hybrid nanomaterial

## 1. INTRODUCTION

Graphene (G)/semiconductor hybrid nanomaterials have demonstrated high potential in enhancing the photocatalytic efficiency of semiconductor nanomaterials [1-10]. There are various materials that show photocatalytic properties, among which, TiO<sub>2</sub> is one of the most widely used heterogeneous photocatalysts [11]. It has excellent physical and chemical stability, electronic and optical properties, and is inexpensive. However, TiO<sub>2</sub> suffers from a large band gap (3.2 eV for anatase TiO<sub>2</sub>) which requires activation by UV light, and a fast electron-hole recombination rate which reduces its photocatalytic efficiency [11,12].

G-TiO<sub>2</sub> hybrid nanomaterials in the literature are mostly prepared by hydrothermal, solvothermal and hydrolysis

reactions [2,3,13-15]. In these cases, graphene oxide (GO) instead of pristine graphene was used. The hybrid materials were prepared by reducing GO in the presence of a TiO<sub>2</sub> precursor [titanium (IV) isopropoxide, titanium (IV) fluoride, titanium (IV) butoxide], resulting in the deposition of TiO<sub>2</sub> particles on the surface of reduced GO. Because reduced GO was used, oxygen-containing species remained and could not be removed completely even after reduction. These defects disrupt the conjugated structure and the electron conduction of graphene [16]. To overcome this issue, we propose to synthesize G-TiO<sub>2</sub> photocatalysts using pristine graphene and pre-made TiO<sub>2</sub> nanoparticles. The goal is to develop high performance G-TiO<sub>2</sub> hybrid nanomaterials with enhanced photocatalytic properties under visible light.

In this hybrid nanomaterials, graphene (G) acts as an electron acceptor to ensure fast charge transfer. Effective charge separation can therefore be achieved to slow down the electron-hole recombination, and as a result, the photocatalytic activity of TiO<sub>2</sub> is enhanced [2,8,17]. Moreover, because graphene can absorb light in the visible region, the photo-excitation wavelength can be extended from

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UV to visible (400~700 nm) [18]. An absorbed photon promotes an electron from graphene, then the electron transfer from graphene into  $\text{TiO}_2$ . Consequently, the photocatalytic reactions can be carried out using the visible light instead of UV. In addition, the large surface area of graphene will increase the concentration of adsorbed reagents as well as the surface interactions [1]. The increased adsorption and interactions with the adsorbed reagents lead to enhanced photocatalytic activities of G- $\text{TiO}_2$  hybrid nanomaterials [2-5].

## 2. METHOD FOR EXPERIMENT

### 2.1 Materials

Methyl pentafluorobenzoate (>97%), sodium azide, graphite flakes (Sigma), AEROXIDE®  $\text{TiO}_2$  P25, acetone, ethyl ether, methanol, triethylamine (>99%), N-methyl-2-pyrrolidone (NMP), hydrochloric acid (37%) were purchased from Sigma-Aldrich, and were used as received without any further purification.

### 2.2 Preparation of PFPA-COOH

4-Azido-2,3,5,6-tetrafluorobenzoic acid (PFPA-COOH) was synthesized following the previously reported protocol [19-21]. Sodium azide was added into solution of methyl 2,3,4,5,6-pentafluorobenzoate in acetone/water (8:3) mixture and then refluxed for 8 h. The azide replaced F in the para-position through a nucleophilic aromatic substitution reaction. The resulting was then hydrolyzed to PFPA-COOH by stirring with 10% NaOH in methanol overnight at room temperature. The solution was neutralized by adding 1 M HCl into the solution until reached pH 3. The compound was extracted with chloroform followed by drying under sodium sulfate. After filtration, the solvent was then removed under vacuum to obtain PFPA-COOH as a pale yellow solid.

### 2.3 Preparation of G- $\text{TiO}_2$ hybrid nanomaterials

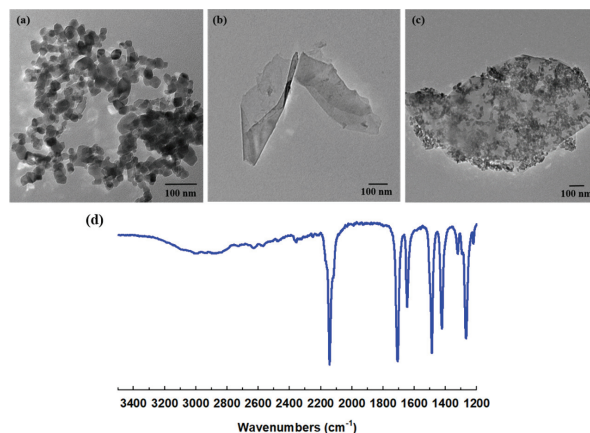
The  $\text{TiO}_2$  particles were functionalized with PFPA-COOH and then covalently conjugated on FLG flakes via UV irradiation for 30 min [22]. For detail,  $\text{TiO}_2$  nanoparticles

were placed in a solution of PFPA-COOH in methanol and the solution was stirred at room temperature for overnight. Unmodified  $\text{TiO}_2$  nanoparticles were removed by centrifuged by repeating 3 times. Liquid phase exfoliated few layer graphene were used in this research. A suspension of G flakes in NMP was mixed with a suspension of PFPA- $\text{TiO}_2$ . The mixture was irradiated with 450 W medium pressure Hg lamp (Ace Glass Inc., Vineland, NJ, USA) for 30 min while stirring. A 280 nm long-path optical filter was placed on top of the samples during irradiation. The resulting reaction mixture was then washed and centrifuged for 3 times.

## 3. RESULTS AND DISCUSSION

Figure 1 shows the transmission electron microscopy (TEM) images and IR spectrum of (a) PFPF- $\text{TiO}_2$ , (b) G, (c)  $\text{TiO}_2$  modified G, and (d) PFPA- $\text{TiO}_2$ . The average  $\text{TiO}_2$  nanoparticles size were 21 nm, measured by TEM. In the IR spectra (Fig. 1(d)), the strong absorption at 2,130 and 1,700  $\text{cm}^{-1}$  due to asymmetric stretch of the azido group and carbonyl group stretching indicating the  $\text{TiO}_2$  nanoparticles have been successfully functionalized with PFPA. After conjugation, nanoparticles were clearly visible on the graphene sheet (Fig. 1(c)).

The particles were placed throughout the sheet although possibility exists that the edges could fold over the basal plane. Control experiments using unfunctionalized  $\text{TiO}_2$



**Fig. 1.** TEM images of (a) PFPF- $\text{TiO}_2$ , (b) graphene flake, (c) G- $\text{TiO}_2$ , and IR spectra of (d) PFPA- $\text{TiO}_2$ .

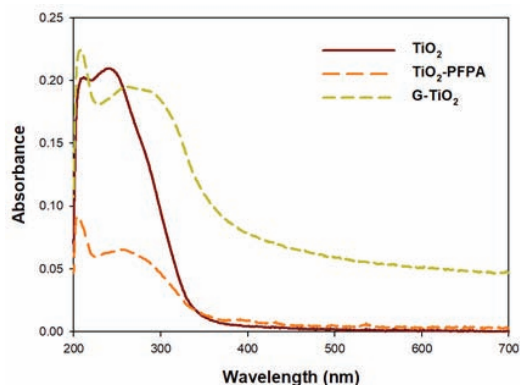


Fig. 2. UV-vis spectra of (a) TiO<sub>2</sub>, (b) TiO<sub>2</sub>-PFPA, and (c) G-TiO<sub>2</sub>.

nanoparticles were carried out under the same experimental conditions and almost no particles were observed on graphene flakes [22].

The UV-Vis spectrum of G-TiO<sub>2</sub> shows a red-shifted absorption compared to TiO<sub>2</sub>, which is absent in TiO<sub>2</sub> and strong absorption in the visible light range (400~700 nm) (Fig. 2). The red-shift of  $\lambda_{\max}$  means the narrowing of the band gap after graphene conjugation. The extended light absorption in the visible region extends the photo excitation wavelength to 400~700 nm, which is a more efficient utilization of the solar spectrum to achieve photocatalysis.

The singlet oxygen sensor green (SOSG, Invitrogen) was used to characterize the photocatalytic activity of the materials. Singlet oxygen is generated when the excited electrons from the photocatalyst are trapped by oxygen in the aqueous solution [23,24]. In the presence of singlet oxygen, SOSG emits a green fluorescence, and the fluorescence intensity increases with the concentration of the singlet oxygen [25].

The experiment was carried out by mixing 10  $\mu\text{g}$  of graphene, TiO<sub>2</sub>, or G-TiO<sub>2</sub> with 2.0  $\mu\text{M}$  SOSG in pH 7.4 PBS buffer, and irradiating the sample with a LED lamp (UHP-Mic-LED-630, Prizmatix) at 630 nm. Fluorescence (525 nm, at 510 nm excitation) was measured every 10 min and the data are reported as  $I/I_0$ , where  $I$  is the fluorescence intensity and  $I_0$  is the initial fluorescence intensity before irradiation (Fig. 3). The fluorescence intensity increased with irradiation time for SOSG due to the degradation of SOSG in solution [26]. Addition of TiO<sub>2</sub> or graphene gave the same result as the SOSG alone. When

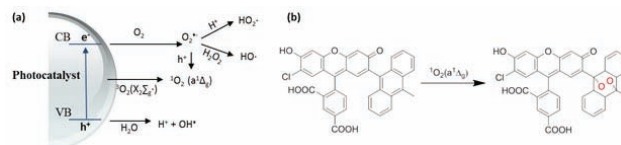


Fig. 3. (a) Photocatalysis mechanism and (b) reaction of SOSG with singlet oxygen. The endoperoxide of SOSG product is highly fluorescent (excitation/emission maxima ~504/525 nm).

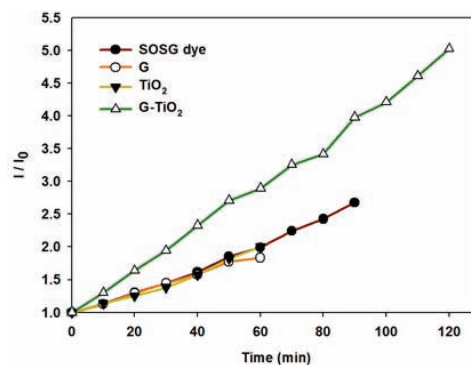


Fig. 4. Photocatalytic activity measurement, measured as  $I/I_0$  (excitation 630 nm).

G-TiO<sub>2</sub> was added, however, the fluorescence intensity increased much more than those of TiO<sub>2</sub> or FLG (Figure 4). The result is encouraging that the photocatalytic activity of TiO<sub>2</sub> was initiated using the visible light (630 nm) instead of UV.

#### 4. CONCLUSION

In summary, we have successfully synthesized G-TiO<sub>2</sub> hybrid nanomaterial. The materials prepared in this research synthesized by covalently attaching P25 TiO<sub>2</sub> nanoparticles onto pristine graphene using the PFPA-mediated coupling chemistry. The mechanism of functionalization of PFPA chemistry on graphene has been proved in our previous study [9,22]. This hybrid nanomaterial showed enhanced photocatalytic activity under the visible light (630 nm) irradiation. The enhanced activities can be attributed by the strong interactions between graphene and the conjugated materials. We believe that the G-TiO<sub>2</sub> hybrid nanomaterial prepared in this study should pave the way for the fabrication of high performance graphene-based photocatalyst that can be activated using visible light.

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