Chemical Identity and Applications of Graphene-Titanium Dioxide

Graphene is a single, two-dimensional nanosheet of aromatic sp² hybridized carbons that enhances the performance of photocatalysts.¹ The most prominent graphene-based photocatalyst is graphene oxide-TiO₂ (GO/TiO₂), the result of graphene oxide’s unpaired π electrons bonding with titanium atoms on the surface of TiO₂.² Though TiO₂ is a widely used and relatively-effective photocatalyst on its own, combining it with graphene oxide (GO) greatly intensifies its photocatalytic abilities. As a good electron collector and transporter, graphene is able to hinder the recombination of photogenerated electron-hole pairs.¹ This hindering is due to being graphene a zero-gap two-dimensional semimetal with a small amount of overlap between its valence and conductance bands, enabling charge carriers that behave as Dirac fermions to move with little scattering under atmospheric conditions.³ Moreover, when TiO₂ is bound to graphene oxide, it increases the absorption of light and extends the light absorption range, which improves the amount of solar energy obtained compared to TiO₂ typical 3%-5% absorption.¹ With these improvements, GO/TiO₂ is a greatly desired photocatalyst for its heightened ability for carbon dioxide reduction, water oxidation, hydrogen synthesis, and the conversion of CO₂ to methanol.⁴ The photocatalytic conversion of CO₂ to hydrocarbons like methanol is potentially the most important application of GO/TiO₂.⁴ The conditions for this redox reaction to occur are quite simple: ambient conditions, CO₂ and water present, and light. As long as light is provided, GO/TiO₂ will continuously oxidize water and reduce CO₂ (Scheme 1).⁴ The highlight of using this photocatalyst is that it is non-toxic, relatively low cost, chemically stable, and readily available.
Scheme 1. Photocatalytic CO\textsubscript{2} Reduction to Methanol and Water Oxidation


Preparation, Structure, and Function of Graphene Oxide/TiO$_2$

A direct and simple method to combine graphene oxide (GO) with semiconductors would be through the process known as solution mixing.$^5$ TiO$_2$ and GO nanocomposites can be prepared using a simple colloidal blending method: sonication and stirring brings about the chemical interaction between surface hydroxyl groups of TiO$_2$ and functional groups of GO and leads to the formation of Ti–O–C bonds in the nanocomposites.$^5$ Electrostatic interaction is the driving force behind this formation. The addition of the graphene oxide co-catalyst provides enhanced activity for the photocurrent generated by TiO$_2$ compared to pure TiO$_2$.$^6$ This allows for more reactivity such as hydrogen production of carbon dioxide reduction.$^6$ The composites also showed an increase in the photoresponsive range of the TiO$_2$.$^6$ The concentration of graphene oxide in starting solution helped to determine the photoelectronic and photocatalytic ability of the GO/TiO$_2$ composites (GOT).$^6$ The design of the GOT is a three-dimensional contact between the Graphene Oxide and the TiO$_2$.$^7$ It is important that the semiconductor species be covered both densely and uniformly in order to maximizes the interaction between two composites, which facilitates the charge separation and the reactivity of the photocatalyst.$^{5,7}$

![Diagram of Graphene Oxide Sheet](image)

**Scheme 2. Synthesis of Graphene Oxide/TiO$_2$ Composites and Graphene Oxide Structure**


Spectroscopic Characterization of Graphene-Titanium Dioxide

The UV-Vis absorption spectrometer measured for various GOTs with different carbon element contents (Figure 1). This showed how varying GOTs change the absorbance of different light energy. Raman spectroscopy is a powerful tool to characterize the crystalline quality of carbon. The Raman spectrum of GO (Figure 2) shows the presence of D, G, and 2D bands at 1340, 1585, and 2701 cm\(^{-1}\), respectively. The G band is common to all sp\(^2\) carbon forms and provides information on the in-plane vibration of sp\(^2\) bonded carbon atoms. Figure 3 shows the diffuse reflective spectra of GO/TiO\(_2\) samples with various amounts of GO (0-1 wt\%). The absorption intensity increases as GO content is increased because GO/TiO\(_2\) absorbs is able to absorb in the entire visible region with the presence of graphitic carbons. To exemplify the enhanced effectiveness of graphene oxide combined with TiO\(_2\), Figure 4 shows how GO/TiO\(_2\) has a much higher level of intensity range and will therefore be able to obtain more solar energy and perform more effectively.
Figure 1. UV–vis absorption spectra of graphene oxide/TiO$_2$ composites (GOT): carbon element contents of GOT-A, GOT-B, GOT-C, GOT-D, and GOT-E are 0.14, 0.15, 0.13, 0.25, and 0.51 wt %, respectively.\textsuperscript{8}
Figure 2. Raman spectra of (A) graphene oxide/TiO$_2$ composites (GOT).
**Figure 3.** Diffuse reflectance UV/Visible spectra of GO (x wt%)/TiO$_2$ composites (x = 0–1.0). The inset shows the magnification of the absorption edge region.$^9$
Figure 4. Raman spectra of GO, TiO$_2$ and GO (1 wt%)/TiO$_2$ showing graphitic modes.
