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A Contemporary Assessment on Composite Titania onto Graphitic Carbon Nitride-Based Catalyst as Photocatalyst

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Abstract

Titanium dioxide (TiO_2) has drawn widespread interest by researchers as a precious semiconductor that is responsive towards photodegradation of various pollutants. This catalyst has its own limitations such as fast electron-hole recombination, wide band gap, and can only be utilised under ultraviolet (UV) region. In order to overcome these problems, the addition of a metal-free dopant is a common practice to prevent electron-hole recombination and enhance photodegradation under visible light. Among various types of metal-free catalysts, carbon nitride material has received much attention due to its numerous benefits such as good in terms of physical and chemical strength, as well as an attractive electronic band combined with a band gap (2.7 eV). This review summarised recent works in the development of titania incorporated with graphitic carbon nitride (g-C_3N_4) for enhanced photocatalytic activity.

Keywords: Photocatalyst; titanium dioxide; graphitic carbon nitride; heterojunction; visible light.

1.0 INTRODUCTION

Recently, the industrial development has caused a major threat towards aquatic life and the environment. This is due to industrial wastewater production such as from pesticides, heavy metals, dyes, pharmaceuticals, and personal care products, which are not simply biodegradable [1, 2]. The utilisation of polluted water resources that are toxic and carcinogenic often leads to human health problem and aquatic life threat [2]. Therefore, many researchers have created various methods to solve this problem by using conventional treatment processes such as adsorption, chemical, and biological treatment. However, some contaminants in wastewater are intractable to degrade by applying these conventional processes. Nowadays, advanced oxidation process (AOP) is the most promising technique and has been explored by researchers to degrade various types of pollutants [3].

The photocatalytic reaction using a heterogeneous catalyst, which is one of the AOPs, has emerged as a destructive method that can mineralise most organic pollutants [4]. The use of semiconductor materials for that purpose has gained attention by many researchers for removal of organic pollutants from an aqueous solution. Various semiconductors such as TiO_2, ZnO, Fe_2O_3, CdS, and ZnS can act as photocatalysts for light-induced redox process. Among them, titania (TiO_2) is the first semiconductor that was initially explored by Fujishima and Honda during photoelectrolysis of water to H_2 in 1972 [3]. TiO_2 has been studied extensively as a photocatalyst due to its inexpensive, chemically and photo-stable, non-toxic, and reusable. However, the fast electron-hole recombination and wide band gap of TiO_2 (~3.2 eV) limit its photoactivity and it is only applicable for ultraviolet (UV) irradiation [3-6]. Hence, many efforts have been devoted to extend the optical response of the

photocatalyst by incorporation of TiO_2 with g-C_3N_4. A short review on recent studies of TiO_2/g-C_3N_4 composite is covered in this paper.

2.0 TITANIUM DIOXIDE

Titanium dioxide (TiO_2) is present in three phases, which are anatase, rutile, and brookite. Anatase and rutile are formed in a tetragonal structure whereas brookite appears in an orthorhombic structure as shown in Figure 1 [7]. These phases are similar based on the octahedral structure with different assembly patterns of each octahedral chain. Among them, anatase TiO_2 is the most widely used in photocatalytic reaction and favoured for modification with other materials due to higher density of localised state that attributed towards slower charge carrier recombination [8, 9].

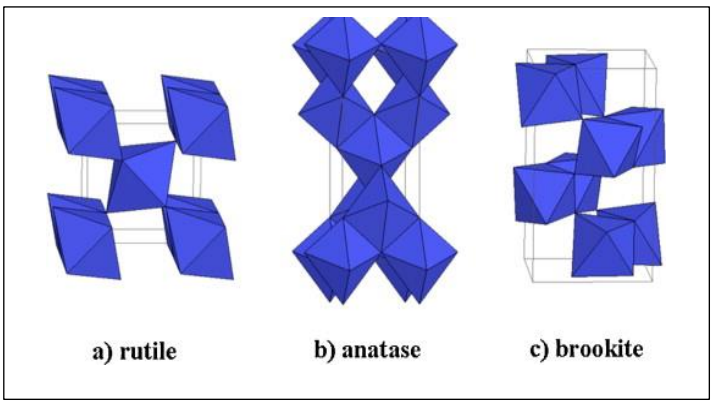

Figure 1. TiO_2 crystal structures [7].

Photocatalysis reaction conducted in visible light irradiation has become the main focus nowadays since it requires low energy for catalyst activation [10]. Even though TiO_2 is a promising photocatalyst, it is unable to absorb visible light due to its wide band gap energy, which limits its application range [6, 8, 10]. Hence, efforts have been devoted to prolong the optical response of TiO_2 from UV to the visible light region and various strategies have been explored including doping with metals or non-metals, dye or semiconductor sensitisation, and surface modification [11-13]. Nevertheless, it is a big challenge to obtain viable visible light active materials that are easily prepared, efficient, stable, and inexpensive.

3.0 GRAPHITIC CARBON NITRIDE (g-C_3N_4)

Polymeric g-C_3N_4 is depicted in Figure 2. Both triazine and heptazine have been discussed as possible tectonic units to constitute stable allotropes of g-C_3N_4. Based on density functional theory (DFT), the structure based on repeating heptazine units is more stable than the triazine units.

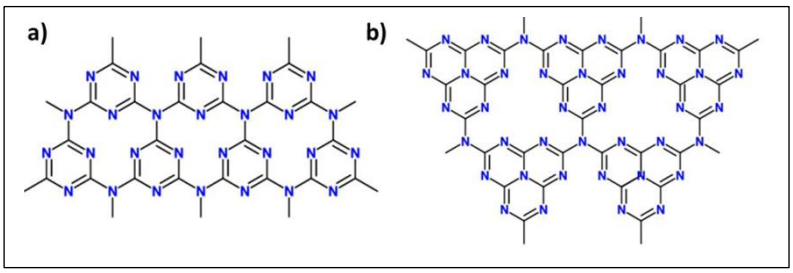

Figure 2. Representation of g-C_3N_4 based on a) triazine and b) heptazine units [14].

Particularly, g-C_3N_4 has become one of the most intensively researched photocatalytic materials due to its capability to be used in visible light radiance [15, 16]. Besides, g-C_3N_4 has high thermal stability, biocompatible, and resistant to oxidation and hydrolysis processes. The constricted band gap of g-C_3N_4 (~2.7 eV) enables it to penetrate visible light up to 460 nm [17].

However, g-C_3N_4 still consists of high recombination probability of photogenerated electron-hole charge carriers that limits photocatalytic efficiency.

4.0 TiO_2/g-C_3N_4 COMPOSITE

In improving photocatalytic activity, one of the strategies is to use a composite of two or more semiconductor photocatalysts that can absorb different parts of solar spectrum [18]. Composite semiconductors can also improve electron-hole separation due to the band off-sets and charge-transfer across interfaces. The coupling of carbon nitrides such as g-C_3N_4 with other semiconductor materials has gained interest of many researchers, for example the production of g-C_3N_4/TiO_2 and or TiO_2/g-C_3N_4 composites [19-21]. These composites show great improvement in the efficiencies of photoactivity, thus promote its applications in energy production and environmental remediation. Recent studies on this photocatalyst are shown in Table 1. The composite catalysts showed high photodegradation performance towards various pollutants under visible light, which are attributed by the optimum band gap factor and better electron-hole pair separation.

Table 1. Recent study on g-C_3N_4/ titania photocatalyst.

Photocatalyst	Synthesis Method	Pollutant	Band Gap (eV)	Performance	References
TiO_2/C_3N_4 core-shell nanowire arrays	Hydrothermal	Bisphenol A	2.90	95%	[21]
Core-shell structure g-C_3N_4@TiO_2	Sol-gel approach in-situ coating re-assembled	Phenol	1.70	30%	[22]
TiO_2/g-C_3N_4 hollow nanotube	Molten salts	Rhodamine B	2.48	95%	[23]
TiO_2/g-C_3N_4 mesostructured nanosheets	Facile calcination-sonication assisted method	Phenol	2.31	93%	[24]
Core-shell TiO_2@g-C_3N_4 hollow microspheres	Two-step self-assembly procedure with the assistance of ultrasonic dispersion	Rhodamine B	2.75	93%	[25]
Porous g-C_3N_4/TiO_2 heterostructure	In-situ assembling of small needle-like TiO2 on the surface of ultrathin g-C3N4 sheets	Acid Orange	2.90	82%	[26]
Mesoporous TiO_2/g-C_3N_4 microspheres	Facile nanocoating	Phenol	1.50	25%	[27]
Brookite/anatase TiO_2/g-C_3N_4 heterojunction	Facile nanocoating	Phenol	1.80	20%	[28]
Carbon nitride/titania nanotubes	High-temperature calculation method	2-chlorophenol	2.60	90%	[29]

5.0 MECHANISM OF TiO_2/g-C_3N_4 COMPOSITE

Most of the TiO_2/g-C_3N_4 composites show a similar proposed mechanism. When TiO_2/g-C_3N_4 is exposed to visible light, the photon could be absorbed directly by g-C_3N_4 to generate the electron-hole pairs in valence band (VB) and conduction band (CB), respectively [30]. The electron from g-C_3N_4 can easily migrate from its CB to the CB of TiO_2 since g-C_3N_4 has more negative CB level (-1.12 eV) than TiO_2 (-0.29 eV) [31]. Meanwhile, the holes from TiO_2 surface will migrate to the VB of g-C_3N_4. The electron on CB of TiO_2 can abduct O_2 to generate superoxide anion radical ($\bullet O^{2-}$), which is one of the active species that can oxidise the pollutant. Meanwhile, the holes on g-C_3N_4 also play an important role in photodegradation process by forming hydroxyl radical (•OH) when reacted with water. The pollutant will be decomposed to form CO_2 and H_2O via photocatalysis with the reactive $\bullet O^{2-}$ and •OH as illustrated in Figure 3.

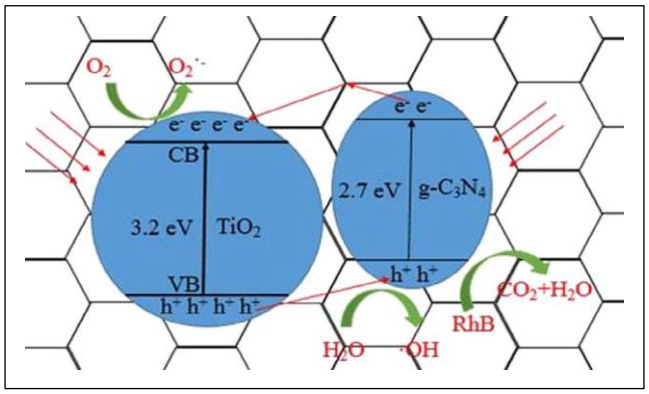

Figure 3. Mechanism for photo-degradation of TiO_2/g-C_3N_4 composite [30].

6.0 CONCLUSION

From this review, it can be concluded that the coupling of these two semiconductors will increase the efficiency of electron transfer separation process. Consequently, the electron life is significantly prolonged and recombination process can be reduced, thus resulting in remarkable photocatalytic degradation of pollutants.

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