

Review

Compositing Two-Dimensional Materials with TiO₂ for Photocatalysis

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Abstract: Energy shortage and environmental pollution problems boost in recent years. Photocatalytic technology is one of the most effective ways to produce clean energy—hydrogen and degrade pollutants under moderate conditions and thus attracts considerable attentions. TiO₂ is considered one of the best photocatalysts because of its well-behaved photo-corrosion resistance and catalytic activity. However, the traditional TiO₂ photocatalyst suffers from limitations of ineffective use of sunlight and rapid carrier recombination rate, which severely suppress its applications in photocatalysis. Surface modification and hybridization of TiO₂ has been developed as an effective method to improve its photocatalysis activity. Due to superior physical and chemical properties such as high surface area, suitable bandgap, structural stability and high charge mobility, two-dimensional (2D) material is an ideal modifier composited with TiO₂ to achieve enhanced photocatalysis process. In this review, we summarized the preparation methods of 2D material/TiO₂ hybrid and drilled down into the role of 2D materials in photocatalysis activities.

Keywords: photocatalysis; 2D materials; TiO₂; composite

1. Introduction

With the massive consumption of fossil energy and serious environmental pollution problems, there is an urgent need for clean energy and more efficient ways to decompose pollutants. Photocatalysis is an advanced technology that uses photon energy to convert chemical reactions occurring under harsh conditions into reactions under mild conditions by appropriate photocatalyst, and thus emerged as recognizable fields such as hydrogen generation [1–4], sewage treatment [5–7], harmful gas removal [8,9], organic pollutant degradation [10–13] and carbon dioxide reduction [14–16].

Since the first report that TiO₂ electrode was applied for hydrogen production by Fujishima and Honda in 1972 [17], TiO₂ has attracted numerous attention in photocatalysis as a typical n-type semiconductor [18–21]. Being non-toxic, inexpensive, highly stable [22–24], TiO₂ is widely investigated in photocatalytic fields. Hoffman proposed the following general mechanism (Table 1) for heterogeneous photocatalysis on TiO₂ [25].

Table 1. Mechanism for heterogeneous photocatalysis on TiO₂.

Primary Process	Characteristic Times
charge-carrier generation	$\text{TiO}_2 + h\nu \rightarrow h\nu_{\text{VB}}^+ + e_{\text{cb}}^-$ (fs)
charge-carrier trapping	$h\nu_{\text{VB}}^+ + >\text{Ti}^{\text{IV}}\text{OH} \rightarrow \{>\text{Ti}^{\text{IV}}\text{OH}\}^{\bullet+}$ $e_{\text{cb}}^- + >\text{Ti}^{\text{IV}}\text{OH} \rightarrow \{>\text{Ti}^{\text{III}}\text{OH}\}$ $e_{\text{cb}}^- + >\text{Ti}^{\text{IV}} \rightarrow >\text{Ti}^{\text{III}}$ fast (10 ns) shallow trap (100 ps) (dynamic equilibrium) deep trap (10 ns) (irreversible)
charge-carrier recombination	$e_{\text{cb}}^- + \{>\text{Ti}^{\text{IV}}\text{OH}\}^{\bullet+} \rightarrow >\text{Ti}^{\text{IV}}\text{OH}$ $h\nu_{\text{VB}}^+ + \{>\text{Ti}^{\text{III}}\text{OH}\} \rightarrow \text{Ti}^{\text{IV}}\text{OH}$ slow (100 ns) fast (10 ns)
interfacial charge transfer	$\{>\text{Ti}^{\text{IV}}\text{OH}\}^{\bullet+} + \text{Red} \rightarrow >\text{Ti}^{\text{IV}}\text{OH} + \text{Red}^{\bullet+}$ $e_{\text{tr}}^- + \text{Ox} \rightarrow \text{Ti}^{\text{IV}}\text{OH} + \text{Ox}^{\bullet-}$ slow (100 ns) very slow (ms)

Where $>\text{TiOH}$ represents the primary hydrated surface functionality of TiO₂, e_{cb}^- is a conduction band (CB) electron, e_{tr}^- is a trapped conduction band electron, $h\nu_{\text{VB}}^+$ is a valence band (VB) hole, Red is an electron donor, Ox is an electron acceptor, $\{>\text{Ti}^{\text{IV}}\text{OH}\}^{\bullet+}$ is the surface-trapped VB hole (i.e., surface-bound hydroxyl radical), and $\{>\text{Ti}^{\text{III}}\text{OH}\}$ is the surface-trapped CB electron. Upon light irradiation, electrons transfer from VB to CB of TiO₂, while both electrons and holes can be trapped by primary hydrated surface functionality of TiO₂, achieving the separation of photo induced electrons and holes. At the same time, the recombination between electrons and holes exits, which competes with charge-carrier trapping process. The competition has thus a negative effect on later interfacial charge transfer. Deliberating on TiO₂ photocatalysis process, some drawbacks exit as following: (1) The wide bandgap of TiO₂ (3.2 eV) means that photons with adequate energy can only excite electrons in the VB to the CB of TiO₂, which limits its effective use of sunlight (UV region, $\lambda \leq 387$ nm); (2) The recombination of excited electrons and holes is inevitable while time for carrier recombination is much shorter than that for charge transfer. Therefore, the effective function of photoexcitation is suppressed greatly.

Considering the above two factors, the improvement of the photocatalytic efficiency of TiO₂ can be obtained through two aspects: the improvement of solar light utilization efficiency and the suppression of recombination of electron and hole pairs. In this text, surface modification and hybridization of TiO₂ such as noble metal loading [26–29] and semiconductor heterojunction [30–32] are effective methods to enhance the photocatalytic performance. The Schottky barrier formed at the interface between the noble metal material and TiO₂ can effectively promote the separation of photogenerated carriers. Similarly, the heterojunction structure can form a matching energy level at the semiconductor interface to suppress the recombination of photogenerated carriers. However, the opportunities of improvements in photocatalysis performances offered by these attempts are narrow, and thus limited their commercial and efficient application. In the past decade, two-dimensional (2D) materials have attracted more and more attention because of the flexible preparation methods, low price and superior physical and chemical properties. In particular, their high surface area, suitable bandgap, structural stability and high charge mobility [33–36] endow these 2D materials with remarkable performances for applications in photocatalysis [37–41]. When combined with TiO₂, not only the utilization of sunlight is improved, but also the matching between energy levels is formed to inhibit the recombination, and the large specific surface area provides support and active sites for the reaction. In this review, we summarize the recent advances of 2D material-TiO₂ composites, including synthesis methods, properties, and catalytic behaviors. Furthermore, the photocatalytic mechanism is deliberated in detail to elaborate the role of 2D materials in the photocatalytic processes.

2. 2D-Material Modified TiO₂

Based on the mobile dimension of electronics, it can be divided into zero-dimensional (0D) materials, one-dimensional (1D) materials, two-dimensional (2D) material and three-dimensional (3D) materials [36], while 2D materials represent an emerging class of materials that possess sheet-like structures with the thickness of only single or a few atom layers [42]. Compared with the bulk structures, the ultrathin 2D structure exhibits superior properties such as modification of energy level

and larger adjustable surface area. The excellent properties of 2D materials make them widely used in many aspects [43–45]. When composited with TiO_2 , the synergistic effect of the two can significantly improve the photocatalytic activity and thus 2D materials is ideal for TiO_2 photocatalysis.

2.1. Graphene Modified TiO_2

Since the first isolation by Geim and Novoselov in 2004, graphene has attracted significant attention [46–49]. Graphene is a 2D honeycomb construction consisting of carbon atoms. The thickness of graphene is only 0.335 nm, which is the thickness of a carbon atom layer. In the sp^2 hybrid distribution form, each carbon atom contributes an unbonded π electron, which can delocalize freely throughout the carbon atom ‘net’ to form an extended π bond. This construction endows graphene excellent properties such as high charge mobility ($200,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), high thermal conductivity ($5000 \text{ W m}^{-1} \text{ K}^{-1}$), and large surface area [35], which is ideal for applications in sensors [50], energy conversion and storage [37], polymer composites [51], drug delivery systems [52], and environmental science [53]. When composited with TiO_2 , graphene can accept photoinduced electrons from TiO_2 and thus greatly enhances the efficiency of carriers’ separation [54–58].

2.1.1. The Synthesis of Graphene/ TiO_2 Composites

Graphite oxide and graphene oxide (GO) intermediates are widely used in the process of combining graphene with other materials [59]. The most widely used technique is chemical reduction of GO as shown in Figure 1, which is usually conducted by Hummers’ method [60]. Graphite is added to a strongly oxidizing solution such as HNO_3 , KMnO_4 , and H_2SO_4 to prepare graphite oxide and the oxygen-containing groups are introduced into the surface or edge of the graphite during the process. The sheets of graphite oxide were exfoliated to obtain GO. The presence of oxygen-containing groups allows GO to provide more surface modification active sites and larger specific surface areas for synthetic graphene-based composites. GO can be converted to reduced graphene oxide (RGO) by chemical reduction to remove these oxygen-containing group. During this process, the number of oxygen-containing groups on the GO decreases drastically, and the conjugated structure of the graphene base will be effectively restored. The presence of oxygen functionalities in GO allows interactions with the cations and provides reactive sites for the nucleation and growth of nanoparticles, which results in the rapid growth of various graphene-based composites. The preparation methods for graphene/ TiO_2 composites are divided into ex-situ hybridization and in-situ growth, the difference between which is the process of TiO_2 formation.

- *Ex-situ hybridization.* The common procedure for ex-situ hybridization is to mix GO and modified TiO_2 with physical process such as ultrasound sonication and heat treatments. Rahmatollah et al. [62] reported a facile one-step solvothermal method to synthesize the TiO_2 -graphene composite sheets by dissolving different mass ratios of GO and TiO_2 nanoparticles in anhydrous ethanol solution. Ultrasound irradiation was used to disperse the GO. Finally, a six-fold enhancement was observed in the photocurrent response compared to the improved photoelectrochemical performance (3%) with the pure TiO_2 . Florina et al. [63] prepared graphene/ TiO_2 -Ag based composites as electrode materials. Similarly, GO suspensions were mixed with prepared TiO_2 -Ag nanoparticles in NaOH solution. The suspensions were sonicated, dried and subjected to thermal treatment. However, the control of modification between the TiO_2 and graphene may lead to a decreased interaction between these two parts [64].
- *In-situ growth.* The in-situ growth method is widely used to prepare graphene-based composite materials, and the method can effectively avoid clustering of nanoparticles on the surface of graphene. According to different preparation process, it might be divided into reduction method, electrochemical deposition method, hydrothermal method and sol-gel method.
 - *Reduction method.* Usually, in a reduction method, GO and TiO_2 metal salts are mixed as precursors. By controlling the hydrolysis of the precursor, TiO_2 crystal nucleus grows on GO,

while GO is reduced to obtain graphene-based TiO₂ composite materials [65]. In addition to the chemical reduction method, other commonly used reduction methods are photocatalytic reduction [66] and microwave-assisted chemical reduction [67].

- *Electrochemical deposition method.* In an electrochemical deposition method, graphene or reduced graphene is used as a working electrode in a dielectric solution containing a metal precursor or its compound [68].
- *Hydrothermal/solvothermal method.* A hydrothermal/solvothermal method is commonly used for preparing inorganic nanomaterials. It is generally carried out in a dispersion of GO. Under high temperature and high pressure, GO and titanium salt precursor are reduced simultaneously [69,70].
- *Sol-gel method.* The sol-gel method takes titanium alkoxide or titanium chloride as precursors, and it can be uniformly bonded with oxygen group on graphene, polycondensed to form a gel. Then TiO₂ nanoparticles are formed through calcining [71,72]. The sol-gel method can obtain loaded nanoparticles with higher uniformity of dispersion.

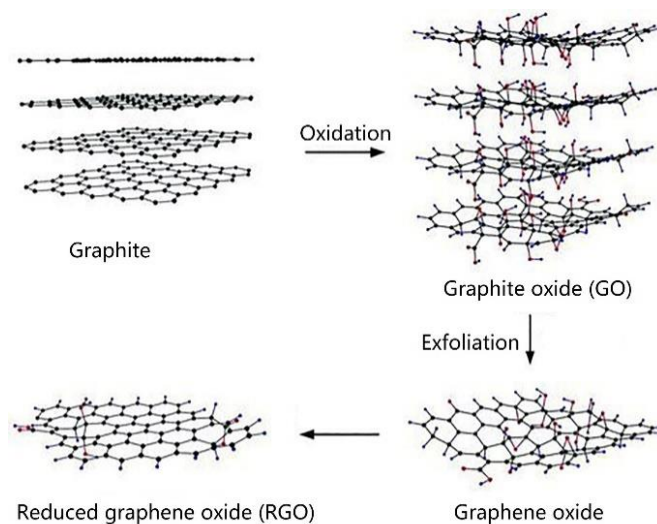


Figure 1. Preparation of graphene by chemical reduction of graphene oxide synthesized by Hummers' method. Reprinted with permission from [61]. Copyright 2011, Wiley-VCH.

2.1.2. The Role of Graphene in TiO₂ Photocatalysis

Due to the large bandgap, the photocatalysis process of pure TiO₂ can only be activated under UV light. Thus, the hybridization of graphene and TiO₂ is essential to ensure a broad light stimulation process. In graphene/TiO₂ system, electrons flow from TiO₂ to graphene through interface because of the higher Fermi level of TiO₂. Then graphene gains excess negative charges while TiO₂ has positive charges, leading to a space charge layer at the interface which is regarded as Schottky junction. The Schottky junction can serve as an electron trap to efficiently capture the photoinduced electrons [73] and thus enhance the photocatalysis activity. Meanwhile, the Schottky barrier also acts as the main obstruction for the electron transport from the graphene to TiO₂. Under visible light, electrons on Fermi level of graphene are irradiated and the Schottky barrier has to overcome to ensure the injection of electrons to conduct band of TiO₂. In the UV light irradiation process, graphene plays a role as electron acceptor and thus promotes the separation of electron-hole pairs [54] (Figure 2).

Different interface interactions have been extensively studied [55,56]. Compared with 0D-2D Degussa P25 (TiO₂)/graphene and 1D-2D TiO₂ nanotube/graphene composites, the 2D-2D TiO₂ nanosheet/graphene hybrid demonstrates higher photocatalytic activity toward the degradation of rhodamine B and 2,4-dichlorophenol under the UV irradiation [56]. The intimate and uniform contact between the two sheets-like nanomaterials allowed for the rapid injection of photogenerated electrons from the excited TiO₂ into graphene across the 2D-2D interface while achieving effective electron-hole

pair separation and promoted radical's generation. In another example of RGO–TiO₂ hybrid, by having a narrower bandgap, the photo-response range of RGO–TiO₂ nanocomposites clearly extended from UV (~390 nm) to visible light (~480 nm), which offered a better utilization of visible light [55]. Raman spectra and other characterization revealed that the narrow bandgap was attributed to the Ti–O–C bond between the two components, and thus caught an intimate interaction between TiO₂ nanoparticles and RGO sheets. What's more, the up-conversion photoluminescence (UCPL) effect of RGO assists the light absorption, and enabled the efficient utilization of both UV light and visible light (Figure 3). It is worth to note that the surface area of RGO–TiO₂ was smaller than that of pure TiO₂ (P25), which revealed that the enhanced photocatalytic activity of RGO–TiO₂ was relevant to the improved conductivity and bandgap structure other than their surface area. RGO nanosheet can play a role in both charge transfer and active sites after doping with heteroatoms. TiO₂/nitrogen (N) doped reduced graphene oxide (TiO₂/NRGO) nanocomposites was applied to photoreduction of CO₂ with H₂O vapor in the gas-phase under the irradiation of a Xe lamp (the wavelength range of 250–400 nm) [57]. Compared with TiO₂, TiO₂/NRGO composites exhibited a narrower bandgap due to chemical bonding between TiO₂ and the specific sites of N-doped graphene. In the photoreduction of carbon dioxide, the function of nitrogen atoms varied in different chemical environments. The pyridinic-N and pyrrolic-N worked as active sites for CO₂ capture and activation while quaternary-N worked as an electron-mobility activation region for the effective transfer of photogenerated electrons from the CB of the TiO₂ [57] (Figure 4). The results reveal that the doped atoms can act as basic sites for anchoring target molecular, adjusting the electronic properties and local surface reactivity of graphene.

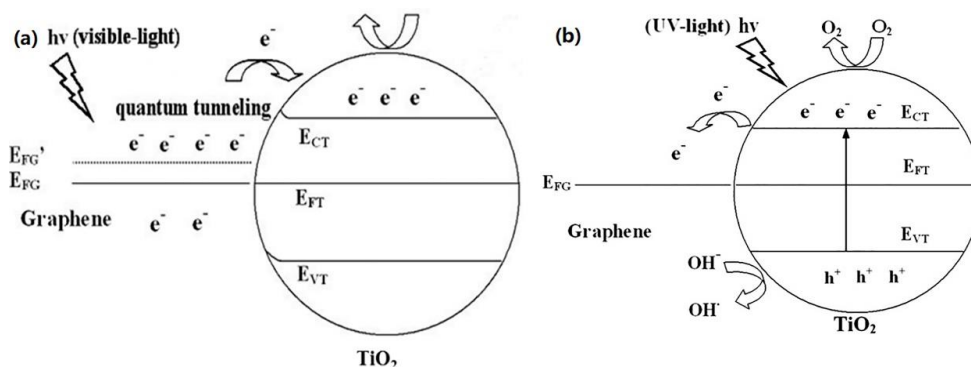


Figure 2. Photocatalytic mechanisms of graphene-TiO₂ composite under (a) visible light (b) UV light. Reprinted with permission from [54]. Copyright 2013, Elsevier.

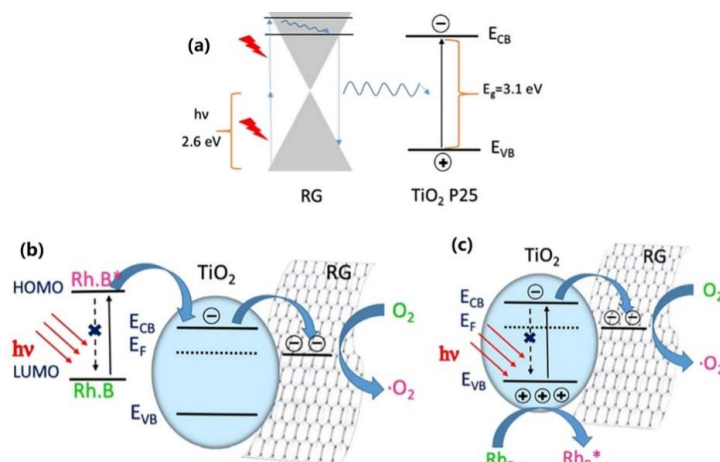


Figure 3. (a) Schematic of up-conversion photoluminescence (UCPL) mechanism for reduced graphene oxide (RGO)–TiO₂ nanocomposite under visible light ($h\nu \sim 2.6$ eV) irradiation; (b,c) Schematics of proposed mechanism of Rh. B photodegradation. Reprinted with permission from [55]. Copyright 2017, Springer.

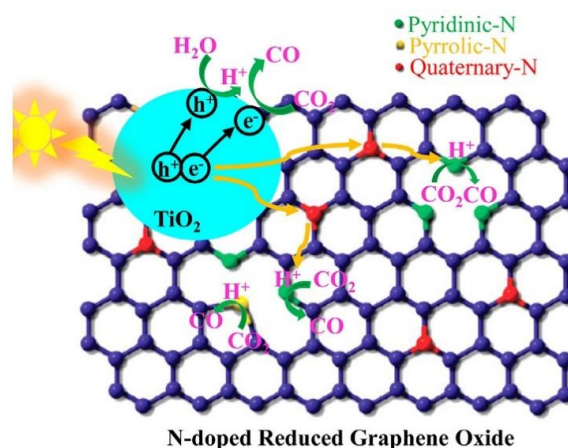


Figure 4. Reaction mechanisms for photoreduction of CO_2 with H_2O over TiO_2/NRGO -300 samples. Reprinted with permission from [57]. Copyright 2017, Elsevier. NRGO: nitrogen doped reduced graphene oxide.

Except for dimension factor and bonding interaction between graphene and TiO_2 , a linkage is introduced to graphene/ TiO_2 system to achieve better interfacial contact as well. A N-doping Graphene- TiO_2 composite nano-capsule for gaseous HCHO degradation was reported [58]. It indicated that wrapping with dopamine on the surface of TiO_2 enhanced interfacial contact between TiO_2 and melamine-doped graphene (MG) sheets, thus promoting the separation and mobility of photoinduced electrons and holes in $\text{TiO}_2@\text{MG-D}$. The dopamine acted as bridge between TiO_2 and MG, creating numerous migration channels for charges and restraining the recombination of electrons and holes (Figure 5). The introduction of linkage can effectively improve the weak interfacial contact and overcome the long distance of electron transport between the graphene and TiO_2 , leading to raised separation and mobility of photoinduced electrons and holes and thus higher photocatalytic activity.

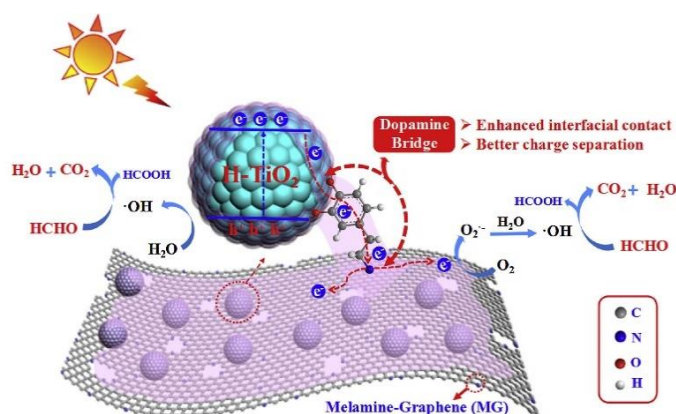


Figure 5. Schematic illustrations for dopamine bridged Melamine-Graphene/ TiO_2 nanocapsule and photocatalytic degradation process of HCHO . Reprinted with permission from [58]. Copyright 2018, Elsevier.

Despite of electron acceptor and electron storage, graphene can also act as a transport bridge between photocatalysts. For example, in the 2D ternary $\text{BiVO}_4/\text{graphene oxide (GO)}/\text{TiO}_2$ system, both the BiVO_4 and the TiO_2 were connected to GO forming a p-n heterogeneous structure. The CB of BiVO_4 was more negative than that of GO and the CB of GO was more negative than that of TiO_2 ; thus, the electrons generated from the CB of BiVO_4 can transfer to the GO and then the electron further moved to the conduction band of TiO_2 (Figure 6). Therefore, the GO can enhance the effective separation of the photo-generated electron-hole pairs due to its superior electrical conductivity. Meanwhile, the large surface area of the GO is also beneficial for dye attachment [74].

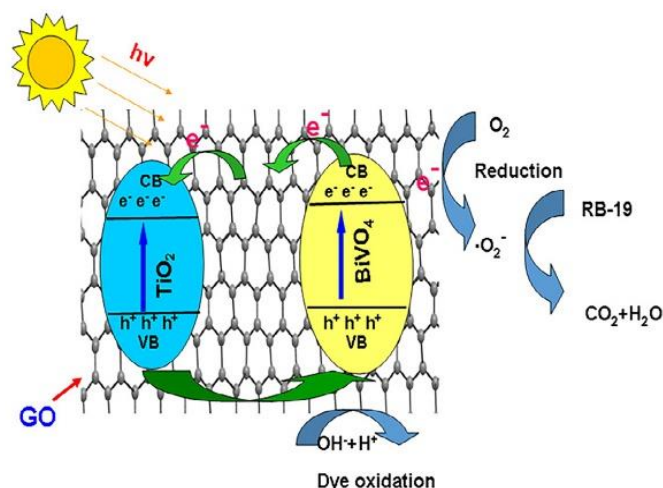


Figure 6. Photodegradation mechanism of BiVO₄/TiO₂/GO photocatalyst. Reprinted with permission from [74]. Copyright 2017, Elsevier.

2.2. Graphdiyne Modified TiO₂

Graphdiyne (GD) is a new carbon allotrope in which the benzene rings are conjugated by 1,3-diyne bonds to form a 2D planar network structure and features both sp and sp² carbon atoms. Since the successful synthesis by Li et al. [75], GD has evoked significant interest in various scientific fields because of unique mechanical, chemical and electrical properties [38,42,76–80]. GD shows potential for photocatalysis with its large surface area as well as high charge mobility. GD features an intrinsic bandgap and exhibits semiconducting property with a measured conductivity of $2.516 \times 10^{-4} \text{ S}\cdot\text{m}^{-1}$ and was predicted to be the most stable structure among various diacetylenic non-natural carbon allotropes [81]. It also provides highly active sites for catalysis. Furthermore, GD with diacetylene linkage can be chemically bonded with TiO₂ [82–85]. Therefore, the TiO₂-graphdiyne composites can greatly improve the photocatalytic activity, and thus their application in photocatalysis has been explored recently [83,84,86].

2.2.1. The Synthesis of GD/TiO₂ Composites

The general preparation of GD film is through a coupling reaction in which hexaethynylbenzene (HEB) acts as precursor and copper foil serves as catalysis. Meanwhile, the copper foil provides a large planar substrate for the directional polymerization growth of the GD film (Figure 7). Despite of film, GD with different morphologies such as nanotube arrays, nanowires, nanowalls and nanosheets have been also prepared for diverse applications [87,88].

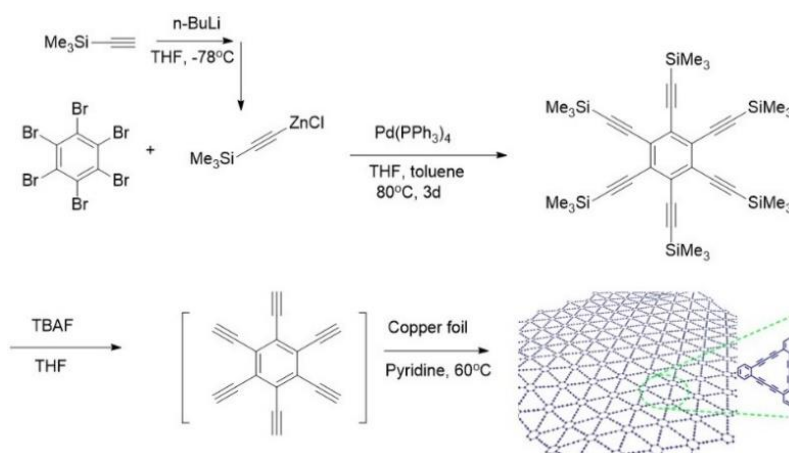


Figure 7. Preparation of graphdiyne (GD) film.

Ex-situ hydrothermal method is commonly used in preparation of GD/TiO₂ composites [83,84,86]. In general, the GD and TiO₂ are prepared separately. Then the pre-prepared GD and TiO₂ are mixed in H₂O/CH₃OH solvent. After stirring to obtain a homogeneous suspension, the suspension is placed in Teflon sealed autoclave and heated to combine the TiO₂ and GD. Being rinsed and dried, the GD/TiO₂ composites are obtained.

2.2.2. The Role of GD in TiO₂ Photocatalysis

Wang et al. [84] were the first to combine GD with TiO₂ for the enhancement of TiO₂ photocatalysis. The resultant GD-P25 composites exhibited higher visible light photocatalytic activity than those of the bare P25, P25-CNT (titania-carbon nanotube), and P25-GR (graphene) materials. By changing the weight percent of GD in the hybrid, the photocatalytic activity of P25-GD can be adjusted. It was speculated that the formation of chemical bonds between P25 and GD can effectively decrease the bandgap of P25 and extended its absorbable light range [84]. Namely, electrons in VB of TiO₂ can easily migrate to impurity band which is attributed to the insertion of carbon *p*-orbitals into the TiO₂ bandgap, and then transfer to CB of TiO₂ thus enhancing the photo-response activity. In order to further explore the role of GD, Yang et al. [83] investigated the chemical structures and electronic properties of TiO₂-GD and TiO₂-GR composites employing first-principles density functional theory (DFT) calculations. The results revealed that for the TiO₂ (001)-GR composite, O and atop C atoms could form C–O σ bond, which acted as a charge transfer bridge at the interface between TiO₂ and GR. Besides the C–O σ bond, another Ti–C π bond is also formed in TiO₂ (001)-GD composite, which makes GD combine with TiO₂ tightly and therefore enhances the charge transfer. In addition, calculated Mulliken charge for the surface of TiO₂ (001)-GD and TiO₂ (001)-GR suggested a stronger electrons' capture ability of former (Figure 8). The calculated results were in accordance with theoretical prediction that TiO₂ (001)-GD composites showed the highest photocatalysis performance among 2D carbon-based TiO₂ composites, confirming that GD could become a promising competitor in the field of photocatalysis. After that, Dong et al. prepared GD-hybridized nitrogen-doped TiO₂ nanosheets with exposed (001) facets (GD-NTNS) [86]. The doped N and incorporated GD efficiently narrowed the bandgap compared with pure TiO₂ and widened response range towards light from UV light to 420 nm visible light. The activity of the GD-NTNS photocatalyst presented the most superior performance compared with bare TiO₂ nanosheets (TNS) and nitrogen-doped TiO₂ nanosheets (NTNS) and GR-NTNS.

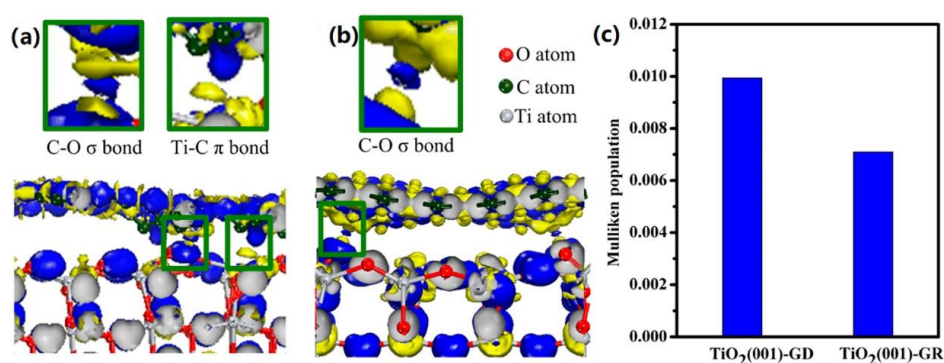


Figure 8. Plots of electron density difference at the composites interfaces: (a) TiO₂ (001)-GD; (b) TiO₂ (001)-GR; (c) Mulliken charge of GD or GR (graphene) surface in the composites. Reprinted with permission from [83]. Copyright 2013, American Chemical Society.

The mechanisms of photocatalysis enhancement by introducing GD remain to be understood. In general, with a lower Fermi level than the conduction band minimum of TiO₂, GD can be regarded as an electron pool which accept electrons excited from TiO₂ [84,89,90] (Figure 9). As a result, it prompts the charge carriers' separation and prevents electron-hole recombination. Moreover, GD can generate an impurity band and thus broaden the visible light absorption in TiO₂-GD composites [91–93].

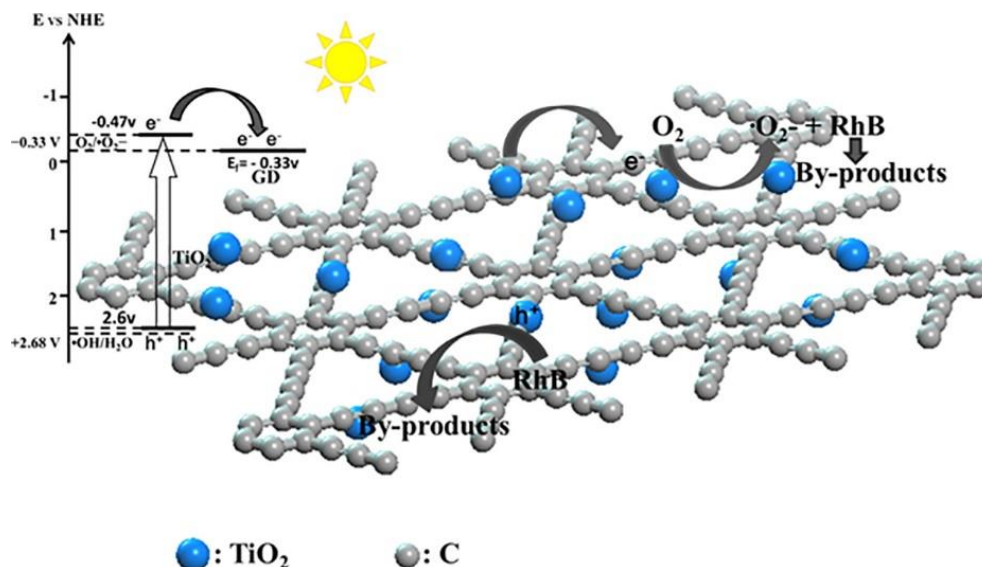


Figure 9. Schematic illustration for the possible mechanism of the visible light-driven photocatalytic degradation for the GD-NTNS composites. Reprinted with permission from [86]. Copyright 2018, Springer.

2.3. C_3N_4 Modified TiO_2

Graphitic carbon nitride ($g-C_3N_4$) is a 2D polymer material which shows broad application prospects in many fields, given the simple synthesis, rich source, along with unique electronic structure, good thermal stability and chemical stability. Its graphene-like structure is composed of triazine (C_3N_3) or tri-s-triazine (C_6N_7) allotropes units (Figure 10). The tri-s-triazine unit structure is more stable and thus draws in extensive studies [34]. Since the first report of $g-C_3N_4$ for water decomposition, $g-C_3N_4$ has attracted wide attention in photocatalyst [40]. The bandgap of $g-C_3N_4$ (2.6–2.7 eV) is moderate and the substantial nitrogen sites and ordered units structure endue $g-C_3N_4$ an ideal material to composite with TiO_2 .

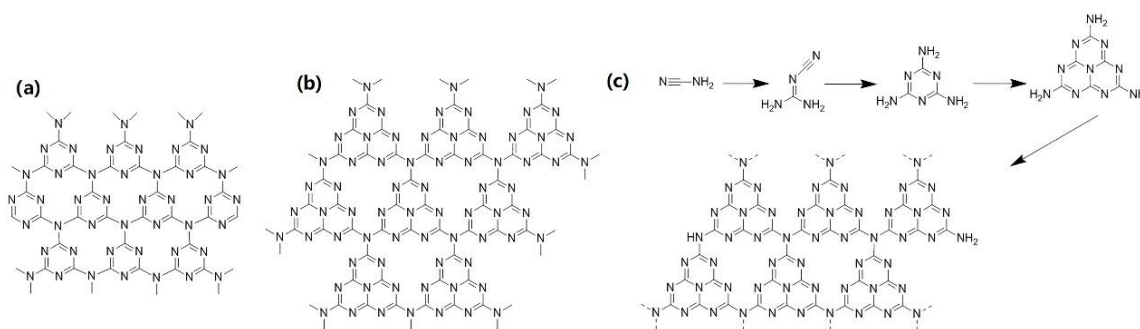


Figure 10. Triazine (a) and tri-s-triazine (b) allotropes units of $g-C_3N_4$; (c) The synthesis of $g-C_3N_4$.

2.3.1. The Synthesis of $g-C_3N_4/TiO_2$ Composites

In general, the synthesis of $g-C_3N_4/TiO_2$ composites can be also divided into ex-situ method and in-situ method.

- In the ex-situ way, both $g-C_3N_4$ and TiO_2 materials are pre-prepared, which can be integrated through physical process such as ball milling [94], solvent evaporation [95,96], etc. Though physical process is easy to operate under moderate conditions, some flaws also exist such as ununiformly dispersing and unstable structure.
- The in-situ method uses one of the materials as a substrate and then the other material grows on the surface of the substrate. For $g-C_3N_4/TiO_2$ composites, both materials can be regarded as substrates.

- When used as substrates, $g\text{-C}_3\text{N}_4$ is pre-prepared by calcinations of precursors. Solvothermal/hydrothermal method is most common for the next step. After mixing $g\text{-C}_3\text{N}_4$ and titanates in a certain solvent, the solution is well dispersed and sealed in the Teflon-lined autoclave, followed by a solvothermal/hydrothermal treatment [97–99]. Furthermore, Atomic Layer Deposition (ALD) was applied to form thin TiO_2 films on $g\text{-C}_3\text{N}_4$ substrates. ALD involves the surface of a substrate exposed alternately to alternating precursor flow. Then the precursor molecule reacts with the surface in a self-limiting way, which guarantees that the reaction stops as all the reactive sites on the substrate reacted with the precursors. It is an effective way to control the thickness and homogeneity of deposited layer [100].
- When TiO_2 was used as substrates, calcination is widely used for the convenience and easy operation. In this process, the solid mixture of TiO_2 and pure urea or melamine or dicyandiamide powder are calcinated under fixed temperature to obtain $g\text{-C}_3\text{N}_4/\text{TiO}_2$ composites. Before calcination, the two components should be evenly dispersed by sonication [101], stirring [102], or grinding [103]. Recently, Tan et al. [104] reported another facile one-step way to prepare nanostructured $g\text{-C}_3\text{N}_4/\text{TiO}_2$ composite. As seen in Figure 11, melamine was at the bottom of the crucible while P25 was on the top of a cylinder put in the crucible. After a 4-h vapor deposition process, nanostructured $g\text{-C}_3\text{N}_4/\text{TiO}_2$ composite was obtained.

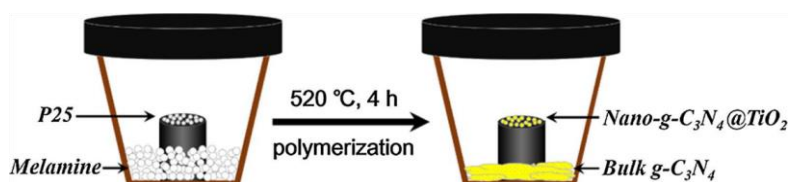


Figure 11. Vapor deposition process in the preparation of $g\text{-C}_3\text{N}_4/\text{TiO}_2$ composite. Reprinted with permission from [104]. Copyright 2018, Elsevier.

2.3.2. The Role of $g\text{-C}_3\text{N}_4$ in Photocatalysis

With a moderate bandgap of ~ 2.7 eV, $g\text{-C}_3\text{N}_4$ shows ability of photocatalyst under visible light, in contrast to TiO_2 , which owns a large bandgap of 3.2 eV (Figure 12). However, because of the rapid recombination of photogenerated electron-hole pairs, the synergistic effect between $g\text{-C}_3\text{N}_4$ and TiO_2 plays important roles. In a photocatalyst system of $g\text{-C}_3\text{N}_4/\text{TiO}_2$ composites, the CB electrons of $g\text{-C}_3\text{N}_4$ transfer to the CB of TiO_2 and the VB holes of TiO_2 transfer to the VB of $g\text{-C}_3\text{N}_4$, which is a typical Type II system [41]. The electron/hole conduction mechanism can effectively separate electrons and holes, and thus enhances the separation efficiency and inhibit the recombination.

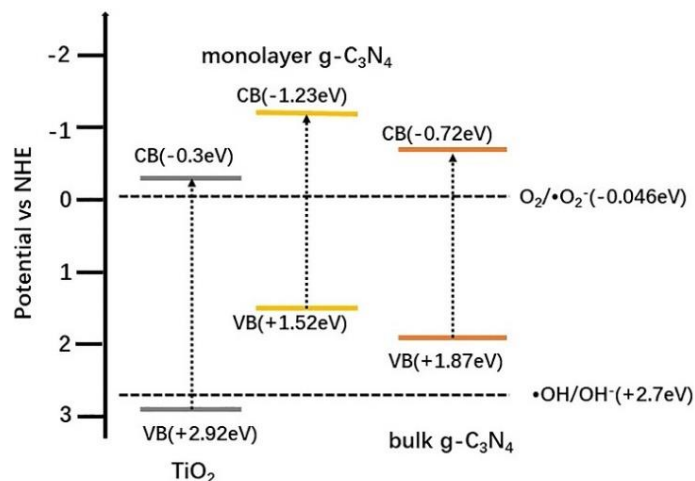


Figure 12. Bandgaps of TiO_2 , monolayer $g\text{-C}_3\text{N}_4$ and bulk $g\text{-C}_3\text{N}_4$.

The structure plays a vital role in enhancing photocatalysis efficiency. g-C₃N₄ nanosheets (NS)-TiO₂ mesocrystals (TMC) composites was prepared by in-situ process [105]. Compared with bulk g-C₃N₄/TMC composites, the H₂ evolution rate of g-C₃N₄ (NS)/TMC was about six times higher, which was possibly due to a larger surface area of g-C₃N₄ (NS)/TMC (57.4 m²g^{−1}) than that of bulk g-C₃N₄/TMC (34.3 m²g^{−1}). What's more, the g-C₃N₄ nanosheets owned a lower surface defect density, given the surface defects normally is seen as recombination centers for photoinduced electrons and holes. However, surface area is not the unparalleled factor of promoted efficiency of photocatalyst, taking the fact that the surface area of g-C₃N₄ NS (31 wt%)/TMC (57.4 m²g^{−1}) and g-C₃N₄ NS (31 wt%)/P25 (52.3 m²g^{−1}) was nearly the same, as the H₂ evolution rate of g-C₃N₄ (NS)/TMC was about 7 times higher. Further research indicated that the tight interface between g-C₃N₄ NS and TMC facilitated the charge transfer, which is a flexible way to promote solar energy utilization of g-C₃N₄/TiO₂ photocatalyst.

Other structures like core-shell was lucubrated to create high photocatalytic activity towards many dyes [106]. After in-situ calcination and growth of cyanamide on the surface of TiO₂, a multiple direction contact structure of TiO₂@g-C₃N₄ hollow core@shell heterojunction photocatalyst (HTCN-1) was synthesized. The g-C₃N₄ nanosheets grew on the surface of TiO₂ caused closer contact between TiO₂ and g-C₃N₄ and a larger interfacial area, as confirmed by XPS analysis [106]. Compared with another core-shell type TiO₂@g-C₃N₄ (C-T) with unidirectional contact structures [107], HTCN-1 possessed higher efficiency in the charge separation and enhanced charge transfer. It demonstrated that multiple direction contact resulted in a large interfacial area, which would provide sufficient channels for efficient and rapid charge transfer (Figure 13) [106]. In another core-shell structure of g-C₃N₄/TiO₂ hybrid, Ag was introduced as interlayers to participate in electrical conduction and bridge the gap between g-C₃N₄ and TiO₂, facilitating the separation of photoexcited charge and reducing the recombination of the photogenerated electron hole (Figure 14) [108]. The surface area of the samples didn't change much upon the introduction of Ag (228.4 m²g^{−1} and 210.3 m²g^{−1} for Ag/TiO₂ microspheres and nonsilver containing TiO₂, respectively). It was worth noting that low content of g-C₃N₄ (2%) in g-C₃N₄/Ag/TiO₂ microspheres had a larger surface area but lower photocatalytic activity than the g-C₃N₄ (4%)/Ag/TiO₂ microsphere sample [108]. The possible reason was that high content of g-C₃N₄ can generate more electron-hole pairs, leading to a higher photocatalytic activity. However, the g-C₃N₄ (6%)/Ag/TiO₂ microsphere sample showed decreased photocatalytic activity due to reduced surface area, which limited the contact between the catalyst and pollutant and thus lowered the photocatalytic reaction. It reflects that proper surface area is needed to provide both active sites and reaction sites.

The doping of g-C₃N₄ is another viable way to realize structure modification process. Sulfur was introduced to g-C₃N₄ nanostructures, and their photocatalytic performance was studied for decomposition of MO dye under visible light. The degradation efficiency over g-C₃N₄-TiO₂ composites (CNT) reached 61% within 90 min, while S-C₃N₄-TiO₂ composites (SCNT) reached nearly 100% within the same period [109]. SEM image showed a more transparent and thinner layer of S-C₃N₄ compared with g-C₃N₄ when composited with TiO₂, leading to an enhanced visible light absorption capability. On the other hand, unique bar-like structure of SCNT provided a pathway for carriers and isolate photon absorption with carriers' collection in perpendicular directions. Meanwhile, TiO₂ nanoparticles were more evenly dispersed on and inside S-C₃N₄ substrate in SCNT sample, which is beneficial for the interfacial carriers' transportation between S-C₃N₄ layer and TiO₂ particle [109]. Calculations revealed that the modified electronic structure with elevation of CB and VB values owing to doped sulfur, contributed to a higher driving force from CB of S-C₃N₄ to CB of TiO₂ and thus promoted the separation efficiency of electron-hole pairs (Figure 15). The doping of sulfur alternated both the structure and level distribution of C₃N₄, causing excellent separation efficiency of electron-hole pair when contacted with TiO₂.

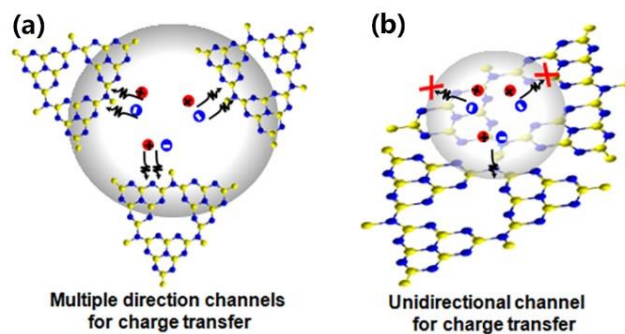


Figure 13. Structure of HTC-N-1 (a) and C-T (b). Reprinted with permission from [106]. Copyright 2018, Elsevier.

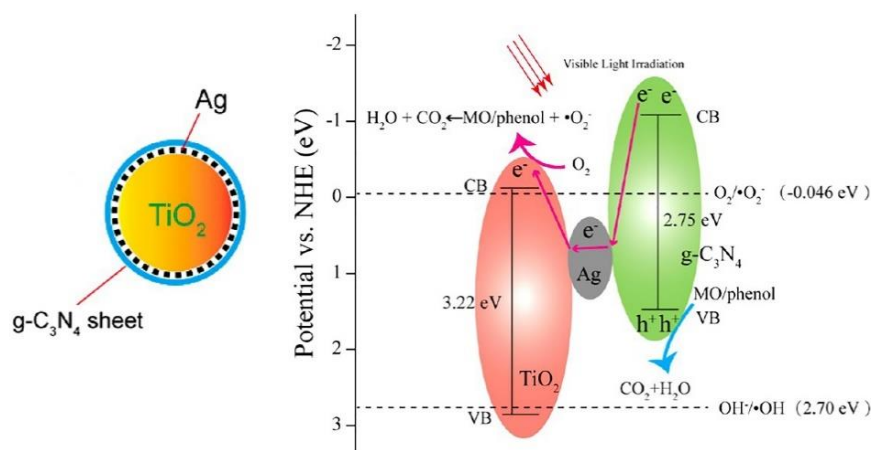


Figure 14. Photocatalytic mechanism scheme of $\text{g-C}_3\text{N}_4/\text{Ag}/\text{TiO}_2$ microspheres under visible light irradiation (>420 nm). Reprinted with permission from [108]. Copyright 2014, American Chemical Society.

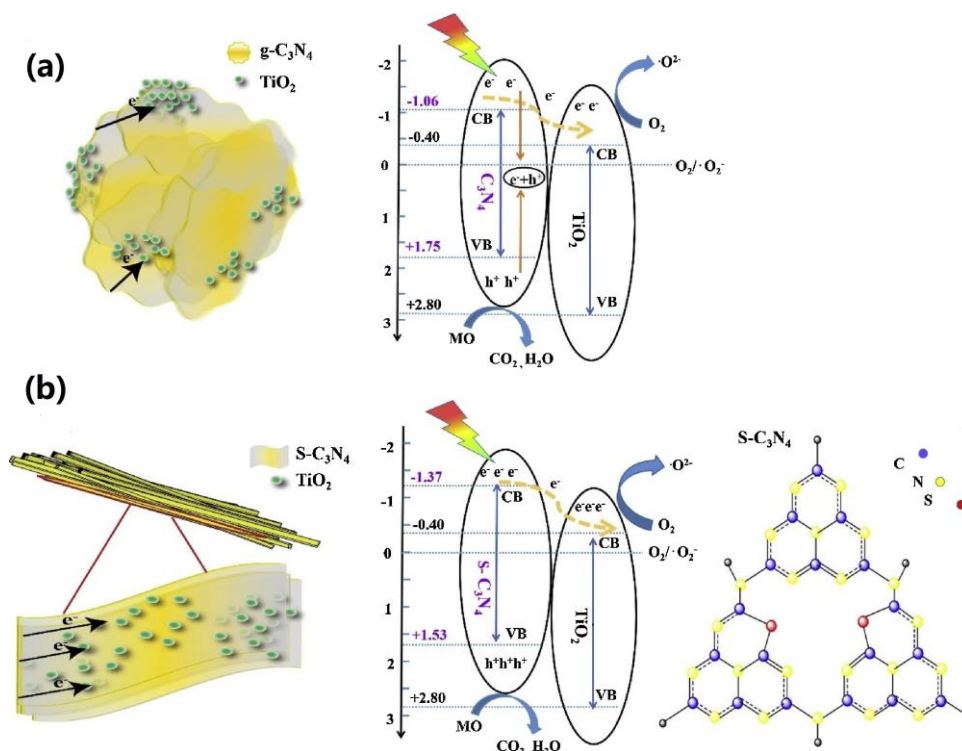


Figure 15. Mechanism of fast charge transfer at the interface between (a) $\text{C}_3\text{N}_4\text{-TiO}_2$ and (b) $\text{S-C}_3\text{N}_4/\text{TiO}_2$. Reprinted with permission from [109]. Copyright 2017, Elsevier.

2.4. MoS₂ Modified TiO₂

2D layered transition metal chalcogenides (TMCs) nanostructures spark a research boom due to its unique physical and chemical properties compared with other 2D materials. The usual formula of TMCs is MX₂, while M is transition metal and X is chalcogenide element, namely, S, Se, or Te. Because of the typical 2D structure with high surface-to-volume ratio and missing coordination at edge (Figure 16), TMCs exhibits high chemical sensitivity [36]. Considering its versatile physicochemical properties, TMCs can be applied in catalyst [41], energy storage [39], and biology [110]. Some TMCs such as WS₂ [111], TiS₂ [112] are also used in TiO₂ photocatalysis. Among TMCs, MoS₂ show extraordinary potential as semiconductors owing to its thickness dependent bandgap and natural abundance. When bulk MoS₂ are stripped into a single layer or several layers of nanosheets, the indirect bandgap (1.3 eV) can be converted to a direct bandgap (1.8 eV) [113] and show excellent performance in photocatalysis after compositing with TiO₂ [114]. Besides, its high surface-to-volume ratio makes up for the limitation of the low theoretical specific capacity of TiO₂. The synergy between MoS₂ and TiO₂ endows the TiO₂/MoS₂ composite superior performance compared to their single material.

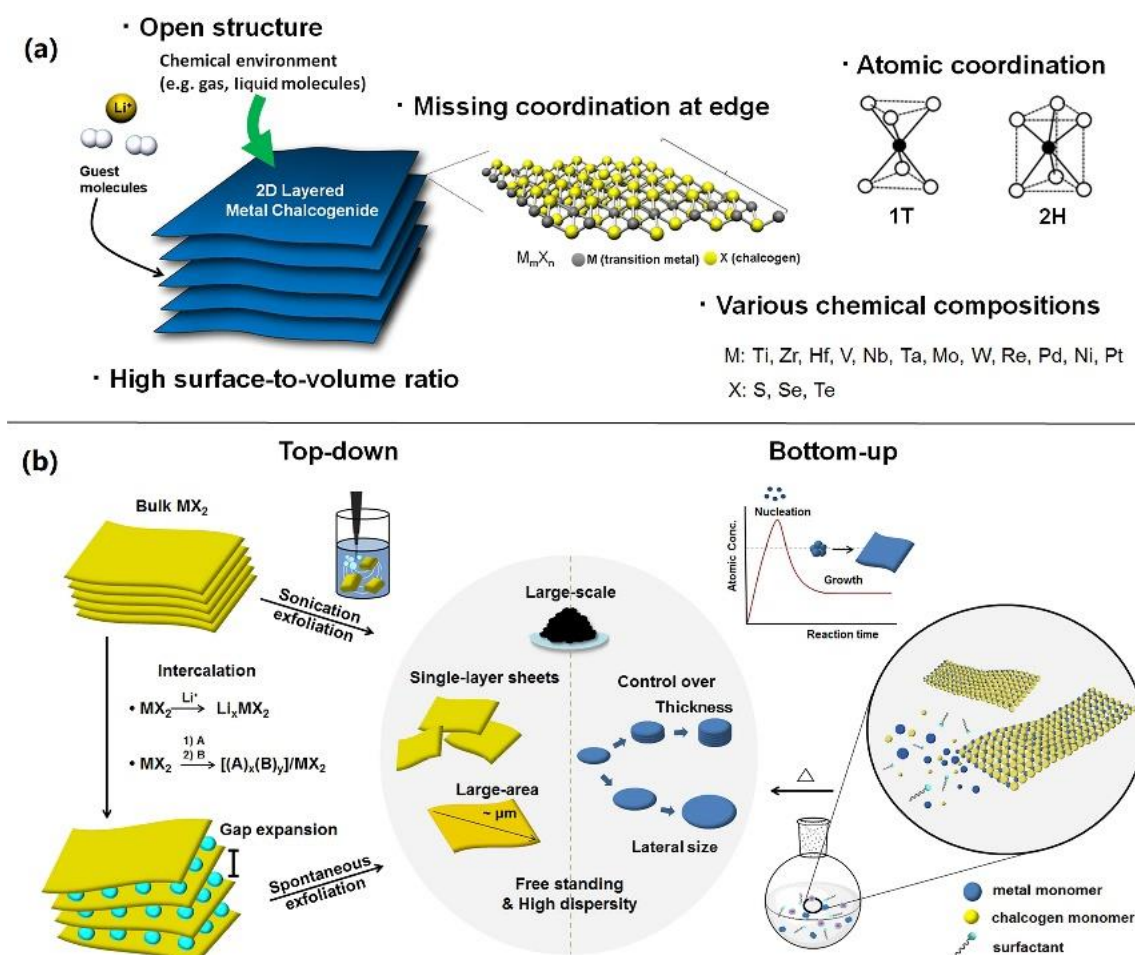


Figure 16. Structure (a) and solution-based preparation (b) of 2D layered transition metal chalcogenides (TMCs) nanosheets based on top-down and bottom-up approaches. Reprinted with permission from [36]. Copyright 2018, American Chemical Society.

2.4.1. The Synthesis of MoS₂/TiO₂ Composites

Similar to the synthesis methods of graphene/TiO₂ composite, the synthesis of MoS₂/TiO₂ composites is also divided into ex-situ methods and in-situ methods. For the in-situ method, TiO₂ and MoS₂ are synthesized separately, then the two are combined by various methods,

such as hydrothermal/solvothermal assembly [115,116], mechanical method [117], drop-casting [118], or sol-gel [119], which can be also applied for in-situ methods [120,121]. The ex-situ method is simple and inexpensive, but the two compounds have poor dispersion and show weak interactions. Despite the same process as ex-situ method, there are chemical vapor deposition [122] and co-reduction precipitation [123] in in-situ process. Among them, the hydrothermal method is simple, easy to operate, and has good controllability, and thus is most commonly used in the preparation of $\text{MoS}_2/\text{TiO}_2$ composite materials. The in-situ reduction method uses one of the materials as a substrate and then coats or loads the other material. This involves the molybdenum disulfide as substrate or TiO_2 as a substrate. The following paragraphs will discuss the two kinds of composites.

- *MoS₂ as substrate.* In this process, MoS_2 are pre-prepared as substrate for the in-situ growth of TiO_2 . Hydrothermal method is widely used in which tetrabutyl titanate serves as titanate source [124,125]. Recently, another approach has been developed to synthesize $\text{MoS}_2@\text{TiO}_2$ composites. Ren et al. [126] reported TiO_2 -modified MoS_2 nanosheet arrays by the ALD process, coating a thin layer of TiO_2 on both the edge and basal planes of TiO_2 (Figure 17). It provides a new insight for the combination of sites at the basal planes of TiO_2 .
- *TiO₂ composite as substrate.* For coated $\text{MoS}_2/\text{TiO}_2$ composites, TiO_2 are usually substrates. Liu et al. [127] reported a $\text{N-TiO}_{2-x}@\text{MoS}_2$ core-shell heterostructure composite. TBT and urea were used to prepare N-doped TiO_2 microspheres (N-TiO_2) with a smooth surface by hydrothermal method. Considering the growth of molybdenum sulfide on the TiO_2 substrate, specific morphology and growth sites of TiO_2 is needed. Sun et al. [128] took a targeted etching route to control the morphology of $\text{TiO}_2/\text{MoS}_2$ nanocomposites. Hollow microspheres structured $\text{TiO}_2/\text{MoS}_2$ showed a higher dye degradation activity due to a larger proportion of interface, compared to $\text{TiO}_2/\text{MoS}_2$ nanocomposites of yolk-shell structures. Other structures such as nanobelts and nanotubes have also been developed [129,130]. In addition to the morphology, the formation of a specific crystal structure of TiO_2 as a substrate has also got attention to prepare high performance $\text{MoS}_2/\text{TiO}_2$ composites [130,131]. He et al. [130] reported a few-layered 1T- MoS_2 coating on Si doped TiO_2 nanotubes ($\text{MoS}_2/\text{TiO}_2$ NTs hybrids) through hydrothermal process. Because of the higher catalytic activity of 1T phase of MoS_2 and Si doped TiO_2 , $\text{MoS}_2/\text{TiO}_2$ NTs hybrids nanocomposites exhibited excellent photocatalytic activity.

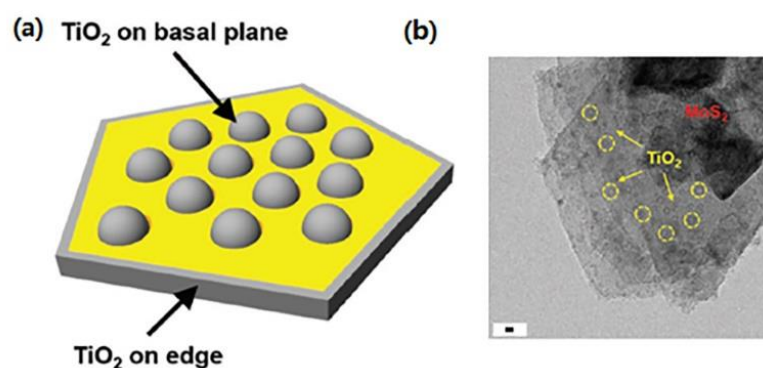


Figure 17. (a) Schematic illustration and (b) TEM image of the ALD TiO_2 coating on pristine MoS_2 . Reprinted with permission from [126]. Copyright 2017, Wiley-VCH.

2.4.2. The Role of MoS_2 in TiO_2 Photocatalysis

During the photocatalysis process, electrons transfer through the interface between TiO_2 and MoS_2 , and therefore the contact between the two is vital for photocatalytic activity. A strategy for construction of 3D semiconductor heterojunction structure by TiO_2 and 2D-structured MoS_2 is proposed to achieve increase of active sites and decrease of electron-hole pair combination [127,132]. For example, a 3D flower-like $\text{N-TiO}_{2-x}@\text{MoS}_2$ was obtained by hydrothermal method. Considering that the smooth TiO_2 nanosphere shows poor affinity when coated with MoS_2 nanosheets, TiO_2 was doped with N and

Ti³⁺. X-ray photoelectron spectroscopy (XPS) shows the existence of electronic interactions between MoS₂ and N-TiO_{2-x} and the strong heterostructure effect between the MoS₂ nanoflower and N-TiO_{2-x} nanosphere [127]. Another study of 3D TiO₂@MoS₂ revealed that the formation of Ti-S bonds made TiO₂ nanoarrays firmly grasp MoS₂, thus affording a marvelous mechanical stability for the integrated architectures [133].

Different phase of MoS₂ exhibits various chemical and physical properties when combined with TiO₂. MoS₂ has two main phases, namely the metallic 1T phase and semiconducting 2H phase. As for 2H phase, the active site with catalytic activity is located at the edge of the MoS₂ layers and the basal surface of MoS₂ is catalytically inactive [134]. Therefore, the 1T phase of MoS₂ with active sites on both edge and basal planes attracts researchers' attention in recent years [118,125,131]. A typical schematic of MoS₂/TiO₂ composites for photocatalytic hydrogen production is shown in Figure 18. The 1T-MoS₂ nanosheets not only provide extra reaction sites on the basal plane, but also play a role in electron delivery. Because of the active site distributing on the edge of 2H-MoS₂ nanosheets, the photogenerated electron from TiO₂ needs a long-distance move before reacted with H₂O. This led to a lower diffusion rate compared with 1T-MoS₂/TiO₂ composites and thus enhanced the separation efficiency of electron-hole pairs. Therefore, the 1T-MoS₂/TiO₂ composites exhibited excellent photocatalytic activity as the hydrogen production rate of 1T-MoS₂/TiO₂ was 5 and 8 times higher than those of bare TiO₂ and 1T-MoS₂/TiO₂ [125]. In another research, 1T-MoS₂ coated onto TiO₂ (001) composite (MST) was synthesized. DFT calculations suggested a closer distance between the interface electrons and MoS₂ surface than that of TiO₂ [131] (Figure 19). Therefore the photo-induced electrons can easily transfer to the conducting channel of MoS₂. Furthermore, the introduction of 1T-MoS₂ prolonged the carrier lifetime remarkably. All the factors led to an enhanced photocatalytic activity.

To further inhibit the recombination of electron-hole pairs, cocatalyst such as graphene is applied to MoS₂/TiO₂ system [115,135,136]. Xiang et al. employed TiO₂/MoS₂/graphene composite as photocatalyst [135]. In this system, photo-induced electrons transfer from VB to CB of TiO₂. Then the electrons are further injected into the graphene sheets or MoS₂ nanoparticles. What is more, graphene sheets can be seen as electrons transport 'highway' through which electrons move from VB of TiO₂ to MoS₂ (Figure 20). The cocatalyst of MoS₂ and graphene enhances the interfacial charge transfer rate, inhibits the recombination of electron-hole pairs and offers a host of active site for adsorption and reaction. Han et al. constructed 3D MoS₂/P25/graphene-aerogel networks. In addition to the above-mentioned advantages, 3D graphene porous architecture has a highly porous ultrafine nanoassembly network structure, excellent electric conductivity, and the maximization of accessible sites [115]. Recently, a 3D double-heterostructured photocatalyst was constructed by connecting a TiO₂-MoS₂ core-shell nanosheets (NSs) on a graphite fiber (GF@MoS₂-TiO₂) [136]. Mechanism of photocatalytic decomposition of dyes under both visible light and UV light was discussed (Figure 21). Anatase TiO₂ has a wide band gap (2.96 eV), while the band gap of MoS₂ is 1.8 eV. Because of the moderate bandgap of MoS₂, the electrons can be irradiated from VB to CB of MoS₂ and then inject into CB of TiO₂ or transfer to graphene through intimate double-heterojunction contact under visible light. Graphene acts as electrons acceptor under both circumstance, leading to a high rate of charge separation and thus depress the charge recombination. The contact interfaces and synergy among graphene, TiO₂ and MoS₂ play an important role in the superior photocatalytic activities.

While the transfer of electrons are paid special attention, the role of capturing the holes are often ignored. To solve this problem, a TiO₂/WO₃@MoS₂ (TWM) hybrid Z-scheme photocatalytic system was structured. TiO₂ and WO₃ have the appropriate energy level matching to form the Z-scheme, while the position of VB in WO₃ is lower than the VB of TiO₂, and the CB of WO₃ is between the CB and VB of TiO₂ [137]. Under UV light irradiation, the VB electrons of all three parts are excited to corresponding CB level. The excited electrons on CB of TiO₂ then transfer to CB of MoS₂ for H₂ evolution, meanwhile the excited electrons on CB of WO₃ were inject to the VB of TiO₂ (Figure 22). This procedure suppressed the recombination of photoinduced electrons and holes in TiO₂,

and therefore the photogenerated electrons and holes can be efficiently separated, which further leads to effective photocatalytic activity [137].

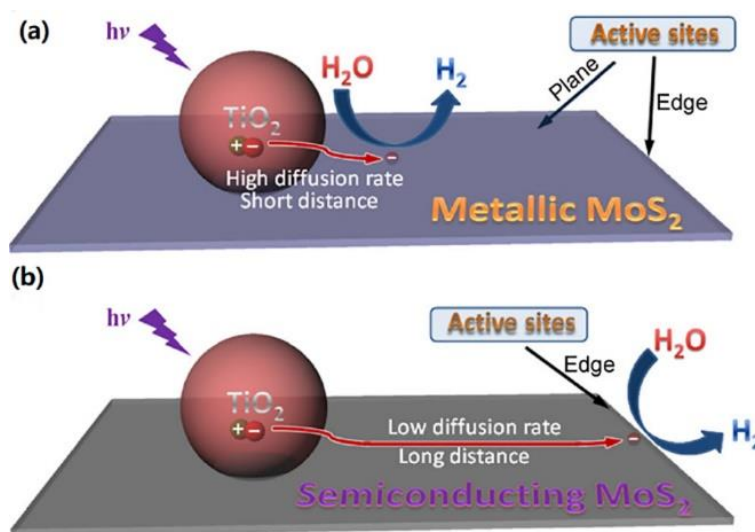


Figure 18. Schematic illustrating charge-transfer behavior and H_2 evolution active sites for (a) 1T-MoS₂/TiO₂ and (b) 2H-MoS₂/TiO₂. Reprinted with permission from [125]. Copyright 2014, Springer.

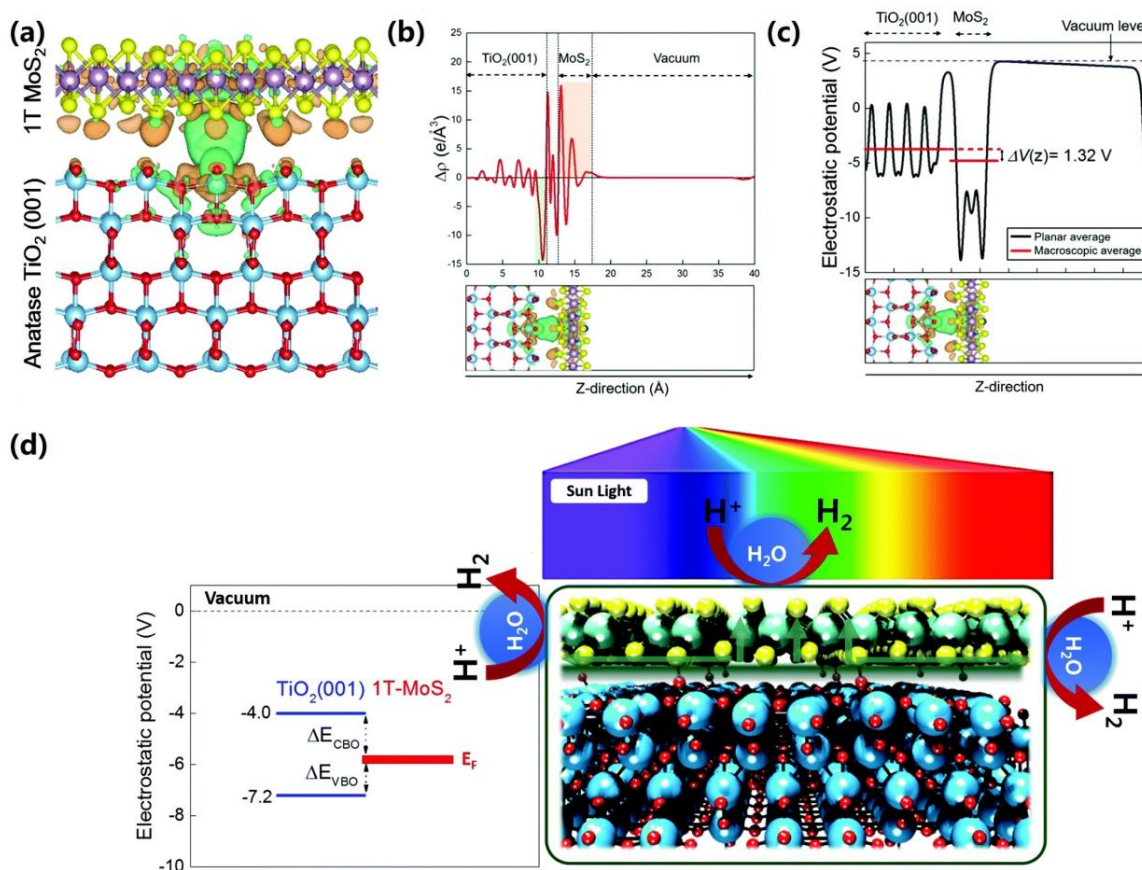


Figure 19. (a) The charge density difference, (b) electrostatic potential and differential charge density of the MoS₂/TiO₂(001) junction; (c) Planar-averaged differential electron density $D_r(z)$ for MoS₂/TiO₂(001); (d) Photocatalytic mechanism for 1T-MoS₂/TiO₂. Reprinted with permission from [131]. Copyright 2017, the Owner Societies.

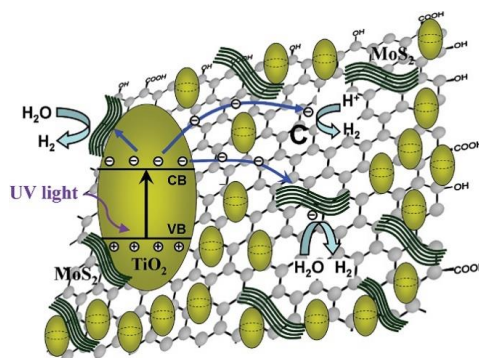


Figure 20. Schematic illustration of the charge transfer in $\text{TiO}_2/\text{MoS}_2/\text{graphene}$ composites. Reprinted with permission from [135]. Copyright 2012, American Chemical Society.

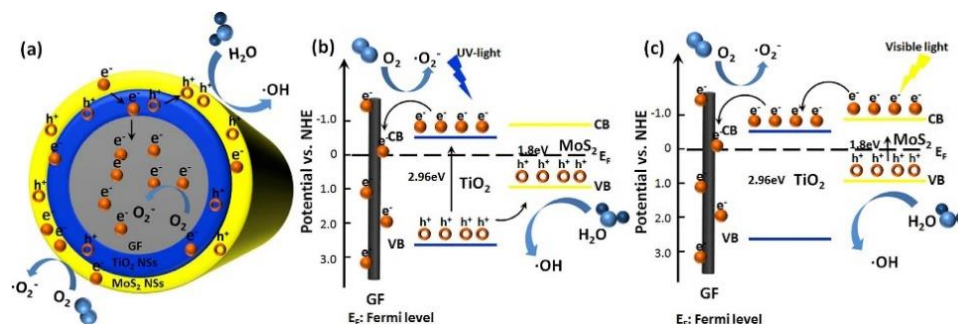


Figure 21. Structure (a) and schematic diagram of electron-hole separation mechanism upon UV (b) and visible light (c) excitation for 3D graphene@ $\text{MoS}_2\text{-TiO}_2$ composites. Reprinted with permission from [136]. Copyright 2017, Elsevier.

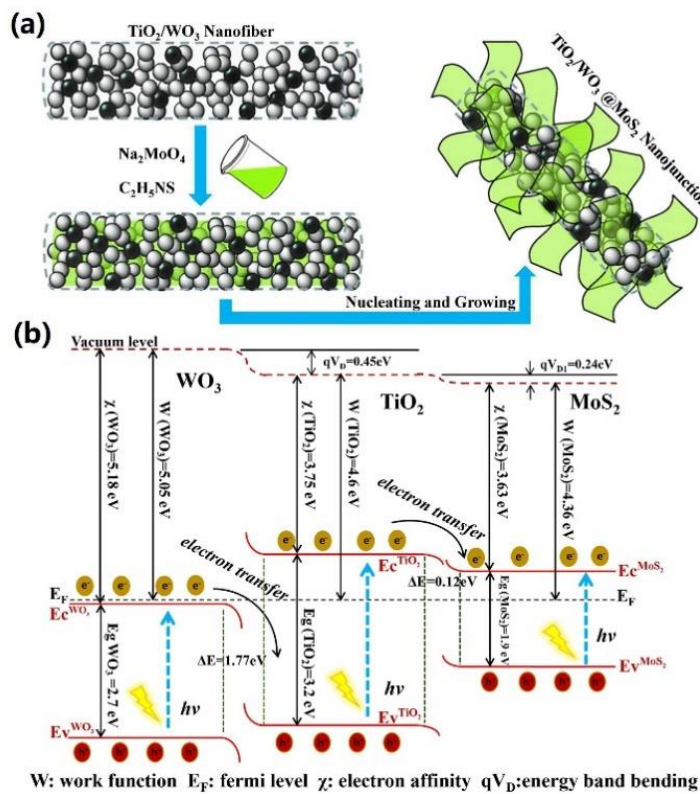


Figure 22. (a) Schematic illustration for the growth of MoS_2 nanosheets (b) Schematic diagram of the photocatalytic H_2 generation over the ternary $\text{TiO}_2/\text{WO}_3@\text{MoS}_2$ heterostructure composite. Reprinted with permission from [137]. Copyright 2017, Elsevier.

3. Conclusions

The coupling between TiO₂ and 2D material has proven to be an efficient approach to enhanced photocatalytic activity. Different methods vary the structures and surface contact of the hybrid and thus can modify the carrier separation process. The synergistic effects show that 2D material plays a vital role in photocatalysis when composited with TiO₂. First, 2D material can act as electrons acceptor or bridge to conduct photoinduced electrons, and therefore represses the recombination of carriers efficiently. Second, the gigantic surface of 2D material provides substantial active sites for substrate capture and reaction, not to mention rapid electrons transfer rate. Third, the 2D material can be decorated to obtain expected properties, for example, non-metal doping to adjust the energy level, specific crystal structure to short the pathway for interfacial charge transfer, and defects or introduced functional group for substrate trapping. What's more, the interfacial heterojunction can adjust energy level to broaden light response range and improve solar utilization. To further enhance the separation efficiency of electron-hole pairs, other photocatalysts are introduced to construct co-catalyst systems among which Z-scheme system can raise the hole trapping rate to some extent, and thus offers a new point to improve the separation of carriers. All factors mentioned above highlight the critical role of 2D material in photocatalyst and the 2D material/TiO₂ hybrid is worth to get further insight for a wider range of applications.

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Conflicts of Interest: The authors declare no conflict of interest.

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