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Black TiO₂ nanobelts/g-C₃N₄ nanosheets Laminated Heterojunctions with Efficient Visible-Light-Driven Photocatalytic Performance

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Black TiO₂ nanobelts/g-C₃N₄ nanosheets laminated heterojunctions (b-TiO₂/g-C₃N₄) as visible-light-driven photocatalysts are fabricated through a simple hydrothermal-calcination process and an *in-situ* solid-state chemical reduction approach, followed by the mild thermal treatment (350 °C) in argon atmosphere. The prepared samples are evidently investigated by X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy, transmission electron microscopy, X-ray photoelectron spectroscopy, N₂ adsorption, and UV-visible diffuse reflectance spectroscopy, respectively. The results show that special laminated heterojunctions are formed between black TiO₂ nanobelts and g-C₃N₄ nanosheets, which favor the separation of photogenerated electron-hole pairs. Furthermore, the presence of Ti³⁺ and g-C₃N₄ greatly enhance the absorption of visible light. The resultant b-TiO₂/g-C₃N₄ materials exhibit higher photocatalytic activity than that of g-C₃N₄, TiO₂, b-TiO₂ and TiO₂/g-C₃N₄ for degradation of methyl orange (95%) and hydrogen evolution (555.8 μmol h⁻¹g⁻¹) under visible light irradiation. The apparent reaction rate constant (k) of b-TiO₂/g-C₃N₄ is ~9 times higher than that of pristine TiO₂. Therefore, the high-efficient laminated heterojunction composites will have potential applications in fields of environment and energy.

The utilization of semiconductor photocatalysts for the treatment of organic pollutants^{1,2} and hydrogen production from water splitting³ has been regarded as a promising method to solve environment issue⁴ and energy crisis⁵. Among various photocatalyst materials, titanium dioxide (TiO₂) is the most famous photocatalysts owing to its low cost, high photocatalytic activity, good stability and nontoxicity⁶⁻⁸. Nevertheless, the wide band-gap (about 3.2 eV for anatase) and the rapid recombination of photoinduced electron-holes are major drawbacks in its poor photocatalytic activity⁹. To date, various methods were developed to improve the visible light absorption of TiO₂, including metal and non-metal elements doping¹⁰, surface sensitization¹¹, semiconductor heterojunction¹², and so on. Among them, semiconductor coupling is an efficient method to reduce the recombination of photoinduced electron-hole pairs.

Recently, graphite-like carbon nitride (g-C₃N₄) has been reported to be a non-toxic, stable and facile metal-free visible light photocatalyst¹³⁻¹⁵. The band-gap of g-C₃N₄ is ~2.7 eV, indicating a strong absorption in visible light region¹⁶. g-C₃N₄ has displayed excellent properties in photodegradation of organic contaminant¹⁷ and H₂ evolution¹⁸. However, the key issue with the high recombination of photoinduced electron-hole pairs is still limited the photocatalytic applications of g-C₃N₄¹⁹. To resolve this problem, coupling g-C₃N₄ with other semiconductors has attracted much attention, which inhibits the recombination of photoinduced electron-hole pairs and thus improves catalytic performance²⁰. There have been many studies on hybrids of g-C₃N₄ with TiO₂.

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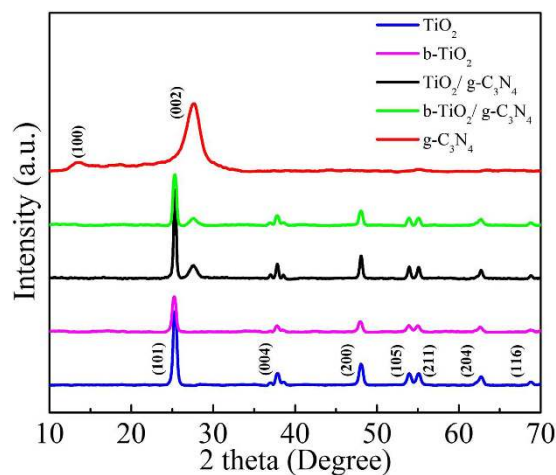


Figure 1. XRD patterns of TiO_2 , $\text{g-C}_3\text{N}_4$, b-TiO_2 , $\text{TiO}_2/\text{g-C}_3\text{N}_4$, and $\text{b-TiO}_2/\text{g-C}_3\text{N}_4$, respectively.

Recent studies on these composites have shown improved photocatalytic performance in dye degradation and H_2 evolution under visible light irradiation^{21–23}.

TiO_2 nanobelts, have attracted great interest because of their large surface areas²⁴, chemical stability²⁵, and provide sufficient space for the new nucleation²⁶. 2D semiconductor materials, such as $\text{g-C}_3\text{N}_4$ nanosheets, possess a unique layered structure and narrow band gap²⁷, which could absorb visible light efficiently. Therefore, it is believed that 2D $\text{g-C}_3\text{N}_4$ nanosheets coupled with TiO_2 nanobelts to form the 3D heterostructure will be a photocatalyst with superior photocatalytic activity. Moreover, the composites with high surface areas maybe produce more reaction active sites and exhibit improved photocatalytic efficiency.

To further expand the $\text{TiO}_2/\text{g-C}_3\text{N}_4$ composite catalyst practical application, it is necessary to enhance the absorption of $\text{TiO}_2/\text{g-C}_3\text{N}_4$ composite photocatalyst in the visible light region. During the past few decades, much effort has been devoted to make colorful TiO_2 for better optical absorption^{28–30}. Recently, Mao *et al.* presented black hydrogenated TiO_2 with enhanced solar light absorption³¹. The black TiO_2 displayed much higher photocatalytic performance over the pristine white TiO_2 , which was attributed to the higher photoinduced electron-hole pairs separation capability. The enhanced solar light absorption of the black TiO_2 was attributed to the formed Ti^{3+} and oxygen vacancies³². Since then, different synthesis methods were proposed to prepare black TiO_2 , including high pressure hydrogenation, plasma assisted hydrogenation, chemical reduction, and high-temperature Al vapor reduction^{33–35}. Therefore, the development of high photocatalytic activity based on black TiO_2 is promising. To the best of our knowledge, up to now, few researchers report black TiO_2 combining with $\text{g-C}_3\text{N}_4$ for pollutants degradation and hydrogen evolution under visible-light irradiation.

In this work, based on a hydrothermal-calcination method, black TiO_2 nanobelts/ $\text{g-C}_3\text{N}_4$ nanosheets laminated heterojunctions were prepared by mixing the melamine and the as-prepared TiO_2 nanobelt, followed by an *in-situ* controllable solid-state reaction approach. The prepared $\text{b-TiO}_2/\text{g-C}_3\text{N}_4$ photocatalyst with a narrow band gap exhibited excellent photocatalytic activity for methyl orange removal and hydrogen evolution under visible-light irradiation.

Results

The samples are characterized by XRD to identify the phase composition of the samples. Figure 1 shows the XRD patterns of TiO_2 , b-TiO_2 , $\text{g-C}_3\text{N}_4$, $\text{TiO}_2/\text{g-C}_3\text{N}_4$, $\text{b-TiO}_2/\text{g-C}_3\text{N}_4$ composites. For pure TiO_2 , the peaks at around 25.3, 37.8, 47.9, 53.8, 55.1, 62.7, and 68.7° are ascribed to the (101), (004), (200), (105), (211), (204), and (116) crystal planes of anatase TiO_2 ^{26,36}, respectively. Moreover, the b-TiO_2 still keeps the pristine crystal phase after the process of treatment with NaBH_4 , indicating that the crystal phase can't be influenced by NaBH_4 . However, the XRD pattern of b-TiO_2 shows a slightly extending characteristic peak at 25.3°, which may be ascribed to the effect of oxygen vacancies (Ov), leading the disorder-induced lattice³⁷. The component $\text{g-C}_3\text{N}_4$ is characterized by two diffraction peaks at around 13.1° and 27.4° are attributed to the (100) plane and (002) plane, which correspond to in-planar structural packing and inter-planar stacking peaks of the aromatic system^{38,39}, respectively. For the $\text{TiO}_2/\text{g-C}_3\text{N}_4$ and $\text{b-TiO}_2/\text{g-C}_3\text{N}_4$ samples, the XRD patterns show the characteristic diffraction peaks of both anatase and $\text{g-C}_3\text{N}_4$, indicating that the composites consisted of both anatase TiO_2 and $\text{g-C}_3\text{N}_4$. No other characteristic peaks are found, revealing the high purity of the as-prepared samples.

The FT-IR spectroscopy is applied to identify the composition of TiO_2 , b-TiO_2 , $\text{g-C}_3\text{N}_4$ and $\text{b-TiO}_2/\text{g-C}_3\text{N}_4$ heterojunction photocatalysts, as shown in Fig. 2. For pure TiO_2 and b-TiO_2 , the main peaks at appearing at 400–700 cm^{-1} is assigned to Ti-O-Ti and Ti-O stretching vibration modes^{40,41}. The peaks at about 1650 and 3400–3500 cm^{-1} are corresponding to hydroxyl group and physically absorbed water on the surface of the TiO_2 ⁴², respectively. In the FT-IR spectrum of $\text{g-C}_3\text{N}_4$, the absorption band at 1640 cm^{-1} can be corresponded to the C-N heterocycle stretching vibration modes⁴³, while the four at 1241, 1320, 1409, and 1567 cm^{-1} to aromatic C-N stretching vibration modes^{44,45}. The peak at 808 cm^{-1} is associated with the breathing mode of triazine units⁴⁶. For the $\text{b-TiO}_2/\text{g-C}_3\text{N}_4$ composite, it can be clearly seen that all the main absorption peaks of $\text{g-C}_3\text{N}_4$ and TiO_2 appeared in $\text{b-TiO}_2/\text{g-C}_3\text{N}_4$ composite, suggesting the presence of TiO_2 and $\text{g-C}_3\text{N}_4$ in the as-prepared composite.

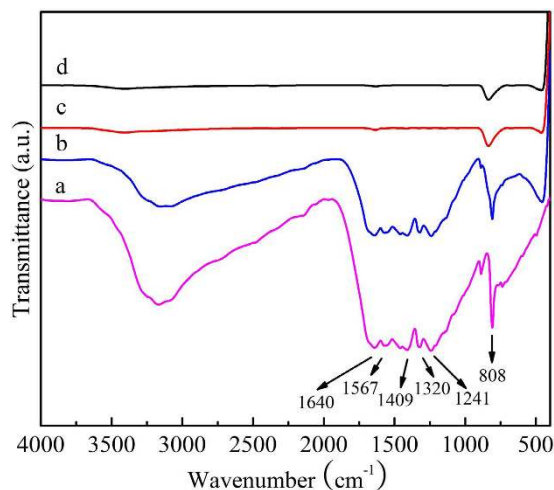


Figure 2. FT-IR spectra of g-C₃N₄ (a), b-TiO₂/g-C₃N₄ (b), TiO₂ (c) and b-TiO₂ (d), respectively.

The morphology and microstructure of samples are studied by SEM and TEM. Figure S1 shows the SEM image of g-C₃N₄, which exhibits a wrinkled sheet structure. It could be found from Figure S2 that TiO₂ nanobelt was about 2–3 μm long, 50–200 nm wide and appeared smooth surface. The SEM image of b-TiO₂/g-C₃N₄ is presented in Fig. 3a. Apparently, when compared with the pure TiO₂ nanobelt, the surface of the b-TiO₂/g-C₃N₄ composite became coarse due to the introduction of g-C₃N₄ nanosheet, indicating that the g-C₃N₄ nanosheet has been coated on the surface of TiO₂ nanobelt and formed the laminated structure. Figure 3b and c display the TEM images of the b-TiO₂/g-C₃N₄ composite, the component g-C₃N₄ shows a sheet shape which is coated on the TiO₂ nanobelt. Importantly, the close contact between g-C₃N₄ nanosheet and TiO₂ nanobelt is necessary for superior catalytic performance. The high-resolution TEM (HRTEM) image of composite is depicted in Fig. 3d, the lattice fringe spacing of 0.35 nm and 0.33 nm corresponded to the (101) crystal plane of TiO₂ and (002) crystal plane of g-C₃N₄, respectively. The result of the HRTEM image clearly indicates the formation of special laminated heterojunctions. All these results confirmed that g-C₃N₄ nanosheets were successfully combined with TiO₂ nanobelts.

In order to examine the surface chemical composition and chemical states of elements in the as-prepared g-C₃N₄ and b-TiO₂/g-C₃N₄ sample, XPS measurements are performed. The survey XPS spectra of g-C₃N₄ and b-TiO₂/g-C₃N₄ sample (Figure S3) reveal the presence of Ti, O, N and C elements. The results of the high-resolution XPS spectra of Ti 2p, O 1s, N 1s and C 1s of the sample are shown in Fig. 4. Figure 4a shows the Ti 2p XPS spectra of the b-TiO₂/g-C₃N₄ sample, the peak located at 464.1, 463.5, 458.3 and 457.8 eV are assigned to Ti⁴⁺ 2p_{1/2}, Ti³⁺ 2p_{1/2}, Ti⁴⁺ 2p_{3/2} and Ti³⁺ 2p_{3/2}, respectively. The Ti³⁺ species are created due to the Ti⁴⁺ reduction of TiO₂ by the treatment with NaBH₄⁴⁷. The O 1s spectra in Fig. 4b can be fitted into two peaks, corresponding to the Ti-O bond (529.8 eV) and the -OH group (532.1 eV) on the surface of the b-TiO₂/g-C₃N₄ sample⁴. Four peaks are observed in the high-resolution XPS spectrum of N 1s for g-C₃N₄ (Fig. 4c). The peak at 398.2 eV is assigned to sp²-hybridized aromatic N bound to C atoms (C=N-C), while the signal at the binding energy of 399.3 eV indicates tertiary nitrogen N-(C)₃. The peaks at 400.9 and 404.2 eV are assigned to C-N-H groups and charging effects⁶. In N 1s XPS spectrum, compared with the g-C₃N₄, the peaks of g-C₃N₄/b-TiO₂ shifted 0.5 eV towards higher binding energy can be attributed to the chemical environment change arising from the close interaction between g-C₃N₄ and TiO₂⁴². The intensity of peaks in g-C₃N₄/b-TiO₂ is higher than in pure g-C₃N₄ due to the existence of N defects in g-C₃N₄ after treatment by NaBH₄. Figure 4d shows the XPS of g-C₃N₄ and b-TiO₂/g-C₃N₄ in the C 1s binding energy regions. Peaks at 284.8 and 287.9 eV can be assigned to the adventitious carbon C-C and N-C=N⁴⁸. Correspondingly, in the C 1s spectrum of the b-TiO₂/g-C₃N₄ sample, the peak of N-C=N shifted 0.5 eV towards higher binding energy. The shifts of the N 1s and C 1s peaks of b-TiO₂/g-C₃N₄ may be attributed to the tight contact at the interface between g-C₃N₄ and TiO₂.

The nitrogen adsorption-desorption isotherms and the pore size distributions curves of pure g-C₃N₄, TiO₂ and b-TiO₂/g-C₃N₄ heterojunction photocatalyst are shown in Fig. 5a and b. It can be seen from Fig. 5a that pure TiO₂ (36.5 m²/g) has a larger surface area than that of g-C₃N₄ (26.5 m²/g). Notably, the BET surface area of the b-TiO₂/g-C₃N₄ composite (29.3 m²/g) is decreased after coupling with TiO₂ due to the relatively low surface area of g-C₃N₄. Figure 5b shows the peak at 21.6 nm of b-TiO₂/g-C₃N₄ is larger than the pure g-C₃N₄ which is the sharp peak at 3.5 nm, indicating that g-C₃N₄ nanosheet coated on the surface of TiO₂ nanobelt.

To study the light absorption ability of as-prepared samples, the UV-vis DRS analysis was performed, as shown in Fig. 6a. The absorption wavelength of g-C₃N₄ is up to 450 nm³⁹. However, the TiO₂ is under 390 nm which means pure TiO₂ can only have a response to UV light⁴⁹. After coupling with g-C₃N₄, the TiO₂/g-C₃N₄ composite exhibits the broader absorption edge and extends to visible light region. For the b-TiO₂, the absorption shows distinctly enhanced in the visible light region, which can be attributed to the introduction of Ti³⁺ and oxygen vacancies³². As can be seen clearly, the b-TiO₂/g-C₃N₄ composite exhibits obvious absorption in the visible light range, due to the synergistic effect between TiO₂, g-C₃N₄ and the Ti³⁺. It has been reported that Ti³⁺ and oxygen vacancies could break the selection rule for indirect transitions of TiO₂ and improve absorption for photon energy⁵⁰.

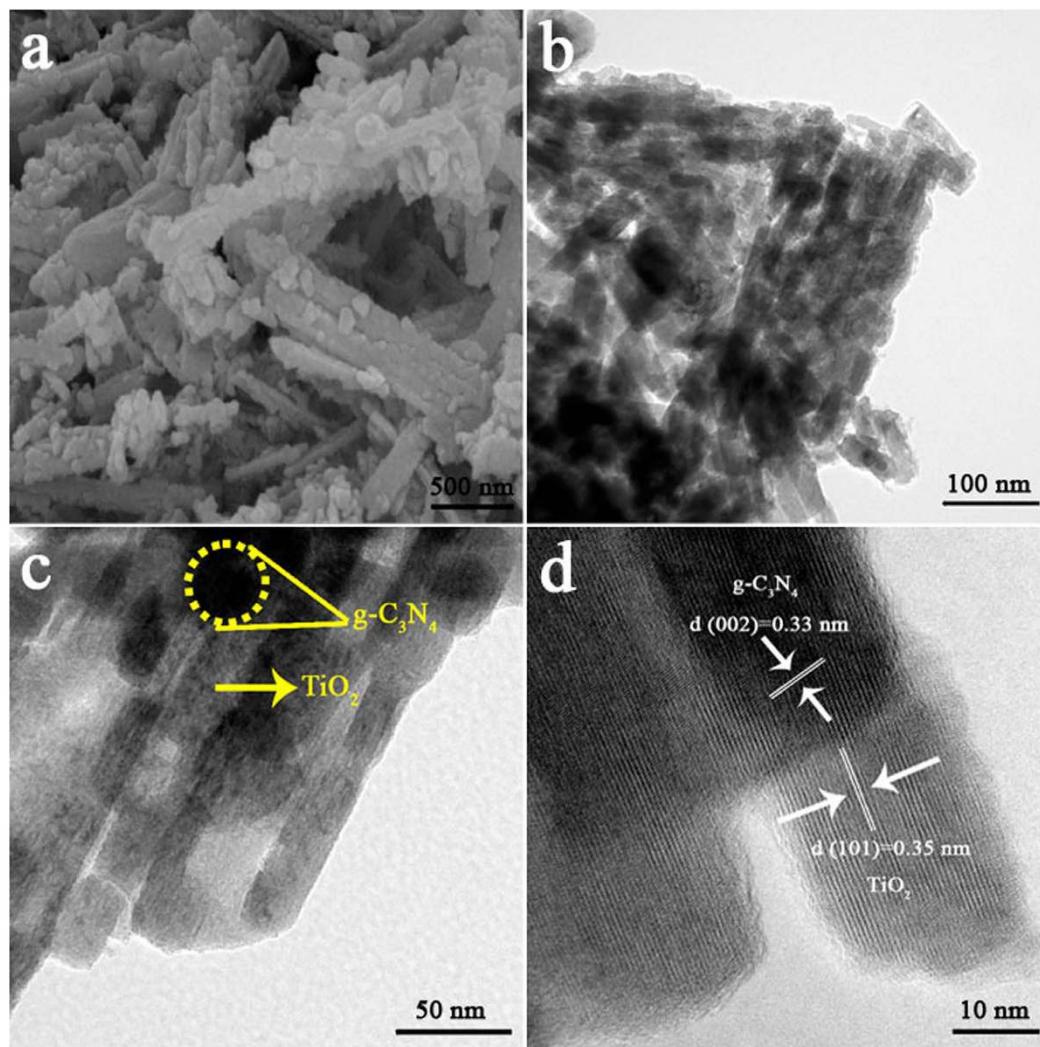


Figure 3. SEM and TEM images of b-TiO₂/g-C₃N₄: SEM image of b-TiO₂/g-C₃N₄ (a), TEM image of b-TiO₂/g-C₃N₄ (b,c), and HRTEM image of b-TiO₂/g-C₃N₄ (d).

Figure 6b shows the band gap energies of all the samples. The band gap of TiO₂, g-C₃N₄, TiO₂/g-C₃N₄, b-TiO₂ and b-TiO₂/g-C₃N₄ are 3.15, 2.62, 2.88, 2.58 and 2.32 eV, respectively. The narrow band gap is beneficial to improve the visible light absorption properties, so the b-TiO₂/g-C₃N₄ can show an enhanced photocatalytic performance.

Figure 7a shows the photocatalytic degradation of MO for different photocatalysts. The blank test demonstrates that MO could not be degraded under visible light irradiation without catalysts, and thus it can be considered that MO is stable. For pure TiO₂ and g-C₃N₄, the concentration of MO is only reduced by about 17.1% and 24.6% under visible light irradiation for 120 min. The TiO₂/g-C₃N₄ and b-TiO₂ show higher photocatalytic activity, which the removal of MO is about 45.6% and 64.7%. As expected, the b-TiO₂/g-C₃N₄ photocatalyst exhibits higher photocatalytic activity than other samples under visible light irradiation. The concentration of MO is reduced by about 95.1%. From Fig. 7b, the apparent reaction rate constant (*k*) values of TiO₂, g-C₃N₄, TiO₂/g-C₃N₄, b-TiO₂ and b-TiO₂/g-C₃N₄ are 0.0016, 0.0025, 0.0052, 0.0074 and 0.0153 min⁻¹, respectively. Moreover, the *k* value of b-g-C₃N₄/TiO₂ is also higher than others, which is about ~9 times higher than that of pure TiO₂. This result suggests that introducing Ti³⁺ of black TiO₂ and a better heterostructured combination between g-C₃N₄ and black TiO₂ could promote the separation of photogenerated carriers and accelerate the electron transfer.

The photocatalytic activity of the as-prepared samples is also evaluated for hydrogen evolution under the simulated solar light (AM 1.5) irradiation. As indicated in Fig. 8a, the pure g-C₃N₄ only shows a H₂ generation rate of 108.2 μmol h⁻¹ g⁻¹. This is probably due to the high recombination of photoinduced electron-holes. For pure TiO₂, very little H₂ is produced. The hydrogen generation rate of b-TiO₂, TiO₂/g-C₃N₄ and b-TiO₂/g-C₃N₄ are 130.5, 388.4 and 555.8 μmol h⁻¹ g⁻¹, respectively. These results indicate that the b-TiO₂/g-C₃N₄ materials have the highest photocatalytic activity among the as-prepared samples, revealing that the Ti³⁺ and the heterojunction structure contribute to high photocatalytic activity. To evaluate the stability of b-TiO₂/g-C₃N₄, recycling experiments were carried out on hydrogen evolution reaction for five times. As shown in Fig. 8b, the b-TiO₂/g-C₃N₄

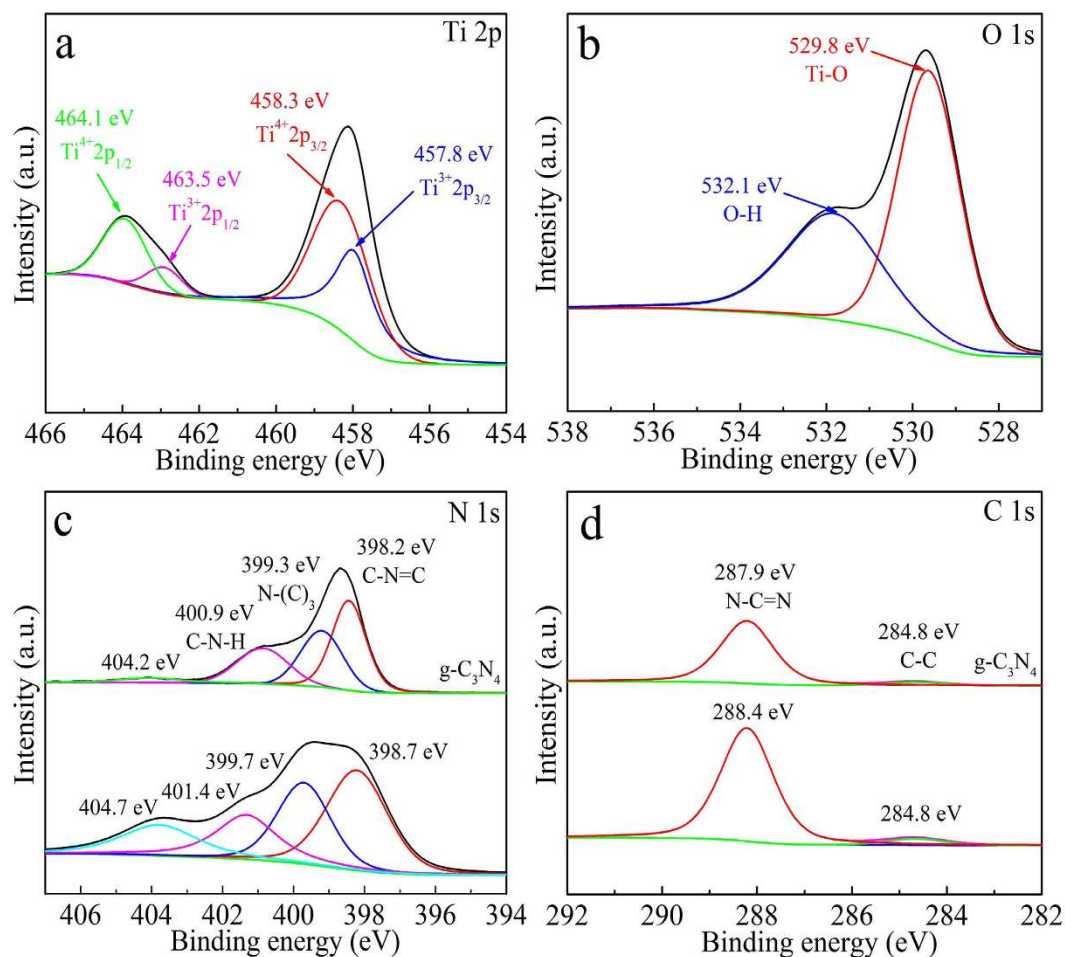


Figure 4. XPS spectra of Ti 2p spectra of b-TiO₂/g-C₃N₄ (a), O 1s spectra of b-TiO₂/g-C₃N₄ (b), N 1s spectra of g-C₃N₄ and b-TiO₂/g-C₃N₄ (c), and C 1s spectra of g-C₃N₄ and b-TiO₂/g-C₃N₄ (d).

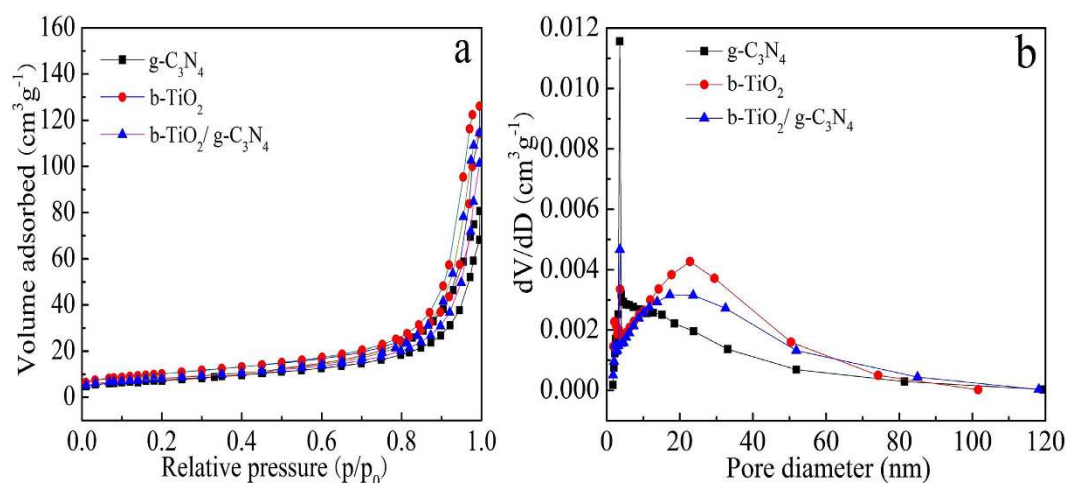


Figure 5. N₂-adsorption/desorption isotherm curves (a) and BJH pore size distribution plots (b) of g-C₃N₄, b-TiO₂, and b-TiO₂/g-C₃N₄, respectively.

exhibits no obvious loss in hydrogen evolution activity after five cycles lasting 25 h in total, indicating the high stability of the photocatalyst.

As can be seen from Fig. 9a, the electrochemical impedance spectra (EIS) result reflects that the impedance arc radius of b-TiO₂/g-C₃N₄ is smaller than that of TiO₂ and g-C₃N₄ under visible light, indicating that b-TiO₂/g-C₃N₄

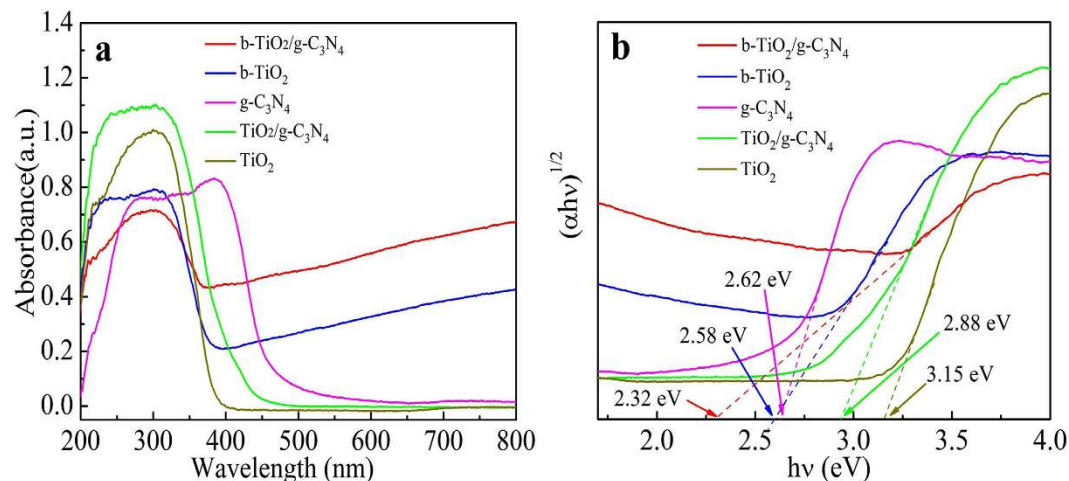


Figure 6. UV-visible diffuse reflectance spectra (a) and determination of the indirect interband transition energies (b) of TiO₂, g-C₃N₄, TiO₂/g-C₃N₄, b-TiO₂ and b-TiO₂/g-C₃N₄, respectively.

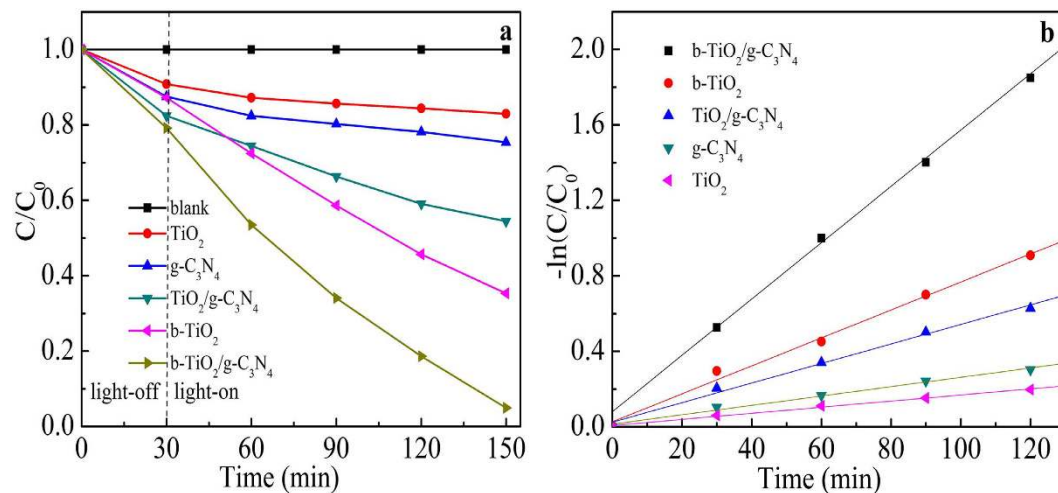


Figure 7. Photodegradation of MO by using different samples under visible-light irradiation (a), and variations of $-\ln(C/C_0)$ versus visible-light irradiation time with different samples (b) (C is the corresponding degradative concentration of MO and C_0 is initial concentration of MO).

composite demonstrates enhanced separation efficiency of the photoexcited charge carriers compared with that of pure TiO₂ and g-C₃N₄. Figure 9b shows the fluorescence (FL) intensity of these samples in 1 h under Xenon lamp irradiation with a 420 nm cut-off filter. It is clearly observed that the fluorescence intensity of b-TiO₂/g-C₃N₄ is the strongest than any other samples at 425 nm, indicating that the b-TiO₂/g-C₃N₄ can produce the largest amount of ·OH radicals under visible light irradiation, consisting with the excellent photodegradation efficiency of MO.

On the basis of the results above, a sufficient contact interface between g-C₃N₄ nanosheet and TiO₂ nanobelt is achieved. As shown in Fig. 10, the Ti³⁺ and oxygen vacancies are detected at the bottom of the TiO₂ conduction band (CB), which can be easily narrow the bandgap of TiO₂ nanobelt and improve the optical absorption properties¹². When the catalyst is exposed to visible-light irradiation, g-C₃N₄ can produce photo-induced electron-hole pairs. The photogenerated electrons in the conduction band of g-C₃N₄ can transfer to the conduction band of TiO₂¹⁹. Since the CB levels of TiO₂ is more negative than the potential of O₂/·O₂⁻ (-0.046 eV vs. NHE at pH = 7), as a result, the electrons in CB of TiO₂ can be trapped by dissolved oxygen to generate ·O₂⁻ radical species. And compared with the potential of ·OH/H₂O (2.27 eV vs. NHE at pH = 7), the remained h⁺ on the VB of g-C₃N₄ can not react with H₂O to generate ·OH radicals due to the lower VB level of g-C₃N₄ (1.63 eV vs. NHE at pH = 7)^{7,51}. Subsequently, the radical species ·O₂⁻ and h⁺ can directly degrade organic pollutants. In this system, the ·OH is mainly produced by the b-TiO₂, not g-C₃N₄. The separated electron-holes separation will enhance the photocatalytic activity as compared to pure TiO₂ and g-C₃N₄ due to the compact interface between the two materials.

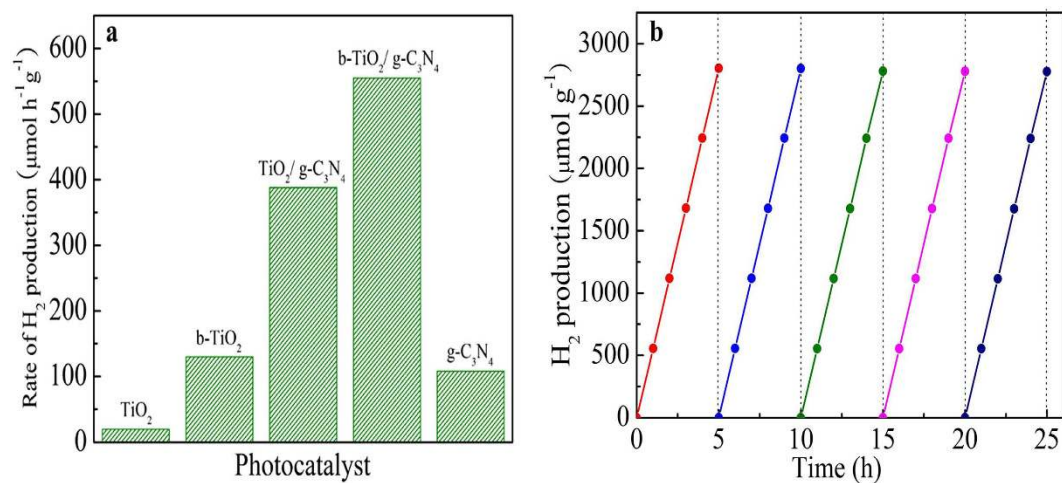


Figure 8. The photocatalytic H₂ evolution of different samples (a) and the recyclability tests of b-TiO₂/g-C₃N₄ during the photocatalytic H₂ evolution under AM 1.5 (b).

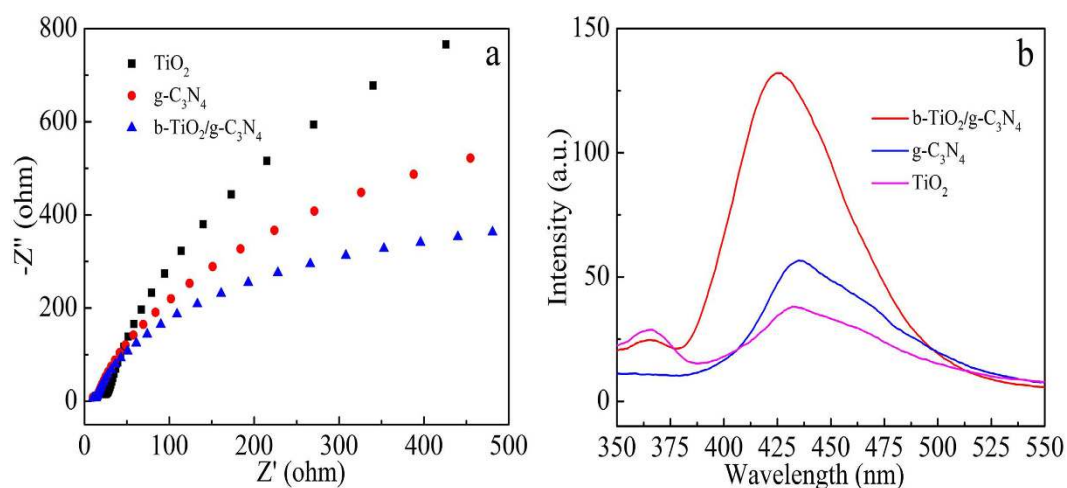


Figure 9. Electrochemical impedance spectra (a) and fluorescence intensity in 1 h (b) of TiO₂, g-C₃N₄ and b-TiO₂/g-C₃N₄, respectively.

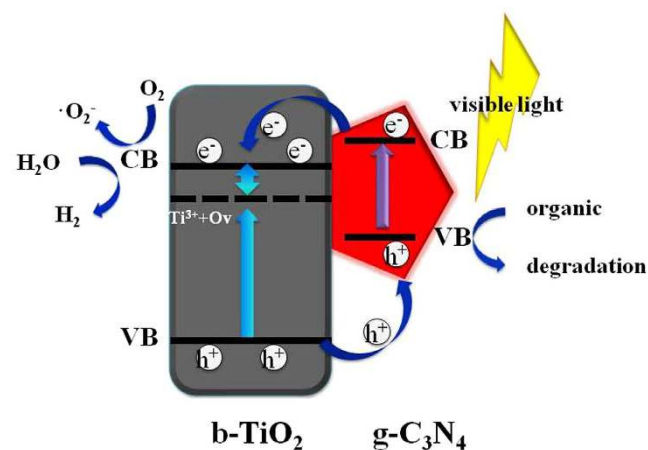


Figure 10. Proposed photocatalytic mechanism of b-TiO₂/g-C₃N₄ composite under visible light irradiation.

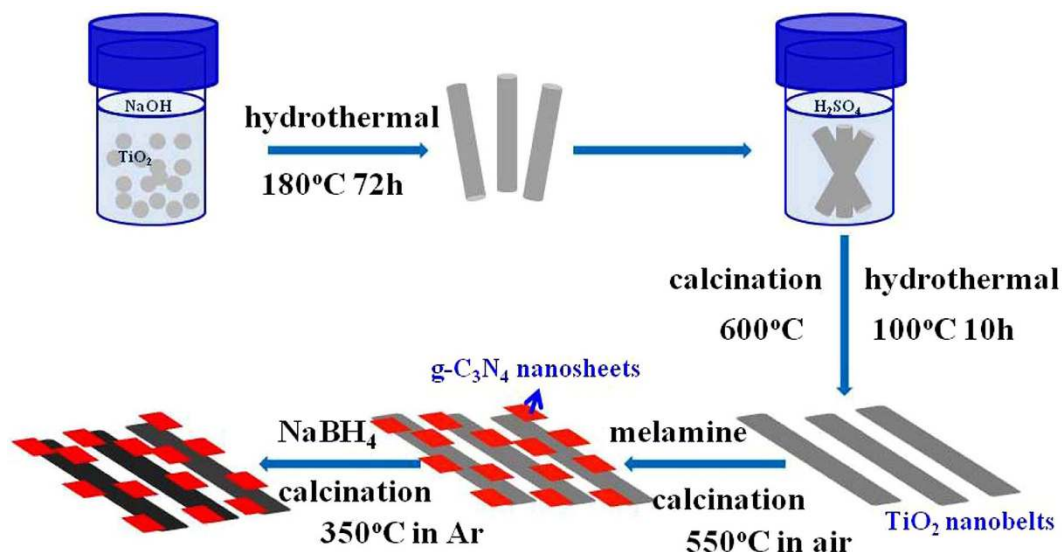


Figure 11. Schematic diagram for the formation of the b-TiO₂/g-C₃N₄ composite.

Conclusions

In conclusion, based on a hydrothermal-calcination method, b-TiO₂/g-C₃N₄ laminated heterojunctions were prepared by mixing the melamine and the as-prepared TiO₂ nanobelt, followed by an *in-situ* controllable solid-state reaction approach. The formation of a strong contact between TiO₂ and g-C₃N₄ by this method greatly enhanced the separation efficiency of photoinduced electrons and holes. The narrow band gap of b-TiO₂/g-C₃N₄ composite was attributed to the introduction of g-C₃N₄ and the Ti³⁺ species. Under visible light irradiation, b-TiO₂/g-C₃N₄ composite exhibited higher photocatalytic activity than g-C₃N₄, TiO₂, b-TiO₂ and TiO₂/g-C₃N₄ towards the degradation of methyl orange and hydrogen evolution. Based on this work, the b-TiO₂/g-C₃N₄ composite is expected to be a highly effective visible light photocatalyst for practical applications.

Methods

Materials. TiO₂ (P25) power was purchased from Degussa Co. Ltd, Germany. Absolute ethanol (EtOH), sulfuric acid (H₂SO₄), and sodium hydroxide (NaOH), were purchased from Tianjin Kermel Chemical Reagent Co. LTD, China. Sodium boron hydride (NaBH₄, 98%) was purchased from Aladdin Reagent Company, China. All reagents used in the experiments were analytical grade and employed without further purification, and the deionized (DI) water was used throughout this study.

Preparation of TiO₂ nanobelt. 0.2 g of P25 was mixed with 40 mL of 10 M NaOH aqueous solution. The suspension was transferred to a 50 mL Teflon-lined autoclave and maintained at 180 °C for 72 h. The obtained products were washed thoroughly with deionized water and immersed in 0.1 M HCl aqueous solution for 24 h. Then the samples were immersed in a 0.02 M H₂SO₄ aqueous solution and maintained at 100 °C for 10 h. Finally, the products were washed with deionized water for several times and dried at 70 °C for 10 h. The sample was annealed at 600 °C for 2 h.

Preparation of TiO₂/g-C₃N₄ photocatalyst. TiO₂/g-C₃N₄ photocatalyst was fabricated by calcining the mixtures of the melamine and TiO₂ nanobelt powder. A given amount of melamine was ground with the TiO₂ nanobelts (weight ratios of TiO₂ nanobelt to melamine: 1:6). Finally, the mixture was calcined in a muffle furnace for 2 h at 550 °C with a heating rate of 20 °C min⁻¹ in air atmosphere. For comparison, g-C₃N₄ was also synthesized by directly calcining melamine under air atmosphere at 550 °C for 2 h.

Preparation of b-TiO₂/g-C₃N₄ photocatalyst. At room temperature, 2 g of the prepared sample was mixed with 4 g of NaBH₄ and the mixture was ground for 30 min thoroughly. Then the mixture was placed in a porcelain boat and heated in a tubular furnace for 1 h at 350 °C with a ramping rate of 5 °C min⁻¹ under Ar atmosphere. After naturally cooling down to room temperature, the b-TiO₂/g-C₃N₄ was obtained (Fig. 11). The obtained sample was washed with deionized water and absolute ethanol for several times. For comparison, the pure black TiO₂ (b-TiO₂) was also synthesized under the same condition.

The Ti³⁺ species are created due to the Ti⁴⁺ reduction of TiO₂ by the treatment with NaBH₄, so the white TiO₂ nanobelt is turned to black⁵². NaBH₄ reduction induces a distinctly increase in the peak intensity of Ti³⁺ and the result shows that more Ti³⁺ is formed on the surface or subsurface of b-TiO₂, which may change the surface chemical bonding environment of TiO₂⁵³.

Characterization. The powder X-ray diffraction (XRD) patterns were acquired on a Bruker D8 Advance diffractometer by using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). X-ray photoelectron spectroscopy (XPS) was measured on a PHI-5700 ESCA instrument with Al-K α X-ray source. The Fourier transform infrared spectra (FT-IR) of the samples

were collected with a PerkinElmer spectrum one system, using KBr as diluents. The morphology of the samples was observed on a field emission scanning electron microscope (FE-SEM, Hitachi S-4800). Transmission electron microscopy (TEM) was performed using a JEM-2100 electron microscope (JEOL, Japan). Surface area determination was performed by the Brunauer-Emmett-Teller (BET) method with an AUTOSORB-1 (Quantachrome Instruments) nitrogen adsorption apparatus. The UV-vis absorption spectra of the samples were measured by a UV-vis spectrophotometer (UV-2550, Shimadzu) with an integrating sphere attachment, and BaSO₄ was used as the reference material. The ·OH radicals were detected by the fluorescence probe technique with terephthalic acid (FL-TA) on a RF-5301PC fluorescence spectrophotometer. The electrochemical impedance spectroscopy (EIS) was performed with a computer-controlled IM6e Impedance measurement unit (Zahner Elektrik, Germany).

Photocatalytic hydrogen evolution. Photocatalytic hydrogen evolution tests were carried out in an online photocatalytic hydrogen generation system (AuLight, Beijing, CEL-SPH2N) at room temperature. The experiments were carried out by taking 50 mg of photocatalysts in a 100 mL of aqueous solution containing the 80 mL of deionized water and 20 mL of methanol used as the sacrificial reagent in closed-gas circulation reaction cell. Prior to the reaction, the system was vacuumized completely to remove O₂ and CO₂ dissolved in water. Then, the mixture solution was irradiated by a 300 W Xe-lamp equipped with an AM 1.5 G filter (Oriel, USA). The hydrogen was periodically analyzed using an on-line gas chromatography with the interval of each 1 h (SP7800, TCD, molecular sieve 5 Å, N₂ carrier, Beijing Keruida, Ltd).

Photocatalytic degradation. The measurement of photocatalytic activity was evaluated by the degradation of methyl orange (MO) under visible light irradiation. A 300 W Xe-lamp with a 420 nm cutoff filter. The experimental procedures were as follows: at room temperature, 30 mg of photocatalyst was added to 30 mL of 10 mg/L MO aqueous solution, which was placed at 20 cm from the light source. Before irradiation, the suspension was magnetically stirred in the dark for 30 min to ensure an adsorption-desorption equilibrium between the photocatalysts and MO. At certain intervals, the reaction solution was centrifuged to remove the particles. Finally, the concentration of MO was measured at $\lambda = 464$ nm by using a T6 UV-vis spectrophotometer.

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Author Contributions

Xing Z.P. and Shen L.Y. conceived the experiments, Xing Z.P., Shen L.Y., Zou J.L., Li Z.Z., Wu X.Y., Zhang Y.C. and Zhu Q. conducted the experiments, Xing Z.P., Yang S.L. and Zhou W. analysed the results. All authors reviewed the manuscript.

Additional Information

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