Black TiO$_2$ nanobelts/g-C$_3$N$_4$ nanosheets Laminated Heterojunctions with Efficient Visible-Light-Driven Photocatalytic Performance

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Black TiO$_2$ nanobelts/g-C$_3$N$_4$ nanosheets laminated heterojunctions (b-TiO$_2$/g-C$_3$N$_4$) 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, N$_2$ adsorption, and UV-visible diffuse reflectance spectroscopy, respectively. The results show that special laminated heterojunctions are formed between black TiO$_2$ nanobelts and g-C$_3$N$_4$ nanosheets, which favor the separation of photogenerated electron-hole pairs. Furthermore, the presence of Ti$^{3+}$ and g-C$_3$N$_4$ greatly enhance the absorption of visible light. The resultant b-TiO$_2$/g-C$_3$N$_4$ materials exhibit higher photocatalytic activity than that of g-C$_3$N$_4$, TiO$_2$, b-TiO$_2$, and TiO$_2$/g-C$_3$N$_4$ for degradation of methyl orange (95%) and hydrogen evolution (555.8 μmol h$^{-1}$ g$^{-1}$) under visible light irradiation. The apparent reaction rate constant (k) of b-TiO$_2$/g-C$_3$N$_4$ is ~9 times higher than that of pristine TiO$_2$. 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$^1$ and hydrogen production from water splitting$^2$ has been regarded as a promising method to solve environment issue$^3$ and energy crisis$^4$. Among various photocatalyst materials, titanium dioxide (TiO$_2$) is the most famous photocatalysts owing to its low cost, high photocatalytic activity, good stability and nontoxicity$^5$–$^8$. 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 activity$^9$. To date, various methods were developed to improve the visible light absorption of TiO$_2$, including metal and non-metal elements doping$^{10}$, surface sensitization$^{11}$, semiconductor heterojunction$^{12}$, 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-C$_3$N$_4$) has been reported to be a non-toxic, stable and facile metal-free visible light photocatalyst$^{13}$–$^{15}$. The band-gap of g-C$_3$N$_4$ is ~2.7 eV, indicating a strong absorption in visible light region$^{16}$. g-C$_3$N$_4$ has displayed excellent properties in photodegradation of organic contaminant$^{17}$ and H$_2$ evolution$^{18}$. However, the key issue with the high recombination of photoinduced electron-hole pairs is still limited the photocatalytic applications of g-C$_3$N$_4$.$^{19}$ To resolve this problem, coupling g-C$_3$N$_4$ with other semiconductors has attracted much attention, which inhibits the recombination of photoinduced electron-hole pairs and thus improves catalytic performance$^{20}$. There have been many studies on hybrids of g-C$_3$N$_4$ with TiO$_2$. 

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Recent studies on these composites have shown improved photocatalytic performance in dye degradation and H₂ evolution under visible light irradiation. TiO₂ nanobelts, have attracted great interest because of their large surface areas, chemical stability, and provide sufficient space for the new nucleation. 2D semiconductor materials, such as g-C₃N₄ nanosheets, possess a unique layered structure and narrow band gap, which could absorb visible light efficiently. Therefore, it is believed that 2D g-C₃N₄ nanosheets coupled with TiO₂ 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 TiO₂/g-C₃N₄ composite catalyst practical application, it is necessary to enhance the absorption of TiO₂/g-C₃N₄ composite photocatalyst in the visible light region. During the past few decades, much effort has been devoted to make colorful TiO₂ for better optical absorption. Recently, Mao et al. presented black hydrogenated TiO₂ with enhanced solar light absorption. The black TiO₂ displayed much higher photocatalytic performance over the pristine white TiO₂, which was attributed to the higher photoinduced electron-hole pairs separation capability. The enhanced solar light absorption of the black TiO₂ was attributed to the formed Ti³⁺ and oxygen vacancies. Since then, different synthesis methods were proposed to prepare black TiO₂, including high pressure hydrogenation, plasma assisted hydrogenation, chemical reduction, and high-temperature Al vapor reduction. Therefore, the development of high photocatalytic activity based on black TiO₂ is promising.

To the best of our knowledge, up to now, few researchers report black TiO₂ combining with g-C₃N₄ for pollutants degradation and hydrogen evolution under visible-light irradiation.

In this work, based on a hydrothermal-calcination method, black TiO₂/g-C₃N₄ composite 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 TiO₂, g-C₃N₄, b-TiO₂, TiO₂/g-C₃N₄, and b-TiO₂/g-C₃N₄ composites. For pure TiO₂, 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 TiO₂. The b-TiO₂ still keeps the pristine crystal phase after the process of treatment with NaBH₄, indicating that the crystal phase can’t be influenced by NaBH₄. However, the XRD pattern of b-TiO₂ shows a slightly extending characteristic peak at 25.3°, which may be ascribed to the effect of oxygen vacancies (Ov), leading the disorder-induced lattice. The component g-C₃N₄ 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. For the TiO₂/g-C₃N₄ and b-TiO₂/g-C₃N₄ samples, the XRD patterns show the characteristic diffraction peaks of both anatase and g-C₃N₄, indicating that the composites consisted of both anatase TiO₂ and g-C₃N₄. 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 TiO₂, b-TiO₂, g-C₃N₄, and b-TiO₂/g-C₃N₄ heterojunction photocatalysts, as shown in Fig. 2. For pure TiO₂ and b-TiO₂, the main peaks at appearing at 400–700 cm⁻¹ is assigned to Ti-O-Ti and Ti-O stretching vibration modes. The peaks at about 1650 and 3400–3500 cm⁻¹ are corresponding to hydroxyl group and physically absorbed water on the surface of the TiO₂, respectively. In the FT-IR spectrum of g-C₃N₄, the absorption band at 1640 cm⁻¹ can be corresponded to the C-N heterocycle stretching vibration modes, while the four at 1241, 1320, 1409, and 1567 cm⁻¹ to aromatic C-N stretching vibration modes. The peak at 808 cm⁻¹ is associated with the breathing mode of triazine units. For the b-TiO₂/g-C₃N₄ composite, it can be clearly seen that all the main absorption peaks of g-C₃N₄ and TiO₂ appeared in b-TiO₂/g-C₃N₄ composite, suggesting the presence of TiO₂ and g-C₃N₄ in the as-prepared composite.
The morphology and microstructure of samples are studied by SEM and TEM. Figure S1 shows the SEM image of g-C$_3$N$_4$, which exhibits a wrinkled sheet structure. It could be found from Figure S2 that TiO$_2$ nanobelt was about 2–3 μm long, 50–200 nm wide and appeared smooth surface. The SEM image of b-TiO$_2$/g-C$_3$N$_4$ is presented in Fig. 3a. Apparently, when compared with the pure TiO$_2$ nanobelt, the surface of the b-TiO$_2$/g-C$_3$N$_4$ composite became coarse due to the introduction of g-C$_3$N$_4$ nanosheet, indicating that the g-C$_3$N$_4$ nanosheet has been coated on the surface of TiO$_2$ nanobelt and formed the laminated structure. Figure 3b and c display the TEM images of the b-TiO$_2$/g-C$_3$N$_4$ composite; the component g-C$_3$N$_4$ shows a sheet shape which is coated on the TiO$_2$ nanobelt. Importantly, the close contact between g-C$_3$N$_4$ nanosheet and TiO$_2$ 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 TiO$_2$ and (002) crystal plane of g-C$_3$N$_4$, respectively. The result of the HRTEM image clearly indicates the formation of special laminated heterojunctions. All these results confirmed that g-C$_3$N$_4$ nanosheets were successfully combined with TiO$_2$ nanobelts.

In order to examine the surface chemical composition and chemical states of elements in the as-prepared g-C$_3$N$_4$ and b-TiO$_2$/g-C$_3$N$_4$ sample, XPS measurements are performed. The survey XPS spectra of g-C$_3$N$_4$ and b-TiO$_2$/g-C$_3$N$_4$ 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-TiO$_2$/g-C$_3$N$_4$ sample, the peak located at 464.1, 463.5, 458.3 and 457.8 eV are assigned to Ti$^{4+}$ 2p$_{3/2}$, Ti$^{4+}$ 2p$_{1/2}$, Ti$^{3+}$ 2p$_{1/2}$ and Ti$^{3+}$ 2p$_{3/2}$, respectively. The Ti$^{4+}$ species are created due to the Ti$^{4+}$ reduction of TiO$_2$ by the treatment with NaBH$_4$. 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-TiO$_2$/g-C$_3$N$_4$ sample. Four peaks are observed in the high-resolution XPS spectrum of N 1s for g-C$_3$N$_4$ (Fig. 4c). The peak at 398.2 eV is assigned to sp$^2$-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 to the Ti-O bond (529.8 eV) and the -OH group (532.1 eV) on the surface of the b-TiO$_2$/g-C$_3$N$_4$ sample. Four sharp carbon C-C and N-C species are created due to the Ti$^{4+}$ reduction of TiO$_2$ by the treatment with NaBH$_4$. Four peaks are observed in the high-resolution XPS spectrum of N 1s for b-TiO$_2$/g-C$_3$N$_4$ (Fig. 4c). The peak at 398.2 eV is assigned to sp$^2$-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 to the Ti-O bond (529.8 eV) and the -OH group (532.1 eV) on the surface of the b-TiO$_2$/g-C$_3$N$_4$ sample. Four peaks are observed in the high-resolution XPS spectrum of N 1s for b-TiO$_2$/g-C$_3$N$_4$ (Fig. 4c). The peak at 398.2 eV is assigned to sp$^2$-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 to the Ti-O bond (529.8 eV) and the -OH group (532.1 eV) on the surface of the b-TiO$_2$/g-C$_3$N$_4$ sample.

The nitrogen adsorption-desorption isotherms and the pore size distributions curves of pure g-C$_3$N$_4$, TiO$_2$ and b-TiO$_2$/g-C$_3$N$_4$ heterojunction catalyst are shown in Fig. 5a and b. It can be seen from Fig. 5a that pure TiO$_2$ (36.5 m$^2$/g) has a larger surface area than that of g-C$_3$N$_4$ (26.5 m$^2$/g). Notably, the BET surface area of the b-TiO$_2$/g-C$_3$N$_4$ composite (29.3 m$^2$/g) is decreased after coupling with TiO$_2$ due to the relatively low surface area of g-C$_3$N$_4$. Figure 5b shows the peak at 21.6 nm of b-TiO$_2$/g-C$_3$N$_4$ is larger than the pure g-C$_3$N$_4$ which is the sharp peak at 3.5 nm, indicating that g-C$_3$N$_4$ nanosheet coated on the surface of TiO$_2$ 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-C$_3$N$_4$ is up to 450 nm. However, the TiO$_2$ is under 390 nm which means pure TiO$_2$ can only have a response to UV light. After coupling with g-C$_3$N$_4$, the TiO$_2$/g-C$_3$N$_4$ composite exhibits the broader absorption edge and extends to visible light region. For the b-TiO$_2$, the absorption shows distinctly enhanced in the visible light region, which can be attributed to the introduction of Ti$^{3+}$ and oxygen vacancies. As can be seen clearly, the b-TiO$_2$/g-C$_3$N$_4$ composite exhibits obvious absorption in the visible light range, due to the synergistic effect between TiO$_2$, g-C$_3$N$_4$ and the Ti$^{3+}$. It has been reported that Ti$^{3+}$ and oxygen vacancies could break the selection rule for indirect transitions of TiO$_2$ and improve absorption for photon energy.

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Figure 2. FT-IR spectra of g-C$_3$N$_4$ (a), b-TiO$_2$/g-C$_3$N$_4$ (b), TiO$_2$ (c) and b-TiO$_2$ (d), respectively.
Figure 6b shows the band gap energies of all the samples. The band gap of TiO$_2$, g-C$_3$N$_4$, TiO$_2$/g-C$_3$N$_4$, b-TiO$_2$ and b-TiO$_2$/g-C$_3$N$_4$ 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-TiO$_2$/g-C$_3$N$_4$ 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 TiO$_2$ and g-C$_3$N$_4$, the concentration of MO is only reduced by about 17.1% and 24.6% under visible light irradiation for 120 min. The TiO$_2$/g-C$_3$N$_4$ and b-TiO$_2$ show higher photocatalytic activity, which the removal of MO is about 45.6% and 64.7%. As expected, the b-TiO$_2$/g-C$_3$N$_4$ 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 TiO$_2$, g-C$_3$N$_4$, TiO$_2$/g-C$_3$N$_4$, b-TiO$_2$ and b-TiO$_2$/g-C$_3$N$_4$ are 0.0016, 0.0025, 0.0052, 0.0074 and 0.0153 min$^{-1}$, respectively.

Moreover, the k value of b-g-C$_3$N$_4$/TiO$_2$ is also higher than others, which is about ~9 times higher than that of pure TiO$_2$. This result suggests that introducing Ti$^{3+}$ of black TiO$_2$ and a better heterostructured combination between g-C$_3$N$_4$ and black TiO$_2$ 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-C$_3$N$_4$ only shows a H$_2$ generation rate of 108.2 μmol h$^{-1}$ g$^{-1}$. This is probably due to the high recombination of photoinduced electron-holes. For pure TiO$_2$, very little H$_2$ is produced. The hydrogen generation rate of b-TiO$_2$, TiO$_2$/g-C$_3$N$_4$ and b-TiO$_2$/g-C$_3$N$_4$ are 130.5, 388.4 and 555.8 μmol h$^{-1}$ g$^{-1}$, respectively. These results indicate that the b-TiO$_2$/g-C$_3$N$_4$ materials have the highest photocatalytic activity among the as-prepared samples, revealing that the Ti$^{3+}$ and the heterojunction structure contribute to high photocatalytic activity. To evaluate the stability of b-TiO$_2$/g-C$_3$N$_4$, recycling experiments were carried out on hydrogen evolution reaction for five times. As shown in Fig. 8b, the b-TiO$_2$/g-C$_3$N$_4$
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
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 properties. 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 TiO2. 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). 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 electrons on the CB of TiO2 can also split water to produce H2. The effective 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 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/C0) versus visible-light irradiation time with different samples (b) (C is the corresponding degradative concentration of MO and C0 is initial concentration of MO).
Figure 8. The photocatalytic H$_2$ evolution of different samples (a) and the recyclability tests of b-TiO$_2$/g-C$_3$N$_4$ during the photocatalytic H$_2$ evolution under AM 1.5 (b).

Figure 9. Electrochemical impedance spectra (a) and fluorescence intensity in 1 h (b) of TiO$_2$, g-C$_3$N$_4$ and b-TiO$_2$/g-C$_3$N$_4$, respectively.

Figure 10. Proposed photocatalytic mechanism of b-TiO$_2$/g-C$_3$N$_4$ composite under visible light irradiation.
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) powder 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 condition 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 Ti 3+ 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 Kα radiation (λ = 1.5406 Å). X-ray photoelectron spectroscopy (XPS) was measured on a PHI-5700 ESCA instrument with Al-Kα X-ray source. The Fourier transform infrared spectra (FT-IR) of the samples
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 Xeon-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 Xeon-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 λ = 464 nm by using a T6 UV-vis spectrophotometer.

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Author Contributions

Zhu Q. conducted the experiments, Xing Z.P., Yang S.L. and Zhou W. analysed the results. All authors reviewed the manuscript.

Additional Information

Supplementary information accompanies this paper at http://www.nature.com/srep

Competing financial interests: The authors declare no competing financial interests.

Acknowledgements

We gratefully acknowledge the support of this research by the National Natural Science Foundation of China (21376065, 81102511, 11573134 and 51672073), the National Science Foundation of Heilongjiang Province (QC2012C001, QC2013C079, and E201456), the Heilongjiang Postdoctoral Startup Fund (LRH-Q14135), the Program for New Century Excellent Talents in University of Heilongjiang Province (1253-NCET-020), the University Nursing Program for Young Scholars with Creative Talents in Heilongjiang Province (UNPYSCT-2015014), and the Science and Technology Innovation Talent Program for Young Scholars in Heilongjiang Province (UNPYSCT-2016018).

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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

Supplementary information accompanies this paper at http://www.nature.com/srep

Competing financial interests: The authors declare no competing financial interests.
