

Short communication

# A novel composite photocatalyst for water splitting hydrogen production

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## Abstract

A novel composite photocatalyst, Pt-TiO<sub>2-x</sub>N<sub>x</sub>-WO<sub>3</sub> was synthesized by the template method and characterized by X-ray diffraction (XRD), ultraviolet–visible light diffusion spectroscopy (UV–vis), and element analysis. XRD spectra indicated that the photocatalyst was in anatase form and the diagnostic peak for WO<sub>3</sub> existed. Combined with the XRD spectra and the results of elemental analysis, the formula of the composite photocatalyst was determined to be Pt-TiO<sub>2-x</sub>N<sub>x</sub>-WO<sub>3</sub>. UV–vis spectra showed the absorption edge was red-shifted to around 750 nm. Under the irradiation of ultraviolet, and with Na<sub>2</sub>S/Na<sub>2</sub>SO<sub>3</sub> as the sacrificial reagent, the composite photocatalyst showed higher hydrogen production activity than anatase TiO<sub>2</sub>, and under irradiation with visible light ( $\lambda > 400$  nm) it showed higher hydrogen production activity than TiO<sub>2-x</sub>N<sub>x</sub> while the anatase TiO<sub>2</sub> showed negligible activity. An explanation was put forward for the mechanism of the red-shift of the absorption edge and the hydrogen production activity improvement.

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## 1. Introduction

Since the discovery of photoelectrochemical splitting of water on n-TiO<sub>2</sub> electrodes [1], the technology of semiconductor-based photocatalytic splitting of water to hydrogen has been one of the most promising technologies to obtain inexpensive hydrogen. To search for suitable photocatalysts, numerous photocatalysts, such as TiO<sub>2</sub> [2], NaTaO<sub>3</sub> [3], etc. have been synthesized and studied. These photocatalysts show very good activities under ultraviolet light, but showed little or no activities under visible light due to their large band gaps. The ultraviolet light accounts for only about 4% of the incoming solar energy, but visible light accounts for about 43% of the incoming solar energy on the surface of the earth. So developing photocatalysts with narrow band gaps and visible light activities has been the main thrust of photocatalyst research.

In recent years, various visible-light photocatalysts were reported. Zou et al. [4–7] developed a series of double and tri-metal oxides visible-light photocatalysts, such as In<sub>1-x</sub>Ni<sub>x</sub>TaO<sub>4</sub>, NiM<sub>2</sub>O<sub>6</sub>, MCo<sub>1/3</sub>Nb<sub>2/3</sub>O<sub>3</sub>, AMn<sub>2</sub>O<sub>4</sub>, etc. Domen and co-

workers [8–11] also developed a series of visible-light photocatalysts, TaON, Ta<sub>3</sub>N<sub>5</sub>, Ln<sub>2</sub>Ti<sub>2</sub>S<sub>2</sub>O<sub>5</sub>, etc. Kudo and co-workers [12–14] synthesized several solid solution visible-light photocatalysts, such as (AgIn)<sub>x</sub>Zn<sub>2(1-x)</sub>S<sub>2</sub>, (CuIn)<sub>x</sub>Zn<sub>2(1-x)</sub>S<sub>2</sub> and ZnS-CuInS<sub>2</sub>-AgInS<sub>2</sub>.

TiO<sub>2</sub> is the most studied photocatalyst. It is stable, of high photocatalytic activity, low cost and easily prepared, but it shows negligible visible-light activity. Thus, much effort has been directed to lowering its band gap and improving its photocatalytic performance under visible light, especially by doping transition metals into TiO<sub>2</sub> [15,16]. But such efforts have only resulted in insignificant changes in the band-gap energy of TiO<sub>2</sub>. In 2001, Asahi et al. [17] found that doping nitrogen into TiO<sub>2</sub> can shift its optical absorption to the visible-light region. The synthesized compound, TiO<sub>2-x</sub>N<sub>x</sub>, could photodegrade methylene blue and gaseous acetaldehyde under visible light ( $\lambda < 500$  nm). In 2002, Khan Shahed et al. [18] synthesized TiO<sub>2-x</sub>C<sub>x</sub> which is capable of absorbing light with wavelengths below 535 nm and could photocatalytically split water into hydrogen and oxygen.

Besides expanding the light absorption edge of the photocatalyst, preventing the recombination of photo-excited electron–hole pairs is another key strategy to improve photocatalytic efficiency. Combining two different semiconductors with

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suitable conduction and valence bands or loading noble metal particles on the surface of the photocatalyst could induce collection of the photogenerated electrons and holes on the different semiconductor surfaces, and enhance the redox reactions of the electrons and holes, respectively.  $\text{WO}_x\text{-TiO}_2$  [19],  $\text{Bi}_2\text{S}_3/\text{TiO}_2$  [20],  $\text{CdS}/\text{TiO}_2$  [20],  $\text{RuS}_2/\text{TiO}_2\text{-SiO}_2$  [21],  $\text{Pt}/\text{TiO}_2$  [22] and  $\text{Au}/\text{TiO}_2$  [23], were reported to be this kind of photocatalyst.

In an attempt to lower the band-gap energy of photocatalysts and to reduce the recombination of photo-excited electron-hole pairs, combining two different semiconductors and loading a noble metal, a novel ternary composite photocatalyst,  $\text{Pt-TiO}_{2-x}\text{N}_x\text{-WO}_3$  was designed and synthesized by the method of templating. Its performance for photocatalytic hydrogen production from water under ultraviolet and visible light was studied.

## 2. Experimental

### 2.1. Preparation and characterization of the photocatalyst

All chemicals were analytical reagent grade and used without further purification.  $2 \times 10^{-4}$  mol  $(\text{NH}_4)_2\text{PtCl}_6$  (Shanghai Chem. Co. I, purity >99%) was dissolved in 25 mL deionized water in a three-orifice flask, and then 250 mL anhydrous ethanol (Xi'an Chem. Co., purity >99.5%) was added to the blend. After the mixture was cooled to  $-70^\circ\text{C}$  by liquid nitrogen, 17 mL (0.05 mol) tetrabutylorthotitanate (Beijing Zhonglian Chem. Co., purity >98.5%) was added slowly drop by drop at  $-70^\circ\text{C}$  under vigorous stirring. Then the pH value of the mixture was adjusted to 7 by  $0.4 \text{ mol L}^{-1}$  ammonia aqueous solution and the blend was stirring for 12 h at  $-70^\circ\text{C}$ . Then 220 mL of  $0.4 \text{ mol L}^{-1}$  ammonia aqueous solution was added to the mixture drop by drop. After its temperature slowly increased to room temperature, the product was filtered to obtain a gel, which was re-dispersed in deionized water using an ultrasonic oscillator. After adding 100 mL of  $0.079 \text{ mol L}^{-1}$  ammonium tungstate (Shanghai Chem. Co. II, purity >99%) aqueous solution, the dispersed mixture was evaporated and dried at  $70^\circ\text{C}$ . The solid mixture was calcined 2 h at  $600^\circ\text{C}$  and the composite photocatalyst powder was obtained. The process is similar to that used in [24].

The pure  $\text{TiO}_2$  used as a reference was synthesized with tetrabutylorthotitanate as the titanium source, using the same process as described above.  $\text{TiO}_{2-x}\text{N}_x$  was synthesized using 2 g pure  $\text{TiO}_2$  gel mixed with 1.68 g  $(\text{NH}_4)_2\text{CO}_3$  (Xi'an Chem. Co.) and calcined for 4 h at  $400^\circ\text{C}$  under  $\text{N}_2$  atmosphere. When the temperature rose,  $(\text{NH}_4)_2\text{CO}_3$  was decomposed in to  $\text{NH}_3$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .  $\text{NH}_3$  could react with the  $\text{TiO}_2$  gel, and some nitrogen atoms substituted some oxygen atoms to form  $\text{TiO}_{2-x}\text{N}_x$  [25,26].

The crystal structure of the sample was identified by XRD (Type Shimadzu Rax-10) with graphite monochromized  $\text{Cu K}\alpha$  radiation (45 kV, 15 mA). SEM images were obtained from a Hitachi-530 scanning electron microscope. The surface area was obtained with the BET method using a surface area analyzer, SA 3100 Plus (Beckman-Coulter Co.). Element analysis was carried out with an EDAX DX-4 (Philips Co.), and the SEM image was obtained from a Hitachi-530 scanning electron microscope.

UV-vis spectrum was obtained with a HITACHI340 UV-vis spectrometer.

The apparent quantum efficiency (A.Q.E.) was defined as the percentage ratio of the number of  $\text{H}_2$  atoms produced to the number of photons from the Hg lamp, and the apparent energy conversion efficiency (A.E.C.E.) was defined as the percentage ratio of the combustion heat energy of  $\text{H}_2$  obtained to the radiation energy from Hg lamp, as showed in the following Eqs. (1) and (2).

$$\begin{aligned} \text{A.Q.E. (\%)} &= \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100 \\ &= \frac{\text{number of evolved } \text{H}_2 \text{ molecules} \times 2}{\text{number of incident photons}} \times 100 \end{aligned} \quad (1)$$

$$\text{A.E.C.E. (\%)} = \frac{\text{combustion enthalpy of evolved } \text{H}_2}{\text{energy of incident photons}} \times 100 \quad (2)$$

The number of photons was measured using  $\text{KFe}[\text{C}_2\text{O}_4]_2$  as the chemical actinometer [27], and was determined with the following equation:

$$\begin{aligned} \text{number of incident photons} \\ &= \text{light intensity} \times \text{irradiated area} \times \text{reaction time.} \end{aligned} \quad (3)$$

### 2.2. Photocatalytic reaction

The photocatalytic reaction was carried out in an inner-irradiation type reactor. The photocatalyst powder (50 mg) was dispersed by a magnetic stirrer in 150 mL aqueous solution containing  $0.1 \text{ mol L}^{-1}$   $\text{Na}_2\text{S}$  and  $0.04 \text{ mol L}^{-1}$   $\text{Na}_2\text{SO}_3$  as the sacrificial reagent. A 300 W high pressure Hg lamp was used as the light source. Before the irradiation, the reactor was deaerated with nitrogen for about 30 min. The gas evolved was gathered and analysed by GC-MS using a C18 column and nitrogen as the carrier gas. During the entire experiment, the reaction temperature was kept at  $25 \pm 0.2^\circ\text{C}$  by eliminating the IR radiation with the circulation water in the water jacket of the reactor.

In the photocatalytic experiment under visible light,  $1 \text{ mol L}^{-1}$   $\text{NaNO}_2$  solution was introduced into the water jacket as an internal circulation cooling medium to eliminate light with a wavelength shorter than 400 nm. UV-vis spectrum of the  $\text{NaNO}_2$  solution showed that it could effectively absorb light with wavelengths below 400 nm and thus act as a cut-off filter.

## 3. Results and discussion

### 3.1. Photocatalyst characterization

Element analysis of the materials indicates that  $\text{Pt-TiO}_{2-x}\text{N}_x\text{-WO}_3$  consists of 4.17 wt.% platinum and 23.47 wt.% tungsten and nitrogen, and the existence of nitrogen in the prepared  $\text{TiO}_{2-x}\text{N}_x$ , indicating the formation of  $\text{TiO}_{2-x}\text{N}_x$ . The XRD pattern (Fig. 1) of  $\text{Pt-TiO}_{2-x}\text{N}_x\text{-WO}_3$  shows that the  $2\theta$  of the highest peak is  $25.2^\circ$ , which shows that  $\text{TiO}_{2-x}\text{N}_x$  in it is of anatase

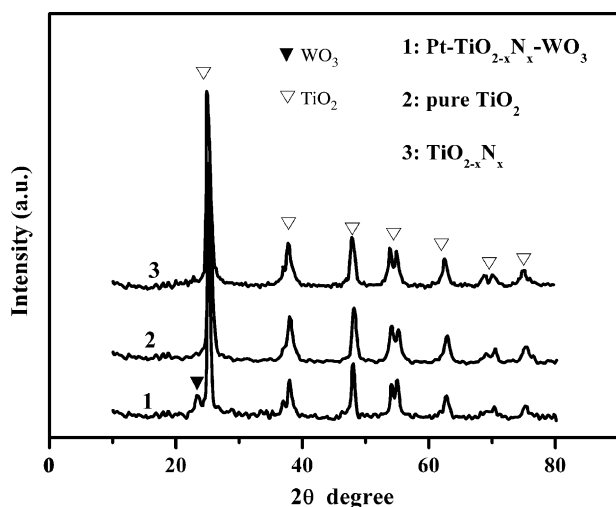


Fig. 1. XRD pattern of Pt-TiO<sub>2-x</sub>N<sub>x</sub>-WO<sub>3</sub>, TiO<sub>2</sub> and TiO<sub>2-x</sub>N<sub>x</sub>.

form, almost the same as that of pure TiO<sub>2</sub> and TiO<sub>2-x</sub>N<sub>x</sub>. The peak at  $2\theta = 23.6^\circ$  is the characteristic peak of WO<sub>3</sub>, which indicates the existence of WO<sub>3</sub> crystals [28]. The average particle size of Pt-TiO<sub>2-x</sub>N<sub>x</sub>-WO<sub>3</sub>, pure TiO<sub>2</sub> and TiO<sub>2-x</sub>N<sub>x</sub> was determined to be 11.6, 10.96 and 10.6 nm, respectively, from the Scherrer formula. The surface areas of these three types of photocatalysts were 51, 64 and 69.1 m<sup>2</sup> g<sup>-1</sup>, respectively, with the Brunauer–Emmett–Teller (BET) method.

UV–vis spectroscopy (Fig. 2) of Pt-TiO<sub>2-x</sub>N<sub>x</sub>-WO<sub>3</sub> showed that the maximum absorption wavelength red-shifted to 750 nm, and the absorption intensity was rather strong. This value is greater than that for TiO<sub>2</sub> (387.5 nm) [19], WO<sub>3</sub> (481 nm) [28], TiO<sub>2-x</sub>N<sub>x</sub> (500 nm) [17], TiO<sub>2-x</sub>C<sub>x</sub> (535 nm) [18] and Pd-TiO<sub>1.72</sub>N<sub>0.28</sub>-WO<sub>3</sub> [24]. Compared with the above listed photocatalysts, Pt-TiO<sub>2-x</sub>N<sub>x</sub>-WO<sub>3</sub> may utilize visible light more efficiently. This phenomenon may be due to multifactor coupling, as shown in Fig. 3. Firstly, in TiO<sub>2-x</sub>N<sub>x</sub>, the dominant

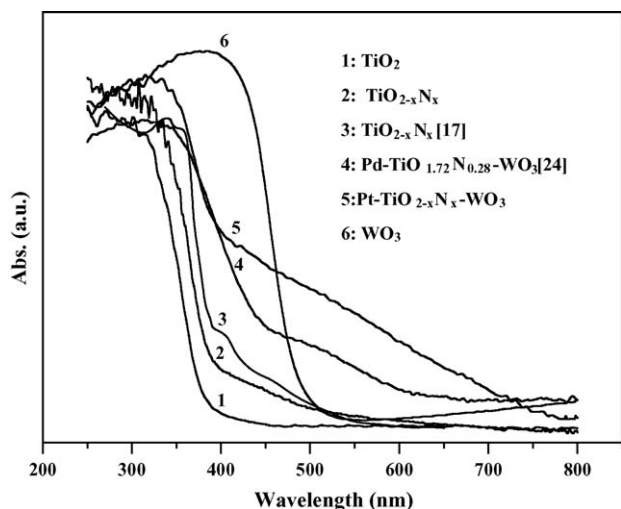


Fig. 2. UV–vis spectroscopy of Pt-TiO<sub>2-x</sub>N<sub>x</sub>-WO<sub>3</sub>, TiO<sub>2</sub>, TiO<sub>2-x</sub>N<sub>x</sub>, TiO<sub>2-x</sub>C<sub>x</sub> and WO<sub>3</sub>.

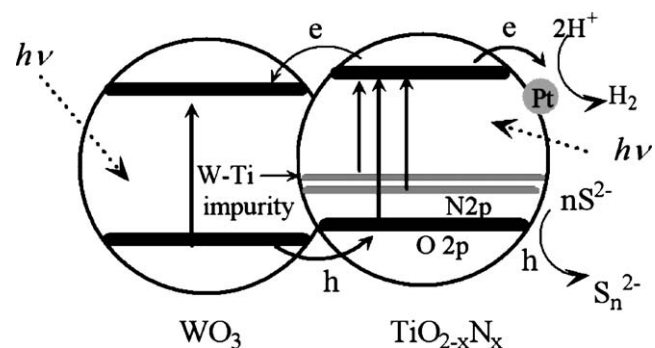


Fig. 3. Transfer of charge carriers in Pt-TiO<sub>2-x</sub>N<sub>x</sub>-WO<sub>3</sub> composite photocatalyst.

transitions at the absorption edge have been identified with those from N 2p<sub>π</sub> to Ti d<sub>xy</sub>, instead of from O 2p<sub>π</sub> as in TiO<sub>2</sub> [17,29]. This change can make the maximum absorption wavelength of TiO<sub>2-x</sub>N<sub>x</sub> red-shift [6]. Secondly, some W<sup>4+</sup> ions were formed when calcining the composite gel [19], the stoichiometric ion exchange between W<sup>4+</sup> and Ti<sup>4+</sup> may occur [30]. Since W<sup>4+</sup> can substitute Ti<sup>4+</sup> in the lattice of TiO<sub>2</sub> because of the similarity in the radius of the two ions, the bond lengths of W–O and Ti–O and the crystal structures of WO<sub>2</sub> and TiO<sub>2</sub> are similar [19], and a nonstoichiometric solid solution W<sub>x</sub>Ti<sub>1-x</sub>O<sub>2</sub> would be formed. W<sub>x</sub>Ti<sub>1-x</sub>O<sub>2</sub> could produce a tungsten impurity energy level, thus introducing WO<sub>3</sub> into TiO<sub>2</sub> can make TiO<sub>2</sub> absorb the longer wavelength light [19]. Furthermore, because the energy level of the 3d electrons of Ti is closer to that of the 5d electrons of W, W<sup>6+</sup> ions can interact with Ti<sup>4+</sup> ions [30]. It is the interaction of the two factors discussed above that makes the absorption wavelength of synthesized compound red-shifted to 750 nm. Additionally, the UV–vis spectra of TiO<sub>2-x</sub>N<sub>x</sub> prepared in this work was almost the same as that of [17], which confirmed the formation of TiO<sub>2-x</sub>N<sub>x</sub> in the other side except for the result of element analysis.

Fig. 4 is the SEM spectrum of Pt-TiO<sub>2-x</sub>N<sub>x</sub>-WO<sub>3</sub>, from which we can see that some of the catalyst particles are of four sided. The possible formation mechanism of the photocatalyst may be explained as below. While adding the template compound (NH<sub>4</sub>)<sub>2</sub>PtCl<sub>6</sub> aqueous solution to the ethanol absolute, micrystals of the template compound are formed. At a temperature of  $-70^\circ\text{C}$ , tetrabutylorthotitanate hydrolyses slowly, and the titanate intermediate species formed by hydrolysing were negatively charged since that the pH of isoelectric point of titania was approximately 6 [32] and the pH of the mixture was 7. It was assumed that the negatively charged titanate intermediate species exchanged with Cl<sup>-</sup> of the template micrystals [31]. Furthermore, the titanate intermediate species can interact with NH<sub>4</sub><sup>+</sup> ions of the template micrystals at the surface of the crystals via hydrogen bonds and electrostatic attraction. According to the interactions described above, titanate intermediate species could anchor on the surface of the micrystals and act as nucleation points, and then TiO<sub>2</sub> grows at the surface of the template micrystal and encloses the template micrystal [31]. Adding the colloids into the ammonium tungstate aqueous solution, ammonium tungstate molecules can diffuse inside and onto



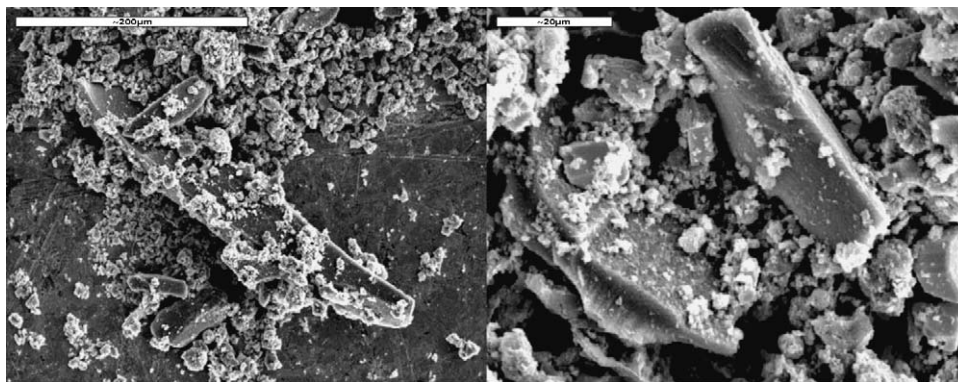


Fig. 4. The SEM photographs of Pt-TiO<sub>2-x</sub>N<sub>x</sub>-WO<sub>3</sub>.

the surface of TiO<sub>2</sub> colloids. In the process of calcining of the obtained colloids mixture under 600 °C, the template molecular decomposed into spongy platinum which is embedded in TiO<sub>2</sub> and the ammonium tungstate decomposed into WO<sub>3</sub> which is attached to TiO<sub>2</sub>. Meanwhile, nitrogen atoms of the NH<sub>4</sub><sup>+</sup> and NH<sub>3</sub> absorbed in the TiO<sub>2</sub> gel from the ammonia solution during the TiO<sub>2</sub> gel preparation were doped into TiO<sub>2</sub> to form nitrogen-doped TiO<sub>2</sub> (TiO<sub>2-x</sub>N<sub>x</sub>) [25,26].

### 3.2. Photocatalytic reaction

Fig. 5a shows the photocatalytic hydrogen production performance of Pt-TiO<sub>2-x</sub>N<sub>x</sub>-WO<sub>3</sub>, TiO<sub>2-x</sub>N<sub>x</sub> and TiO<sub>2</sub> under ultraviolet light. The hydrogen evolution rate of Pt-TiO<sub>2-x</sub>N<sub>x</sub>-WO<sub>3</sub> is 23.69 mmol (h g catal.)<sup>-1</sup>, 30.3% higher than that of TiO<sub>2</sub> at 18.18 mmol (h g catal.)<sup>-1</sup> and 100.3% higher than that of TiO<sub>2-x</sub>N<sub>x</sub> at 11.83 mmol (h g catal.)<sup>-1</sup>. The apparent quantum efficiencies of Pt-TiO<sub>2-x</sub>N<sub>x</sub>-WO<sub>3</sub>, TiO<sub>2</sub> and TiO<sub>2-x</sub>N<sub>x</sub> under ultraviolet light were determined to be 2.66%, 1.88% and 1.49% from Eq. (1) and their apparent energy conversion efficiencies were determined to be 1.13%, 0.79% and 0.63% from Eq. (2), respectively. In addition, the rate of hydrogen evolution of the synthesized catalyst is steady.

Hydrogen evolution performance of Pt-TiO<sub>2-x</sub>N<sub>x</sub>-WO<sub>3</sub>, TiO<sub>2-x</sub>N<sub>x</sub> and TiO<sub>2</sub> under visible-light irradiation is shown in Fig. 5b. The visible light is obtained by removing light with wavelength shorter than 400 nm with 1 mol L<sup>-1</sup> NaNO<sub>2</sub>. The composite semiconductor catalysts exhibit the activity of photocatalytic hydrogen production under visible light. The rate of hydrogen production was up to 603 μmol (h g catal.)<sup>-1</sup> in the first 3 h and it is 56.7% higher than that of TiO<sub>2-x</sub>N<sub>x</sub> at 384.9 μmol (h g catal.)<sup>-1</sup>, while negligible hydrogen evolution is detected with TiO<sub>2</sub>. The apparent quantum efficiencies of Pt-TiO<sub>2-x</sub>N<sub>x</sub>-WO<sub>3</sub> and TiO<sub>2-x</sub>N<sub>x</sub> under visible light were determined to be 0.24% and 0.14% from Eq. (1) and their apparent energy conversion efficiencies were determined to be 0.12% and 0.07% from Eq. (2), respectively. Since it is impossible to measure the light absorbed by the photocatalysts, the total incident light was assumed to be absorbed completely. It is affirmative that the real quantum efficiencies and energy conversion efficiencies will be higher than the apparent quantum efficiencies and apparent energy conversion efficiencies showed above.

### 3.3. Photocatalytic reaction mechanism

There are two forms of electron-hole recombination, surface recombination and bulk recombination, and both can lower the efficiency of the photocatalysis. The mechanism proposed is illustrated in Fig. 3. The Fermi energy level of Pt is lower than that of TiO<sub>2-x</sub>N<sub>x</sub>, and because of combining to each other, the electron would transfer from TiO<sub>2-x</sub>N<sub>x</sub> to Pt, until the Fermi energy level become equal. Thus, the transfer reduces the surface electron-hole recombination, and increases the efficiency

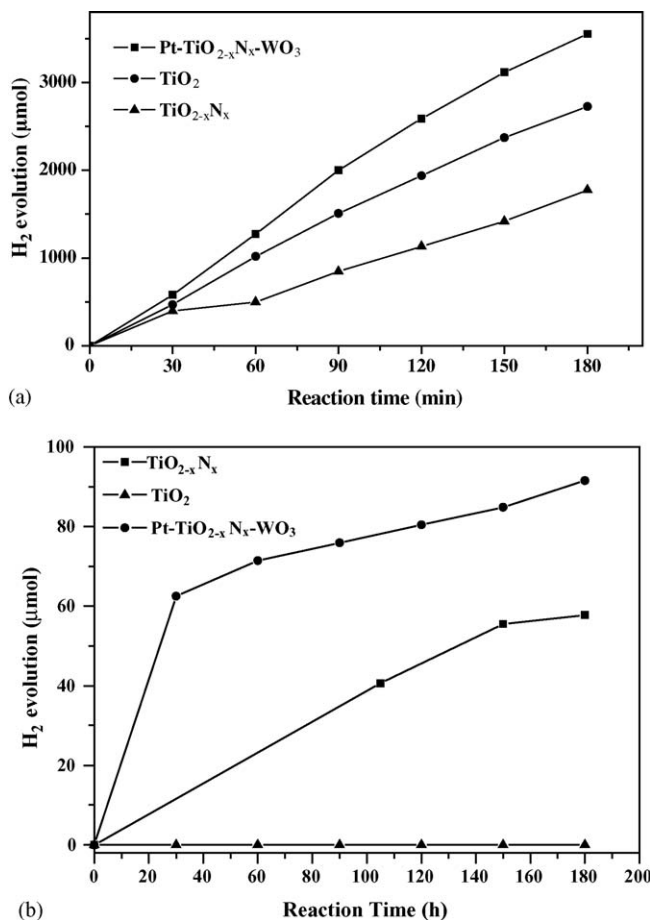
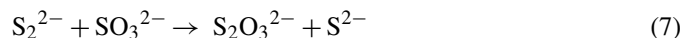


Fig. 5. Hydrogen production performance of Pt-TiO<sub>2-x</sub>N<sub>x</sub>-WO<sub>3</sub>, pure TiO<sub>2</sub> and TiO<sub>2-x</sub>N<sub>x</sub> under (a) ultraviolet and (b) visible light ( $\lambda > 400$  nm).

of photocatalysis. When irradiated by light with enough energy, the band-to-band transition will occur simultaneously in both  $\text{TiO}_{2-x}\text{N}_x$  and  $\text{WO}_3$  in  $\text{Pt-TiO}_{2-x}\text{N}_x\text{-WO}_3$ . Because  $\text{TiO}_{2-x}\text{N}_x$  and  $\text{WO}_3$  have different conduction band and valence band potential levels, some of the electrons in the conduction band of  $\text{TiO}_{2-x}\text{N}_x$  will transfer to the low-level conduction band of  $\text{WO}_3$ , and the holes will accumulate in the high-level valence band of  $\text{TiO}_{2-x}\text{N}_x$ . Thus, the separation efficiency of photogenerated electron–hole couple is higher than that of  $\text{TiO}_{2-x}\text{N}_x$  and  $\text{WO}_3$ .

Because the conduction band potential of  $\text{WO}_3$  is more positive than the potential of  $\text{H}^+/\text{H}_2$ , the electrons accumulating in the conduction band of  $\text{WO}_3$  cannot reduce  $\text{H}^+$  to  $\text{H}_2$ . However, as shown in Fig. 5a, even if there is such a disadvantage, the hydrogen evolution rate of  $\text{Pt-TiO}_{2-x}\text{N}_x\text{-WO}_3$  is still higher than that of  $\text{TiO}_2$ , indicating that combining Pt,  $\text{WO}_3$  and  $\text{TiO}_{2-x}\text{N}_x$  has some advantage. This work provides only a direction for future work. Thus, seeking a narrow band-gap semiconductor with a conduction band potential more negative than the potential of  $\text{H}^+/\text{H}_2$  to replace  $\text{WO}_3$  in the composite catalyst, may achieve higher activity of hydrogen production. This research is underway.

Besides the separation of holes and electrons by the photocatalysts, the holes should be consumed to prolong the lifetime of electrons and thus improve the hydrogen production efficiency. The ideal condition is that holes are consumed by oxidizing water to produce oxygen, as shown in Eqs. (4) and (5). At present, few photocatalysts can decompose water into hydrogen and oxygen [4]. So sacrificial reagents were needed to assist in hydrogen production. In this work, a sacrificial electron donor system,  $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$ , was employed to scavenge the photogenerated holes in the valence band of the composite photocatalyst [7,33]. The  $\text{S}^{2-}$  could consume the holes effectively and generate  $\text{S}_2^{2-}$ , which was in turn recycled to  $\text{S}^{2-}$  by  $\text{SO}_3^{2-}$ , as shown in Eqs. (6) and (7).



#### 4. Conclusion

A composite photocatalyst  $\text{Pt-TiO}_{2-x}\text{N}_x\text{-WO}_3$  was synthesized using Pt,  $\text{TiO}_{2-x}\text{N}_x$  and  $\text{WO}_3$  as components by the template method. The maximum absorption wavelength of the photocatalyst red-shifted to about 750 nm, which was much further than that of  $\text{TiO}_{2-x}\text{N}_x$ ,  $\text{WO}_3$ ,  $\text{TiO}_{2-x}\text{C}_x$  and  $\text{Pd-TiO}_{1.72}\text{O}_{0.28}\text{-WO}_3$  [24]. The new catalyst shows a higher activity for hydrogen production than either  $\text{TiO}_2$  on  $\text{TiO}_{2-x}\text{N}_x$  under ultraviolet light. It also showed a higher hydrogen production activity than  $\text{TiO}_{2-x}\text{N}_x$  under visible light. In addition, a possible mechanism was presented to explain the improved photocatalytic activity of this composite catalyst.

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