Green hydrogen production by solar photocatalysis using Pt-TiO₂ nanosheets with reactive facets

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ABSTRACT

Green production of hydrogen is essential for the development of a hydrogen economy. In this study, the photocatalytic water-splitting technology is developed to harness solar energy for production of renewable hydrogen. Pt-TiO₂ nanosheets were fabricated by a facile hydrothermal method, followed by photo-reduction of Pt(acac)₃ on B,F-codoped TiO₂ with reactive facets. The as-prepared photocatalysts were characterised by transmission electron microscopy (TEM), X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDX) and UV-vis diffuse reflectance spectroscopy (DRS). The photocatalytic hydrogen production performance was systematically investigated under UV-visible irradiation. The parametric results indicate that the TiO₂ nanosheet structure, Pt loading and photocatalyst concentration have significant impacts on the photocatalytic hydrogen production. The highest hydrogen production rate obtained is 5,086 $\mu\text{mol h}^{-1}\text{g}^{-1}$.

KEYWORDS Titanium dioxide; nanosheets; photocatalysis; hydrogen production; semiconductors

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1. Introduction

Photocatalytic hydrogen production over semiconductors has received considerable interest in recent years. Among various semiconductors, titanium dioxide (TiO₂) is regarded as one of the promising candidates for solar energy harvesting owing to its high photostability, environmental benignity and low cost (Murdoch et al., 2011). Yet, the photocatalytic performance of pure phase TiO₂ is somewhat limited as it has a wide band gap (3.2 eV) and thus only the UV spectral region can induce activation. Therefore, the main challenges in solar photocatalytic H₂ production are to enhance visible-light activities and reduce the recombination rate of electrons and holes. One strategy to improve the photocatalytic performance is by modifying TiO₂ with noble metal co-catalysts to reduce the recombination rate of the charge carriers. Co-catalysts can act as electron collectors to effectively separate the photo-generated electron-hole pairs and the active sites for proton reduction to produce H₂. Among various co-catalysts, study has shown that Pt has the lowest overpotential and the best activity for H₂ evolution (Leung et al., 2010). Moreover, anion modified TiO₂ samples have been synthesised and investigated for photocatalysis applications, such as N-TiO₂ (Bakar and Ribeiro, 2016) and C-TiO₂ (Varnagiris et al., 2019). Recently, modifying TiO₂ with multiple anions has also been regarded as an effective strategy to improve photocatalytic performance. For instance, Xiang et al. reported that N,S co-doped TiO₂ nanosheets with exposed facets showed much higher photocatalytic activity than

pristine TiO₂ nanosheets (2011). Li et. al. also reported a B,N co-doped black TiO₂ developed to improve hydrogen production (2019). In our previous work, we have also reported an effective photocatalyst, namely B,F codoped TiO₂ nanosheets, which exhibited higher photocatalytic dye degradation activity than commercial P25 (Wang et al., 2013). Herein, we further modified the B,F-codoped TiO₂ nanosheets with Pt nanoparticles for photocatalytic H₂ production under UV-visible irradiation. The effects of Pt loading, TiO₂ size and photocatalyst loading on photocatalytic H₂ production were systematically investigated.

2. Experimental section

2.1. Material synthesis

B,F-codoped TiO₂ nanosheets of different sizes were prepared by one-pot hydrothermal method developed in our previous work (Wang et al., 2013). In brief, 10 mL of Ti(OBu)₄ was reacted with different HBF₄ quantities of 0.4 mL, 0.8 mL, 1.2 mL and 1.6 mL, which were abbreviated as TiO₂-NS-1, TiO₂-NS-2, TiO₂-NS-3 and TiO₂-NS-4, respectively. Subsequently, Pt nanoparticles were deposited on the as-prepared B,F-codoped TiO₂ nanosheets *via* photo-reduction method to form Pt deposited B,F-codoped TiO₂ nanosheets. In a typical synthesis, 0.2 g of the as-prepared TiO₂ was dispersed in 50 mL of DI water (Millipore, Inc., 18 M $\Omega\cdot\text{cm}^{-1}$) and platinum (II) acetylacetonate

(Pt(acac)₃, Sigma Aldrich, 99.99%) dissolved in ethanol (Sigma Aldrich, 99.9%) was added to the suspension under magnetic stirring. A 300 W xenon lamp (Aulight, CEL-HX UV300, 200 nm ~ 2000 nm) was used as the light source to initiate the photo reduction of Pt precursors. Under irradiation, ethanol in the suspension played the role of sacrificial reagent to enhance the charge separation. After irradiation for 30 minutes, the liquid sample was centrifuged and washed with DI water three times. Finally, the as-prepared product was dried at 60°C for 12 hours before use. Different Pt loadings (from 0.5 wt.% to 4.0 wt.%) were obtained by changing the amount of Pt precursor added.

2.2. Material Characterisation

The morphology of the as-prepared Pt-B,F codoped TiO₂ nanosheets was characterised by transmission electron microscope (TEM, FEI Tecnai G2 20 scanning). The crystal phase of the as-prepared Pt- B,F codoped TiO₂ nanosheets was confirmed with X-ray diffractometer (XRD, Bruker) equipped with Cu K_{α12} X-ray radiation and a LynxEye detector. The UV-vis spectra of TiO₂ (TiO₂-NS-2) and TiO₂-Pt (TiO₂-NS-2-Pt) were also recorded on diffusion reflectance UV-vis spectrometer (Hitachi, UV-3010).

2.3. Photocatalytic Performance

The photocatalytic activities of the as-prepared Pt-TiO₂ nanosheets with different Pt loadings were investigated via H₂ production test using LabSolar H₂ production system (Trustech, Beijing) at room temperature under UV-vis irradiation. In a typical run, 20 mg of photocatalyst was suspended with sonication in 100 mL of 10 vol% methanol (Sigma Aldrich, 99%) solution. The resulting photocatalyst suspension was bubbled with N₂ gas (HKO, 99%) for one hour to purge out the dissolved oxygen. Subsequently, the photocatalyst suspension was added to a photo reactor with a quartz cover and was magnetically stirred. The top of the reactor was filled with DI water in order to filter out the IR from the light source. During hydrogen production test, the gas composition in the headspace of the photo reactor was periodically analysed by a gas chromatograph (GC-2010, Shimadzu) equipped with MolSieve 5A capillary column (Restek, 30 m × 0.53 mm × 50 μm) and a thermal conductivity detector (TCD). The entire process was conducted under vacuum condition and an electromagnetic air pump was also employed to accelerate gas circulation in the system. Helium gas was used as a carrier gas at a flow rate of 30 mL/minute. The inlet, column and detector temperatures were controlled at 35°C, 35°C and 120°C respectively. A 300 W Xe lamp (Aulight, CEL-HX UV300) was used as the radiation source to evaluate the photocatalytic activities of the as-prepared Pt-TiO₂ nanosheets.

3. Results and Discussion

The detailed morphology and crystal phase analysis of B,F-codoped TiO₂ nanosheets were reported in our previous work (Wang et al., 2013). Figure 1 displays the XRD patterns of Pt-TiO₂ with the same Pt loading (1 wt.%). The diffraction peaks of Pt-TiO₂ are similar to the diffraction peaks of anatase TiO₂ (PDF#21-1272), while Pt cannot be detected by XRD due to low concentration (*ca.* 1 wt.%). The TEM analysis shown in Figure 2 indicates that as-prepared TiO₂-NS-2 is composed of nanosheets with 10 nm side length and 2.5 nm in thickness. In addition, many Pt nanoparticles of a few nanometers in diameter can be observed in Figure 2(a) - (b). The lattice structure can be clearly found in Figure 2(b), indicating the presence of TiO₂ nanosheets. The fast Fourier transform image (Figure 2(c)) implies the existence of TiO₂ (101) facets. Figure 2 (d) shows the typical morphology of TiO₂ nanosheets decorated with Pt nanoparticles. As seen in Figure 3, C, Ti, O, F, Cu and Pt can be detected by energy-dispersive X-ray (EDX) spectroscopy. Cu and C are supposed to come from the grid holder of the TEM analyser. Ti, O, F and Pt are from the as-prepared Pt-TiO₂ product. The fluorine dopant can be determined while boron is not detectable due to its low concentration (Wang et al., 2013). Figure 4(a) shows the typical morphology of Pt nanoparticle prepared by photo-reduction method. The small Pt size is ascribed to the low energy from UV light. The histogram analysis of Pt size distribution in Figure 4(b) reveals that the size of Pt nanoparticles mostly falls into the range of 2.0 ± 0.2 nm.

Figure 1. XRD patterns of TiO₂-Pt photocatalysts.

Figure 2. TEM analysis of Pt-TiO₂-NS-2 (a, b, d) TiO₂ nanosheets deposited with Pt nanoparticles. (c) fast Fourier transform image of (b).

Figure 3. Typical EDX analysis of Pt-TiO₂ nanosheets.

Figure 4. TEM images of Pt nanoparticles and histogram analysis of Pt size distribution.

Figure 5 displays the UV-vis absorption spectra of TiO₂-NS-2 and Pt-TiO₂-NS-2. A significant increase in light absorption of Pt-TiO₂ is found in the UV and visible light regions in comparison with TiO₂. Based on previous study, the addition of Pt in TiO₂ could affect visible light absorption of TiO₂ (Yu and Jaroniec, 2010a). The enhanced visible light absorption is ascribed to the resonance between photon frequency and collective excitations of conduction electrons from Pt nanoparticles. The phenomenon is known as localised surface plasmon resonance (LSPR) (Yu et al., 2010b). The band gap of Pt-TiO₂ photocatalyst is remarkably reduced by Pt modification. The absorption edges of Pt-TiO₂ and TiO₂ are 437 nm and 410 nm, respectively. Thus, the band gaps of Pt-TiO₂ and TiO₂ are 2.8 eV and 3.0 eV, respectively. The band gap of TiO₂ nanosheets is smaller than that of anatase TiO₂ (3.2 eV) due to the addition of dopants (e.g. fluorine and boron) into TiO₂. The red shift is ascribed to the excitation of electrons from the impurity energy levels located above the valence band edge (O 2p states) (Li et al., 2008). The reduction in band gap results in improved solar photocatalytic performance.

Figure 5. UV-vis absorption spectra of TiO₂ and TiO₂-Pt photocatalysts.

Figure 6 presents photocatalytic H₂ production over Pt-TiO₂ nanosheets synthesised with different Pt loadings and TiO₂ dimensions. As shown in Figure 6(a), pristine TiO₂-NS-2 shows poor performance in H₂ production, probably due to the fast electron-hole recombination and the absence of active sites for H₂ evolution. When TiO₂-NS-2 is loaded with 0.5 wt.% Pt, photocatalytic H₂ production performance is significantly enhanced, suggesting that Pt sites are beneficial for the decrease in overpotential for H₂ production. The highest H₂ production of 329 μmol within 4 hours is found at TiO₂-NS-2 loaded with 1.0 wt.% Pt. However, further increase in the Pt loading does not raise the performance of photocatalytic H₂ production. TiO₂-NS-2 loaded with 2.0 wt.% shows similar performance with 1.0 wt.% Pt loading. The performance of TiO₂-NS-2 modified with 4.0 wt.% Pt is even worse than that of 0.5

wt.% Pt. This is because higher Pt loading onto TiO₂ can block the light penetration into the photosensitive sites for photocatalytic reaction. In addition, overloading of Pt can increase the Pt-TiO₂ contact area, which can bring higher probability for the recombination of electron-hole pairs (Sun et al., 2003). Therefore, overloading Pt can reduce the overall photocatalytic activity of TiO₂. According to the literature, the optimal Pt loading onto TiO₂ photocatalysts for water splitting is 0.2 wt.% ~ 2.0 wt.% (Lin et al., 2008; Kandiel et al., 2011), depending on morphology, crystal phase, porosity and particle size of TiO₂. In this work, the optimal Pt loading found is 1.0 wt.% for B,F-codoped TiO₂ nanosheets, well in consistence with previous studies.

Figure 6(b) shows the effect of TiO₂ dimensions and morphology on photocatalytic H₂ production over 20 mg Pt-TiO₂ photocatalysts with 1.0 wt.% Pt loading. The particle size of TiO₂-NP-1 is around 5 nm. For Pt loaded TiO₂-NP-1, the amount of generated H₂ is 172 μmol after four hours of operation. Among other samples, Pt loaded TiO₂-NS-2 yields the best performance in H₂ production. The nanosheet morphology has dimensions of 10 $\times$ 10 $\times$ 2.5 nm. When TiO₂ size increases from 10 nm to 30–45 nm, the H₂ production rate abruptly decreases, implying that TiO₂ size can strongly affect photocatalytic H₂ production. The smaller TiO₂ size with nanosheet morphology is beneficial for photocatalytic activity improvement.

Figure 6(c) presents the effect of Pt-TiO₂ loadings on photocatalytic H₂ production. TiO₂-NS-2-1.0Pt was selected as the model photocatalysts and the photocatalyst loadings varied from 5 mg to 30 mg in 10 vol.% methanol solution. When photocatalyst loading is less than 20 mg, the amount of generated H₂ increases from 102 μmol to 329 μmol . However, when the loading further increases to 30 mg, the amount of hydrogen produced decreases to 275 μmol . Previous work suggested that photocatalytic reaction was dominantly governed by the active sites which should have

access to light and reactants (Daskalaki and Kongdarides, 2009). When the concentration of photocatalyst was larger than the optimal value, the light was scattered or blocked by the excess photocatalysts, leading to the shield of the active sites.

Table 1 summarises the properties of Pt-TiO₂ and photocatalytic H₂ production rate. The highest H₂ production rate of 5086 $\mu\text{mol h}^{-1} \text{g}^{-1}$ is found at TiO₂-NS-2-1.0Pt of 5 mg suspended in 10 vol.% methanol solution. Yi et al. reported that TiO₂ mesoporous nanopowder with 1.0 wt.% Pt loading can produce H₂ at a rate of 6,000 $\mu\text{mol h}^{-1} \text{g}^{-1}$ (2008). However, Sreethawong and Yoshikawa reported TiO₂ modified with 1.5 wt.% CuO and 1.0 wt.% PdO can achieve a H₂ production rate of 1,800 $\mu\text{mol h}^{-1} \text{g}^{-1}$ and 2,100 $\mu\text{mol h}^{-1} \text{g}^{-1}$, respectively (2005). Therefore, Pt is considered as a better co-catalyst for photocatalytic H₂ production. Moreover, TiO₂-based photocatalysts show higher photocatalytic activity for H₂ production than metal sulphide catalysts. Silva et al. reported a H₂ production rate of 1,000 $\mu\text{mol h}^{-1} \text{g}^{-1}$ obtained with CdS-Pt composites in the presence of Na₂S and Na₂SO₃ (2008). The main problems for metal sulphide photocatalysts include photo-corrosion by valence band holes and the limitation of salts (Na₂S and Na₂SO₃ as hole scavengers) used in suspension (Koca and Şahin, 2002; Chen et al., 2010). In this work, we have achieved superior performance of Pt-TiO₂ due to the anion doping (fluorine and boron) and nanosheet morphology of TiO₂. The major mechanisms of solar photocatalytic hydrogen production are depicted in Figure 7. With the presence of B and F dopants, the band gap of TiO₂ photocatalyst is reduced from 3.2 eV to 3.0 eV, as indicated by UV-vis absorption spectra. Further deposition of Pt nanoparticles could lead to lower band gap to 2.8 eV, which could maximise the utilisation of the solar light spectrum for photocatalytic hydrogen production.

Figure 6. Photocatalytic hydrogen production over Pt-TiO₂ nanosheets (a) the effect of Pt loading; (b) the effect of TiO₂ size and morphology; (c) the effect of photocatalyst loadings.

Table 1. Summary of the properties of Pt-TiO₂ and photocatalytic hydrogen production rate.

No.	Photocatalyst	TiO ₂ size (nm)	Pt loading (wt.%)	Photocatalyst loading (mg)	H ₂ production rate (μmol h ⁻¹ g ⁻¹)
1	TiO ₂ -NS-2	10×10×2.5	0	20	81
2	TiO ₂ -NS-2-0.5Pt	10×10×2.5	0.5	20	2877
3	TiO ₂ -NS-2-1.0Pt	10×10×2.5	1.0	20	4107
4	TiO ₂ -NS-2-2.0Pt	10×10×2.5	2.0	20	3884
5	TiO ₂ -NS-2-4.0Pt	10×10×2.5	4.0	20	2675
6	TiO ₂ -NS-1-1.0Pt	5	1.0	20	2145
7	TiO ₂ -NS-3-1.0Pt	30×30×6.0	1.0	20	2633
8	TiO ₂ -NS-4-1.0Pt	45×45×6.5	1.0	20	2499
9	TiO ₂ -NS-2-1.0Pt	10×10×2.5	1.0	5	5086
10	TiO ₂ -NS-2-1.0Pt	10×10×2.5	1.0	10	4694
11	TiO ₂ -NS-2-1.0Pt	10×10×2.5	1.0	30	2287

Figure 7. Schematic diagram of solar photocatalytic hydrogen production using Pt deposited B,F-codoped TiO₂ nanosheets.

4. Conclusions

In summary, B,F-codoped TiO₂ nanosheets deposited with ~ 2 nm Pt nanoparticles was successfully prepared by a facile hydrothermal method, followed by a photo-deposition method. The major design parameters for solar photocatalytic H₂ production include the TiO₂ morphology, size, Pt loading and photocatalyst loading. The highest H₂ production rate of 5,086 μmol h⁻¹g⁻¹ was obtained by using TiO₂-NS-2 nanosheets with 1.0 wt.% Pt loading. The results revealed that TiO₂ nanosheets exhibit better photocatalytic property than TiO₂ nanoparticles. Moreover, TiO₂ nanosheets of small size possess higher photocatalytic H₂ production activity.

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