Catal Lett (2009) 127:319–322
DOI 10.1007/s10562-008-9681-4

Hydrogen Evolution Over Heteropoly Blue-Sensitized Pt/TiO$_2$ Under Visible Light Irradiation

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Received: 15 June 2008 / Accepted: 16 September 2008 / Published online: 10 October 2008

Abstract We report the visible light-induced hydrogen generation over heteropoly blue (HPB) sensitized Pt/TiO$_2$ photocatalyst. HPB was obtained via UV-induced reduction of heteropoly acid $K_5(BW_{11}O_{39}H_4) \cdot 12.8H_2O$ (BW_{11}) in glycerol aqueous solution. The photocatalytic activity for hydrogen generation was found to be dependent on the concentration of HPB in the solution.

Keywords Photocatalyst · Sensitization · Heteropoly blue (HPB) · Visible light

1 Introduction

Due to the consistent emission of carbon dioxide and the fast exhaustion of fossil resources, the global-warming and energy pressure becomes seriously in coming years. The extensive endeavour has been made for exploration of new techniques both of replacing fossil resources by renewable energy and new methods of energy application. From both points of view, hydrogen for fuel cell from solar energy is a promising way. The photocatalytic hydrogen generation from water is the best possible route. Some photocatalysts were reported active for hydrogen generation under UV light irradiation, such as TiO$_2$ [1], NiO-SrTiO$_3$ [2], Ta$_2$O$_5$ [3], $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ [4] and $BaM_{1/3}N_{2/3}O_3$($M = Ni, Zn; N = Nb, Ta$) [5]. Among these semiconductors, TiO$_2$ has been identified as a chemical stable, low cost, low-toxicity, and electronic material [6, 7]. However, TiO$_2$ is a large band gap semiconductor ($E_g > 3.2$ eV) and can only be excited by UV light. In addition, visible light sensitive photocatalyst is highly desirable because visible light (>400 nm) is the major component (ca. 43%) of sunlight input on the earth. In order to achieve hydrogen generation from solar energy over TiO$_2$ based catalyst, it is necessary to extend the absorption of TiO$_2$ based photocatalyst to visible light region. In the attempted efforts, the sensitization of TiO$_2$ with the photosensitive dyes (e.g., phthalocyanines, $Ru(bpy)_3^{2+}$ and derivatives, and 8-hydroxyquinoline complex) seems to be a successful route [8–21]. The sensitization of TiO$_2$ was identified very successful in solar cell. The efficiency from solar energy to electricity was achieved up to 11% by Grätzel et al. [22]. Recently, some attempts to replace organic dyes with inorganic semiconductor quantum dots have been made, such as using CdSe [23], CdS, PbS, Ag$_2$S, Sb$_2$S$_3$, and Bi$_2$S$_3$ [24]. Exploring new inorganic dye as sensitizer is still an attractive route for modifying TiO$_2$.

Heteropoly acids (HPAs) are inorganic clusters with well-defined structure [25]. It is easy to change their properties and metal-oxygen frameworks via variation of the composition and the method of pre-treatment [26]. For example, irradiation of heteropoly tungstate with UV light yields dark blue heteropoly blue (HPB) in the presence of electron donor, which shows new absorption bands in visible light region. However, the photo activity of HPB under visible light has only been studied in recent years.

Electronic supplementary material The online version of this article (doi:10.1007/s10562-008-9681-4) contains supplementary material, which is available to authorized users.

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For instance, the excited-state HPB (HPB[*]) catalyzed the reduction of methyl orange was reported [27]. The encapsulation of HPA into the TiHY zeolite could also work as an inorganic photosynthetic reaction center for water reduction [28]. It was found that HPB[*] donated the excited electrons to the transition metal in the zeolite and further reduced methyl orange [29]. Those studies suggest HPB could be excited with visible light and HPB[*] is formed. So HPB may be used as a new inorganic dye for sensitization of TiO_2 in reduction of water to H_2. In this work, we reported a catalyst, in which HPB was employed as an antenna molecule to absorb visible light ($\lambda > 420$ nm) for sensitization of TiO_2. In addition, glycerol was used as electron donor because it was an oversupplied compound of biodiesel production and using glycerol was a logical step in moving toward a more sustainable economy [30].

2 Experimental

P25 TiO_2 powder (70% anatase and 30% rutile, Degussa, Germany), Chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$), glycerol, sodium tungstate, boric acid, potassium chloride, and hydrochloric acid were of analytical grade and used without further purification. The 0.5 wt.% Pt/TiO_2 photocatalyst was prepared by a photoreduction method [31]. $K_5(BW_{11}O_{39}H_4) \cdot nH_2O$ was synthesized by a modified method according to ref [32]. The lacunary structure of $K_5(BW_{11}O_{39}H_4) \cdot nH_2O$ was identified by IR spectrum [33]. IR (cm^{-1}): 997 (m, v (B−O_a)), 952 (s, v (W−O_d)), 883 (vs, v (B−O_a)), 870 (vw, v (W−O_b)), 795 and 722(s, v (W−O_c)). Thermogravimetry results show that water content $x = 12.8$. Anal. Calcd. for $K_5(BW_{11}O_{39}H_4)$ (%): K, 6.31; B, 0.35; W, 65.52; Found: K, 5.95; B, 0.30; W, 65.32.

For photoelectrochemical measurements, a platinum electrode and a saturated calomel electrode (SCE) were used as the counter electrode and the reference electrode, respectively. The photocatalyst films on ITO glad slide were used as the working electrode and prepared using the dip-coating method. TiO_2 suspensions were first deposited onto the surface of ITO and allowed to dry under infrared lamp irradiation. Then the ITO coated with TiO_2 was cut into pieces to ensure that identical films were immersed in HPA solution (1 mg mL^{-1} HPA aqueous solution, pH 0.5). Finally, the film was dried under infrared lamp irradiation. The thickness of the film was about 0.5–0.8 μm. The surface of semiconductor working electrode exposed to the electrolyte was circular-films with a geometrical surface area of 1.6 cm^2. All photoelectrochemical measurements were carried out using a standard three-electrode system equipped with a quartz window. A 200 W high-pressure mercury-lamp was used as UV light source. After HPB was generated by UV irradiation, UV light was cut-off with a 420 nm cutoff filter in order to act as visible light source. The switch of visible light was controlled manually. 0.1 mol L^{-1} Na_2SO_4 20 (v/v) % glycerol-water solution was used as the supporting electrolyte. The applied voltage was 0 V for the ITO working electrode.

Photocatalytic experiments were performed in a Pyrex cell (ca. 140 cm^3) having a flat window ca. 10.2 cm^2 for irradiation. The cell was sealed with a silicone rubber septum. A 250 W high-pressure Hg lamp and a 300 W halogen lamp were used as the UV light source and the visible light source for photocatalytic reaction, respectively. The visible light source was equipped with a cut-off filter (Toshiba Y 44.2, $\lambda > 420$ nm) to remove radiation below 420 nm and to ensure irradiation by visible light only.

Typically, 50 mg of 0.5 wt.% Pt/TiO_2 photocatalyst and amount of HPA were suspended in 80 mL 20 (v/v) % glycerol aqueous solutions by a magnetic stirrer. Argon gas was bubbled through the reaction mixture for 40 min to remove oxygen and the suspension of the catalyst was achieved by ultrasonic prior to irradiation. HPB was obtained under UV light irradiation at room temperature, then the UV light was turned off and the reaction was continued under visible light irradiation or in the dark. The range of light intensity of the visible light used for the photo reaction is ca. 260–280 μmol(photons) m^{-2} s^{-1}. The H_2 evolved by reduction of water with reduced HPA have been deducted.

3 Results and Discussion

A framework of dye-sensitized semiconductor nanoparticles (photo-electrode) can be used for converting visible light into electricity efficiently [34–36]. If indeed TiO_2 is capable of accepting electrons from HPB[*], we should be able to collect these charges at electrode surface in a photoelectrochemical cell. Therefore, the photosensitization of HPB for Pt/TiO_2 can be confirmed by the photo-electrochemical measurements. Figure 1 shows the unbiased potential photocurrent-time curves of Pt/TiO_2–HPB and Pt/TiO_2 ITO electrodes under visible light irradiation ($\lambda > 420$ nm). The curve a shows that the photocurrent increases when the irradiation of visible light ($\lambda > 420$ nm) is turned on, and then decreases when the irradiation is turned off; and the current value is 5.1×10^{-2} μA. The photocurrent response is prompt and reproducible at several cycles of illumination. In contrast, photocurrents cannot be observed on the Pt/TiO_2 ITO electrode (curve b) because TiO_2 has no photo activity of visible light. The results indicate that HPB is the key role for photo-electrochemical response, and the role of HPB[*] works as “dye”

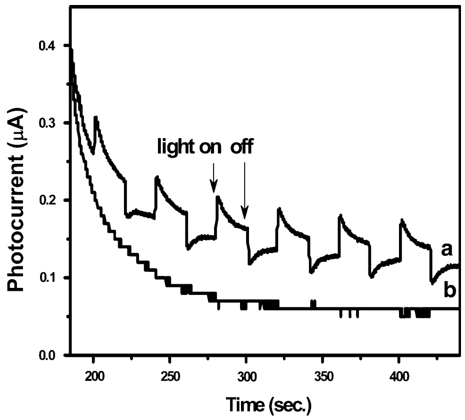

Fig. 1 Unbiased potential photocurrent versus time curves of the Pt/TiO$_2$–HPB (**a**) and pure Pt/TiO$_2$ (**b**). Conditions: 20 (v/v) % glycerol aqueous solution with 0.1 mol L^{-1} Na$_2$SO$_4$, pH = 0.5, $\lambda > 420$ nm

here and is similar to the role in dye/TiO$_2$ Grätzel cell [22]. In conclusion, the energy absorbed by HPB* is transferred to TiO$_2$ via interfacial electron transfer from HPB* to the TiO$_2$ conduction band.

Fluorescence (FL) measurement is an extremely useful method to evaluate the behavior of electron transfer. To further understand the interaction between HPB and TiO$_2$, the effects of TiO$_2$ on the FL of HPB were investigated as shown in Fig. 2. The excitation wavelength was 388 nm, and an emission peak centered at ca. 446 nm was observed in both samples, which was attributed to the recombination process of the photogenerated electron-hole pairs. The FL intensity of HPB reached 67. After TiO$_2$ was added, FL quenching was observed and the intensity decreased to 24. The phenomenon could be explained as follow: when excited electrons were transferred from HPB* to TiO$_2$, the recombination of e^-–h^+ was restrained, so the FL quenching was observed. The FL results also conformed the electron transfer from HPB* to TiO$_2$.

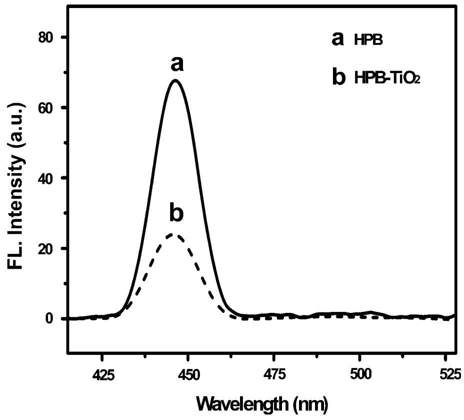

Fig 2 Fluorescence spectra (FL) of HPB (**a**) and HPB–TiO$_2$ (**b**) at pH 0.5. The excitation wavelength is 388 nm

Figure 3 demonstrates that H$_2$ continuously produced over HPB–Pt/TiO$_2$ catalysts under visible light irradiation (>420 nm). As Pt/TiO$_2$ has no photo activity in 420–900 nm region, the H$_2$ formation may be due to the sensitization of HPB* and related water reduction reaction on the TiO$_2$ surface. In this process, HPB absorbs visible light giving rise to its excited-state, then, the electron injection occurs from HPB* to the CB of TiO$_2$, and subsequently the electron is trapped by Pt particles for further reducing H$^+$ to H atom. If visible light irradiation of HPB–Pt/TiO$_2$ went on, a gradual decrease of H$_2$ evolution rate was noted. The reason may be due to the decay of HPB which took place within a long time under visible light irradiation [27]. The inset of Fig. 3 shows the decay of HPB at 730 nm along the reaction. It is clear that the decay is quite weak. As the picture below shown, the deep-blue of HPB* was remained even after 300 min irradiation of visible light (>420 nm).

To further illustrate the effect of the HPB formation on the H$_2$ evolution rate, the dependence of the H$_2$ evolution rate on the absorbance of HPB were investigated. As shown in the inset of Fig. 4, when UV irradiation was prolonged, the absorption intensity was increased accordingly, indicating more HPB was formed. Moreover, the H$_2$ evolution rate increased significantly with the absorption intensity as shown in Fig. 4. This indicates that HPB is the

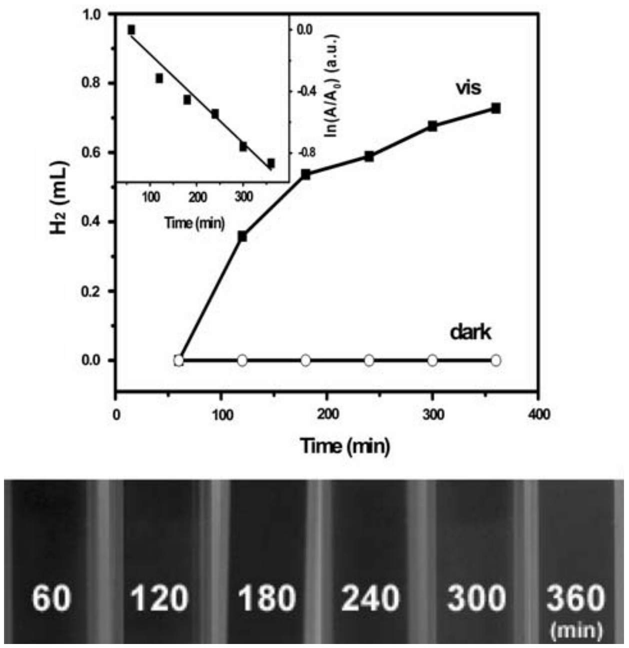

Fig. 3 Time course of H$_2$ evolution over HPB–Pt/TiO$_2$ catalysts under visible light irradiation. The inset is time course of decay of HPB under visible light irradiation. The bottom image is decay of HPB with time. Conditions: pH = 0.5, BW$_{11}$ 1.0 × 10^{-3} mol L^{-1} in 20 (v/v) % glycerol aqueous solution, $\lambda > 420$ nm

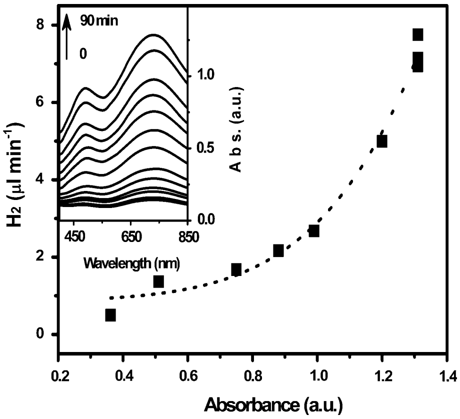

Fig. 4 The dependence of the H_2 generation rate on the absorption intensity of HPB. The inset is the increase of absorbance of HPB with UV irradiation. Conditions: pH $= 0.5$, 1.0×10^{-3} mol L^{-1} BW_{11} in 20(v/v)% glycerol aqueous solution, $\lambda > 420$ nm

key role for H_2 evolution over HPB–Pt/TiO_2 catalysts and higher concentration of HPB results in higher H_2 evolution rate.

4 Conclusions

In conclusion, sensitization of TiO_2 by HPB to achieve H_2 evolution under visible light was identified. Under visible light irradiation ($\lambda > 420$ nm), HPB was excited and the produced electron was transferred to the TiO_2 for efficiently photocatalytic hydrogen generation. The photocatalytic activity of HPB sensitized Pt/TiO_2 was dependent on the concentration of HPB. HPB could vary its character by changing addenda atom (e.g., W) and central atom (e.g., B). Therefore, further work on optimization of the sensitization of TiO_2 with HPB is currently under way.

Acknowledgments This work has been financially supported by Chinese Academy of Sciences, Department of Sciences and Technology of China (2003CB214503).

References

1. Tabata S, Nishida H, Masaki Y, Tabata K (1995) Catal Lett 34:245
2. Domen K, Kudo A, Onishi T (1986) J Catal 102:92
3. Sayama K, Arakawa H (1994) J Photochem Photobiol A 77:243
4. Maeda K, Teramura K, Lu D, Takata T, Saito N, Inoue Y, Domen K (2006) Nature 440:295
5. Yin J, Zou Z, Ye J (2004) J Phys Chem B 108:8888
6. Linsebigler AL, Lu G, Yates JT (1995) Chem Rev 95:735
7. Fujishima A, Rao TN, Tryk DA (2000) J Photochem Photobiol C 1:1
8. Fan F-RF, Bard AJ (1979) J Am Chem Soc 101:6139
9. Desilvestro J, Graetzel M, Kavan L, Moser J, Augustynski J (1985) J Am Chem Soc 107:2988
10. Houlding VH, Gratzel M (1983) J Am Chem Soc 105:5695
11. Jin Z, Zhang X, Li Y, Li S, Lu G (2007) Catal Commun 8:1267
12. Abe R, Sayama K, Arakawa H (2002) Chem Phys Lett 362:441
13. Abe R, Hara K, Sayama K, Domen K, Arakawa H (2000) J Photochem Photobiol A 137:63
14. Abe R, Sayama K, Arakawa H (2004) J Photochem Photobiol A 166:115
15. Abe R, Sayama K, Arakawa H (2003) Chem Phys Lett 379:230
16. Sugihara H, Sano S, Yamaguchi T, Yanagida M, Sato T, Abe Y, Nagao Y, Arakawa H (2004) J Photochem Photobiol A 166:81
17. Sayama K, Tsukagoshi S, Mori T, Hara K, Ohga Y, Shinpou A, Abe Y, Suga S, Arakawa H (2003) Sol Energy Mater Sol Cells 80:47
18. Zhang X, Jin Z, Li Y, Li S, Lu G (2007) J Power Sources 166:74
19. Li Q, Ji Z, Peng Z, Li Y, Li S, Lu G (2007) J Phys Chem C 111:8237
20. Li Q, Lu G (2007) J Mol Catal A: Chem 266:75
21. Jin Z, Zhang X, Lu G, Li S (2006) J Mol Catal A: Chem 259:275
22. Grätzel M (2001) Nature 414:338
23. Underwood DF, Kippeny T, Rosenthal SJ (2001) J Phys Chem B 105:436
24. Peter LM, Wijayantha KGU, Riley DJ, Waggett JP (2003) J Phys Chem B 107:8378
25. Huang D, Wang YJ, Yang LM, Luo GS (2006) Microporous Mesoporous Mater 96:301
26. Liu S, Kurth DG, Bredenkötter B, Volkmer D (2002) J Am Chem Soc 124:12279
27. Yoon M, Chang JA, Kim Y, Choi JR, Kim K, Lee SJ (2001) J Phys Chem B 105:2539
28. Anandan S, Yoon M (2003) J Photochem Photobiol A 160:181
29. Chatti R, Rayalu SS, Dubey N, Labhsetwar N, Devotta S (2007) Sol Energy Mater Sol Cells 91:180
30. Maris EP, Ketchie WC, Murayama M, Davis RJ (2007) J Catal 251:281
31. Herrmann JM, Disdier J, Pichat P (1986) J Phys Chem B 90:6028
32. Teze A, Michelon M, Herve G (1997) Inorg Chem 36:505
33. Wang EB, Hu CW, Xu L (2002) A concise polyoxometalate. Chemical Industry Press, Beijing, p 36
34. Bisquert J, Zaban A, Salvador P (2002) J Phys Chem B 106:8774
35. Gerischer H (1972) Photochem Photobiol 16:243
36. Memming R (1972) Photochem Photobiol 16:325