Highly efficient Pt/TiO$_2$ photocatalyst prepared by plasma-enhanced impregnation method

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Abstract

Highly efficient Pt/TiO$_2$ photocatalyst has been prepared using plasma-enhanced impregnation method. Impregnated 0.5 wt% Pt/TiO$_2$ was treated by plasma followed with thermal calcinations and hydrogen reduction. The catalyst characterizations show that Pt is highly dispersed with a size of 3–5 nm. UV–Vis reflection spectrum suggests it a high photosensitivity in near UV region. Such plasma prepared catalyst exhibits a much higher activity and better metal stability for hydrogen generation from methanol/water mixture, compared to the catalyst prepared conventionally. This highly efficient photocatalyst should have extensive applications in photocatalytic processes.
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1. Introduction

Titanium dioxide supported Pt catalyst (Pt/TiO$_2$) is extensively used as photocatalyst in hydrogen generation and pollutant degradation [1–5]. Especially, photocatalytic hydrogen generation has attracted much attention because photon energy can be utilized this way and clean hydrogen can be produced. The role of photocatalyst is to convert photon energy into chemical energy. Loaded Pt particles can help the separation of electrons and holes generated in illuminated TiO$_2$ and act as H$_2$ evolution sites [4–6]. Many investigations have been conducted to improve the efficiency of Pt/TiO$_2$-catalyzed reactions towards practical application and utilization of solar light directly. It has been reported that addition of carbonate or iodide has a significant effect on liquid water splitting into H$_2$ and O$_2$ over Pt/TiO$_2$ [7,8]. Hydrogen formation can also be enhanced when Pt/TiO$_2$ is suspended in water with oil emulsion [9]. In fact, these additives work as co-catalysts and the activity of Pt/TiO$_2$ itself is not promoted. The effects of loading amount, particle size and pre-treatment have been investigated for methanol/water system but few significant improvements were achieved [10,11]. To further improve the photocatalytic efficiency of Pt/TiO$_2$, more attentions should be paid to the catalyst preparation.

There are two typical methods to load Pt on TiO$_2$: photodeposition and impregnation. For photodeposition method, the precursors of Pt are reduced by ultraviolet (UV) illumination and deposited on TiO$_2$ in aqueous solution [2–4,8,10]. A simpler way is to directly add these precursors into the reaction system (called in situ photodeposition) [7]. Impregnation includes impregnation of TiO$_2$ with H$_2$PtCl$_6$ solution, drying and hydrogen reduction [6,9,11]. Pt/TiO$_2$ prepared by

impregnation with O_2 treatment was reported to show identical activities for liquid alcohols dehydrogenation [11]. Recently, Pt/TiO_2 nanocomposite thin films with unique optical and chemical properties are synthesized using rf magnetron co-sputtering of Pt and TiO_2 [12]. This film is latterly synthesized from single bi-combinant target materials using pulsed laser deposition [13]. It exhibits an optical band gap <2.3 eV and can be used as excellent photoelectrode. However, it is difficult to be used as photocatalyst powders.

We have successfully utilized plasma treatment to improve conventional impregnation method for catalyst preparation. The metal dispersion and activity of Pd/HZSM-5, Pt/NaZSM-5, Ni/Al_2O_3 and $Ni–Fe/Al_2O_3$ are remarkably enhanced by plasma treatment followed with thermal calcinations [14–18]. In the present work, we attempt to use this plasma-enhanced impregnation for the preparation of Pt/TiO_2. The prepared catalyst exhibits an excellent near-UV absorption and a remarkably high activity for hydrogen generation from methanol/water mixture.

2. Experimental and setup

TiO_2 powders were prepared through sol–gel method. About 30 ml de-ionized water was added drop-wise into a mixture of 20 ml $Ti(C_4H_9O)_4$ and 100 ml ethanol under vigorous stirring at room temperature. After filtered and dried at 110 °C for 10 h, the obtained TiO_2 sample was calcined at 600 °C for 2 h. For the preparation of Pt/TiO_2 catalyst, TiO_2 powders were first impregnated with H_2PtCl_6 solution. The Pt loading was 0.5 wt%. After dried at ambient conditions for 24 h, the obtained samples were treated by glow discharge plasma for 30 min. The setup for plasma treatment has been described previously [14,15,18]. The plasma was initiated by a high DC voltage generator (made by Tianda Cutting and Welding Setup Inc. Ltd., Tianjin, China) with Argon as plasma-forming gas. At last, these plasma-treated catalysts were calcined in air for 2 h and reduced using flowing hydrogen for 2 h at 300 °C, respectively. The prepared catalysts were referred as $Pt/TiO_2(P)$. For the purpose of comparison, the conventional catalysts prepared with calcinations and reduction (but no plasma treatment) were also prepared and referred as $Pt/TiO_2(C)$.

All prepared catalysts were characterized using XRD (Rigaku, D/max-2500, Cu Kα), TEM (Philips,Tecnai G^2 F20), XPS (PHI1600), H_2-chemisorption (Quantachrome, Autosorb-1-C), and UV–Vis spectrometry (Shimadzu, UV-2100S). The Pt amounts on the used catalysts were analyzed by inductively coupled plasma spectrometry (ICP) (Vista-MPX, ICP-OES).

The photocatalytic activity of prepared Pt/TiO_2 was evaluated in an inner irradiation quartz reactor equipped with a 300 W high-pressure Hg lamp. Catalyst powders (0.5 g) were dispersed in a mixture of 150 ml methanol and 200 ml water by a magnetic stirrer. The initial pressure in the reactor was 20 kPa filled by Ar. The evolution of H_2 was measured by both a mass spectrometer (Pfeiffer, Omnistar) and a manometer. After 7.5 h irradiation, the reaction was stopped and the used catalysts were collected for ICP analysis.

3. Results and discussion

XRD characterization shows that the TiO_2 powder used has a mixed anatase and rutile structure with the weight percentage of the anatase phase of 80.6% [19]. The crystal size calculated using Scherrer equation is 30.4 nm, in agreement with the TEM observations in Fig. 1. For $Pt/TiO_2(P)$ and $Pt/TiO_2(C)$, no Pt peaks are determined by XRD because of the low loading amount. Fig. 1a shows that Pt particles are well dispersed on the surface of $Pt/TiO_2(P)$ with particle diameter in the range of 3–5 nm. For $Pt/TiO_2(C)$, however, less Pt particles are observed randomly locating on TiO_2
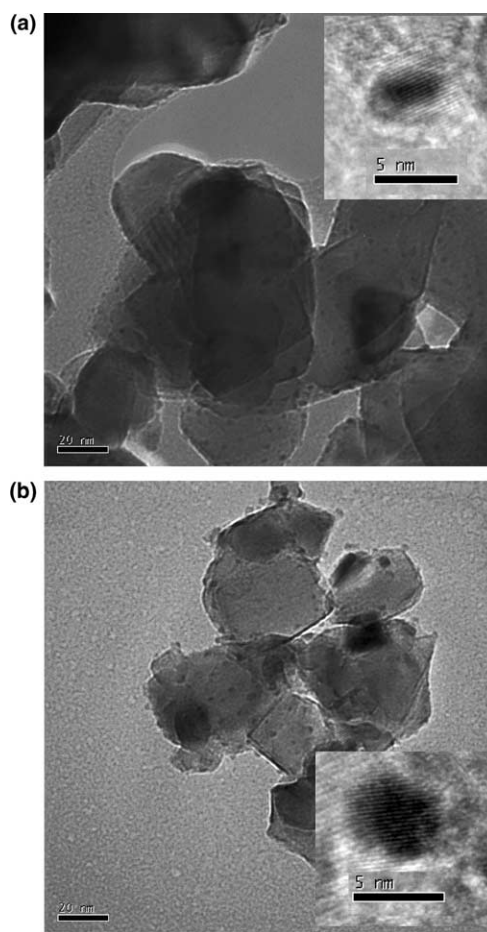

Fig. 1. TEM photographs of: (a) $Pt/TiO_2(P)$; (b) $Pt/TiO_2(C)$. The inset is high-resolution TEM of single Pt particle.

with particle size as 5–7 nm, as shown in Fig. 1b, which indicates a relatively worse metal distribution. This suggests that catalyst prepared by plasma method has a better metal dispersion than that obtained by conventional impregnation.

Fig. 2 shows the XPS spectra of Pt_{4f} for $Pt/TiO_2(P)$ and $Pt/TiO_2(C)$. The binding energy of Pt_{4f5} (74.98 eV) and Pt_{4f7} (70.37 eV) confirms the presence of Pt^0 metal on the TiO_2 surface. The peak intensity of Pt for $Pt/TiO_2(P)$ is much larger than that for $Pt/TiO_2(C)$. The Pt/Ti surface ratio for $Pt/TiO_2(P)$ and $Pt/TiO_2(C)$ is 0.026 and 0.017, respectively. It means that more Pt atoms exist on the surface of $Pt/TiO_2(P)$. Furthermore, Pt should be dispersed into more particles but with smaller size over $Pt/TiO_2(P)$ compared with $Pt/TiO_2(C)$, as shown by TEM photographs. Meanwhile, The Pt/Ti ratio for 10 wt% Pt/TiO_2 film synsesized by pulsed laser deposition is about 0.034 [13]. Regarding that the Pt loading in our catalyst is only 0.5 wt%, the catalyst prepared by impregnation has a better metal dispersion, especially, the plasma prepared one.

H_2-chemisorption shows that the metal dispersion of $Pt/TiO_2(P)$ is 12.7%, which is twice high than the 6.1% dispersion of $Pt/TiO_2(C)$. Evidently, a much better metal dispersion over the plasma-treated Pt/TiO_2 has been obtained. Accordingly, the metal surface area of $Pt/TiO_2(P)$ (0.158-m^2/g catalyst) is also double of that of $Pt/TiO_2(C)$ (0.075-m^2/g catalyst). It should be noted that, the chemisorption is conducted at 50 °C and the hydrogen spillover from Pt to TiO_2 cannot be completely avoided and uncertainty of measurement may exist [20,21]. However, it can be regarded as system deviation for all the measurements and the comparison of the data still give valid conclusion.

The UV–Vis spectra of catalysts are shown in Fig. 3. In the UV region (<340 nm), both catalysts have complete absorption. In the near UV region (340–400 nm), however, $Pt/TiO_2(P)$ exhibits a larger absorption and thus a higher photosensitivity in contrast with $Pt/TiO_2(C)$. The absorption in region above 400 nm is caused by Pt and has no catalytic activity. It has been
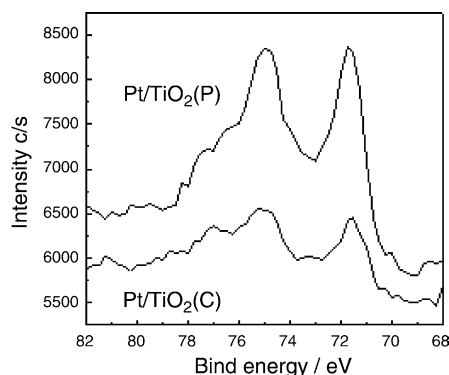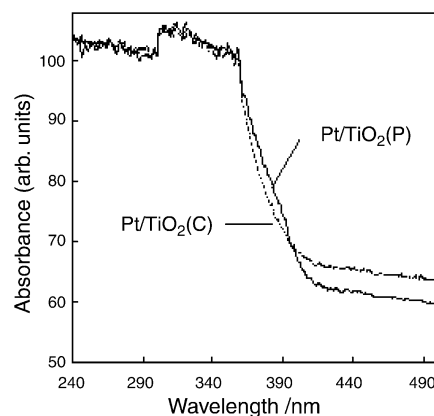

Fig. 3. UV–Vis absorption spectra of $Pt/TiO_2(P)$ and $Pt/TiO_2(C)$.

reported that the near UV absorption intensity is proportional to the Pt-loading [5,6]. For an effective absorption, photogenerated electrons in the conduction band of TiO_2 must migrate to Pt through the interface between Pt and TiO_2. Well-dispersed $Pt/TiO_2(P)$ has a larger metal-support interface than $Pt/TiO_2(C)$, thereby it can promote electron–hole separation and absorb more photons. It also have been concluded that small metallic particles widely dispersed on TiO_2 show a modulation of the semiconductor bands [22,23]. Simultaneously, nanocomposite Pt/TiO_2 prepared via laser ablation shows a narrow band gap [13]. Plasma preparation produces a homogeneous and discontinuous Pt layer on TiO_2. At the same time, plasma treatment followed with thermal calcinations may induce strong metal-support interaction [24]. Therefore the discontinuous Pt layer can impact the band structure of exterior TiO_2, resulting in a high optical absorbing ability.

Compared with $Pt/TiO_2(C)$, two advantages of $Pt/TiO_2(P)$ can be concluded: high metal dispersion and high photosensitivity. Metal particles loaded on semiconductor are regarded as H_2 hydrogen generation sites [4–6]. Recent study identifies that hydrogen evolution reaction takes place at the boundary between metal and support [25]. $Pt/TiO_2(P)$ has a high Pt dispersion and thus a longer interface boundary, consequently exhibits high hydrogen generation efficiency. Furthermore, more photoinduced electrons for hydrogen generation will be generated in TiO_2 as $Pt/TiO_2(P)$ can absorb more near UV light. Therefore, $Pt/TiO_2(P)$ should exhibit a high H_2 evolution efficiency. Fig. 4 illustrates the photocatalytic activity of Pt/TiO_2 prepared by different methods. It is noticed the activity of catalyst prepared by conventional impregnation is slightly higher than that by in situ phtodecomposition. The H_2 evolving rate for $Pt/TiO_2(C)$ is 1.92 mmol/h. However, $Pt/TiO_2(P)$ has a much higher evolving rate of 4.28 mmol/h. It is clear that Pt/TiO_2 prepared by plasma-enhanced impregnation exhibits a remarkably high photocatalytic activity.
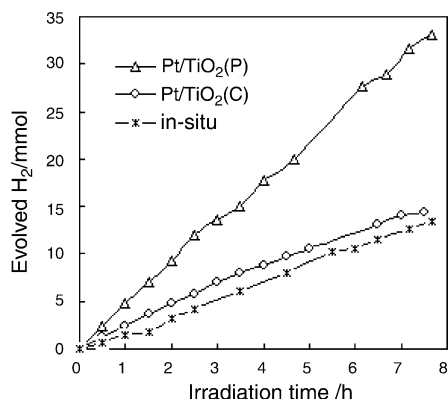

Fig. 2. Pt_{4f} XPS spectra of $Pt/TiO_2(P)$ and $Pt/TiO_2(C)$.

Fig. 4. Photocatalytic hydrogen evolution from methanol/water mixture. In situ means that H_2PtCl_6 (0.5 wt% Pt) and TiO_2 (0.5 g) are directly added in the mixture.

ICP analysis shows that part of supported Pt is lost during the reaction. After 7.5 h reaction, the 0.5 wt% Pt-loading decreases to 0.456 and 0.284 wt% for Pt/TiO_2(P) and Pt/TiO_2(C), respectively. This result indicates that the Pt/TiO_2(P) also has a better metal stability, probably because of its large Pt–TiO_2 interface inducing a strong interaction to anchor Pt tightly on TiO_2 surface.

4. Conclusion

We have demonstrated a highly efficient Pt/TiO_2 photocatalyst prepared by plasma-enhanced impregnation method including plasma treatment, calcinations and hydrogen reduction. The Pt particles are 3–5 nm in diameter and homogeneously distributed on TiO_2. This highly dispersed catalyst exhibits an intensive absorption in the range of 340–400 nm. It shows a remarkable high activity and a high metal stability for hydrogen generation from methanol/water mixture.

References

[1] T. Kawai, T. Sakata, J. Chem. Soc. Chem. Commun. (1980) 694.
[2] T. Sakata, T. Kawai, Chem. Phys. Lett. 80 (1981) 341.
[3] Y. Li, G. Lu, S. Li, Appl. Catal. A: Gen. 214 (2001) 179.
[4] Z. Zhang, C.-C. Wang, R. Zakaria, J.Y. Ying, J. Phys. Chem. B 102 (1998) 10871.
[5] M. Ashokkumar, Int. J. Hydrogen Energ. 23 (1998) 427.
[6] A. Furube, T. Asahi, H. Masuhara, H. Yamashita, M. Anpo, Chem. Phys. Lett. 336 (2001) 424.
[7] K. Sayama, H. Arakawa, J. Chem. Soc., Faraday Trans. 93 (1997) 1647.
[8] R. Abe, K. Sayama, H. Arakawa, Chem. Phys. Lett. 371 (2003) 360.
[9] T. Miyao, Y. Suzuki, S. Naito, Catal. Lett. 66 (2000) 197.
[10] T. Maruyama, T. Nishimoto, Ind. Eng. Chem. Res. 30 (1991) 1634.
[11] F.H. Hussein, R. Rudham, J. Chem. Soc., Faraday Trans. I 83 (1987) 1647.
[12] T. Sasaki, R. Rozbicki, Y. Matsumoto, N. Koshizaki, S.-Y. Terauchi, H. Umehara, Mater. Res. Soc. Symp. Proc. 457 (1997) 425.
[13] K.M. Beck, T. Sasaki, N. Koshizaki, Chem. Phys. Lett. 301 (1999) 336.
[14] C.-J. Liu, G.P. Vissokov, B. Jang, Catal. Today 72 (2002) 173.
[15] C.-J. Liu, Y.-P. Zhang, X.L. Zhu, F. Hei, B. Eliasson, Appl. Catal. B: Environ. 47 (2004) 95.
[16] Y.-P. Zhang, P.-S. Ma, X.L. Zhu, C.-J. Liu, Y.-T. Shen, Catal. Commun. 5 (2004) 35.
[17] J.-G. Wang, C.-J. Liu, Y.-P. Zhang, K.-L. Yu, X.L. Zhu, F. Hei, Catal. Today 89 (2004) 183.
[18] C.-J. Liu, D.-G. Cheng, Y.-P. Zhang, K.-L. Yu, Q. Xia, J.-G. Wang, X.L. Zhu, Catal. Surv. Asia 8 (2004) 111.
[19] D. Mardare, M. Tasca, M. Delibas, G.I. Rusu, Appl. Surf. Sci. 156 (2000) 200.
[20] S. Khoobiar, J. Phys. Chem. 68 (1964) 411.
[21] V. Perrichon, L. Retailleau, P. Bazin, M. Daturi, J.C. Lavalley, Appl. Catal. A: Gen. 160 (2004) 1.
[22] Y. Nakato, H. Tsubomura, J. Photochem. 29 (1985) 257.
[23] G. Munuera, A.R. González, A. Fernández, P. Malet, J.P. Espinós, J. Chem. Soc., Faraday Trans. I 85 (1989) 1279.
[24] Y. Li, Y. Fan, H. Yang, B. Xu, L. Feng, M. Yang, Y. Chen, Chem. Phys. Lett. 372 (2003) 160.
[25] M. Bowker, D. James, P. Stone, R. Bennett, N. Perkins, L. Millard, J. Greaves, A. Dickinson, J. Catal. 217 (2003) 427.