Pt Deposites on TiO$_2$ for Photocatalytic H$_2$ Evolution: Pt Is Not Only the Cocatalyst, but Also the Defect Repair Agent

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Abstract: Pt, as a common cocatalyst, has been widely used in photocatalytic H$_2$ evolution. However, the specific role of Pt in photocatalytic H$_2$ evolution has not been thoroughly studied. In this paper, by employing three Pt sources with different charges (positive, negative and neutral), we systematically studied the charge effect of Pt sources on photocatalytic H$_2$ evolution via TiO$_2$ catalyst. According to the results of Raman, X-ray photoelectron spectroscopy (XPS), recycle experiments and photocurrent characterizations, it was found that TiO$_2$ would produce electropositive defects during photocatalytic H$_2$ evolution, inevitably leading to the decline of H$_2$ production activity. Thanks to the electrostatic interaction, the electronegative Pt source not only promoted charge separation, but preferential deposited on electropositive defects, which acted as the defect repair agent, and thus resulted in the increased photocatalytic stability. This work may provide a new perspective for enhancing photocatalytic stability of hydrogen production.

Keywords: photocatalytic stability; electropositive defect; Pt sources; electrostatic interaction; defect repair

1. Introduction

Since Fujishima A and Honda K of the University of Tokyo first reported the phenomenon of photocatalytic H$_2$ evolution in 1972, photocatalytic H$_2$ evolution has gradually become a focus of academic research [1]. In recent years, researchers have reported a large number of semiconductor photocatalysts with excellent performances of H$_2$ production, such as TiO$_2$, CdS and SrTiO$_3$ [2–7]. However, the problem of poor photostability is still found on these semiconductor photocatalysts [8], which hinders the large-scale industrial application. As a common photocatalyst, TiO$_2$ has been proposed to have the excellent photocatalytic activity. Generally, TiO$_2$ was believed as a stable catalyst [9,10], but some literatures have shown that after several cycles of photocatalytic reaction, the H$_2$ evolution activity gradually decreased on TiO$_2$ catalyst, which might indicate its instability [11].

Recent studies considered that the decrease in activity is mainly due to the interaction of photo-generated electron-hole pairs with water and oxygen in the surrounding environment. The interaction resulted in the redox reaction of the semiconductor itself and the destruction of its structure [12,13]. Akihito Imanishi et al. studied the mechanism of water photooxidation reaction on TiO$_2$ surface, and found that the surface roughness variation at the atomic level occurred with
photoreaction, due to the fracture of Ti–O bond during the photoreaction [14]. Yang et al. also observed that the light irradiation could cause the entire TiO₂ nanowire crystalline surface convert to the amorphous structure, which was attributed to hole-guided photocorrosion [11]. The above studies suggested that the activity of most semiconductor materials will inevitably decrease under light irradiation. On the basis of that, the design and modification of semiconductor catalysts are necessary to improve their stability [15].

The noble metal of Pt is widely used as a cocatalyst in photocatalytic H₂ evolution, due to its large work function and efficient electron migration capability [16,17]. Cao et al. investigated the role of single Pt atom in photocatalytic H₂ evolution reaction, and proposed that the Pt single atoms with electron-deficient 5d orbitals on g-C₃N₄ nanosheets not only facilitated the separation of electron-hole pairs, but also optimized the water reduction kinetics on the surface [18]. In addition, Xing et al. studied the active sites on Pt/TiO₂ photocatalytic H₂ evolution. It is reported that the metallic Pt nanoparticles have little contribution to the activity of photocatalytic H₂ evolution, while the oxidized Pt species is the key species to the activity [19]. At present, most researchers focused on the fact that the Pt cocatalyst helps photo-generated electron migrate, while the role of Pt cocatalyst on the catalyst stability was less investigated.

In this work, the effects of Pt sources with different charges (positive, negative and neutral) on the reaction stability of TiO₂ photocatalytic H₂ evolution were investigated in details. The characterizations of Transmission electron microscopy (TEM), X-Ray Diffraction (XRD), XPS, Raman and photocurrent were carried out to reveal the origin of the improvement on photostability. It was found that the positive charged defects were generated on the TiO₂ surface in the photocatalytic reaction, leading to the decreased stability. Considering that H₂PtCl₆ is slightly negative charged, loaded Pt with H₂PtCl₆, can not only improve the photocatalytic H₂ evolution activity of TiO₂ catalyst, but also act as the defect repair agent to improve the stability of TiO₂. The possible scheme of H₂PtCl₆ improving photostability of TiO₂ was proposed.

2. Results and Discussions

2.1. Photocatalytic H₂ Evolution Activity

The photocatalytic H₂ evolution performances of Pt/TiO₂ and TiO₂ catalysts with different Pt sources were shown in Figure S1. The photocatalytic H₂ evolution performance of pure TiO₂ catalyst without Pt cocatalyst was the worst. When three kinds of Pt were introduced into the system, i.e., positive charged Pt source PtCl₄ (TiO₂-Pt⁴⁺), negative charged Pt source H₂PtCl₆ (TiO₂-PtCl₆²⁻) and neutral Pt particles (TiO₂-Pt⁰), the photocatalytic H₂ evolution activities were significantly improved. The photocatalytic H₂ evolution activity of TiO₂–Pt⁰ was slightly lower than TiO₂–PtCl₆²⁻ and TiO₂–Pt⁴⁺ (14 mmol/g), but it also reached 11 mmol/g, which was much higher than that of pure TiO₂. The phenomenon suggests that once the Pt species is introduced into the system, the cocatalyst Pt can greatly improve the H₂ production performance of TiO₂ photocatalyst.

Furthermore, the photocatalytic stabilities of TiO₂-based samples were measured, and the difference of Pt sources (PtCl₆²⁻, Pt⁴⁺ and Pt⁰) in the photostability of Pt/TiO₂ were investigated in comparison. As observed in Figure 1a, the activities of all the samples decreased after three cycles, which indicated that the TiO₂ catalyst seemed not as stable as we think. Moreover, there were photostability differences of the three Pt samples after three cycles (Figure 1b). The activity of the last cycle was compared with that of the first one. As shown in Figure 1b, the H₂ production of TiO₂–PtCl₆²⁻ was 11 mmol/g after the three cycle, which was 70% of the H₂ production in the first cycle. While the H₂ production of TiO₂ loaded with Pt was only 5.5 mmol/g, which was 50% of the first cycle. In addition, the H₂ production of TiO₂–Pt⁴⁺ was 8 mmol/g after three cycles, which was 60% of the first cycle and lower than TiO₂–PtCl₆²⁻. It was observed that the negative charged Pt source loaded on TiO₂ greatly enhanced the photostability of TiO₂ in comparison with the two others, indicating that the different
Pt sources play an important role in the stability of Pt/TiO\textsubscript{2} catalysts, and the key factor might be the electrical properties of Pt sources.

**Figure 1.** (a) Recycle experiments on TiO\textsubscript{2}, TiO\textsubscript{2}-Pt\textsuperscript{0}, TiO\textsubscript{2}-PtCl\textsubscript{6}\textsuperscript{2-} and TiO\textsubscript{2}-Pt\textsuperscript{4+}; (b) The ratios of the third cycle activity to the first one of TiO\textsubscript{2}, TiO\textsubscript{2}-Pt\textsuperscript{0}, TiO\textsubscript{2}-PtCl\textsubscript{6}\textsuperscript{2-} and TiO\textsubscript{2}-Pt\textsuperscript{4+} (C\textsubscript{3} is the third cycle activity and C\textsubscript{1} is the first cycle activity).

2.2. Changes of TiO\textsubscript{2} Catalyst during Photocatalytic H\textsubscript{2} Evolution

In order to explore the improved stability of Pt/TiO\textsubscript{2}, the reason for the decreased photostability on TiO\textsubscript{2} was investigated. The texture properties of TiO\textsubscript{2} catalysts before and after the photoactivation were determined. In XRD patterns (Figure S2), only diffraction peaks belonging to anatase TiO\textsubscript{2} were detected for both TiO\textsubscript{2} catalysts before and after photocatalytic H\textsubscript{2} evolution test, and no other peaks of impurities were found [20]. This result indicates the crystal structure of TiO\textsubscript{2} bulk is stable during photoreaction process. In addition, the N\textsubscript{2} adsorption and desorption (Figures S3 and S4, Table S1) results showed that the specific surface areas of TiO\textsubscript{2} before and after the reaction were around 100 m\textsuperscript{2}/g, with little change before and after the reaction. Therefore, the photoreaction process will not change the specific surface area of TiO\textsubscript{2} [21]. On the basis of that, it was found that the texture properties of TiO\textsubscript{2} before and after the reaction are similar.

Furthermore, the surface structures of TiO\textsubscript{2} before and after the reaction were measured. Firstly, the Raman characterization was carried out for its sensitivity. As shown in Figure 2a, both the two TiO\textsubscript{2} samples exhibited E\textsubscript{g} modes (143 cm\textsuperscript{-1}, 198 cm\textsuperscript{-1} and 639 cm\textsuperscript{-1}), B\textsubscript{1g} mode (399 cm\textsuperscript{-1}) and A\textsubscript{1g} mode (515 cm\textsuperscript{-1}) [22]. However, compared to TiO\textsubscript{2} before the reaction, the peak at 143 cm\textsuperscript{-1} of TiO\textsubscript{2} had a slight blue shift after the photoreaction. Generally, the formation of oxygen defects in TiO\textsubscript{2} will lead to the rupture of the Ti-O bond, which in turn causes the TiO\textsubscript{2} lattice to shrink, and then the bond length of the Ti-O bond becomes shorter, finally resulted in the blue shift [23,24]. On the basis of that, it was suggested that the blue shift on the used TiO\textsubscript{2} catalyst was resulted from the oxygen defects. In addition, the phenomenon was also reported by Du et al. [25]. Therefore, it was inferred that the stability decline of TiO\textsubscript{2} was attributed to the positive-charged oxygen defects generated in the photoreaction.

The electron spin resonance (ESR) analyses were also carried out and the results were shown in Figure 2b. The signal with g value near 2.002 appeared in ESR curve of TiO\textsubscript{2} after the photoreaction, which was attributed to the oxygen defects in anatase [26]. This result confirms our hypothesis that a certain amount of oxygen defects is generated on the TiO\textsubscript{2} surface after the reaction of photocatalytic H\textsubscript{2} production. The XPS characterization was employed to confirm the formation of defects on the used TiO\textsubscript{2} photocatalyst. Figure 2c showed the XPS spectra of O1s. Compared with the fresh TiO\textsubscript{2} (529.38 eV) sample, the peak positions of used TiO\textsubscript{2} shifted to higher binding energy (529.75 eV), implying that more oxygen defects were generated on the TiO\textsubscript{2} catalyst after the reaction [27].

Generally, most of the defects will become the recombination center of electron and hole, leading to a decline in the activity [28]. Thus, the photocurrent test was used to compare the degree of electron-hole recombination on TiO\textsubscript{2} samples before and after the reaction, displayed in Figure 2d. The results...
showed that the photocurrent of the used TiO$_2$ catalyst was only half of the fresh one, which suggests that there are more defects generated on TiO$_2$ after the reaction. The defects lead to the increased recombination of electron-hole and the decreased photocurrent intensity [29]. This phenomenon was also observed by Zhang et al., they proposed that the defects of ZnO after a long time of photoreaction played an important role in the decreased photostability [30]. Therefore, combined with the results of Raman, ESR and XPS, we speculate that the generation of defects with positive charge on TiO$_2$ surface was the main reason for the declined photostability.

![Figure 2](image-url)  
*Figure 2.* TiO$_2$ and TiO$_2$-A: (a) Raman spectra, inset was the locally magnified Raman spectra (100–200 cm$^{-1}$); (b) EPR spectra; (c) O 1s XPS spectra; (d) photocurrent result.

2.3. The Influences of Different Pt Sources on Photostability

In order to reveal the influences of different charged Pt sources on the stability of photocatalytic H$_2$ evolution, the contents, valence states and particle sizes of Pt on Pt/TiO$_2$ catalysts were investigated in comparison. The Inductively coupled plasma-atomic emission spectroscopy (ICP) test was employed to study the contents of Pt on three kinds of Pt/TiO$_2$ catalysts. As shown in Table S1, the Pt weight ratio of Pt/Ti of all the samples were ca. 0.60 wt%, demonstrating that the contents of Pt were similar. Then the XPS characterization was used to study the valence state of the generated Pt on three Pt/TiO$_2$ samples. In Pt 4f XPS spectra (Figure 3), only the Pt 4f$_{7/2}$ and Pt 4f$_{5/2}$ peaks at 70.7 eV and 74.1 eV assigned to Pt$^0$ could be detected [31,32], which indicates that the valence states of Pt introduced via three different sources are consistent. Furthermore, the TEM characterization was carried out to determine the Pt particle size, and the results were shown in Figure 4a–c. The dark spots in TEM images are Pt species. It was observed that Pt is highly dispersed on TiO$_2$ surface. The Pt particle size of all the samples is similar, i.e., 2 nm. While for the TiO$_2$ sample, its particle size is 20 nm. Therefore, the Pt introduced by three Pt sources have the same content, valence state and particle size on the Pt/TiO$_2$ catalysts, suggesting that the different stabilities have little relationship with the Pt properties.
In addition, the texture properties of the used Pt/TiO\textsubscript{2} samples via three different Pt sources were explored in details. Firstly, the specific surface areas were determined (Table S1). The results showed that the specific surface areas of all the sample were around 100 m\textsuperscript{2}/g. Moreover, the BET measurements—adsorption isotherms and pore size distribution—of the samples have been determined in Figures S3 and S4. Compared with the Pt/TiO\textsubscript{2} samples via three different Pt sources, it could be found that the results of BJH pore size distribution and N\textsubscript{2}-sorption isotherm are similar, which suggest that the difference in photostability is not mainly resulted from the pore structure and specific surface

Figure 3. Pt 4f XPS spectra of the used Pt/TiO\textsubscript{2} samples via three different Pt sources.

Figure 4. TEM images of the used Pt/TiO\textsubscript{2} samples via three different Pt sources and the size distributions of Pt particles (a) TiO\textsubscript{2}-Pt\textsuperscript{0}, (b) TiO\textsubscript{2}-Pt\textsuperscript{4+} and (c) TiO\textsubscript{2}-PtCl\textsubscript{6}\textsuperscript{2-}.
area. Subsequently, the XRD method was used to detect the phase structures of all the used Pt/TiO₂ samples, as displayed in Figure S5. There was no peak shift of the TiO₂ and the other species generation, indicating that the different Pt sources have no effect on the TiO₂ crystal structure. In general, different charged Pt sources have little change on the structures of Pt and TiO₂.

In order to further reveal the reason for the different stabilities on Pt/TiO₂ samples via three different Pt sources, the XPS (Figure 5) spectra of O 1s on the used Pt/TiO₂ were carried out. The O 1s spectra for the used Pt/TiO₂ were fitted into three peaks, i.e., 529.4, 531.6 and 532.9 eV, which were assigned to the O lattice (Oₐ), oxygen vacancies (Oᵥ), and the adsorbed oxygen species on defect sites of TiO₂ (Oc) [33]. The results showed that all the peak positions of Oc of the used Pt/TiO₂ shift to lower binding energy compared with TiO₂-A (529.75 eV). Among them, TiO₂-PtCl₆²⁻-A had the lowest binding energy (529.38 eV), which was similar to the TiO₂ before the reaction, suggesting that there were few defects generated on the TiO₂-PtCl₆²⁻ catalyst after the reaction. In addition (Table S1), the ratio of peak areas of A(Oc + Oᵥ)/Aₐ on TiO₂-PtCl₆²⁻ is also the lowest (10.6%) compared with other used Pt/TiO₂ samples, which indicates that the introduction of the negative charged PtCl₆²⁻ can reduce the amount of defects generated on TiO₂ in the photocatalytic H₂ evolution, and thus improve the photocatalytic stability.

**Figure 5.** O 1s XPS spectra of the used Pt/TiO₂ samples via three different Pt sources.

In addition, the Raman spectra were performed to investigate the repair effect of different Pt sources on the defects formed on TiO₂ in photocatalytic H₂ evolution (Figure 6). It was observed that after loaded with Pt, the blue shift of the peaks attributed to the Ti-O bond was decreased, compared with TiO₂-A (156 cm⁻¹). The used TiO₂-PtCl₆²⁻-A has the smallest blue shift (153 cm⁻¹), TiO₂-Pt⁺⁺-A followed, and TiO₂-Pt⁰-A had the biggest blue shift. It is suspected that the Pt sources have entered the defects generated by photocorrosion, which repairs the rupture of the Ti-O bond, and thus the blue shift of Raman peak is reduced [34]. Surprisingly, it was found that the blue shift of TiO₂-PtCl₆²⁻-A is smaller than others, indicating that the effect of electrostatic attraction resulted in the maximum degree of Pt species entering the defects, and thus the repairing ability of H₂PtCl₆ source is the best.

Based on the above characterization results, we proposed a possible scheme for the influence of different Pt sources on the stability, as shown in Figure 7. Under light illumination, the photo-generated electrons and holes were present on TiO₂. Due to the worst ability of charge transfer on TiO₂, the surface defects with slightly positive charge gradually appeared, which acted as the recombination center of electrons and holes, and thus led to the decrease of stability. Thanks to the electrostatic interaction,
We compared the ratio of photocurrent intensity between the first and the third cycle of different Pt sources on the stability, as shown in Figure 7. Under light illumination, the photocurrent intensity of TiO$_2$-PtCl$_6^{2-}$ in the third cycle was 80% of the first cycle, but the photocurrent in the third cycle was 70% of the first cycle, which was better than TiO$_2$-Pt$^0$ and TiO$_2$ (60%). The performances are consistent with the results of the Raman and recycle experiments, which confirm that Pt deposited on TiO$_2$ can reduce the recombination of electrons and holes, and H$_2$PtCl$_6$ source can efficiently improve the photostability.

In order to verify the advantageous defect repairing ability of PtCl$_6^{2-}$ source, the photocurrent characterization was performed on TiO$_2$ samples. In the photocurrent test, the Pt sources with different charges were firstly added into the reaction cell, and in-situ deposited under light irradiation, respectively. As shown in Figure 8a, the maximum photocurrents of all samples decreased gradually with the increase of the on-off cycles, which indicates that the surface defects are produced [35]. We compared the ratio of photocurrent intensity between the first and the third cycle of different samples. The decreased photocurrent intensity of TiO$_2$-PtCl$_6^{2-}$ in the third cycle was 80% of the first cycle, and its stability was better than that of other samples. The decreased photocurrent of TiO$_2$-Pt$^{4+}$ was more obvious than TiO$_2$-PtCl$_6^{2-}$, but the photocurrent in the third cycle was 70% of the first cycle, which was better than TiO$_2$-Pt$^0$ and TiO$_2$ (60%). The performances are consistent with the results of the Raman and recycle experiments, which confirm that Pt deposited on TiO$_2$ can reduce the recombination of electrons and holes, and H$_2$PtCl$_6$ source can efficiently improve the photostability.
Moreover, the above phenomenon is also suitable for ZnO catalyst, which is that Pt could act as the defect repairing agent, and the results were shown in Figure S6. Similar to TiO$_2$, the photocatalytic activity of ZnO gradually decreased \[36,37\]. After three cycles of hydrogen production test, the improvement of the stability of the catalysts prepared by different Pt sources follow the sequence: PtCl$_6^{2-}$ > Pt$^{4+}$ > Pt$^0$ (Figure 9). Compared with TiO$_2$, ZnO catalyst would easily have the oxygen defects with positive charge. On the basis of that, the negative charged Pt source can act as the highly efficient defect repairing agent. Therefore, the possible mechanism in the work would provide us a basis to design photocatalysts with better stabilities.

![Figure 8](image_url)  
**Figure 8.** (a) Photocurrents of TiO$_2$, TiO$_2$-Pt$^0$, TiO$_2$-PtCl$_6^{2-}$ and TiO$_2$-Pt$^{4+}$; and (b) maximum photocurrent ratios ($D_3$ is the third cycle photocurrent and $D_1$ is the first cycle photocurrent).

3. Experimental Section

3.1. Materials

All chemicals used in this study were of analytical grade. Anatase titanium dioxide (TiO$_2$), hydrofluoric acid (HF), triethanolamine ($C_6H_{15}NO_3$), chloroplatinic acid ($H_2PtCl_6$), platinum tetrachloride (PtCl$_4$), zinc oxide (ZnO) and absolute ethyl alcohol ($C_2H_6O$) were purchased from “Nanjing chemical reagent co. LTD”, China. Deionized water (resistivity 18.2 MΩ cm$^{-1}$) was used for all samples. All chemicals were used without further purification.

3.2. Preparation of Samples

3.2.1. TiO$_2$-Pt$^0$

0.1 g TiO$_2$ was dispersed in 100 mL deionized water, and then stirred with 0.41 mL $H_2PtCl_6$ (10 g/L) adding. The dissolved oxygen in the water was removed by vacuum. A 300 W xenon lamp was used to irradiate sample. After reaction, the products were collected by centrifugation method and washed with ethyl alcohol for three times. Then the samples were dried overnight at 80 °C in the oven. The sample was noted as TiO$_2$-Pt$^0$. 

![Figure 9](image_url)  
**Figure 9.** The activity ratio of the third cycle to the first of ZnO, ZnO-Pt$^0$, ZnO-PtCl$_6^{2-}$ and ZnO-Pt$^{4+}$.
3.2.2. TiO$_2$-Pt$^{4+}$ and TiO$_2$-PtCl$_6^{2−}$

0.1 g TiO$_2$ photocatalyst was dispersed in 90 mL water, then stirred with 10 mL of triethanolamine adding. The 1.07 mL (2.5 g/L) positive charged Pt source PtCl$_4$ or 0.41 mL (10 g/L) negative charged Pt source H$_2$PtCl$_6$ were added into the above solution, which irradiated under 300 W xenon lamp for 2.5 h. Finally, TiO$_2$-Pt$^{4+}$ and TiO$_2$-PtCl$_6^{2−}$ samples were obtained, respectively. The corresponding description have been added in the revised manuscript.

3.3. Characterization

X-ray diffraction (XRD) patterns of the samples were obtained on a Philips X pert Pro diffractometer with Cu Ka radiation ($λ = 0.15418$ nm) and Ni filter plate (Shimadzu, Tokyo, Japan). The X-ray tube was operated at 40 kV and 40 mA. BET surface areas were measured by nitrogen adsorption at 77 K on a Micrometrics ASAP 2020 adsorption apparatus (Micromeritics, Shanghai, China). Before adsorption measurements, the samples were degassed for 3 h at 300 $°$C. UV-visible diffuse reflection (UV-vis DRS) was performed on a Shimadzu UV–2401 spectrometer (Shimadzu, Tokyo, Japan) with BaSO$_4$ as a standard sample. X-ray photoelectron spectroscopy (XPS) was performed on the Phl 5000 Versa Probe energy spectrum instrument (ULVAC-PHI, Tokyo, Japan). Transmission electron microscopy (TEM) images were obtained on JEM-2100 instrument at an accelerating voltage of 200 Kv (JEOL, Akishima City, Japan). The samples were dispersed in A.R. grade ethanol and the resulting suspensions were dried on carbon film supported copper grids. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis was determined on an Optima 5300DV inductively coupled plasma-atomic emission spectrometer (PerkinElmer, Waltham, MA, USA). Laser Raman spectroscopy was performed on a LabRAM HR Evolution spectrometer with an excitation source of 532 nm (HORIBA, LTD, China). The electron spin resonance (ESR) signal was examined at 77 K on ESR JES FA200 (JEOL) spectrometer (Bruker, Kleve, Germany).

3.4. Photocurrent Tests

Electrochemical measurements were carried out on an Ivium electrochemical workstation (Tianjin Deshang Instrument, Inc China) using a standard three-electrode cell. The prepared samples were deposited on In-doped SnO$_2$-coated glass (ITO glass) electrode as the working electrodes with an active area of ca. 1 cm$^2$ with a Pt wire as the counter electrode, saturated calomel electrode as a reference electrode, and 0.5 M Na$_2$SO$_4$ aqueous solution as electrolyte. A 300 W Xe lamp with the 420 nm cut-off filter served as a light source. The working electrodes were prepared as followed: 2 mg photocatalyst was ground with 5 mL ethanol and 10 uL 5% Nafion (DuPont) to make a slurry. Afterwards, the slurry was coated onto a 1 cm $×$ 2 cm ITO glass electrode. After air-drying, a homogeneous film could be obtained. The transient photocurrent densities of the as-prepared electrodes were tested at 0.5 V versus saturated calomel electrode under visible light irradiation.

3.5. Catalytic Performances Measurement

3.5.1. TiO$_2$ and TiO$_2$-Pt$^0$

Photocatalytic H$_2$ evolution reaction was carried out under a 300 W Xe lamp (Perfect Light, Microsolar300, $λ > 300$ nm). Typically, 100 mg of sample was added to 100 mL of aqueous solution containing 10 mL triethanolamine as the sacrificial electron donor and kept it stirring vigorously. The hydrogen amount was periodically detected by an online gas chromatograph (GC, 4000) (Aulight, Beijing, China) with a thermal conductivity detector (TCD) (Aulight, Beijing, China) using Ar as a carrier gas. After reaction, the products were collected by centrifugation method and washed with ethyl alcohol for three times. The samples after the reaction were recorded as sample-A.
3.5.2. TiO₂-Pt⁴⁺ and TiO₂-PtCl₆²⁻

A total of 0.1 g TiO₂ photocatalyst was dispersed in 90 mL water, then stirred with 10 mL of triethanolamine adding. Metal Pt was introduced into the system with 1.07 mL (2.5 g/L) positive charged Pt source PtCl₄ or 0.41 mL (10 g/L) negative charged Pt source H₂PtCl₆. The dissolved oxygen in the water was removed by vacuum. A 300 W xenon lamp was used to irradiate samples. After reaction, the products were collected by centrifugation method and washed with ethyl alcohol for 3 times. The samples were noted as TiO₂-Pt⁴⁺ and TiO₂-PtCl₆²⁻, respectively. The samples after the photoreaction were recorded as sample-A.

The recycle experiment was performed as followed: every cycle was carried out for 2.5 h. During the interruption of each cycle, 3 mL triethanolamine was added into the reaction and the system was vacuumed for 30 min.

4. Conclusions

In this study, the charge effects of Pt sources (positive, negative and neutral) on the reaction stability of TiO₂ photocatalytic H₂ evolution were investigated. It was found that Pt could be not only the cocatalyst, but also it acts as an agent which repair defects. In summary, the defects with positive charge are gradually formed on TiO₂ during the photocatalytic H₂ evolution; these defects are centers for recombination of electrons and holes process which leads to lower stability. Due to the charge interaction, Pt sources with negative charge (H₂PtCl₆) could preferentially deposit on the positive defects, repair the recombination centers and, thus, improve the photocatalytic performance.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/10/9/1047/s1, Figure S1: Hydrogen evolution of TiO₂, TiO₂-Pt⁰, TiO₂-PtCl₆²⁻ and TiO₂-Pt⁴⁺, Figure S2: XRD patterns of TiO₂ and TiO₂-A, Figure S3: BJH pore size distribution of catalysts, Figure S4: N₂-sorption isotherm linear plot of the used Pt/TiO₂ samples via three different Pt sources, Figure S5: XRD patterns of the used Pt/TiO₂ samples via three different Pt sources, Figure S6: Recycle experiments on H₂ evolution of ZnO, ZnO-Pt⁰, ZnO-PtCl₆²⁻ and ZnO-Pt⁴⁺, Table S1: Content, surface area, XPS information of samples.

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