

Research Article

Facet-Dependent Activity of Pt Nanoparticles as Cocatalyst on TiO₂ Photocatalyst for Dye-Sensitized Visible-Light Hydrogen Generation

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The photocatalytic activities of polyoriented and preferential Pt(111) nanoparticles supported on TiO₂ (Pt(poly)/TiO₂ and Pt(111)/TiO₂) were investigated by the photocatalytic hydrogen generation from water under visible-light irradiation. The photocatalytic hydrogen production rate of Pt(111)/TiO₂ was 1.6 times higher than that of Pt(poly)/TiO₂. The corresponding apparent activation energy on Pt(111)/TiO₂ was about 2.39 KJ/mol, while on Pt(poly)/TiO₂, it was about 4.83 KJ/mol. The difference in the apparent activation energies was probably due to the diversity in the number of surface atoms at corners and edges between the Pt(poly) and Pt(111) nanoparticles. The photocurrent of Pt(111)/TiO₂ was also bigger than that of Pt(poly)/TiO₂, implying that the surface structure of Pt(111) nanoparticles can improve the transfer efficiency of photo-induced electrons from the conduction band of TiO₂ to Pt nanoparticles. As a result, the surface structure of Pt nanoparticles played an important role in the reactivity and kinetics performance of hydrogen evolution. Therefore, the photocatalytic properties of Pt/TiO₂ strongly depended on the surface structure of Pt nanoparticles.

1. Introduction

TiO₂ is the most widely used photocatalyst. Up to now, the energy conversion efficiency from solar to hydrogen by TiO₂ photocatalytic water splitting is still low, mainly resulting from the following reasons: (1) the quick recombination of photo-generated electron/hole pairs; (2) the fast backward reaction, that is, the recombination reaction of hydrogen and oxygen into water; (3) the wide band-gap only excited by ultraviolet irradiation [1]. In order to resolve the above problems, numerous efforts have been made to promote the photocatalytic activity and enhance the visible-light response, such as addition of electron donors (hole scavengers), addition of carbonate salts, noble metal loading, metal ion doping, anion doping, and dye sensitization.

Loading of noble metal particles on the surface of TiO₂ can inhibit the photo-induced charge recombination [2–19].

It was found that the loading concentration, nanoparticle size, and introduction order of Pt have great influence on the hydrogen production rate [1, 20–23]. However, there were still no reports about the effect of the surface structure of loaded platinum nanoparticles on photocatalytic activity of TiO₂. Solla-Gullón et al. demonstrated that the formic acid electrooxidation activity on preferential Pt(111) electrodes was higher than that on Pt(poly) electrodes, because the Pt(poly) electrode has only a small amount of (111) domains [24]. Marković et al. found that the activity for oxygen reduction in 0.1M HClO₄ decreased in the sequence Pt(110) > Pt(111) > Pt(100). Since O₂ reduction mainly involved a four-electron reduction to water as the main product, the kinetics were found to be first order with respect to O₂ on all three low-index surfaces [25, 26]. Employing the same method, ElKadiri et al. found that O₂ reduction in 1M HClO₄ was essentially insensitive to the Pt surface structure but was

structure-sensitive to anions in solutions. The structure sensitivity arose from structure-sensitive adsorption of anions which impeded the reaction. The activity of the platinum single crystals in solutions containing strongly adsorbing anions increased in the order Pt(111) < Pt(100) < Pt(110) [27]. Marković et al. also found that, in oxygen reduction reaction, the reactivity on Pt(100) was higher than that on Pt(111) owing to the different adsorption rate of sulfates on these facets [25]. Nevertheless, it was desirable to exploit the influence of Pt nanoparticles with different surface structure on photocatalytic activity of TiO₂ so as to improve hydrogen evolution efficiency and significantly reduce consumption of the Pt loaded on TiO₂ while maintaining the high photocatalytic activity.

In the present work, the study of water photolysis for hydrogen production on Pt(111)/TiO₂ and Pt(poly)/TiO₂ has been carried out. Pt/TiO₂ photocatalysts with different surface structure of Pt nanoparticles were prepared by microemulsion and colloidal method. We found that the different surface structure of Pt nanoparticles had significant influence on the photocatalytic activity of TiO₂ in suspension solution. The particle size, shape, and chemical state of Pt nanoparticles as well as their effect on photocatalytic activity for hydrogen evolution from water were studied in detail.

2. Experimental Sections

2.1. Preparation. All the reagents were of analytical grade and were used without further purification.

2.1.1. Pt(poly)/TiO₂ Photocatalyst Preparation. (Poly) Pt/TiO₂ photocatalyst was prepared by the water-in-oil microemulsion method (water/polyethylene glycol dodecyl ether (Brij30)/n-heptane). NaBH₄ was used as reducing agent [28–31]. Subsequently, the Pt nanoparticles solution was loaded on TiO₂. The precipitate was washed several times with acetone and deionized water in order to eliminate surfactant molecules, and then the product was annealed at temperature of 423 K for 2 h in muffle furnace. The resulting sample contained about 0.5% Pt by weight.

2.1.2. Pt(111)/TiO₂ Photocatalyst Preparation. Pt(111)/TiO₂ photocatalyst was prepared by colloidal method. In brief, an aqueous solution (30 mL) of H₂ PtCl₆ (5 mg/mL) containing PVP (polymer/Pt = 1/10, mol/mol) was purged with Ar for 10 min and the Pt ions were reduced by bubbling H₂ for 3 min. In the second approach, a certain amount of TiO₂ was added into Pt sol, keeping stirring for 24 h. The mixture was washed 3 times in deionized water and methanol, respectively, and then the product was annealed at temperature of 423 K for 2 h in muffle furnace. The resulting sample contained about 0.5% Pt by weight.

2.2. Photocatalytic Activity Test. Photocatalytic hydrogen evolution experiments were performed in a 190 mL quartz flask with a flat window, the openings of which were sealed with a silicone rubber septum for sampling at ambient temperature and atmospheric pressure. A 300-W Xenon lamp

equipped with a 420 nm cutoff filter was used as a light source. The reactant mixtures containing 100 mg of powder photocatalyst, 35.7 mg of Eosin Y, and 100 mL of aqueous triethanolamine (TEOA, 15 (v/v) %, pH = 7.00) solution were placed in a quartz reaction flask and dispersed by ultrasonication. The pH values of the reaction solution were adjusted by addition of nitric acid or sodium hydroxide. Before irradiation, the reaction mixture was purged with argon gas for 40 min to remove the dissolved oxygen. During the photocatalytic process, agitation of the solution ensured uniform irradiation of the catalyst suspension and a 0.5 mL gas sample in the top of reactor was collected intermittently through the septum. The amount of hydrogen evolution was measured with gas chromatography (Agilent 6820, TCD, 13x column, Ar carrier).

2.3. Working Electrode Preparation and Photoelectrochemical Measurement. Photocurrent responses of samples were measured using an electrochemical analyzer (CHI660A) in a homemade standard three-compartment cell. Platinum foil was used as counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The working electrodes were prepared by drop-coating a certain volume of sample suspensions onto the conductive surface of pre-cleaned indium tin oxide glass (ITO glass) by microsyringe and dried under an infrared heat lamp. The geometrical surface area of working electrode exposed to the electrolyte was a circular film of 1.6 cm². Aqueous 15 vol% TEOA (pH = 7.00) solution was used as supporting electrolyte. A 300 W Xenon lamp with optical cutoff filter ($\lambda \geq 420$ nm) was used for excitation.

2.4. Characterization. Transmission electron microscopy (TEM) images were taken with a Tecnai-G2-F30 field emission transmission electron microscope operating at accelerating voltage of 300 kV. Photoluminescence spectra were recorded by a FluoroMax-4 spectrofluorometer spectrometer. The fluorescence decay times were measured using the Horiba Jobin Yvon DataStation HUB operating in time-correlated single photon counting (TCSPC) mode with the time resolution of 200 ps. Nano-LED diode emitting pulses at 460 nm with 1 MHz repetition rate and pulse duration of 1.3 ns was used as an excitation source. Light-scattering Ludox solution was used to obtain the instrument response function (prompt). The time ranges are 0.055 ns/channel, in 4096 effective channels. Horiba Jobin Yvon DAS6 fluorescence decay analysis software was used to fit the model functions (one- and two-exponential decays) to the experimental data.

3. Results and Discussion

3.1. Characterization. Figure 1 shows representative TEM images and size distribution of Pt(poly)/TiO₂ and Pt(111)/TiO₂ samples. Images of (a-1)–(a-4) and (b-1)–(b-4) correspond to Pt(poly)/TiO₂ and Pt(111)/TiO₂, respectively. The Pt nanoparticles prepared in microemulsion showed a quasispherical shape (Figure 1(a-1)) with particle size of 3.0 ± 1 nm and the size distribution was relatively uniform.

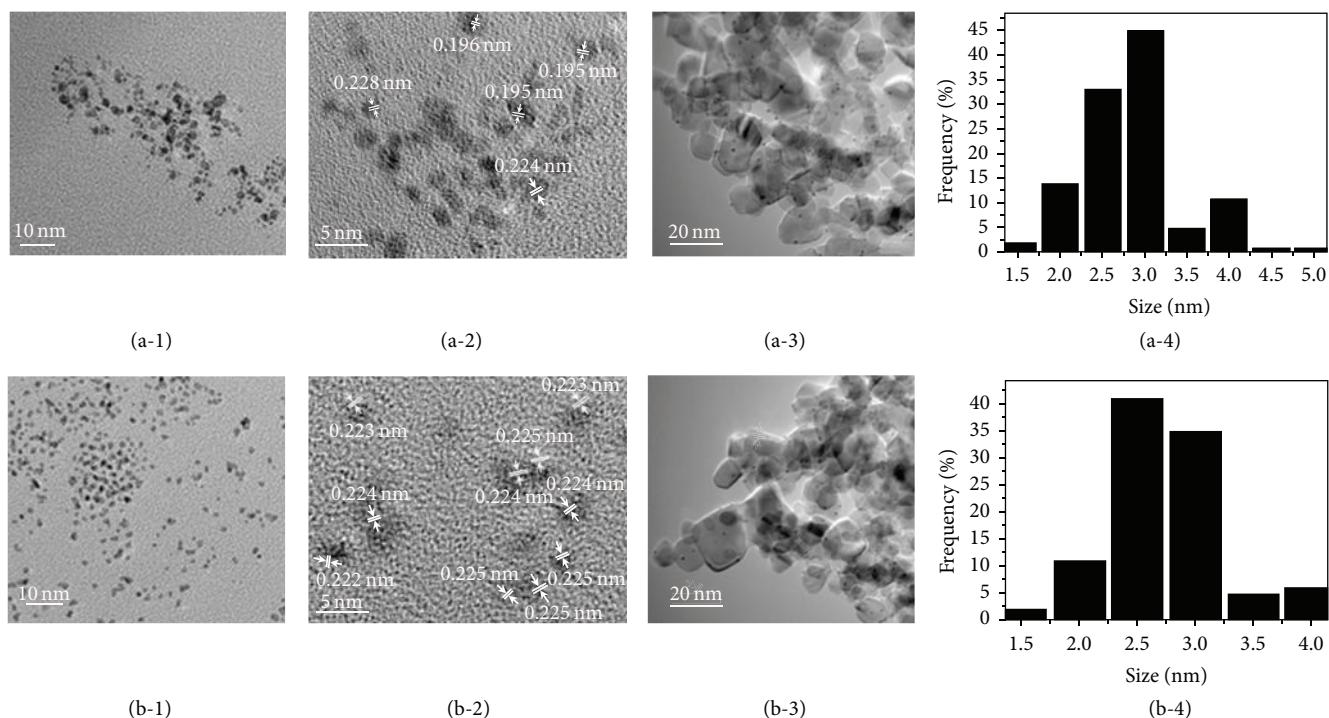


FIGURE 1: TEM images ((a-1)–(a-3) and (b-1)–(b-3)) and Pt nanoparticles' size distribution ((a-4) and (b-4)) of Pt(poly)/TiO₂ and Pt(111)/TiO₂ samples, respectively.

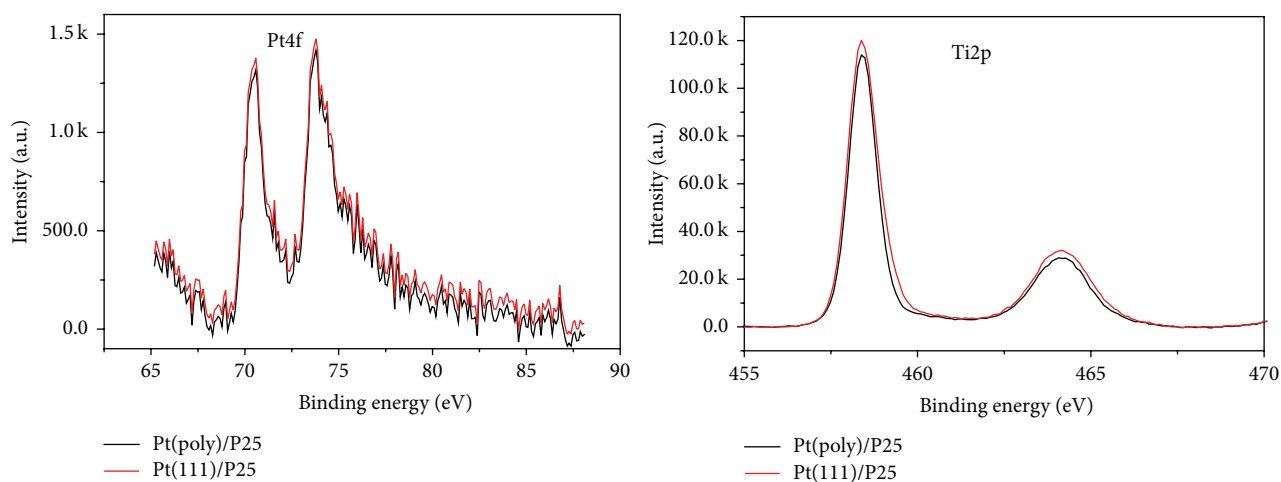


FIGURE 2: Pt4f spectrum and Ti2p spectrum from Pt(poly)/TiO₂ and Pt(111)/TiO₂.

As shown in Figure 1(a-2), there were two lattice spacings of 0.228 nm and 0.1955 nm, which were assigned to Pt(111) and Pt(100) facets, respectively. It indicated that the Pt nanoparticles were non-specifically structured. On the other hand, the TEM and HRTEM images of Pt(111) nanoparticles are shown in Figure 1(b). According to the HRTEM analysis (Figure 1(b-2)), the lattice spacing between 0.222 nm and 0.225 nm all corresponds to (111) facets of Pt. Since the most of Pt nanoparticles (Figure 1(b-2)) were observed with (111) facets, they formed a preferential (111) surface structure. In this sample, the size of Pt particles varied in the range of

2.5 ± 0.5 nm. Therefore, the particle size distribution in this case was also near-uniform. In both samples (Figures 1(a-3) and 1(b-3)), the sizes of Pt(111) and Pt(poly) nanoparticles were comparable and these nanoparticles were evenly dispersed over TiO₂ surface. The two kinds of platinum particles on TiO₂ retained their initial structures after calcination at 423 K [32].

The XPS results of Pt and Ti elements are shown in Figure 2. There was obviously no shift between the centers of Pt peaks of two samples, and the Ti XPS peaks for both samples were also identical, indicating that, for both samples,

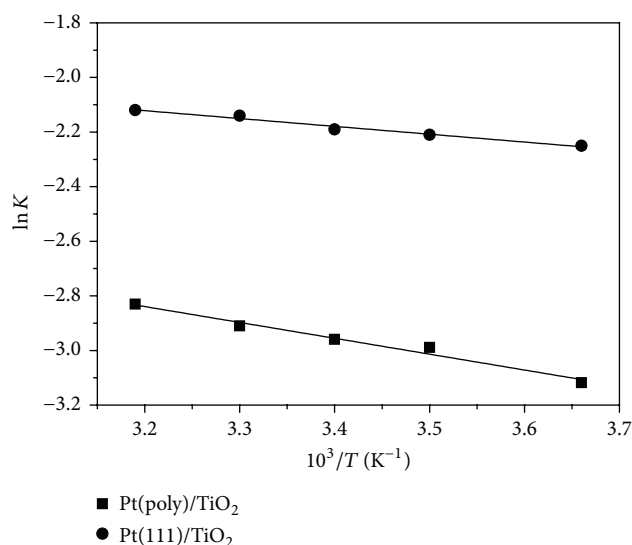


FIGURE 3: Arrhenius plots of the natural logarithm of rate constant versus $1/T$ for Pt(poly)/TiO₂ and Pt(111)/TiO₂.

the chemical state of Pt and Ti species on TiO₂ surface and the interaction between Pt and TiO₂ were the same. Therefore, for both samples, the effect of TiO₂ was the same.

3.2. Comparison of Photocatalytic Activities of Pt/TiO₂ Photocatalysts. The photocatalytic activities of Pt/TiO₂ photocatalysts were evaluated under visible-light irradiation ($\lambda \geq 420$ nm) using TEOA and EY as sacrificial donor and photosensitizer, respectively. Control experiments indicated that no appreciable hydrogen evolution was detected in the absence of either irradiation or EY. The hydrogen evolution rate of Pt(111)/TiO₂ and Pt(poly)/TiO₂ was 171.4 and 107.1 mL/g·h, respectively; that is, the photocatalytic hydrogen production rate of Pt(111)/TiO₂ was 1.6 times higher than that of Pt(poly)/TiO₂. It indicated that compared with Pt(poly) nanoparticles, Pt(111) nanoparticles have a more positive effect on photocatalytic activity enhancement.

The photocatalytic water splitting reaction by semiconductor was a first-order reaction [33]. However, in our reaction system, the concentration of reactants did not change, so we considered it as a quasi-zero-order reaction. The specific rate constant k at different temperatures was calculated from the average reaction rates. Figure 3 presents the Arrhenius plots of photocatalytic water splitting reaction on Pt(poly)/TiO₂ and Pt(111)/TiO₂. The apparent activation energies on Pt(poly)/TiO₂ and Pt(111)/TiO₂ were 4.83 and 2.39 KJ/mol, respectively, which were basically consistent with the previous reports [34–40]. The reactions were repeated twice, and the reproducibility was satisfactory. The lower apparent activation energies obtained on Pt(111)/TiO₂ may be attributed to the bigger number of atoms at corner and edge sites [41–44]. With analogous average size distributions, the number of atoms at corners and edges of Pt(111) nanoparticles was about 9 times larger than that of Pt(poly) nanoparticles [24, 44, 45]. On the other hand, the apparent activation energy was often associated

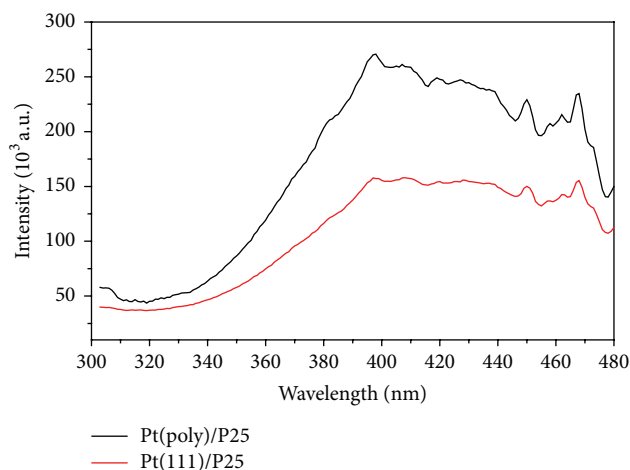


FIGURE 4: Photoluminescence spectra of Pt(poly)/TiO₂ and Pt(111)/TiO₂.

with the adsorption-desorption properties [46], the diffusion behavior of reactants and products [47], or the solid-state properties of photocatalysts [48–50]. Hisatomi et al. believed that the mobility of photo-excited carriers was one of the influence factors on the apparent activation energy of water splitting reaction [51]. To some extent, the lower apparent activation energy corresponded to the faster transferring rate and the smaller recombination efficiency of photo-excited carriers. The hydrogen evolution reaction ($H^+ + e^- \rightarrow H, 2H \rightarrow H_2$) took place on Pt nanoparticles surface, and thus the physical and chemical properties of Pt nanoparticles surface were the main influential factors on hydrogen evolution reaction. The results of HRTEM and XPS analysis showed that, for Pt(poly)/TiO₂ and Pt(111)/TiO₂, the size, morphology, and chemical state of Pt nanoparticles were all similar. So it was reasonable to conclude that the different apparent activation energies originated from the different surface structure between Pt(poly) and Pt(111) nanoparticles.

To determine the electron-hole recombination characteristics on the above photocatalysts, photoluminescence (PL) studies were undertaken. PL emission is a useful technique to determine the trapping and migration efficiency of charge carriers, which was used to study the behavior of the electron-hole pairs [52, 53]. It is well known that PL emission results from the recombination of excited electrons and holes. The lower the PL intensity, the smaller the recombination rate [54]. Figure 4 presents the PL spectra of Pt(poly)/TiO₂ and Pt(111)/TiO₂. The figure showed that the PL intensity of Pt(111)/TiO₂ sample was smaller than that of Pt(poly)/TiO₂, which was in accord with the change trend of hydrogen production rate and PL decay curves (Figure 5). The PL signal reflected the transition of electrons from the excited state to the ground state. Generally, when semiconductor materials receive energy from the outside generating photo-excited electron-hole pairs, the electrons will transfer from the ground state to the excited state, but the electrons are unstable due to the high energy state and they return to

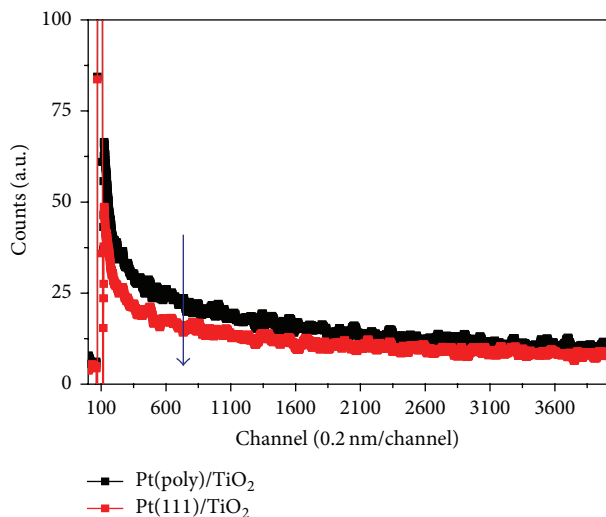


FIGURE 5: The PL decay curves of Pt(poly)/TiO₂ and Pt(111)/TiO₂.

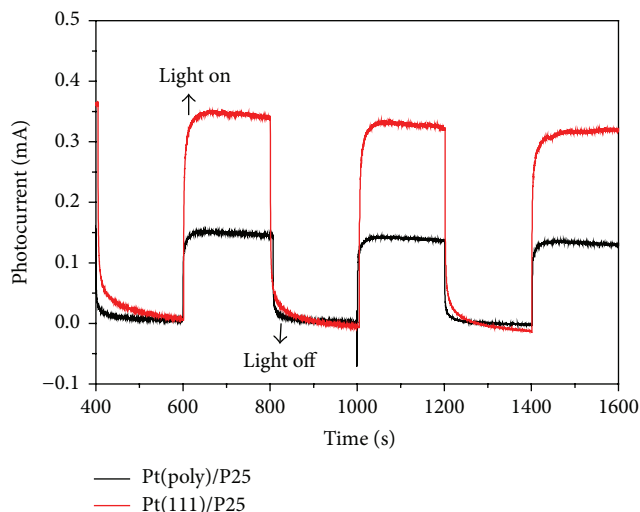


FIGURE 6: Transient photocurrent-time profiles of Pt(poly)/TiO₂ and Pt(111)/TiO₂.

the ground state, so fluorescent light is emitted. A higher PL intensity represents a bigger recombination rate between photo-generated electrons and holes. Pt(111)/TiO₂ sample exhibited a weaker PL intensity indicating that the radiative charge recombination on it was suppressed relatively stronger. To give further evidence on the above statements, the transient photocurrent responses of Pt(poly)/TiO₂ and Pt(111)/TiO₂ samples were investigated for several on-off cycles of intermittent irradiation (200 s). Figure 6 shows *i-t* curves for the aforementioned two samples. The photocurrent on Pt(111)/TiO₂ sample was larger than that on Pt(poly)/TiO₂, indicating that under the same conditions the photo-excited electron transfer was more efficient on the former. It was reasonable to conclude that the Pt(111) facet significantly retarded the electrons recombination with holes, resulting in an enhanced photocatalytic hydrogen evolution activity. Therefore, the surface structure of Pt nanoparticles

had a strong influence on the electron transfer from the conduction band of TiO₂ to Pt particles surface.

4. Conclusions

Pt(poly)/TiO₂ and Pt(111)/TiO₂ photocatalysts were prepared by water-in-oil microemulsion and colloidal methods, respectively. The particle sizes of Pt nanoparticles were similar for Pt(poly)/TiO₂ and Pt(111)/TiO₂. The photocatalytic activity for hydrogen generation of Pt(111)/TiO₂ was about 1.6 times higher than that of Pt(poly)/TiO₂. For Pt(111)/TiO₂, the apparent activation energy was 2.86 KJ/mol while for Pt(poly)/TiO₂, it was 4.83 KJ/mol. Therefore, under the same conditions, the water photocatalysis reaction on Pt(111)/TiO₂ was more effective. The results of PL spectra and PL decay implied that the rate of photo-generated electrons transfer on Pt(111)/TiO₂ was bigger than that on Pt(poly)/TiO₂, which was in favor of impeding the recombination of electrons and holes. The significant lower apparent activation energy and bigger photo-induced electron transfer rate of Pt(111)/TiO₂ may be attributed to the bigger number of corner and edge sites on Pt(111) nanoparticles compared with that on Pt(poly) nanoparticles.

Competing Interests

The authors declare that they have no competing interests.

Acknowledgments

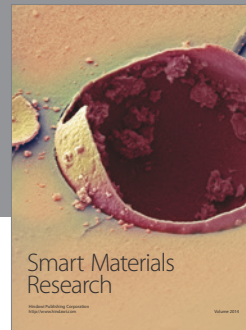
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