Enhancing the Photocatalytic Activity of Anatase TiO2 by Improving the Specific Facet-Induced Spontaneous Separation of Photogenerated Electrons and Holes

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Abstract: Recently, it has been proven that directional flow of photogenerated charge carriers occurs on specific facets of TiO2 nanocrystals. Herein, we demonstrate that the photocatalytic activity of anatase TiO2 nanocrystals in both photoreduction and photooxidation processes can be enhanced by selectively depositing Pt nanoparticles on the [101] facets, which strengthens spontaneously surface-induced separation between photogenerated electrons and holes in the photocatalysis process. An optimal ratio of the oxidative [001] facets to the reductive [101] facets exists with regard to the photocatalysis of the faceted TiO2 nanocrystals, and this is crucial for balancing the recombination and redox reaction rates of photogenerated electrons and holes. The present work might help us gain deeper insight into the relation between the specific surface of semiconductor photocatalysts and their photocatalytic activities and provides us with a new route to design photocatalysts with high photocatalytic activity.

Keywords: hydrogen evolution · nanostructures · photocatalysis · surface chemistry · titanium

Introduction

Photogenerated electrons and holes are the most essential driving force in photochemical reactions. However, the photocatalytic activity of semiconductor photocatalysts is generally restrained owing to the easy electron–hole recombination. It has been found that anisotropic-shaped semiconductor particles would display a lower charge recombination rate than spherical particles. This phenomenon can be explained by the fact that photogenerated electrons and holes might spontaneously separate towards different crystal faces in the photochemical processes. Anatase TiO2, which is recognized as one of the most important semiconductors on account of its wide applications in photovoltaics and photocatalysis, is also governed by this rule. By means of photochemical deposition or a single-molecule fluorescence probe, it has been demonstrated that the [001] facets of anatase TiO2 are the oxidative sites, whereas the [101] facets are the reductive sites in the photoreaction on account of different preferential transport directions of photogenerated carriers. These results suggest that strengthening such specific facet-induced spontaneous separation efficiency between photogenerated carriers by means of rational design on those faceted TiO2 particles is potentially an effective method to enhance the photocatalytic activities of TiO2 photocatalysts.

In addition, with regard to the surface-dependent photocatalytic activity of photocatalysts, the difference between surface energies of different facets is believed to be another factor. A theoretical calculation has demonstrated that the [001] surface of anatase TiO2 has higher surface energy (0.90 J m⁻²) than the [101] surface (0.44 J m⁻²). A large number of studies have also demonstrated that such highly exposed [001] facets are indeed favorable for enhancing the photocatalytic performance of anatase TiO2 both in the photodegradation of organic pollutants, and H₂ (or O₂) evolution from water splitting. Therefore various synthetic routes have been successively developed to fabricate anatase TiO2 crystallites with high percentages of exposed [001] facets. However, it might not be absolutely true that high-energy surfaces should possess higher photocatalytic activities. Recent studies have found that some low-energy surfaces (e.g., [100] and [101] facets) possess even higher photocatalytic activities than those of high-energy [001] facets. These contradictory results indicate that for semiconductor photocatalysts a deeper understanding of the photochemical behavior and a more valid design are urgently needed.

Herein, we demonstrate that the photocatalytic activity of anatase TiO2 nanocrystals (NCS) in both photoreduction and photooxidation processes can be enhanced by selectively depositing Pt nanoparticles onto the [101] facets. Compared to nonselective deposition (i.e., Pt was deposited on both the [101] and [001] facets), the selective deposition of...
Pt nanoparticles on the [101] facets result in higher separation efficiencies between photogenerated electrons and holes, and thus higher photocatalytic activities. In addition, we found that an optimal ratio of the oxidative [001] facets to the reductive [101] facets was crucial for balancing the recombination and redox reaction rates of photogenerated electrons and holes during the photocatalysis process.

Results and Discussion

Selective Deposition of Pt Nanoparticles on [101] Facets of Anatase TiO2 NCs

Separation efficiency between photogenerated electrons and holes is one of the most important factors for the activity of photocatalysts, including TiO2. This efficiency can be enhanced by depositing noble metals onto TiO2 NCs, as the Schottky barrier between the metals and TiO2 can facilitate separation of photogenerated electrons and holes.[27,28] For the TiO2 NCs enclosed with [101] and [001] facets, photogenerated electrons are concentrated on [101] facets, whereas photogenerated holes are concentrated on [001] facets.[11,12] Accordingly, it is reasonable to believe that the selective deposition of metals on [101] facets should enhance such a facet-induced spontaneous separation of photogenerated electrons and holes, and thus enhance the catalytic activity of TiO2 NCs. Here, in our experiment, we chose platinum (Pt) as the deposited metal, as Pt is one of the best metals to facilitate charge capture.[29–31]

Figures 1 and 2 show the TEM images and size distribution of anatase TiO2 NCs with nonselective Pt deposition by chemical reduction and selective Pt deposition by photochemical reduction, respectively. The as-prepared products are denoted as TiO2-Pt(NS-X)% and TiO2-Pt(S-X)% (NS: nonselective deposition, S: selective deposition, X: the mass ratio of Pt element to TiO2 in raw solution).

Figure 1. a) SEM image of as-prepared TiO2 NCs with the assistance of HMTA (0.70 g, 5 mmol). b) TEM image of an individual TiO2 NC viewed along the [001] direction; the inset is the corresponding SAED pattern.

Figure 2. TEM images and size distribution of anatase TiO2 NCs a) with nonselective Pt deposition by chemical reduction and b) with selective Pt deposition by photochemical reduction. The top right insets are high-magnification TEM images and the bottom right insets are corresponding models. The particle-size analysis of 200 Pt nanoparticles is selected from both samples.
that there is no clear difference in the adsorption abilities with the Pt precursor on the [101] and [001] facets of TiO$_2$ NCs. In contrast, in the photochemical-reduction process, Pt nanoparticles are only deposited on the [101] facets rather than the [001] facets (Figure 2c). The above results indicate that, when induced by specific facets, photogenerated carriers spontaneously have different preferential migration pathways, with electrons toward [101] facets and holes toward [001] facets.$^{[11,12]}$ Consequently, the [101] facets provide reduction sites in the photocatalytic reaction process, thereby resulting in the selective reduction of Pt on the [101] facets. Note that the size of Pt nanoparticles deposited by photochemical reduction is mainly in the range of (1.7 ± 0.5) nm, which is a little larger than that deposited by chemical reduction, (1.5 ± 0.5) nm (Figure 2b, d).

**Enhanced Photocatalytic Activities of TiO$_2$ NCs with Pt Selectively Deposited**

Practically, rational utilization of such specific facet-induced spontaneous separation between photogenerated electrons and holes is very important for improving the photocatalytic activity of anatase TiO$_2$ NCs. Owing to the lower Fermi energy, deposition of Pt onto the surface of TiO$_2$ NCs facilitates the transfer of electrons from TiO$_2$ to noble metals and reduces recombination between photogenerated electrons and holes during the transport process from the bulk to surface.$^{[10]}$ Relative to different preferential transport directions of photogenerated carriers, the selective deposition of Pt onto TiO$_2$ [101] facets might further enhance spontaneous separation between photogenerated electrons and holes, thereby greatly improving the photocatalytic activities of TiO$_2$ NCs. To confirm this idea, herein we investigated in detail the influence of Pt deposition on the photooxidation and photoreduction activities of different exposed facets. The naked TiO$_2$ particles (naked TiO$_2$), nonselectively Pt-deposited TiO$_2$ particles (TiO$_2$-Pt(NS)-0.5%), and selectively Pt-deposited TiO$_2$ particles (TiO$_2$-Pt(S)-0.5%) were measured in the study.

We first investigated the photooxidation activities of the three samples by monitoring the formation of active hydroxyl radicals (‘OH) that originate from the capture of the photogenerated holes by the surface-bound OH.$^{[26]}$ Terephthalic acid (TA) was used as a fluorescence probe, which can produce 2-hydroxyterephthalic acid (TAOH) with a fluorescence peak at 426 nm by reacting with ‘OH in basic solution.$^{[16e,22]}$ Among the three samples, TiO$_2$ NCs with selective Pt deposition on the [101] facets (i.e., the TiO$_2$-Pt(S)-0.5% sample) shows the best photooxidation activity, whereas TiO$_2$ NCs with nonselective Pt deposition (i.e., the TiO$_2$-Pt(S)-0.5% sample) show even lower activity than the naked TiO$_2$ NCs (Figure 3a).

The ‘OH radicals are one of the most important oxidative species in the photocatalysis process. They are responsible for the oxidation decomposition of organic pollutants. In our study, the photocatalytic degradation of methylene orange (MO) as a model pollutant was carried out (Figure 3b). It is seen that the photocatalytic degradation activity of three samples follows the sequence of TiO$_2$-Pt(S)-0.5% > naked TiO$_2$ > TiO$_2$-Pt(NS)-0.5%, which is consistent with the results in the detection of active ‘OH radicals. Noticeably, the curves of ln[C/C$_0$] versus time present a good linear relationship (Figure 3b, inset). This indicates that the photocatalytic degradation of MO follows pseudo-first-order kinetics ln[C/C$_0$] = –kt,$^{[23]}$ in which $C$/$C_0$ is the normalized MO concentration, $t$ is the reaction time, and $k$ is the pseudo-first-order rate constant. The apparent rate constant of MO photodegradation for the TiO$_2$-Pt(S)-0.5% sample with Pt selectively deposited is calculated to be 0.212 min$^{-1}$, almost three times that (0.075 min$^{-1}$) of the naked TiO$_2$, and four times that (0.045 min$^{-1}$) of the sample TiO$_2$-Pt(NS)-0.5% without selective Pt deposition. On the basis of the above results, it can be concluded that the selective Pt deposition on the [101] facets can indeed enhance the photocatalytic activities of anatase TiO$_2$ in the photooxidation process; on the contrary, nonselective deposition of Pt reduces the photooxidation activities. In fact, the photoreduction activity of anatase TiO$_2$ would be likely enhanced on account of more effective separation of electrons and holes by the same method. In this study, the photocatalytic H$_2$ production experiments were further carried out to evaluate the photoreduction activity of TiO$_2$ NCs. As we know, both photooxidation and photoreduction simultaneously occur in the reaction system; therefore we used an excess amount of methanol as a sacrificial agent for photogenerated holes in our experiments and focused on in-
vestigating the photoreduction activities of anatase TiO$_2$ through detecting the amount of H$_2$ production. Generally, the naked TiO$_2$ particles without loading Pt have poor photocatalytic ability. In the early research, Pt nanoparticles deposited onto the TiO$_2$ surface have been demonstrated to play an important role in the producing H$_2$ system. They trap the excited electrons and become the catalytic centers for hydrogen photoproduction: 

\[ \text{e}^-_{\text{tr}} + \text{Pt} + \text{H}^+ \rightarrow \text{H}^- + \frac{1}{2} \text{H}_2. \] 

Figure 4 shows the H$_2$ production in the presence of three samples under UV irradiation for 6 h. As expected, the amount of hydrogen production from the TiO$_2$-Pt(S)-0.5% sample with Pt selectively deposited on the [101] facets is 30 times higher than that of the naked TiO$_2$, and 5 times that of the sample TiO$_2$-Pt(NS)-0.5% with nonselective Pt loading.

In particular, it should be pointed out that the deposition amount of Pt nanoparticles is very important for the photocatalytic activities in hydrogen evolution. At a lower concentration, Pt nanoparticles act as centers for capturing electrons, which might decrease the recombination of photogenerated electrons and holes. Nevertheless, the excessive Pt loading might hinder the incident light from irradiating TiO$_2$, thereby resulting in an incomplete excitation of photocatalysts; on the other hand, too many loaded Pt nanoparticles might serve as recombination centers for holes and electrons, which would lead to a decrease in photocatalytic activities.\[35\]

To make clear whether or not the differences in photocatalytic activities between TiO$_2$-Pt(NS) and TiO$_2$-Pt(S)-0.5% originate from the effect of Pt deposition amounts, we systematically compared hydrogen production activities of TiO$_2$ NCs with different Pt deposition amounts from 0.25 to 1.5% (Figure 5a). It can be clearly seen that the TiO$_2$ NCs exhibit an optimum amount for Pt deposition, regardless of the deposition routes. For the samples prepared by means of the photochemical-reduction route, the photocatalytic activity reaches its highest point at 0.5% of the Pt amount and then gradually decreases as the Pt amount increases. For the samples prepared by means of the chemical-reduction route, however, the photocatalytic activity increases as the Pt amount increases within the range from 0.25 to 1.0%. Note that on the whole the photocatalytic activities of TiO$_2$-Pt NCs prepared by photochemical reduction are much higher than those prepared by chemical reduction. It should be stated that the amount of Pt herein refers to the mass ratio of elemental Pt to TiO$_2$ in a raw solution. The effective Pt deposition amounts were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES). As shown in Figure 5b, the effective deposition amounts of Pt on TiO$_2$ NCs are lower than the mass ratio of elemental Pt to TiO$_2$ in raw solution for all the samples prepared by both chemical reduction and photochemical reduction. By contrast, the effective deposition amounts of Pt on TiO$_2$ NCs prepared by chemical reduction are a little higher than those prepared by photochemical reduction. Typically, for the TiO$_2$-Pt(NS)-0.5% and TiO$_2$-Pt(S)-0.5% samples, the effective Pt deposition amounts on TiO$_2$ NCs are 0.29 and 0.33%, respectively.

Figure 4. Hydrogen production of naked TiO$_2$ NCs, TiO$_2$ NCs with selective deposition of Pt on [101] facets (TiO$_2$-Pt(S)-0.5%), and TiO$_2$ NCs with nonselective deposition of Pt (TiO$_2$-Pt(NS)-0.5%), respectively.

Figure 5. a) Hydrogen production amounts and b) effective Pt deposition amounts of Pt deposited TiO$_2$ NCs by means of photochemical-reduction (■) and chemical-reduction routes (▲). SEM images of TiO$_2$ NCs with different Pt-loading amounts prepared by c) chemical reduction and d) photochemical reduction, respectively.
To probe the essential reason for the influence of different Pt depositions, the real deposition status of Pt nanoparticles on TiO₂ NCs was further surveyed by TEM. For the samples prepared by means of chemical reduction, Pt nanoparticles were randomly deposited on all exposed facets, with the deposition density gradually increasing over the whole range from 0.25 to 1.5%, as shown in Figure 5c. For the samples prepared by means of photoreduction, Pt nanoparticles were selectively deposited on the {101} facets at high loading amounts (i.e., 0.25 and 0.5%), whereas a small number of Pt nanoparticles appear on the {001} facets at high loading amounts (i.e., 1 and 1.5%). Along with the changes of those TiO₂ NCs in photocatalytic activities, the above TEM observations demonstrate convincingly that the enhancement in photocatalytic activity of the sample TiO₂-Pt(S)-0.5% originates from the selective deposition of Pt on the {101} facets.

From the above results, it can be seen that the deposition status of Pt has a great influence on both the photooxidation and photoreduction activities of TiO₂ NCs. This phenomenon can be easily explained by selective Pt deposition-enhanced spontaneous separation between photogenerated electrons and holes. It is well known that Pt nanoparticles can provide a space for electronic enrichment, and thus the deposition of Pt makes the photogenerated electrons migrate towards them. As TiO₂ {101} facets are essentially the preferential migration direction, the flow of electrons to {101} facets can be reinforced by the selective Pt deposition on {101}, and accordingly more holes can be photogenerated on {001} facets. Consequently, both the photooxidation activities of {001} facets and the photoreduction activities of {101} facets for the selective Pt-deposited TiO₂ NCs are greatly enhanced. On the contrary, the TiO₂ {001} facets possess sites of hole enrichment, and thus the Pt nanoparticles deposited on the {001} facets might become the centers of hole–electron recombination. Accordingly, the photocatalytic activity of TiO₂ NCs is reduced.

**Influence of the Ratio of Exposed {001} to {101} Facets on Photocatalytic Activities of TiO₂ NCs**

As we have demonstrated, different crystal facets of anatase TiO₂ NCs play different roles in the photochemical reaction. The {101} facets of anatase particles provide the effective reduction sites and the {001} facets work as the oxidation sites in the photocatalytic process. It seems that increasing the percentage of the oxidative {001} facets improves the photocatalytic activities of TiO₂ NCs in the photooxidation process (e.g., photodegradation of organic pollutants), and increasing the percentage of the reductive {101} facets benefits the photocatalytic activities of TiO₂ NCs in the photoreduction process (e.g., H₂ production by water splitting). However, the photocatalytic activity of a semiconductor also depends on the electron–hole recombination rate. We have demonstrated that photogenerated holes prefer to move towards {001} facets of TiO₂ NCs, whereas {101} facets are likely to trap electrons. To avoid recombination of photogenerated electrons and holes, there should be an optimum pathway length of photogenerated carriers in TiO₂ NCs, and therefore an optimum ratio of the areas of adjacent {001} and {101} facets for the effective separation of photogenerated charges might exist.

To optimize the synergetic effect of adjacent crystal facets on the separation of photogenerated charges, tetragonal bipyramidal TiO₂ NCs enclosed by eight {101} facets and truncated tetragonal bipyramidal TiO₂ NCs enclosed by {101} and {001} facets were prepared at different concentrations of hexamethylenetetramine (HMTA), and are shown in Figure 6a–e. In the absence of HMTA, the product (TiO₂ NCs-1) was composed of tetragonal bipyramids without being truncated; two tips in the longitudinal direction were very sharp (Figure 6a). Viewed from the [010] direction, it can be seen that the angle of the two adjacent sides surface is about 44 or 136°, which is consistent with that of an ideal model fully enclosed by eight {101} facets. This indicates that these tetragonal bipyramidal TiO₂ NCs are enclosed by {101} facets, the crystal planes with the lowest surface energy. In the presence of HMTA, two tips of these tetragonal bipyramids are truncated, thereby resulting in the appearance of high-energy {001} facets (Figure 6b–e). Notably, the truncated degree of TiO₂ NCs clearly increases along the edge.
with the HMTA concentration. The average lengths of the maximum (A) and minimum (B) sides of the square [001] faces in every particle were acquired by measuring more than 100 TiO2 NCs by means of SEM observation, and the length ratio (B:A) was used to indicate the percentage of different facets (see Table 1). As shown in Figure 6f, the

Table 1. Synthetic conditions of as-prepared TiO2 NCs with different percentages of [001] facets.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>KTNWs [g]</th>
<th>HMTA [mmol]</th>
<th>Water [mL]</th>
<th>B:A [%]</th>
<th>Percentage of [001] facets</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO2</td>
<td>0.010</td>
<td>0</td>
<td>6.0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>NCs-1</td>
<td>0.010</td>
<td>0.1</td>
<td>6.0</td>
<td>0.40</td>
<td>7.1</td>
</tr>
<tr>
<td>NCs-2</td>
<td>0.010</td>
<td>1.0</td>
<td>6.0</td>
<td>0.55</td>
<td>14.9</td>
</tr>
<tr>
<td>NCs-3</td>
<td>0.010</td>
<td>5.0</td>
<td>6.0</td>
<td>0.70</td>
<td>27.9</td>
</tr>
<tr>
<td>NCs-4</td>
<td>0.010</td>
<td>17.0</td>
<td>6.0</td>
<td>0.85</td>
<td>51.2</td>
</tr>
<tr>
<td>NCs-5</td>
<td>0.010</td>
<td>60.0</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

[a] A and B correspond to the maximum and minimum side of the square [001] faces, respectively.

length ratios B:A for the as-prepared samples (TiO2 NCs-2, 3, 4, and 5) are 0.40, 0.55, 0.70, and 0.85, which correspond to 7.1, 14.9, 27.9, and 51.2% [001] facets exposed on the surface of TiO2 NCs, respectively.

Figure 7 shows the hydrogen production activities of five kinds of anatase TiO2 exposed with different percentages of [001] facets. It should be noted that we do not deposit Pt onto the surfaces of TiO2 NCs to avoid any nonuniform deposition of Pt and other unexpected effects. From the experimental results, it can be found that an optimal ratio of the oxidative [001] facets to the reductive [101] facets exists for the photocatalytic H2 production. The truncated tetragonal bipyramidal TiO2 NCs with 14.9% [001] facets showed the highest photocatalytic activity for H2 production, whereas the octahedral TiO2 NCs fully enclosed by [101] facets possess very low photocatalytic activity for H2 production.

Generally, the photocatalytic activity of a semiconductor mainly depends upon two factors, including 1) the energy-band structure, and 2) the electron–hole recombination rate. In this study, tetragonal bipyramidal anatase TiO2 NCs with different percentages of exposed [001] and [101] facets have been obtained with the assistance of HMTA. Selectively depositing Pt nanoparticles onto the [101] facets is an effective method to improve photocatalytic activity of anatase TiO2 NCs in both photoreduction and photooxidation processes. The spontaneous separation could be reinforced by selective deposition of Pt nanoparticles on the reductive [101] facets, and consequently, the photocatalytic activities of TiO2 NCs could be greatly enhanced. Furthermore, an optimal ratio of the oxidative [001] facets to the reductive [101] facets is crucial for balancing the recombination and redox reaction rates of photogenerated electrons and holes. It should be noted that the photocatalytic activity of TiO2 NCs relates to many factors, including the size, phase, crystallinity, surface area, defects in the bulk or the surface, orientation of the exposed surface, and so on. Optimal conditions should be sought by taking these considerations into account and can vary from case to case. The results presented in this work might help us to gain a deeper insight into the relation between the specific surface of semiconductor photocatalysts and their photocatalytic activities. In addition, it provides us with a new route for designing photocatalysts with high photocatalytic activity.

Conclusion

In this study, the dependence of photocatalytic efficiency of TiO2 NCs on the ratio of exposed percentages of [001] to [101] should be mainly attributed to the latter factor. For example, in the TiO2 NCs-1 sample, the tetragonal bipyramidal TiO2 NCs fully enclosed by [101] facets, only exhibits very slight photocatalytic activity for H2 production, although it provides the maximum reductive sites, as shown in Figure 7. In this extreme case, the absence of [001] facets might compel photogenerated holes to transport towards [101] facets, too, which markedly increases the recombination probability between electrons and holes. As a result, the photocatalytic activity of TiO2 NCs-1 becomes the lowest one. For other samples that consist of both [101] and [001] facets, the photogenerated electrons and holes in the bulk migrate to different surfaces, respectively. From the bulk to the surface, an optimal transport distance for electrons and holes reasonably exists to avoid the recombination during their transportation to their preferred surfaces, and therefore the optimal ratio of [101] to [001] facets indeed exists.

Experimental Section

Material

Potassium hydroxide (KOH, 99%), hexamethylenetetramine (HMTA, 99%), sodium borohydride (NaBH4, 99%), methanol (CH3OH, 99.5%), potassium hydroxide (KOH, 90%), methylene orange (MO, analytical reagent) were purchased from Sinopharm Chemical Reagent Co., Ltd. Hexachloroplatinate hexahydrate (H2PtCl6·6H2O, 99.95%) and terephthalic acid (TA, 98%) were pur-
Chased from Alfa Aesar. Degussa P25 was purchased from Shanghai Haisty Co. All reagents were used as received without further purification.

Syntheses of Tetragonal Bipyramidal Anatase TiO$_2$ NCs with Exposed {101} and {001} Facets

First, potassium titanate nanowires (KTNWs) were prepared at 200 °C over 24 h under hydrothermal conditions with Degussa P25 and a high-concentration KOH solution according to the literature method.\(^{101}\) Then anatase TiO$_2$ NCs with different percentages of exposed {001} facets and {101} facets were prepared by means of a facial hydrothermal route and by using KTNWs as a precursor and HMTA as a shape regulator. In a typical experiment, KTNWs (0.01 g) and HMTA (0.70 g, 5 mmol) were dispersed in distilled water (6 mL) under intense ultrasonic treatment. The resulting solution was then transferred into a 25 mL Teflon-lined stainless-steel autoclave and was kept at 200 °C for 12 h. After the reaction reached completion, the white precipitate in the autoclave was collected by centrifugation, washed with distilled water and ethanol 3 times, and finally dried in an oven. The percentage of exposed {001} facets of anatase TiO$_2$ nanocrystals were tuned by adjusting the concentration of HMTA added (see Table 1 for the detailed experimental conditions).

Deposition of Pt Nanoparticles on the Surface of Tetragonal Bipyramidal Anatase TiO$_2$ NCs

Pt nanoparticles were deposited on the as-prepared TiO$_2$ NCs by means of photoreduction and chemical reduction, and the as-prepared products are denoted as TiO$_2$-Pt(NX)-X% and TiO$_2$-Pt(S)-X% (X is the mass ratio of Pt element to TiO$_2$ in raw solution), respectively; for example: 0.5% Pt loading on TiO$_2$ NCs. In the photochemical-reduction process, TiO$_2$ NCs (50 mg) were dispersed in deionized water (100 mL), and then an H$_2$PtCl$_6$ aqueous solution (1.282 mL, 1 mm) was impregnated into the above solution. The resulting suspension was stirred magnetically and irradiated under a 300 W Xe lamp for 1 h at room temperature. The final product was collected by high-speed centrifugation, and washed with water and ethanol three times. In the chemical-reduction process, a NaBH$_4$ solution (0.1 mL, 0.1 M) was impregnated into the aforementioned suspension of TiO$_2$ and H$_2$PtCl$_6$ under magnetic stirring and kept in an ice–water bath for 2 h. Finally, the product was collected and treated in the same way.

Composition and Structure Characterization of Samples

The morphology of products was observed by SEM (Hitachi S4800) and TEM (JEM-2100) with an acceleration voltage of 200 kV. All TEM samples were prepared by depositing a drop of diluted suspensions in ethanol on a carbon-film-coated copper grid, followed by drying under infrared light. The effective Pt loading amounts on TiO$_2$ NCs were determined by inductively coupled plasma–atomic emission spectrometry (ICP-AES, Baird PS-4).

Photocatalytic Generation of Active Hydroxyl Radicals (OH)•

TA was chosen as a fluorescent label to study the photocatalytic ability of anatase TiO$_2$ NCs.\(^{126, 127}\) Typically, a TiO$_2$ sample (10 mg) was dispersed in an aqueous solution (40 mL) that contained NaOH (0.01 M) and TA (3.0 mM) in the dark. Before exposure to light irradiation (300 W Xe lamp), the resulting suspension was magnetically stirred for 30 min. After irradiation, 4 mL of suspension was removed every 20 min. The photocatalysts were removed from the solution by centrifugation, and the remaining clear liquid was used for fluorescence spectrum measurements. The excitation light used in recording fluorescence spectra is 320 nm. The light source employed in photo-reactions is a 150 W Xe lamp with a maximum emission at 466 nm.

Photocatalytic Degradation of MO

MO was chosen as a model pollutant to explore the photodegradation activity of anatase TiO$_2$ NCs. All the experiments were carried out at a temperature of (25 ± 2) °C. Typically, a TiO$_2$ sample (10 mg) was dispersed in an MO aqueous solution (30 mL, 4 × 10$^{-3}$ M) under ultrasonication to form a suspension, and the suspension was magnetically stirred for 30 min in the dark. After irradiation under a 300 W Xe lamp, 4 mL of the dispersion was sampled every 5 min and centrifuged to remove the photocatalyst. The photodegradation efficiency was monitored by measuring the absorbance of the centrifuged solutions at the maximum absorption wavelength of MO (465 nm) with UV/Vis spectroscopy (SHIMADZU, UV-2550) at room temperature.

Photocatalytic Production of H$_2$ by Water Splitting

The photocatalytic H$_2$ production experiments were carried out with a homemade top-irradiation vessel connected to a stainless-steel closed gas circulation system. Typically, a TiO$_2$ sample (50 mg) was thoroughly dispersed in a mixed solution of deionized water (80 mL) and methanol (20 mL) under magnetic stirring. The reaction temperature was maintained at room temperature with cooling water circulation. A 300 W Xe lamp (PLS-SXE-300UV, Beijing Trusttech Co. Ltd) with a wavelength of 220–770 nm was employed as light source. Before irradiation, the system was pumped to remove the air, then Ar gas (99.9999%) was inflated as the carrier gas until the system reached atmospheric pressure. The amount of H$_2$ evolved was determined by means of gas chromatography (GC 2060) with a TCD detector.

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