Research Article

Enhancing Photocatalytic Performance through Tuning the Interfacial Process between TiO₂-Assembled and Pt-Loaded Microspheres

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This work reports on a simple two-step approach to rutile TiO₂-assembled microspheres loaded by Pt with an aim to tune semiconductor-metal interfacial processes for enhancing the photocatalytic performance. Systematic sample characterizations and structural analysis indicate that Pt loading did not produce any significant influences on the lattice structure of TiO₂-assembled microspheres. Instead, upon Pt loading, Schottky barrier was formed in the interfaces between microspheres and Pt nanoparticles, which inhabited efficiently the recombination of photo-generated electron-hole pairs essential for the photocatalytic activities. In addition, TiO₂ microspheres also showed a capacity of electrons storage and releasing as represented by a high dielectric constant, which increased the utility rate of photogenerated electrons. All these structural advantages contribute to the excellent photocatalytic activity under ultraviolet light irradiation. The interfacial process between microspheres and Pt nanoparticles was further tuned through adjusting the loading Pt content of metal Pt. As a consequence, the best photocatalytic activity on TiO₂ was obtained at 0.85 wt% Pt loading, above or below which photocatalytic activity was apparently decreased.

1. Introduction

Degradation of organic pollutants by photocatalytic technology has attracted increasing attention [1, 2]. In all kinds of photocatalysts, simple oxide semiconductors (e.g., TiO₂, ZnO, and SnO₂) have been extensively studied [3–6], among which TiO₂ nanomaterials characterized by the advantages of nontoxicity, stability, cheapness, and high activity have become the basis of promising photocatalysts [7, 8]. However, due to the wide bandgap and low quantum efficiency, the practical applications are always restricted [9–11]. Therefore, some endeavors (like doping foreign elements [12, 13] and coupled semiconductors or composites [5]) have been implemented, and some gains are obtained. Even so, efficient methods in enhancing photocatalytic activity are still challenging, since the elements introduced into the semiconductors often act as the recombination of

photogenerated electrons and holes that would decrease the quantum efficiency.

One has to execute some other routes such as imputing external fields or depositing some noble metals. For example, when H₂ [14] and magnetic field [15] are involved into the systems, the photocatalytic activities can be significantly improved, while the reaction systems became complicated, seemly not favorable for comprehension of photocatalytic process. In addition, loading noble metal (e.g., Au, Ag, Pt, Pd) onto semiconductors has been observed to greatly improve the photocatalytic activity [9, 16–18], in which the efficient utility of photogenerated electrons in the photo-degradation process is critical but often ignored.

In this work, we synthesized TiO₂-assembled microspheres with different Pt loading content through microsphere formation with a subsequent photoreduction deposition of Pt nanoparticles. With tuning the loading quantity of

FIGURE 1: SEM images of the samples: (a, b) PureTiO₂ and (c, d) 1.0-Pt-TiO₂.

metal Pt, an optimum photocatalytic activity was achieved at a loading of 0.85 wt% Pt. Further, the impacts of Pt loading content were investigated as a measure for the interfacial process between microspheres and Pt nanoparticles responsible for the enhanced photocatalytic activities.

2. Experimental Section

2.1. Sample Preparation. All reagents employed in the experiments were analytical grade and used without further purification. TiO₂ microspheres were of fabricated according to the solution chemistry described in our previous work [19]. Briefly, 20.5 mL TiCl₄ (Alpha, 99%) was added dropwise into 60 mL distilled water at 0°C in an ice-water bath under vigorously magnetic stirring to form a given concentration aqueous solution. After stirring for about 1 h, the solution was transferred to a Teflon-lined stainless steel autoclave (100 mL). After reaction at 160°C for 2 h, the autoclave was allowed to cool to room temperature naturally, and the final product was washed carefully with distilled water to remove Cl⁻ in the residue solution. The resulting product was dried at 80°C for 4 h in air.

Pt-deposited TiO₂ microspheres were prepared via a photoreduction process. Generally, 0.5 g of the as-prepared

TiO₂ microspheres was immersed into 100 mL solution of H₂PtCl₄ (Sino-Platinum Co., Ltd.) in distilled water. 0.1 M acetic acid (Sinopharm Chemical Reagent Co., Ltd.) was used to adjust the pH of suspension to about 3. Then, high-purity nitrogen passes through the suspension for 15 min to remove the oxygen in suspension. After stirring for 3 h, the mixture solution was irradiated for 3.5 h by a 300 W high-pressure xenon lamp while stirring. Finally, the specimen was centrifuged and washed with distilled water until no Cl⁻ was detected in the rinsing water. The quantity of H₂PtCl₄ needed was set according to the mass ratio of metal Pt to TiO₂ as 0.1 wt%, 0.5 wt%, 1.0 wt%, and 3 wt%, and the corresponding samples were named as 0.1-Pt-TiO₂, 0.5-Pt-TiO₂, 1.0-Pt-TiO₂, and 3.0-Pt-TiO₂. After being dried in vacuum at 80°C, the resulting products were obtained.

2.2. Sample Characterization. Powder X-ray diffraction (XRD) patterns of the samples were collected on Rigaku MinFlex benchtop X-ray diffractometer with Cu K_α irradiation. The crystallite sizes for the samples were calculated according to Scherrer formula, $D = 0.89\lambda / \beta \cos \theta$, where λ is the X-ray wavelength employed, θ is the diffraction angle matches along with diffraction peak (110), and β is defined as

FIGURE 2: XRD patterns of the samples: (a) PureTiO₂, (b) 0.1-Pt-TiO₂, (c) 0.5-Pt-TiO₂, (d) 1.0-Pt-TiO₂, and (e) 3.0-Pt-TiO₂. Vertical bars represent the standard diffraction data for bulk rutile TiO₂. *represents the diffraction lines of internal standard nickel.

the peak width at half height after the instrumental broadening is subtracted. The lattice parameters of the samples were calculated by a least-squares method using Rietica Rietveld software. Ni powder serves as an internal standard for peak position determination. Morphologies of the samples were observed by field emission scanning electron microscopy (FE-SEM) (JEOL JSM-6700). The specific loading contents of Pt for all samples were measured by Inductively Coupled Plasma OES spectrometer (ICP) (Ultima2). UV-vis diffuse reflectance spectra of the samples were obtained using a Varian Cary 500 UV-vis-NIR spectrometer. Infrared spectra of the samples were measured on a Perkin-Elmer IR spectrophotometer at a resolution of 4 cm^{-1} using the KBr pellet technique.

2.3. Photocatalytic Activity Evaluation. Photocatalytic activities test of samples was implemented on a UV light photoreactor, which was constructed by a quartz tube (4.6 cm in inner diameter and 17 cm in length) surrounded by four UV lamps ($\lambda = 254\text{ nm}$, 4 W). Methyl orange (MO) was taken as a probe molecule for evaluating the photocatalytic activity. All experiments were performed at room temperature. Namely, 100 mg of the sample was dispersed in 100 mL MO (10 mg/L) solution and magnetically stirred for 5 h to establish adsorption/desorption equilibrium of MO solution on the sample surfaces before illumination. Then, the suspension solution was irradiated by light and

collected at a regular time interval. Finally, the collected solution was centrifuged at a rate of 8500 rpm to remove the solid power and UV-vis absorption spectra of the supernatant were measured with a Perkin-Elmer UV lambda 35 spectrophotometer.

3. Results and Discussion

Figure 1 shows the SEM images of pure TiO₂ and 1.0-Pt-TiO₂ samples. It is explicit to found that pure TiO₂ sample exhibits a microsize spherical morphology as constructed by bundles of nanowires, in which nanowires grew from the center of microsphere to the outward surface along with the direction [001], exposing the outer surface (110) of nanowire and tip (001) of nanowire while keeping a roughly parallel configuration [19]. Upon photoreduction deposition, very small Pt particles are dispersed uniformly onto the microspheres, since there are no obvious changes in the microsphere morphology. Further, Pt deposited onto the microspheres is in metallic state as indicated by XPS and TEM [20].

The exact loading contents of metal Pt for all samples were determined by ICP. For sample 0.1-Pt-TiO₂, the Pt content measured was 0.1 wt%, which is close to the initial one. With increasing the initial Pt content, the corresponding measured Pt increased, such as from 0.43 wt% for 0.5-Pt-TiO₂ to 0.85 wt% for 1.0-Pt-TiO₂ and further to 1.46 wt% for 3.0-Pt-TiO₂.

XRD patterns for TiO₂ microspheres with and without Pt deposition were shown in Figure 2. Without Pt deposition, TiO₂ microspheres were highly crystallized, as indicated by strong diffraction peaks. All diffraction peaks matched well with the standard diffraction data for rutile phase (JCPDS, No. 21-1276), which demonstrated the formation of a pure rutile phase for TiO₂ microspheres. After Pt deposition, no significant changes were seen in XRD patterns. Based on the Scherrer formula' calculation, the primary particle sizes for TiO₂ samples with and without Pt modification were all about 6.2 nm. Therefore, Pt modification has no apparent influence on the particle size of TiO₂ microspheres. Besides this, no traces of metal Pt were detected from the XRD patterns in the Pt-TiO₂ series samples, regardless of Pt content. One of the primary reasons for this phenomenon is that Pt content in Pt-TiO₂ samples is too low to be detected.

Further, Pt deposition has no apparent effects on the lattice structure of rutile TiO₂. As indicated by structural refinements, the lattice parameters of all samples almost kept the same within the experimental errors. For instance, the lattice parameters for 3.0-Pt-TiO₂ were $a = 0.46143 (\pm 0.00009)\text{ nm}$ and $c = 0.29582 (\pm 0.00006)$, respectively, which are closer to that of $a = 0.46160 (\pm 0.0005)$, $c = 0.29622 (\pm 0.0004)$ of pure TiO₂. Combining the analytic results of SEM and XRD, it can be concluded that the structure of rutile TiO₂ microspheres remained unchanged after Pt loading.

It is well known that the premise of photocatalytic reaction is the adsorption of incidence light by catalysts. Therefore, UV-visible diffuse spectrum measurements appear to

FIGURE 3: UV-visible diffusion reflectance spectra of TiO_2 microspheres with Pt loaded.

be particularly important. Figure 3 shows the UV-visible diffuse reflectance spectrum (UV-Vis DRS) of all samples prepared. Pure TiO_2 microspheres reflect above 90% visible light and all samples showed intense absorbance in the UV region ($200 < \lambda < 400 \text{ nm}$). Differently, as the content of Pt loading increases, strong plasma response was observed in the visible region. Pt deposition is thus playing a critical role in the visible light adsorption because highly dispersed Pt nanoparticles can absorb nearly all the incident light [21]. It is worth emphasizing that this absorbance of visible light does not contribute a lot to the UV-light activity likely because visible light with a low energy does not allow an efficient light excitation.

Degradation of MO molecules is employed for the photocatalytic property evaluation of the samples. Specific degradation rate of MO molecule in the solution is monitored by examining the intensity variation of characteristic absorption peak of MO at 464 nm. As shown in Figure 4, all Pt-loaded microspheres exhibited a fast degradation of MO molecules. Particularly in the starting 30 min, all Pt-loaded microspheres showed a high removal of MO molecule beyond 67%, while less than 27% MO molecules were degraded by the pure TiO_2 microspheres in this period of irradiation (Figure 4(c)). Moreover, the photocatalytic performance of 1.0-Pt- TiO_2 sample is comparable with that of P25. Further, with increasing the Pt loading content, the photocatalytic activities became better, as indicated by the observation that the complete degradation time of MO became shortened from 80 min to 40 min as the loading quantity increased from 0.1 wt% to 0.85 wt%. Loading content to 0.85 wt% led to an optimum photocatalytic activity as indicated by a fast degradation of MO molecule in 40 min. However, higher Pt loading does not always mean high

photocatalytic efficiency. For instance, the photocatalytic efficiency of 3.0-Pt- TiO_2 was only half of that for 1.0-Pt- TiO_2 in the whole photocatalytic process.

The optimized photocatalytic activities with Pt loading described above might be interpreted as follows. Firstly, loading metal Pt onto surfaces of TiO_2 microspheres is beneficial for electronic transfer that decreases the recombination of photoinduced electrons and holes and thereby can greatly enhance the photoquantum efficiency. Nevertheless, too much metal Pt loadings may hinder the direct interaction between the incident light and microspheres, which leads to an incomplete excitement of photocatalysts. On the other hand, Pt nanoparticles loaded may attract holes to serve as recombination centers through recombining with electrons, which leads to a decrease in quantum efficiency [22]. As proposed in Scheme 1, metal Pt loaded was mainly deposited onto the face (110) and photogenerated electrons migrated predominantly along the direction [110] to metal Pt [20]. However, too much Pt loading led to the covering of the external surface of TiO_2 microsphere with Pt nanoparticles (Scheme 1(b)), which contribute negatively to the photocatalytic activity because of the not enough direct interaction between incident light and semiconductor. Consequently, overfull Pt loading does not help to increase the photocatalytic activity. Also, the above phenomenon indicates that metal Pt loading only favored to the transfer of electrons and does not possess photocatalytic activity inherently or the activity is far less than TiO_2 sample prepared in this work.

FT-IR spectra of Pure TiO_2 and 1.0-Pt- TiO_2 samples after MO degradation were given in Figure 5. For comparison, the FT-IR spectrum for Pure TiO_2 microspheres was also shown. The surface chemistry of the microspheres is characterized

FIGURE 4: (a) Typical time-dependent absorption spectra of MO solution in the presence of 3.0-Pt-TiO₂ under ultraviolet light irradiation; (b) C/C_0 as a function of irradiating time of MO solution for different samples in 90 min under UV light irradiation; (c) degradation rate for different Pt loading content of TiO₂ after irradiation for 30 min under UV light with a wavelength of 254 nm irradiation. The photocatalytic performances of PureTiO₂ and commercial P25-TiO₂ were measured in the same conditions for comparison.

by a band observed around 1625 cm^{-1} for the H–O flexural vibration [23] and the bands centered at 1250 and 1155 cm^{-1} for the vibrations of –C–O– bonds. The lattice nature for the microspheres is represented by the bands observed between 700 and 500 cm^{-1} for the stretching bending vibrations of TiO₂, the band around 500 cm^{-1} for the stretching vibration of Ti–O–Ti, and that around 600 cm^{-1} for bending vibration band of Ti–O and O–Ti–O. It is striking that some new weak bands appeared at 1250 and 1155 cm^{-1} for both PureTiO₂ and 1.0-Pt-TiO₂ after photocatalytic reaction, which are not observed before the photocatalytic reaction as for PureTiO₂. These new bands are probably due to the residual segments

of the organic molecules degraded. Moreover, the vibration signals of these new bands for PureTiO₂ sample are stronger than those for 1.0-Pt-TiO₂ sample, which indicates that the adsorbed residual organic pieces after MO degradation by PureTiO₂ are much more. Therefore, Pt loading is in favor of the complete degradation of organic molecules.

Based on the previous experimental results, one can see that loading metal Pt onto TiO₂ microspheres greatly improved the photocatalytic efficiency. This finding can be explained in terms of the special assembly structure of TiO₂ microspheres and the interfacial interactions between metal Pt and microspheres. As shown in Scheme 2, excitement of

SCHEME 1: Pictures illustrating the loading of Pt onto TiO_2 microspheres: (a) <0.85 wt% Pt and (b) >0.85 wt% Pt.

FIGURE 5: FT-IR spectra for given samples: (a) Pure TiO_2 sample after photocatalytic reaction; (b) 1.0-Pt- TiO_2 sample after photocatalytic reaction; (c) Pure TiO_2 sample before photocatalytic reaction.

microspheres by ultraviolet light leads to the separation of photogenerated electron-hole pairs. Since the work function of metal Pt is $\phi_m = 5.36$ eV, larger than that of 4.2 eV for the face (110) of TiO_2 [24], the Fermi energy level for microspheres locates above that of metal Pt. Therefore, electrons can easily transfer from the conduction band of TiO_2 to metal Pt. Continuous transfer of electrons leads to the formation of Schottky barriers at the interfaces between Pt and TiO_2 microspheres. Due to the existence of Schottky barriers [7], reverse process for electrons migration from metal Pt to TiO_2 is hard to occur. Therefore, recombination of photogenerated electrons and holes can be efficiently inhibited and photoquantum efficiency increased spontaneously.

SCHEME 2: Reaction mechanism proposed for the photocatalytic removal of MO molecules.

It is well known that the separation of light-induced electron-hole pairs is critical in the photocatalytic reaction. However, some photochemical processes except for the enhancement of photoquantum efficiency are hardly discussed. For example, the highly efficient utility of photo-generated electrons and holes in photo-degradation process plays an important role in enhancing the photocatalytic efficiency. In our recent work, self-assembled TiO_2 microspheres sample has been found to exhibit a giant dielectric property [25], which is closely related to the cavities structure in between the parallel adjacent nanowires within the microspheres that can be taken as microcapacitors. These microcapacitors possess a giant dielectric constant and therefore might provide a superior electronic storage capacity. Because the production of light-induced electrons is faster than the degradation of MO molecule in photocatalytic reaction, compensating the time difference of photogenerated electrons and degradation reaction participated by electrons is pretty necessary. Due to the existences of microcapacitors, the accumulation and releasing of electrons can enhance the utility of electrons, while avoiding the recombination of electrons and holes. Therefore, dual roles from Pt deposition and special structure of TiO_2 microspheres contribute to the efficient separation of light-induced electrons and holes that greatly enhances the utility of electrons in favor of the optimum photocatalytic activities.

4. Conclusions

We have fabricated the Pt-TiO₂ microspheres by a solution chemistry with a subsequent Pt loading through a photoreduction. Pt loading led to an efficient separation of photogenerated electron-hole pairs. Meanwhile, electrons stored in the “microcapacitor” of TiO₂ microspheres contributed to the enhancement of photocatalytic activity under UV light irradiation. Varying the Pt loading content gives rise to an optimum catalytic efficiency. By monitoring the surface chemistry of Pt-TiO₂ microspheres before and after photocatalytic reactions, we found that the degradation of MO molecules was more complete in the presence of Pt loading.

Acknowledgments

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