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Size-Dependent Mie's Scattering Effect on TiO₂ Spheres for the Superior Photoactivity of H₂ Evolution

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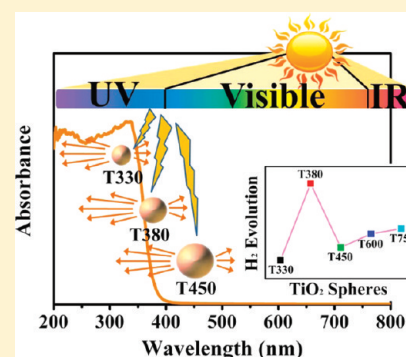
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ABSTRACT: A novel strategy of coupling Mie's scattering effect into the light-absorption region of TiO₂ was developed to enhance the photocatalytic performance of H₂ evolution over TiO₂ spheres. The TiO₂ spheres with different diameters (330–750 nm) were controllably fabricated via adopting different sized polymer poly(methyl methacrylate) (PMMA) templates. The UV–visible absorption and reflectance spectra were employed for studying the absorption and scattering properties of these TiO₂ spheres. It was found that the scattering resonant peaks that indicate the strongly efficient scattering in different wavelength regions were largely dependent on the sizes of the TiO₂ spheres. The scattering resonant peaks have been detected around 366, 400, and 440 nm for the TiO₂ spheres with diameters of 380, 450, and 600 nm, respectively. Moreover, the photocatalytic efficiency of the H₂ evolution was found to be dependent on the size of the TiO₂ spheres. Among them, the TiO₂ spheres with a diameter of 380 nm exhibited the highest photocatalytic activity (313 μmol/(h·m²)), about 5 times and 3 times of that of 330 and 450 nm sized TiO₂ spheres, respectively. The highest activity observed on 380 nm sized TiO₂ may be attributed to its optimized diameter, which can result in a highly efficient scattering effect in the light-absorption region of TiO₂ (λ < 387 nm).



INTRODUCTION

Photocatalysis is an environmentally friendly and promising technology to convert solar energy into chemical energy.^{1–5} In 1972, Fujishima and Honda reported that TiO₂ electrode could photocatalytically split water into H₂ and O₂ under some bias potential and UV light irradiation. After that, much work has been carried out on TiO₂ to enhance the photocatalytic activity.⁶ In order to achieve this goal, the extensive efforts have been mainly focused on three aspects. One is the modification of the electronic structure to extend the light-absorption region, such as a series of anion doped TiO₂.^{7–13} The other way is to fabricate single-crystalline TiO₂ with high-surface-energy crystal facets exposed^{14–17} or mesoporous TiO₂ with large surface area,¹⁸ which can offer more active sites during the photocatalytic reaction process. Third, improving the light utilization efficiency via the spatial structuring control (e.g., semi-hollow spheres) is also an effective method, but the relevant study is very limited.¹⁹

In general, the TiO₂ photocatalytic cycle comprises three steps: first, light excitation induces the transition of electrons from valence band to the conduction band, leaving an equal number of vacant sites (holes); second, the excited electrons and holes migrate to the surface of TiO₂; third, they react with the adsorbed electron donors and electron acceptors, respectively. Since the first step for the photocatalysis is the light excitation process, a high-efficient utilization of the

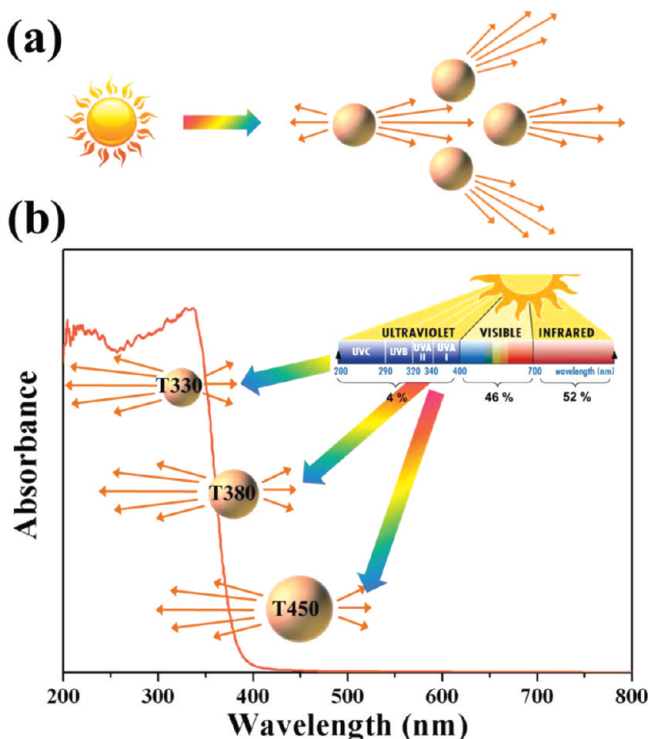
incident light is an effective method to enhance the photocatalytic performance. Light can be scattered and redirected in many directions. Particularly, when the size of the particles is comparable to the wavelength of the incident light, the Mie's scattering happens. In the atmosphere, the clouds appear white, attributing to the Mie's scattering effect, which can scatter all wavelength of the visible light by the various sized dusts. If we introduce the Mie's scattering phenomenon into the TiO₂ spheres, when the light collides with the TiO₂ sphere with size comparable to its wavelength, the light scatters strongly along the forward direction. This scattering produces a pattern like an antenna lobe, with a sharper and more intense forward lobe (Scheme 1a).²⁰ Therefore, the path length of the incident light between the neighbored spheres will be increased,²¹ leading to a promoted light utilization efficiency over the TiO₂ spheres. The scattering phenomenon has been applied in the dye-sensitized solar cells (DSSC) before;^{22,23} however, to the best of our knowledge, there are few studies available on the light scattering effect over TiO₂ in the application of H₂ evolution. Previous work reported that the light scattering efficiency is largely dependent on the

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Scheme 1. Schematic Illustration of the Mie's Scattering Phenomenon among the TiO₂ Spheres (a) and the Simulated Scattering Region for the TiO₂ Spheres with Different Diameters (T330, T380, and T450 Represent the TiO₂ Spheres with Diameters of 330 nm, 380 nm, and 450 nm, Respectively) (b)



size of the scattering particle, and the wavelength of the incident light.²⁴ Therefore, fabrication of TiO₂ spheres with suitable diameter is critical to induce the Mie's scattering effect happening in the light absorption region of TiO₂.

In this work, we develop a strategy of coupling Mie's scattering into the light-absorption region of TiO₂ to enhance the light-utilization efficiency of the TiO₂ spheres. The band gap of TiO₂ is 3.2 eV, which can only be excited by the light with wavelength smaller than 387 nm. According to the Mie's scattering theory, the light will be strongly scattered on the surface of TiO₂ with an appropriate size comparable to its wavelength. When the scattering cross-section exhibits a number of resonances for a given particle size of TiO₂ sphere, the scattering will be very efficient at these wavelengths. Therefore, the scattering efficiency in different wavelength regions of the incident light spectrum is largely dependent on the diameter of TiO₂ spheres. Only when the scattering resonant peak, which indicates the strongly efficient scattering,²⁵ is coupled into the light-absorption region of TiO₂, the scattering and absorption for the TiO₂ is effective, followed with the highest light utilization efficiency. As shown in Scheme 1b, the scattering phenomenon occurs on the TiO₂ spheres with diameters of smaller (330 nm), comparable (380 nm), and larger (450 nm) than the light absorption edge of TiO₂ (about 387 nm) is depicted. We can assume that the scattering effect that happens on the TiO₂ spheres will be various and related to the different diameters. On the basis of the above assumption, herein, the TiO₂ spheres with different sizes (330 nm, 380 nm, 450 nm, 600 nm, and 750 nm) have been selectively fabricated. The scattering resonant peaks over the TiO₂ spheres were

checked to study the correlation between the particle size and the scattering efficiency. The further photocatalytic H₂ evolution and photoelectrochemical measurements over the TiO₂ spheres were investigated to test the validity of the coupling strategy of the size-dependent Mie's scattering effect.

EXPERIMENTAL SECTION

Synthesis of TiO₂ Spheres. The TiO₂ spheres were prepared via a facile sol-gel method²⁶ by the coagulation of titanium tetra-*n*-butyl (TBOT) with the polymer poly(methyl methacrylate) (PMMA) spheres as templates. Typically, 0.05 g PMMA spheres and 0.6 mL ammonium were first added into a mixed solution of 75 mL of ethanol and 25 mL of acetonitrile. In this step, the PMMA spheres were negatively charged, while the ammonium was selected to electrostatically stabilize the PMMA template because of the positively charged NH₄⁺. After being stirred for 20 min, 3 mmol of TBOT was subsequently added and adsorbed on the surface of the NH₄⁺/PMMA⁻ spheres, followed with a series of hydrolysis processes to form the amorphous TiO₂ via magnetic stirring at room temperature for 24 h. Finally, the white precipitation was heated at 500 °C for 2 h with a temperature ramping rate of 1 °C/min, all the PMMA polymers were removed, leading to the formation of TiO₂ hollow spheres. By using different sized PMMA spheres as the template, TiO₂ spheres with different diameters were selectively prepared. The diameters of the TiO₂ spheres were controlled to be 330, 380, 450, 600, and 750 nm (denoted as T330, T380, T450, T600, and T750) by adopting 170, 260, 330, 450, and 670 nm sized PMMA spheres, respectively.

Preparation of TiO₂ Films. The TiO₂ films used for the photoelectrochemical test were prepared via a spin-coating method. The 20 mg of TiO₂ samples were first dispersed into 10 mL of ethanol solvent by ultrasonic treatment, then spin-coated on the ITO substrate layer by layer for 50 times. In the procedure of spin coating, every drop of the TiO₂ suspension was about 0.05 mL. In each cycle, 3 drops of suspension was dripped on the ITO substrate. The spin speed and time were 800 rpm for 5 s followed with 1000 rpm for 30 s. Finally, the coated films were heated to 500 °C at a rate of 1 °C/min and kept at this temperature for 2 h.

Characterization. The X-ray diffraction (XRD) patterns of the prepared samples were conducted on a Rigaku Multiflex diffractometer (RINT 2000; Rigaku Corp., Japan) with monochromatized Cu K α radiation ($\lambda=1.54178$ Å). The size and morphology of the samples were observed by a scanning electron microscope (SEM, JSM-6701F, JEOL Co., Japan) and transmission electron microscope (TEM, JEM-200 CX, JEOL Co., Japan) operating at 200 kV. The Brunauer-Emmett-Teller (BET) surface areas were recorded by a surface area analyzer (Tristar 3000, Micromeritics Inc., USA) with nitrogen absorption at 77 K. The UV-visible diffuse reflectance spectra were measured on a UV-visible spectrophotometer (UV-2500PC, Shimadzu Co., Japan).

Photocatalytic H₂ Evolution Process. Photocatalytic reactions of H₂ evolution were carried out in a closed gas circulation system with an external-irradiation Pyrex-cell. The light source was a 300 W xenon lamp. The intensity of the light at 300–800 nm was measured to be 242.3 mW/cm² using a spectroradiometer (USR-40; Ushio Inc., Japan). The cocatalyst Pt was loaded by an in situ photodeposition method. The 0.5 wt % Pt-loaded catalyst (0.09 g) was first ultrasonically dispersed into monodispersed spheres suspended in a methanol aqueous solution (50 mL of methanol and 220 mL of water).

Then, magnetic stirring was used to stabilize the suspension during the whole photocatalytic H₂ evolution process. The evolved gas including H₂ was analyzed by an online gas chromatograph (GC-8A; Shimadzu Corp., Japan) equipped with a thermal conductivity detector.

Photoelectrochemical Measurement. Photocurrent measurements were performed with an electrochemical station (ALS/CH model 650A, Japan) using a three-electrode mode with 0.1 M Na₂SO₄ solution as the electrolyte. The TiO₂ photoanodes were used as working electrodes; a Pt wire served as a counter electrode. The Ag/AgCl electrode was used as the reference electrodes. The illumination source was a 500 W Xe lamp (Optical ModuleX; Ushio Inc., Japan). The intensity of the light at 300–800 nm was measured to be 140.4 mW/cm² using a spectroradiometer (USR-40; Ushio Inc., Japan). In the photocurrent–time measurement, the TiO₂ photoelectrodes were illuminated at normal incidence of light through a quartz window. The voltage-scan speed was 0.1 V/s, and light was chopped manually at regular intervals.

RESULTS AND DISCUSSION

The XRD patterns of the as-prepared TiO₂ samples are shown in Figure 1. The XRD profiles of all the samples can be

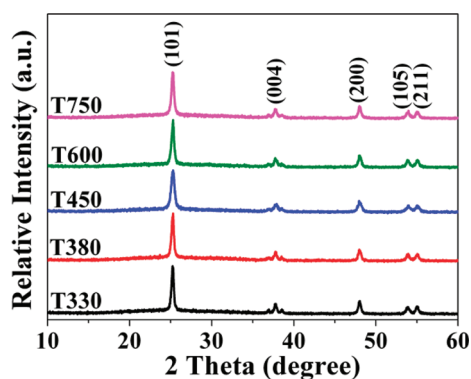


Figure 1. XRD patterns of the as-prepared TiO₂ spheres.

coincidentally indexed by the standard anatase TiO₂ pattern (JCPDS file No. 71–1167). The peaks at 25.25, 37.72, 48.03, 53.91, and 54.99 degree can be assigned to (101), (004), (200), (105), and (211) crystal planes of anatase TiO₂, respectively. Meanwhile, the average crystallite sizes of the TiO₂ samples were calculated by the Scherrer's formula: $D = K\lambda/\beta \cos \theta$, where λ was the wavelength of the X-ray radiation ($\lambda = 0.15418$ nm), K was the Scherrer constant ($K = 0.89$), θ was the position of X-ray diffraction peak, and β was the full width at half-maximum (fwhm) of the (101) plane for anatase TiO₂. The calculated sizes are 22.8, 25.6, 22.1, 21.2, and 22.3 nm for T330, T380, T450, T600, and T750, respectively. Therefore, the crystallinity for all the TiO₂ samples is not obviously different. It is well-known that the crystallinity of the TiO₂ during the crystal growth process is largely dependent on the water content, the solution acidity, and the calcination temperature. Since the TiO₂ spheres were prepared in the same procedure and similar preparation environment (0.06 mL ammonium added and calcination at 500 °C for 2 h), thus leading to the similar crystallinity for all the TiO₂ samples.

The size and morphology of the TiO₂ samples can be observed by the SEM images (Figure 2a–e). There is no obvious difference in the surface morphology except for the size

among the TiO₂ spheres with different diameters around 330, 380, 450, 600, and 750 nm, respectively. Furthermore, the TEM image confirms the spherical structure with an average size of 380 nm for T380 (Figure 2f). Meanwhile, the contrast between the bold dark ring and the bright inner circle indicates that the sphere is hollow, which is resulted from the removal of the PMMA template via calcination. The enlarged representative surface of the TiO₂ sphere (Figure 2g) reveals that the TiO₂ sphere consists of a large amount of tiny nanoparticles (~3 nm). The spacing of the lattice fringes is 0.350 nm as shown in the HRTEM image (Figure 2h), which is associated with the (101) lattice plane of the anatase TiO₂.

As shown in Figure 3, the N₂ adsorption–desorption isotherms of T380 exhibit a typical Type IV isotherm with a hysteresis loop, which is associated with capillary condensation taking place in mesopores, and the limiting uptake over a range of high P/P_0 .²⁷ Moreover, the pore-size distribution curve of T380 (inset of Figure 3) indicates that the TiO₂ samples contain mesopores with diameter smaller than 10 nm, this result is well consistent with the TEM image as shown in Figure 2g. The TiO₂ spheres are made of large amounts of small nanoparticles and the mesopores are resulted from the aggregates of the nanoparticles. Therefore, besides the contribution of the external and internal surface areas of the hollow sphere, the pores resulting from the aggregation of the small TiO₂ nanocrystalline consisting in the TiO₂ sphere also make an effort to the total surface area. Finally, the Brunauer–Emmett–Teller (BET) specific surface areas are recorded as 13.8, 9.4, 10.1, 10.2, and 8.8 m²/g for T330, T380, T450, T600, and T750, respectively (as listed in Table 1).

The optical properties of the TiO₂ sphere powders are shown in Figure 4. All the TiO₂ samples exhibit the similar light absorption edge around 380 nm (Figure 4a), while little differences exist in the reflectance spectra, especially in the region of 335–370 nm (inset of Figure 4b), which reveals that T380 presents a relatively higher reflectance intensity compared with other TiO₂ samples. It is well-known that the light-scattering performance of TiO₂ is strongly dependent on the particle size, and the size dependency of the scattering effect can be evaluated by the reflectance spectra to some extent.²⁸ Therefore, since T380 exhibits the strongest reflectance intensity in the region of 335–370 nm, it might have a strong scattering efficiency in this region.

The photocatalytic activities of the H₂ evolution were tested for all the TiO₂ sphere samples. The amounts of the evolved H₂ over the TiO₂ samples were 76, 265, 94, 136, and 131 μmol/h for T330, T380, T450, T600, and T750, respectively (as depicted in Table 1). Among which, T380 exhibited obviously higher photocatalytic activity compared with the other TiO₂ samples. Usually the photocatalytic performance of TiO₂ is affected by various factors such as the morphology, the phase composition, the crystallinity, the surface area, and so on. In this work, considering that the crystallinity is not appreciably different for these TiO₂ samples (Figure 1), the effect of the crystallinity on the photocatalytic performance can be ignored. Moreover, taking the surface area into account, the photocatalytic activities of the TiO₂ samples are 61, 313, 103, 148, and 165 μmol/(h·m²) for T330, T380, T450, T600, and T750, respectively (Figure 5), in which the photoactivity of T380 is also superior to that of other TiO₂ samples. Therefore, the highest photocatalytic activity of the H₂ evolution over T380 can be attributed to the fact that the unique diameter can result in a strongly efficient scattering effect in the light absorption

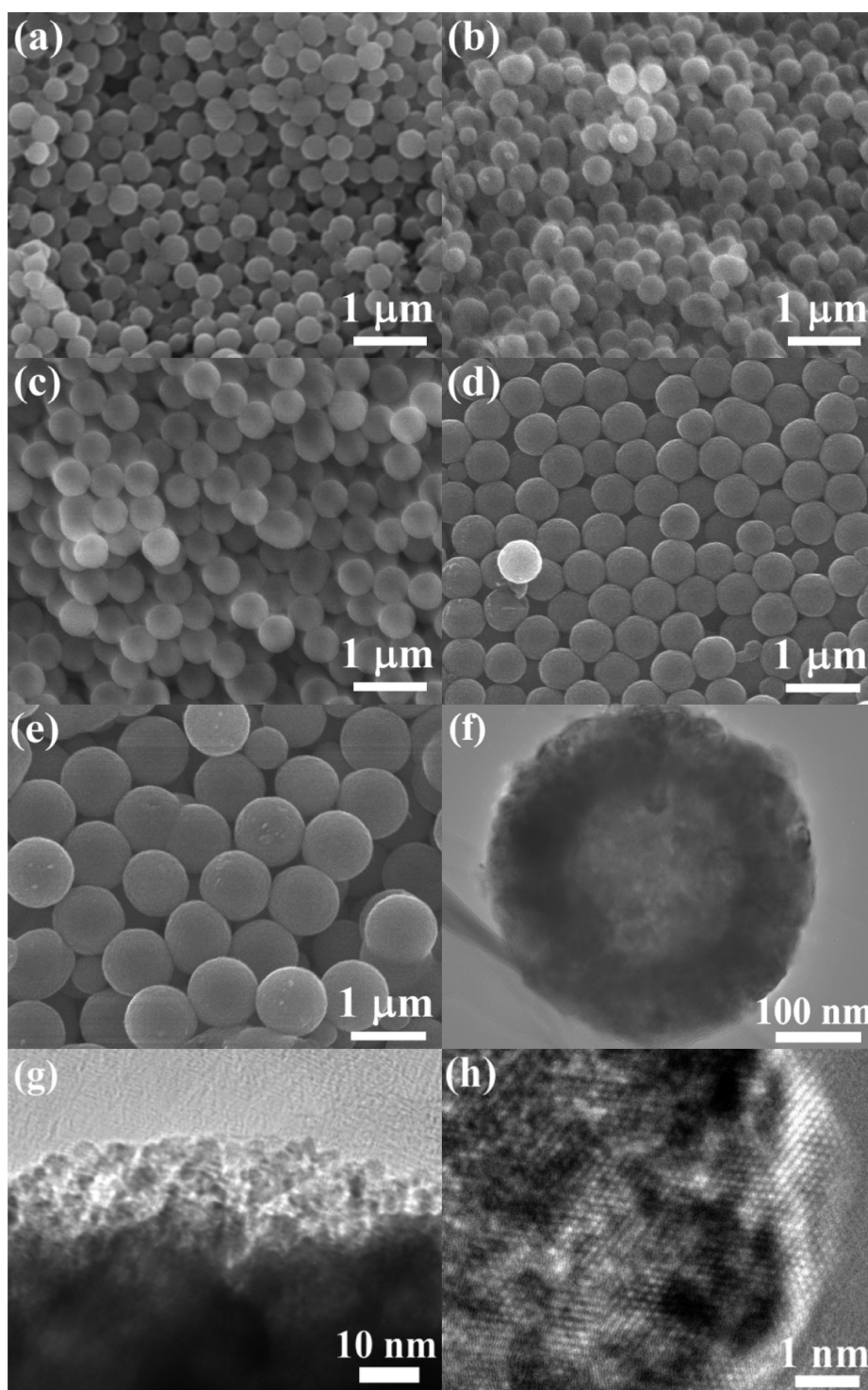


Figure 2. SEM images of the TiO₂ spheres, (a) T330, (b) T380, (c) T450, (d) T600, and (e) T750; the TEM image (f), the high-magnified TEM image (g), and HRTEM image (h) of T380.

region of TiO₂ and thus lead to the enhanced photocatalytic performance.

The strong scattering effect is largely dependent on the particle size, which can be theoretically explained as follows. When the size of sphere is comparable to the incident-light wavelength, the Mie's scattering occurs. Theoretically, the scattered wave is found to be necessary to obtain the right boundary conditions between incident wave and the field inside the sphere. For an incident light wavelength λ , the scattering

behavior of a system, which consists of dispersed spherical particles, can be fully described by the radius of sphere r and the complex refractive index m . The complex Mie coefficients a_n and b_n can be deduced by the complex Bessel–Riccati functions ψ and ζ

$$a_n = \frac{\psi'_n(mx)\psi_n(x) - m\psi_n(mx)\psi'_n(x)}{\psi'_n(mx)\zeta_n(x) - m\psi_n(mx)\zeta'_n(x)}$$

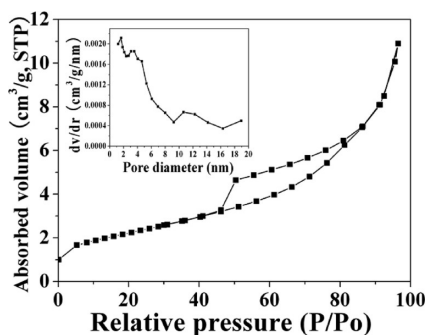


Figure 3. Nitrogen adsorption–desorption isotherms and pore-size distribution curve (inset) of the prepared TiO₂ sample (T380).

Table 1. BET Surface Areas, Photocatalytic Activities, and Photoelectrochemical Properties of the As-Prepared TiO₂ Spheres

	T330	T380	T450	T600	T750
BET surface area (m ² /g)	13.8	9.4	10.1	10.2	8.8
amounts of H ₂ evolution (μmol/h)	76	265	94	136	131
photocurrent density (μA/cm ²)	14.9	59.2	36.9	13.0	9.2

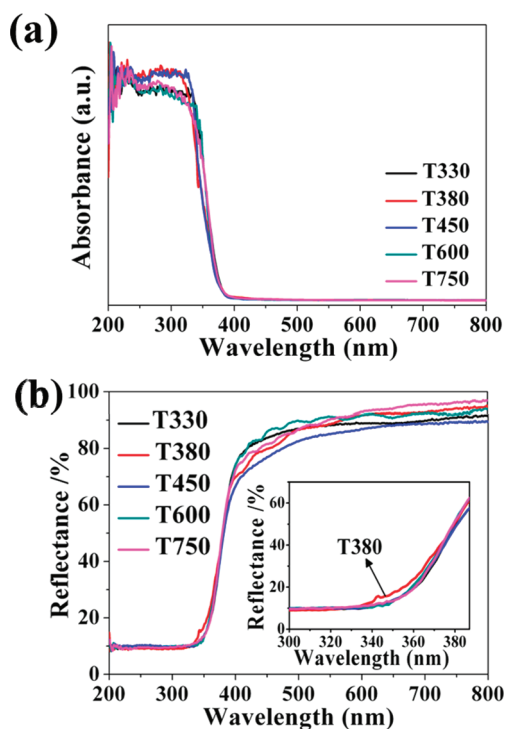


Figure 4. (a) UV–visible absorption spectra of the TiO₂ powders; and (b) the UV–visible diffuse reflectance spectra of the TiO₂ powders and the enlarged part in the region of 300–387 nm (inset).

$$b_n = \frac{m\psi'_n(mx)\psi_n(x) - \psi_n(mx)\psi'_n(x)}{m\psi'_n(mx)\zeta_n(x) - \psi_n(mx)\zeta'_n(x)}$$

where the size parameter x is taken as $x = 2\pi r/\lambda$.

The Mie coefficients a_n and b_n are functions with numerous poles in the complex plane. The scattering, absorption, and

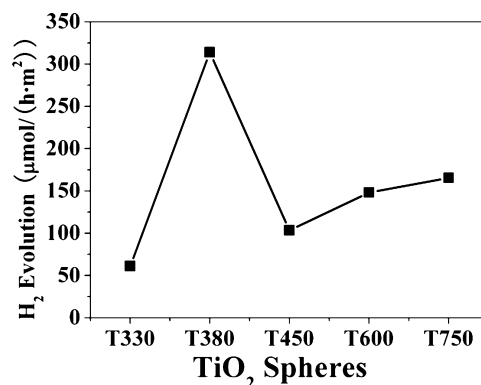


Figure 5. Photocatalytic activities of H₂ evolution over the different sized TiO₂ spheres (with 0.5 wt % Pt loaded) under UV–visible light irradiation ($\lambda > 300$ nm).

extinction efficiencies are given by

$$Q_{\text{sca}} = \frac{2}{x^2} \sum_{n=1}^{\infty} (2n+1)(|a_n|^2 + |b_n|^2)$$

$$Q_{\text{abs}} = Q_{\text{ext}} - Q_{\text{sca}}$$

$$Q_{\text{ext}} = \frac{2}{x^2} \sum_{n=1}^{\infty} (2n+1)\text{Re}(a_n + b_n)$$

Therefore, the scattering cross-section exhibits a number of resonances for a given particle size; at these wavelengths, the scattering is very efficient.^{29,30}

To verify the existence of the scattering effect in the H₂ evolution process, the TiO₂ suspensions obtained after the H₂ evolution test were used to check the scattering resonant peaks by the UV–visible reflectance spectra from 300 to 800 nm.^{25,31} As shown in Figure 6, the experimental results reveal that the

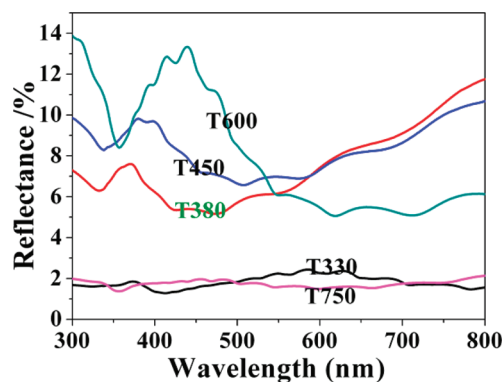


Figure 6. UV–visible reflectance spectra of the TiO₂ suspensions obtained after the H₂ evolution test to detect the scattering resonant peaks of the TiO₂ spheres.

scattering effect for the various sized TiO₂ spheres in the incident light spectrum are obviously different. The TiO₂ sample with a diameter of 380 nm exhibits the strong resonant peak around 366 nm, indicating that the incident light strongly scatters on the 380 nm sized TiO₂ sphere at wavelength around 366 nm. The scattered light then transfers to and is absorbed by the neighbored spheres, thus inducing more photoexcited electrons to reduce the H⁺ ions into H₂ molecules. For TiO₂ spheres, only for the light with wavelengths shorter than the

absorption edge ($\lambda < 387$ nm), scattering and absorption is effective. As for the TiO₂ spheres with diameters of 450 and 600 nm, the peaks of scattering resonances locate at 400 and 440 nm, thus the scattering effects are relatively limited to the enhancement of light absorption for TiO₂. For the 750 nm sized TiO₂ sample, a very weak and broad peak between 350 and 600 nm can be detected with careful observation. The weak scattering resonance peak might be attributed to the low scattering coefficient reported by Thiele and his co-workers.³² In the photocatalytic H₂ evolution process, more light can be absorbed by the TiO₂ samples, more electrons will be excited and take part in the H⁺ reduction reaction, thus lead to a higher H₂ output efficiency. Since the TiO₂ sample with a diameter of 380 nm exhibits the strong effective scattering effect in the light-absorption region of TiO₂, more light will be scattered and absorbed by the TiO₂, thus the light utilization efficiency will be largely enhanced followed with the superior photocatalytic activity, which is well in accordance with our photocatalytic tests that T380 showed the higher photocatalytic activity of H₂ evolution compared with other TiO₂ samples (T330, T450, T600, and T750). In conclusion, only the scattering and absorption that happened in the light absorption region of TiO₂ can make a great contribution to the effective light-utilization efficiency followed with the enhancement of photocatalytic performance.

In order to further confirm that the photon-to-electron conversion efficiency of the TiO₂ sphere is affected by the size-dependent Mie's scattering effect, the photoelectrochemical measurements of the TiO₂ photoanodes have been conducted. Figure 7a shows the photocurrent–time ($I-t$) curves measured with a three-electrode mode and 0.1 M Na₂SO₄ solution as the

electrolyte. Under a bias potential of 0.6 V, the photocurrent densities of the TiO₂ spheres are 14.9, 59.2, 36.9, 13.0, and 9.2 $\mu\text{A}/\text{cm}^2$ for T330, T380, T450, T600, and T750, respectively, in which the photocurrent intensity of T380 is the highest (Figure 7b), indicating that T380 has the best photon-to-electron conversion efficiency. This result is consistent with the results from the photocatalytic H₂ evolution tests. In the photocatalytic H₂ evolution process, the photoexcited electrons will reduce the protons (H⁺) into H₂, thus an enhanced light-utilization efficiency followed with the better photon-to-electron conversion performance might result in a superior output efficiency of H₂.

CONCLUSIONS

In summary, the Mie's scattering effect was introduced into the application of photocatalytic H₂ evolution over TiO₂ spheres. TiO₂ spheres with different diameters (330–750 nm) were fabricated to investigate the correlation between the particle size and the scattering effect. In contrast to the 450 and 600 nm sized TiO₂ spheres, the TiO₂ with a diameter of 380 nm exhibited the strong efficient scattering effect in the light absorption region of TiO₂, thus leading to a higher light-utilization efficiency, followed with a considerable enhancement of the photocatalytic activity. This study proposes a novel strategy that coupling the effect of Mie's scattering into the light absorption region of TiO₂ via morphological modulation can improve the photocatalytic performance in the H₂ evolution. Moreover, it will provide a potential and promising approach to effectively enhance the light utilization efficiency for other semiconductor photocatalysts, especially for the visible-light-driven photocatalysts with the optimized diameter.

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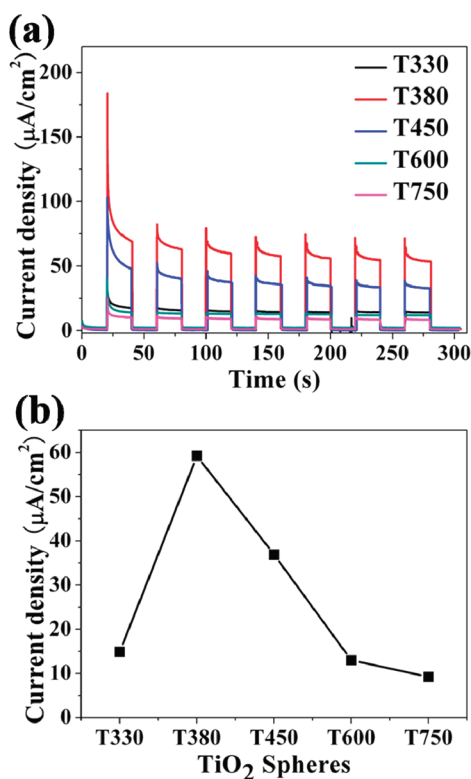


Figure 7. (a) Photocurrent curves ($I-t$) of the as-prepared TiO₂ photoanodes measured under UV–visible light irradiation ($\lambda > 300$ nm); (b) the comparison of the photoelectrochemical properties of the TiO₂ thin films samples.

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