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Short Communication

Visible-Light Photocatalyst of Tetramethoxyphenylporphyrin Sensitized TiO_2 Nanotube

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Abstract: *This paper investigated the performance of photocatalysts of TiO_2 nanotubes sensitized by photosensitizers of tetramethoxyphenylporphyrin(TMPP) for producing H_2 from water under visible light. This photocatalyst might have a smaller band gap (2.6 eV). The investigation shows that a photosensitized catalyst combined TiO_2 nanotube with TMPP can be used to extend the absorption of solar light region and enhance the efficiency of energy conversion, and the quantity of H_2 evolution is 1.427 L $m^{-2}h^{-1}g^{-1}$. It was a way to apply the dye sensitized TiO_2 nanotubes photocatalyst in the visible light for clean energy.*

Keywords: nanotube; photocatalyst; sensitizer; tetramethoxyphenylporphyrin; TiO_2

1. INTRODUCTION

Semiconductor photocatalysis is an efficient way for the utilization of solar light as clean energy. The important feature of the reaction is that H_2 is produced by a photocatalytic reaction when photocatalysts are irradiated with sunlight. Since photoinduced producing H_2 from water on TiO_2 electrode was discovered in 1972 [1], TiO_2-based photocatalysts have attracted much attention. Although TiO_2 has the advantages for its high stability, low cost, non-toxicity and high efficiency for degradation of difficult-to-remove pollutants and other aspects, it can be activated only by ultraviolet light due to the wide band gap energies (3.0 eV for rutile and 3.2 eV for anatase). Only a small fraction (~4%) of the solar energy can be utilized in practical application. Therefore many attempts have been made to sensitize TiO_2 to use a larger part of the visible light (~43 % of the solar light).

Narrowing the band gap has been reported in crystalline TiO_2 doped with N, C and F [2] to extend the absorption range of TiO_2 from ultraviolet region to the visible light region. The processes are always complicated and require special equipment. Another way to shift the optical absorption is to sensitize the TiO_2 by a photosensitizer, such as Ru (Ⅱ) quaterpyridinium complexes [3] and metalloporphyrins [4]. These complexes absorb light in the visible wavelength range. The resulting excited complex may lose energy by ejection of an electron if a suitable acceptor is available. The acceptor may be other dyes in the aqueous phase, or the acceptor may be a solid semiconductor, but in either case the acceptor must be located sufficiently close so that diffusion to the acceptor is possible within the lifetime of the excited complex. The main problem with the sensitized photocatalyst is that the phocatalysts are easily degraded and lose their stability.

Recently, our group used a microwave irradiation method utilizing anatase TiO_2 nanoparticle in a concentrated NaOH solution to produce a highly pure TiO_2 nanotube [5]. TiO_2 nanotubes have a much larger surface area and a stronger capacity for absorption than that of typical TiO_2 nanoparticle. Even though the nanotubes had a band gap with 3.8 eV, it had advantages of the separation of excited electron-hole pair, acceleration of the transfer of the electrons, and inhibition of recombination. Nanotubes with a one-dimensional structure have recently been successfully used as catalyst supports to prepare Pt/TiO_2 nanotube catalysts to generate H_2 gas from neat ethanol under a UV lamp [6]. Novel carbon-doped TiO_2 nanotube arrays, with a high photocatalytic activity and enhanced visible light response. [7]. It found that the TiO_2 nanotube arrays could harvest solar light more effectively. In addition, the TiO_2 nanotube structure also showed a steeper increase in photocatalytic activity. Thus, with the TiO_2 nanotubes, e--h+ pairs induced by photon absorption split more readily compared to nanoparticles.

In this paper we report the sensitization of TiO_2 nanotubes by

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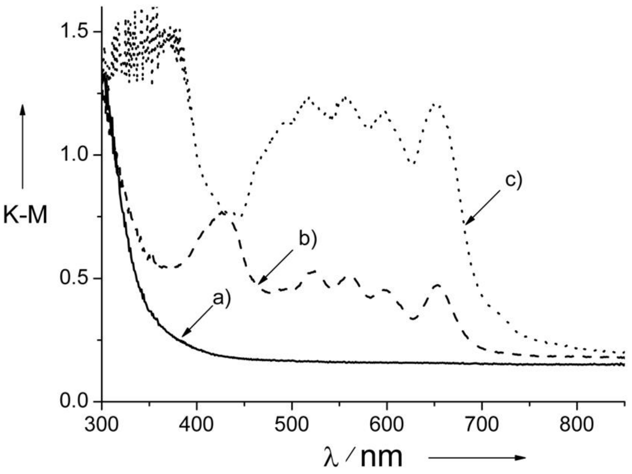

Figure 1. Diffuse reflection spectra of TiO_2 nanotube (a), TMPP sensitized TiO_2 nanotubes (b), and TMPP (c). K-M=diffuse reflection spectra converted into absorbance by the Kubelka-Munk method (arbitrary units).

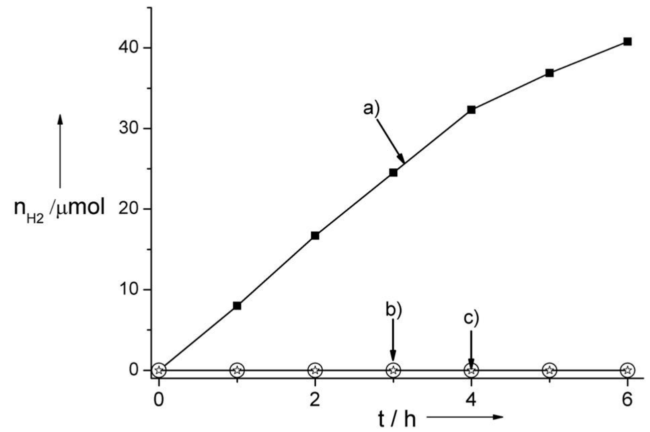

Figure 2. Photocatalytic H_2 evolution from water under simulated sunlight irradiation with a cut-off filter over TMPP sensitized TiO_2 nanotube photocatalyst (a), pure TiO_2 nanotube (b), and TMPP (c).solar simulator: 350 W Xe lamp with 420 nm cut-off filter; reaction cell: top-window pyrex cell; irradated area: 12.56 cm^2.

tetramethoxyphenylporphyrin (TMPP) to explore the binding of a photosensitizer to TiO_2 nanotubes both as a way of isolating the catalyst, and more importantly, to determine whether the catalysts have a adequate excited lifetime for water splitting in photocatalytic process under direct artificial visible light.

2. EXPERIMENTAL

2.1. Preparation of photocatalysts

TiO_2 nanoparticles were synthesized by co-deposition and added-crystalline particle methods in our group. They acted as the precursor for TiO_2 nanotube fabrication. 0.15 g of the precursor was mixed with 50 mL NaOH aqueous solution (10 $mol·L^{-1}$). The mixture was encased in Teflon autoclave, sonicated for 5 min, and heated by microwave irradiation in a microwave reactorwith 195 W of power for 90 min. After filtration, washing, and drying under vacuum at 90 °C, TiO_2 nanotubes were obtained [5].

Tetramethoxyphenylporphyrin (TMPP) was synthesized by using the experimental protocol described in the literature [8]. 0.0045 g TMPP was dissolved in CH_2Cl_2. After 0.125g TiO_2 nanotubes were added into the above solution, the mixture was refluxed in a water bath at 50 °C with a magnetic stirrer. The product was placed over 12 h and treated by a rotatory evaporator. The photocatalyst was dried under vacuum at 90 °C for 12 h.

2.2. Analysis of trace CH_2Cl_2

The chromatographic conditions for trace CH_2Cl_2 analysis: a Agilent 6890N gas chromatograph equipped with an electron-capture detector was used for the experiments. The carrier gas was ultrapure nitrogen (>99.999%) with a flow-rate of 1.5 ml/min. The gas chromatograph was operated in a splitless mode and the splitless time was 9 min. The injector was maintained between 240 and 300 ℃. The temperature of detector was maintained at 280 °C. The column was held at 50 ℃ for 4 min, increased to 200 at a rate of 8 °C/min to 230 °C, held for 3 min, and ramped to 250 °C at a rate of 4 °C/min, and then held for 3 min.

2.3. Photochemical experiments

Photocatalytic activity was carried out in a top-irradiation type reactor made of quartz under a 300 W Xe lamp (Shanghai Dianguang Device Co., China) as a light source. A series of cut-off filters (Shanghai Colour Glass Co., China) were used to provide the incident lights with different wavelengths. The photocatalyst powder (100 mg) was dispersed by a magnetic stirrer in an aqueous solution (that is 60 mL pure water (18 Ωm)). Before irradiation, the reactor was deaerated by Ar gas until air (O_2 and N_2) almost cannot be detected by TCD gas chromatography (using 5A molecular sieves, Ar as the carrier gas, and a GC9160, China), by which the amounts of gases including H_2 or O_2 evolved were determined. UV-Vis adsorption spectra of solution were achieved using a UV-Vis spectrophotometer (TU1901, China).

3. RESULTS AND DISCUSSION

Figure 1 shows UV-Vis spectra of TiO_2 nanotubes, TMPP, and TMPP sensitized TiO_2 nanotubes catalysts powders. From the spectra, it is obvious that the TMPP has a strong Soret band at about 420 nm. In the region of 500-700 nm, the TMPP and the sensitized photocatalyst have four absorption bands.The TiO_2 nanotubes have absorption at about 350 nm and thus the estimated band-gap energy is about 3.5 eV. The absorption edge of the sensitized photocatalyst is at a longer wavelength (480 nm) than the TiO_2 nanotube, as indicated by arrow b). The band-gap energy can be etimated according to the following equament:

$$Eg=1240/\lambda g \quad (eV)$$

where λg is the absorption edge of the photocatalyst. The band-gap energy of the sensitized photocatalyst is about 2.6eV. It is concluded that the sensitized catalyst has absorption in the visible region.

Figure 2 gives the results of H_2 evolution, from water under irradiation, on TMPP sensitized TiO_2 nanotube photocatalyst, pure TiO_2 nanotube, and TMPP. The simulated sunlight source was a

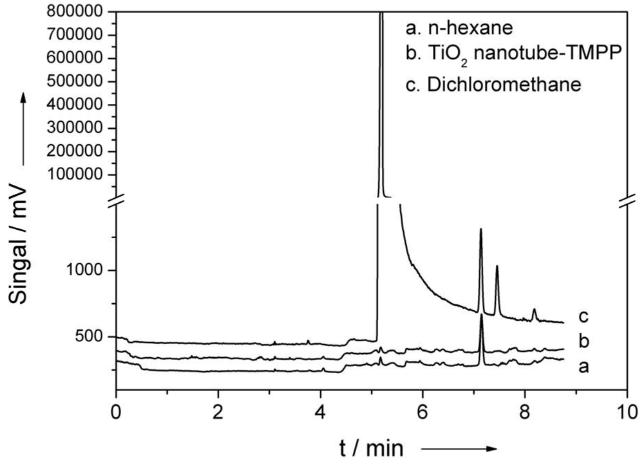

Figure 3. GC-ECD chromatogram maps of 1 μL diluting solutions of n-hexane blank a), 1 μL TMPP sensitized TiO_2 nanotube photocatalysts b), and 1 μL standard solution of dichloromethane c). Other conditions list in experimental section.

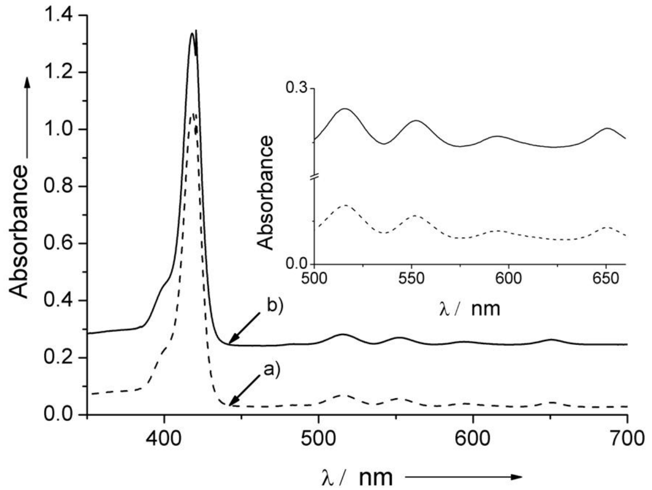

Figure 4. UV-Vis spectra of TMPP sensitized TiO_2 nanotubes photocatalysts after reaction (a), and before reaction (b). The samples were solved in acetone during the UV-Vis detection.

350 W Xe lamp with a 420 nm cut-off filter. There was clear evidence for H_2 evolution from pure water on TMPP sensitized TiO_2 nanotube, whereas no H_2 evolution was observed on pure TiO_2 nanotubes and TMPP under visible light. TiO_2 nanotube have a wide band-gap (~3.5 eV) that cannot be excited by visible light. TMPP can adsorb the energy of visible light. If there are no appropriate acceptors, the excited energy will lost before electron transfer. In the case of the TMPP sensitized TiO_2 nanotube catalyst, the energy of the TMPP from visible light can transfer to TiO_2 nanotubes, which yield electron-hole pairs for water splitting. Even under the pure water, the initial rate of H_2 evolution over 0.1 g TMPP sensitized catalyst is 8 μmol·h. Considering the irradiated area (12.56 cm^2), the quantity of H2 evolution is 1.427 L $m^{-2}h^{-1}g^{-1}$. Although a slight deactivation was observed during the photocatalytic reaction, the activity remained comparatively stable over 6 h under pure water.

To confirm that the H_2 evolution was indeed from pure water a further series of measurements were taken. An Agilent 6890N gas chromatograoh (GC) equipped with an electron-capture detector (ECD) was used to detect any residual CH_2Cl_2 in the sensitized catalyst. However, the possibility of release of hydrogen from CH_2Cl_2 by a photocatalytic is very remote. Figure 3 shows a set of chromatograms for 1μL n-hexane blank, 1μL of the sensitized catalyst and 1μL of CH_2Cl_2. No treace of CH_2Cl_2 was found in the sensitized catalyst. The initial vacuum drying at 90°C was sufficient to remove all the CH_2Cl_2. It was concluded that the evolved hydrogen came from water.

UV-Vis spectroscopy was used to examine the photocatalyst before and after the photocatalytic reaction. The results are given in figure 4. The spectra of TMPP sensitized TiO_2 nanotube photocatalyst did not undergo changes. The Soret band (420 nm) is unchanged after the photocatalytic reaction. And the four absorption bands between 500 nm and 700 nm were the same. This indicated that the photocatalytic reaction, over a 6h period, did not destroy the skeleton of the photosensitizer.

4. CONCLUSION

In conclusion, we have demonstrated significant progress towards the goal of enhancing the photocatalytic activity of TiO_2 nanotube under visible light, which was sensitized by TMPP, by using TiO_2 nanotube as a starting material for preparing a novel photocatalyst with a smaller band gap (2.6 eV). The investigation shows that a photosensitized catalyst combined TiO_2 nanotube with TMPP can be used to extend the absorption of solar light region and enhance the efficiency of energy conversion. Although in this study quantity of H_2 evolution from water was not too high, it was a way to apply the dye sensitized TiO_2 nanotubes photocatalyst in the visible light for clean energy and TiO_2 nanotubes could find use in other applications. Overall speaking, our interpretation on this observed improvement is still quite preliminary, and further mechanistic investigation is still under way in our research group.

5. ACKNOWLEDGEMENT

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