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Research Article

Photocatalytic Reduction of CO_2 to Methane on Pt/TiO_2 Nanosheet Porous Film

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Anatase TiO_2 nanosheet porous films were prepared by calcination of the orthorhombic titanic acid films at 400°C. They showed an excellent photocatalytic activity for CO_2 photoreduction to methane, which should be related to their special porous structure and large Brunauer-Emmett-Teller (BET) surface area. In order to further improve the photocatalytic activity, Pt nanoparticles were loaded uniformly with the average size of 3-4 nm on TiO_2 porous films by the photoreduction method. It was found that the loading of Pt expanded the light absorption ability of the porous film and improved the transformation efficiency of CO_2 to methane. The conversion yield of CO_2 to methane on Pt/TiO_2 film reached 20.51 ppm/h·cm^2. The Pt/TiO_2 nanosheet porous film was characterized by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscope (TEM), and ultraviolet-visible light diffuse reflectance spectra (UV-vis DRS). Moreover, the transient photocurrent-time curves showed that the Pt/TiO_2 nanosheet porous film exhibited higher photocurrent, indicating that the higher separation efficiency of the photogenerated charge carriers was achieved.

1. Introduction

Fossil fuels are our primary source of energy. Unfortunately, CO_2 emissions generated in using these fuels have drastically increased in atmosphere in recent years, and the fast-growing CO_2 leads to climate change, which has become one of the greatest threats of environmental problems. It is very urgent to reduce the accumulation of CO_2 in the atmosphere. In general, the photocatalytic reduction of CO_2 is a possible avenue to convert CO_2 into hydrocarbon fuels, because reducing the amount of CO_2 will not only meet the purpose of environmental protection but also provide raw materials for chemical industry. This process utilizes ultraviolet (UV) and/or visible light as the excitation source for semiconductor catalysts, and the photoexcited electrons reduce CO_2 with H_2O on the catalyst surface and form energy-bearing products such as carbon monoxide (CO), methane (CH_4), methanol (CH_3OH), formaldehyde (HCHO), and formic acid (HCOOH) [1].

Many researchers [2] have shown that CO_2 could be reduced by water vapor or solvent with photocatalysts. Among these photocatalysts, TiO_2 or TiO_2-based materials may promote the photoreduction of CO_2 to useful organic compounds [3–9]. Moreover, TiO_2 is one of the most intensively studied and widely used photocatalysts as a result of a number of advantageous features such as low cost, relatively high catalytic activity, low toxicity, and high chemical stability [10–12]. Especially modification of TiO_2 through noble metal supporting is increasingly being considered for maximising its photocatalytic efficiency. These metals may facilitate electron-hole separation and promote interfacial electron transfer or they may decrease the TiO_2 band gap, which benefits electrons transfer from the valence band to the conduction band, facilitating the formation of oxidative species. The TiO_2-based nanomaterials, especially the titanate network films, obtained by the hydrothermal method often have large BET surface area and strong adsorption ability [13]. It is noticeable that the surface network structure of the film can enhance the adsorption of the reactive species and absorption efficiency of the incident light and further improve the photocatalytic activity [14–16].

Herein, anatase TiO_2 nanosheet porous films were obtained by calcination of the orthorhombic titanic acid films at 400°C. Because the surface of titanic acid consists of

the porous network structure [17], the obtained anatase TiO_2 has stronger absorption ability and higher photocatalytic performance compared with the film prepared by sol-gel method in the same condition. Moreover, it is noticeable that the porous structure of the film also can enhance the adsorption of the reactive species and absorption efficiency of the incident light [14–16]. In order to further improve the photocatalytic activity, Pt nanoparticles were loaded on the surface of it as an electron trapper to capture the photogenerated electrons by the photoreduction method. The relationship between the morphology, structure, and their photocatalytic activity was investigated in detail.

2. Experimental

2.1. Preparation of TiO_2 and Pt-TiO_2 Nanosheet Porous Films. The precursor for preparing TiO_2 porous film was titanate nanotube (TAN) porous film, and the typical preparing process of TAN film was as follows: a Ti thin foil with a size of $2*4\ cm^2$ was put into 100 mL of 10 M NaOH aqueous solution, followed by the hydrothermal treatment in a 120 mL Teflon-lined autoclave at 120°C for 24 h. After cooling down, the obtained titanate network film was washed with distilled water several times and then immersed in a 0.1 M HCl aqueous solution overnight. After that, the product was washed several times with water and then dried in the N_2 stream.

TiO_2 nanosheet porous films were prepared by calcination of TAN films at 400°C for 4 h in air. Then, Pt nanoparticles were loaded by the photoreduction method in H_2PtCl_6 ethanol solution. The solution was illuminated under UV light for 1 h. After that, the sample was washed with deionized water and dried. For a comparison, a TiO_2 film prepared by a sol-gel method was used as a reference [18]; the sample was denoted by R-TiO_2.

2.2. Characterization. UV-vis diffuse reflectance spectra (DRS) were obtained on a Shimadzu U-3010 spectrometer, using $BaSO_4$ as a reference. X-ray diffraction (XRD) patterns were measured on an X'Pert Philips diffractometer (Cu Kα radiation; 2θ range 5–90°, step size 0.08°, accelerating voltage 40 kV, and applied current 40 mA). The particle size and surface morphology of the samples were observed using a scanning electron microscope (SEM) (JSM-7100F, JEOL Co., Japan) and transmission electron microscope (TEM) (JEM-2010, JEOL Co., Japan).

2.3. Photoelectrochemical Measurements. The transient photocurrent-time (I-t) experiments were conducted using a conventional three-electrode system on the electrochemical analyzer (IM6ex, Germany). The photocatalyst film served as the working electrode, and a Pt meshwork and an Ag/AgCl electrode (SCE) acted as the counter electrode and reference electrode, respectively. The electrolyte was Na_2SO_4 with a concentration of $0.5\ mol{\cdot}L^{-1}$.

2.4. Photocatalytic Activity Evaluation. The photocatalytic reduction of CO_2 was conducted in a flat closed reactor with the inner capacity of 358 mL containing 20 mL 0.1 mol/L $KHCO_3$ solution. The prepared TiO_2 nanosheet porous film was located in the center of the reactor and then the ultrapure gaseous CO_2 and water vapor was flowed through the reactor for 2 h to achieve the adsorption-desorption equilibrium. Before illumination, the reactor was sealed. The light source was the high pressure Hg lamp with 300 W, and the intensity of the incident light was measured to be $10.4\ mW/cm^2$. The photocatalytic reaction was typically performed at room temperature for 6 h. The products were measured by gas chromatography (GC). The comparison tests consisted of a reaction under light without the catalysts and a reaction in dark with the catalysts. The results indicated that there was almost no methane production in the comparison experiments.

3. Results and Discussions

3.1. Phase Structure, Morphology, and Optical Absorption of Pt-Loaded TiO_2 Nanosheet Porous Film. The phase structure of the titania films was analyzed by the XRD technique. As shown in Figure 1(a), the TiO_2 film belongs to the typical anatase phase. In our previous work, we knew that TAN precursor belonged to the orthorhombic system [19]. This indicated that the orthorhombic TAN has been transformed to anatase TiO_2 completely after being calcined at 400°C for 4 h. There still existed some characteristic peaks of metallic Ti at 40.2°, 63.1°, and 70.7°, indicating that only the surface of the Ti foil reacted with NaOH, and the interior still remained as Ti metal. When Pt nanoparticles were loaded on the surface of TiO_2 nanosheet porous films, the anatase phase did not change. And no apparent Pt diffraction signals appeared; this may be due to the ultrafine dispersion of Pt nanoparticles on TiO_2 nanosheet porous films and its low loading amount. However, the EDS results verified that Pt nanoparticles were successfully modified on the TiO_2 nanosheet porous films (as shown in Figure 1(b)); the mole ratio of Pt to TiO_2 was estimated to be ca. 0.14%.

Figure 2 shows the surface morphology of the Pt-loaded TiO_2 nanosheet porous films. As can be seen from Figure 2(a), anatase TiO_2 film consisted of many thin nanosheets, and the surface of the film looks like porous structure. Figure 2(b) showed that some Pt nanoparticles were successfully deposited on the surface of TiO_2 nanosheet porous film and were homogeneous both in size and in shape. To further observe the morphology of TiO_2 film, some powders were peeled off from the substrate, and their TEM images are shown in Figures 2(c) and 2(d); we can clearly see that Pt nanoparticles are very uniform, and their particle sizes are only 3-4 nm. On one hand, the porous nanosheet structure of this kind of TiO_2 film occupied larger BET surface area than the common TiO_2 film obtained by the sol-gel method, so it can increase the adsorption amount of the reactive species and then accelerate the photocatalytic reaction rate. On the other hand, more irradiated light can be utilized for the porous TiO_2 film because of the multiple scattering and reflection of the incident light in the channels of the porous film [17, 20, 21], so the utilization efficiency

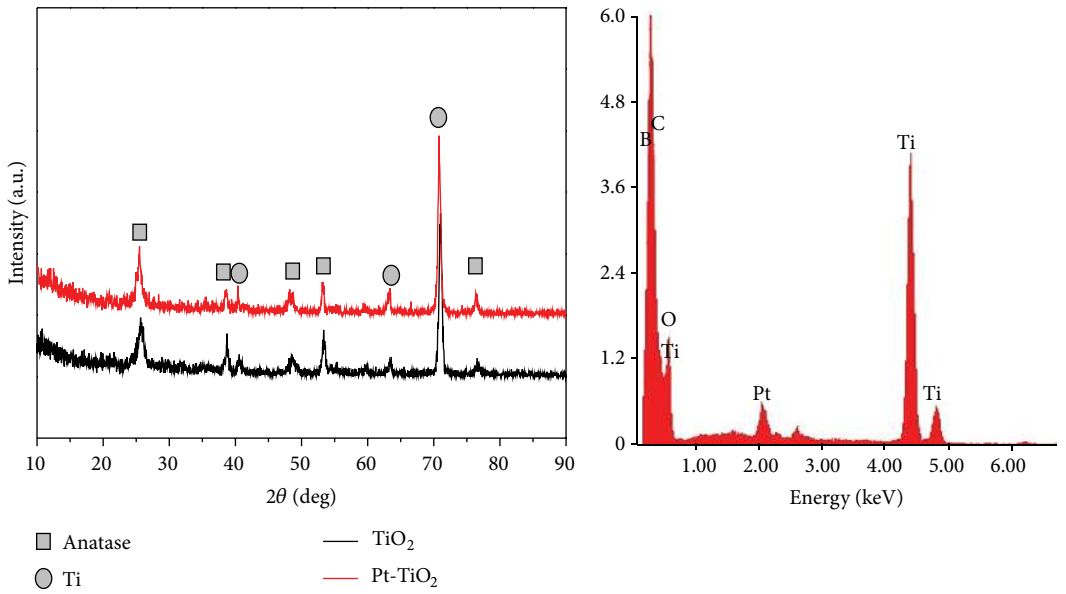

FIGURE 1: XRD patterns of TiO_2 and Pt-TiO_2 nanosheet films.

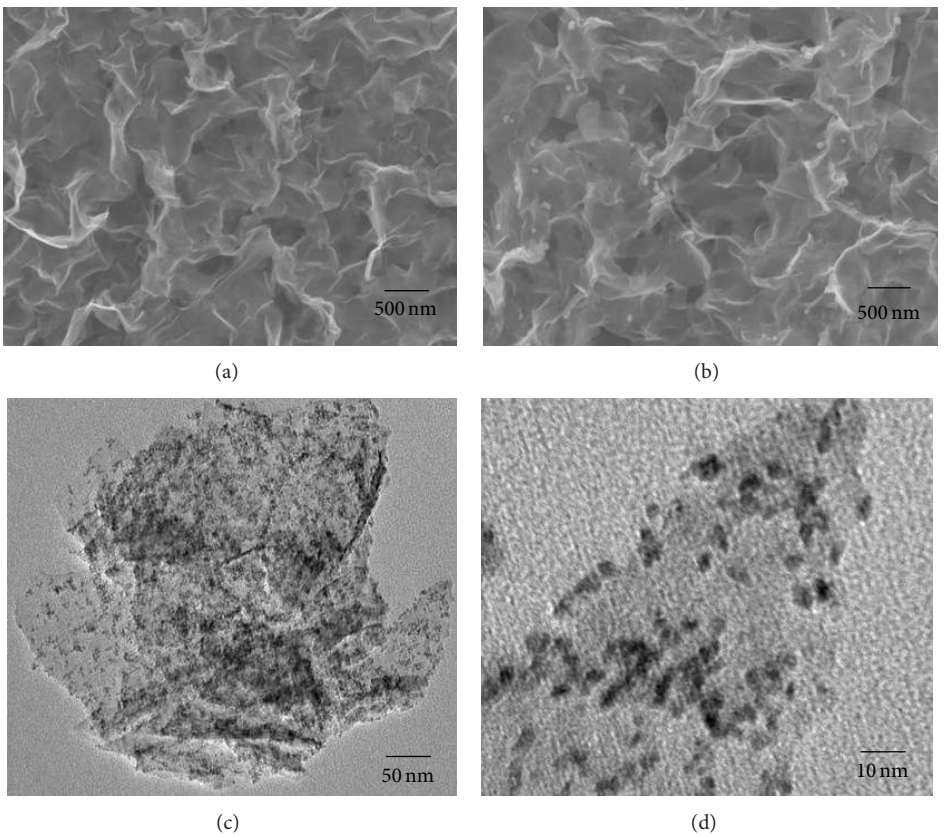

FIGURE 2: SEM images of TiO_2 and Pt-TiO_2 nanosheet films.

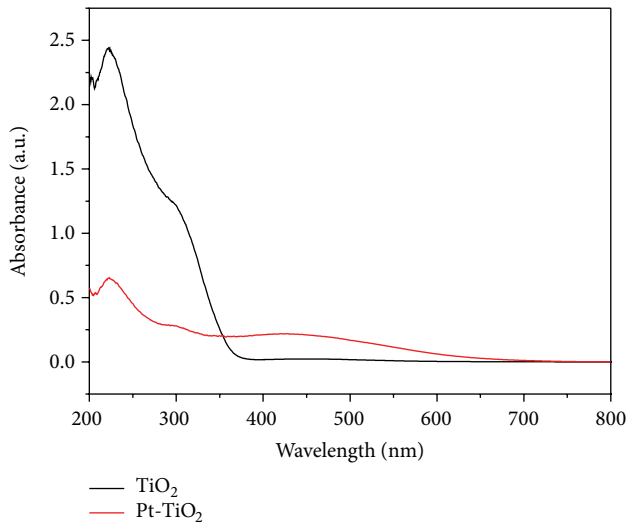

FIGURE 3: UV-vis DRS spectra of TiO_2 and Pt-TiO_2 nanosheet films.

of the incident light was increased and thereby did favor for improving the photocatalytic activity.

The optical absorption of the nanosheet porous films was shown in Figure 3. The absorption band edge of TiO_2 porous film was 380 nm. In our previous work [13, 22], we found that the onset absorption of the titanate acid was about 350–360 nm. So from the change of the absorption band, we can conclude that the titanate acid had transformed to anatase TiO_2 successfully by the calcination of 400°C. While Pt nanoparticles were loaded on the surface of the TiO_2 porous film, a broad peak at around 350–550 nm was observed, which should be due to the plasma resonance absorption of the Pt nanoparticles [23]. Moreover, the absorbance intensity of the film in the UV light region reduced, which should be because the loaded Pt nanoparticles shield some absorption of TiO_2 nanosheets.

3.2. Photoreduction of CO_2 on Pt-Loaded TiO_2 Nanosheet Porous Film. The photoreduction of CO_2 to methane was tested as a probe reaction to evaluate the photocatalytic activity of the catalyst films. As shown in Figure 4(a), the production rate of CH_4 on Pt-loaded TiO_2 nanosheet porous film reached 20.51 ppm/h·cm^2. To confirm the photocatalytic reduction process of CO_2 to CH_4, the related reference experiments were carried out. When the system was kept in dark, there was no CH_4 produced, indicating that the photoexcited process of Pt-loaded TiO_2 was essential in the photoreduction of CO_2. When the experiment was carried out in the absence of H_2O, almost no CH_4 was detected. That implying that water is also one of the key roles for CO_2 photoreduction. When a blank Ti foil with the same area of Pt-loaded TiO_2 film was put into the system, the production rate of CH_4 was only 1.01 ppm/h·cm^2. This slow production rate of CH_4 should be due to the thin oxide layer on Ti foil surface.

In addition, some comparative experiments about Pt-loaded TiO_2, TiO_2 porous film, and ordinary R-TiO_2 obtained by the sol-gel method proceeded. As can be seen, under the same experiment conditions, the production rate of CH_4 on Pt-loaded TiO_2, TiO_2, and R-TiO_2 was 20.51, 3.71, and 1.45 ppm/h·cm^2, respectively. Obviously, the photocatalytic activity of the Pt-TiO_2 nanosheet porous film was much higher than that of TiO_2 and R-TiO_2 film; the possible reasons were listed as follows. Firstly, it is commonly known that Pt could promote the interparticle charge migration and facilitate the photogenerated electrons transfer from conduction band of the TiO_2 to Pt particles, so as to provide adequate electrons for the reduction of carbon dioxide to methane [24]. The charge carrier separation ability of Pt nanoparticles was verified by the transient photocurrent-time curve. As shown in Figure 4(b), the photocurrent density of TiO_2 and Pt-TiO_2 nanosheet film was 0.006 and 0.017 mA·cm^{-2}, respectively. The photocurrent density of Pt-TiO_2 was apparently larger than that of TiO_2, indicating that its separation efficiency of the photogenerated charge carriers was higher. Secondly, the large BET surface area and strong adsorption ability of the TiO_2 nanosheet porous structure can provide more adsorption sites for CO_2 molecules, so the localized concentration of CO_2 on the surface of TiO_2 porous film would be higher, which would accelerate the photoreduction reaction of CO_2 to methane. Thirdly, the porous and incompact structure of the TiO_2 nanosheet porous film would facilitate the use of more irradiated light, because more light can be scattered and reflected in the channels and pores of TiO_2 film [25].

3.3. Proposal of the Photoreduction Mechanism of CO_2 to Methane on Pt-Loaded TiO_2 Nanosheet Porous Film. The photoreduction mechanism of CO_2 to methane on Pt-loaded TiO_2 nanosheet porous film was proposed in Figure 5. Most researchers agree that this process is based on proton-assisted multielectron transfer instead of single electron transfer, as the electrochemical potential of −2.14 V versus SCE for a single electron process is highly unfavorable [26]. When Pt-loaded TiO_2 nanosheet porous film was illuminated by UV light, photon-generated electrons (e^-) and holes (h^+) are created on the surface of the TiO_2 nanosheets. The excited holes reacted with adsorbed water molecules on the catalyst surface to produce hydroxyl radicals ($^\bullet$OH) and hydrogen ions (H^+) and further oxidized by $^\bullet$OH radicals to produce O_2 and H^+ [27]. And H^+ would interact with the excited electrons to form $^\bullet$H radicals. At the same time, the photogenerated electrons on the conduction band of TiO_2 can be easily trapped by Pt nanoparticles because of the lower Fermi energy level of the noble metal [28], and then they would transfer rapidly to the absorbed CO_2 for photoreduction reaction. CO_2 molecules would interact with the excited electrons to form to $^\bullet CO_2^-$ radicals, and then reacted with $^\bullet$H on the catalyst surface to produce CH_4 [1, 28, 29]. It is known that the formation of CH_4 requires eight electrons, and the enriched electron density on Pt nanoparticles would favor the formation of CH_4, which is thermodynamically

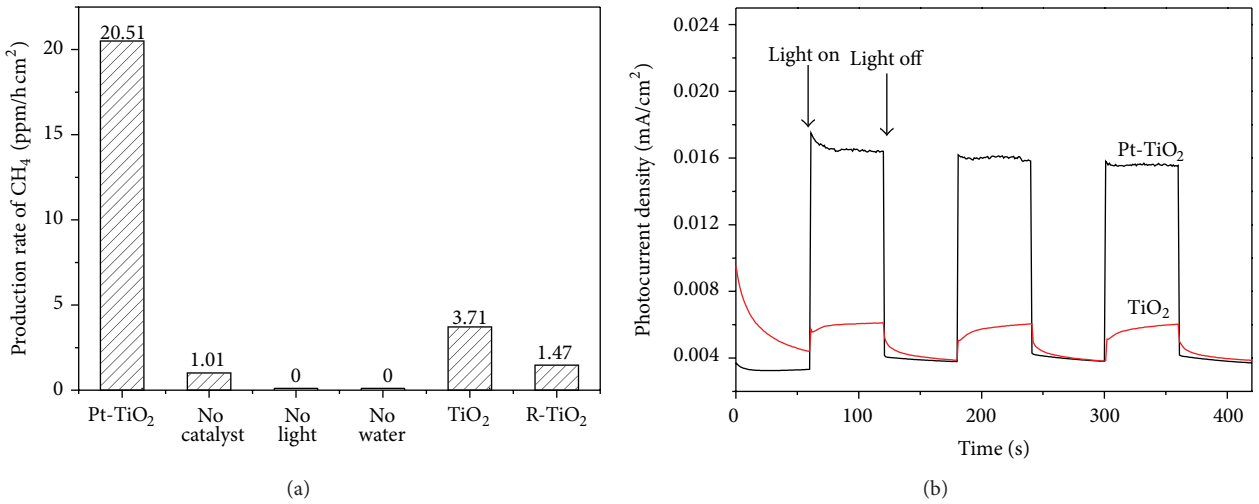

FIGURE 4: Evolution yield of CH_4 and photocurrent-time curve of TiO_2 and Pt-TiO_2 network film under UV irradiation in same conditions.

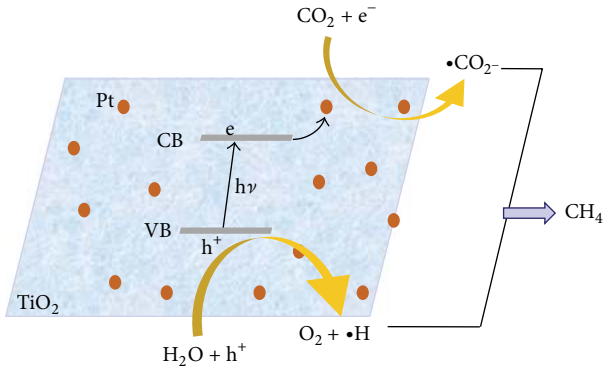

FIGURE 5: Photoreduction mechanism of CO_2 to methane on Pt-loaded TiO_2 nanosheet porous film.

more feasible. The possible process would have undergone the following pathway:

$$
\begin{aligned}
&TiO_2 \xrightarrow{h\nu} h^+ + e^- \\
&H_2O + h^+ \longrightarrow {}^{\bullet}OH + H^+ \\
&{}^{\bullet}OH + H_2O + 3h^+ \longrightarrow 3H^+ + O_2 \\
&H^+ + e^- \longrightarrow {}^{\bullet}H \\
&CO_2 + e^- \longrightarrow {}^{\bullet}CO_2^- \\
&CO_2 + 2\,{}^{\bullet}H \longrightarrow CO + H_2O \\
&{}^{\bullet}CO_2^- + 8\,{}^{\bullet}H + h^+ \longrightarrow CH_4 + H_2O \\
&CO + 6\,{}^{\bullet}H \longrightarrow CH_4 + H_2O
\end{aligned}
\tag{1}
$$

4. Conclusions

Anatase TiO_2 nanosheet porous films obtained by calcination of the orthorhombic titanic acid films exhibited better performance for the photoreduction of CO_2 to methane. In order to further improve the photoactivity, Pt nanoparticles with the particle size of 3-4 nm were loaded on the TiO_2 porous films uniformly. The EDS results confirmed the mole ratio of Pt to TiO_2 was ca. 0.14%. The conversion yield of CO_2 to methane on Pt/TiO_2 film reached 20.51 ppm/h·cm^2. The transient photocurrent-time curves showed that the Pt/TiO_2 nanosheet porous film exhibited higher photocurrent, so the higher separation efficiency of the photogenerated charge carriers should be the main reason for the high photoreduction activity of CO_2.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Authors' Contribution

Li Qiu-ye and Zong Lan-lan contributed equally to this work.

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