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Photoreduction of \( \text{CO}_2 \) on \( \text{TiO}_2/\text{SrTiO}_3 \) Heterojunction Network Film

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Abstract

Nanotube titanic acid (NTA) network film has a porous structure and large BET surface area, which lead them to possessing high utilization of the incident light and strong adsorption ability. We used NTA as the precursor to fabricate a \( \text{TiO}_2/\text{SrTiO}_3 \) heterojunction film by the hydrothermal method. In the process of the reaction, part of NTA reacted with \( \text{SrCl}_2 \) to form \( \text{SrTiO}_3 \) nanocubes, and the remainder dehydrated to transform to the rutile \( \text{TiO}_2 \). The ratio of \( \text{TiO}_2 \) and \( \text{SrTiO}_3 \) varied with the hydrothermal reaction time. SEM and TEM images indicated that \( \text{SrTiO}_3 \) nanocubes dispersed uniformly on \( \text{TiO}_2 \) film, and the particle size and crystallinity of \( \text{SrTiO}_3 \) nanocubes increased with the reaction time prolonging. The \( \text{TiO}_2/\text{SrTiO}_3 \) heterojunction obtained by 1 h showed the best activity for \( \text{CO}_2 \) photoreduction, where the mole ratio of \( \text{TiO}_2 \) and \( \text{SrTiO}_3 \) was 4:1. And the photo-conversion efficiency of \( \text{CO}_2 \) to \( \text{CH}_4 \) improved remarkably after the foreign electron traps of Pt and Pd nanoparticles were loaded. The highest photocatalytic production rate of \( \text{CH}_4 \) reached 20.83 ppm/h cm\(^2\). In addition, the selectivity of photoreduction product of \( \text{CO}_2 \) was also increased apparently when Pd acted as the cocatalyst on \( \text{TiO}_2/\text{SrTiO}_3 \) heterojunction film.

Keywords: Nanotube titanic acid; Porous network film; \( \text{TiO}_2/\text{SrTiO}_3 \) heterojunction; \( \text{CO}_2 \) photoreduction; Product selectivity

Background

Nowadays, the fossil fuels are still the main energy resource for our society. However, the shortage of fossil fuels and the growing environmental concerns due to the emission of large amounts of \( \text{CO}_2 \) during the combustion of fossil fuels have become the global problems. Conversion of \( \text{CO}_2 \) into useful hydrocarbon fuels is a possible avenue to develop alternative fuels, and prevent the green house effect on the global temperature. For example, the chemical conversion of \( \text{CO}_2 \) into industrially beneficial compounds is advantageous in terms of green and sustainable chemistry because \( \text{CO}_2 \) is an inexpensive, nontoxic and abundant C1 feedstock [1]. Particularly, catalytic conversion of \( \text{CO}_2 \) to hydrocarbon fuels and chemicals have attracted much attention in recent years [2–6]. At the same time, \( \text{TiO}_2 \)-based materials are the most common photocatalysts because of their many advantages. Especially, one-dimensional \( \text{TiO}_2 \) nanostructures have become of increasing importance in applications of photocatalysis, photoelectron-chemical process, and dye-sensitized solar cells due to their superior properties in comparison with other \( \text{TiO}_2 \) nanstructured counterparts [7–12]. Besides, \( \text{TiO}_2 \)-based nanomaterials, especially the layered titanate nanotubes, obtained by the hydrothermal method possess the large BET surface area, strong ion-exchange capacity, and strong adsorption ability [13]. The high recombination of the photo-generated charge carriers leads to the low photocatalytic activity of \( \text{TiO}_2 \)-based nanomaterials. In order to overcome this drawback, forming a heterojunction structure by combing \( \text{TiO}_2 \) with another semiconductor is considered to be one of the efficient ways to suppress the recombination of the photo-excited electron-hole pairs and to enhance the photocatalytic efficiency [14, 15]. \( \text{SrTiO}_3 \) with the perovskite structure is one of semiconductors with a flat band potential lower than that of \( \text{TiO}_2 \), and it is easily to be formed a heterojunction structure with \( \text{TiO}_2 \) in the preparation process [16–19]. In this regard, the photo-generated electrons would centralize on the conduction band of \( \text{TiO}_2 \), and the holes would concentrate on the valence band of \( \text{SrTiO}_3 \).
under UV light irradiation, and as a result, the recombination efficiency of the photo-generated charge carriers is inhibited, and thereby the photocatalytic activity would be improved [20].

On the basis of above consideration, we intent to fabricate the TiO$_2$/SrTiO$_3$ heterojunction structure film by the hydrothermal method. Herein, the cubic SrTiO$_3$ was achieved by hydrothermal treatment of the orthorhombic titanic acid in SrCl$_2$ aqueous solution by adjusting pH = 13. Notably, by simply tuning reaction time, the crystallinity, morphology and the amount of SrTiO$_3$ nanostructures can be controlled easily. The TiO$_2$/SrTiO$_3$ heterostructure film exhibited the good photocatalytic performance for CO$_2$ photoreduction. In order to further improve the transformation yield, the foreign electron traps of Pt and Pd nanoparticles were loaded on the film by the photoreduction approach. The relationship between the photocatalytic properties of TiO$_2$/SrTiO$_3$ heterostructure film with their morphology and structure was investigated systematically.

**Methods**

**Preparation of the Film Photocatalysts**

Ti foil with a size of 2 cm $\times$ 4 cm was put into an autoclave containing a concentrated 10 M NaOH aqueous solution, and then reacted at 120 °C for 24 h. After cooling down, the obtained film was washed with distilled water several times, and then immersed in 0.1 M HCl aqueous solution for 12 h to obtain the titanic acid nanotubes film (TAN). After that, TAN was put into an autoclave containing 80 mL 0.05 M SrCl$_2$ aqueous solution, and the pH value of the solution was adjusted to 13 by NaOH solution. The autoclave was kept at 120 °C for 1 h, 2 h, and 3 h respectively. The as-fabricated films were washed with deionized water several times, and then dried with the stream of N$_2$. The samples obtained in the different reaction time were denoted as TS1, TS2, and TS3, respectively. In order to further increase the photocatalytic performance, the foreign electron traps of Pt and Pd nanoparticles were deposited on the TS1 surface by photoreduction of H$_2$PtCl$_6$ and PdCl$_2$ solution under the irradiation of the high-pressure mercury lamp for 1 h. The obtained products were denoted as TS1-Pt and TS1-Pd.

**Characterization**

X-Ray powder diffraction (XRD) patterns of the films were measured on a Philips X’Pert Pro X-ray diffractometer (Holland) (Cu Kα radiation; 2θ range 5 ~ 70°, step size 0.08°, time per step 1.0 s, accelerating voltage 40 kV, and applied current 40 mA). The morphologies of the samples were taken on SEM (JSM-7100 F, JEOL Co., Japan) and TEM (JEM-2010, JEOL Co., Japan). X-ray photoelectron spectra (XPS) were recorded with a Kratos AXIS Ultra spectrometer (excitation source: monochromatized Al Kα (hv = 1486.6 eV); voltage 15 kV, current 10 mA). And the C 1 s binding energy of hydrocarbon (284.8 eV) was used as the standard for the correction of charging shift.

**Evaluation of Photocatalytic Activity**

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 samples were located in the center of the reactor and then the ultra-pure 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$^2$. Both sides of the Ti foil have transformed to TiO$_2$/SrTiO$_3$ heterojunction film, but only one side under the light irradiation took part in the CO$_2$ photo-reduction reaction. The photocatalytic reaction was typically performed at room temperature for 6 h. The concentration of CO, CO$_2$, and CH$_4$ were measured by a gas-chromatography (GC). Moreover, the electrochemical impedance spectroscopy (EIS) properties were measured in 0.05 M Na$_2$SO$_3$ aqueous solution using a three-electrode photoelectrochemical cell with TS film as the working electrode, an Ag/AgCl electrode as the reference, and a platinum meshwork as the counter electrode.

**Results and Discussion**

**Phase Structure of the Porous Film**

The phase structure of the films was measured by the XRD technique. As illustrated in Fig. 1, curve a showed that the titanic acid nanotube (TAN) film belongs to the orthorhombic structure, which is consistent with our
previous work [21]. There are some characteristic peaks at 38.5°, 40.2°, 63.1°, and 70.7°, which were indexed to the metallic Ti. That indicated only the surface of the Ti foil transformed to TAN after reacting with NaOH, and the interior part still remained as Ti metal. After hydrothermal treatment of TAN film in SrCl₂ solution at 120 °C for 1 h, additional diffraction peaks at 22.7°, 32.2°, 46.3°, 57.6°, and 67.8° appeared, which were corresponded to the (100), (110), (200), (211), and (220) crystal planes of cubic SrTiO₃, respectively (as shown in curve b). This result indicated that part of TAN successfully converted into the cubic SrTiO₃. At the same time, two peaks at about 27.46° and 44.08° of rutile TiO₂ appeared, indicating that the residue TAN converted to rutile in the base solution. When the reaction time prolonged to 2 h, the peaks of TiO₂ disappeared, that illustrated TAN transformed into SrTiO₃ completely (as shown in curve c). As the increase of the reaction time, the peak intensity of SrTiO₃ increased by comparing curve b and c, which indicated that the crystallinity of the cubic SrTiO₃ improved.

**Morphology and Composition Analysis of TiO₂/SrTiO₃ Heterostructure**

Figure 2 shows the FE-SEM images of TAN and TiO₂/SrTiO₃ heterostructure films. From Fig. 2a, we can see that TAN film consisted of a large amount of nanotubes, and many nanotubes intertwined together to form a porous an incompact structure. The diameters of TAN nanotubes were uniform, and their lengths expanded to several micrometers. The inset figure showed that the thickness of TAN film was about 1.6 μm. Figure 2b illustrated that some cubic nanoparticles emerged in TAN films, indicated that part of TAN has transformed to SrTiO₃. As the increase of the reaction time, TAN disappeared and transformed to SrTiO₃ nanoparticles completely (shown in Fig. 2c). When the reaction time increased to 3 h, the irregular SrTiO₃ nanoparticles grew to the regular SrTiO₃ nanocubes, indicating that the crystallinity becomes better. The above results were in accordance very well with the XRD results. And the average particle size of SrTiO₃ nanocubes in Fig. 2d was about 70–80 nm. To further observe the morphology of TiO₂/SrTiO₃ heterojunction strucuture, some powders were peeled off from the film. The TEM images in Fig. 3 illustrated that, TiO₂ nanotubes and SrTiO₃ nanocubes co-existed in the TiO₂/SrTiO₃ heterojunction strucuture. The diameter of TiO₂ nanotubes was about 8–10 nm, and SrTiO₃ nanocubes were ca. 80 nm, which consisted with the SEM results. From Fig. 3b, we can obviously found that the figure lattice spacing of SrTiO₃ nanocubes was regular and clear, indicating that the crystallinity of SrTiO₃ was very good. And Fig. 3c showed that TiO₂ nanotubes and SrTiO₃ nanocubes formed a very closely heterjunction structure, which should be favorable for the separation of the charge carriers. The phase composition of TiO₂/SrTiO₃ heterojunction was also measured by XPS techniques (shown in Fig. 3d). The XPS spectrum of Ti 2p was wide and asymmetric, which indicated that there could be more than one chemical state according to the binding energy [20, 22]. Using the XPS Peak fitting program, the Ti 2p XPS spectrum could be fitted to two kinds of chemical states, that was ascribed to Ti⁴⁺/TiO₂ and Ti⁴⁺/SrTiO₃, respectively [23]. The mole ratio of TiO₂ and SrTiO₃ was tested to be 4:1.
Photoreduction of CO$_2$ on TiO$_2$/SrTiO$_3$ Heterojunction Films

The photo-reduction reaction of CO$_2$ was selected to evaluate the photocatalytic activity of TiO$_2$/SrTiO$_3$ heterojunction films. As shown in Fig. 4, the production rate of CH$_4$ on TS1, TS2, and TS3 films was 3.67, 2.73, and 3.37 ppm/h·cm$^2$, respectively. From the above XRD and SEM result, we knew that TS1 was TiO$_2$/SrTiO$_3$ heterojunction films, and the main composition of TS2 and TS3 was SrTiO$_3$. These results indicated that the TiO$_2$/SrTiO$_3$ heterojunction exhibited the best photocatalytic activity of CO$_2$ photoreduction to CH$_4$. The reasons of the high photo-activity of TiO$_2$/SrTiO$_3$ film can be attributed to three aspects. Firstly, the efficient heterojunction by direct coupling of TiO$_2$ and SrTiO$_3$ nanostructures during short duration hydrothermal treatment caused the Fermi level to equilibrate and reduced the recombination of charge carriers at the surface of the heterostructure. And thus favored the separation of photogenerated electrons-holes pairs and improved the photo-conversion efficiency [24]. Secondly, the large BET surface areas and strong adsorption capability of the TiO$_2$/SrTiO$_3$ network structure would facilitate more CO$_2$ molecules to adsorb, and thus the localized concentration of CO$_2$ molecules would be higher, which would enhance the photoreduction reaction rate of CO$_2$ to methane. Thirdly, more light can be scattered or reflected in the porous and incompact structure of the TiO$_2$/SrTiO$_3$ network film, so the utilization yield of the irradiated light would be improved [25]. Comparison the photoactivity of TS2 and TS3, we found that the photoreduction rate of CO$_2$ on TS3 was higher, which should be due to the high crystallinity of TS3 nanocubes.

As an effective tool for probing the features of surface-modified electrodes, electrochemical impedance spectroscopy (EIS) was employed to analyze the electron transport properties of TiO$_2$/SrTiO$_3$ (TS) electrodes. As shown in Fig. 5, the impedance arc radius of TS1 was much smaller than TS2 and TS3, and that of TS2 was the largest. EIS spectrum often displays the conductivity of an electrode, and a larger arc radius usually illustrates
a higher charge transfer resistance [26–28]. So, the EIS results indicated that the separation and transfer efficiency of the photo-generated charge carriers of TS1 was much higher than that of TS2 and TS3, which is consistent very well with their photocatalytic activity.

To confirm the real photocatalytic reduction process of CO$_2$ to CH$_4$ on TiO$_2$/SrTiO$_3$ heterojunction films, some related reference experiments were conducted. When the reaction was preceded in dark, there was no CH$_4$ detectable, indicating that the photo-excited process of TS film was essential in the photo-reduction of CO$_2$. When the experiment was conducted in the absence of H$_2$O, almost no CH$_4$ was produced. That should be due to no reduce species (H$^+$) took part in the photo-reduction of CO$_2$. If we use the NTA nanotube film to replace TS film, there was also no photoactivity. The above comparison experiments illustrated that the conversion of CO$_2$ to CH$_4$ on TS films was indeed the photo-reduction process.

Photocatalytic Activity on Pt (or Pd) Loaded TiO$_2$/SrTiO$_3$ Heterojunction Films

In order to further raise the photocatalytic activity of TS film, Pt and Pd nanoparticles were loaded on TS1 film by the photoreduction method. As shown in Fig. 6, Pt and Pd nanoparticles with the average size of 4–6 nm dispersed uniformly on TiO$_2$ nanotubes. Due to the similar size of Pt (or Pd) nanoparticles and the TiO$_2$ nanotube diameters, so it is easily to observe and distinguish the loaded noble metals. However, the particle size of SrTiO$_3$ nanocubes is about 70–80 nm, and the crystallinity of SrTiO$_3$ in TS1 is not very good, and thus the borderline of SrTiO$_3$ nanocubes is not clear, so it is difficult to differentiate the loaded small Pt and Pd nanoparticles. Because Pt and Pd nanoparticles were loaded on TS1 by the photoreduction, they should be dispersed on both TiO$_2$ nanotubes and SrTiO$_3$ nanocubes. The activity of CO$_2$ photo-reduction on Pt or Pd loaded TiO$_2$/SrTiO$_3$ heterojunction films were illustrated in Fig. 7. Compared with the bare TS1 film, the photocatalytic activity for CH$_4$ and CO production after loading Pt or Pd nanoparticles increased remarkably. The production rate of CH$_4$ increased from 3.67 to 11.37 and 20.83 ppm/h cm$^2$ when Pt and Pd loaded on TS1. In the meantime, the production rate of CO increased from 2.93 to 5.38 and 7.49, respectively. Pt or Pd nanoparticles are often used as the co-catalysts to increase the separation efficiency of the photo-generated electron-hole pairs [29, 30]. In this work, they indeed played the important role to enhance the photocatalytic activity for CO$_2$ reduction. In addition, comparison TS1-Pt and TS1-Pd film, we found that the loaded noble metals played different effect on the enhancement of the photoactivity. When Pt loaded TS1, the production rate of CH$_4$ increased 2.1 times. While for Pd loaded TS1, it increased 4.7 times, indicating that Pd is more efficient to improve the photoactivity of CH$_4$ production. Moreover, the production rate of CH$_4$
and CO increased 4.7 times and 1.6 times on TS1-Pd than TS1, implying that loading Pd nanoparticles on TS1 film is favorable to improve the selectivity of CO₂ phoreduction to CH₄.

**Conclusions**

In summary, TiO₂/SrTiO₃ heterojunction network films were prepared successfully by hydrothermal method using nanotube titanate acid film (NTA) as the precursor. In the basic reaction process, part of NTA reacted with SrCl₂ to form SrTiO₃ naocubes, and the residues transformed to rutile TiO₂. As prolonging the reaction time to 2 h, NTA transformed to SrTiO₃ naocubes completely. The TiO₂/SrTiO₃ heterojunctions obtained at 1 h exhibit the best photocatalytic performance for the photoreduction of CO₂. The increased photocatalytic activity can be responded by the enhanced charge separation derived from the coupling effect the TiO₂ and SrTiO₃ components, large surface area (BET) and strong adsorption ability of TS1 network porous film. In addition, the photoreduction activity of CO₂ to CH₄ increased from 3.67 to 11.37 and 20.83 ppm/h cm² when Pt and Pd loaded on TS1 film. Especially, Pd also played the important role to increase the selectivity of photoreduction CO₂ to CH₄.

**Competing interests**

The authors declare that they have no competing interests.

**Authors’ contributions**

YB and LZ carried out the total experiment. CL and JY participated in the date analysis. QL supervised the project, and provided the facilities and discussions related to them. All authors read and approved the final manuscript.

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