Enhanced activity of TiO_2 foam combined with CdS for the visible light photocatalytic reduction of CO_2 to solar fuel

JUANGANG WANG*, FEI WANG
Anhui Key Laboratory of Energetic Materials, College of Chemistry and Material Science, Huaibei Normal University, Huaibei 235000, Anhui, China

The latest progress of photocatalytic technology has highlighted the important role of improving the conversion efficiency of CO_2 reduction reaction. In this study, TiO_2 foam combined with CdS (FCC) was prepared to optimize their carbon dioxide photoreduction processes. The results showed that the formation rate of methanol in FCC is 22.6 μmol g^{-1} h^{-1}, roughly 1.33 times higher than that of TiO_2 nanoparticulate combined with CdS (NCC). The fast transmission of photoinduced charge carriers and the slow charge carriers recombination in TiO_2 foam were the main reasons attributable for the enhancement.

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1. Introduction

Carbon dioxide is known to be the main greenhouse gas over the past few centuries [1]. Therefore, effective utilization of CO_2 is one of the most important projects [2-4]. There are many ways to convert CO_2 into fuel. Photocatalytic reduction of CO_2 by H_2O can not only reduce the concentration of CO_2, but also produce energy. [4-7]. It is well known that one of the most important problems in the photoelectrochemical processes is highly efficient separation and transmission of photoinduced electron-hole pairs. In order to suppress the recombination and improve transmission of electron-hole pairs, researchers have designed many schemes. A novel type of hierarchical nanocomposites consisted of MoS_2 nanosheet coating on the self-ordered TiO_2 nanotube arrays is prepared to significantly improve the photocatalytic activity [8]. F. Zhan etc have prepared TiO_2 nanorods films on FTO substrates, which exhibit a longer electron lifetime and more effective separation of photogenerated electron-hole pairs [9]. A highly efficient Pt-TiO_2 nanostructured films with fast electron-transfer rate and the efficient electron-hole separation by the Pt nanoparticles is reported [10]. In this paper, we propose a material model of TiO_2 foam bonded with CdS, the result showed its photocatalytic performance is superior to that of CdS bound to conventional TiO_2 nanoparticles.

2. Experimental section

Ti $(OC_2H_5)_4$ was dissolved in ethanol, glycerol and water at room temperature. The weight ratio of ethanol / glycerin / water is 2: 15: 1. The concentration of titanium in solution was 1 mmol dm^{-3}. The substrate was put into autoclave and sealed, then heated in oven for 6 days at 180 °C. The FTO glass (4×5 cm^2) was coated with a thin film of the above titania powders, then the substrate is placed in a sealed polytetrafluoroethylene reactor (200 ml), containing 0.1 mM $Ti(OC_2H_5)_4$, 1 mM tetrabutylammonium fluoride and 5mM 1-(1-Butoxy-2-propoxy)-2-propanol at 180°C for 6 days. The substrate was baked at 450°C for 50 min to optimize the photoreduction performance of CO_2.

The CdS–TiO_2 heterostructure photocatalysts were prepared using a simple precipitation method. The FTO film of prepared interconnected TiO_2 nanowires was dispersed in a certain volume of 0.1 M $Cd(NO_3)_2$ aqueous, using same capacity of 0.1 M Na_2S aqueous solution as the precipitator introduced by dripping slowly. Then rinse the film several times with deionized water.

3. Results and discussions

3.1. Morphological characteristics and phase structures

The morphology of TiO_2 on FTO glass was studied by SEM (Fig. 1). Fig. 1a indicates the TiO_2 film of micron

size. In order to observe the films clearly, Fig. 1b shows an enlarged SEM image of the film packaging by TiO_2 foam. Fig. 1c displays magnified SEM of the TiO_2 foam covered with CdS nanosized crystallites. Their phase structures were studied by XRD. Fig. 1d shows the XRD diagram of TiO_2 foam, indicating formation of the anatase phase. The diffraction peak of TiO_2 can be seen by observing the XRD diagram of CdS@TiO_2 composite. The CdS XRD spectra of the complexes can be attributed to cubic CdS.

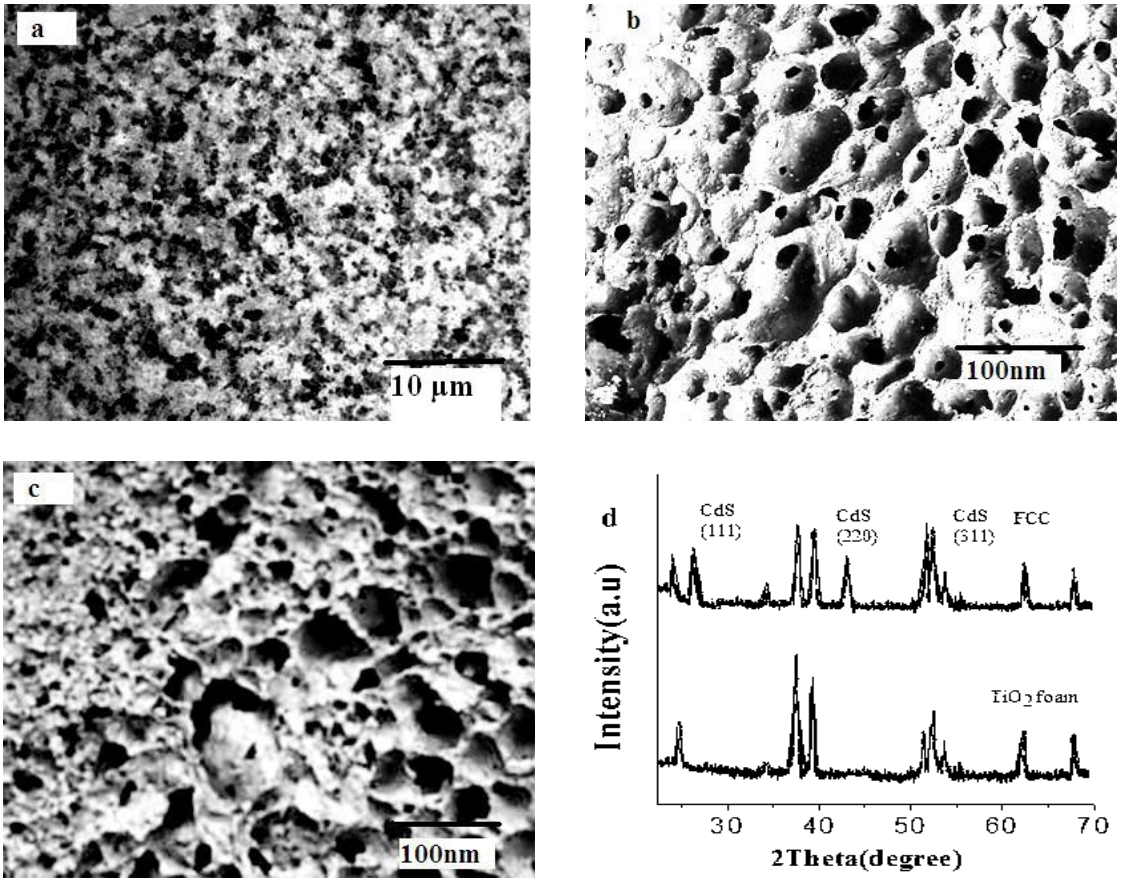

Fig. 1. Morphology of the FCC. (a) SEM image of the top view of the FCC. (b) A magnified SEM image of the TiO_2 foam. (c) A magnified SEM image of the FCC. (d) XRD pattern of the FCC and TiO_2 foam

3.2. Transmission and recombination time constants

The transmission and recombination of photoinduced electrons are the main determinants of the efficiency of CO_2 photoreduction, thus, the study of these effects in FCC is of great significance for the further development of CO_2 photoreduction process. Intensity modulated photocurrent spectroscopy was used to measure the transmission characteristics and intensity modulated photovoltage spectroscopy was used to measure recombination characteristics. Fig. 2a compares the transmission time constants of TiO_2 foam and nano-titanium dioxide particles (Aladdin, 15-25 nm) combined with CdS as light intensity functions. The transmission time constant τ_c of FCC is 2.27×10^{-4} s at the light intensity (8.11×10^{16} cm^{-2} s^{-1}) and 2.61×10^{-3} s at the light intensity (1.46×10^{15} cm^{-2} s^{-1}). Meanwhile, the transmission time constant τ_c of NCC is 8.27×10^{-4} s at 8.14×10^{16} cm^2 s^{-1} and 9.15×10^{-3} s at 1.49×10^{15} cm^{-2} s^{-1}. The electron transmission between TiO_2 nanoparticles and CdS is slower than that of FCC film, it may be due to the electron's residence time in the trap of the particle network (for example, the number of connections between particles) and the region of contact between particles that limits it [11]. That is to say, the TiO_2 foam is fine electrical conductive body along the orientation of the strip axes relative to TiO_2 nanoparticles. Fig. 2b shows the recombination time constant of NNCC is two or three orders of magnitude larger than that of NCC in the studied range of light intensity. Slower carrier recombination indicates the TiO_2 foam have less surface recombination sites than TiO_2 nanoparticles.

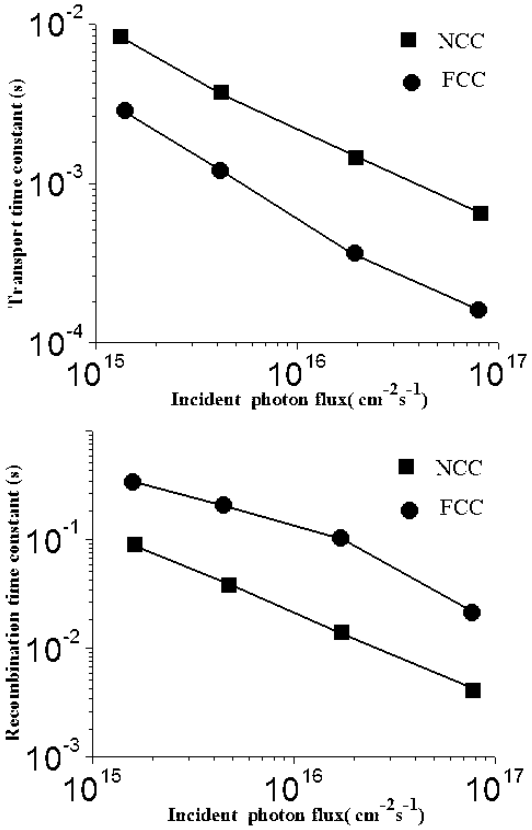

Fig. 2. Comparison of transmission and recombination time constants for TiO_2 foam and TiO_2 nanoparticulate

3.3. Photocatalytic reduction activity

A self-made 100 mL quartz reactor was used for photocatalytic CO_2 reduction. A 400 W xenon lamp with a 420 nm cut off filter was used as the optical source. Gas products from photocatalytic reduction of CO_2 were collected with a 1-micron syringe and analyzed rapidly by the gas chromatograph (SP-7890) with the flame ionization detector. Fig. 3 present the methanol and methane formation rates of NCC and FCC in 5 h of irradiation. It is noteworthy that the yield of methanol (Fig. 3a) is much higher than that of methane (Fig. 3b). The results showed that the methanol production rate of FCC was 22.6 μmol $g^{-1}h^{-1}$, which is 1.33 times higher than that of NCC. It can be seen the FCC achieve a methane formation rate of 4.83μmol g^{-1} h^{-1}, 1.73 times higher than that of NCC. The geometry structure of TiO_2 foam can significantly improve its CO_2 photoreduction performance. When visible light irradiates the photocatalyst, CdS acts as a sensitizer at this time, converting the TiO_2 response from ultraviolet to visible light. The photogenerated electrons transferred from CdS to the conduction band of TiO_2 can reduce CO_2 into the negative and metastable superoxide ($\bullet CO_2^-$) radicals, which can eventually lead to the formation of CH_4 or CH_3OH. Meanwhile, the photogenerated holes left in the valence band of CdS could oxidize H_2O. The electron transmission between TiO_2 foam and CdS is faster than that of NCC film, thereby inhibiting recombination with hole.

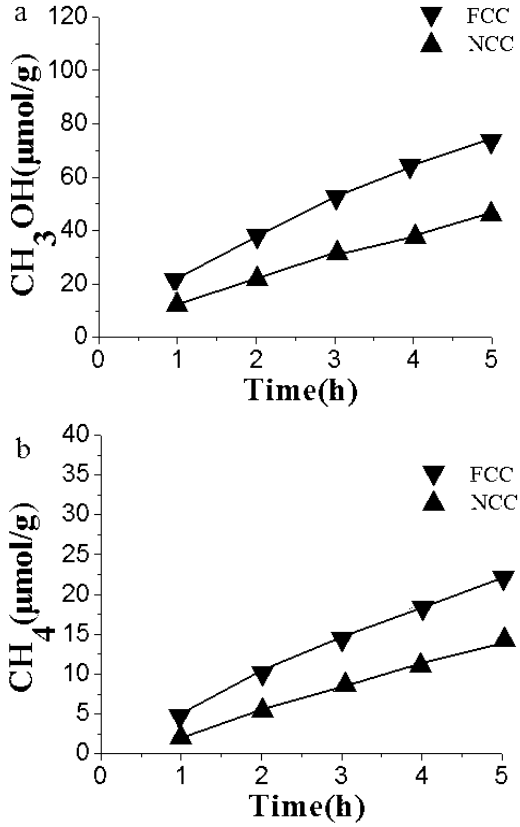

Fig. 3. Yield of (a) CH_3OH and (b) CH_4 upon photoreduction of CO_2 as a function of time under visible light by using FCC and NCC

4. Conclusions

The TiO_2 foam coated CdS was successfully synthesized by solvothermal method. The excellent conductivity of TiO_2 foam significantly improves the electron transfer, thus suppressing the recombination of electron hole pairs. This work presents a simple and affordable way to design structures that improve the renewable energy sources for electron transfer CO_2 conversion.

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*Corresponding author: shanxiwangjuangang@126.com