Enhanced photoreduction CO\(_2\) efficiency by criss-crossed TiO\(_2\) nanoflakes combined with CdS under visible light

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In this paper, a novel photocatalyst CNCC with excellent visible light photocatalytic performance was successfully prepared to optimize the CO\(_2\) photoreduction performance. The results showed that the methanol formation rate of CNCC was 24.7 \(\mu\)mol g\(^{-1}\) h\(^{-1}\), which was 1.42 times higher than that of NCC. The enhanced photoactivity is attributed to the rapid propagation of charge carriers induced by light from the constructed composite structure.

1. Introduction

Photocatalysis is increasingly being seen as a potential alternative to solar fuel production [1–4]. In addition to the formation of hydrogen from water, another focus is photocatalytic reduction in CO\(_2\). Because of the technical difficulties associated with hydrogen storage, products [5–8] from CO\(_2\), such as methane and methanol, can easily be used as current energy sources. It is well known that one of the most significant challenges in photoelectrochemical processes is highly efficient separation and transmission of photoinduced electron–hole pairs. To suppress a recombination and improve transmission of electron–hole pairs, researchers have designed many schemes. A novel photocatalyst Ag\(_3\)PO\(_4\)@MWCNTs@PANI and Z-scheme heterojunction photocatalyst Ag\(_3\)PO\(_4\)@MWCNTs@Cr:SiTiO\(_3\) were successfully prepared by a facile in situ precipitation method [9,10]. The MWCNTs penetrating in the bulk phase of Ag\(_3\)PO\(_4\) could serve as conductors of photogenerated electrons and rapidly migrated electrons to the surface of the photocatalysts. Han et al. [11] synthesized uniform spherical CdS/TiO\(_2\) core–shell nanoparticles with different TiO\(_2\) shell thicknesses, generating an energy gradient at the interface to spatially separate the electrons and holes. Zhan et al. [12] have prepared TiO\(_2\) nanorod films on FTO substrates, which exhibit a longer electron lifetime and more
effective separation of photogenerated electron–hole pairs. A highly efficient Pt–TiO2 nanostructured film, with fast electron-transfer rate and efficient electron–hole separation by the Pt nanoparticles, is reported [13]. In this paper, we propose a material model of criss-crossed TiO2 nanoflakes combined with CdS (CNCC) and compared its photocatalytic activity with that of the usual TiO2 nanoparticles with CdS (NCC). The geometry structure of criss-crossed TiO2 nanoflakes is conductive to charge separation, therefore inhibiting recombination can significantly improve its CO2 photoreduction performance.

2. Experimental methods

All chemicals used in the experiment (Tianjin Chemical Reagent Company) are analytical reagent grade. The FTO glass (5 × 5 cm²) was cleaned, and then coated with TiO2 nanowire in ethanol solution. FTO glass was placed in a tetrafluoroethylene reactor (200 ml), 110 ml ethanol, 5 ml deionized water, 1 mmol Ti(OC₂H₅)₄, 1 mmol trihydroxytriethylamine, 1 mmol urea glycoside and 1 mmol hexadecanol were added, and then placed in an oven at 180°C for 7 days. The substrate was washed and baked at 450°C for 50 min to optimize the photoreduction performance of CO₂.

The CdS–TiO2 heterostructure photocatalysts were prepared using a simple precipitation method. The FTO film of prepared interconnected TiO2 nanowires was dispersed in a certain volume of 0.1 M Cd(NO₃)₂ aqueous solution, using the same capacity of 0.1 M Na₂S aqueous solution as the precipitator introduced by dripping slowly. Then the film was rinsed several times with deionized water. The anatase TiO2 nanoparticles (15 nm primary particle size) were purchased from Aladdin. The synthetic procedures of TiO2 nanoparticles combined with CdS were almost the same as the procedures of criss-crossed TiO2 nanoflakes combined with CdS.

3. Results and discussion

3.1. Morphological characteristics and phase structures

The morphology of TiO2 on FTO glass was studied by SEM. Figure 1a indicates the micrometre-sized TiO2 film. A magnified SEM image in figure 1b clearly demonstrates the highly organized structure of the film packaging by criss-crossed TiO2 nanoflakes, which provide more surface area and active sites for the next catalytic reaction [14,15]. Figure 1c displays magnified SEM of the criss-crossed TiO2 nanoflakes covered with CdS-nanosized crystallites. The CdS particle size is about 8 nm. Transmission electron microscopy (TEM) images for TiO2 and TiO2–CdS composite are presented in figure 1d,e to explore the nanostructure. As shown in figure 1d, criss-crossed nanoflakes were distinctly observed. From figure 1e, it can be seen that the porous surface is composed of nanoparticles with a diameter of less than 10 nm. EDX mapping images (figure 1f–i) indicate that the sample contains Ti, O, Cd and S; this finding further confirms the coexistence of titanium dioxide and cadmium sulfide. Ti, O, Cd and S are well dispersed in the samples; thus, CdS nanoparticles are uniformly dispersed on the surface of TiO2. Their phase structures were studied by XRD. Figure 1j shows the XRD diagram of criss-crossed TiO2 nanoflakes, indicating formation of the anatase phase. The diffraction peak of TiO2 can be seen by observing the XRD diagram of CdS@TiO2 composite. The peaks located at 26.5°, 44.4° and 52° could be indexed to the (111), (220) and (311) crystal planes of cubic CdS phase, respectively.

3.2. Transportation time and recombination time constants

The transmission and recombination of photoinduced electrons are the main determinants of the efficiency of CO2 photoreduction; thus, the study of these effects in CNCC is of great significance for the further development of the CO2 photoreduction process. Intensity-modulated photocurrent spectroscopy was used to measure the transmission characteristics and intensity-modulated photovoltage spectroscopy was used to measure recombination characteristics [16]. Figure 2a compares the transmission time constants of TiO2 nanoflakes and nano-titanium dioxide particles combined with CdS as light intensity functions. The transmission time constant τ of CNCC is 2.24 × 10⁻⁴ s at the light intensity (9.12 × 10¹⁶ cm⁻² s⁻¹) and 3.31 × 10⁻³ s at the light intensity (1.15 × 10¹⁵ cm⁻² s⁻¹). Meanwhile, the transmission time constant τ of NCC is 8.34 × 10⁻⁴ s at 9.19 × 10¹⁶ cm⁻² s⁻¹ and 8.04 × 10⁻³ s at 1.18 × 10¹⁵ cm⁻² s⁻¹. The electron transmission between TiO2 nanoparticles and CdS is slower than that of CNCC film; this 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 [17]. That is to say, the
criss-crossed TiO2 nanoflakes are a fine electrical conductive body along the orientation of the strip axes relative to TiO2 nanoparticles. Figure 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 criss-crossed TiO2 nanoflakes have less surface recombination sites than TiO2 nanoparticles.

Figure 1. Morphology of the CNCC. (a) SEM image of the top view of the criss-crossed TiO2 nanoflakes. (b) A magnified SEM image of the criss-crossed TiO2 nanoflakes (c) A magnified FESEM image of the CNCC. TEM images of TiO2 (d) and TiO2–Cds (e) composite. (f–i) Composed elemental mapping image. (j) XRD pattern of the CNCC and the criss-crossed TiO2 nanoflakes.
3.3. Photocatalytic reduction activity

A self-made 100 ml quartz reactor was used for photocatalytic CO2 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 CO2 were collected with a 1 mm syringe and analysed rapidly by the gas chromatograph (SP-7890) with a flame ionization detector. Detailed experimental procedures of photocatalytic CO2 reduction can be found in supplementary materials. Figure 3 presents the methanol and methane formation rates of NCC and CNCC in 5 h of irradiation. For CNCC and NCC, it is noteworthy that the yield of methanol (figure 3a) is much higher than that of methane (figure 3b). It can be seen that CNCC achieves a methanol formation rate of 24.7 \( \mu \text{mol g}^{-1} \text{h}^{-1} \), 1.42 times higher than that of NCC. The results show that the methane production rate of CNCC was 4.59 \( \mu \text{mol g}^{-1} \text{h}^{-1} \), 1.68 times higher than that of NCC. The geometry structure of criss-crossed TiO2 nanoflakes can significantly improve its CO2 photoreduction performance. When visible light irradiates the photocatalyst, CdS acts as a sensitizer at this time, converting the TiO2 response from ultraviolet to visible light. Photoinduced electrons from CdS to the conductive bands of TiO2 can reduce carbon dioxide to negative electrodes, resulting in the formation of methane or methanol. The electron transmission between criss-crossed TiO2 nanoflakes and CdS is faster than that of NCC film, thereby inhibiting recombination with holes.

4. Conclusion

The criss-crossed TiO2 nanoflakes combined with CdS were successfully synthesized by a simple solvothermal method using hexadecanol as hydrophobic modifier. The CNCC composites exhibited good CO2 reduction photocatalytic activity under visible light. The results showed that the methane production rate of CNCC was 4.59 \( \mu \text{mol g}^{-1} \text{h}^{-1} \), which is 1.68 times higher than that of NCC. CNCC achieves a methanol formation rate of 24.7 \( \mu \text{mol g}^{-1} \text{h}^{-1} \), which is 1.42 times higher than that of NCC. The increase in CH4 and CH3OH yields can be attributed to the fast electron–hole transmission of TiO2 nanoflakes. This provides a new photocatalytic method for the efficient conversion of CO2 by solar energy.
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