Synthesis and characterization of Co_3O_4@TiO_2 photoelectrode materials

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Abstract. The Co_3O_4@TiO_2 photoelectrode was prepared in two steps on the F-doped SnO_2 conductive glass (FTO). The appearance and internal structure of the samples were tested by XRD and SEM, The photoelectric properties of the electrodes were tested by an electrochemical workstation. Photoelectrochemical (PEC) test results shows that the photocurrent density of Co_3O_4@TiO_2 photoelectric electrode is 0.8mA ▪ cm^{-2}.

Keywords: Photoelectrochemical, Titanium oxide, Cobalt Oxide, Hydrolysis.

1 Introduction

With the aggravation of the greenhouse effect, energy consumption and environmental pollution, clean energy has attracted the attention of the international community. Because of its non-toxicity, super hydrophilicity, good chemical stability, cheap and ease to get, TiO_2 become the most ideal photocatalyst especially in dealing with water pollution. Fujishima et al. first used TiO_2 as a photoanode for photoelectrochemical water decomposition to produce hydrogen [1]. Subsequently, more and more scholars start to study of photoelectrochemical water decomposition at TiO_2. But TiO_2 has a wide bandgap (3.20 eV for anatase, 3.03 eV for rutile, and 3.40 eV for slate), The wide bandgap means that TiO_2 can only utilize ultraviolet light, and the electron-hole pairs excited by ultraviolet light are very easy to compound [2,3,8]

As a narrow bandgap p-type semiconductor, Co_3O_4 is widely used in magnetic materials, sensors, supercapacitors, lithium-ion batteries and catalytic materials. The bandgap of Co_3O_4 is about 2.07 eV, which can only absorb the main visible light in sunlight. The analysis of the band structures of Co_3O_4 and TiO_2 in theory suggests that the combination of visible light active Co_3O_4 and ultraviolet (UV) light active TiO_2 could obtain a broad spectrum photocatalytic material from UV to visible as well as the enhanced separation of photogenerated electrons and holes. Recent studies have demonstrated the improved UV−visible light photodegradation performance of Co_3O_4@TiO_2 heterostructures [2-5]. However, to our knowledge, the study on the fabrication of Co_3O_4@TiO_2 on an FTO glass substrate and their application as a photoanode for photoelectric water decomposition is still rarely reported.

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In this study, we used the improved hydrothermal method method to grow three-dimensional conical nano TiO_2 arrays on FTO conductive glass substrate, and Co_3O_4 was rotary coated on it. TiO_2 nanocone as the 3D frame, Co_3O_4 as spin-coated cover. In this 3D structure, the Co3O4 in the above structure was used to gather visible light, and the TiO_2 skeleton growing on the FTO glass substrate is used to capture ultraviolet light to generate photoelectron-hole pairs, and act as an electron transfer path. In our work, photocurrent and electrochemical impedance spectroscopic results were used to demonstrate low charge transfer resistance of the 3D structure, and excellent PEC performance under visible light illumination.

2 Experimental section

2.1 Synthesis of 3D TiO_2 nanocones

Analytical grade reagents were used, unless otherwise specified. In a typical synthesis process, 4.73mmol citrate, 4.73mmol tetrabutyl titanate and 50mL hydrochloric acid were added to 50mL deionized water, and the mixture was stirred for a defined period. After stirring, the liquid was transferred to a 100mL reaction kettle, and the FTO conductive substrate was immersed in the precursor solution. And the conductive surface was titled downward. The reaction at 150℃ for 6 h and dried at 80℃ for 2 h.

2.2 Synthesis of 3D Co_3O_4@TiO_2

In our work, 5 mM of $Co(NO_3)_2 \cdot 6H_2O$ was dissolved in anhydrous ethanol, and the Co_3O_4 coating was spin-coated on the TiO_2 nanocones synthesized in Section 2.1 using a spin-coater (Easy Coater 6, LS52147), dried, and calcination at 400°C.

The final sample was characterized by X-ray diffractometer (XRD; Rigaku D/max 2500), scanning electron microscope (SEM; Hitachi S-4800). Electrochemical impedance spectroscopy (EIS) tests were performed by an electrochemical workstation (Autolab; PGSTAT302N; The electrolyte is 0.5M Na_2SO_4, the bias voltage of 1 V and a frequency of 0.1-105 Hz). The amperometric current versus time (I-t) curves of the electrodes was tested using the three-electrode method and a solar simulator (WXS-80C-3, 100 mW/cm^2) under the same electrolyte conditions as above.

3 Results and Discussion

As shown in Figure 1(a), TiO_2 nanocones are evenly staggered on the entire FTO surface. The enlarged image (Figure 2(b)) shows that TiO_2 nanocones are smooth four-pyramid shapes with wide bottom and a narrow top, and the bottom width is about 500nm. Figure 1(c) shows that the Co_3O_4@TiO_2 is relatively uniform, with the canopy scattered on the surface of the TiO_2 nanocone, and the TiO_2 nanocones interspersed on the Co_3O_4 canopy. The morphological structure of the material affects the properties of the material, and this special three-dimensional structure can greatly increase the light capture and contact area with electrolytes. Meanwhile, the TiO_2 nanocone can be used as an electron transport path to migrate electrons to FTO conductive glass.

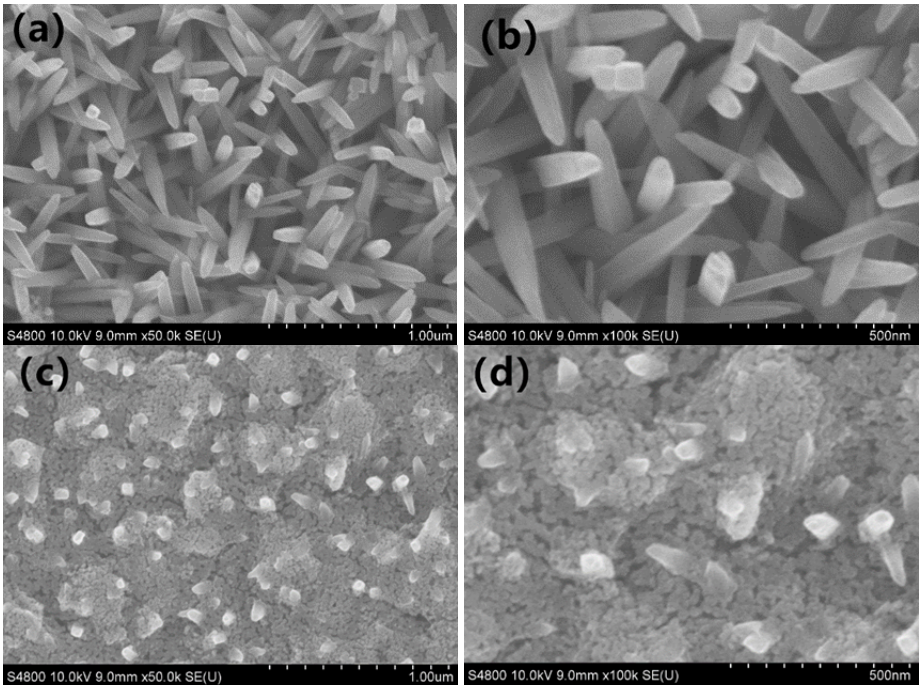

Fig. 1. SEM image of (a,b) TiO_2 nanocones, (c,d) Co_3O_4@TiO_2 photoelectrode.

The XRD patterns of TiO_2 nanocones are shown in Figure 2(b), it can be determined from the peak that the prepared nanocone is tetragonal rutile TiO_2 (Corresponding to the diffraction peak of standard card JCPDS No.88-1175) [6]. XRD patterns of the Co_3O_4@TiO_2 in Figure 2(c) confirm the presence of spinel Co_3O_4 (Corresponding to the diffraction peak of standard card JCPDS No.76-1802) [4].

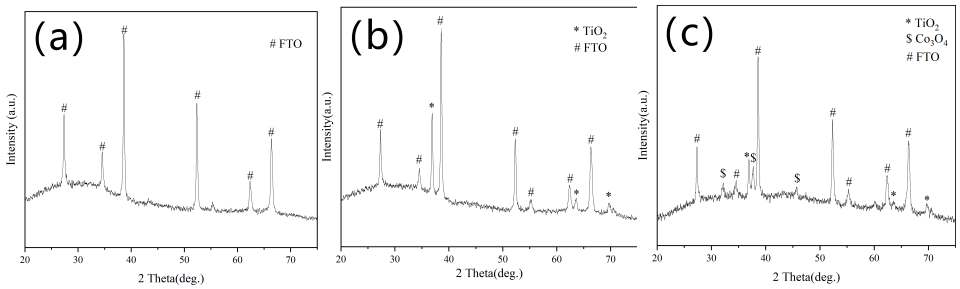

Fig. 2. XRD patterns of (a) FTO ,(b) the TiO_2 nanocones and (c) Co_3O_4@TiO_2 photoelectrode.

Figure 3 shows the photocurrent density curve for a light on/off cycle every 60s, All the electrodes showed a rapid light response. The photocurrent density of the three-dimensional nanostructure array Co_3O_4@TiO_2 photoelectrode increases gradually when the light source is turned on, and the maximum is close to 0.8mA/cm^2, which is nearly 4 times that of the TiO_2 nanocones. Generally, the photocurrent density reflects the separation efficiency of the semiconductor photogenerated electron-hole pair [3]. The electron hole separation efficiency of the photoelectrode prepared by us is much higher than that of TiO_2 nanocones.

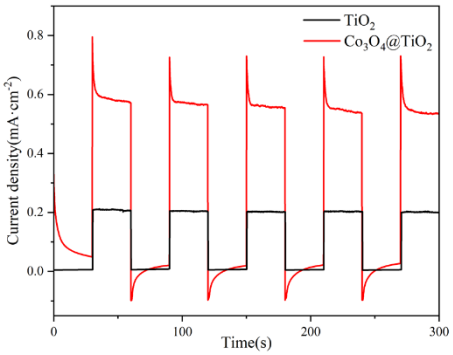

Fig. 3. I-t curves of TiO_2 nanocones and Co_3O_4@TiO_2 photoelectrode.

Figure 4 shows the EIS plots of TiO_2 nanocone and Co_3O_4@TiO_2. All EIS plots shows a high-frequency hemisphere whose diameter represents the electron transfer resistance of the electrode surface dynamics, the smaller the semicircle diameter, the easier the charge migration and the more efficient the electron-hole pair separation is [7]. The semicircular diameter of Co_3O_4@TiO_2 photoelectrodes is much less than that of TiO_2 nanocones. This indicates that the three-dimensional structure array formed by the Co_3O_4 coating distributed on the TiO_2 skeleton stalk is more suitable for carrier transfer compared with TiO_2 and the introduction of Co_3O_4 inhibits the electron-hole recombination and improves the charge transfer performance.

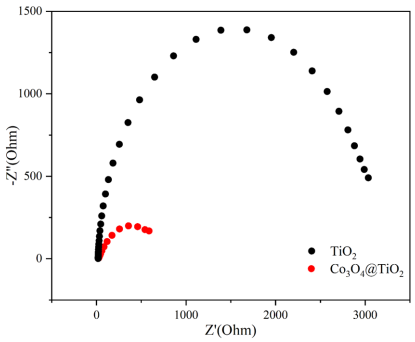

Fig. 4. EIS plots for TiO_2 and Co_3O_4@TiO_2 photoelectrode.

4 Conclusions

In conclusion, we have successfully synthesized a Co_3O_4@TiO_2 nanoarray on an FTO conductive glass substrate. Compared with TiO_2 nanocones, the photoelectrode we synthesized has lower charge transfer resistance and higher photocurrent, while the separation efficiency of semiconductor photogenerated electron hole pairs is easily affected by the material morphology. Our synthesized photoelectric electrode has a unique three-dimensional morphology, which increases the surface area of the electrode, enhances the absorption capacity of light, and improves the separation efficiency of electrons and holes in the photoelectric aurora. Our work provides a reference for the design of novel photocatalytic degradation materials and photoelectrochemical water decomposition electrodes, and this simple and low-cost preparation method also provides ideas for the design and synthesis of novel catalytic and photoelectric conversion nanostructures.

References

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