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Article

A $\text{TiN}_{0.3}/\text{CeO}_2$ photo-anode and its photo-electrocatalytic performance

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ABSTRACT

A $\text{TiN}_{0.3}/\text{CeO}_2$ photo-anode was synthesized by the electro-deposition of CeO_2 on $\text{TiN}_{0.3}$ supported on a Ti substrate. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to study its structure and morphology. The crystalline nature of $\text{TiN}_{0.3}$ and CeO_2 was confirmed by XRD, and SEM images showed that CeO_2 spheres uniformly distributed on the $\text{TiN}_{0.3}$ surface. In addition to visible light absorption by $\text{TiN}_{0.3}$, UV light was also harvested by the outer CeO_2 component on the $\text{TiN}_{0.3}/\text{CeO}_2$ combined photo-anode. In the photo-electrochemical measurement, $\text{TiN}_{0.3}/\text{CeO}_2$ showed four times higher photo-current density than $\text{TiN}_{0.3}$ or CeO_2 , and the photo-current stabilization was also significantly improved compared to $\text{TiN}_{0.3}$ or CeO_2 . The specific double-layer structure of $\text{TiN}_{0.3}/\text{CeO}_2$ contributed to its improved photo-electrocatalytic performance. Electron transfer from CeO_2 to $\text{TiN}_{0.3}$ driven by the hetero-junction and hole consumption by Ce^{3+} at the $\text{TiN}_{0.3}/\text{CeO}_2$ interface promoted the separation of electron and hole in the CeO_2 layer, which improved the photo-current generation. Ce^{3+} that existed in CeO_2 acted as the adsorption and activation site for H_2O and accelerated the oxidation of H_2O on the CeO_2 surface, which further led to the high and stable photo-current density generated in $\text{TiN}_{0.3}/\text{CeO}_2$. This finding is useful for the design and synthesis of an effective photo-electrocatalysis material for solar energy conversion.

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1. Introduction

Photo-electrocatalysis is an efficient way to convert solar energy into chemical energy. Extending the light absorption region of the photo-electrode material is a key step to obtaining high conversion efficiency. Most investigations so far have focused on titanium oxide for its high activity and excellent chemical stability for energy conversion under UV light [1–3]. The doping of N into TiO_2 can extend the light response into the visible region as the band gap is narrowed with N doping [4–6], such as in the oxide/nitride compounds of Ta_3N_5 [7], TaON [8], and N-TiO [9]. In contrast to these oxide/nitride semiconduc-

tors with a specific conduction band and valence band, TiN_x exhibits metallic property in a particular energy state [10,11], which is favorable for electron transfer in TiN_x [12–14]. In a previous report, TiN_x was reported to show photo-catalytic activity for H_2 generation under visible light in water with CH_3OH , with Na_2SO_3 and Na_2S as sacrificial electron donors [15]. However, the non-stoichiometric nature of TiN_x inhibited its application in photo-electrocatalysis because its intrinsic defects/vacancies can act as the recombination centers to reduce the conversion efficiency.

Cerium oxide (CeO_2) has been widely studied in catalysis for its unique redox property. Recent research indicated that CeO_2

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is also a potential photo-catalyst [16–19]. We have reported that the redox property of CeO_2 is favorable for the consumption of photo-holes in the photo-catalytic reaction for H_2 generation in Na_2S and Na_2SO_3 aqueous solution [20]. In this manuscript, a composite photo-anode of $\text{TiN}_x/\text{CeO}_2$ was fabricated with the electrodeposited method and its photo-electrocatalytic performance was evaluated by photo-current measurement. $\text{TiN}_x/\text{CeO}_2$ gave four times larger photo-current than the pristine TiN_x and CeO_2 , and the photo-current stabilization was significantly increased relative to TiN_x and CeO_2 . The photo-electrocatalytic mechanism is discussed with consideration of the light harvest, separation efficiency of photo-electrons and photo-holes, and the interfacial electrochemical reaction rate.

2. Experimental

2.1. Preparation of $\text{TiN}_{0.3}$

$\text{TiN}_{0.3}$ was obtained by calcining a Ti sheet (Taijin Company, China) under NH_3 at 600 °C for 3 h. Before calcination, the Ti sheet of 2.5 cm × 1.2 cm size was polished and then washed by deionized water, acetone, and deionized water.

2.2. Preparation of $\text{TiN}_{0.3}/\text{CeO}_2$

$\text{TiN}_{0.3}/\text{CeO}_2$ was obtained by electrodepositing CeO_2 on $\text{TiN}_{0.3}$ in a two electrode cell with a current of 2 mA for 10 min. The synthesis recipe was reported in Ref. [20]. $\text{TiN}_{0.3}$ and a graphite rod were used as the working electrode and counter electrode, respectively. The CeO_2 grew on the TiN_x substrate in a solution containing $\text{Ce}(\text{NO}_3)_3$ (0.01 mol/L), NH_4Cl (0.1 mol/L), and KCl (0.03 mol/L) at 70 °C. A Ti/CeO_2 photo-electrode was prepared by the same method for comparison.

2.3. Characterization

The crystal structure of $\text{TiN}_{0.3}$, $\text{TiN}_{0.3}/\text{CeO}_2$, and Ti/CeO_2 was characterized by a D8 Advance X-ray diffractometer (Bruker, Germany) with $\text{Cu K}\alpha$ radiation source at a scanning rate of 5°/min. The morphology of the samples was observed with a Thermal FE Environment scanning electron microscope (SEM) (FEI, Quanta 400F, Holland). Diffuse reflection spectra (DSR) were recorded on a UV-Vis spectrophotometer (Shimadzu, UV-3150, Japan; equipped with an integrating sphere) to characterize the optical properties of the samples.

2.4. Photo-electrocatalytic performance

The photo-electrocatalytic performance of $\text{TiN}_{0.3}$, $\text{TiN}_{0.3}/\text{CeO}_2$, and Ti/CeO_2 was evaluated with photo-current measurement without an external potential in addition to the open circuit voltage. The test was carried out in a three-electrode cell equipped with a Pt counterelectrode and saturated calomel reference electrode. The potential was generated and the current was analyzed with a potentiostat (Chenhua, 756d, Shanghai) controlled by a computer. A 10 mL Na_2SO_4 aqueous solu-

tion (0.1 mol/L) was used as the electrolyte. The photo-current was measured under light-on and light-off with a 10 s interval. Light for the photo-electrochemical measurement was produced by a Xe lamp (Changtuo, PLS-SXE300/300UV, Beijing) with 130 mW/cm^2 intensity (Zhongjiaojinyuan, CEL-VIS400, Beijing).

3. Results and discussion

3.1. Crystal structure and morphology

Figure 1 shows the XRD patterns of the Ti sheet and $\text{TiN}_{0.3}$, $\text{TiN}_{0.3}/\text{CeO}_2$, and Ti/CeO_2 samples. The diffraction peaks at 35.0°, 38.4°, 40.2°, 52.8°, 62.7°, and 70.1° (Fig. 1(1)) were consistent with JCPDS 44-1294, and indicated the Ti crystalline structure. After calcining the Ti sheet in a NH_3 atmosphere, a series of shoulder peaks at 37.5°, 39.7°, 52.1°, and 69.2° appeared in Fig. 1(2), in addition to the Ti characteristic peaks. These peaks are from hexagonal $\text{TiN}_{0.3}$ according to JCPDS 41-1352 ($a = b = 0.2974$ nm, $c = 0.4792$ nm, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$). In Fig. 1(3) and (4), a new peak at 28.5° was observed for $\text{TiN}_{0.3}/\text{CeO}_2$ and Ti/CeO_2 , in addition to the diffraction peaks of $\text{TiN}_{0.3}$ and Ti substrates. This peak was identified as the (111) diffraction peak of cubic CeO_2 according to JCPDS 65-2975 ($a = b = c = 0.424$ nm, $\alpha = \beta = \gamma = 90^\circ$), and indicated that CeO_2 was deposited on the $\text{TiN}_{0.3}$ and Ti substrates successfully.

SEM was employed to study the morphology of $\text{TiN}_{0.3}/\text{CeO}_2$ and Ti/CeO_2 . The images are shown in Fig. 2. Spherical CeO_2 particles were uniformly dispersed on the surface of the $\text{TiN}_{0.3}$ and Ti substrates. The change of substrates did not influence the dispersion and particle size of CeO_2 .

3.2. Optical absorption

The optical absorption characterization results of $\text{TiN}_{0.3}$ and $\text{TiN}_{0.3}/\text{CeO}_2$ are shown in Fig. 3. A broad absorption band cen-

Fig. 1. XRD patterns of (1) Ti, (2) $\text{TiN}_{0.3}$, (3) $\text{TiN}_{0.3}/\text{CeO}_2$, and (4) Ti/CeO_2 .

Fig. 2. SEM images of (a) $\text{TiN}_{0.3}/\text{CeO}_2$ and (b) Ti/CeO_2 .

tered at 680 nm was observed for pristine $\text{TiN}_{0.3}$. Compared to TiO_2 with a UV response, the visible light harvest by $\text{TiN}_{0.3}$ originated from the reduction of the energy level structure due to the atomic substitution of N for O. After electrodepositing CeO_2 on $\text{TiN}_{0.3}$, the visible absorption band was weakened and blue-shifted to 550 nm. Meanwhile, a UV absorption band starting at 400 nm was observed. The outer CeO_2 was responsible for the UV absorption of $\text{TiN}_{0.3}/\text{CeO}_2$ [20], and it also caused the attenuation of visible light transmission to the $\text{TiN}_{0.3}$ layer. For the shift of the visible absorption band, we proposed that it was related to an interaction between $\text{TiN}_{0.3}$ and CeO_2 .

3.3. Photo-electrocatalytic performance

The photo-electrocatalytic performance (i - t) of the $\text{TiN}_{0.3}$, Ti/CeO_2 , and $\text{TiN}_{0.3}/\text{CeO}_2$ samples is shown in Fig. 4. A $7 \mu\text{A}/\text{cm}^2$ photo-current was instantly observed for $\text{TiN}_{0.3}$ once the light was turned on. This photo-current quickly decayed within 1 s to $2.0 \mu\text{A}/\text{cm}^2$, and then slowly decayed thereafter. With the CeO_2 photo-anode, the photo-current showed a similar generation and decay as with $\text{TiN}_{0.3}$, except that it slowly decayed within 10 s to $1 \mu\text{A}/\text{cm}^2$. For the $\text{TiN}_{0.3}/\text{CeO}_2$ sample, an instant photo-current of $8.4 \mu\text{A}/\text{cm}^2$ was generated by irradiating, and it remained constantly in the following light-on time. However, after two light-on/off cycles, the photo-current was slightly reduced at the end of the light-on time.

The photo-current measurement was carried out in Na_2SO_4 aqueous solution without an external potential. In this electro-

Fig. 3. UV-Vis absorption spectra of the $\text{TiN}_{0.3}$ and $\text{TiN}_{0.3}/\text{CeO}_2$ samples.

Fig. 4. i - t plots of $\text{TiN}_{0.3}$, $\text{TiN}_{0.3}/\text{CeO}_2$, and Ti/CeO_2 .

lyte, the observed anodic photo-current originated from photo-electrocatalytic H_2O oxidation. The four times larger photo-current density of $\text{TiN}_{0.3}/\text{CeO}_2$ than those of $\text{TiN}_{0.3}$ and CeO_2 indicated its higher photo-electrocatalytic activity. The photo-current generation begins with the generation of photo-carriers under light irradiation on the photo-anode. After the separation of the photo-electrons and photo-holes inside the semiconductor, photo-electrons are transferred to the Ti substrate and arrive at the Pt counterelectrode through the outer circuit to form the observed photo-current. Meanwhile, photo-holes diffuse to the interface between the electrode and electrolyte to complete the electrochemical reaction. Therefore, the light harvest and photo-carriers separation in the semiconductor directly influence the intensity of the photo-current. In contrast to the light absorption and photo-carriers separation on the nanosecond scale, the slow electrochemical reaction rate at the electrode/solution interface gave a current stabilization on the time scale of seconds.

There are many vacancies and defects in $\text{TiN}_{0.3}$ due to its non-stoichiometric nature. These defects act as recombination centers in the photo-electrocatalytic process, and lead to the fast decay of the photo-current in $\text{TiN}_{0.3}$. For the single CeO_2 photo-anode, Ce^{3+} is oxidized to Ce^{4+} by the photo-holes, while it can be reproduced by Ce^{4+} reduction by trapping the photo-electron. That is, the Ce^{3+} centers act as the recombination centers of electrons and holes, which is unfavorable for photo-current generation in the photo-electrocatalytic H_2O oxidation process.

Compared to $\text{TiN}_{0.3}$ and CeO_2 , the combined $\text{TiN}_{0.3}/\text{CeO}_2$ photo-anode exhibited the highest light utilization efficiency since both UV and visible light can be harvested for the generation of free carriers. Figure 5(a) shows the straddling gap (type I) heterojunction structure of $\text{TiN}_{0.3}$ and CeO_2 . This energy band structure has no effect on the transfer of carriers in the $\text{TiN}_{0.3}$ layer, but it allows the transfer of electrons and holes in the CeO_2 layer to $\text{TiN}_{0.3}$. Photo-electrons in $\text{TiN}_{0.3}$ are recombined with photo-holes at the defect sites in $\text{TiN}_{0.3}$, which is similar to the single $\text{TiN}_{0.3}$ photo-anode. In contrast to $\text{TiN}_{0.3}$, photo-electrons in CeO_2 transferred to $\text{TiN}_{0.3}$ conduction band are driven by the energy difference between CeO_2 and $\text{TiN}_{0.3}$. But

Fig. 5. (a) Energy band structure of CeO₂ and TiN_{0.3}; (b) Schematic of photo-current generation in TiN_{0.3}/CeO₂.

the photo-hole transfer from CeO₂ to TiN_{0.3} was inhibited as they were consumed by Ce³⁺ that existed in the interface of TiN_{0.3}/CeO₂. That is, the carrier recombination in CeO₂ was inhibited by the specific double-layer structure of TiN_{0.3}/CeO₂. Therefore, the photo-current in the TiN_{0.3}/CeO₂ photo-anode was significantly enhanced.

In addition to the enhancement of the photo-current in the TiN_{0.3}/CeO₂ combined photo-anode, the stabilization of the photo-current was also promoted. The oxidation of H₂O occurs in the interface between CeO₂ and the electrolyte. As an important catalyst, CeO₂ has drawn much attention for its special storage and release of oxygen as oxygen vacancies, i.e., Ce³⁺ [21–23]. The Ce³⁺ at the CeO₂ surface acts as the adsorption site

for the activation of H₂O, which accelerates the H₂O oxidation reaction. As a result, the stabilization of the photo-current was improved in the TiN_{0.3}/CeO₂ photo-anode. A scheme of photo-current generation in TiN_{0.3}/CeO₂ is shown in Fig. 5(b). Concerning the slight decline of the photo-current after several cycles with TiN_{0.3}/CeO₂, we believe it was related to a side reaction of the electrode. More work is now underway.

4. Conclusions

A TiN_{0.3}/CeO₂ photo-anode was fabricated by the electro-deposition of CeO₂ spheres on the surface of TiN_{0.3} supported on a Ti substrate. The double-layer structure in TiN_{0.3}/CeO₂ increased the light harvest efficiency since both visible light and UV light were absorbed by TiN_{0.3} and CeO₂, respectively. The photo-electrochemical measurement indicated that the stabilization and magnitude of the photo-current were significantly improved by the combination of TiN_{0.3} and CeO₂. The separation of electrons and holes in the CeO₂ layer was promoted due to electron transfer to TiN_{0.3} driven by the heterojunction and hole consumption by Ce³⁺ in the TiN_{0.3}-CeO₂ interface. The electrochemical reaction was also accelerated due to the adsorption and activation of H₂O on Ce³⁺ sites. The TiN_{0.3}/CeO₂ photo-anode has potential application in photo-catalysis and photo-electrocatalytic reactions.

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Graphical Abstract

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A TiN_{0.3}/CeO₂ photo-anode and its photo-electrocatalytic performance

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TiN_{0.3}/CeO₂ has improved photo-electrocatalytic performance due to enhanced separation of electron and hole at the interface between TiN_{0.3} and CeO₂, and accelerated H₂O oxidation at the interface between CeO₂ and electrolyte.

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TiN_{0.3}/CeO₂光阳极材料的构筑及其光电催化性能

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摘要: 采用高温氮化法在Ti片基底上生长一层TiN_{0.3}薄膜, 进一步利用电化学沉积法在TiN_{0.3}薄膜上生长CeO₂, 制备了TiN_{0.3}/CeO₂复合材料. 分别用X射线衍射和扫描电镜研究了复合材料的晶体和形貌结构, 用紫外-可见光谱探究了材料的光学吸收性能. 结果表明, 球状CeO₂颗粒均匀地分布在TiN_{0.3}表面; 该复合光阳极除了TiN_{0.3}对可见光的吸收外, 外层的CeO₂同时实现了对紫外光的吸收. 光电催化性能研究发现, TiN_{0.3}/CeO₂复合光阳极能够显著提高TiN_{0.3}或CeO₂的光电流密度, 同时增加光电流的稳定性. TiN_{0.3}/CeO₂独特的双层结构是其光电催化性能提高的主要原因. 在TiN_{0.3}与CeO₂界面处异质结构的驱动下, CeO₂层中的光生电子迁移至TiN_{0.3}层, 而相应的光生空穴在界面处被Ce³⁺所消耗, 从而提高了CeO₂层中电子和空穴的分离效率, 光电流密度也随之提高; 同时, 位于CeO₂与电解液界面处的Ce³⁺作为水分子的吸附中心和反应活性中心, 加快了界面处水的氧化反应, 从而进一步促进了稳定光电流的产生. 鉴于TiN_{0.3}/CeO₂光阳极材料优良的光电催化性能, 其在太阳能光电催化领域具有潜在的应用, 对于新型高效光电转化材料的设计与合成具有借鉴作用.

关键词: 氮化钛; 氧化铈; TiN_{0.3}/CeO₂; 光阳极; 光电催化

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