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Article

Multifarious function layers photoanode based on g-C₃N₄ for photoelectrochemical water splitting

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ABSTRACT

We report on a novel g-C₃N₄/TiO₂/Co-Pi photoanode combining a TiO₂ protection layer, Co-Pi hole capture layer, and g-C₃N₄ light-absorption layer for photoelectrochemical (PEC) water splitting to generate hydrogen for the first time. This new photoanode with three function layers exhibits enhanced PEC performance with a photocurrent density of 0.346 mA·cm⁻² at 1.1 V (vs. RHE), which is approximately 3.6 times that of pure g-C₃N₄ photoanode. The enhanced PEC performance of g-C₃N₄/TiO₂/Co-Pi photoanode benefits from the following: (1) excellent visible light absorption of g-C₃N₄; (2) stable protection of TiO₂ to improve the durability of g-C₃N₄ film; and (3) photogenerated holes capture Co-Pi to separate photogenerated electron-hole pairs efficiently. This promising multifarious function layers structure provides a new perspective for PEC water splitting to generate hydrogen.

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1. Introduction

Hunting for solutions to the energy crisis and environment issue, clean hydrogen fuel has been extensively explored owing to its high energy density, easy storage, and transportability [1]. Of particular note is that photoelectrochemical (PEC) water splitting to generate hydrogen is an excellent device, where solar energy acts as energy provider and a semiconductor electrode acts as catalyst to decrease overpotential for the hydrogen evolution reaction (HER) [2]. However, to achieve efficient hydrogen generation by PEC water splitting, the semiconductor electrodes need to meet following critical factors simultaneously: (1) wide light response and absorption range; (2) efficient charge separation and transportation; and (3) high durability. Beginning with the first study by Fujishima et al. [3] in 1972, TiO₂ has been widely studied as an n-type semiconductor

electrode for PEC water splitting. In order to fully utilize solar energy, most studies have focused on developing new visible semiconductor electrodes such as Bi₂O₃ [4], WO₃ [5], α-Fe₂O₃ [6], and mpg-C₃N₄ [7].

Metal-free g-C₃N₄ composed of C and N elements has attracted increased attention owing to its improved optical properties, low cost, non-toxicity, and excellent chemical-Phys.stability [8–12]. Moreover, g-C₃N₄ is a medium band gap semiconductor of ~2.7 eV and an efficient photocatalyst is employed for a wide variety of reactions in water, including dye degradation and photocatalytic H₂ evolution [12,13]. Wang et al. [12] prepared bulk g-C₃N₄, which exhibits absorbance edge of 420 nm and photocatalytic H₂ evolution rate of 0.5 μmol·h⁻¹. Gao et al. [13] synthesized g-C₃N₄ nanosheets with absorbance edge of 450 nm, which shows a certain degradation ability of methylene blue. However, there are few reports about g-C₃N₄

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photoanodes for PEC water splitting to generate hydrogen. Based on the outstanding visible absorption and high stability of g-C₃N₄, we fabricated g-C₃N₄ film directly on fluorine-doped tin oxide (FTO) glass substrate as the photoanode for PEC water splitting to generate hydrogen [14].

The g-C₃N₄ film on FTO substrate was employed as the photoanode of the PEC device to generate hydrogen in water, which is easily recycled compared with dispersed g-C₃N₄ powder. Moreover, the durability of photoelectrodes must be also considered, especially after adding bias potential and immersing in water for a long time. Protective layers have been successfully developed to improve durability. Hu et al. [15] reviewed the protective thin layers (e.g., TiO₂, ZrO₂, SnO₂, SiO₂, etc) utilized on photoanodes for hydrogen evolution. Hou et al. [16] synthesized Co₃O₄ nanoparticles which were surrounded by the N-doped porous carbon (N-PC) hybrid act as a protective layer to stabilize the Co₃O₄ nanoparticles, and make the Co₃O₄/N-PC more stable during the test. Li et al. [17] designed the Pt/TiO₂/Ga₂O₃/Cu₂O electrode (TiO₂ as protective layer) which achieves a stable current for 2 h under continuous illumination of a 500-W Xe lamp. TiO₂ is one of the most excellent thin protective layers owing to its low price, optical transparency, and facile preparation. However, research on the use of TiO₂ thin layer to protect g-C₃N₄ photoanode is rare.

Unfortunately, the widespread application of g-C₃N₄ is limited by its inherent fast charge recombination [12]. It is noteworthy that co-catalyst loading has been attempted to suppress charge recombination and promote charge separation [18,19]. For example, some noble metal co-catalysts like Au and Pt were employed to inhibit charge recombination and accelerate charge transportation to improve the photocatalytic hydrogen generation efficiency of g-C₃N₄ [20,21]. Recently, non-noble-metal co-catalysts have been widely researched because of their excellent performance and low cost. Yu et al. [22] introduced Ni(OH)₂ as a non-noble-metal co-catalyst that promotes the transportation of photogenerated electrons from g-C₃N₄ to Ni(OH)₂ in order to improve the photocatalytic H₂ generation activity of g-C₃N₄. Meanwhile, it was also found that the H₂ production rate of 7.6 μmol·h⁻¹ of 0.5 mol% Ni(OH)₂/g-C₃N₄ approached that of 8.2 μmol·h⁻¹ of 1.0 wt% Pt/g-C₃N₄.

Cobalt-phosphate (Co-Pi) is a non-noble-metal co-catalyst that has become increasingly important because of its availability, ion permeability, and self-repair; thus, it can be self-assembled as an amorphous film on the surface of various material by a photoelectric deposition method [23,24]. More importantly, Co-Pi can decrease overpotential of water splitting, increase semiconductor band bending near the semiconductor/liquid junction, capture and extend lifetimes for photogenerated holes, suppress photogenerated electron-hole pair recombination, and promote or induce onset potential negative shift [23–26]. Tong et al. [27] fabricated TiO₂/BiVO₄/Co-Pi nanorod arrays on the FTO substrate as photoanode for PEC water splitting. Their electrochemical impedance spectroscopy results show that Co-Pi can promote charge transfer and separation by greatly decreasing the charge transfer resistance at the TiO₂/BiVO₄/Co-Pi and electrolyte interface. However, sys-

tematic studies of both the protective layer and hole capture layer on the g-C₃N₄ photoanode remain few.

Here, we report a novel g-C₃N₄/TiO₂/Co-Pi photoanode with multifarious function layers for PEC water splitting to generate hydrogen. The g-C₃N₄ film as light-absorption layer is directly synthesized on the FTO substrate by a thermal vapor liquid-polymerization method. The TiO₂ film as protective layer is covered on the g-C₃N₄ film to improve the durability of g-C₃N₄. The Co-Pi as hole capture layer is employed to promote photogenerated electron-hole pair separation. The g-C₃N₄/TiO₂/Co-Pi photoanode exhibits enhanced PEC performance with increased photocurrent density of 0.346 mA·cm⁻² at 1.1 V (vs. RHE), and shows quite good durability.

2. Experimental

2.1. The preparation of g-C₃N₄ film

The g-C₃N₄ film was directly grown on the FTO substrate by a thermal vapor liquid-polymerization method. Thiourea was chosen as a precursor of g-C₃N₄ because of its low price. Thiourea particles were ground into fine powder. Next, 7 g of thiourea powder were transferred into a small ceramic ark, and then the FTO substrate with the conductive surface faced downward covered the ceramic ark. Subsequently, these were put in a muffle furnace and heated to 500 °C for 1 h. After cooling down to room temperature, the g-C₃N₄ film on the FTO substrate was acquired.

2.2. The preparation of TiO₂ thin layer

The TiO₂ thin layer was prepared on the surface of g-C₃N₄ film by a dip-coating method. Firstly, TiO₂ sol was prepared. In a typical synthesis process, 10 mL of titanium butoxide was added to 40 mL ethanol and subjected to magnetic stirring for 15 min. Diethanolamine was slowly added and stirred for 2 h. Subsequently, water and ethanol were added and stirred for another 2 h. After seven days, TiO₂ sol was coated on the surface of the g-C₃N₄ film by a dip-coating method. Finally, the g-C₃N₄/TiO₂ film was heated in a muffle furnace at 500 °C for 1 h to ensure that TiO₂ was well crystallized.

2.3. The preparation of Co-Pi layer

The Co-Pi layer was synthesized directly on the surface of the g-C₃N₄/TiO₂ film using an electrochemical workstation (LK2005A) and Xe lamp (CHF-XM500, 100 mW·cm⁻²) by a photoelectric deposition method. A three-electrode system was utilized, consisting of the g-C₃N₄/TiO₂ film on the FTO substrate as the working electrode, Ag/AgCl as the reference electrode, and Pt foil as the counter electrode. Then, 0.4 V vs. Ag/AgCl was Appl. in a solution (pH = 7) containing 0.5 mmol·L⁻¹ cobalt nitrate and 0.1 mol·L⁻¹ potassium phosphate. The thickness of Co-Pi was controlled by the deposition time, which ranged between 10 and 60 s. The Co-Pi layer was deposited on the g-C₃N₄/TiO₂ film and then washed with deionized water. The g-C₃N₄/TiO₂/Co-Pi film was obtained after drying in an air ov-

en.

2.4. Characterization

The morphology and structure of as-prepared samples were analyzed by a JEOL JSM-7800F scanning electron microscope (SEM). The energy dispersive X-ray spectroscopy (EDS) characterization of as-prepared samples was carried out under SEM observation. The crystal structure of as-prepared samples was identified by Rigaku D/max-2500 X-ray diffraction (XRD) with Cu K_{α} radiation ($\lambda = 0.154059$ nm). The optical absorption capability of as-prepared samples was investigated by DU-8B UV-Vis double-beam spectrophotometer using the FTO substructure as reference. All as-prepared samples were used as photoanodes in the PEC device, and their PEC performance was investigated in 0.1 mol·L⁻¹ Na₂SO₄ aqueous solution by an electrochemical workstation (LK2005A) and Xe lamp (CHF-XM500, 100 mW·cm⁻²) with global AM 1.5 G. A Pt foil and saturated Ag/AgCl were used as the counter electrode and reference electrode, respectively. The pH value was tested based on 0.1 mol·L⁻¹ Na₂SO₄, which is approximately 7.1. The Ag/AgCl potential was converted to the reversible hydrogen electrode (RHE) according to the Nernst equation as follows:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \text{ pH} + 0.1976 \text{ V}$$

The incident photon-to-current conversion efficiency (IPCE) plots are recorded in the range 300–900 nm at 1.1 V (vs. RHE) under AM 1.5 G illumination. The electrochemical impedance spectroscopy (EIS) measurements were performed by an electrochemical workstation under the illumination of a Xe lamp (100 mW·cm⁻²). The potential value of the EIS data is 1.1 V (vs. RHE).

3. Results and discussion

The schematic illustration of the synthesis of g-C₃N₄/TiO₂/Co-Pi film is displayed in Fig. 1. In Step 1, thiourea particles were ground into powder and transferred to a ceramic ark, which was covered by the FTO substrate with the conductive surface facing downward. The g-C₃N₄ film on the FTO

Fig. 1. Diagram of the synthesis of g-C₃N₄/TiO₂/Co-Pi film.

substrate was acquired after heating in a muffle furnace at 500 °C for 1 h. In Step 2, the TiO₂ thin layer was prepared on the surface of the g-C₃N₄ film by a dip-coat method. In Step 3, the Co-Pi thin layer was photoelectrically deposited on the surface of the g-C₃N₄/TiO₂ film at 0.4 V vs. Ag/AgCl in a solution (pH = 7) containing 0.5 mmol·L⁻¹ cobalt nitrate and 0.1 mol·L⁻¹ potassium phosphate for a time. Finally, as-prepared g-C₃N₄/TiO₂/Co-Pi film was obtained.

As shown by the top-view SEM image in Fig. 2(a), the surface of as-prepared g-C₃N₄ film has plenty of irregular pores with different sizes in contact with each other to form a framework structure, which provides a higher surface area to promote the PEC reaction because the area of a curved surface is larger than that of a plane surface in the same space. The relevant cross-section SEM image is displayed in Fig. 2(b). It can be observed that the film thickness of as-prepared g-C₃N₄ is approximately 2 μm, which indicates that as-prepared g-C₃N₄ film is well grown on the FTO substrate.

The XRD pattern is presented in Fig. 2(c). Two obvious diffraction peaks, a weak peak at approximately 13.1° and a strong peak at approximately 27.4°, can be indexed to the (100) facet and (002) facet of g-C₃N₄, respectively, in accordance with the reports of previous literature about g-C₃N₄ [11–13]. Other diffraction peaks belong to the FTO substrate (JCPDS Card No. 46–1088). Therefore, g-C₃N₄ film on the FTO substructure has been obtained successfully.

The UV-Vis absorption spectra in the wavelength range of 300–900 nm is presented in Fig. 2(d). It can be noted that the absorption edge of the g-C₃N₄ film reaches 470 nm to realize outstanding absorption function within visible light range. Meanwhile, the absorbance of the g-C₃N₄ film is higher, which can be attributed to the improved light-harvesting ability of the framework structure owing to its increased light reflection. Subsequently, the plot of $(\alpha h\nu)^2$ of the g-C₃N₄ film is presented in Fig. S1. Its band gap was calculated according to the following equation [14]:

$$(\alpha h\nu)^n = A(h\nu - E_g) \quad (1)$$

where α represents the absorbance, h represents the Planck constant, ν represents the light frequency, and A is a constant, when n is 2 or 1/2 for the direct or indirect band gap, respectively. The band gap of the g-C₃N₄ film is ~2.6 eV. As expected, its band gap is applicable for visible light absorption. Thus, the g-C₃N₄ film can be a light-absorption layer layer to harvest and absorb visible light.

The top-view SEM image of as-prepared g-C₃N₄/TiO₂/Co-Pi film is shown in Fig. 3(a). It can be noted that the surface of film is evenly covered by plenty of particles, which should be Co-Pi according to the preparation process. As can be seen from the inset of Fig. 3(a), these Co-Pi particles are approximately 100 nm, and are distributed and aggregated randomly on the surface of film. The corresponding cross-section SEM image of as-prepared g-C₃N₄/TiO₂/Co-Pi film is presented in Fig. 3(b). The as-prepared g-C₃N₄/TiO₂/Co-Pi film is ~3 μm in height on average, which is 1 μm higher than that of pure g-C₃N₄ film. The XRD pattern of as-prepared g-C₃N₄/TiO₂/Co-Pi film is displayed in Fig. 3(c). The strongest diffraction peak at approximately 27.4° is the characteristic peak of g-C₃N₄ corresponding to the

Fig. 2. Top-view (a), cross-section (b) SEM images, XRD pattern (c), and UV-Vis absorbance spectrum (d) of g-C₃N₄ film.

Fig. 3. Top-view (a), and cross-section (b) SEM images, and XRD pattern (c) of g-C₃N₄/TiO₂/Co-Pi film.

(002) facet. The diffraction peak of g-C₃N₄ at approximately 13.1° disappears, which can be attributed to the second heating. Other peaks marked with “●” are consistent with the diffraction peaks of FTO substrate matched with JCPDS Card No. 46–1088. Apart from the peaks of the FTO and g-C₃N₄, of particular interest is some diffraction peaks at $2\theta \approx 31.5^\circ$, 33.6° , 55.1° , 61.3° , and 65.7° , which correspond to (002), (221), (411), (420), and (004) facets of hexagonal TiO₂ (JCPDS Card No. 33–1381), respectively. Other diffraction peaks at approximately 30.0° , 37.8° , 43.6° and 44.6° , which correspond to (401), (401), (003), and (511) facets of monoclinic TiO₂ (JCPDS Card No. 33–1381), respectively. The obtained TiO₂ belongs to two different crystal systems; the specific reason why is not clear and needs further study, but it is worth noting that TiO₂ is highly pure and well crystallized. There are no obvious diffraction peaks of Co-Pi because it is a kind of amorphous material.

To further verify the successful synthesis of Co-Pi, EDS characterization of as-prepared g-C₃N₄/TiO₂/Co-Pi film was carried out under SEM observation. As shown in Fig. 4, the detection area of element distribution mappings was randomly selected under SEM observation. The elemental distribution mappings indicate the obvious existence of C, N, Ti, O, Co, and Pi elements in the detection area, which manifests that Co and Pi

elements are distributed uniformly on the film. All SEM, XRD, and EDS analyses results prove that g-C₃N₄/TiO₂/Co-Pi film was successfully synthesized.

The photocurrent density-voltage (*I*-*V*) curves of g-C₃N₄ and g-C₃N₄/TiO₂/Co-Pi photoanodes are shown in Fig. 5(a). It can be seen that the photocurrent density of the g-C₃N₄ photoanode is approximately 0.095 mA·cm⁻² at 1.1 V (vs. RHE); that of g-C₃N₄/TiO₂/Co-Pi photoanode reaches ~0.346 mA·cm⁻², which is ~3.6 times as large as the former. This may be due to the combined effect of both the TiO₂ layer and Co-Pi layer on the g-C₃N₄ light-absorption layer layer. In order to determine the specific reasons for increased photocurrent density, the photocurrent density of g-C₃N₄/TiO₂ photoanode was measured

Fig. 4. Element distribution mappings of g-C₃N₄/TiO₂/Co-Pi film.

Fig. 5. (a) Photocurrent density-voltage curves and (b) photocurrent density-time curves at 1.1 V vs. RHE with a 60 s light on/off of g-C₃N₄ film and g-C₃N₄/TiO₂/Co-Pi film.

under the same conditions, as shown in Fig. S2(a). What can be clearly seen is that the photocurrent density of g-C₃N₄/TiO₂ photoanode is far away from that of the g-C₃N₄ photoanode and g-C₃N₄/TiO₂/Co-Pi photoanode, which indicates that the individual TiO₂ layer is not able to improve the photocurrent density of g-C₃N₄ photoanode, and the ameliorative PEC performance mainly relies on the Co-Pi layer. Additionally, the onset potential of g-C₃N₄/TiO₂/Co-Pi photoanode is more negative than that of g-C₃N₄ photoanode, which is consistent with previous reports about Co-Pi [24,25,28]. The positive shift of the photocurrent onset potential is caused by the slow kinetics and/or surface recombination [24]. Thus, the negative shift of the onset potential of g-C₃N₄/TiO₂/Co-Pi photoanode should be that Co-Pi layer could capture photogenerated holes to suppress charge recombination and promote charge transport. The actual effect of the Co-Pi layer is further studied below.

To further investigate the photoresponse performance of the g-C₃N₄ photoanode and g-C₃N₄/TiO₂/Co-Pi photoanode, the transient photocurrent density-time (*I*-*t*) curves were obtained at 1.1 eV (vs. RHE) under chopped light irradiation. As shown in Fig. 5(b), both the g-C₃N₄ photoanode and g-C₃N₄/TiO₂/Co-Pi photoanode display good photoresponse performance according to the rapid rise/decline in photocurrent with the light on/off, which suggests that these photoanodes have a good charge transport ability [4], especially the g-C₃N₄/TiO₂/Co-Pi photoanode. After the first stable light irradiation period, the photocurrent densities of the g-C₃N₄ photoanode and g-C₃N₄/TiO₂/Co-Pi photoanode basically agreed with the values in Fig. 5(a). It can be seen that photocurrent and dark current densities of the g-C₃N₄ photoanode have a certain decrease along with the increase in light on/off cycles, and dark current density starts to decline at a certain value until it reaches zero. This indicates that the durability of the g-C₃N₄ photoanode needs to be further improved. The dark current density of the g-C₃N₄/TiO₂/Co-Pi photoanode is always zero, and its photocurrent density has a certain decline along with increased light on/off cycles. The decrease in photocurrent density of g-C₃N₄/TiO₂/Co-Pi photoanode is influenced by chopped light irradiation. Some photogenerated electron-hole pairs excited by the first light irradiation could recombine with those excited by the second light irradiation. The transport and separation of

photogenerated electron-hole pairs is not sufficiently stable under short chopped light irradiation, which leads to the decrease in photocurrent density of g-C₃N₄/TiO₂/Co-Pi. Therefore, the photocurrent density of g-C₃N₄/TiO₂/Co-Pi photoanode was further measured under continuous light irradiation, as shown in Fig. S2(b). What can be clearly noted is that the photocurrent density of g-C₃N₄/TiO₂/Co-Pi photoanode is quite stable and has no obvious decrease for 2 h. Under long light irradiation, the transport and separation of photogenerated electron-hole pairs achieve enough stability; thus, the photocurrent density of g-C₃N₄/TiO₂/Co-Pi photoanode is quite stable. In a word, the durability of g-C₃N₄/TiO₂/Co-Pi photoanode is higher than that of g-C₃N₄ photoanode, which is attributed to the protective TiO₂ and Co-Pi layers, especially the TiO₂ layer. The role of the TiO₂ layer in protecting g-C₃N₄ film on the FTO substrate starts from the photoelectric deposition of Co-Pi to the PEC performance tests.

Furthermore, to illustrate the relationship between the wavelength of the incident light and photoelectrochemical activity based on g-C₃N₄ photoanode and g-C₃N₄/TiO₂/Co-Pi photoanode, IPCE plots in range 300–900 nm at 1.1 V (vs. RHE) are presented in Fig. 6(a). It can be noted that the IPCE outline of the g-C₃N₄/TiO₂/Co-Pi photoanode displays improved photon-to-current conversion activity compared to that of g-C₃N₄ photoanode over the visible light region, which is attributed to the effect of light absorption of g-C₃N₄ and the good charge transport ability of Co-Pi. The charge transfer and separation performance of g-C₃N₄ photoanode and g-C₃N₄/TiO₂/Co-Pi photoanode were tested using the same electrochemical workstation. The EIS of all photoanodes is shown in Fig. 6(b). All EIS Nyquist plots of these photoanodes include semicircles. Of particular note is that the arc radius of g-C₃N₄/TiO₂/Co-Pi photoanode is smaller than that of g-C₃N₄ photoanode, which implies that the charge transfer resistance of g-C₃N₄/TiO₂/Co-Pi photoanode is less than that of g-C₃N₄ photoanode. Therefore, the photogenerated electron-hole pairs of g-C₃N₄/TiO₂/Co-Pi photoanode can be transferred easily, which is attributed to the fact that the Co-Pi layer can catch or trap the photogenerated holes to promote the separation of photogenerated electron-hole pairs. The g-C₃N₄ layer as light-absorption layer layer can be excited to generate photogenerated electron-hole pairs

Fig. 6. (a) Incident photon-to-current conversion efficiency (IPCE) plots and (b) electrochemical impedance spectroscopy of g-C₃N₄ film and g-C₃N₄/TiO₂/Co-Pi film.

under light irradiation. The photogenerated electrons reach the conduction band of g-C₃N₄ from its valence band, and then flow into the counter electrode through a wire. Finally, the photogenerated electrons participate in water splitting to generate hydrogen. The TiO₂ layer, as the protective layer, can protect the g-C₃N₄ film on the FTO substrate all the time. The Co-Pi layer, as the hole capture layer, can trap the photogenerated holes and promote the separation of photogenerated electron-hole pairs to improve the PEC performance.

4. Conclusions

In summary, we designed a novel photoanode with a multiple function layers structure, including a g-C₃N₄ light-absorption layer layer, TiO₂ protective layer, and Co-Pi hole capture layer, which was Appl. in PEC water splitting to generate hydrogen. The g-C₃N₄/TiO₂/Co-Pi photoanode presents enhanced PEC performance with photocurrent density of 0.346 mA·cm⁻² at 1.1 V (vs. RHE) owing to its outstanding visible light absorption, photogenerated electron-hole pair separation, and durability. This promising multifarious function layered structure provides a new strategy for PEC water splitting

to generate hydrogen.

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Graphical Abstract

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g-C₃N₄/TiO₂/Co-Pi photoanode for PEC water splitting to generate hydrogen. g-C₃N₄ as light-absorption layer layer, TiO₂ as protection layer and Co-Pi as hole capture layer. Enhanced performances due to outstanding light absorption, charges separation and durability.

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g-C₃N₄ 基多功能层光阳极在光电化学水分解中的应用

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摘要: 光电化学分解水制氢可以一并解决环境问题和能源危机, 因而成为研究热点. 由于 TiO₂ 禁带宽度较大, 不能有效吸收太阳光中的可见光, 使光电化学分解水制氢的应用受限. g-C₃N₄ 的禁带宽度约为 2.7 eV, 能有效吸收可见光, 但 g-C₃N₄ 薄膜制备研究较少. 我们通过热聚缩合法直接在 FTO 导电玻璃上制备出 g-C₃N₄ 薄膜, 发现其光电化学分解水制氢稳定性不高, 选择易制备的 TiO₂ 作为保护层可以提高 g-C₃N₄ 的耐用性. 此外, 为提高 g-C₃N₄ 光生电子空穴对的分离能力, 依靠 Co-Pi 对光生空穴的捕获作用而将其覆盖在最外层. 因此本文首次制备一种新型的 g-C₃N₄/TiO₂/Co-Pi 光阳极用于光电化学分解水制氢, 其中 g-C₃N₄ 用作光吸收层, TiO₂ 用作保护层, Co-Pi 用作空穴捕获层. 并在此基础上, 通过扫描电子显微镜 (SEM), X 射线衍射 (XRD), 紫外可见光谱 (UV-Vis) 等手段研究了 g-C₃N₄/TiO₂/Co-Pi 光阳极的形貌特征和光电化学性能.

SEM、EDS 和 XRD 结果表明, g-C₃N₄/TiO₂/Co-Pi 光阳极被成功制备在了 FTO 导电玻璃上, 厚度约为 3 μm. UV-Vis 测试表明, g-C₃N₄ 的光吸收边约为 470 nm, 可以有效地吸收可见光, 并且 g-C₃N₄ 的框架结构使光多次反射折射增加了光的捕获能力, 由此可见, g-C₃N₄ 能够发挥很好的光吸收层作用. 通过对 g-C₃N₄ 光阳极, g-C₃N₄/TiO₂ 光阳极和 g-C₃N₄/TiO₂/Co-Pi 光阳极的电流电压测试发现, g-C₃N₄/TiO₂ 光阳极的光电流密度小于 g-C₃N₄ 光阳极, 而 g-C₃N₄/TiO₂/Co-Pi 光阳极的光电流密度在可逆氢电极 1.1 V 下达到了 0.346 mA·cm⁻², 约为单独 g-C₃N₄ 光阳极的 3.6 倍. 这说明 Co-Pi 是提升 g-C₃N₄ 光电化学性能的主要因素. 电化学阻抗测试结果发现, g-C₃N₄/TiO₂/Co-Pi 光阳极的界面电荷转移电阻小于 g-C₃N₄ 光阳极的, 这表明 g-C₃N₄/TiO₂/Co-Pi 光阳极界面处载流子转移较快, 同时也能促进内部光生电子空穴对的分离, 整体性能的提高应该主要归因于 Co-Pi 对光生空穴的捕获作用. 恒电压时间测试展示出 g-C₃N₄/TiO₂/Co-Pi 光阳极的光电流密度在 2 h 测试过程中没有明显下降, 表明 g-C₃N₄/TiO₂/Co-Pi 光阳极是相当稳定的, 具有良好的耐用性, 归因于 TiO₂ 和 Co-Pi 的共同保护作用, 主要归因于 TiO₂ 层对 FTO 导电玻璃上的 g-C₃N₄ 薄膜保护, 从电化学沉积 Co-Pi 到所有测试结束. 总体而言, g-C₃N₄/TiO₂/Co-Pi 光阳极加强的光电化学性能归因于以下几个因素: (1) g-C₃N₄ 优异的光吸收能力; (2) TiO₂ 稳定的保护提升了 g-C₃N₄ 薄膜的耐用性; (3) Co-Pi 对光生空穴的捕获有效促进了光生电子空穴对的分离.

关键词: g-C₃N₄; TiO₂; Co-Pi; 光阳极; 光电化学水分解

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