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Electrodeposition of $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4$ heterojunction film on an FTO substrate for enhancing visible light photoelectrochemical water splitting

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ABSTRACT

An immobilized $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4$ heterojunction film was successfully made on an FTO substrate by electrophoretic deposition of $\text{g-C}_3\text{N}_4$ on a Cu_2O thin film. The photoelectrochemical (PEC) performance for water splitting by the $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4$ film was better than pure $\text{g-C}_3\text{N}_4$ and pure Cu_2O film. Under -0.4 V external bias and visible light irradiation, the photocurrent density and PEC hydrogen evolution efficiency of the optimized $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4$ film was -1.38 mA/cm^2 and $0.48\text{ mL h}^{-1}\text{ cm}^{-2}$, respectively. The enhanced PEC performance of $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4$ was attributed to the synergistic effect of light coupling and a matching energy band structure between $\text{g-C}_3\text{N}_4$ and Cu_2O as well as the external bias.

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1. Introduction

In the past several decades, photoelectrochemical (PEC) hydrogen evolution from water using semiconductors as photocatalyst has attracted extensive attention because it is a promising clean and renewable energy technology [1–5]. Among the various semiconductors, p-type cuprous oxide (Cu_2O) is one of the most promising visible light PEC materials for water splitting [6–8]. On the one hand, Cu_2O gives a higher

photoconversion efficiency with a conduction band (CB) of -1.4 eV versus NHE and a direct band gap of $2.0\text{--}2.4\text{ eV}$ [9,10]. On the other hand, the photocurrent and light-to-hydrogen conversion efficiency of Cu_2O can be as high as -14.8 mA/cm^2 and 18.7% , respectively, in theory [11]. However, the reported photoconversion efficiency of Cu_2O is far below the theoretical value [12,13]. Furthermore, pure Cu_2O suffers from inadequate stability in the presence of visible light [12,14]. Therefore, attention was focused on improving the PEC performance and

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stability of Cu₂O [15,16].

It is well known that graphitic carbon nitride (g-C₃N₄) or composites based on g-C₃N₄ are promising visible light photocatalysts for the PEC or photocatalytic (PC) hydrogen evolution due to their low band gap energy of 2.7 eV, and their metal-free semiconductivity, nontoxicity, and natural abundance [17–24]. In addition, the CB and VB positions of g-C₃N₄ are –1.1 and 1.6 eV vs. NHE, respectively [25,26], which exactly matches the band potentials of Cu₂O [9,10]. Many works have reported that the photocatalytic activity of a Cu₂O/g-C₃N₄ heterojunction photocatalyst was greatly improved compared to pure Cu₂O and pure C₃N₄ [27–32]. For example, our study showed that a g-C₃N₄/Cu₂O composite powder displayed an enhanced photocatalytic performance compared to pure g-C₃N₄ and pure Cu₂O because of the better separation of photogenerated charges (electron-hole pairs) in the two semiconductors [32]. However, reported Cu₂O/g-C₃N₄ composites are almost all powder photocatalysts, which are difficult to separate from liquid systems. Furthermore, it is necessary to add sacrificial agent as electron donors and deposit the co-catalyst on Cu₂O/g-C₃N₄ in the photocatalytic process.

It will broaden the application of g-C₃N₄/Cu₂O composites as visible light photocatalysts to immobilize g-C₃N₄ on a Cu₂O film based on the FTO substrate because the PEC performance can be improved by the reduction of electron-hole recombination and the photoelectrode can be easily recycled and reused. In this study, we fabricated a Cu₂O/g-C₃N₄ heterojunction film on an FTO substrate by an electrochemical deposition method. The Cu₂O/g-C₃N₄ film showed excellent activity and reusability for visible light PEC water splitting.

2. Experimental

2.1. Materials and synthesis

The Cu₂O films on the FTO substrate were grown by the electrochemical deposition method in a three-electrode cell using FTO glass (3.5 × 2 cm²), Pt plate and Ag/Cl (SAE) as the working, counter and reference electrodes, respectively [33]. A solution of 0.4 mol/L CuSO₄ and 3.0 mol/L lactic acid was applied as the electrolyte. The electrolyte was adjusted to pH = 10.0 with 5.0 mol/L NaOH aqueous solution. The electrochemical deposition potential was –0.8 V_{SAE} and deposition time was 100 s. The samples obtained were cleaned with deionized water and dried overnight in vacuum.

The g-C₃N₄ nanoparticles were fabricated by a general sol-gel method reported in our previous reports [32,33]. The g-C₃N₄ nanoparticles were deposited on the Cu₂O film on the FTO substrate by an electrophoretic deposition process [34]. Briefly, g-C₃N₄ nanoparticles loaded on the Cu₂O films of the FTO substrate were obtained in a two-electrode cell using a deposition potential of 50 V, and the FTO substrate with the Cu₂O film and Pt plate were used as the cathode and anode, respectively. The two electrodes were immersed in the electrolyte and then 40 mg g-C₃N₄ and 10 mg iodine powder were added to 50 mL acetone and sonicated for 20 min. The content of g-C₃N₄ in the Cu₂O/g-C₃N₄ heterojunction film was controlled

by the deposition time. In the process, iodine in the solution reacts with acetone and generated H⁺, which made the g-C₃N₄ particles positively charged. Four Cu₂O/g-C₃N₄ samples were prepared by varying the deposition time as 5, 10, 15 and 20 s, and are denoted as Cu₂O/g-C₃N₄-5, Cu₂O/g-C₃N₄-10, Cu₂O/g-C₃N₄-15 and Cu₂O/g-C₃N₄-20, respectively. Pure Cu₂O and g-C₃N₄ films were also fabricated for comparison. The deposition time of pure g-C₃N₄ on FTO was 15 s. Finally, the obtained samples were dried in vacuum at 80 °C.

2.2. Characterization

The surface morphology of the samples was viewed on a field emission scanning electron microscope (FESEM, LEO 1530VP, Germany) and a model JEOL-2010 transmission electron microscope (TEM, Japan) with an operation voltage of 200 kV. The element contents of the samples were analyzed by energy dispersive X-ray spectroscopy (EDX, JEM-2100). The crystal structure of the samples was determined using a Model D/max 2500v/pc X-ray diffractometer (XRD, Rigaku, Japan). Diffuse reflectance absorption spectra were recorded using an ultraviolet-visible (UV-vis) spectrometer (U3010, Hitachi).

2.3. Evaluation

PEC tests were performed with a three-electrode cell described in our previous report [33]. The PEC experiments for hydrogen and oxygen production were completed in a 150 mL temperature controlled three-electrode sealed cell (NBeT, Beijing) at an applied potential of –0.4 V under visible light (100 mW/cm²) illumination. The light was from a 300W Xe arc lamp equipped with an ultraviolet cutoff filter to provide visible light with $\lambda \geq 400$ nm (PLS-SXE300UV Xe lamp, 100 mW/cm²). A 0.1 mol/L NaNO₃ solution was used as supporting electrolyte, Ag/AgCl as reference electrode, and the Cu₂O/g-C₃N₄ film on the FTO substrate (2.0 × 2.0 cm²) as working electrode and Pt wire as counter electrode. A gas sample of 100 μ L was withdrawn from the cell headspace every 1 h with a glass syringe and analyzed using a gas chromatograph (GC-14C, Shimadzu, Japan, TCD) equipped with a 5 Å molecular sieve column and high purity nitrogen as carrier gas.

3. Results and discussion

3.1. Structure and composition

Two distinct diffraction peaks was observed in the XRD pattern of the pure Cu₂O film on the FTO substrate (Fig. 1). The stronger peak located at $2\theta = 36.52^\circ$ was due to the (111) plane of Cu₂O, and the other one located at $2\theta = 42.44^\circ$ was attributed to the (200) plane of Cu₂O [33,35]. For the pure g-C₃N₄ film on the FTO substrate, one characteristic peak at $2\theta = 27.53^\circ$, corresponding to the interlayer stacker structural packing, was observed. The weak diffraction peak at $2\theta = 13.12^\circ$ for g-C₃N₄ reported in our previous work [32] was not observed. The possible reason was the appearance of the strong characteristic peak at 37.70° of the FTO substrate. Also shown in Fig.

Fig. 1. XRD patterns of the different samples. (1) Cu₂O; (2) Cu₂O/g-C₃N₄-5; (3) Cu₂O/g-C₃N₄-10; (4) Cu₂O/g-C₃N₄-15; (5) Cu₂O/g-C₃N₄-20; (6) g-C₃N₄.

1(2)–(5), with increase in the deposition time, a diffraction peak located at $2\theta = 27.53^\circ$ corresponding to g-C₃N₄ was observed, and the peak intensity increased gradually. The results confirmed that g-C₃N₄ nanoparticles were successful loaded on the Cu₂O nano-film.

3.2. Morphology

Fig. 2(a) shows the top view image of the as-prepared Cu₂O particles on the FTO substrate. The Cu₂O particles exhibited a polyhedral shape and a relatively smooth surface with side length of 90 nm. The growth of g-C₃N₄ on the Cu₂O film on the FTO substrate is demonstrated in Fig. 2(b)–(e). With electro-

deposition time increase, the amount of g-C₃N₄ nanoparticles deposited on the surface of Cu₂O film increased. Fig. 2(c) clearly shows that g-C₃N₄ nanoparticles with the size of 15 nm were deposited on the surface of Cu₂O. Fig. 2(d) displays that g-C₃N₄ nanoparticles almost cover all of the surface of the Cu₂O film when the electrophoretic deposition time was 15 s. Furthermore, the shape of the original Cu₂O was still preserved as polyhedron, indicating that g-C₃N₄ could be uniformly loaded on the surface of Cu₂O by the electrophoretic deposition method. After 20 s of electrophoretic deposition, g-C₃N₄ nanoparticles aggregated on the Cu₂O surface as shown in Fig. 2(e). Fig. 2(f) shows that pure g-C₃N₄ nanoparticles with the size of 15 nm were uniformly deposited on the surface of the FTO substrate, indicating that the electrophoretic deposition process has no effect on the morphology of the g-C₃N₄ nanoparticles. The EDX spectrum (Fig. 2(g)) revealed that the Cu₂O/g-C₃N₄-15 film on the FTO glass was composed of C, N, O, Cu, Si and Sn. The Si and Sn and part of the O elements were from the FTO glass. The atom counting rate of C to N in the selected region was nearly 3:4, which matched well with the molecular structure of g-C₃N₄. From the calculated atom% of C and Cu elements, the relative molar ratio of Cu₂O and g-C₃N₄ on the Cu₂O/g-C₃N₄-15 electrode is 1.22.

The TEM images of the Cu₂O/g-C₃N₄-15 sample are shown in Fig. 3. The sample was peeled from the FTO glass using a blade and then sonicated in ethanol before it was dripped onto a copper screen. Fig. 3(a) shows that the morphology of the g-C₃N₄ particles did not change significantly. The HRTEM (Fig. 3(b)) showed the observed lattice spacing of 0.24 nm corresponded to the (111) crystal plane of the Cu₂O (JCPDS 005-0667), which is in accordance with the XRD result. Fig. 3(b) also implied that g-C₃N₄ and Cu₂O nanoparticles were well contacted and an intimate interface, i.e., heterojunction, was

Fig. 2. Top view FESEM images of Cu₂O (a), Cu₂O/g-C₃N₄-5 (b), Cu₂O/g-C₃N₄-10 (c), Cu₂O/g-C₃N₄-15 (d), Cu₂O/g-C₃N₄-20 (e) and g-C₃N₄ (f). EDX spectrum and element contents of Cu₂O/g-C₃N₄-15 (g).

Fig. 3. TEM (a), HRTEM (b) images and (c) element mapping of Cu, O, N and C of the $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4$ -15 sample.

formed between $\text{g-C}_3\text{N}_4$ and Cu_2O . The heterojunction helps charge transfer between $\text{g-C}_3\text{N}_4$ and Cu_2O and suppresses the recombination of photogenerated electron-hole pairs, thus resulting in an enhancement of the PEC performance over that of a pure Cu_2O film. Fig. 3(c) displays the elemental mapping of Cu, O, N and C of the $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4$ -15 sample. The mappings of the four elements have some overlap, confirming that $\text{g-C}_3\text{N}_4$ nanoparticles were successfully coupled with the surface of the Cu_2O film.

3.3. Optical property

The UV-vis light absorption curves of the $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4$ heterojunction composites with different contents of $\text{g-C}_3\text{N}_4$, and pure $\text{g-C}_3\text{N}_4$ and pure Cu_2O films on the FTO substrate are shown in Fig. 4. The pure Cu_2O film gave an absorption edge at 520 nm, with a band gap (E_g) calculated to be 2.39 eV by Kubelka-Munk theory. However, in our previous work [32], the E_g of Cu_2O nanoparticles was 2.03 eV. This difference was attributed to the different nanoparticle sizes [29]. The calculated E_g of pure $\text{g-C}_3\text{N}_4$ was 2.70 eV, which was the same as reported in our previous work. Fig. 4 also displays that the absorption intensities of $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4$ were reduced in the visible light

range with the increase of the deposition time of $\text{g-C}_3\text{N}_4$, and the intensity of all the $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4$ heterojunction films were located between the intensity values of pure Cu_2O and pure $\text{g-C}_3\text{N}_4$. From the optical photographs of the $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4$ film shown in the insets in Fig. 4, it can be seen that the color of the as-prepared films changed from deep yellow (Cu_2O) to light yellow ($\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4$ -15) and then white ($\text{g-C}_3\text{N}_4$), demonstrating that the visible light absorption ability of $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4$ decreases with the increase of deposition time of $\text{g-C}_3\text{N}_4$.

3.4. Photoelectrochemical performance and mechanism

Fig. 5 displays the PEC performance of the $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4$ heterojunction films, pure Cu_2O film and pure $\text{g-C}_3\text{N}_4$ film. From the transient photocurrent response curve of the different $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4$ heterojunction films shown in Fig. 5(a), it can be seen that there was almost no photocurrent in the absence of light irradiation for all the samples. The photocurrent densities of the pure $\text{g-C}_3\text{N}_4$ film and pure Cu_2O film at 40 s were -0.07 and -0.22 mA/cm^2 , respectively. With increased deposition time of $\text{g-C}_3\text{N}_4$, the photocurrent density of the $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4$ heterojunction films increased and reached a maximum value of 1.38 mA/cm^2 negative at 15 s deposition time. When the deposition time of $\text{g-C}_3\text{N}_4$ was increased further, the photocurrent density of the $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4$ heterojunction films decreased.

Fig. 5(b) shows the linear sweep voltammograms (LSV) of pure Cu_2O , $\text{g-C}_3\text{N}_4$ and $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4$ -15 heterojunction film on the FTO substrate in the dark and under visible light irradiation from -0.4 to 0 V. It can be seen that no photocurrent was observed in the dark for the three samples. A clear increase of the current was seen only below -0.15 V potential when the samples were exposed to visible light. The negative photocurrent generated by the $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4$ -15 composite photoelectrode was significantly higher than that of the plain $\text{g-C}_3\text{N}_4$ or Cu_2O photoelectrode. An exceptionally high cathode photocurrent response was achieved with the $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4$ -15 film, showing that it possessed superior visible light activity. In addition, the stability of the pure $\text{g-C}_3\text{N}_4$, Cu_2O and $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4$ -15 heterojunction films was evaluated by measuring the photocurrents for 20 min under visible light illumination of 100 mW/cm^2 .

As shown in Fig. 5(c), the plot revealed good stability of the $\text{g-C}_3\text{N}_4$ film, but the photoresponse activity was inefficient. It also shows that the photocurrent density of the pure Cu_2O film

Fig. 4. UV-vis absorption spectra of the different samples. (1) Cu_2O ; (2) $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4$ -5; (3) $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4$ -10; (4) $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4$ -15; (5) $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4$ -20; (6) $\text{g-C}_3\text{N}_4$.

Fig. 5. (a) Transient photocurrent response of the samples at a bias potential of -0.4 V (vs. Ag/AgCl) under visible light. (1) Cu_2O ; (2) $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4-5$; (3) $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4-10$; (4) $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4-15$; (5) $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4-20$; (6) $\text{g-C}_3\text{N}_4$. (b) Linear sweep voltammograms of Cu_2O , $\text{g-C}_3\text{N}_4$ and $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4-15$ films in the dark and with visible light. (c) The stability of Cu_2O , $\text{g-C}_3\text{N}_4$ and $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4-15$ electrode after 20 min.

decreased after 20 min under visible light irradiation. It is widely recognized that pure Cu_2O suffers from photocorrosion [12,14]. In contrast, after coupling with $\text{g-C}_3\text{N}_4$, i.e., $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4-15$, both the PEC activity and stability of the $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4$ photocatalyst were increased significantly. At -0.4 V, the photocurrent was stable at -1.32 mA/cm^2 for 20 min under continuous visible light illumination for a $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4-15$ photocathode. This result suggested that the $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4$ film was suitable for PEC splitting of water for hydrogen and oxygen evolution under visible light illumination.

PEC water splitting tests were performed at -0.4 V external bias. The gas generated in the sealed cell was collected with a 100 μL glass syringe and analyzed using a gas chromatograph. Fig. 6 displays the time courses of PEC water splitting from the $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4-15$ film under visible light irradiation. The reaction was tested for 3 cycles. The first cycle showed that the hydrogen evolution rate reached 0.48 $\text{mL h}^{-1} \text{cm}^{-2}$. After three cycles, the PEC water splitting efficiency had decreased only 10.8%, suggesting that the $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4-15$ heterojunction film on the FTO substrate was stable and has good reusability. It is noted that H_2 and O_2 evolution proceeded continuously in a molar ratio of H_2/O_2 of 2, demonstrating that visible light PEC water splitting on the $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4$ heterojunction film was

Fig. 6. Measured gas production from the $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4-15$ film at -0.4 V vs. Ag/AgCl under visible light of 100 mW/cm^2 illumination.

achieved.

Based on the above results, a mechanism was proposed for the photogenerated charge excitation and their transfer in the $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4$ heterojunction film on the FTO substrate, as well as the PEC water splitting process under visible light irradiation. As shown in the left side of Fig. 7, under visible light irradiation, electron-hole pairs were generated in both Cu_2O and $\text{g-C}_3\text{N}_4$ [36,37]. When $\text{g-C}_3\text{N}_4$ is in good contact with Cu_2O , the photoexcited electrons (e^-) in the CB of Cu_2O can transfer to the CB of $\text{g-C}_3\text{N}_4$ because the CB bottom of Cu_2O is more negative than that of $\text{g-C}_3\text{N}_4$. Similarly, the photoexcited holes (h^+) can transfer from the VB of $\text{g-C}_3\text{N}_4$ to the VB of Cu_2O because the VB top of $\text{g-C}_3\text{N}_4$ is more positive than that of Cu_2O [9,10,25], resulting in effective e^- - h^+ pair separation. In the PEC processes as shown in the right side of Fig. 7, the h^+ in the VB of Cu_2O can combine with electrons from the counter electrode due to the external bias. The electrons are generated from the reaction of H_2O (or OH^-) which was transformed into O_2 . The e^- in the CB of $\text{g-C}_3\text{N}_4$ can reduce H_2O (or H^+) to yield H_2 because of the positive potential (vs. NHE, $\text{pH} = 0$) of the CB of $\text{g-C}_3\text{N}_4$. When more e^- - h^+ pairs are separated on the $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4$ heterojunction film, more H_2 and O_2 production are achieved. As a result, the PEC water splitting efficiency of the Cu_2O film on the FTO substrate under visible light irradiation was improved significantly through the coupling with $\text{g-C}_3\text{N}_4$ nanoparticles to form a $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4$ heterojunction film.

Fig. 7. Schematic pathway for photoelectron excitation and transfer in the $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4$ film and the photoelectrochemical process under visible light irradiation.

4. Conclusions

An immobilized $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4$ heterojunction film on an FTO substrate was made by a two-step electrodeposition method. The XRD, SEM and HRTEM results confirmed that $\text{g-C}_3\text{N}_4$ nanoparticles were deposited on the Cu_2O surface. The photocurrent density of the Cu_2O film on the FTO substrate under visible light irradiation was increased significantly when it was coupled with $\text{g-C}_3\text{N}_4$ nanoparticles. PEC water splitting tests showed that the $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4$ heterojunction film on the FTO substrate was stable and exhibited good reusability. When the deposition time of $\text{g-C}_3\text{N}_4$ was 15 s, the $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4$ -15 heterojunction film displayed the highest PEC activity for water splitting under visible light irradiation.

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Graphical Abstract

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Electrodeposition of $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4$ heterojunction film on an FTO substrate for enhancing visible light photoelectrochemical water splitting

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$\text{g-C}_3\text{N}_4$ nanoparticles have been immobilized on a Cu_2O film with FTO substrate, resulting in a $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4$ heterojunction nanocomposite formation for efficient photoelectrochemical water splitting under visible light irradiation.

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在FTO导电玻璃上电化学沉积高效可见光光电化学分解水 Cu₂O/g-C₃N₄异质结膜

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摘要: 近几十年来, 光电化学分解水制氢作为一种洁净的、能持续利用太阳能的技术受到极大关注。在众多光催化材料中, p型半导体氧化亚铜(Cu₂O)被认为是最有前途的可见光光电分解水材料之一。理论上, 它的光能转换为氢能的效率可达到18.7%。然而, 目前所报道的Cu₂O光转换效率远远低于此值; 同时, 纯Cu₂O在光照条件下的稳定性较差。研究表明, Cu₂O与其它半导体复合可以增强其光电转换效率和提高稳定性。如Cu₂O和能带匹配的石墨相氮化碳(g-C₃N₄)复合后, 光催化性能和稳定性都有较大提高。但目前所报道的Cu₂O/g-C₃N₄复合物几乎都是粉末状催化剂, 不利于回收和重复使用。

本文首先采用电化学方法在FTO导电玻璃上沉积Cu₂O薄膜, 采用溶胶凝胶法制备g-C₃N₄纳米颗粒材料, 然后采用电化学法在Cu₂O薄膜表面沉积一层g-C₃N₄纳米颗粒, 得到了Cu₂O/g-C₃N₄异质结膜。分别利用X射线粉末衍射(XRD)、高分辨透射电子显微镜(HRTEM)、扫描电子显微镜(SEM)、紫外可见光谱(UV-Vis)和光电化学分解水实验分析了Cu₂O/g-C₃N₄异质结的组成结构、表面形貌、光吸收性能及催化剂活性和稳定性。

XRD和HRTEM表征显示, 本文成功合成了Cu₂O/g-C₃N₄异质结材料, SEM图表明g-C₃N₄纳米颗粒在Cu₂O表面分布均匀, 大小均一。可见光光电化学分解水结果显示, 异质结薄膜的光电化学性能比纯的Cu₂O和g-C₃N₄薄膜材料有极大提高。当在Cu₂O表面沉积g-C₃N₄的时间为15 s时, 得到样品Cu₂O/g-C₃N₄-15异质结膜, 其在-0.4 V和可见光照射条件下, 光电流密度达到了-1.38 mA/cm², 分别是纯Cu₂O和g-C₃N₄薄膜材料的19.7和6.3倍。产氢速率也达到了0.48 mL h⁻¹ cm⁻², 且产氢和产氧的速率之比约为2, 说明此异质结材料在可见光作用下能全分解水。经过三次循环实验, 光电化学分解水的效率仅降低10.8%, 表明该材料具有良好的稳定性。根据UV-Vis表征和光电化学性能对比, Cu₂O/g-C₃N₄-15的光电性能最好, 但其光吸收性能并不是最好, 说明光电化学性能与光吸收不是成正比关系, 主要是由于Cu₂O和g-C₃N₄两个半导体相互起到了协同作用。机理分析表明, Cu₂O/g-C₃N₄异质结薄膜在光照下, 由于两者能带匹配, Cu₂O的光生电子从其导带转移到g-C₃N₄的导带上, g-C₃N₄价带上的空穴转移到Cu₂O的价带上, 从而降低了光生电子和空穴的复合, 提高了其光催化性能。由于g-C₃N₄的导带位置高于H₂O (或H⁺)还原为H₂的电势, Cu₂O的价带位置低于H₂O (或OH⁻)还原为O₂的电势, 所以在外加-0.4 V偏压和可见光照射条件下, Cu₂O/g-C₃N₄能全分解水, 光生载流子越多, 光电化学分解水的速率越大。综上所述, 在Cu₂O薄膜上沉积g-C₃N₄后得到的异质结薄膜具有高效的光能转换为氢能性能。

关键词: 氧化亚铜; 石墨相氮化碳; 异质结薄膜; 电化学沉积; 可见光; 光电化学分解水; 产氢

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