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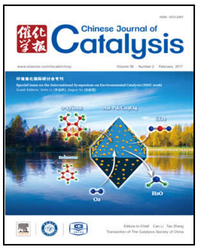

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Electrodeposition of Cu_2O/g-C_3N_4 heterojunction film on an FTO substrate for enhancing visible light photoelectrochemical water splitting

Shengsen Zhang [a,b], Jie Yan [a], Siyuan Yang [a], Yuehua Xu [a], Xin Cai [a], Xin Li [a], Xiangchao Zhang [c], Feng Peng [b,*], Yueping Fang [a,#]

[a] College of Materials and Energy, South China Agricultural University, Guangzhou 510643, Guangdong, China
[b] School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510641, Guangdong, China
[c] Hunan Key Laboratory of Applied Environmental Photocatalysis, Changsha University, Changsha 410022, Hunan, China

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ABSTRACT

An immobilized Cu_2O/g-C_3N_4 heterojunction film was successfully made on an FTO substrate by electrophoretic deposition of g-C_3N_4 on a Cu_2O thin film. The photoelectrochemical (PEC) performance for water splitting by the Cu_2O/g-C_3N_4 film was better than pure g-C_3N_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 Cu_2O/g-C_3N_4 film was –1.38 mA/cm^2 and 0.48 mL h^{-1} cm^{-2}, respectively. The enhanced PEC performance of Cu_2O/g-C_3N_4 was attributed to the synergistic effect of light coupling and a matching energy band structure between g-C_3N_4 and Cu_2O as well as the external bias.

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 2.0–2.4 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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* Corresponding author. Tel/Fax: +86-20-87114916; E-mail: cefpeng@scut.edu.cn
# Corresponding author. Tel/Fax: +86-20-85280319; E-mail: ypfang@scau.edu.cn

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stability of Cu_2O [15,16].

It is well known that graphitic carbon nitride (g-C_3N_4) or composites based on g-C_3N_4 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-C_3N_4 are –1.1 and 1.6 eV vs. NHE, respectively [25,26], which exactly matches the band potentials of Cu_2O [9,10]. Many works have reported that the photocatalytic activity of a Cu_2O/g-C_3N_4 heterojunction photocatalyst was greatly improved compared to pure Cu_2O and pure C_3N_4 [27–32]. For example, our study showed that a g-C_3N_4/Cu_2O composite powder displayed an enhanced photocatalytic performance compared to pure g-C_3N_4 and pure Cu_2O because of the better separation of photogenerated charges (electron-hole pairs) in the two semiconductors [32]. However, reported Cu_2O/g-C_3N_4 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 Cu_2O/g-C_3N_4 in the photocatalytic process.

It will broaden the application of g-C_3N_4/Cu_2O composites as visible light photocatalysts to immobilize g-C_3N_4 on a Cu_2O 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 Cu_2O/g-C_3N_4 heterojunction film on an FTO substrate by an electrochemical deposition method. The Cu_2O/g-C_3N_4 film showed excellent activity and reusability for visible light PEC water splitting.

2. Experimental

2.1. Materials and synthesis

The Cu_2O films on the FTO substrate were grown by the electrochemical deposition method in a three-electrode cell using FTO glass (3.5×2 cm^2), Pt plate and Ag/Cl (SAE) as the working, counter and reference electrodes, respectively [33]. A solution of 0.4 mol/L $CuSO_4$ 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-C_3N_4 nanoparticles were fabricated by a general sol-gel method reported in our previous reports [32,33]. The g-C_3N_4 nanoparticles were deposited on the Cu_2O film on the FTO substrate by an electrophoretic deposition process [34]. Briefly, g-C_3N_4 nanoparticles loaded on the Cu_2O 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 Cu_2O 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-C_3N_4 and 10 mg iodine powder were added to 50 mL acetone and sonicated for 20 min. The content of g-C_3N_4 in the Cu_2O/g-C_3N_4 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-C_3N_4 particles positively charged. Four Cu_2O/g-C_3N_4 samples were prepared by varying the deposition time as 5, 10, 15 and 20 s, and are denoted as Cu_2O/g-C_3N_4-5, Cu_2O/g-C_3N_4-10, Cu_2O/g-C_3N_4-15 and Cu_2O/g-C_3N_4-20, respectively. Pure Cu_2O and g-C_3N_4 films were also fabricated for comparison. The deposition time of pure g-C_3N_4 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/cm^2) 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/cm^2). A 0.1 mol/L $NaNO_3$ solution was used as supporting electrolyte, Ag/AgCl as reference electrode, and the Cu_2O/g-C_3N_4 film on the FTO substrate (2.0×2.0 cm^2) as working electrode and Pt wire as counter electrode. A gas sample of 100 μL 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 Cu_2O film on the FTO substrate (Fig. 1). The stronger peak located at $2\theta = 36.52°$ was due to the (111) plane of Cu_2O, and the other one located at $2\theta = 42.44°$ was attributed to the (200) plane of Cu_2O [33,35]. For the pure g-C_3N_4 film on the FTO substrate, one characteristic peak at $2\theta = 27.53°$, corresponding to the interlayer stacker structural packing, was observed. The weak diffraction peak at $2\theta = 13.12°$ for g-C_3N_4 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.