



# Facile synthesis of interlocking g-C<sub>3</sub>N<sub>4</sub>/CdS photoanode for stable photoelectrochemical hydrogen production

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## ARTICLE INFO

### Article history:

Received 12 February 2018

Received in revised form

26 April 2018

Accepted 11 May 2018

Available online 12 May 2018

### Keywords:

Carbon nitride

CdS

Heterojunction

Photocatalysis

H<sub>2</sub> production

## ABSTRACT

A simple and facile two-step method, including electrophoretic deposition and chemical bath deposition strategies, has been used to fabricate a novel interlocking g-C<sub>3</sub>N<sub>4</sub>/CdS photoanode on conductive substrate. Integrating a large area of intercontact g-C<sub>3</sub>N<sub>4</sub>/CdS heterojunction with an intimate connection between the photocatalysts and the substrate, the separation and migration of the photogenerated carriers by g-C<sub>3</sub>N<sub>4</sub> and CdS are significantly improved, and the internal resistance of the photoanode is effectively reduced. The optimal g-C<sub>3</sub>N<sub>4</sub>/CdS photoanode exhibits an excellent visible light photocurrent density of 5.4 mA cm<sup>-2</sup> at 0.0 V bias (vs. Ag/AgCl) and the photoelectrochemical H<sub>2</sub> production rate reaches 81.1 μmol h<sup>-1</sup> cm<sup>-2</sup>. Moreover, the stability of this interlocking g-C<sub>3</sub>N<sub>4</sub>/CdS photoanode not only reflects in a 9-hour long time recycling photoelectrochemical H<sub>2</sub> production test, but also in an outstanding steady structure which even be stabilized in an ultrasonic treatment. The present study provides a practical and convenient technique to develop such an earth abundant and low-cost CdS/C<sub>3</sub>N<sub>4</sub> photoanode which can be used for high efficiency and stable photoelectrochemical solar energy conversion.

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## 1. Introduction

Utilizing semiconductor based photocatalysts to convert inexhaustible solar energy into environmentally friendly chemical energy, such as hydrogen fuel, through photocatalytic (PC) or photoelectrochemical (PEC) water splitting technologies has attracted considerable attention [1–6]. As almost 50% of the solar energy received by the earth falls within the light wavelength range from 400 to 800 nm, the research directions in this field have been mainly focused on the development and fabrication of effective semiconductor photocatalysts which have a visible light absorption quality and high energy conversion efficiency.

CdS, as one of the most promising candidate, has attracted significant attention due to its great visible light response with a suitable narrow band gap (~2.4 eV) and excellent PC or PEC

properties for H<sub>2</sub> production [7–9]. However, two major drawbacks cannot be ignored, the serious self-photocorrosion and high photoinduced charge carriers recombination rate, which have largely obstructed the practical application of CdS. Coupling CdS with other coordinated band structure semiconductors to synthesize heterojunction photocatalysts has been regarded as one of the most efficient strategies to overcome these drawbacks and can further enhance the photocatalytic property. Graphene-like C<sub>3</sub>N<sub>4</sub>, due to its high stability, nontoxicity and easy synthesis has been considered as a very suitable material to combine with CdS [10–14]. Numerous g-C<sub>3</sub>N<sub>4</sub>/CdS heterojunction photocatalysts have been successfully fabricated to harvest solar energy for PC water splitting [15–17], such as CdS quantum dot-coupled g-C<sub>3</sub>N<sub>4</sub> nanoparticles, core/shell g-C<sub>3</sub>N<sub>4</sub>/CdS nanowires [17]. In our previous work, we exploited an in-suit growth strategy to create g-C<sub>3</sub>N<sub>4</sub>/CdS hybrid photocatalyst [18]. Combined with suitable cocatalysts NiS, this powder photocatalyst exhibited a super high PC water splitting performance with a H<sub>2</sub> production rate of ca. 2.6 mmol h<sup>-1</sup> g<sup>-1</sup> under visible light irradiation. Unfortunately, limited by the common features of powder samples, the recycling and reusing of this g-C<sub>3</sub>N<sub>4</sub>/CdS photocatalyst is still inconvenient and unsatisfactory.

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Moreover, it is also noted that, like  $g\text{-C}_3\text{N}_4/\text{CdS}$  photocatalysts, when the powder samples are used to fabricate a photoanode on the conductive FTO substrate through a typical deposition-annealing process, the PEC properties of this kind of photoanode are far from practical applications on account of its low solar energy conversion efficiency with the very small microampere level photoelectrical current density. As is well known, PEC water splitting system has been considered more promising in practical application than PC system, and a high efficient PEC activity largely depends on the rapid charge-holes separation and transfer between the heterojunction photocatalysts and the conductive substrate [19,20]. Therefore, in order to apply such an excellent visible light respond, earth abundant and low-cost  $g\text{-C}_3\text{N}_4/\text{CdS}$  photocatalyst in the PEC water splitting system, there are three key points should be taken into account during the design and fabrication of the  $g\text{-C}_3\text{N}_4/\text{CdS}$  photoanodes: (i) an intimate and large area contact heterojunction between the CdS and  $g\text{-C}_3\text{N}_4$  can assist the migration and separation of photo-induced electrons and holes [21–24], (ii) a compact connection between the photocatalysts and the FTO substrate is advantaged to reduce the internal resistance in the PEC system and can accelerate the transposition of the electrons [24], (iii) with the higher conduction band (CB) and valence band (VB) of  $g\text{-C}_3\text{N}_4$  than the corresponding levels of CdS, a reasonable stratified arrangement between FTO, CdS and  $g\text{-C}_3\text{N}_4$  is beneficial to a directional conduction of the electrons from  $g\text{-C}_3\text{N}_4$  to CdS and then to FTO [25,26]. Up to now, it is still challenging to develop such a  $g\text{-C}_3\text{N}_4/\text{CdS}$  photoanode with high efficiency and stability.

In this work, a simple and facile two-step method, including electrophoretic deposition and chemical bath deposition (CBD), was used to fabricate a novel interlocking  $g\text{-C}_3\text{N}_4/\text{CdS}$  photoanode. This innovative structure integrates the above three key motives and realizes (i) large contact interface between CdS and  $g\text{-C}_3\text{N}_4$ , (ii) steady in-suit connection between the  $g\text{-C}_3\text{N}_4/\text{CdS}$  and FTO substrate, and (iii) a reasonable and directional electron-holes separation and transport route. The morphologies, microstructures, optical properties, and in particular the interaction between two components were investigated in detail. Charge transfer property was investigated by electrochemical impedance spectroscopy (EIS) and PEC response. The PEC hydrogen production activities under visible light irradiation of the  $g\text{-C}_3\text{N}_4/\text{CdS}$  photoanodes were evaluated. Furthermore, the stability of the obtained composites was studied by an ultrasonic treatment method. On the basis of above results, a possible mechanism of the enhanced PEC activity was also proposed.

## 2. Experimental details

### 2.1. Synthesis of $g\text{-C}_3\text{N}_4$ powder

The  $g\text{-C}_3\text{N}_4$  was prepared via a typical urea thermal decomposition process according to the previous report [27]. Briefly, 10 g of urea was put in a covered alumina crucible and heated to 550 °C for 4 h in a muffle furnace. The sample was then naturally cooled to the room temperature after calculating.

### 2.2. Preparation of interlocking $g\text{-C}_3\text{N}_4/\text{CdS}$ photoanode

The schematic of the two-step process for the preparation of interlocking  $g\text{-C}_3\text{N}_4/\text{CdS}$  photoanode is proposed in Fig. 1. (1) Electrochemical deposition coating  $g\text{-C}_3\text{N}_4$  thin film on FTO substrate as previous report [28]. Firstly, 40 mg of  $g\text{-C}_3\text{N}_4$  powder and 10 mg of iodine powder were dispersed into 50 ml of acetone with mechanically stirring for 10 min. Then, the mixture was sonicated for another 1 h to obtain uniformly dispersed slurry. The slurry were transferred into a two-electrode cell, where two pieces of

parallel FTO glass ( $2 \times 3.5 \text{ cm}^2$ ) were respectively used as cathode and anode with a distance of 1.5 cm. A  $g\text{-C}_3\text{N}_4$  thin film was electrodeposited on the cathodic FTO glass at a potential of 50 V for 5 s. The film was further dried in vacuum at 60 °C. (2) In-situ chemical bath deposition CdS on FTO/ $g\text{-C}_3\text{N}_4$  (CBD). Briefly, 0.005 M  $\text{CdCl}_2$  and 0.038 M  $\text{NH}_4\text{Cl}$  were mixed in 500 mL deionized water and stirred vigorously for 10 min. Then an appropriate amount of  $\text{NH}_3 \cdot \text{H}_2\text{O}$  (~12 M) was dipped into the above mixed solution while stirring for another 5 min to adjust the pH to 9.5. Three pieces of as-prepared FTO/ $g\text{-C}_3\text{N}_4$  samples were immersed into the above mixed solution for 10 min to absorb  $\text{Cd}(\text{NH}_3)_2^{2+}$ . And then 0.017 M thiocarbamide was introduced in and stirred gently for another 5 min. After that, the mixed solution containing FTO/ $g\text{-C}_3\text{N}_4$  samples was heated to 80 °C and remained for a certain period of time to deposit CdS on FTO/ $g\text{-C}_3\text{N}_4$ . Finally, the as-prepared  $g\text{-C}_3\text{N}_4/\text{CdS}/\text{FTO}$  samples were rinsed with ethanol and deionized water alternately to remove excess precursors. The final obtained films were denoted as  $g\text{-C}_3\text{N}_4/\text{CdS}$ -1h,  $g\text{-C}_3\text{N}_4/\text{CdS}$ -2h and  $g\text{-C}_3\text{N}_4/\text{CdS}$ -3h according to the different depositing time of 1 h, 2 h and 3 h, respectively. As contrast samples, the pure  $g\text{-C}_3\text{N}_4$  and CdS thin film were also deposited on the FTO substrate through the same process without CdS and  $g\text{-C}_3\text{N}_4$  deposition, respectively. All the  $g\text{-C}_3\text{N}_4$ , CdS-2h and final  $g\text{-C}_3\text{N}_4/\text{CdS}$  heterojunction films were annealed in a muffle furnace at 400 °C for 1 h with a heating rate of 3 °C  $\text{min}^{-1}$ .

### 2.3. Characterization

The morphologies of the as-prepared  $g\text{-C}_3\text{N}_4/\text{CdS}$  were observed on a transmission electron microscopy (TEM, JEOL-2010 microscope) operated at 200 kV and a scanning electron microscopy (SEM, FEI Quanta 200 FEG). The XRD patterns were collected on an X-ray diffractometer (XRD, Rigaku, D/max 2500 v/pc) at a scanning speed of 4°  $\text{min}^{-1}$ . X-ray photoelectron spectra (XPS) were detected using a Krato Axis Ultra DLD spectrometer with  $\text{Al K}_\alpha$  radiation. The UV–Visible absorption spectra were recorded on a UV–Vis spectrophotometer (DRS, V-560, Jasco) equipped with an integrating sphere taking  $\text{BaSO}_4$  as reference. The photoluminescence (PL) spectra were detected on a LS 50 B fluorescence spectrometer (Perkin Elmer, Inc., USA) with an excitation wavelength of 379 nm and the PL decay plots were obtained using an Edinburgh Instruments F980 at room temperature. The incident photon-to-current conversion efficiency (IPCE) spectra were collected by a Keithley 2000 multimeter incorporated with a Spectral Product DK240 monochromator. EIS was examined at a 5 mV of alternating current signal in the frequency range of 0.01–10<sup>6</sup> Hz on a PGSTAT30 Eco Chemie B. V. electrochemical workstation.

### 2.4. PEC performance

The PEC performance was measured via standard three-electrode configuration by AUTOLAB PGSTAT302 electrochemical workstation. An aqueous solution of 0.5 M of  $\text{Na}_2\text{S}$  and 0.5 M  $\text{Na}_2\text{SO}_3$  (pH = 12.4) was used as electrolyte. The as-prepared  $g\text{-C}_3\text{N}_4/\text{CdS}$  thin film, platinum wire and Ag/AgCl electrode were employed as working electrode, counter electrode and reference electrode, respectively. The visible light with intensity of 100  $\text{mW cm}^{-2}$  was obtained from a 300 W xenon lamp (PLS-SXE 300UV) coupled with a 420-nm cutoff filter to eliminate the ultraviolet light. The PEC hydrogen evolution experiment was carried out on a homemade device. A Pt wire was impaled on the bottom of a 5-mL graduated centrifuge tube and sealed with glue to avoid gas leakage. The evolved gas from the Pt wire was collected by tube using displacement method [29]. Briefly, the tube with Pt wire was filled with electrolyte and inverted in the reaction cell. During the PEC hydrogen production, the electrolyte in the tube was

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