Graphical Abstract

**Facile synthesis of interlocking g-C₃N₄/CdS photoanode for stable
photoelectrochemical hydrogen production**

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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-C₃N₄/CdS photoanode on conductive substrate. Integrating a large area of intercontact g-C₃N₄/CdS heterojunction with an intimate connection between the photocatalysts and the substrate, the separation and migration of the photogenerated carriers by g-C₃N₄ and CdS are significantly improved, and the internal resistance of the photoanode is effectively reduced. The optimal g-C₃N₄/CdS photoanode exhibits an excellent visible light photocurrent density of 5.4 mA cm⁻² at 0.0 V bias (vs. Ag/AgCl) and the photoelectrochemical H₂ production rate reaches 81.1 μmol h⁻¹ cm⁻². Moreover, the stability of this interlocking g-C₃N₄/CdS photoanode not only reflects in a 9-hour long time recycling photoelectrochemical H₂ 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/C₃N₄ photoanode which can be used for high efficiency and stable photoelectrochemical solar energy conversion.

Keywords: Carbon nitride; CdS; Heterojunction; Photocatalysis; H₂ production

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_2 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_3N_4 , 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_3N_4 /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_3N_4 nanoparticles, core/shell g- C_3N_4 /CdS nanowires

[17]. In our previous work, we exploited an in-suit growth strategy to create g-C₃N₄/CdS hybrid photocatalyst [18]. Combined with suitable cocatalysts NiS, this powder photocatalyst exhibited a super high PC water splitting performance with a H₂ production rate of ca. 2.6 mmol h⁻¹ g⁻¹ under visible light irradiation. Unfortunately, limited by the common features of powder samples, the recycling and reusing of this g-C₃N₄/CdS photocatalyst is still inconvenient and unsatisfactory. Moreover, it is also noted that, like g-C₃N₄/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-C₃N₄/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-C₃N₄/CdS photoanodes: (i) an intimate and large area contact heterojunction between the CdS and g-C₃N₄ 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-C₃N₄/CdS photoanode.

The schematic of the two-step process for the preparation of interlocking g-C₃N₄/CdS photoanode is proposed in Fig. 1. (1) Electrochemical deposition coating g-C₃N₄ thin film on FTO substrate as previous report [28]. Firstly, 40 mg of g-C₃N₄ 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 (2×3.5 cm²) were respectively used as cathode and anode with a distance of 1.5 cm. A g-C₃N₄ 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-C₃N₄ (CBD). Briefly, 0.005 M CdCl₂ and 0.038 M NH₄Cl were mixed in 500 mL deionized water and stirred vigorously for 10 min. Then an appropriate amount of NH₃·H₂O (~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-C₃N₄ samples were immersed into the above mixed solution for 10 min to absorb Cd(NH₃)_n²⁺. And then 0.017 M thiocarbamide was introduced in and stirred gently for another 5 min. After that, the mixed solution containing FTO/g-C₃N₄ samples was heated to 80 °C and remained for a certain period of time to deposit CdS on FTO/g-C₃N₄. Finally, the as-prepared g-C₃N₄/CdS/FTO samples were rinsed with ethanol and deionized water alternately to

remove excess precursors. The final obtained films were denoted as g-C₃N₄/CdS-1h, g-C₃N₄/CdS-2h and g-C₃N₄/CdS-3h according to the different depositing time of 1 h, 2 h and 3 h, respectively. As contrast samples, the pure g-C₃N₄ and CdS thin film were also deposited on the FTO substrate through the same process without CdS and g-C₃N₄ deposition, respectively. All the g-C₃N₄, CdS-2h and final g-C₃N₄/CdS heterojunction films were annealed in a muffle furnace at 400 °C for 1 h with a heating rate of 3 °C min⁻¹.

2.3. Characterization

The morphologies of the as-prepared g-C₃N₄/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 ° min⁻¹. X-ray photoelectron spectra (XPS) were detected using a Krato Axis Ultra DLD spectrometer with Al K_α radiation. The UV-Visible absorption spectra were recorded on a UV-Vis spectrophotometer (DRS, V-560, Jasco) equipped with an integrating sphere taking BaSO₄ 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 0.01-10⁶ 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 Na₂S and 0.5 M Na₂SO₃ (pH=12.4) was used as electrolyte. The as-prepared g-C₃N₄/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 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 discharged by the gas generated on the Pt wire. The volume of gas in the tube was measured every 1 hour.

3. Results and discussion

3.1 Compositions and morphology analysis of the g-C₃N₄/CdS photoelectrode

Fig. 2A shows the XRD patterns of g-C₃N₄, CdS and g-C₃N₄/CdS thin films. The characteristic diffraction peaks of FTO can be observed in all the samples. For pure

g-C₃N₄ film, the weak characteristic peak at $2\theta = 27.5^\circ$ corresponds to the interlayer stacker structural packing of g-C₃N₄, indicating the g-C₃N₄ has successfully loaded on the FTO glass by the electrophoretic deposition method [28]. For g-C₃N₄/CdS, two new diffraction peaks at 44.2° and 52.3° appear, which can be attributed to the (220) and (311) crystal planes of cubic crystalline structure of CdS (JCPDS: 41-1049) [30], respectively. After loading CdS nanoparticles, the peaks of FTO decrease and the peak of g-C₃N₄ even disappears because CdS attached on the FTO/g-C₃N₄, which blocks the detection ability of X-ray to FTO and g-C₃N₄. The reason for the enhancement of intensity at 26.9° is overlapped the peak of CdS (26.7°) and FTO substrate. These results indicate that CdS has been successfully assembled on the surface of FTO/g-C₃N₄ film.

FT-IR spectroscopy of g-C₃N₄/CdS-2h is illustrated in Fig. 2B. The obvious band at 3450 cm^{-1} attributes to the formation of O-H from the surface adsorption of water molecules [31]. Two weak stretching bands at 2927 and 2769 cm^{-1} are assigned to C-H stretching and N-H stretching, respectively, which are originated from g-C₃N₄ [28]. Three strong characteristic stretching bands observed at 1490 , 1358 and 1608 cm^{-1} can be ascribed to the typical stretching modes of C $\equiv$ N hetero-cycles in g-C₃N₄ [31, 32]. The broad band near 3335 cm^{-1} corresponds to the stretching modes of terminal NH₂ or NH groups at the defect sites of the aromatic ring [32]. The characteristic stretching bands at 1128 and 661 cm^{-1} are originated from the vibrations of Cd-S bond [24]. The above FT-IR analysis results evidently reveal the obtained g-C₃N₄/CdS-2h film contains two fundamental components of g-C₃N₄ and CdS.

XPS measurement was performed to determine the chemical element composition and surface chemical state of the as-prepared g-C₃N₄/CdS-2h thin film. The C 1s peak can be de-convoluted into two peaks at 288.2 eV and 284.8 eV (Fig. 2C). The main peak at 288.2 eV is ascribed to N-C=N from g-C₃N₄, which further verifies the existence of g-C₃N₄. The peak at 284.8 eV is identified as sp² C-C bonds in graphitic carbon, which can be attributed to the surface adventitious carbon [24]. The N 1s spectrum can be fitted into three peaks located at 398.3 eV, 398.7 eV and 399.3 eV as shown in Fig. 2D [34]. The main peak at 398.7 eV belongs to C-N=C dominated in g-C₃N₄. The N 1s peak at 399.3 eV is assigned to N-(C)₃, and another peak at 398.3 eV belongs to C=N-C. The XPS peaks for Cd 3d appear at 404.9 eV (3d_{5/2}) and 411.7 eV (3d_{3/2}), which are attributed to Cd²⁺ ions in CdS (Fig. 2E) [30]. The S 2p peaks at 161.5 eV (S 2p_{3/2}) and 162.6 eV (S 2p_{1/2}) shown in Fig. 2F are in accordance with S²⁻ in CdS [35]. The above results from XPS spectra further confirm that the sample is a composite of g-C₃N₄ and CdS.

The FESEM results show that g-C₃N₄ disperses on FTO with obvious gaps between clusters (Fig. 3A). Obviously, except for the presence of fungus-like g-C₃N₄ on the FTO substrate, no other species were founded. After one hour of CBD process, sphere-like particles with average particle size of ~100 nm are deposited uniformly on the leaf of fungus-like g-C₃N₄ (Fig. 3B). With a carefully contrast the FTO glass surfaces before and after the CdS CBD process, as seen in Fig. 3A and Fig. 3B, it is found that the new formed small CdS sphere not only located on the g-C₃N₄ nanosheets but also deposited on the surface of FTO substrate. After the CBD time

increasing to 2 h, the surface of g-C₃N₄ is entirely covered by CdS microspheres and the average size of CdS also increases to ~140 nm (Fig. 3C). When the CBD time increases to 3 h, larger particles of g-C₃N₄ (~180 nm) can be hardly observed on the top of the film and CdS film becomes more compact, and the particles contact each other more closely (Fig. 3D). The cross-section image of g-C₃N₄/CdS-2 (Fig. 3E) shows there are three layers in the film, i.e. glass, FTO and g-C₃N₄/CdS layers, and the thickness of the g-C₃N₄/CdS layer is about 2.0 μm. Furthermore, the elemental mappings of the corresponding cross-sectional view of g-C₃N₄/CdS-2h film were characterized to investigate the longitudinal distribution of CdS and g-C₃N₄. The results display that the upper part of the film is CdS and g-C₃N₄ and both of them contact with each other closely even inside the film. These FESEM and cross-sectional elemental distribution mappings suggest that the size, structure and composition of g-C₃N₄/CdS thin film can be designed and well-controlled by in-situ assembling CdS on the surface of g-C₃N₄ thin film.

TEM images of g-C₃N₄/CdS-2h (Fig 3F) reflect the interface information between CdS and g-C₃N₄. It is obviously revealed that along with the CBD deposition last to 2 h, the fungus-like g-C₃N₄ were inter-locked by the big CdS microspheres which has a diameter of ~ 40 nm and composed by the accumulated small CdS nanoparticles. This TEM image consisted well with the corresponding SEM results (Fig. 3C) and further proved the intrinsic inter-locking structures between the CdS and g-C₃N₄. The lattice spacing of 0.34 nm as shown in Fig. 3G can be indexed as (002) crystal planes of CdS [29]. The intimate interface between CdS and g-C₃N₄ suggests the formation of

heterostructure, which is important for promoting the separation and transfer of photogenerated electron-hole pairs and thus enhancing photoactivity of the g-C₃N₄/CdS film.

3.2 Optical and PEC properties of the g-C₃N₄/CdS electrode

Fig. 4A displays the UV-Vis diffuse reflectance spectra of the samples. It can be observed that the pure g-C₃N₄ presents a very weak light absorption when the wavelength is larger than 460 nm, attributed to its fundamental absorption edge ($E_g=2.7$ eV) [10]. After CdS loading, the absorption edges of all the g-C₃N₄/CdS samples exhibit systematic red shift. The light absorption property of the samples is strengthened with the increasing of the loading content of CdS. Optical photographs (insets in Fig. 4A) shows the colors of the samples change from light yellow (g-C₃N₄) to deep red (g-C₃N₄/CdS-3h) with the increase of deposited CdS. The different colors and absorbance intensity between g-C₃N₄/CdS composites and pristine CdS can be attributed to the combination of g-C₃N₄ and CdS.

The photoluminescence spectroscopy (PL) measurement was carried out to investigate the charge separation of CdS/g-C₃N₄ composites. Fig. 4B shows the PL spectra of the g-C₃N₄/CdS composites at an excitation wavelength of 379 nm. The intense and wide emission peak at 450 nm in 'line a' indicate a strong electron-hole pairs recombination rate for pure g-C₃N₄. However, for the g-C₃N₄/CdS films (line b to d), the emission peaks at 450 nm are large reduced, which indicating that the deposited CdS can effectively accelerate the photoinduced charge separation of g-C₃N₄. It is also noticed that with the increasing of CdS contents, new PL emission

peaks at around 575 nm are appeared, which belonging to the charge recombination of CdS. Obviously, g-C₃N₄/CdS-2h has the weakest PL peaks indicates the effective separation of photoinduced charge carriers in the composite. Associated with the HERTEM analyses, these PL results further confirm that the photoinduced charge recombination on both g-C₃N₄ and CdS have been effectively prevent with the formation of heterojunction structure between CdS and g-C₃N₄.

Under visible light irradiation, the photocurrent (I_{ph}) response plots of the pure g-C₃N₄, CdS-2h and g-C₃N₄/CdS composites for four on-off cycles at 0.0 V are shown in Fig. 4C. The photocurrent intensity of the g-C₃N₄/CdS composites is clearly stronger than the pure g-C₃N₄ and CdS. The maximum photocurrent of g-C₃N₄/CdS-2h is reached 5.4 mA·cm⁻², which is far higher than that of the pure g-C₃N₄ (0.01 mA cm⁻²) and CdS-2h (3.1 mA cm⁻²). To evaluate the relationship between photocurrent density and applied potentials, a series of linear sweeping voltammetry (LSV) were investigated for different samples (Fig. 4D). The g-C₃N₄/CdS-2h also exhibits a maximum photocurrent density of 6.5 mA cm⁻² at 0.2 V vs Ag/AgCl. These results suggest that g-C₃N₄/CdS composites can provide more efficient photogenerated carriers to participate in the PEC process. Nevertheless, when CBD time exceeds 2 h, the photocurrent density of the as-prepared g-C₃N₄/CdS is decrease. The possible reason could be that the excessive CdS particles hinder the light absorption of C₃N₄ and restrain the separation of photogenerated electron-hole pairs and further prevent the photogenerated electrons transferring from CdS to g-C₃N₄ and FTO [24, 36]. Basing on the LSV results, the applied bias photo to current

conversion efficiency (ABPE), which plays a significant role in characterizing the PEC system, were calculated and displayed in Fig. 4E. As expected, the g-C₃N₄/CdS-2h gets the highest ABPE value of 1.56%. The wavelength dependence incident photon to electron conversion efficiency (IPCE) action is another important parameter to quantitatively investigate the photoelectrical activity of the photoanodes in a PEC cell. Fig. 4F shows the IPCE of the samples with the potential of 0.0 V vs. Ag/AgCl. In comparison to the pristine CdS-2h, the g-C₃N₄/CdS-2h exhibits a higher photoactivity with a wider photoresponse range from 300 to 600 nm. The maximum IPCE efficiency of ~ 42% is obtained for g-C₃N₄/CdS-2h at 350 nm. It indicates that the effective separation and transfer of the carriers in g-C₃N₄/CdS-2h give rise to the well PEC activity compared to pristine g-C₃N₄ and CdS.

The hydrogen generations of the pure g-C₃N₄, CdS-2h and g-C₃N₄/CdS composites photoanodes were investigated under the illumination of visible light (100 mW cm⁻²) with a potential of 0.0 V vs Ag/AgCl. Fig. 5 shows the hydrogen evolution rates of different samples under visible light illumination. Pure g-C₃N₄ displays the weakest PEC activity for its worst visible light absorption and the most rapid recombination rate of electrons and holes [37]. After coupling with CdS, the PEC hydrogen evolution rates of the g-C₃N₄/CdS photoanodes are significantly increased. With the CBD time increasing, the hydrogen evolution rate of the g-C₃N₄/CdS heterojunction increases and reaches a maximum value of 81.1 μmol h⁻¹ cm⁻² at 2 h of CBD time. When the CBD time of CdS increases further, the PEC hydrogen production rate decreases gradually. For pure CdS-2h, the hydrogen evolution rate is only 18.0 μmol

$\text{h}^{-1} \text{cm}^{-2}$.

To explore the intrinsic reasons for the high PEC efficiency, PL and electrochemical impedance spectroscopy (EIS) decay character of the as-prepared samples were further measured. The PL decay times of the g-C₃N₄/CdS-2h and CdS-2h film were measured by monitoring the emission intensity at 340 nm (Fig. 6A). The fitting results show the PL decay time of g-C₃N₄/CdS-2h (1.21 ns) is shorter than that of CdS-2h (2.98 ns). It is indicated that the lifetimes of charge carriers in g-C₃N₄/CdS-2h are synergistically lengthened by the combination of g-C₃N₄ and CdS nanoparticles [38]. The accelerated PL decay and the PL intensity confirmed that rapid charge transfer occurred between the g-C₃N₄ and CdS, hence partially addressing their proverbial severe surface charge recombination issue. Fig. 6B demonstrates the EIS Nyquist plots of the composites under the irradiation of visible light. Compared to that of the pure g-C₃N₄ and CdS electrodes, the g-C₃N₄/CdS-2h electrode exhibits the smallest arc radius, revealing that the charge-transfer resistance obviously decreased for the g-C₃N₄/CdS-2h film. Therefore, the pronounced PL decay and the decrease of the charge-transfer resistance by incorporating g-C₃N₄ and CdS clearly validates the better charge separation and transport ability of the g-C₃N₄/CdS film, especially for g-C₃N₄/CdS-2h which exhibited the best PEC performance of the samples.

3.3 Mechanism discussion

According to the above results, possible PEC hydrogen production mechanism of g-C₃N₄/CdS-2h is discussed. It is well known that both g-C₃N₄ and CdS can be

excited by visible light due to their narrow band gaps and perfect band energy match. As shown in the Fig. 7, under the visible light irradiation, the excitation electrons of g-C₃N₄ directly transfer to CdS, and the holes in the valance band of CdS move to the conduction band of g-C₃N₄ at the same time as the conduction band (CB) and valance band (CB) of g-C₃N₄ are both higher than those of CdS. The separated electrons coming from CdS and g-C₃N₄ transfer to the external circuit *via* FTO under the potential bias of 0.0 V, and react with H⁺ to generate H₂ on Pt wire electrode finally. Meanwhile the holes left on the conduction band of g-C₃N₄ can be consumed by sacrificial agent. Therefore, the efficient separation and transfer of the electron-hole pairs inhibit the recombination of the carriers, and avoid the photocorrosion of CdS by the holes simultaneously.

3.4. Stability of the g-C₃N₄/CdS photoanodes

Besides the PEC activity, the photostability is also an important factor to evaluate the performance of PEC photoanode. Fig. 8A shows a cycling PEC hydrogen evolution running in the presence of g-C₃N₄/CdS-2h heterojunction and CdS-2h thin films. After three cycles, the hydrogen evolution rate of CdS-2h decreases by 26.8% comparing to the initial cycle, and the hydrogen evolution rate of g-C₃N₄/CdS-2h heterojunction is quite stable and preserves about 95.4% of the initial cycle. It is indicated that in-situ assembling CdS on the surface of g-C₃N₄ thin film can notably promote its hydrogen evolution rate and stability. The photocurrent response of CdS-2h and g-C₃N₄/CdS-2h composites with 9 h of visible light irradiation was recorded to verify their photostability as shown in Fig. 8B. It is evident that the

photocurrent of g-C₃N₄/CdS-2h heterojunction is much more stable than that of the pure CdS-2h. The photocurrent density of CdS-2h decreases rapidly by 46.5% over the first 2.7 h and then becomes to relatively flat. While the photocurrent density of g-C₃N₄/CdS-2h declines extremely slow and decreases by only 7.2% after 9 h of visible light irradiation.

Here, we have also explored the structure stability in g-C₃N₄/CdS-2h and CdS-2h photoanode before and after the electrochemical reduction by comparing the XRD and HRTEM characters, respectively. As shown in Fig. 8C, almost no obvious change occurred in the phase composition of the g-C₃N₄/CdS-2h heterojunction after 9 h of visible light irradiation. However, for pure CdS-2h, regardless of the decreased diffraction intensity at the peak of 26.7 ° corresponding to (002) crystal plane, two new diffraction peaks at 24.8° and 28.2° corresponding to (100) and (101) hexagonal planes of CdS (JCPDS: 41-1049) were observed (Fig. 8D) [39]. The HRTEM of g-C₃N₄/CdS-2h and CdS-2h after PEC measurement were observed and shown in Fig. 8E and F, respectively. As shown in Fig. 8E, for the g-C₃N₄/CdS-2h, the CdS and g-C₃N₄ are still tightly coupled with each other, and two kinds of founded lattice fringes of 0.21 nm and 0.34 nm on the surface of sample corresponded to the CdS crystal planes of (110) and (002), respectively. However, there are four kinds of lattice fringes of 0.21 nm, 0.35 nm, 0.34 nm and 0.32 nm on the surface of CdS (Fig. 8F) were observed, corresponding to the CdS crystal planes of (110), (100) (002) and (101), respectively. The lattice fringes of CdS after reaction showed in HRTEM images are clearly imaged and consistent with the results of XRD pattern, which have

been demonstrated to be induced by the photocorrosion of CdS nanocrystal, and negative to the PC reaction of CdS [36, 40].

Moreover, the stability of this g-C₃N₄/CdS-2h photoanode not only reflected in an unchanged structure between g-C₃N₄ and CdS during the 9-hour long time recycling PEC H₂ production, but also in an outstanding steady structure between g-C₃N₄/CdS and the FTO substrate, which can even be stabilized in an ultrasonic treatment. The impressive adhesion ability of g-C₃N₄/CdS thin film to FTO glass can be explained by the in-situ “ion by ion” CdS growth mechanism during the CBD process as following [41]:

i: The Cd²⁺ firstly combined with ammonia to generate Cd(NH₃)_n²⁺ ions (formula (1) and (2)), these Cd(NH₃)_n²⁺ ions are prefer to accumulated on the surface of the nearby substrate, i.e., g-C₃N₄ and FTO [42].

ii: The Cd(NH₃)_n²⁺ ions reversible generated Cd(OH)₂ species on the surface of the substrate, formula (3):

iii: The Cd(OH)₂ species reacted with the subsequent injected thiourea forming a metastable complex with the dihydroxycadmium adsorption species (Cd(OH)₂SC(NH₂)₂), as formula (4);

iv: The [Cd(OH)₂SC(NH₂)₂]_{ads} in-situ decomposes to form CdS (formula (5)).

The in-situ growth CdS on one hand can tightly lock-in the g-C₃N₄ on the FTO substrate, and on the other hand it also assured an intimately contacting interfaces among CdS, g-C₃N₄ and FTO substrate, which is very important for improving the separation and transfer of the photogenerated carriers and thus increases PEC activity [43]. From the above ion by ion mechanism, CdS nanocrystals can contact with both FTO and g-C₃N₄ closely, resulting in a dense, flat and stable g-C₃N₄/CdS thin film. Therefore, the as-obtained interlocking g-C₃N₄/CdS heterojunction film exhibits significantly enhanced PEC activity and stability under visible light irradiation.

4. Conclusions

A novel interlocking g-C₃N₄/CdS heterojunction thin film contacting strongly with FTO is obtained via electrophoretic deposition and subsequent CBD method. The g-C₃N₄/CdS thin film possesses a large contacting area between CdS and g-C₃N₄ and better adhesion ability on FTO substrates. The PEC activity and stability of g-C₃N₄/CdS heterojunction thin film are significantly enhanced through the combination of g-C₃N₄ and CdS. Under the visible light irradiation, the maximum PEC hydrogen evolution yield of g-C₃N₄/CdS is 81.1 μmol h⁻¹ cm⁻² and exhibits excellent stability in a 9-hour long time recycling PEC H₂ production test. This work offers a practical and convenient technique to develop the promising C₃N₄/CdS photoanode with a high energy efficiency and stable cycling performance for PEC solar energy conversion.

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Legends

Fig. 1. Schematic illustration of the formation process of the g-C₃N₄/CdS.

Fig. 2. (A) XRD patterns of (a) g-C₃N₄, (b) g-C₃N₄/CdS-1h, (c) g-C₃N₄/CdS-2h, (d) g-C₃N₄/CdS-3h, (e) CdS-2h; FT-IR spectrum (B), XPS spectra of C 1s (C); N 1s (D); Cd 3d (E) and S 2p (F) of g-C₃N₄/CdS-2h.

Fig. 3. FESEM images of the g-C₃N₄ (A), g-C₃N₄/CdS-1h (B), g-C₃N₄/CdS-2h (C) and g-C₃N₄/CdS-3h (D) samples; The cross-section SEM image and corresponding elemental mappings of g-C₃N₄/CdS-2h film (E). TEM (F) and HRTEM (G) analysis of the sample g-C₃N₄/CdS-2h, HRTEM image of the selected G section in image F.

Fig. 4. UV-Vis absorption spectra and the corresponding optical photographs (insets) (A), PL (B), photocurrent response (C), linear sweeping voltammetry (LSV) (D), ABPE (E) and IPCE (F) of different samples. (a. g-C₃N₄, b. g-C₃N₄/CdS-1h, c. g-C₃N₄/CdS-2h, d. g-C₃N₄/CdS-3h, e. CdS-2h)

Fig. 5. PEC hydrogen evolution activities of g-C₃N₄ (a), g-C₃N₄/CdS-1h (b), g-C₃N₄/CdS-2h (c), g-C₃N₄/CdS-3h (d) and CdS-2h (e).

Fig. 6. (A) Time-resolved PL decay spectra of CdS-2h and g-C₃N₄/CdS-2h, (B) EIS Nyquist plots recorded of g-C₃N₄ (a), g-C₃N₄/CdS-1h (b), g-C₃N₄/CdS-2h (c), g-C₃N₄/CdS-3h (d) and CdS-2h (e).

Fig. 7. Schematic diagrams of possible electron transfer pathway for visible light PEC hydrogen production system of dense g-C₃N₄/CdS film.

Fig. 8. The reusability (A) and the corresponding photocurrent (B) of g-C₃N₄/CdS-2h and CdS-2h; XRD pattern of g-C₃N₄/CdS-2h (C) and CdS-2h (D) before and after the PEC hydrogen production; HRTEM images of g-C₃N₄/CdS-2h (E) and CdS-2h (F) after the PEC hydrogen production for 9 h.

Figures

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.

Fig. 8.

Research Highlights

- ◆ An interlocking g-C₃N₄/CdS photoanode was fabricated by a simple two-step method.
- ◆ The in-situ growth CdS tightly locked g-C₃N₄ on a FTO substrate.
- ◆ An extensive contact interface between CdS and g-C₃N₄ has been achieved.
- ◆ A steady connection between the g-C₃N₄/CdS and FTO has been realized.
- ◆ The photoanode has a high activity and extremely stability for PEC H₂ evolution.

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Facile synthesis of interlocking g-C₃N₄/CdS photoanode for stable photoelectrochemical hydrogen production

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