Surface localization of CdZnS quantum dots onto 2D g-C₃N₄ ultrathin microribbons: Highly efficient visible light-induced H₂-generation

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Abstract

The construction of new semiconductor photocatalysts toward high-efficiency splitting water has played an important role in developing sustainable and clean hydrogen energy. In this work, new type of micro/nano-sized hybrids were synthesized based on the assembly of 0D CdₓZn₁₋ₓS quantum dots (QDs, size: ca. 5 nm) onto 2D graphitic carbon nitride (g-C₃N₄) ultrathin microribbons (thickness: ca. 4 nm) via an in-situ growth hydrothermal method. The CdₓZn₁₋ₓS 32 wt%g-C₃N₄ composite exhibits the highest visible-light-driven H₂-generation rate of 33.41 mmol h⁻¹ g⁻¹ without any noble-metal as cocatalyst, and the apparent quantum efficiency is 46.65% at 450 nm. Such H₂-generation rate is higher than the pristine g-C₃N₄ and CdₓZn₁₋ₓS by a factor of 27.39 and 9.18 respectively, which is significantly enhanced compared with most as-reported noble-metal-free semiconductor catalysts to date. In addition, compared with the pristine CdₓZn₁₋ₓS, the photocatalytical stability of CdₓZn₁₋ₓS QDs@g-C₃N₄ is highly improved. The enhanced H₂-generation performance can be attributed to the well-matched energy level and strong electronic coupling between two components at the g-C₃N₄ interface as well as enhanced visible-light absorption. The uniform dispersion of CdₓZn₁₋ₓS QDs onto the g-C₃N₄ ultrathin microribbons also facilitates the depression of electron-hole recombination from potential aggregation of CdₓZn₁₋ₓS. Therefore, this work supplies an effective way to obtain promising 2D micro/nanostructures for high-efficiency visible light-induced H₂-generation.

1. Introduction

During last few decades, high dependence and overuse of fossil fuels have led to serious energy crisis and environment concern. Thus, the development of clean, low-cost and efficient alternative to fossil fuels is a matter of utmost urgency [1,2]. Hydrogen (H₂) is considered as an effective clean energy resource and idealized substitution for fossil fuels, because of its high specific enthalpy and environmentally-friendly combustion products. Recently, water splitting with the aid of semiconductor photocatalysts has been perceived as one of the most promising technologies to obtain H₂ [3,4]. Moreover, the design and construction of high-efficiency noble-metal-free photocatalysts are quite appealing with the aim of providing sustainable and cost-competitive H₂ [5].

In this sense, graphitic carbon nitride (g-C₃N₄), as an intriguing earth-abundant photocatalysts has attracted dramatically increasing interest in visible-light-driven H₂-generation due to the unique two-dimensional (2D) layered structure, high chemical stability and facile preparation [6,7]. However, the pure g-C₃N₄ is usually restricted by low photocatalytic efficiency because of the rapid recombination of photo-induced electron-hole pairs, small specific surface area and low visible light utilization [8,9]. To solve these problems, many approaches have been devoted to the enhancement of its photocatalytic activity (such as exfoliated g-C₃N₄ nanosheets [10,11], formation of mesoporous and O-doping g-C₃N₄ [12,13], hybridization with ZnO and CdS [14,15], loading of Pt particles [16], fabrication of nanojunctions with MoS₂ [17], and cooperation with carbon quantum dots [18,19]), the H₂-generation rate was, however, not satisfactory to date. Furthermore, to enhance the visible-light absorption and to obtain high active sites of g-C₃N₄, optimizing appropriate band structure and integrating multi-functional composites are reasonable ways towards efficient visible-light utilization and high photocatalytic activity in the process of splitting water [20,21].

Among various semiconductor photocatalysts, the CdZnS solid solutions have been proven to be efficient photocatalysts due to the relatively narrow band gap, which can serve as a light harvesting antenna for effective absorption of the solar energy...
However, similar to CdS, pure CdZnS tends to form large particle aggregation and photocorrosion layer, resulting in a higher recombination rate of photo-induced electron-hole pairs and unstable structures, which have limited the further enhancement of photocatalytic efficiency [25]. To achieve the deaggregation of CdZnS and to develop high-efficiency noble-metal-free photo-catalysts, herein, we have put forward the strategy that localizing CdZnS QDs onto the 2D layercd g-C3N4 micro/nanostructures (Scheme 1). Firstly, the visible-light-absorption efficiency can be improved by the high dispersion of the QDs in the 2D host interface. Secondly, the electronic structures of CdZnS QDs and g-C3N4 are strongly coupled and the matched band structure between two components could promote the photogenerated charge separation and transfer, which lowers charge recombination possibility. Thirdly, the nano-sized CdZnS QDs present a sufficient contact with g-C3N4, which leads to efficient electronic mobile channel and short migration distance, and thus resulting in increased reactive sites. Therefore, it is expected that the combination of CdZnS and g-C3N4 can be an ideal model to overcome the disadvantages that exist in both g-C3N4 and CdZnS simultaneously.

In this work, 2D g-C3N4 microribbons have been fabricated firstly via a combination of thermal exfoliation and liquid exfoliation, which were then used as a host supporter for anchoring Cd0.5Zn0.5S QDs (particle size: ca. 5 nm). The Cd0.5Zn0.5S QDs are highly dispersed and localized onto the surface of the g-C3N4 microribbons as con

2. Experimental section

2.1. Preparation of the g-C3N4 microribbons

All chemicals (analytical grade purity) used in this research were purchased from Aladdin (Shanghai) Chemistry Co., Ltd and used without further purification. The bulk g-C3N4 powders were prepared via pyrolysis of urea in a tube furnace. In a typical synthesis, 4 g of urea was placed into a porcelain boat with cover and heated to 550 °C for 2 h at 2 °C/min heating rate. After cooling naturally to room temperature, the resultant powder was then direct thermal exfoliation heated to 550 °C for 2 h at 2 °C/min heating rate in air. g-C3N4 microribbons were fabricated by a one-pot exfoliation of as-thermal-exfoliated g-C3N4 in water. In a typical fabrication, 200 mg of thermal exfoliated g-C3N4 were added into 800 ml beaker with 400 ml of water, and then the sealed beaker was sonicated for 6 h. Thus, the white exfoliated g-C3N4 microribbons were obtained. The select of precursor and control of heating temperature are keys to obtain g-C3N4 microribbons.

2.2. Preparation of the Cd0.5Zn0.5S@g-C3N4 photocatalyst

In-situ growth of Cd0.5Zn0.5S QDs on g-C3N4 microribbons was prepared by a hydrothermal method. All of the reagents were purchased from Aladdin (Shanghai) Chemistry Co., Ltd without further purification. Deionized (DI) water was used in all experiments. In a typical synthesis of the composites, a varying amount of the Cd(Ac)2·2H2O and Zn(Ac)2·2H2O (0.02, 0.05, 0.1, 0.2, 0.4 mmol, respectively) were disperse in 25 ml of g-C3N4 micro-ribbons, and then adding thiourea (0.01 mol), and ethylenediamine (2 ml). Next, the obtained mixed solution was transferred into a 100 ml Teflon-lined autoclave and held at 180 °C for 24 h after vigorous stirring for 60 min After that, the precipitates from the mixture were allowed to cool to room temperature and collected by centrifugation, and then rinsed with water and ethanol several times. The final product was dried in an oven at 60 °C for 12 h. The weight ratios of Cd0.5Zn0.5S to g-C3N4 microribbons were 0, 16 wt%, 32 wt%, 51 wt%, 66 wt% and 79 wt%, and the obtained samples were labeled as Cd0.5Zn0.5S, Cd0.5Zn0.5S 16%@C3N4.
Cd$_{0.5}$Zn$_{0.5}$S 32%@C$_3$N$_4$, Cd$_{0.5}$Zn$_{0.5}$S 51%@C$_3$N$_4$, Cd$_{0.5}$Zn$_{0.5}$S 66% @C$_3$N$_4$, and Cd$_{0.5}$Zn$_{0.5}$S 79%@C$_3$N$_4$, respectively.

2.3. Material characterization

The crystal structure and phase purity of the resultant samples were analyzed by powder X-ray diffraction (PXRD) recorded on a Bruker D8 Advance X-ray diffractometer using Cu-Kα radiation. The structural information for samples was measured by Fourier transform infrared spectrophotometer (FTIR, Thermo IFS) in the range of 4000–400 cm$^{-1}$ using the standard KBr disk method. The morphology and microstructure of the samples were observed by scanning electron microscopy (JEOL-JEOL-4800) and transmission electron microscopy (JEOL JEM-2010). The surface roughness and thickness data were obtained using a Bruker Multimode 8 atomic force microscope (AFM). The surface composition was analyzed by X-ray photoelectron spectroscopy (XPS) on ESCALAB 250 electron spectrometer. UV–vis absorption spectra were performed on a UV–vis spectrophotometer (TU-1901) using BaSO$_4$ as the reference. The spectrum of the visible light from the xenon lamp (300 W, CEL-HXF300, Jinjuan, λ = 420–760 nm) was detected on an optical spectrum analyzer Avaspec-NIR256 (avantes, Netherlands). The photocurrent performance was performed on a CHI660D electrochemical workstation, where Pt electrode and saturated Ag/AgCl electrode were employed as counter and reference electrode, respectively.

2.4. Photocatalytic experiments

Photocatalytic tests were carried out in a Pyrex top-irradiation reaction vessel connected to a closed glass gas system. The hydrogen production experiment was carried out in a quartz reactor cooled by running water. A xenon arc lamp (300 W, CEL-HXF300, Jinjuan) with a UV light cutoff filter (λ = 420–760 nm) was used as the visible light source to offer photons, where the power density of visible light radiated on the photocatalyst was measured to be 1.5 mW/cm$^2$. The photocatalytic hydrogen evolution was measured with Zhejiang university N2000 gas chromatography system by using N$_2$ as carrier. In a typical photocatalytic experiment, 20 mg of the prepared Cd$_{0.5}$Zn$_{0.5}$S@C$_3$N$_4$ and Cd$_{0.5}$Zn$_{0.5}$S (50 mg) were evaluated by measuring the hydrogen evolution from 100 ml 0.5 M Na$_2$S and 0.15 M Na$_2$SO$_3$ aqueous solution under visible light irradiation at 5 °C. For determination of stability, another four circles of hydrogen production were taken without replacing the sacrificial agents under the same photocatalytic condition. For g-C$_3$N$_4$, hydrogen production was performed by 100 ml aqueous solution of 0.5 mg/ml g-C$_3$N$_4$ microribbons containing triethanolamine (10 vol%) as a sacrificial electron donor. Co-catalysts Pt nanoparticles were introduced by in-situ photodeposition method, where 3 wt% (respect to Pt) H$_2$PtCl$_6$·6H$_2$O was added and well distributed in the reaction solution.

The apparent quantum efficiency (QE) was measured under the same photocatalytic reaction condition except that the catalyst solution was irradiated by a 300 W Xe lamp applying a λ = 450 ± 20 nm band-pass filter. The average intensity of irradiation was measured as 1.5 mW/cm$^2$ and the irradiation area was controlled as 23.75 cm$^2$. The produced H$_2$ reached to 525 µmol in 5 h (Fig. S13), and the QE was calculated according to the equation [18]:

$$\text{QE} = \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 2 \times \text{number of incident photons}.$$  

2.5. Photoelectrochemical measurements

Photocurrents were measured by using an electrochemical analyzer (CHI 660C Instruments) in a standard three-electrode system with the as-prepared powers as the working electrode, a Pt wire as counter electrode, and Ag/AgCl (saturated KCl) as reference electrode. Aqueous Na$_2$SO$_3$ solution (0.5 M) was used as the electrolyte. The modified electrodes were prepared as follows: 0.5 mg of the as-prepared photocatalyst Cd$_{0.5}$Zn$_{0.5}$S@C$_3$N$_4$ was suspended in 1 ml of ethanol and solution of liquid exfoliated g-C$_3$N$_4$ with 20 µl of 5 wt% Nafion solution to produce slurry, respectively. Then 10 µl of the resulting colloidal dispersion was dropped onto a glassy carbon electrode.

3. Results and discussion

3.1. Synthesis of g-C$_3$N$_4$ microribbons

As shown in Scheme 1, bulk g-C$_3$N$_4$ was prepared by heating urea at 550 °C for 2 h followed by thermal exfoliation for another 2 h at 550 °C to obtain g-C$_3$N$_4$ [10,26]. Then, pale-yellow g-C$_3$N$_4$ were suspended in water (concentration: 0.5 mg/ml), and then sonicated at room temperature for 6 h to exfoliate and get uniformly dispersed g-C$_3$N$_4$ product. The white homogenous dispersion of g-C$_3$N$_4$ was highly stable, and showed no precipitation even after being stored for 1 month under ambient conditions (Fig. S1). Tyndall phenomenon can be observed when the dispersed g-C$_3$N$_4$ was diluted for 100 times. However, obvious precipitation was formed in the pale-yellow dispersion of thermal exfoliated g-C$_3$N$_4$ after stored for 2 h.

3.2. Structure and morphology of the g-C$_3$N$_4$ microribbons

Elemental analysis showed the approximate component of thermal exfoliated g-C$_3$N$_4$ is C$_{2.98}$N$_{4.27}$H$_{1.91}$ (Table S1) with an average C/N ratio of 0.69 (theoretical value for g-C$_3$N$_4$: 0.75). Powder X-ray diffraction (PXRD) was employed to monitor the crystal phase of the obtained g-C$_3$N$_4$ (Fig. 1a): a low-angle reflection peak appeared at 12.91°, stemmed from the lattice plane parallel to the c-axis with an interplanar distance of 0.685 nm. For the bulk g-C$_3$N$_4$ (shown in Fig. S2) the strongest peak at 27.52° reflect the characteristic interlayer-stacking of aromatic systems (002), which gives an interplanar distance d = 0.325 nm [27,28]. After the bulk g-C$_3$N$_4$ was thermal exfoliated, the (002) peak of g-C$_3$N$_4$ shifts to a higher angle of 27.74°, which gives an interplanar distance of d = 0.321 nm, indicating a decreased gallery distance between the basic units in the g-C$_3$N$_4$ [11,29].

The crystal structure of the thermal exfoliated g-C$_3$N$_4$ can be further confirmed by FTIR spectroscopy (Fig. 1b). The peak at 813 cm$^{-1}$ corresponds to aromatic C–N stretching. The band near 3000 cm$^{-1}$ is consistent with modes involving N–H stretching vibrations; the bands observed in the 1200–1600 cm$^{-1}$ region are typical molecular framework containing CN heterocycles, which are generally associated with the skeletal stretch vibrations of these aromatic rings. The prominent absorption bands at 1207, 1237 and 1316 cm$^{-1}$ can be assigned to the characteristic vibrations of C–NH-C units [30,31]. The absorption bands at 1574 and 1637 cm$^{-1}$ are attributed to C–N stretching. The FTIR results are in fairly accordance with the as-reported g-C$_3$N$_4$ materials [32]. Solid-state $^{13}$C NMR spectrum (Fig. 1c) shows a very strong signal at δ ~ 165 ppm, which is attributed to the characteristic peak of the ring carbon of the triazine or heptazine moiety. The peak of δ ~ 157 ppm can be assigned to the CN$_3$ moieties on the g-C$_3$N$_4$ [31,33]. These results indicated that g-C$_3$N$_4$ was synthesized successfully using urea as precursor.

The morphology and texture of liquid exfoliated g-C$_3$N$_4$ sample were detected using scanning electron microscopy (SEM). The typical SEM image of g-C$_3$N$_4$ (Fig. 1d) showed that the morphology of as-exfoliated g-C$_3$N$_4$ is well-orderly ribbon structure with length of about 10 µm and width of about 2 µm. Moreover, atomic
force microscope (AFM) showed that the thickness of the g-C₃N₄ microribbons is ca. 4 nm (Fig. 1e and f). These results confirmed that g-C₃N₄ ultrathin microribbons have been obtained successfully via thermal and liquid exfoliation processes. To the best of our knowledge, such 2D ultrathin morphology of g-C₃N₄ has seldom been reported in the previous works.

3.3. Synthesis, structure and morphology of Cd₀.₅Zn₀.₅S@g-C₃N₄ composites

The white homogenous dispersion of g-C₃N₄ microribbons obtained by liquid exfoliation was used as support layer to hybrid with thiourea and Zn²⁺/Cd²⁺. A composite photocatalyst was

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Fig. 1. Analysis of g-C₃N₄ sample: (a) XRD pattern, (b) FTIR spectra, (c) solid-state 13C NMR spectra, (d) the image of SEM, (e) the image of AFM, (f) estimation of thickness along the white line in (e) for g-C₃N₄ microribbons.

Fig. 2. (a) XRD of CdS, Cd₀.₅Zn₀.₅S and Cd₀.₅Zn₀.₅S 32% @C₃N₄; (b, c, d) The TEM images of Cd₀.₅Zn₀.₅S 32%@C₃N₄, the HRTEM images of Cd₀.₅Zn₀.₅S 32%@C₃N₄ (inset in c) and the corresponding SAED pattern (inset in b).
synthesized via an in-situ growth of Cd$_{0.5}$Zn$_{0.5}$S QDs on g-C$_3$N$_4$ microribbons in a green hydrothermal process, and the obtained Cd$_{0.5}$Zn$_{0.5}$S@g-C$_3$N$_4$ binary micro/nanocomposites were labeled as Cd$_{0.5}$Zn$_{0.5}$S$_x$%@g-C$_3$N$_4$ (x%: the mass concentration of Cd$_{0.5}$Zn$_{0.5}$S in the total amount of Cd$_{0.5}$Zn$_{0.5}$S and g-C$_3$N$_4$, x = 0, 16 wt%, 32 wt%, 51 wt%, 66 wt%, 79 wt%, 100 wt%). PXRD was performed on the as-prepared samples to confirm the crystal phase and to investigate the influence of g-C$_3$N$_4$ microribbons on the crystallinity in the composites. For the pristine Cd$_{0.5}$Zn$_{0.5}$S, the crystal structure has retained the same with CdS after Zn doped (JSPDS no. 1-783). Upon hybridization with g-C$_3$N$_4$ microribbons, all diffraction peaks of the Cd$_{0.5}$Zn$_{0.5}$S$_x$%@g-C$_3$N$_4$ can be indexed to hexagonal wurtzite Cd$_{0.5}$Zn$_{0.5}$S solid solution (Fig. S3) [34]. Taking the sample Cd$_{0.5}$Zn$_{0.5}$S 32%@g-C$_3$N$_4$ as an example, no obvious peak shift was observed when Cd$_{0.5}$Zn$_{0.5}$S was introduced into the g-C$_3$N$_4$ microribbons (Fig. 2a). In addition, no evident diffraction peaks of g-C$_3$N$_4$ microribbons was observed in the Cd$_{0.5}$Zn$_{0.5}$S 32%@g-C$_3$N$_4$ composite, owing to the relatively low diffraction intensity of peak at 12.91° and overlapping with the peak of 27.75° [15,35]. Based on the PXRD results, it can be concluded that the g-C$_3$N$_4$ and Cd$_{0.5}$Zn$_{0.5}$S have maintained their own phases in the Cd$_{0.5}$Zn$_{0.5}$S@g-C$_3$N$_4$ composites. Furthermore, TEM and HRTEM images were taken to directly analyze the fine structure of the Cd$_{0.5}$Zn$_{0.5}$S@g-C$_3$N$_4$ samples. For the Cd$_{0.5}$Zn$_{0.5}$S 32%@g-C$_3$N$_4$, it can be observed that the sample maintained the 2D sheet-like morphology upon immobilized by Cd$_{0.5}$Zn$_{0.5}$S. The hybrid is easily imaged under TEM due to the ultrathin sheet of g-C$_3$N$_4$ (Fig. 2b). By magnification of the sample, it was shown that the nano-sized Cd$_{0.5}$Zn$_{0.5}$S QDs are uniformly dispersed and tightly anchored on the g-C$_3$N$_4$ microribbons. The HRTEM image (inset in Fig. 2c) shows that the size of Cd$_{0.5}$Zn$_{0.5}$S QDs is around 5 nm, and the lattice fringes with d-spacing of 0.33 nm can be assigned to the (111) crystal plane of hexagonal wurtzite Cd$_{0.5}$Zn$_{0.5}$S. Besides the position at the interfaces of the g-C$_3$N$_4$ microribbons, the Cd$_{0.5}$Zn$_{0.5}$S QDs are also highly located at the edge of the g-C$_3$N$_4$ microribbons (Fig. 2d), and this may be beneficial to the full exposure of the active sites for photocatalytic application. To better understand the influence of the g-C$_3$N$_4$ microribbons on the growth process of Cd$_{0.5}$Zn$_{0.5}$S QDs, the pristine Cd$_{0.5}$Zn$_{0.5}$S sample was also prepared under the same hydrothermal condition without g-C$_3$N$_4$. It can be observed that a significant aggregation occurred, and the Cd$_{0.5}$Zn$_{0.5}$S nanoparticles further assembled into microspheres with the diameters of ca. 500 nm (Fig. S4). Therefore, the interaction between g-C$_3$N$_4$ microribbons and Cd$_{0.5}$Zn$_{0.5}$S can reduce the aggregation of QDs effectively. For example, the oxygen-containing defects and the amino groups on g-C$_3$N$_4$ surfaces could serve as anchoring sites to stabilize the Cd$^{2+}$ and Zn$^{2+}$ precursors, and achieve a fast heterogeneous crystal nucleation of Cd$_{0.5}$Zn$_{0.5}$S QDs on the g-C$_3$N$_4$ microribbons. The confinement of isolated Cd$_{0.5}$Zn$_{0.5}$S QDs from the diffusion resistance on g-C$_3$N$_4$ surface can further prevent their aggregation. By further increasing the precursor contents of Cd$_{0.5}$Zn$_{0.5}$S, the morphology of Cd$_{0.5}$Zn$_{0.5}$S@g-C$_3$N$_4$ composites has also changed, and the aggregation morphology containing rod-like and sphere-like Cd$_{0.5}$Zn$_{0.5}$S appeared (Fig. S5), which can be attributed to the homogenous crystal nucleation occurs at high ratios of QDs precursor.

To study the chemical states of g-C$_3$N$_4$, Cd$_{0.5}$Zn$_{0.5}$S and Cd$_{0.5}$Zn$_{0.5}$S@g-C$_3$N$_4$, the X-ray photoelectron spectrometer (XPS) was carried out. The full XPS spectra of g-C$_3$N$_4$, Cd$_{0.5}$Zn$_{0.5}$S, and Cd$_{0.5}$Zn$_{0.5}$S@g-C$_3$N$_4$ are shown in Fig. 3. The XPS spectra of g-C$_3$N$_4$, Cd$_{0.5}$Zn$_{0.5}$S 32%@g-C$_3$N$_4$, and Cd$_{0.5}$Zn$_{0.5}$S@g-C$_3$N$_4$.
The high electronegativity of sp2-C and N in C–N–C units has decreased. These are related to the electron-withdrawing effect of Cd0.5Zn0.5S QDs on g-C3N4 microribbons [37,38]. Furthermore, it is noted that the binding energies of S 2p, Zn 2p and Cd 3d have systematically shifted towards higher binding energy with 0.2–0.38 eV (Fig. S7), which is attributed to the high electronegativity of sp2-C and N in g-C3N4 as well as the partial electron transfer from Cd0.5Zn0.5S to g-C3N4 [39]. These results indicate a strong electronic interaction between Cd0.5Zn0.5S QDs and g-C3N4. In addition, the XPS can also be used to study the band positions of the Cd0.5Zn0.5S@C3N4 and Cd0.5Zn0.5S composites. The pristine Cd0.5Zn0.5S@C3N4 is located at 470 nm upon excitation at 350 nm. For the Cd0.5Zn0.5S@C3N4, there is a drastic decrease in the PL intensity, indicating a significant depression of electron-hole recombination. The PL quenching demonstrates that the efficient charge separation occurs at Cd0.5Zn0.5S@C3N4. This can be understood by the internal holes transfer between Cd0.5Zn0.5S and g-C3N4 components, as illustrated in their band structures in Scheme S1. According to band gap theory, the CB levels of g-C3N4 are sufficiently negative relative to the CB of Cd0.5Zn0.5S, the electron transfer from the CB of g-C3N4 to the CB of Cd0.5Zn0.5S is therefore reasonable, while holes generated in VB of Cd0.5Zn0.5S QDs transfer to VB of g-C3N4. Such charge transfers result in mutual activation of both g-C3N4 and Cd0.5Zn0.5S QDs [43].

3.5. Enhancement of photocatalytic activity and photocurrent

To date, sulphide/g-C3N4 composites composed of two visible-light responsive semiconductors have been continuously developed (Table S2). To the best of our knowledge, the as-reported the highest rate H2-generation was 9.29 mmol h⁻¹ g⁻¹ [44]. In this work, the photocatalytic H2-production activity of Cd0.5Zn0.5S@g-C3N4 composite was tested by monitoring the time-dependent production of H2 gas in visible-light-illumination without noble-metal cocatalyst. No appreciable H2-generation was detected in the absence of either irradiation or photocatalyst, suggesting that hydrogen was generated by photocatalytic reaction in the present of photocatalyst. Fig. 6a summarizes the H2-generation rates with the samples of pure g-C3N4, pure Cd0.5Zn0.5S and Cd0.5Zn0.5S@g-C3N4 micro/nanocomposites as photocatalysts. For the pristine g-C3N4 microribbons, its H2-generation rate is 1.22 mmol h⁻¹ g⁻¹ in the presence of Pt (3 wt%) as co-catalyst. However, after hybridization of g-C3N4 microribbons with Cd0.5Zn0.5S QDs, the Cd0.5Zn0.5S@g-C3N4 samples exhibited a high performance of H2-generation without noble-metal as cocatalyst. With 16 wt% Cd0.5Zn0.5S QDs, the H2-generation rate of Cd0.5Zn0.5S 16%g-C3N4 composite was significant increased (6.03 mmol h⁻¹ g⁻¹), which is higher than that of the pure Cd0.5Zn0.5S (3.64 mmol h⁻¹ g⁻¹) due to the high aggregation of QDs for the latter one. Furthermore, all the binary
Cd$_{0.5}$Zn$_{0.5}$S@C$_3$N$_4$ could produce H$_2$ under visible-light irradiation ($\lambda \geq$ 420 nm) effectively. The photocatalytic rate of all the binary Cd$_{0.5}$Zn$_{0.5}$S@C$_3$N$_4$ systems was higher than that of pure g-C$_3$N$_4$ microribbons and pure Cd$_{0.5}$Zn$_{0.5}$S, highlighting the utilization of Cd$_{0.5}$Zn$_{0.5}$S QDs as the sensitizers for g-C$_3$N$_4$ microribbons in improving the photocatalytic activity. At an optimal Cd$_{0.5}$Zn$_{0.5}$S content of 32 wt%, the Cd$_{0.5}$Zn$_{0.5}$S@C$_3$N$_4$ micro/nanocomposite exhibits the highest H$_2$-generation rate of 33.41 mmol h$^{-1}$ g$^{-1}$ (corresponding to the electron transfer number of ca. $1.12 \times 10^{19}$ g$^{-1}$ C$^{-1}$) and the apparent quantum efficiency is estimated as 46.65% at 450 nm. In this regard, the photocatalytic rate of sample Cd$_{0.5}$Zn$_{0.5}$S@C$_3$N$_4$ is higher than that of pristine g-C$_3$N$_4$ and Cd$_{0.5}$Zn$_{0.5}$S by a factor of 27.39 and 9.18 respectively, and such H$_2$-generation rate is significantly higher than most of as-reported noble-metal-free semiconductor catalysts to date (Table S3).

Therefore, the in-situ anchoring of Cd$_{0.5}$Zn$_{0.5}$S QDs on the 2D g-C$_3$N$_4$ ultrathin microribbons can noticeably improves the photocatalytic H$_2$-generation activity. The obvious improvement of the photocatalytic activity should be related to both the decrease of the band gap energy, and the electronic coupling between the Cd$_{0.5}$Zn$_{0.5}$S and the band gap energy, and the electronic coupling between the Cd$_{0.5}$Zn$_{0.5}$S and Cd$_{0.5}$Zn$_{0.5}$S@C$_3$N$_4$. The photocurrent responses of pure Cd$_{0.5}$Zn$_{0.5}$S@C$_3$N$_4$ were also performed under the same experimental condition, and it can be observe in Fig. 7b, the H$_2$-generation has highly reduced after 3rd circulation. In particularly, the H$_2$-generation rate has a sharp decrease in the 5th photocatalytic reaction due to the photocorrosion. These results proved that Cd$_{0.5}$Zn$_{0.5}$S@C$_3$N$_4$ has much higher stability than pure Cd$_{0.5}$Zn$_{0.5}$S on the account of the localization and stabilization onto the 2D g-C$_3$N$_4$ microribbons host.

The photocatalytic performance is positively correlated with density of the photocurrent, a higher photocurrent indicates a higher efficiency in the separation of the photon-generated electrons and holes [45,46]. Fig. 6b shows the transient photocurrent response obtained from both the pure g-C$_3$N$_4$ microribbons and Cd$_{0.5}$Zn$_{0.5}$S 32%@C$_3$N$_4$ with several on-off cycles under visible-light irradiation at a bias potential of 0.5 V. Pure g-C$_3$N$_4$ microribbons shows a lower photocurrent response under visible-light irradiation, which indicates that photo-generated electrons and holes are inefficiently transferred at the sample/electrolyte interface to produce photocurrent [47]. When 32 wt% Cd$_{0.5}$Zn$_{0.5}$S is introduced into the g-C$_3$N$_4$ microribbons, an anodic photocurrent spike occurs at the initial time of irradiation, and then the photocurrent continuously decreases with time until a constant current is reached. Such photocurrent decay in the Cd$_{0.5}$Zn$_{0.5}$S 32%@C$_3$N$_4$ composite is related to the fact: besides photogenerated electrons, a certain number of photogenerated holes are also transferred to the g-C$_3$N$_4$ microribbons due to the intimate contact between Cd$_{0.5}$Zn$_{0.5}$S QDs and g-C$_3$N$_4$. These holes accumulate at the g-C$_3$N$_4$ surface, and their competitive recombination with electrons and reduced species in the electrolyte results in the decreased photocurrent. After equilibration of competitive separation and recombination of electron-hole pairs, the photocurrent reaches a constant [48,49]. Notably, the stable photocurrent value of Cd$_{0.5}$Zn$_{0.5}$S 32%@C$_3$N$_4$ is about 5.0 times as high as that of pure g-C$_3$N$_4$ microribbons, indicating more effective separation and transfer of photon-generated electrons and holes, which lead to higher photocatalytic activity of the nanocomposites.

**Fig. 5.** Photoemission spectra of g-C$_3$N$_4$, Cd$_{0.5}$Zn$_{0.5}$S and Cd$_{0.5}$Zn$_{0.5}$S 32%@C$_3$N$_4$ with an excitation wavelength of 350 nm.

**Fig. 6.** (a) H$_2$ production under visible-light irradiation and the rate of H$_2$ production of Cd$_{0.5}$Zn$_{0.5}$S, Cd$_{0.5}$Zn$_{0.5}$S 32%@C$_3$N$_4$ (with Na$_2$S and Na$_2$SO$_3$ were used as the hole scavengers without noble-mental cocatalysts) and g-C$_3$N$_4$ microribbons (with triethanolamine used as the hole scavengers and Pt [3 wt%] as cocatalyst); (b) Transient photocurrent responses of pure g-C$_3$N$_4$ microribbons and Cd$_{0.5}$Zn$_{0.5}$S 32%@C$_3$N$_4$. 

The photocatalytic activity should be related to both the decrease of the band gap energy, and the electronic coupling between the Cd$_{0.5}$Zn$_{0.5}$S and Cd$_{0.5}$Zn$_{0.5}$S@C$_3$N$_4$. These holes accumulate at the g-C$_3$N$_4$ surface, and their competitive recombination with electrons and reduced species in the electrolyte results in the decreased photocurrent. After equilibration of competitive separation and recombination of electron-hole pairs, the photocurrent reaches a constant [48,49]. Notably, the stable photocurrent value of Cd$_{0.5}$Zn$_{0.5}$S 32%@C$_3$N$_4$ is about 5.0 times as high as that of pure g-C$_3$N$_4$ microribbons, indicating more effective separation and transfer of photon-generated electrons and holes, which lead to higher photocatalytic activity of the nanocomposites.
than the single-component counterparts. The results of PL spectrum and transient photocurrent demonstrate that the g-C3N4 function as a holes collector, while the Cd0.5Zn0.5S function as an electron collector and transporter, which is significant to lengthen the lifetime of the charge carriers, consequently improve the charge separation and photocatalytic activity [50].

To further prove the synergistic effect between Cd0.5Zn0.5S QDs and g-C3N4 microribbons, two control compositions of Cd0.5Zn0.5S 32%@C3N4 were further synthesized. One is a mechanical mixture containing the pure Cd0.5Zn0.5S QDs and pure g-C3N4; another is prepared under the same condition with the thermal exfoliated g-C3N4 as a precursor. As displayed in Fig. S10, the obtained composites showed a relative lower photocatalytic H2-generation activity (16.23 mmol h⁻¹ g⁻¹ for the mechanical mixture; 20.85 mmol h⁻¹ g⁻¹ for the composite using un-exfoliated g-C3N4). These results thus confirm that the electronic coupling between Cd0.5Zn0.5S QDs and g-C3N4 microribbons as well as the uniform dispersion of Cd0.5Zn0.5S played an important role in enhancing photocatalytic H2-generation activity. Additionally, the exfoliated g-C3N4 ultrathin microribbons can also supply more highly active sites during the photocatalytic process.

Furthermore, we have detected how the different morphologies of g-C3N4 can influence the photocatalytic H2-generation activities, and two bulk g-C3N4 samples were also fabricated from two different precursors (dicyanodiamine and melamine, Table S1) respectively. The photocatalytic H2-generation rates of two Cd0.5Zn0.5S@C3N4 samples (32%, dicyanodiamine and melamine as the precursors) are 11.2 mmol h⁻¹ g⁻¹ and 7.37 mmol h⁻¹ g⁻¹ respectively (Fig. S11). As shown in SEM images (Fig. S12), it can be observed that the obtained two powdered Cd0.5Zn0.5S@C3N4 samples present obvious nanoparticle aggregation, and this may contribute to the relative lower hydrogen production rate of two control samples. These comparisons proved that the 2D sheet-like g-C3N4 microribbons could supply an effective host matrix and give rise to a higher photocatalytic activity.

4. Conclusions

In summary, 2D g-C3N4 ultrathin microribbons were prepared by a thermal exfoliation and liquid exfoliation process, and a new type Cd0.5Zn0.5S QDs sensitized g-C3N4 microribbons photocatalysts can be further obtained via an in-situ hydrothermal method. The Cd0.5Zn0.5S QDs@C3N4 micro/nanostructures present a high-efficiency photocatalytic H2-generation rate during water splitting process under visible-light irradiation. The Cd0.5Zn0.5S QDs in the hybrids have largely enhanced visible-light absorption; the electronic coupling between Cd0.5Zn0.5S QDs and g-C3N4 microribbons has achieved a high-efficiency separation of photo-induced electron-hole pairs, and inhibited their recombination. In addition, the high dispersion of Cd0.5Zn0.5S QDs on the g-C3N4 microribbons made an important contribution to increasing photocatalytic activities due to the full exposure of active sites of QDs. The optimal weight percentage of Cd0.5Zn0.5S QDs was found to be 32 wt%, which resulted in a high visible-light photocatalytic H2-generation rate of 33.41 mmol h⁻¹ g⁻¹ without noble-metal as a cocatalyst; this rate is also higher than most of state-of-the-art metal sulphide sensitized g-C3N4 composites (Table S3). Therefore, this work not only demonstrates that the 2D ultrathin microribbon of g-C3N4 can serve as an excellent supporting material for anchoring and localizing visible-light-sensitizer QDs, but also confirms that the electronic coupling between Cd0.5Zn0.5S QDs and g-C3N4 at the micro/nano-sized interface can largely enhance the visible light-induced H2-generation. It was expected that the strategy based on the rational hybridization of micro/nano-sized materials can be extended to other energy-matched semiconductor systems for potential applications in solar energy conversion.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.nanoen.2016.05.031.

References