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1T-phase MoS₂ quantum dots as a superior co-catalyst to Pt decorated on carbon nitride nanorods for photocatalytic hydrogen evolution from water†

 Zhangqian Liang, Yichen Guo, Yanjun Xue, Hongzhi Cui * and Jian Tian *

Molybdenum disulfide (MoS₂) has been confirmed to be a promising non-precious-metal co-catalyst for photocatalytic hydrogen (H₂) evolution; however, its low-density of active sites and poor electron transfer efficiency have essentially limited its photocatalytic properties. Here we report that 1T-MoS₂ quantum dots (QDs) can exceed the performance of noble metals like Pt as co-catalysts in assisting photocatalytic H₂ evolution upon forming a heterostructure with C₃N₄ nanorods (denoted as 1T-MoS₂@C₃N₄ NRs). The presence of 1T-MoS₂ QDs is found to improve light harvesting, enhance electronic conductivity as well as boost the density of active sites, resulting in an excellent light absorption range up to the near-infrared (NIR) region and a highly efficient spatial charge separation and transfer process. As a result, the optimized 1T-MoS₂@C₃N₄ NR composite (5.0 wt%) exhibits an extraordinary photocatalytic H₂ production rate of 565 μmol h⁻¹ g⁻¹ under simulated solar light irradiation, obviously higher than that of noble metal Pt loaded C₃N₄ NRs (318 μmol h⁻¹ g⁻¹). Moreover, the 1T-MoS₂@C₃N₄ NR composites exhibit good stability in the cyclic runs for photocatalytic H₂ production. This study indicates that the highly active MoS₂ as a co-catalyst is highly promising as a substitute for Pt for photocatalytic H₂ evolution.

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1. Introduction

Due to the emerging energy crisis and global environmental awareness,^{1–3} the conversion of solar energy into perfect hydrogen (H₂) energy *via* photocatalytic water splitting using semiconductors as catalysts has attracted significant attention.^{4–7} Hydrogen is considered as an ideal, clean and sustainable candidate to replace exhaustible fossil fuels.^{8–11} Until now, a rich variety of semiconductor materials have been explored as photocatalysts for hydrogen production.^{12–15} As a promising semiconductor photocatalyst, C₃N₄ nanorods (NRs) exhibit a suitable band gap (about 1.38 eV), broader visible-light absorption range than g-C₃N₄ nanosheets (about 2.47 eV) and a negative conduction band edge potential (below the reduction potential of H₂O/H₂) for splitting water.^{16,17} However, bare C₃N₄ NRs show extremely low activity for the photocatalytic H₂ evolution reaction due to the rapid recombination of photogenerated electrons and holes and lack of active sites for photocatalysis.¹⁸ Integration of co-catalysts, such as noble metals Au and Pt, into C₃N₄ NRs has proven to be an effective way for suppressing electron-hole

recombination and accelerating photocatalytic H₂ evolution.¹⁹ However, the scale-up application of the commonly used noble metal co-catalysts is still largely restricted due to their low abundance and high cost.^{19,20} Therefore, there is an urgent need to seek noble-metal free alternative co-catalysts compounded with C₃N₄ NRs for synthesizing C₃N₄ NR-based heterostructures with significantly enhanced photocatalytic activity.

As a typical layered transition metal sulfide, molybdenum disulfide (MoS₂), with a sandwich structure of three stacked atomic layers (S–Mo–S), has been considered a promising alternative for noble-metal co-catalysts due to its abundance and low cost.^{21–24} MoS₂ has been designed with various nanostructures, such as nanoparticles,^{25,26} nanowires,^{27,28} nanoflowers,^{29,30} nanosheets,^{31,32} and quantum dots (QDs).^{33,34} Interestingly, MoS₂ QDs have attracted more significant attention due to their better solubility in aqueous solvents and more edge atoms compared with other MoS₂ nanostructures or bulk-MoS₂.³⁵ It is well known that MoS₂ usually has two phase structures, including a trigonal phase (1T-MoS₂) and a hexagonal phase (2H-MoS₂).^{36,37} Natural MoS₂ usually exists in the stable 2H phase, showing semiconducting properties with a tunable bandgap of 1.3–1.9 eV.²¹ However, the inherent semiconducting character of 2H-MoS₂ with a low density of active sites and poor conductivity restricts its catalytic performance.¹ As reported previously,³⁸ 1T-MoS₂ offers dense active sites containing catalytically active edges and basal planes,

School of Materials Science and Engineering, Shandong University of Science and Technology, Qingdao, 266590, China. E-mail: cuihongzhi1965@163.com, jiantian@sdust.edu.cn

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while 2H-MoS₂ only possesses edge sites. Besides, compared to 2H-MoS₂, the metallic 1T-MoS₂ displays excellent conductivity characteristics at ambient temperature, making it suitable as a co-catalyst to accept the electrons for H₂ evolution.³⁹

This study aims to prepare highly active MoS₂ substituting for noble metal Pt for photocatalytic H₂ evolution and clearly certify the electron transfer process between C₃N₄ and MoS₂. Herein, we prepare 1T-MoS₂ QD decorated C₃N₄ NRs (1T-MoS₂@C₃N₄ NRs) by a sonication-assisted hydrothermal method. The obtained 1T-MoS₂@C₃N₄ NR composites exhibit a broad visible and near-infrared (NIR) light absorption range, excellent photocurrent response and charge transfer activity. The 1T-MoS₂@C₃N₄ NR composite with optimal 1T-MoS₂ QD loading of 5.0 wt% exhibits a drastically enhanced photocatalytic H₂ evolution rate of 565 μmol h⁻¹ g⁻¹, which is almost 1.8 times higher than that of Pt@C₃N₄ NRs (318 μmol h⁻¹ g⁻¹) under simulated solar light irradiation, as well as good stability in photocatalytic cyclic runs. The 1T-MoS₂ QDs apparently show metallic characteristics like Pt, and a series of experimental studies have proven the photo-generated electron transfer process and photocatalytic mechanism.

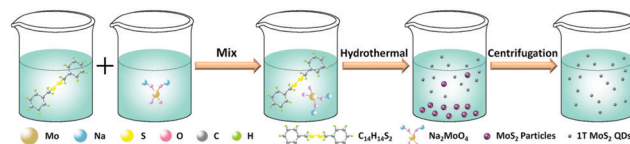
2. Experimental section

2.1. Synthesis of C₃N₄ nanorods (NRs)

In a typical procedure (Scheme 1), 2.7675 g of 1,3,5-trichlorotriazine and 0.9459 g of melamine powder were dissolved in 60 mL of acetonitrile. The mixture was stirred for 12 h, and then put into a 100 mL Teflon-lined stainless steel autoclave, which was sealed and maintained at 180 °C for 96 h. After heating at a certain temperature, the autoclave was allowed to cool to room temperature naturally. The obtained product was sequentially washed with acetonitrile, distilled water and absolute ethanol several times to remove residual impurities and then the resulting powder was dried at 60 °C for 12 h to get the final products.

2.2. Preparation of 1T-MoS₂ quantum dots (QDs)

1T-MoS₂ QDs were prepared by a simple hydrothermal method (Scheme 2). Specifically, 0.4 g of Na₂MoO₄·2H₂O and 0.38 g of C₁₄H₁₄S₂ were dissolved in 30 mL of deionized water and 30 mL of ethanol with sonication for 30 min, respectively. Then, C₁₄H₁₄S₂ solution was added to the Na₂MoO₄·2H₂O solution. After sonication for 30 min, the mixture was then transferred to a 100 mL Teflon-lined stainless steel autoclave and heated at 180 °C for 20 h. After the autoclave was cooled to room temperature naturally, the light yellow supernatant was discarded and then



Scheme 2 Schematic illustration of the synthetic route for 1T-MoS₂ QDs through a hydrothermal technique.

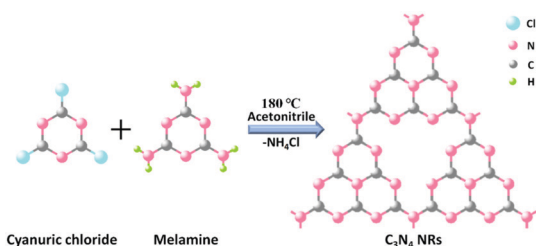
30 mL of deionized water was added to disperse the black product. The resulting suspension was then centrifuged for 90 min at 12 000 rpm to separate the supernatant and sediment, and the supernatant was 1T-MoS₂ QDs. In order to determine the concentration of the 1T-MoS₂ QD solution, the supernatant was treated by freeze drying to obtain a powder. Therefore, the concentration of the as-prepared 1T-MoS₂ QD solution was determined to be about 0.2 mg mL⁻¹ in terms of the measured weight and the volume of solution before freeze drying.

2.3. Preparation of 1T-MoS₂@C₃N₄ NR composites

200 mg of C₃N₄ NRs and 50 mL (0.2 mg mL⁻¹) of the as-prepared 1T-MoS₂ QD solution were mixed and then sonicated for over 2 h. Subsequently, the obtained mixture was centrifuged and dried at 60 °C to gain the target product (1T-MoS₂@C₃N₄ NRs with 1T-MoS₂ QD loading of 5.0 wt%). Similarly, a series of hybrid catalysts, including 1T-MoS₂@C₃N₄ NRs with 1T-MoS₂ QD loading of 0.5 wt%, 1.0 wt%, 3.0 wt% and 7.0 wt%, were obtained by adjusting the volume of the 1T-MoS₂ QD solution as 5, 10, 30 and 70 mL, respectively.

2.4. Characterization

The synthesized products were characterized by X-ray diffraction (XRD, D/Max 2500PC Rigaku, Japan) utilizing a Cu Kα (λ = 1.5418 Å) radiation source operated at 40 kV at a scan rate of 4° min⁻¹. The nanostructure and surface characteristics of the products were studied on a high-resolution scanning electron microscope (FESEM, FEI Nova Nanosem 450, USA). The morphology and crystal structure of the samples were characterized by transmission electron microscopy (TEM) and high resolution TEM (HRTEM) (JEOL JEM 2100F) with an accelerating voltage of 200 kV, and their composition was examined using energy-dispersive X-ray spectroscopy (EDS) attached to the TEM instrument. X-ray photoelectron spectroscopy (XPS) was carried out with a Thermo ESCALAB 250XI spectrometer using Al Kα radiation at a voltage of 1486.6 eV and calibrated with the C 1s binding energy of 284.8 eV. The XPS results were deconvoluted with XPSPEAK software. The UV-vis-NIR diffuse reflectance spectra (DRS) of the samples were recorded on a UV-vis-NIR spectrophotometer (Hitachi UV-3101) with an integrating sphere attachment within the 200–2000 nm range and with BaSO₄ as the reflectance standard. The Brunauer–Emmett–Teller (BET) specific surface area measurements were carried out by N₂ adsorption at 77 K using a Micromeritics ASAP2020 nitrogen adsorption–desorption apparatus with prior out gassing of the sample overnight at 120 °C under a primary vacuum. Raman spectra were measured with solid samples using a HORIBA LabRAM HR Evolution Raman microscope. Transient photoluminescence curves of the as-prepared samples were obtained on a FLS980 Series fluorescence lifetime spectrophotometer.



Scheme 1 Schematic illustration of the C₃N₄ NR reaction.

2.5. Photoelectrochemical measurements

The photocurrent response and electrochemical impedance of the samples were tested by using an electrochemical workstation (Shanghai Chenhua CHI660D) in a three-electrode system, in which the sample electrode was used as the photocathode, Ag/AgCl as the reference electrode, a Pt wire as the counter electrode, and 0.5 M Na₂SO₄ aqueous solution as the electrolyte. The working electrodes were prepared as follows: 5 mg of the photocatalyst (1T-MoS₂@C₃N₄ NRs composites) and 1 mg of ethyl cellulose were dispersed into a solution containing 250 μ L of ethanol and 250 μ L of terpineol by 60 min sonication to prepare a homogeneous slurry. Then, 250 μ L of the slurry was dropped onto pretreated stannic oxide (FTO) conductive glass with an exposed area of 4.0 cm² (2 cm $\times$ 2 cm). A 500 W Xe arc lamp equipped with an AM-1.5 filter was adopted as the light source.

2.6. Photocatalytic H₂ evolution

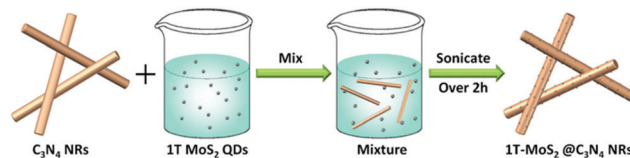
Photocatalytic H₂ production experiments were carried out in an outer irradiation type photoreactor (100 mL quartz glass) in a N₂ environment. 20 mg of the 1T-MoS₂@C₃N₄ NR composite photocatalyst was dispersed with mechanical stirring in 100 mL of an aqueous solution containing 20 vol% triethanolamine for further photocatalytic H₂ production experiments. Before irradiation, the photocatalytic system was thoroughly degassed to remove air by bubbling N₂ for 20 min. The irradiation light source used in this study was a 300 W Xe arc lamp (CELHXF300, Beijing China Education Au-light Co., Ltd), which was equipped with an AM-1.5 filter. The evolved gas was analyzed using a gas chromatograph (Techcomp GC-7920) equipped with a thermal conductivity detector (TCD). The apparent quantum efficiency (AQE) was measured under similar photocatalytic reaction conditions except that a 300 W Xe arc lamp with an AM-1.5 filter was used as the light source. The focused intensity for the 300 W Xe arc lamp with the AM-1.5 filter was *ca.* 4601.7 W m⁻². The apparent quantum efficiency (AQE) was measured and calculated according to the equation:

$$\text{AQE} = \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100$$

$$= \frac{\text{number of evolved H}_2 \text{ molecules} \times 2}{\text{number of incident photons}} \times 100\%$$

3. Results and discussion

Firstly, the C₃N₄ NRs were prepared by solvothermally treating cyanuric chloride and melamine in acetonitrile solution at 180 $^{\circ}$ C for 96 h. Under these conditions, the C₃N₄ frameworks could be formed due to the condensation of triazine tectons from cyanuric chloride and melamine, accompanied by the release of NH₄Cl (Scheme 1). Then, 1T-MoS₂ QDs were fabricated by a simple hydrothermal method (Scheme 2). The obtained 1T-MoS₂ QDs not only act as electron acceptors with high electrical conductivity, but also offer abundant reaction sites for H₂ evolution. Ultimately, 1T-MoS₂@C₃N₄ NR composite photocatalysts were prepared *via* ultrasonic mixing; in this process, 1T-MoS₂ QDs were perfectly decorated on the surface of



Scheme 3 Schematic illustration for the formation of 1T-MoS₂@C₃N₄ NR composites.

C₃N₄ NRs and offer dense active sites containing catalytically active edges and basal planes, just as schematically shown in Scheme 3.

The phases of C₃N₄ NRs and 1T-MoS₂@C₃N₄ NR composites with varying loadings of 1T-MoS₂ QDs (0.5, 1.0, 3.0, 5.0 and 7.0 wt%) were investigated by the X-ray diffraction (XRD) patterns (Fig. 1). For comparison, g-C₃N₄ was obtained by the thermal polymerization of urea. As shown in Fig. S1 (ESI[†]), g-C₃N₄ exhibits two peaks located at 13.0 $^{\circ}$ and 27.5 $^{\circ}$, which can be well indexed to the (100) and (002) planes of g-C₃N₄, respectively.^{40,41} Compared with g-C₃N₄, C₃N₄ NRs only display one characteristic diffraction peak located at 27.5 $^{\circ}$, which corresponds to the (002) plane of g-C₃N₄ due to the interlayer stacking of the conjugated aromatic systems.⁴² After 1T-MoS₂ QD decoration, all 1T-MoS₂@C₃N₄ NR samples exhibit similar diffraction patterns and show no XRD peak shift compared to pure C₃N₄ NRs. This indicates that the C₃N₄ NR is the basic structure of the obtained samples, and its structure does not change after 1T-MoS₂ QD loading.⁴² It is obvious that no diffraction peaks of 1T-MoS₂ QDs can be observed even for 1T-MoS₂@C₃N₄ NRs (7.0 wt%) due to the low concentration and/or low crystallinity of 1T-MoS₂ in the composites.^{43,44}

The elemental composition and chemical status of 1T-MoS₂@C₃N₄ NR composites were further investigated by X-ray photoelectron spectroscopy (XPS). The XPS survey spectrum (Fig. S2, ESI[†]) indicates that the 1T-MoS₂@C₃N₄ NR composites are composed of C, N, Mo and S elements. In addition, the O 1s peak can also be found, due to the surface absorption and oxidation during the preparation process.⁴⁵ To further analyze the 1T-MoS₂@C₃N₄ NR composites, the high-resolution spectra for C 1s, N 1s, Mo 3d and S 2p of the 1T-MoS₂@C₃N₄ NR

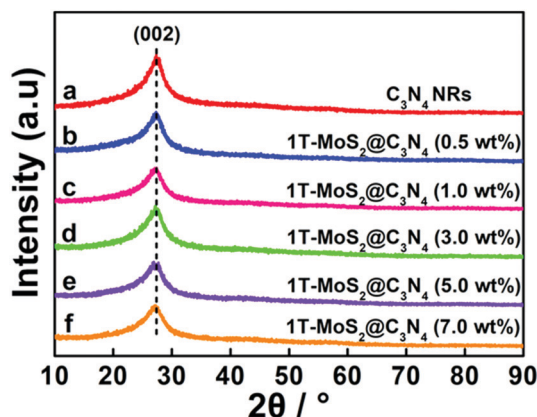


Fig. 1 XRD patterns of C₃N₄ NRs and 1T-MoS₂@C₃N₄ NR composites containing different amounts of 1T-MoS₂ QDs (0.5, 1.0, 3.0, 5.0 and 7.0 wt%).

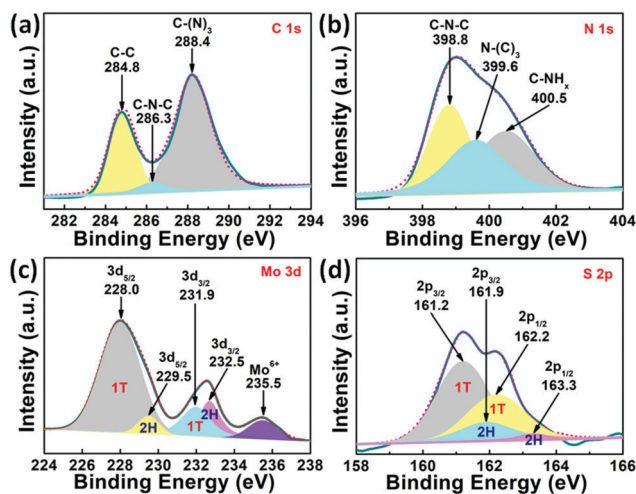


Fig. 2 High-resolution peak-fitting XPS spectra of (a) C 1s, (b) N 1s, (c) Mo 3d and (d) S 2p of 1T-MoS₂@C₃N₄ NR composites (5.0 wt%).

composites are depicted (Fig. 2). The C 1s spectrum (Fig. 2a) of the samples shows three peaks at 284.8, 286.3 and 288.4 eV, which can be attributed to the carbon nitride matrix group (C-C), the sp²-hybridized carbon atoms bonded to nitrogen atom in the aromatic ring group (C-N-C) and the sp²-hybridized carbon atoms bonded to three nitrogen atoms in the aromatic ring attached to the NH₂ group (C-(N)₃), respectively.^{46,47} The N 1s spectrum (Fig. 2b) can be fitted into three peaks at 398.8, 399.6 and 400.5 eV, which arise from the sp²-hybridized nitrogen atom (C-N-C), sp³-hybridized nitrogen atom (N-(C)₃) and amino groups carrying hydrogen (C-NH_x), respectively.^{16,48} To better illustrate the existence of 1T-MoS₂, the Mo 3d and S 2p XPS spectra of the 1T-MoS₂@C₃N₄ NR composites are given in Fig. 2c and d. The Mo 3d spectrum (Fig. 2c) can be resolved into five peaks. The two small peaks located at 229.5 eV (Mo 3d_{5/2}) and 232.5 eV (Mo 3d_{3/2}) indicate the 4+ oxidation state of 2H-phase MoS₂, and the main peaks at 228.0 and 231.9 eV suggest the formation of 1T-phase MoS₂.^{49,50} The peak located at 235.5 eV was assigned to Mo⁶⁺, probably owing to the oxidation of 1T-MoS₂@C₃N₄ NRs by the exposure to air. Fig. 2d shows the S 2p spectrum, in which the main two peaks at 161.2 eV (S 2p_{3/2}) and 162.2 eV (S 2p_{1/2}) represent the 1T-phase MoS₂, and the two small peaks at 161.9 eV (S 2p_{3/2}) and 163.3 eV (S 2p_{1/2}) indicate the 2H-phase MoS₂.^{49,50} The concentration of the 1T phase in the 1T-MoS₂@C₃N₄ NR composites is approximately calculated to be ~79%, which indicates the predominance of the 1T phase over its 2H counterpart. The above results further confirm the existence of C₃N₄ and 1T-MoS₂ in 1T-MoS₂@C₃N₄ NR samples. The vibrational properties of the prepared C₃N₄ NRs and 1T-MoS₂@C₃N₄ NR composites (5.0 wt%) were determined by Raman spectroscopy. As can be seen in Fig. S3 (ESI[†]), the band at 978 cm⁻¹ corresponds to the stretching vibration of the CN heterocycle in the g-C₃N₄ structure.⁵¹ The band at 740 cm⁻¹ is also ascribed to g-C₃N₄, which appears in both spectra. No peaks ascribed to 1T-MoS₂ QDs can be detected in the 1T-MoS₂@C₃N₄ NRs (5.0 wt%), due to the low content of MoS₂ in the hybrid. This result is consistent with the XRD data as shown in Fig. 1.

The morphology and size of C₃N₄ NRs and 1T-MoS₂@C₃N₄ NR composites were investigated by scanning electron microscopy (SEM). Obviously, the C₃N₄ sample exhibits a rod-like structure with a length of 300–500 nm (Fig. 3a). Subsequently, the surface decoration of C₃N₄ NRs with 1T-MoS₂ QDs was carried out by sonication of the C₃N₄ NRs in an aqueous solution of 1T-MoS₂ QDs for over 2 h. In this process, 1T-MoS₂ QDs could be absorbed on the surface of C₃N₄ NRs, resulting in the assembly of 1T-MoS₂ QDs on C₃N₄ NRs (Scheme 3). The obtained 1T-MoS₂@C₃N₄ NR composites still retained the rod-shaped structure (Fig. 3b). 1T-MoS₂ QDs were difficult to discern through SEM due to their very small size.

In order to further visualize the morphology and micro-structure of the as-prepared pure 1T-MoS₂ QDs and 1T-MoS₂@C₃N₄ NR composites, TEM images were employed (Fig. 4 and 5). Obviously, Fig. 4a reveals that pure 1T-MoS₂ QDs are distributed homogeneously without apparent aggregation, which possess well-dispersed ultrasmall particles of size about 2–3 nm. From the HRTEM image (Fig. 4b) of 1T-MoS₂ QDs, no typical (002) lattice plane of crystalline MoS₂ is observed, indicating that 1T-MoS₂ QDs contain only a single layer or very few layers.⁵² The atomic force microscopy (AFM) image shown in Fig. S4 (ESI[†]) also confirms the formation of the 1T-MoS₂ QDs with good dispersion. Furthermore, the 1T-phase MoS₂ can be clearly visualized (inset in Fig. 4b), evidently displaying the trigonal lattice areas (octahedral coordination) of the 1T phase of MoS₂ QDs.^{50,53} As displayed in Fig. 5a, the 1T-MoS₂@C₃N₄ NR composites exhibit a 1D rod-shaped morphology. However, plenty of black dot-like structures (the regions enclosed by the red circles) are seen decorating the nanorod with a diameter of several nanometers (Fig. 5b). A closer inspection of the TEM image

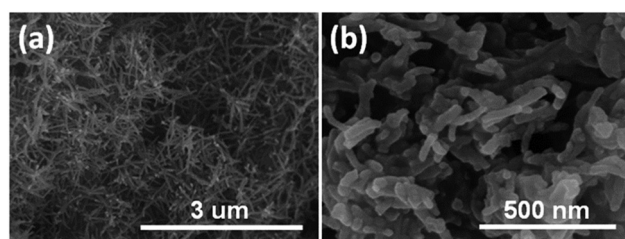


Fig. 3 SEM images of (a) C₃N₄ NRs and (b) 1T-MoS₂@C₃N₄ NR composites (5.0 wt%).

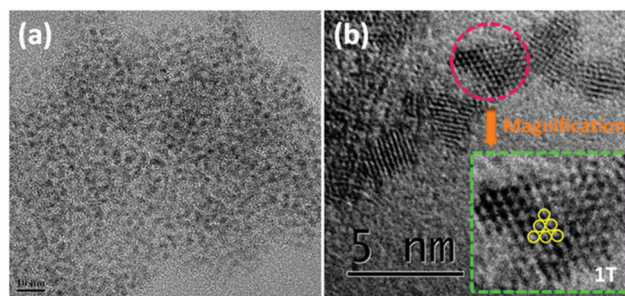


Fig. 4 (a) TEM images and (b) HRTEM image of 1T-MoS₂ QDs (the inset shows the magnification of the region enclosed by the pink circle).

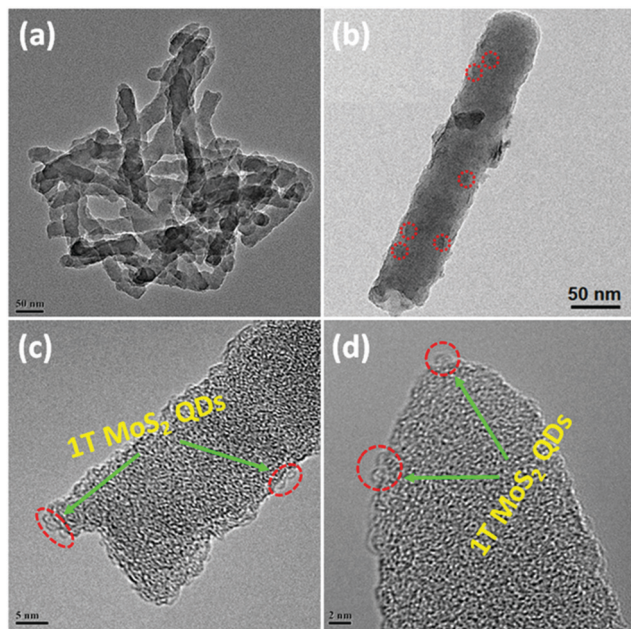


Fig. 5 TEM image of 1T-MoS₂@C₃N₄ NR composites (5.0 wt%).

(Fig. 5c and d) indicates that these nanodots (1T-MoS₂ QDs) are closely attached on the surface of the nanorod. Such a heterostructure with close contact interfaces ensures the fast separation and transfer of charge carriers across the interfaces. Moreover, the EDS mapping (Fig. 6) analysis of 1T-MoS₂@C₃N₄ NR composites displays the uniform distribution of C, N, Mo and S, further confirming that 1T-MoS₂ QDs are successfully loaded on the surface of C₃N₄ NRs.

To determine the surface area of the as-synthesized samples, the N₂ adsorption-desorption isotherms were measured for the samples. The nitrogen adsorption-desorption isotherms and the corresponding pore size distribution curves of the samples are shown in Fig. S5 (ESI[†]), and the specific surface areas of the samples are listed in Table S1 (ESI[†]). The N₂ adsorption-desorption isotherms of all the samples are typical Langmuir type IV isotherms with a typical H₃ hysteresis loop at high pressure, indicating the presence of mesopores in all samples.^{54,55} The pore size distribution curves (Fig. S5b–f, ESI[†] inset) reveal that the pore size diameter of the 1T-MoS₂@C₃N₄ NR composites is about 2 nm, while the pore size diameter of pure C₃N₄ NRs is about 4 nm (Fig. S5a, ESI[†] inset). Besides, the results show that the 1T-MoS₂@C₃N₄ NR composites containing different amounts of 1T-MoS₂ QDs have similar specific surface areas (Table S1, ESI[†]). Thus, the effect of the BET surface area on the hydrogen evolution activity of the 1T-MoS₂@C₃N₄ NR composites is uncertain in this work.

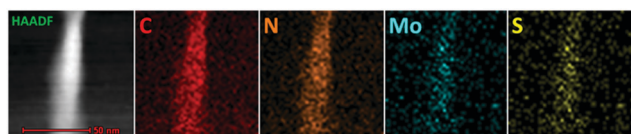


Fig. 6 Selected HAADF image and corresponding EDS elemental mappings of 1T-MoS₂@C₃N₄ NR composites (5.0 wt%).

The optical properties of the samples were measured by UV-vis-NIR diffuse reflectance spectroscopy (DRS) (Fig. 7 and Fig. S6a, ESI[†]). As shown in Fig. S6a (ESI[†]), g-C₃N₄ nanosheets exhibit a short-wavelength absorption with an edge at ~470 nm. For the C₃N₄ NR sample, it exhibits a wide photoabsorption range from the UV to visible region with an absorption edge at ~754 nm, indicating a large redshift compared with that of pure g-C₃N₄ (~470 nm). The UV-vis-NIR absorption spectrum of 1T-MoS₂ QDs gives a smooth line without any obvious absorption band (Fig. S7, ESI[†]), confirming the metallic characteristics of 1T-MoS₂ QDs. Furthermore, it is obvious that loading the 1T-MoS₂ QD co-catalysts onto the surface of C₃N₄ NRs can broaden the absorption range to the NIR light region (Fig. 7). Importantly, the 1T-MoS₂@C₃N₄ NR composites (5.0 wt%) display stronger optical absorption with an edge at ~850 nm, indicating a large red-shift compared with that of C₃N₄ NRs and 1T-MoS₂@C₃N₄ NR composites containing other amounts of 1T-MoS₂ QDs (0.5, 1.0, 3.0 and 7.0 wt%). Thus, the enhanced light absorption of 1T-MoS₂@C₃N₄ NR composites is favorable to produce more photo-generated electrons and holes, which is in turn beneficial to the photocatalytic HER activity.⁵⁶ Furthermore, the band gap energy of g-C₃N₄ and C₃N₄ NRs could be computed from the formula $(\alpha h\nu)^{1/2} \propto h\nu - E_g$, where α , h , ν , and E_g are the absorption coefficient, Planck's constant, light frequency, and band gap energy, respectively. Then the estimated E_g of g-C₃N₄ and C₃N₄ NRs is 2.47 and 1.38 eV, respectively (Fig. S6b, ESI[†]).

We further tested the photoexcited charge carrier lifetimes of pure C₃N₄ NRs and 1T-MoS₂@C₃N₄ NR composites by using time-resolved fluorescence decay spectroscopy. As shown in Fig. 8, by fitting the fluorescence lifetime decay curve, we conclude that both pure C₃N₄ NRs and 1T-MoS₂@C₃N₄ NR composites show single exponential decay. The intensity-average lifetime (τ) of pure C₃N₄ NRs is 0.1545 ns, which is lower than that of the 1T-MoS₂@C₃N₄ NR composites (0.3585 ns). The extension of the trapped carrier lifetimes in 1T-MoS₂@C₃N₄ NR composites indicates the advantages of surface decoration of C₃N₄ NRs by 1T-MoS₂ QDs, which promotes electron-hole separation and hinders their efficient recombination.

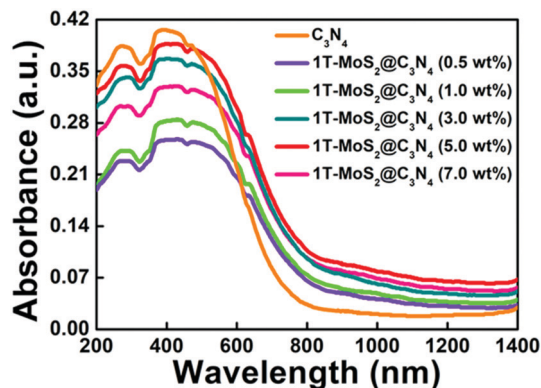


Fig. 7 UV-vis-NIR light absorption spectra of C₃N₄ NRs and 1T-MoS₂@C₃N₄ NR composites containing different amounts of 1T-MoS₂ QDs (0.5, 1.0, 3.0, 5.0 and 7.0 wt%).

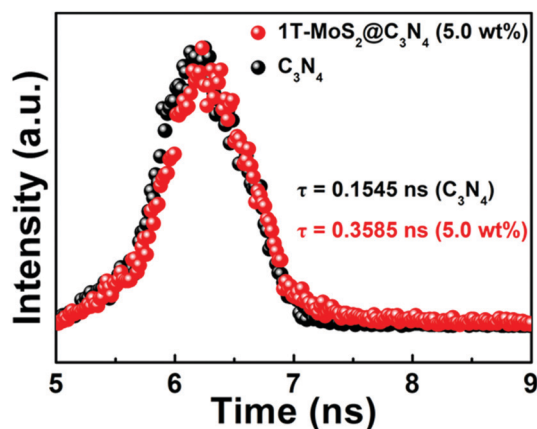


Fig. 8 Luminescence decay curves of pure C_3N_4 NRs and 1T- $MoS_2@C_3N_4$ NR composites (5.0 wt%).

To gain deep insights into the charge transfer behaviors in the 1T- $MoS_2@C_3N_4$ NR composites, the photocurrent responses were studied and electrochemical impedance spectroscopy (EIS) was carried out. Fig. 9a shows the periodic on/off photocurrent response of all samples when irradiated under solar light. It can be seen that all the samples show an immediate rise in the photocurrent response when the light is on. In contrast, the photocurrent rapidly decreases to zero when the light is turned off. The on-off cycles of photocurrent are reproducible, which indicates that the photogenerated electrons are transferred to the back contact across the samples to form the photocurrent under light irradiation.⁵⁷ The pure C_3N_4 NR electrode generates a relatively low photocurrent density of $0.019 \mu A cm^{-2}$. The photocurrent response curves (Fig. 9a) show an increased current density in all 1T- $MoS_2@C_3N_4$ NR samples as compared with pure C_3N_4 NRs, indicating a noticeable improvement of the electron-hole separation efficiency by the introduction of 1T MoS_2 QD co-catalysts.⁵⁶ The 1T- $MoS_2@C_3N_4$ NR composite (5.0 wt%) electrode shows the highest photocurrent density of $0.108 \mu A cm^{-2}$, which is about 5.7 times higher than that of a bare C_3N_4 NR electrode. On the one hand, 1T- $MoS_2@C_3N_4$ NR composites (5.0 wt%) have a wider absorption range and stronger photoabsorption ability, resulting in more photogenerated carriers. On the other hand, 1T- MoS_2 QDs can act as electron acceptors to capture photo-generated electrons before they recombine with holes, leading to more effective separation of electron-hole pairs. The EIS measurement is also an effective approach to study the charge transfer process. In general, a smaller arc radius on an EIS Nyquist plot means a

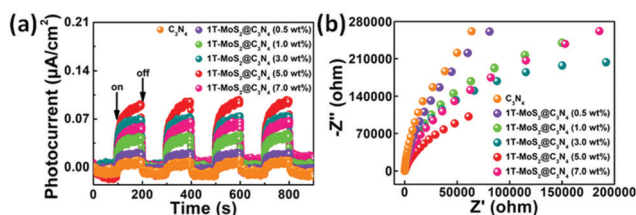


Fig. 9 (a) The transient photocurrent responses and (b) the electrochemical impedance spectra (EIS) of the samples under solar light irradiation.

smaller charge-transfer resistance on the electrode surface and a higher separation efficiency of electron-hole pairs.⁵⁸ As illustrated in Fig. 9b, the order of arc size for the samples under solar light irradiation is 1T- $MoS_2@C_3N_4$ NR composites (5.0 wt%) < 1T- $MoS_2@C_3N_4$ NR composites (3.0 wt%) < 1T- $MoS_2@C_3N_4$ NR composites (7.0 wt%) < 1T- $MoS_2@C_3N_4$ NR composites (1.0 wt%) < 1T- $MoS_2@C_3N_4$ NR composites (0.5 wt%) < pure C_3N_4 NRs, suggesting that the 1T- $MoS_2@C_3N_4$ NR composites (5.0 wt%) display the most effective separation of photogenerated charges. Apparently, this is in good agreement with luminescence decay and photocurrent results, validating that the 1T- $MoS_2@C_3N_4$ NR composites would obviously improve the charge transfer rate. Note that the higher interfacial charge transfer ability of the 1T- $MoS_2@C_3N_4$ NR composites implies that the recombination rate of electrons and holes has been reduced, thereby contributing to the enhanced photocatalytic efficiency and stability toward hydrogen production.

The photocatalytic activity for H_2 evolution was evaluated under simulated sunlight irradiation using a 300 W Xe arc lamp with an AM-1.5 filter. Fig. 10 presents a comparison of the photocatalytic H_2 production activities of C_3N_4 NRs (Pt as co-catalyst) and 1T- $MoS_2@C_3N_4$ NR composites containing different amounts of co-catalyst (0.5, 1.0, 3.0, 5.0 and 7.0 wt% 1T- MoS_2 QDs) in aqueous solution with TEOA. It can be seen that no H_2 is detected for C_3N_4 NRs in the absence of a co-catalyst (Fig. S8, ESI†), which can be ascribed to their limited light-harvesting efficiency and fast recombination of photoinduced charge carriers. Notably, after the assembly of 1T- MoS_2 QDs, a significantly improved photocatalytic performance was observed, with the highest photocatalytic H_2 evolution rate of $565 \mu mol h^{-1} g^{-1}$ occurring for the 5.0 wt% MoS_2 sample (Fig. 10). The 1T- $MoS_2@C_3N_4$ NR composites (0.5, 1.0 and 3.0 wt%), which are composed of a small amount of MoS_2 , display a lower photocatalytic performance compared with 1T- $MoS_2@C_3N_4$ NR composites (5.0 wt%), because of the relatively poor light absorption (Fig. 7). Furthermore, with increasing the content of MoS_2 from 5.0 wt% to 7.0 wt%, a decrease in the photocatalytic activity of the 1T- $MoS_2@C_3N_4$ NR composites is discovered, which is due to the light-screening effect of the excessive amount of co-catalysts.^{59,60}

Besides, the photocatalytic H_2 evolution rate of 1T- $MoS_2@C_3N_4$ NR composites (5.0 wt%) also exceeds that of Pt@ C_3N_4

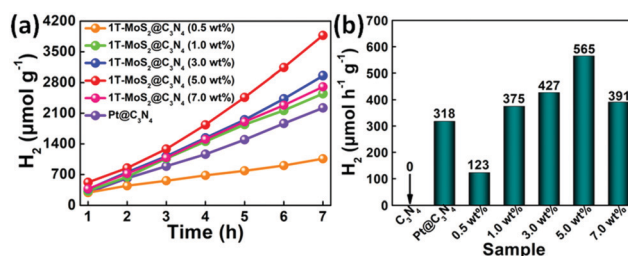


Fig. 10 (a) Cumulated evolution and (b) photocatalytic H_2 evolution rate of C_3N_4 NRs ($H_2PtCl_6 \cdot 6H_2O$ as co-catalyst) and 1T- $MoS_2@C_3N_4$ NR composites containing different amounts of co-catalyst (0.5, 1.0, 3.0, 5.0 and 7.0 wt% 1T- MoS_2 QDs) under simulated solar light.

NRs ($318 \mu\text{mol h}^{-1} \text{g}^{-1}$). Moreover, the photocatalytic H_2 production catalyzed by 1T-MoS₂@C₃N₄ NR composites (5.0 wt%) is measured under prolonged simulated solar light irradiation for 21 h (Fig. S9, ESI[†]), and no obvious decay of photocatalytic HER is discerned, suggesting good durability and practical application for 1T-MoS₂@C₃N₄ NR composites. High-resolution peak-fitting XPS spectra of Mo 3d of 1T-MoS₂@C₃N₄ NR composites (5.0 wt%) after cycling under simulated solar light irradiation are measured (Fig. S10, ESI[†]). As shown in Fig. S10 (ESI[†]), there is almost no change in the Mo⁶⁺ (MoO₃) XPS peaks of the 1T-MoS₂@C₃N₄ NR composites (5.0 wt%) before cycling and after cycling, which further confirms the excellent stability of the 1T-MoS₂@C₃N₄ NR composites. We further evaluated the apparent quantum efficiency (AQE) of the samples under a 300 W Xe arc lamp with an AM-1.5 optical filter. Table S2 (ESI[†]) shows the comparison of AQE values over C₃N₄ NRs, Pt@C₃N₄ NRs and 1T-MoS₂@C₃N₄ NR composites containing different amounts of 1T-MoS₂ QDs (0.5, 1.0, 3.0, 5.0 and 7.0 wt%): 0 (C₃N₄ NRs) < 0.47% (1T-MoS₂@C₃N₄-0.5 wt%) < 0.99% (Pt@C₃N₄ NRs) < 1.13% (1T-MoS₂@C₃N₄-1.0 wt%) < 1.21% (1T-MoS₂@C₃N₄-7.0 wt%) < 1.31% (1T-MoS₂@C₃N₄-3.0 wt%) < 1.73% (1T-MoS₂@C₃N₄-5.0 wt%). Therefore, the 1T-MoS₂@C₃N₄ NR composites can be used as an efficient and stable photocatalyst.

To further explore the photocatalytic mechanism of 1T-MoS₂@C₃N₄ NR composites, Mott-Schottky plots were recorded to evaluate the conduction band (CB) levels of C₃N₄ NRs. As shown in Fig. S11 (ESI[†]), by extrapolating the x intercept of the linear region, the flat band potentials (E_{FB}) of C₃N₄ NRs were obtained to be -0.71 V vs. Ag/AgCl from the Mott-Schottky plots, corresponding to -0.51 V vs. the normal hydrogen electrode (NHE). It is widely accepted that the conduction band potential (E_{CB}) of an n-type semiconductor is more negative by about 0.1 V than its E_{FB} value,⁶¹ therefore, the E_{CB} of C₃N₄ NRs could be approximated to be -0.61 V vs. NHE. Combined with the E_{g} of C₃N₄ NRs (1.38 eV) obtained from the UV-vis DRS spectra (Fig. S6b, ESI[†]), the estimated valence band potential (E_{VB}) of C₃N₄ NRs is 0.77 eV vs. NHE.

Based on the above results, a possible photocatalytic HER process of 1T-MoS₂@C₃N₄ NR composites under simulated solar light irradiation is proposed and schematically displayed in Scheme 4. Typically, under simulated solar light irradiation, electron-hole pairs are generated in C₃N₄ NRs, and then the photo-excited electrons rapidly transfer to the 1T-MoS₂ QD

co-catalyst quickly, because the 1T-MoS₂ QDs are good electron acceptors due to their metallic characteristics. As photoelectron acceptors, 1T-MoS₂ QDs act as active sites for H_2 evolution. In addition, in the 1T-MoS₂@C₃N₄ NR composites, small-sized 1T-MoS₂ QDs well attached on the C₃N₄ NRs enable electron transfer from C₃N₄ NRs to 1T-MoS₂ QDs in a short distance and simultaneously provide more reaction sites on both basal planes and edges for the evolution of H_2 . The holes would react with the sacrificial agent (TEOA) (Scheme 4). This effective electron transport between C₃N₄ NRs and 1T-MoS₂ QDs tremendously decreases the recombination of electron-hole pairs and prolong the charge lifetime.

4. Conclusions

1T-MoS₂ QDs were successfully synthesized and subsequently assembled with C₃N₄ NRs as effective co-catalysts for photocatalytic H_2 evolution over noble metal Pt. Specifically, an optimized 1T-MoS₂@C₃N₄ NR composite (5.0 wt%) attains a remarkable increased solar light photocatalytic H_2 evolution rate of $565 \mu\text{mol h}^{-1} \text{g}^{-1}$ which is apparently higher than that of Pt@C₃N₄ NRs ($318 \mu\text{mol h}^{-1} \text{g}^{-1}$). The highly efficient photocatalytic performance of the 1T-MoS₂@C₃N₄ NR composite is primarily attributed to the following facts: (1) 1T-MoS₂ QDs in cooperation with C₃N₄ NRs can enhance the light absorption intensity and broaden the light absorption range to NIR light; (2) the tiny particle size of 1T-MoS₂ QD co-catalysts can provide more active sites, which is helpful for the photocatalytic reaction; (3) the close contact layer between metallic 1T-MoS₂ QDs and C₃N₄ NRs is more favorable to transfer photo-generated electrons from the CB of C₃N₄ to the surface of conductive 1T-MoS₂, and then the electrons would rapidly participate in photocatalytic HER.

Conflicts of interest

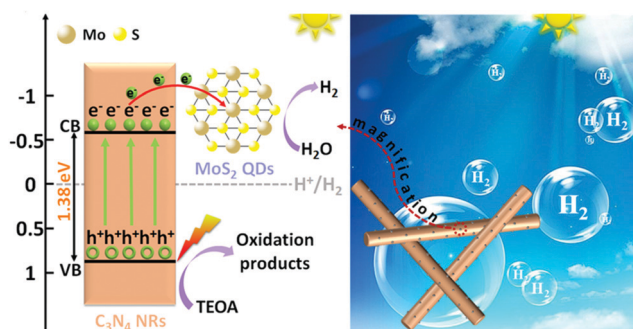
There are no conflicts to declare.

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Scheme 4 Schematic illustration of the photocatalytic mechanism of 1T-MoS₂@C₃N₄ NR composites under simulated solar light irradiation.

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