

RESEARCH ARTICLE

Air-condition process for scalable fabrication of CdS/ZnS 1D/2D heterojunctions toward efficient and stable photocatalytic hydrogen production

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Abstract

We report the scalable fabrication of CdS/ZnS 1D/2D heterojunctions under ambient air conditions (i.e., room temperature and atmospheric pressure) in which ZnS nanoparticles are anchored on the surface of CdS nanosheets. The as-formed heterojunctions exhibit a significantly enhanced photocatalytic H₂ evolution rate of 14.02 mmol h⁻¹ g⁻¹ when irradiated with visible light, which is ~10 and 85 times higher than those of pristine CdS nanosheets and CdS nanoparticles, respectively, and superior to most of the CdS-based photocatalysts reported to date. Furthermore, they provide robust photocatalytic performance with demonstrable stability over 58 h, indicating their potential for practical applications. The formation of 1D/2D heterojunctions not only provides improved exposed active sites that respond to illumination but also provides a rapid pathway to generate photogenerated carriers for efficient separation and transfer through the matrix of single-crystalline CdS nanosheets. In addition, first-principles simulations demonstrate that the existence of rich Zn vacancies increases the energy level of the ZnS valence band maximum to construct type-II and Z-scheme mixed heterojunctions, which plays a critical role in suppressing the recombination of carriers with limited photocorrosion of CdS to enhance photocatalytic behavior.

KEYWORDS

air condition, CdS, heterojunctions, photocatalytic hydrogen production, ZnS

1 | INTRODUCTION

Photocatalytic hydrogen evolution from water splitting is emerging as an attractive approach for exploring clean energy,^{1–10} where one of the crucial challenges is to develop efficient and stable photocatalysts.^{11–15} To date, there are

popular strategies to enhance the performance of photocatalysts: (i) creating blocks in a low-dimensional and single-crystalline configuration to facilitate the transport of photogenerated carriers^{16–21}; (ii) increasing the surface area to improve light harvesting and the number of active sites^{22–24}; (iii) constructing homo/heterojunctions for

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energy band engineering to strengthen light absorption and charge separation efficiency.^{25–31} Although the well-known type-I/II heterojunctions are effective in improving photocatalytic activity, the redox ability of transferred electrons and holes is often weakened due to the release of partial potential energy, which is unfavorable for hydrogen production.^{32,33} In comparison, the formation of a Z-scheme heterojunction not only promotes the separation of photo-induced carriers but maintains the redox capability to enhance photocatalytic hydrogen generation,^{34–37} which has, therefore, been recognized as an effective technique for exploring advanced photocatalysts.

Among the family of semiconductor photocatalysts, cadmium sulfide (CdS) is an intriguing *n*-type semiconductor for photocatalytic H₂ production due to its relatively narrow band gap ($E_g \sim 2.4$ eV), which can be highly active for harvesting visible light.^{38–41} As a result, a number of strategies have been explored for growing CdS and CdS-based nanostructures, including hydrothermal,^{42–44} solvothermal,^{45–47} template,⁴⁸ and chemical deposition⁴⁹ methods, along with other techniques.^{50–52} Of particular note is that the majority of the reported works to date have often used high processing temperatures and pressures, organic/toxic reagents, and involved a time-consuming process.

Here, we report the kilogram-scale production of CdS nanosheets (CdS NSs)/ZnS nanoparticles (ZnS NPs) as 1D/2D heterojunctions (CdS-NSs/ZnS-NPs) under ambient air condition (room temperature [RT] and atmospheric pressure) based on a sonochemical strategy. The as-fabricated photocatalysts with rationally designed structures exhibit a significantly enhanced photocatalytic H₂ evolution rate of 14.02 mmol h^{−1} g^{−1} when irradiated with visible light ($\lambda > 400$ nm), which is ~ 10 and ~ 85 times higher than those of pristine CdS NSs and CdS nanoparticles (CdS NPs), respectively. Furthermore, they exhibit highly stable photocatalytic behavior for over 58 h with an internal quantum yield of 2.76% when irradiated with 400 nm light, thereby demonstrating their potential as highly efficient and stable photocatalysts for practical applications. The mechanism for the enhanced photocatalytic activities of as-formed CdS-NSs/ZnS-NPs type-II and Z-scheme mixed 1D/2D heterojunctions is also proposed based on first-principles simulations.

2 | EXPERIMENTAL SECTION

2.1 | Materials

The source materials of zinc acetate dihydrate (Zn (Ac)₂·2H₂O), sodium sulfide (Na₂S·9H₂O), cadmium chloride hydrate (CdCl₂·2.5H₂O), thiourea (CH₄N₂S), and sodium sulfite (Na₂SO₃) were obtained from Sigma-Aldrich.

Ethylenediamine (EDA) was obtained from Sinopharm Chemical Reagent Co., Ltd. Deionized water (DI H₂O) was used for all experiments. All reagents were used in as-received conditions without further purification.

2.2 | Sonochemical synthesis of ZnS NPs

For the fabrication of ZnS NPs based on the sonochemical method under ambient air conditions (i.e., RT and atmospheric pressure), in a typical process, 1 mmol Zn (Ac)₂·2H₂O with 1 mmol Na₂S·9H₂O was dissolved in 15 mL DI H₂O to form a white slurry solution while magnetic stirring at RT. The obtained solution was subjected to ultrasonic treatment at a frequency of 40 kHz for 30 min, followed by naturally cooling to RT. Subsequently, the ZnS NPs product was obtained by centrifugation and washed three times with DI H₂O and ethanol, followed by freeze-drying overnight.

2.3 | Sonochemical synthesis of CdS NPs

For fabrication of CdS NPs based on the sonochemical method under ambient air conditions, in a typical process, 1 mmol CdCl₂·2.5H₂O and 1 mmol Na₂S·9H₂O were dissolved in 15 mL DI H₂O to form an orange solution while magnetic stirring condition at RT. The obtained solution was then subject to ultrasonic treatment at a frequency of 40 kHz for 120 min, followed by naturally cooling to RT. Finally, the orange precipitates of CdS NPs were obtained by centrifugation and washing three times with DI H₂O and ethanol, followed by freeze-drying overnight.

2.4 | Sonochemical synthesis of CdS NSs

For the fabrication of CdS NSs based on the sonochemical method under ambient air conditions, in a typical procedure, 5 mmol of CdCl₂·2.5H₂O and 15 mmol of CH₄N₂S were dissolved in 10 mL of ethylenediamine and 5 mL DI H₂O, which were subjected to ultrasonic treatment at a frequency of 40 kHz for 120 min, followed by naturally cooling to RT. Finally, the yellow precipitate of CdS NSs was obtained by centrifugation and washing three times with DI H₂O and ethanol, followed by freeze-drying overnight.

2.5 | Sonochemical synthesis of CdS-NSs/ZnS-NPs heterojunctions

As for the fabrication of CdS-NSs/ZnS-NPs heterojunctions based on the sonochemical method under air

conditions, in a typical process, 1.0 mmol as-prepared CdS NSs, different amounts of $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ (0.2, 0.4, 0.6, 0.8, and 1.0 mmol) and $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ (the molar ratio of $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ to Na_2S was kept at 1, and the corresponding samples were labeled as CdS-NSs/ZnS-NPs-0.2, CdS-NSs/ZnS-NPs-0.4, CdS-NSs/ZnS-NPs-0.6, CdS-NSs/ZnS-NPs-0.8, and CdS-NSs/ZnS-NPs-1.0, respectively) were dispersed into 15 mL DI H_2O under magnetic stirring, which was subjected to ultrasonic treatment at a frequency of 40 kHz for 30 min, followed by naturally cooling to RT. Finally, the product CdS-NSs/ZnS-NPs heterojunctions were collected by centrifugation and washed three times with DI H_2O and ethanol, followed by freeze-drying overnight.

2.6 | Kilogram-scale synthesis of CdS-NSs/ZnS-NPs heterojunctions

To demonstrate the capacity of kilogram-scale fabrication of CdS-NSs/ZnS-NPs heterojunctions, first, the source materials were extended up to 200 mmol (45.76 g) of $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ and 200 mmol (45.76 g) of $\text{CH}_4\text{N}_2\text{S}$, which were dissolved in 400 mL of ethylenediamine and 200 mL DI H_2O . They were then mixed together and subjected to ultrasonic treatment at a frequency of 40 kHz for 120 min, followed by naturally cooling to RT. Finally, a yellow precipitate was obtained by centrifugation and washing three times with DI H_2O and ethanol, followed by freeze-drying overnight for the large-scale fabrication of CdS NSs. Second, the as-prepared CdS NSs with $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ and $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ (the molar ratio of CdS NSs: $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$: Na_2S = 0.6:1:1) were dispersed into 500 mL DI H_2O while magnetic stirring and subjected to ultrasonic treatment at a frequency of 40 kHz for 30 min, followed by naturally cooling to RT. Finally, the CdS-NSs/ZnS-NPs heterojunctions were collected by centrifugation and washing three times with DI H_2O and ethanol, followed by freeze-drying overnight. Similar experiments were repeated five times, leading to the fabrication of 102.45 g of CdS-NSs/ZnS-NPs heterojunctions.

2.7 | Characterizations

Powder X-ray diffraction (PXRD; D8 Advance; Bruker) was utilized to evaluate the phase compositions under $\text{Cu K}\alpha$ X-ray radiation ($\lambda = 1.5406 \text{ \AA}$). The microstructure and morphology of as-prepared samples were observed under a field emission scanning electron microscope (FESEM; S-4800; Hitachi) and high-resolution transmission electron microscopy (HRTEM; JEM-2100F; JEOL) equipped with

energy dispersive X-ray spectroscopy (EDX; Quantax-STEM; Bruker). The compositions and valence band of the product were analyzed by X-ray photoelectron spectroscopy (XPS; Scientific K-Alpha; Thermo Fisher Scientific) with a reference of C 1s peak at 284.6 eV. The UV-Vis absorption spectrum was recorded on a UV-Vis scanning spectrophotometer (U-3900; Hitachi). Electron paramagnetic resonance (EPR) was conducted on a spectrometer (Bruker A300) at RT, while the radicals were captured by 5,5-dimethyl-1-pyrroline N-oxide (DMPO) under Xe lamp irradiation. The photoluminescence (PL) and time-resolved photoluminescence (TRPL) spectra were tested on a spectrometer (FLS-1000; Edinburgh) excited at 380 nm. The porous properties of as-prepared samples were characterized using N_2 adsorption at 77 K on a specific surface area and porosity analyzer (Micromeritics; ASAP 2020 M).

2.8 | Photocatalytic hydrogen evolution

The analyses on the photocatalytic H_2 evolution of the as-fabricated samples were performed on a top-irradiation quartz cell connected to a photocatalytic H_2 evolution system (CEL-SPH2N). In a typical experiment, 10 mg of the as-prepared sample was suspended in 100 mL of distilled water containing 0.25 M sodium sulfite (Na_2SO_3) and 0.35 M sodium sulfide (Na_2S) as sacrificial agents. Before the irradiation, the reactant system was degassed by evacuation to remove the air, which ensured that the reaction system was under anaerobic conditions. After that, the system was irradiated by a 300-W Xe lamp with a cutoff filter of 400 nm for H_2 evolution under magnetic stirring conditions. A thermal conductivity detector gas phase chromatograph (GC-7920) was employed to determine the amount of H_2 evolution with the carrier gas of nitrogen (N_2). Over the photocatalytic reaction, the temperature was maintained at 6°C by a flow of cooling water.

2.9 | Photoelectrochemical (PEC) measurement

PEC measurements were performed on an electrochemical analyzer (Chenhua CHI 660D) in a standard three-electrode cell with photocatalyst-coated fluorine-doped tin oxide (FTO) as the working electrode (active area: $\sim 1 \text{ cm}^2$), Ag/AgCl as the reference electrode, and a Pt plate as the counter electrode. A 300 W Xe lamp with a cut-off filter ($\lambda > 400 \text{ nm}$) was used as the light source, and the Na_2SO_4 (0.5 M, pH = 6.8) aqueous solution was used as a supporting electrolyte. The working electrodes

were prepared by dropping a suspension (20 μL) made of samples ZnS NPs, CdS NSs, and CdS NSs/ZnS-NPs-0.6 with a given concentration of 5 mg mL^{-1} onto the surface of a precleaned FTO plate, followed by drying in air at RT. The Mott-Schottky (MS) curves were measured in the dark at a frequency of 0.5, 1.0, and 2.0 kHz, respectively. Transient photocurrent measurements (achieved by light on and off alternating every 5 s) were recorded under visible light irradiation, with an optical cutoff filter of 400 nm installed on a 300 W Xe lamp for visible light excitation. Electrochemical impedance spectra (EIS) were collected at an off-line potential with frequencies ranging from 100 kHz to 0.1 Hz and modulation amplitude of 5.0 mV. The measured potentials (V vs. Ag/AgCl) were converted to the normal hydrogen electrode (NHE) scale according to the Nernst equation: $E(\text{NHE}) = E(\text{Ag/AgCl}) + 0.197$. In addition, the apparent quantum yield (AQY) was measured under the same photocatalytic reaction conditions with different single wavelengths of 400, 420, 450, and 520 nm band-pass filters. The AQY was calculated using the following equation:

$$\text{AQY}(\%) = \frac{\text{Number of evolved hydrogen atoms } (N_{\text{H}})}{\text{Number of incident photons } (N_{\text{P}})} \times 100,$$

$$N_{\text{P}} \frac{A \times I}{E} \times t = \frac{A \times I}{(hc/\lambda)} \times t,$$

$$N_{\text{H}} = 2 \times n_{\text{H}_2} \times N_{\text{A}},$$

where n_{H_2} is the moles of evolved hydrogen molecular, N_{A} is the Avogadro constant ($6.02 \times 10^{23} \text{ mol}^{-1}$), I is the light intensity at 400, 420, 450 and 520 nm, A is the illuminated area, E is the photon energy, h is the Planck constant ($6.63 \times 10^{-34} \text{ J s}$), and c is the light rate ($3 \times 10^8 \text{ m/s}$).

2.10 | Density functional theory (DFT) calculations

To investigate the band structures of ZnS and CdS in the heterojunctions, we performed ab initio calculations employing DFT, as implemented in Vienna Ab-initio Simulation Package,⁵⁴ which was based on the projector-augmented wave potentials.⁵⁵ The energy cutoff of 400 eV was used for plane-wave expansion of electron wave functions based on the convergence test. The generalized gradient approximation with the Perdew Burke Ernzerhof functional was chosen to examine the exchange-correlation potential.⁵³ The following valence electron configurations are used: $4s^2 3d^{10}$ of Zn, $5s^2 4d^{10}$ of Cd, $3s^2 3p^4$ of S. For ZnS/CdS heterojunctions, they were composed of a ZnS (111) surface and a CdS (002) surface with a lattice mismatch smaller than 5%. To prevent unphysical

charge transfer between the top and bottom slab surfaces, pseudohydrogens with fractional charges were used to saturate the dangling bonds of Cd atoms at the bottom and S atoms on the top of the heterojunctions. A 15-Å-thick vacuum layer was used for all the surfaces to isolate the slabs. A $4 \times 4 \times 1$ Γ -centered k -points mesh was used for the sampling of Brillouin zone integration in the calculation of ZnS/CdS heterojunctions. We also built a neutral Zn vacancy (V_{Zn}) in the interface of ZnS/CdS heterojunctions to investigate the influence of V_{Zn} on the band structures. All ZnS/CdS heterojunctions were fully relaxed in structure optimization with an energy convergence tolerance of $1.0 \times 10^{-4} \text{ eV/atom}$ and a maximum force less than $0.05 \text{ eV/\AA}$.

The surface energy was determined by the slab calculations:

$$\sigma = (E_{\text{slab}} - nE_{\text{bulk}})/2A,$$

where E_{slab} , E_{bulk} , n , and A were referred to the total energies of unrelaxed slab model and bulk phase, the number of bulk phases in the slab model, and the surface area of the slab model, respectively.

3 | RESULTS AND DISCUSSION

With regard to the growth of CdS nanosheets (CdS NSs), $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ precursors with different sulfur sources are introduced into the solvent and then subjected to ultrasonic treatment at air conditions, namely, at RT and atmospheric pressure (see the details in Section 2). Notably, when using $\text{H}_2\text{O} + \text{Na}_2\text{S}$ as the sulfur source, only CdS nanoparticles (CdS NPs) could be grown (Figure S1). Interestingly, when using $\text{EDA} + \text{H}_2\text{O} + \text{CH}_4\text{N}_2\text{S}$ as the sulfur source, the growth of CdS NSs is accomplished, implying that the growth of CdS nanostructures is tunable in terms of morphology, which is primarily attributed to the difference in polarity between H_2O and EDA. To demonstrate the detailed growth of CdS NSs with a volume ratio of $\text{H}_2\text{O} : \text{EDA} = 2:1$ as the source materials, the time-dependent evolution of Cd NSs at fixed sonication times from 0.5 to 2 h with an interval of 0.5 h is recorded, as shown in Figure 1A–D. It is seen that, for a sonication time of 0.5 h, numerous fine-scale CdS NPs are formed, as shown in Figure 1A. However, when the reaction time is extended to 1 h, thin CdS NSs are formed (Figure 1B). On further increasing the reaction time to 1.5 h, the CdS NSs grow continuously, as outlined in Figure 1C. Finally, for a reaction time of 2 h, a flower-like configuration is produced (see Figure 1D and Figure S2). In summary, as schematically shown in Figure 1E, the

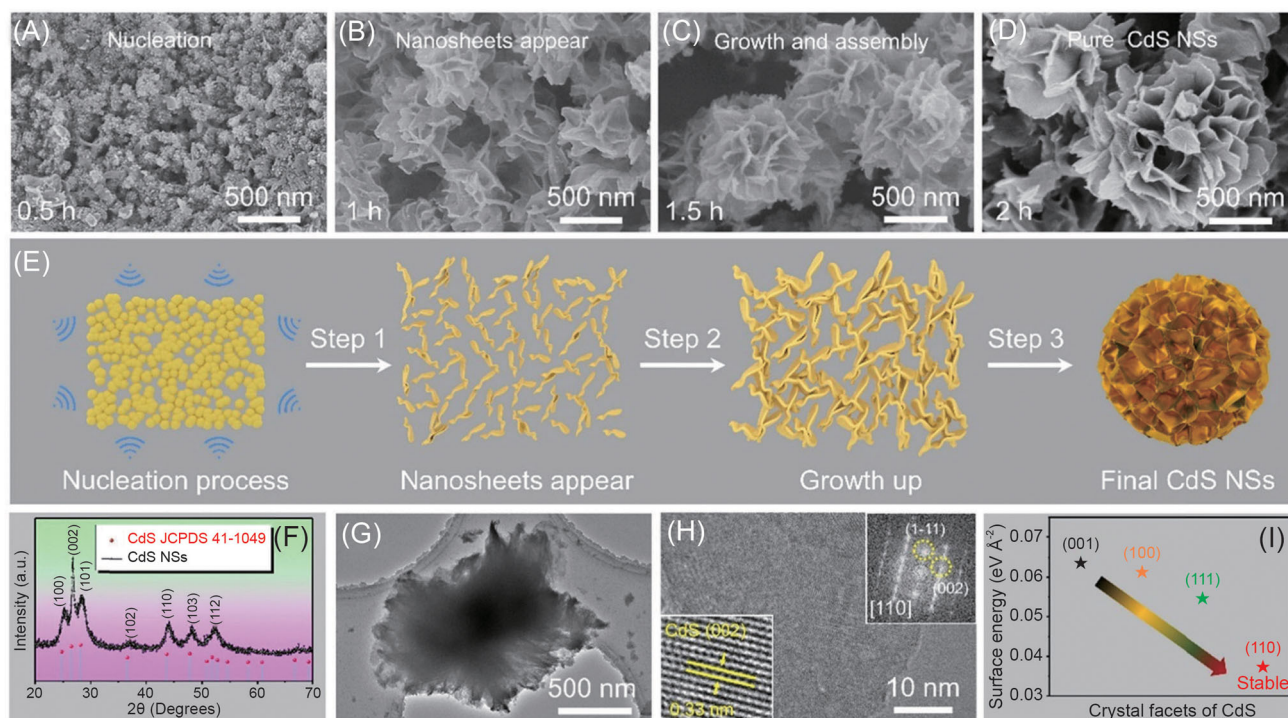


FIGURE 1 Growth details of CdS NSs. (A–D) Typical SEM images of products with fixed ultrasonic treatment times of 0.5, 1, 1.5, and 2 h, respectively. (E) Schematic of the growth process of CdS NSs. (F) XRD pattern of pure CdS NSs. (G,H) TEM and HRTEM images of CdS NSs, respectively. Inset in (H) is the corresponding FFT pattern. (I) DFT calculations of the surface energies of CdS. DFT, density functional theory; FFT, fast Fourier transition; HRTEM, high-resolution transmission electron microscopy; NS, nanosheet; SEM, scanning electron microscopy; TEM, transmission electron microscopy; XRD, X-ray diffraction.

growth of CdS NSs involves three primary stages, namely (i) the nucleation of CdS NSs (Step 1 in Figure 1E), (ii) the continued growth of CdS NSs (Step 2 in Figure 1E), and (iii) final assembly into a flower-like configuration (Step 3 in Figure 1E). Figure 1F provides a typical XRD pattern, showing their pure hexagonal crystal structure (JCPDS Card No. 41-1409). Figure 1G and Figure S3 present typical transmission electron microscopy (TEM) images of as-synthesized CdS NSs, further demonstrating their typical flower-like shape morphology. HRTEM analysis in Figure 1H and fast Fourier transition (FFT) analysis (the inset of Figure 1H) of individual nanosheets indicate their single-crystalline nature with an exposed close-packed plane of (110).⁵⁶ According to our DFT calculation in Figure 1I, it is confirmed that the surface energy of the (110) plane is the most thermodynamically stable plane, which, therefore, leads to the formation of nanosheets rather than nanoparticles.⁵⁷

Figure 2A is a schematic of a typical process for fabricating CdS-nanosheets/ZnS-nanoparticles (CdS-NSs/ZnS-NPs) heterojunctions based on the sonochemical method under air conditions (i.e., RT and atmospheric pressure), of which the exact details are outlined in Section 2. The approach involves two main steps, namely, the initial growth of CdS NSs and subsequent growth of

ZnS NPs on the surface of CdS NSs, both of which are performed by a sonochemical process under ambient conditions. For performance comparison, pure ZnS NPs are also fabricated, and the details are described in Section 2 and Figure S4. As a representative sample, the CdS-NSs/ZnS-NPs-0.6 heterojunctions refer to the product formed using source materials of 1.0 mmol as-grown CdS NSs, 0.6 mmol $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ and 0.6 mmol $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, and the details are provided in Section 2. In contrast to the pure CdS NSs in Figure 1D, the nanosheet surfaces become rough, indicating the deposition of ZnS NPs onto the CdS NPs, as seen in Figure 2B,C and Figure S5. SEM images of the products incorporating a variety of ZnS NPs amounts of 0.2, 0.4, 0.8, and 1.0 mmol (referred to as samples CdS-NSs/ZnS-NPs-0.2, CdS-NSs/ZnS-NPs-0.4, CdS-NSs/ZnS-NPs-0.8 and CdS-NSs/ZnS-NPs-1.0, respectively) are presented in Figure S6. Figure 2D provides the XRD pattern of sample CdS-NSs/ZnS-NPs-0.6 heterojunctions, and the samples with other mole ratios of ZnS NPs are presented in Figure S7. It can be seen that strong diffractions from hexagonal CdS NSs appear in all samples (JCPDS Card No. 41-1049), with detectable diffractions from cubic ZnS, as indicated by the blue dotted lines in Figure 2D and Figure S8 (JCPDS Card No. 05-0566).^{58,59} The XRD pattern of pure CdS NSs in Figure 1F also

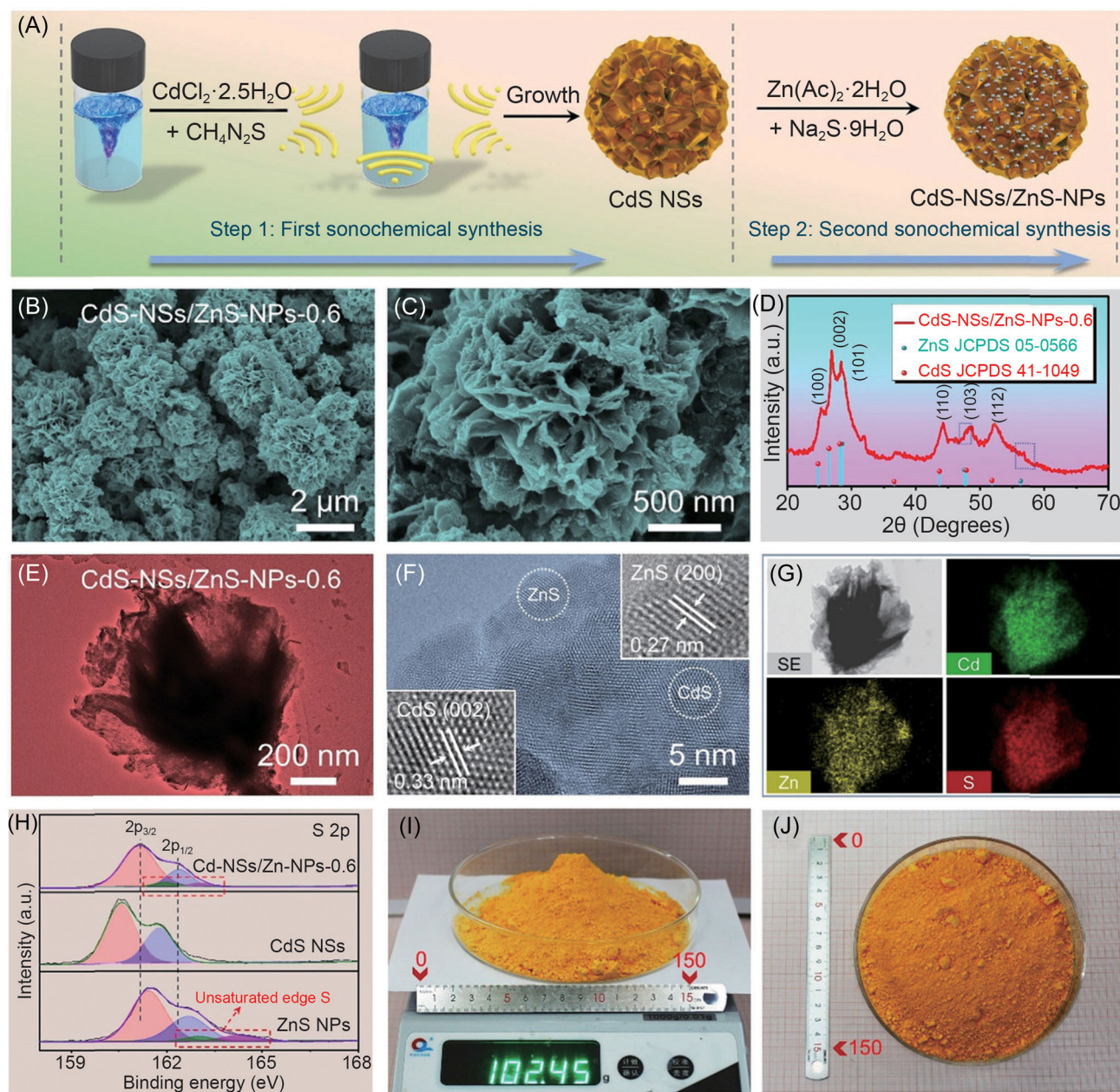


FIGURE 2 Fabrication and microstructural characterization of CdS-NSs/ZnS-NPs heterojunctions. (A) Schematic of the fabrication of CdS-NSs/ZnS-NPs heterojunctions. (B–G) Typical SEM images, XRD pattern, TEM, HRTEM, and element mappings images of sample CdS-NSs/ZnS-NPs-0.6. (H) High-resolution XPS spectra of S 2p of ZnS NPs, CdS NSs, and CdS-NSs/ZnS-NPs-0.6. (I, J) Digital photographs showing kilogram-scale production of CdS-NSs/ZnS-NPs heterojunctions. HRTEM, high-resolution transmission electron microscopy; NS, nanosheet; NPs, nanoparticles; SEM, scanning electron microscopy; TEM, transmission electron microscopy; XPS, X-ray photoelectron spectroscopy; XRD, X-ray diffraction.

indicates that the introduced ZnS has not affected the crystallinity of CdS, suggesting that the ZnS NPs are simply anchored onto the surface of CdS NSs. Figure 2E–F show the typical TEM and HRTEM images of CdS-NSs/ZnS-NPs-0.6 heterojunctions, where the observed 0.27 nm lattice fringes are attributable to the (200) plane of cubic ZnS, while those with 0.33 nm fringes are indexed to the (002) plane of hexagonal CdS, in agreement with the XRD

characterization (Figure 1F and Figure S8). The corresponding EDX analyses are shown in Figure 2G and Figure S9, clarifying that it is mainly composed of Zn, Cd, and S. Moreover, the EDX characterization data demonstrate that the ZnS NPs have a uniform spatial distribution on the surface of CdS NSs, leading to the formation of 1D/2D heterojunctions. Furthermore, XPS analyses indicate the presence of unsaturated edge S atoms on the

surfaces of the CdS-NSs/ZnS-NPs-0.6 sample and ZnS NPs, as shown by the red dotted lines in Figure 2H.^{58,60} In comparison to the ZnS NPs, the high-resolution XPS spectrum of S 2p of pure ZnS has only two peaks at 161.75 and 162.93 eV (Figure S10A), which can be assigned to S 2p_{3/2} and S 2p_{1/2}, respectively. The binding energies for Zn 2p_{3/2} and Zn 2p_{1/2} of pure ZnS observed at 1021.91 and 1045.01 eV (Figure S10B) have a shift of ~0.7 eV toward higher binding energy. The binding energies for Zn 2p and S 2p of ZnS NPs exhibit a shift to lower energy, as compared to pure ZnS, which can be attributed to the presence of rich defect states within the ZnS NPs. In such circumstances, a single negatively charged Zn vacancy is located near S²⁻, leading to an increase in the electron density around the Zn vacancy and a decrease in the binding energy of S²⁻. The XPS (Table S1) and inductively coupled plasma mass spectrometry (Table S2) analyses indicate that the ratio of Zn and S elements in the ZnS NPs is considerably lower than that in pure ZnS, also highlighting the presence of Zn defects in ZnS NPs. To obtain more information about the Zn vacancy defects, EPR measurement is also performed, and a very strong ESR signal at $g = 2.007$ was observed (Figure S11), which can be attributed to the presence of abundant Zn vacancies. In addition, the observed shifts of S 2p and Cd 3d within sample CdS-NSs/ZnS-NPs-0.6 suggest the presence of strong interactions among the CdS and ZnS (Figure 2H and Figure S12). Furthermore, as shown in Figure S13, the BET surface area of the CdS-NSs/ZnS-NPs-0.6 sample is fundamentally improved, in comparison to those of ZnS NPs samples, which is also beneficial to increasing the photocatalytic hydrogen reactive sites. To show the potential for mass production of CdS-NSs/ZnS-NPs-0.6 heterojunctions under ambient air conditions, the source materials of CdCl₂·2.5H₂O and CH₄N₂S are extended in size up to 45.67 g (see the details in Section 2). Consequently, after a two-step sonication treatment, 102.45 g of CdS-NSs/ZnS-NPs-0.6 photocatalysts could be obtained, as shown in Figure 2I,J. It should be noted that their phase composition (Figure S14A) and morphology (Figure S14B) are well maintained, similar to those in Figures 2C and 2D, underscoring that the present strategy is simple, efficient, and appropriate for mass production of CdS-NSs/ZnS-NPs heterojunctions under air conditions. It is worth noting that the whole process for fabricating CdS/ZnS heterojunctions is performed under ambient air conditions, which excludes the assistance of externally applied high temperatures and high pressures, as required in most other work concerning the synthesis of CdS-based nanostructures reported to date.^{42–47}

The photocatalytic hydrogen production activity of the as-synthesized products is characterized under visible light irradiation ($\lambda > 400$ nm), as shown in Figure 3A. The results indicate that the pure CdS NSs deliver an H₂ evolution rate of 1.39 mmol h⁻¹ g⁻¹, which is approximately eight times higher than that of CdS NPs (0.16 mmol h⁻¹ g⁻¹). The H₂ production efficiency of pure ZnS NPs under visible light is even lower at 0.12 mmol h⁻¹ g⁻¹. With respect to the CdS-NSs/ZnS-NPs heterojunctions, the H₂ evolution rates are ca. 3.79, 11.99, 14.02, 13.01, and 8.24 mmol h⁻¹ g⁻¹ for samples CdS-NSs/ZnS-NPs-0.2, CdS-NSs/ZnS-NPs-0.4, CdS-NSs/ZnS-NPs-0.6, CdS-NSs/ZnS-NPs-0.8, and CdS-NSs/ZnS-NPs-1.0, respectively, indicating that the highest rate of H₂ production is achieved once the introduced ZnS NPs are fixed at a molar ratio of 0.6. The optimized one of 14.02 mmol h⁻¹ g⁻¹ is ~10 and 85 times higher than those of pure CdS NSs (1.39 mmol h⁻¹ g⁻¹) and CdS NPs (0.16 mmol h⁻¹ g⁻¹), respectively, superior to most of the CdS-based photocatalysts and other systems ever reported, as summarized in Figure 3B and Tables S3 and S4.^{44,61–75} Moreover, as shown in Figure 3C, sample CdS-NSs/ZnS-NPs-0.6 exhibits a stable photocatalytic activity over four cycles for 12 h, suggesting excellent stability against H₂ production. Moreover, after a 12 h reaction time, its morphology (Figure S15A–C) and phase composition (Figure S15D) are almost the same as those before H₂ production, further reflecting its robust stability to be employed as a stable photocatalyst. More importantly, the long-term stability of sample CdS-NSs/ZnS-NPs-0.6 for H₂ production demonstrates that the H₂ production rate is highly stable with 313.92 mmol g⁻¹ H₂ produced over 58 h of irradiation, as shown in Figure 3D. To evaluate the light harvest efficiency, the wavelength-dependent AQY of photocatalytic H₂ evolution for CdS-NSs/ZnS-NPs-0.6 heterojunctions is calculated as ~2.76% at 400 nm (Figure 3E). The excellent photocatalytic performance can be assumed to be a consequence of the rationally designed CdS-NSs/ZnS-NPs 1D/2D heterojunctions in which not only both the CdS NSs and ZnS NPs have sufficient exposed active sites to respond to the illumination but also the matrix of single-crystalline CdS NSs can provide an ideal pathway for the separation and transfer of photogenerated carriers.

UV-Vis diffuse reflectance absorbance spectrum is performed to investigate the optical properties of the photocatalysts, as shown in Figure 4A. The corresponding Tauc plots are used to estimate their band gaps, as disclosed in Figure 4B. Both CdS NSs and CdS-NSs/ZnS-NPs-0.6 heterojunctions exhibit strong absorption over the region from UV to visible light, due to the relatively narrow band gaps of CdS ($E_g \sim 2.41$ eV) and CdS-NSs/ZnS-NPs-0.6

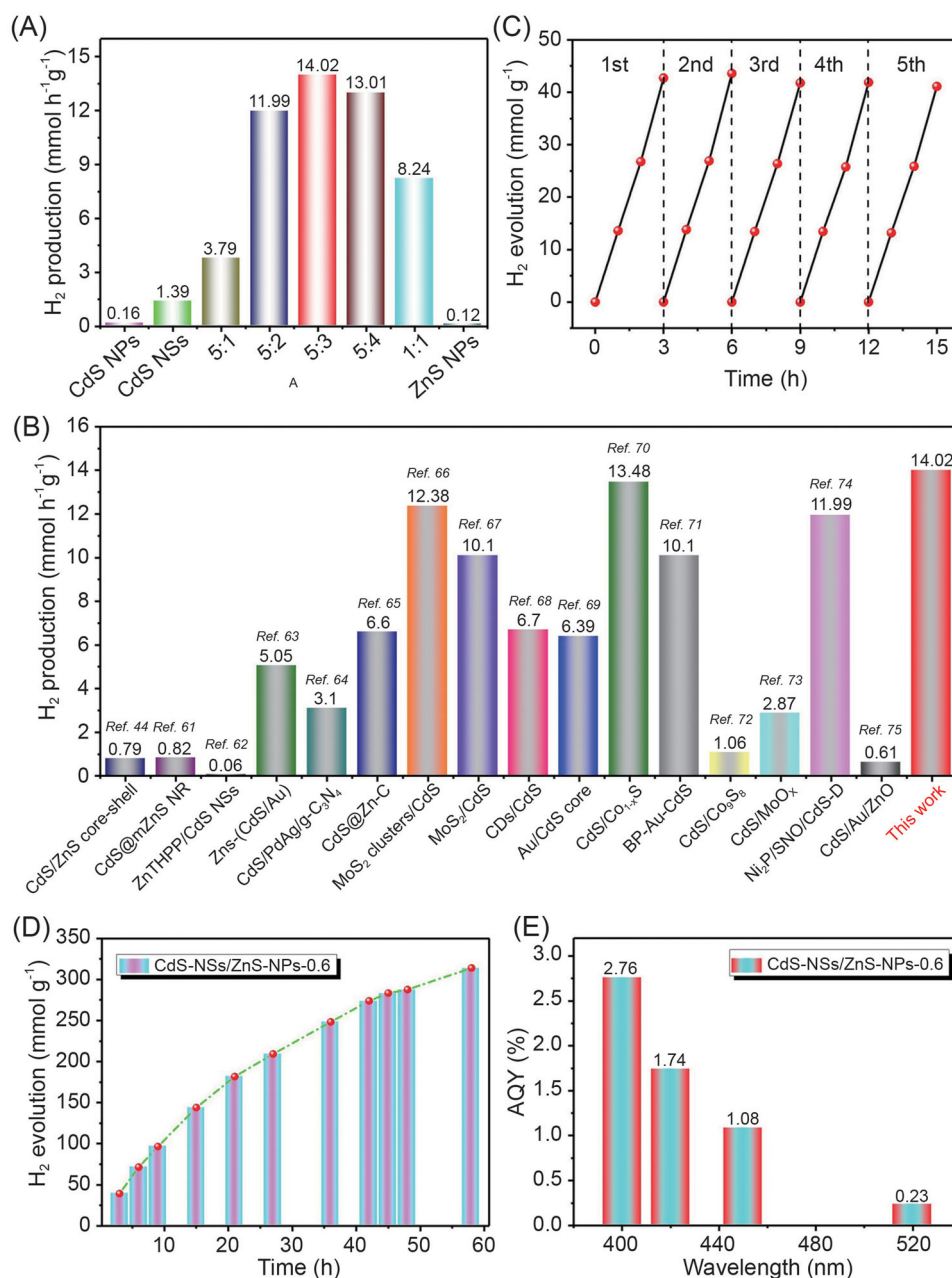


FIGURE 3 Visible-light-driven photocatalytic H_2 evolution performance. (A) Average photocatalytic H_2 evolution rates for different samples. (B) Typical H_2 evolution rates of CdS-based photocatalysts reported to date.^{44,61–75} (C) Photocatalytic stability of CdS-NSs/ZnS-NPs-0.6. (D) Long-term photocatalytic stability of sample CdS-NSs/ZnS-NPs-0.6 for 58 h. (E) Wavelength-dependent AQY of CdS-NSs/ZnS-NPs-0.6. AQY, apparent quantum yield; NP, nanoparticle; NS, nanosheet.

($E_g \sim 2.44$ eV).⁷⁶ In comparison, the ZnS NPs only exhibit relatively strong absorption over the UV region, as a result of their intrinsically wide band gap ($E_g \sim 2.99$ eV). Meanwhile, as shown in Figure 4C, the photocurrent density of CdS-NSs/ZnS-NPs-0.6 heterojunctions is higher than those of ZnS NPs and CdS NSs, indicating the significantly enhanced transfer and separation efficiencies of photogenerated charge carriers. According to the EIS measurements in Figure 4D, the CdS-NSs/ZnS-NPs-0.6 heterojunctions exhibit the smallest arc

size in comparison to those of CdS NSs and ZnS NPs, clarifying their smaller electron transport resistance and the formation of an intimate interface between CdS NSs and ZnS NPs. As shown in Figure 4E,F, the recorded MS plots reveal that the flat band (E_{FB}) potential of ZnS NPs is -0.77 eV^{59,60} (vs. NHE, $E(NHE) = E(Ag/AgCl) + 0.197$), which is more negative than that of CdS NSs (-0.55 eV vs. NHE).² The flat band potential for CdS-NSs/ZnS-NPs-0.6 heterojunctions is estimated to be 0.66 eV (vs. NHE), as shown in Figure S16.

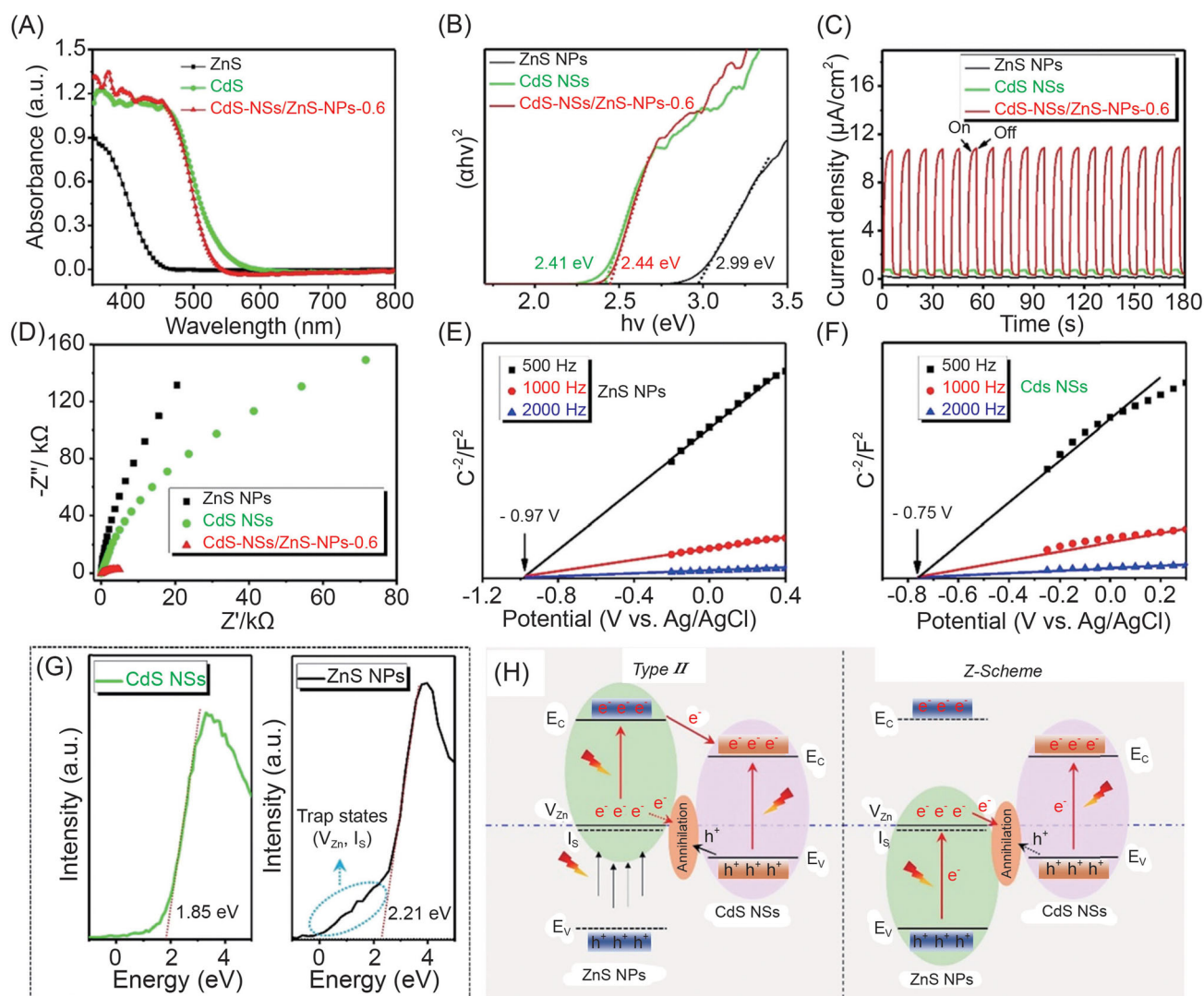


FIGURE 4 Mechanism of photocatalytic H₂ production. (A) UV-Vis diffuse reflectance spectra of a range of samples. (B) Calculated optical band gaps. (C) Transient photocurrent responses of a range of samples. (D) EIS of samples. (E,F) Mott-Schottky plots of ZnS NPs and CdS NSs, respectively. (G) VB XPS analysis of CdS and ZnS, showing the existence of trap states in ZnS. (H) Schematic of photocatalytic H₂ production over type-II and Z-scheme mixed CdS/ZnS heterojunction. EIS, electrochemical impedance spectra; NP, nanoparticle; NS, nanosheet; VB, valence band; XPS, X-ray photoelectron spectroscopy.

The shift of flat band potential witnesses the strong interaction among 1D ZnS NPs and 2D CdS NSs nanosheets, which favors the transfer of photogenerated carriers. It is known that, for *n*-type semiconductors, the position of the flat band potential is similar to that of the conduction band (E_{CB}). Namely, the conduction bands of ZnS NPs and CdS NSs should be located at -0.77 and -0.55 eV, respectively. Accordingly, the valence band (E_{VB}) of the ZnS NPs and CdS NSs can be calculated by $E_{VB} = E_{CB} + E_g$, which are located at 2.22 and 1.86 eV, respectively, in agreement with the results of XPS VB spectra in Figure 4G. Furthermore, the XPS VB of the ZnS NPs shows the density of states within the valence band, in comparison with pure ZnS, as shown by the blue dotted lines in Figure 4G and Figure S17. These

results indicate the existence of trap states of V_{Zn} and I_S within the resultant heterojunctions, in agreement with the XPS and EPR analyses provided in Figure 2H and Figures S10 and S11. The separation and transfer processes of photogenerated charge carriers are investigated by the steady-state PL and TRPL spectroscopy, as shown in Figure S18. These results confirm that as-built CdS-NSs/ZnS-NPs-0.6 heterojunction could suppress the recombination of photo-induced charge carriers. Besides, the long-lived photogenerated electrons of NSs/ZnS-NPs-0.6 (17.06 ns) indicate that the charge recombination of CdS in the heterojunction is inhibited, implying that the transfer pathway hinders the recombination of charge carriers. Furthermore, in terms of the higher DMPO·OH intensity

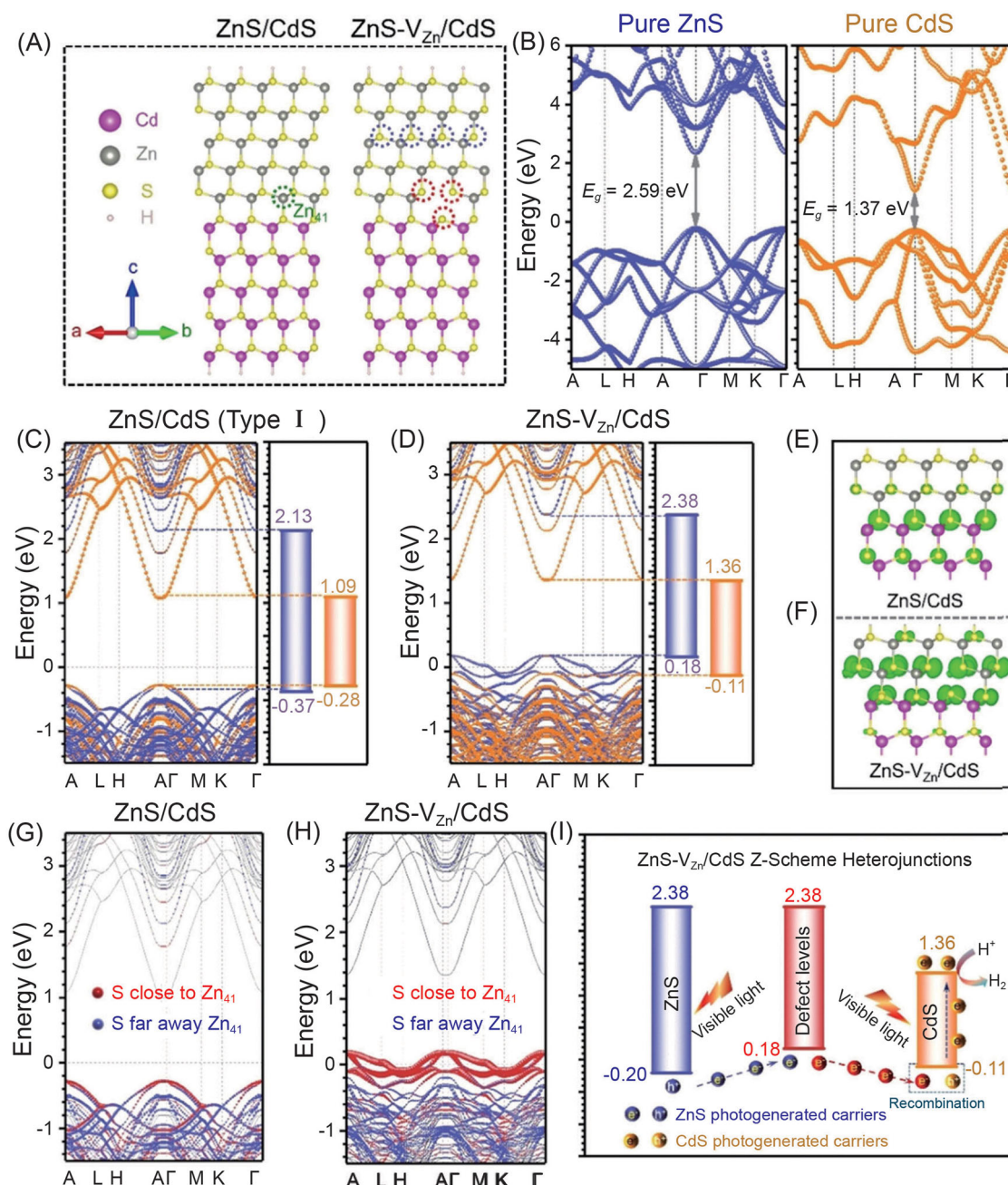


FIGURE 5 Theoretical investigation on photocatalytic H₂ production. (A) Crystal structures of ZnS/CdS heterostructure with and without Zn vacancy, with an example of Zn₄₁ (the green, blue, and red dotted circle represents Zn atom No. 41 (labeled as Zn₄₁), S far away from Zn₄₁, and S close to Zn₄₁, respectively). (B) Energy band structures of pure ZnS (left) and CdS (right). (C,D) Energy band structures of ZnS/CdS heterostructure with and without Zn vacancy, respectively. The blue and yellow dotted regions represent the isolated ZnS and CdS band structures, respectively. (E,F) Partial charge densities at VBM of ZnS/CdS heterojunctions without and with V_{Zn}, respectively. (G,H) Contributions of S atoms close to and far away from Zn₄₁ on the band structure of ZnS/CdS heterojunction with and without Zn vacancy, respectively. (I) Carrier transport within Z-scheme ZnS/CdS heterojunction. VBM, valence band maximum; V_{Zn}, Zn vacancy.

of CdS-NSs/ZnS-NPs-0.6 heterojunction (Figure S19), it suggests that the electron transfer mechanism does not follow the conventional type-I heterojunction mechanism. Based on the abovementioned analyses, the mechanism concerning the enhanced activity of photocatalytic H₂ evolution is illustrated schematically in Figure 4H, and it

suggests that the improved photocatalytic performance primarily originates from the defect energy levels produced by Zn vacancies, which helps to build the desired type-II (the left part in Figure 4H) and Z-scheme (the right part in Figure 4H) mixed heterojunction. This facilitates an improved trapping capacity under visible light, with efficient

separation and transfer of photogenerated carriers. Consequently, the photogenerated electrons in the E_{CB} of CdS NSs is available to effectively reduce protons for producing H_2 . Additionally, the high stability of the heterojunctions could be attributed to the fact that the photogenerated holes within CdS NSs is rapidly combined with electrons that exist within the defect levels of ZnS NPs, resulting in a suppressed hole-led photocorrosion of CdS.

To provide a deeper insight into the electronic structure of as-fabricated CdS-NSs/ZnS-NPs heterojunctions, their bandgap alignments are theoretically investigated. In terms of the small lattice mismatch (<5%) between the ZnS (111) surface with/without V_{Zn} and CdS (002) surfaces, the ZnS/CdS heterojunction is constructed, as shown in Figure 5A. For comparison, the electronic structures of pure bulk ZnS and CdS are provided in Figure 5B. For the ZnS materials, it has a direct band gap of $E_g \sim 2.59$ eV, with both the conduction band minimum (CBM) and valence band maximum (VBM) located at the Γ point. For CdS, it possesses a direct band gap of $E_g \sim 1.37$ eV at Γ point. Figure 5C,D shows the band structures of ZnS/CdS heterojunctions without and with V_{Zn} , respectively. It is observed that the electronic structures of both heterojunctions have a clean band gap, without midgap states. With respect to the condition without V_{Zn} , once the V_{Zn} is introduced into the interface of heterojunction, as shown in the right part of Figure 5A, significant modification of the electronic structure occurs. This suggests that both the CBM and VBM of ZnS- V_{Zn} are moved upward for the CdS component, inducing a change from a type-I heterojunction to a type-II one (the left part in Figure 4H). As a result, the photogenerated electrons of ZnS will be trapped in the defect levels, which is followed by recombination with the holes within the VB of CdS and partly transferred to the CB of CdS at the heterojunction interfaces.^{44,77,78} Such a tailored band alignment would prevent the recombination of photogenerated carriers, facilitating a longer carrier lifetime to enhance photocatalytic behavior. Moreover, the partial charge densities at the VBM of ZnS/CdS without and with V_{Zn} are calculated, as shown in Figure 5E,F and Figure S20, which indicate the areas for generating photoinduced holes. In terms of the condition without V_{Zn} , the holes are located in the ZnS component. However, as shown by the movement of the charge density in the case with V_{Zn} , the holes will transfer from CdS to ZnS components, indicating that the V_{Zn} could pull up the energy level of VBM of ZnS. In addition, the contributions of S atoms close to and far away from Zn_{41} (as an example for Zn-vacancy defects in Figure 5A) in the band structure of ZnS/CdS without Zn vacancy are investigated, presenting that the electronic states of both type-S atoms are almost overlapped (Figure 5G). However, once the V_{Zn} is

generated at the Zn_{41} site, an energy level split occurs, which makes the electronic states of the S atoms close to V_{Zn} for dominating the valence band edge (Figure 5H), which thus accounts for the upshift of VBM in ZnS. In terms of the breaking S-Zn bonds, the S atoms close to V_{Zn} become unsaturated, which is accompanied by the generation of dangling bonds around the VBM. Meanwhile, the electronic states of S atoms far away from the V_{Zn} are almost fixed due to the negligible effect of V_{Zn} . As a result, the existence of V_{Zn} , as confirmed by the XPS analyses in Figure 2H, favors the formation of Z-scheme heterojunctions within sample CdS-NSs/ZnS-NPs, as schematically shown in Figure 5I and the right part in Figure 4H. As a result, the photogenerated electrons of bulk ZnS (the blue column in inset of Figure 5I) will be trapped in the defect levels (the red line and column in Figures 5H and 5I, respectively), which is followed by recombination with holes within the VB of CdS at the heterojunction interfaces (the orange column in Figure 5I). In such a process, the electrons within the CB of CdS would be facilitated to participate in H_2 evolution reactions, favoring a limited photocorrosion of CdS. Overall, the enhanced spatial separation of photogenerated carriers induced by the constructed type-II and Z-scheme mixed 1D/2D heterojunctions plays a critical and important role in suppressing the recombination of charge carriers with limited photocorrosion of CdS, which thus leads to an enhanced photocatalytic behavior.

4 | CONCLUSION

In summary, we have demonstrated a sonochemistry strategy for kilogram-scale fabrication of CdS/ZnS 1D/2D heterojunctions under ambient air conditions (i.e., RT and atmospheric pressure), whereby uniformly distributed ZnS nanoparticles are anchored on the surface of CdS nanosheets. The resultant CdS-NSs/ZnS-NPs heterojunctions deliver a significantly enhanced photocatalytic H_2 evolution rate of $14.02 \text{ mmol h}^{-1} \text{ g}^{-1}$ under visible-light irradiation ($\lambda > 400 \text{ nm}$), which is ~ 10 and ~ 85 times higher than those of pristine CdS NSs and CdS NPs, respectively, and superior to most of the CdS-based photoanodes reported to date. Moreover, the heterojunctions provide excellent photocatalytic stability over 58 h, highlighting their potential for practical applications. The enhanced photocatalytic activity is attributed to the following key points: (i) the formed 1D/2D heterojunctions provide sufficient exposed active sites to respond to illumination by light and also provide a fast pathway for efficient separation and transfer of photogenerated carriers through the matrix of single-crystalline CdS NSs; (ii) the constructed type-II and Z-scheme mixed

heterojunctions are directed by the defect energy level of Zn vacancies, which increase the energy level of valence band maximum in ZnS. As a result, such heterojunctions play a critical role in suppressing the recombination of carriers with limited photocorrosion of CdS, thus enabling an enhanced photocatalytic behavior. The work has the potential to open a new door for large-scale production of advanced photocatalysts with rationally designed structures toward highly efficient and stable visible-light-driven photocatalytic H₂ evolution.

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CONFLICT OF INTEREST

The authors declare no conflict of interests.

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SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

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