

S-scheme unidirectional transmission of CdS-CuO heterojunction benefits for superior photocatalytic hydrogen evolution efficiency

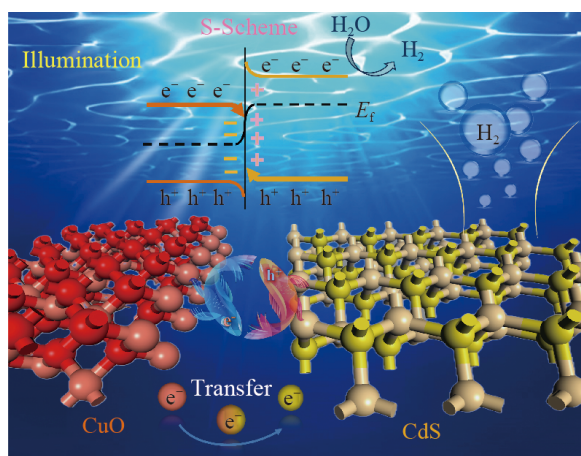
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Abstract: The efficiency and stability of catalysts for photocatalytic hydrogen evolution (PHE) are largely governed by the charge transfer behaviors across the heterojunction interfaces. In this study, CuO, a typical semiconductor featuring a broad spectral absorption range, is successfully employed as the electron acceptor to combine with CdS for constructing a S-scheme heterojunction. The optimized photocatalyst (CdS-CuO₂:1) delivers an exceptional hydrogen evolution rate of 18.89 mmol/(g·h), 4.15-fold higher compared with bare CdS. X-ray photoelectron spectroscopy (XPS) and ultraviolet-visible diffuse reflection absorption spectroscopy (UV-vis DRS) confirmed the S-scheme band structure of the composites. Moreover, the surface photovoltage (SPV) and electron paramagnetic resonance

(EPR) indicated that the photogenerated electrons and photogenerated holes of CdS-CuO₂:1 were respectively transferred to the conduction band (CB) of CdS with a higher reduction potential and the valence band (VB) of CuO with a higher oxidation potential under illumination, as expected for the S-scheme mechanism. Density-functional-theory calculations of the electron density difference (EDD) disclose an interfacial electric field oriented from CdS to CuO. This built-in field suppresses charge recombination and accelerates carrier migration, rationalizing the markedly enhanced PHE activity. This study offers a novel strategy for designing S-scheme heterojunctions with high light harvesting and charge utilization toward sustainable solar-to-hydrogen conversion.

Key words: photocatalytic hydrogen evolution; CdS-CuO S-scheme heterojunction; electron directional transmission; interfacial electric field; DFT calculation



Solar-driven photocatalytic hydrogen evolution (PHE) offers a carbon-neutral approach to convert the endless solar-energy to chemical fuels^[1-3], yet its practical viability is impeded by the poor light absorption and low electron transfer efficiency of the traditional photocatalysts^[4-5]. Transition metal sulfides (TMSs), such as CdS, ZnS, ZnIn₂S₄, have emerged as appealing alternatives because of their exceptional light response and splendid photoelectric properties^[6-7]. Among them, CdS possess an ideal band gap and a conduction-band minimum for proton reduction, thus presenting a great future potential^[8-11]. However, rapid recombination of photo-generated electron-hole pairs and

inefficient interfacial charge extraction severely curtail its quantum efficiency^[12-13].

Many efforts have been devoted to enhance the charge separation efficiency, among which the crafted design of heterojunction catalysts is regarded as a promising strategy^[14]. Among them, the effective strategy to construct heterojunctions by coupling semiconductors with different work functions is largely explored and has shown significant prospect. A rich library of CdS-based heterojunctions, such as CdS/BiVO₄^[15], Co₉S₈ QDs/NiS/CdS^[16], g-C₃N₄/CdS^[17], CdS/MnO_x-BiVO₄^[18], CdS/NiAl-LDH^[19], COF/CdS^[20], MnO₂/CdS^[21] and

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$\text{W}_{18}\text{O}_{49}/\text{CdS}$ ^[22] have presented markedly improved PHE efficiencies. The driving force in these systems originates from the Fermi-level offset between adjoining semiconductors, which established a strong interfacial electric field (IEF) at the interfaces. Induced by the driving force of IEF, the spatial separation and transmission of carriers would be largely accelerated, finally realizing a high quantum efficiency.

Copper oxide (CuO), a narrow band gap semiconductor, has been widely explored for photocatalytic applications due to its suitable band gap energy, abundant oxygen deficiency, and tunable electronic structure^[8,23–25]. Previous investigations have highlighted the potential of combination CuO with CdS to fabricate heterojunctions, capitalizing on their well-aligned valence band (VB) and conduction band (CB) positions for Type-II band alignment^[8,26]. However, the IEF in type II heterojunctions drives the photogenerated charges toward lower energy bands, which significantly reduces their redox ability. Therefore, despite improved photocatalytic performance, these systems remain fundamentally limited by weak redox potentials. Recently, the step-scheme (S-scheme) heterojunctions have emerged as promising alternatives, demonstrating superior photocatalytic activity^[27–31]. Unlike traditional heterojunctions, S-scheme systems leverage work function differences between semiconductors to achieve efficient charge separation. Here, photogenerated electrons in the CB of oxidation photocatalysts (OP) recombine with holes in the VB of reduction photocatalysts (RP)^[32–36]. This process establishes an IEF that preserves high-energy electrons and holes with strong redox capacities while inducing band bending to facilitate directional charge migration^[37–38]. Accordingly, the rational spatial separation of photoexcited charges can maximally display the respective superiority of CdS and CuO, thus endowing the S-scheme heterojunction with both excellent activity and stability. Nevertheless, it is still a formidable challenge on how to realize the fabrication of the S-scheme heterojunction with CdS and CuO.

Critically, matching Fermi energy levels and the work functions are prerequisites for the designation of S-scheme heterojunctions. Through DFT calculations (the work function and energy band structure), it is certified that the intrinsic properties of CuO and CdS are qualified for assembling S-type heterojunction, which should generate a powerful IEF to drive charge transfer. To address the challenges in fabrication, we propose a facile method involving impregnation and grinding to synthesize the heterojunction. It is observed that the resulting material exhibits uniform and intimate interfacial contact between CdS and CuO, delivering competitive photocatalytic hydrogen evolution (PHE) performance with remarkable stability. X-ray photoelectron spectroscopy (XPS) and surface photovoltage (SPV) analyses reveal that the as-prepared photo-catalyst bears a powerful charge transfer ability originated from the IEF inside the heterojunction. Integrating with the characterizations of spin-trapping

electron paramagnetic resonance (EPR) and DFT calculations (electron density difference (EDD) and Planar-averaged electron density difference), the role of IEF is analyzed and discussed, by which the PHE mechanism is ultimately confirmed.

1 Materials and method

1.1 Materials

Cadmium chloride pentahydrate ($\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$, AR, 98%), ethylenediamine monohydrate (AR, 98%) was obtained from Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). Sodium dodecyl benzene sulfonate (SDBS, AR, 90%), thiourea ($\text{CH}_4\text{N}_2\text{S}$, AR, 99%), sodium sulfide nonahydrate ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, AR, 98%), sodium sulfite (Na_2SO_3 , AR, 98%), ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, AR, 99%) were obtained from Maclin Biochemical Technology Co., Ltd. (Shanghai, China). Sodium hydroxide (NaOH, AR, 98%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Anhydrous ethanol ($\text{C}_2\text{H}_5\text{OH}$, AR, 99.7%) was purchased from Tianjin Fuyu Fine Chemical Co., Ltd (Tianjin, China). The reagents above were all of analytical grade and used directly without further purification. The deionized water used in this study was obtained from local sources.

1.2 Synthesis of CdS

For the synthesis of the CdS, 0.003 mol $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$, 0.009 mol ethylenediamine monohydrate, 0.6 g sodium dodecyl benzene sulfonate (SDBS) (0.010 g/mL), and 0.006 mol thiourea were added into beaker with 60 mL deionized water under continuous stirring for 30 min. Then, the resulting mixture was transferred into a Teflon-lined stainless autoclave of 100 mL capacity, which thereafter was maintained at 100 °C for 5 h. After being cooled down to room temperature naturally, the resulted products were alternately washed for 3 times with deionized water and ethanol absolute. Finally, the final products were dried at 60 °C for 6 h for further use.

1.3 Synthesis of the CuO

CuO was synthesized according to a previously reported method^[23]. Briefly, 0.6 g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was resolved in 25 mL deionized water (DW) and then 0.4 g of NaOH solution in 25 mL of DW was dropped in this solution. The mixture, after being stirred for 30 min, was transferred to a stainless-steel autoclave and heated at 180 °C for 20 h. The composed CuO nanoparticles were centrifuged at 4000 r/min for 5 min and dried at 70 °C overnight after being washed by DW and ethanol for three times.

1.4 Synthesis of the CdS-CuO Heterojunctions

The CdS-CuO heterojunctions were synthesized by wet impregnation method. Initially, CdS and CuO were mixed in absolute ethanol at a molar ratio of 1:2, 1:1, 2:1, 3:1 and 4:1. Then the mixture was ultrasonicated in a sealed vial for 3 h at 40 °C. After that, it was centrifuged and was dried in the lyophilizer overnight. The mixed powder of CdS and CuO was thoroughly mixed by grinding for 30 min to ensure that they were evenly mixed and calcined in a tube furnace where nitrogen was introduced for 30 min to isolate the air at 80 °C under N₂ condition for 2 h. The molar ratios of CdS:CuO heterojunctions were set to be 1:2, 1:1, 2:1, 3:1, 4:1, based on which the obtained samples were denoted as CdS-CuO1:2, CdS-CuO1:1, CdS-CuO2:1, CdS-CuO3:1, CdS-CuO4:1.

1.5 Characterizations

Powder X-ray diffraction (XRD) patterns were collected using a Rigaku D/max-gB X-ray diffractometer with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$) at 293 K and the distribution of the elements was detected by SEM equipped with energy dispersive spectrometer (EDS). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were obtained via a JEOL JEM-2100 electron microscope. X-ray photoelectron spectroscopy (XPS) spectra were obtained using an ESCALAB 250 instrument. All the spectra are obtained after 284.8 eV calibration of C 1s. Ultraviolet-visible diffuse reflectance spectra (UV-vis DRS) were measured by UV-3600 (Shimadzu). The lock-in amplifier-based surface photovoltage (SPV) consists of a monochromatic light source, a lock-in amplifier (SR830-DSP) with a light chopper (SR540), and a 500 W Xe lamp (CHF-XM-500 W, Global Xenon lamp power) serve as the light source. The monochromatic light is provided by passing light from the Xe lamp through a grating monochromator (Omni-5007, Zolix). JES-FA300 (JEOL) was used for the characterization of electron paramagnetic resonance (EPR) with 300 W Xenon lamp at room temperature.

1.6 Photocatalytic H₂ evolution

The photocatalytic H₂ evolution was tested to evaluate the photocatalytic activities of the CdS-CuO heterojunctions. The photocatalytic H₂ evolution was tested by MC-SPB10 (Magnesium catalytic tester, Beijing Magnesium Richen Technology Co., Ltd.), using Na₂S and Na₂SO₃ as sacrificial reagents to evaluate the photocatalytic activities of CdS-CuO heterojunctions. Typically, 10 mg of photocatalyst was dispersed in a 50 mL mixed aqueous solution of 0.35 mol/L Na₂S and 0.5 mol/L Na₂SO₃ in a photocatalytic reactor. Na₂S and Na₂SO₃ served as sacrificial reagents to consume holes in the system. Then, the reactor was vertically illuminated by using a 300 W

Xenon lamp as the light source. H₂ amounts were quantitatively analyzed via a GC9790Plus gas chromatograph equipped with a thermal conductivity detector (TCD).

1.7 Photoelectrochemical characterization

Electrochemistry impedance spectroscopy (EIS) Nyquist plots and transient photocurrent spectra were measured in Na₂SO₄ aqueous solution (0.1 mol/L) with a standard three-electrode system (Pt plate, counter electrode; Ag/AgCl, reference electrode; sample/ITO, working electrode).

1.8 DFT calculations

Density functional theory (DFT) calculation was accomplished based on the CASTEP module in Materials Studio software. Perdew-Burke-Ernzerhof (PBE) of the exchange-correlation function was employed within the generalized gradient approximation (GGA). Here, the electronic energy was considered to be self-consistent when the energy change was $<10^{-5}$ eV. A geometry optimization was considered to be convergent when the force change was $<0.02 \text{ eV/\AA}$. For the model of CdS (220) and CuO (002) slab, a plane wave basis was set with a cutoff energy of 500 eV and a Monkhorst-Pack grids of $7 \times 7 \times 1$ k-point, and the ultrasoft pseudopotential was used to approximate the interaction between the atomic real and valence electrons to accurately describe the hybridization and transfer of valence electrons. Thus, geometric optimization was carried out and the properties of the band structure and density of states (DOS) were calculated.

For the CdS-CuO heterojunction model, a $1 \times 1 \times 2$ supercell for CdS and $1 \times 1 \times 3$ supercell for CuO was built as the surface and a vacuum layer of 20 Å was applied in the z-direction to build the CdS-CuO heterojunction model. The Monkhorst-Pack sampling scheme of the Brillouin zone was adopted to generate the $2 \times 3 \times 1$ k-point grids and the kinetic energy cutoff of 400 eV was used, and the norm conserving pseudopotential was used to approximate the interaction between atomic real and valence electrons for geometric optimization, and the band structure, density of states (DOS) and EDD calculations were carried out.

2 Results and discussion

2.1 Structure and morphology of the CdS-CuO heterojunction

Figure 1(a) displays the overall preparation procedure, in which CdS and CuO were initially prepared by hydrothermal method, and afterwards the composite catalyst was synthesized via grinding the CdS and CuO with ethyl alcohol to integrate the two components evenly and intimately. The crystal structures of the as-prepared samples

CdS, CuO and CdS-CuO₂:1 were characterized by X-ray diffraction (XRD) as depicted in Figure 1(b). In the pattern of sample CdS, the prominent peaks at 26.5°, 43.9° and

52.0° are assigned to the (111), (220) and (311) planes of the cubic CdS (PDF#75-1546), respectively^[14,39–40].

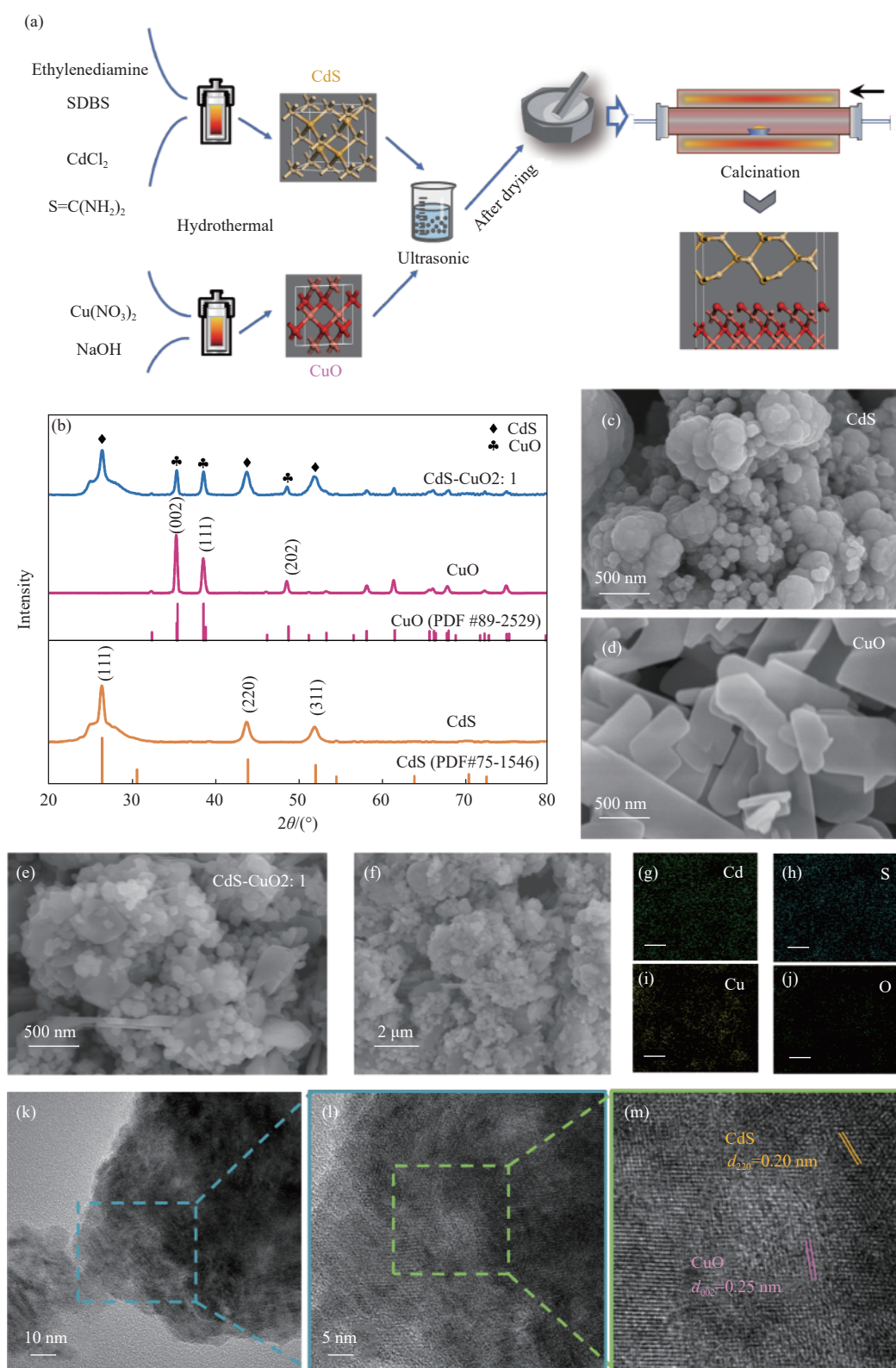


Fig. 1 (a) Schematic illustration of the synthesis of the CdS-CuO composites; (b) XRD patterns for CdS, CuO and CdS-CuO₂:1; SEM image of (c) CdS, (d) CuO and (e) CdS-CuO₂:1; (f–j) EDS mapping of the CdS-CuO₂:1; and (k–m) TEM and HRTEM images of the CdS-CuO₂:1

For sample CuO, the characteristic peaks at 35.5° , 38.6° and 48.8° could be indexed to the (002), (111) and (202) planes of the monoclinic CuO (PDF#89-2529)^[23]. The XRD patterns of sample CdS-CuO2:1 include the diffraction peaks of both CdS and CuO, indicating the successful fabrication of the composite catalyst^[41–42].

The morphology and elemental distribution of the CdS-CuO2:1 sample were studied by SEM, HRTEM and EDS mappings. Figure 1(c) exhibits the microscopic structure of CdS, which presents uniform nanospheres with the diameter of 100–300 nm, and the image of CuO (Figure 1(d)) exhibits a 2D micro-chip morphology. As to the CdS-CuO2:1 composite (Figure 1(e)), it is found that CdS nanoparticles were evenly deposited on the CuO surface, demonstrating a well interwoven states of CuO and CdS, which is favored in forming heterojunctions^[43]. The EDS elemental mapping as illustrated in Figure 1(f)–(g) reveals that the involved elements, Cd, S, Cu and O, uniformly distribute over the surface of CdS-CuO2:1, wherein the atomic ratio of Cd and Cu is close to 2:1 (Figure S1, Supporting Information), agreeing well with the initial feeding. To obtain more detailed information, HRTEM image was recorded as illustrated in Figure 1(k)–(m), in which two sets of visible lattice fringes with the spacing of 0.25 and 0.20 nm fit well with the (220) and (002) crystal planes of CdS and CuO. This observation indicates the physical coalesce between CdS and CuO, and thus provides a solid basis for IEF formation and efficient charge transfer^[44].

X-ray photoelectron spectroscopy (XPS) was adopted to examine the surface chemical states and probe the electron

transfer in heterojunctions (Figure 2^[34,45]). For clarity, the XPS survey spectra of CdS, CuO and CdS-CuO2:1 are shown in Figure S2 (Supporting Information), in which the elements Cd, S, Cu and O can be detected, consistent with the EDS mapping (Figure 1(f)). Figure 2(a) shows the high-resolution XPS profile of Cd 3d orbitals in CdS, in which the peaks at 405.08 and 411.81 eV are ascribed to Cd 3d_{5/2} and Cd 3d_{3/2} orbitals, respectively^[14]. By contrast, the corresponding peaks for Cd 3d in the CdS-CuO2:1 spectrum positively shift (~ 0.25 eV) to 405.33 and 412.06 eV. The higher binding energies should be attributed to the interfacial electron transfer to CuO. In the case of S 2p spectra (Figure 2(b)), the peaks at 161.42 and 162.61 eV in original CdS are respectively assigned to the S 2p_{3/2} and S 2p_{1/2} orbitals^[42]. Notably, the two peaks of S 2p orbitals in the spectrum of the CdS-CuO2:1 are also positively shifted (~ 0.30 eV) to 161.70 and 162.91 eV, which agrees well with the trend in the Cd 3d peaks, thus further demonstrating the strong interaction between CdS and CuO. Meanwhile, the core level Cu 2p spectrum reveals to be doublet (Figure 2(c)), which locate at 933.70 and 953.47 eV, respectively representing Cu 2p_{3/2} and Cu 2p_{1/2} orbitals^[46]. It has been acknowledged that the appearance of two satellites at ~ 942 and ~ 962 eV signifies the paramagnetic state of Cu²⁺^[47]. Herein, one can ascertain that the interaction between CdS and CuO is responsible for the decrease of Cu 2p binding energies to 933.46 and 953.31 eV. Figure 2(d) shows the O 1s XPS spectra, in which the pure CuO are fitted at 529.78 and 531.39 eV, corresponding to the lattice oxygen (O_{lat}) and adsorbed oxygen (O_{ads}) species^[42,47–48].

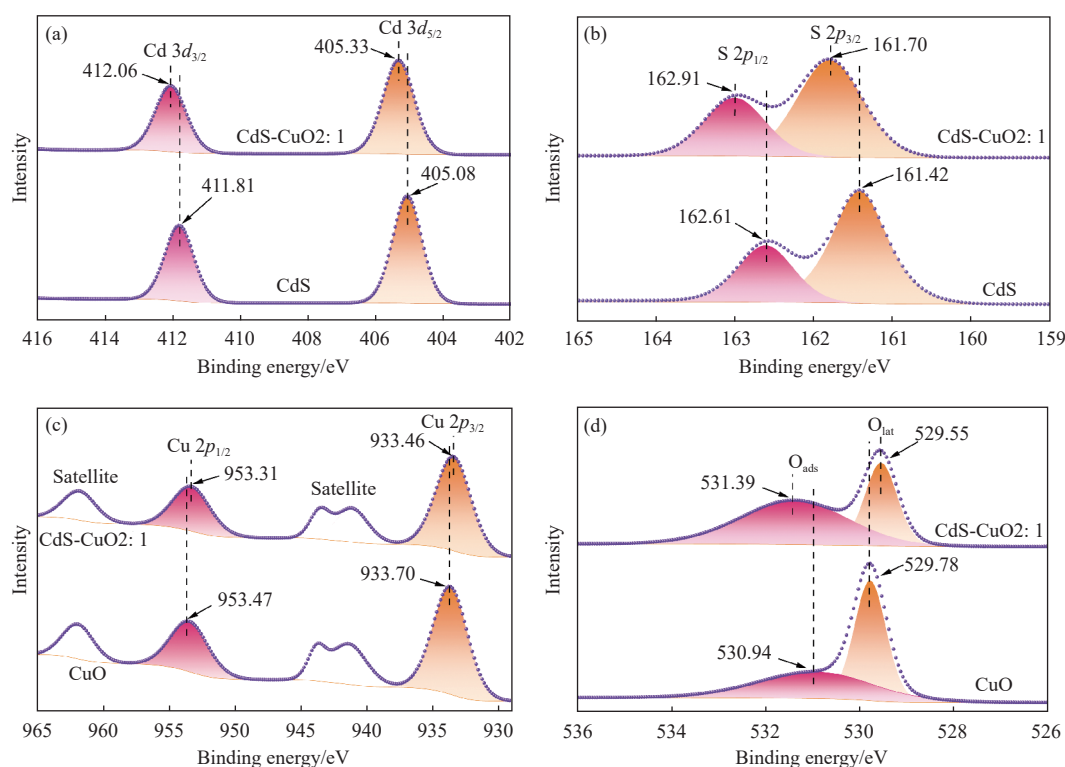


Fig. 2 High-resolution XPS spectra for (a) Cd 3d orbital and (b) S 2p orbital of the CdS and the CdS-CuO2:1; High-resolution XPS spectra for (c) Cu 2p orbital and (d) O 1s orbital of the CuO and the CdS-CuO2:1

Besides, the one of O_{lat} negatively shifts to 529.55 eV after construction of the heterojunction with CdS. These variations of binding energies not only confirm the strong interaction between CdS and CuO, but also confirm that in the composites of CdS and CuO, due to the difference in E_F , electrons spontaneously diffuse from CdS to CuO^[49–50]. Such electron transfer can effectively facilitate the electric field at the interface of the CdS-CuO heterojunctions, which is in compliance with the setting of the S-scheme heterojunction^[1,4,51–52].

2.2 Photocatalytic activity of the CdS-CuO heterojunctions

The photocatalytic H_2 evolution performance was evaluated by using Na_2S and Na_2SO_3 as sacrificial reagents under light irradiation, and the results are shown in Figure 3(a) and (b). It can be seen that the pristine CdS and CuO exhibit low H_2 evolution performance, which were 4.55 and 3.21 mmol/(g·h) respectively. By contrast, the CdS-CuO composite delivers greatly increased H_2 evolution rates. Explicitly, the H_2 production is closely dependent to the molar ratio of CdS and CuO. When the molar ratios of

CdS and CuO is set as 1:2, the H_2 evolution rate reaches 13.13 mmol O 1s. Further increasing the proportion of CdS, a volcanic trend is presented, and the maximum rate of 18.89 mmol O 1s is achieved with the molar ratio of 2:1 (CdS:CuO).

Based on the XPS analyses above, it is proposed that the promoted photocatalytic activity can be ascribed to the improved charge separation after the construction of heterojunctions. The combination of CdS and CuO creates an IEF, which allows the photogenerated electrons to drift to the surface of CdS (higher reduction potential) driven by the electric field force. Thus, the proton reduction on the CdS surface is enhanced. In this case, the appropriate proportion of CdS and CuO can guarantee both efficient light excitation and transmission of electrons. Of note, by comparing with previously reported CdS-based photocatalysts, the PHE efficiency of this S-scheme heterojunction catalyst (CdS-CuO2:1) is rather competitive (Table S1, Supporting Information).

The durability of CdS-CuO2:1 sample for PHE application was evaluated by the cycling H_2 evolution experiments. Based on the results in Figure 3(c), no obvious decrease on H_2 evolution can be observed even after four cycles.

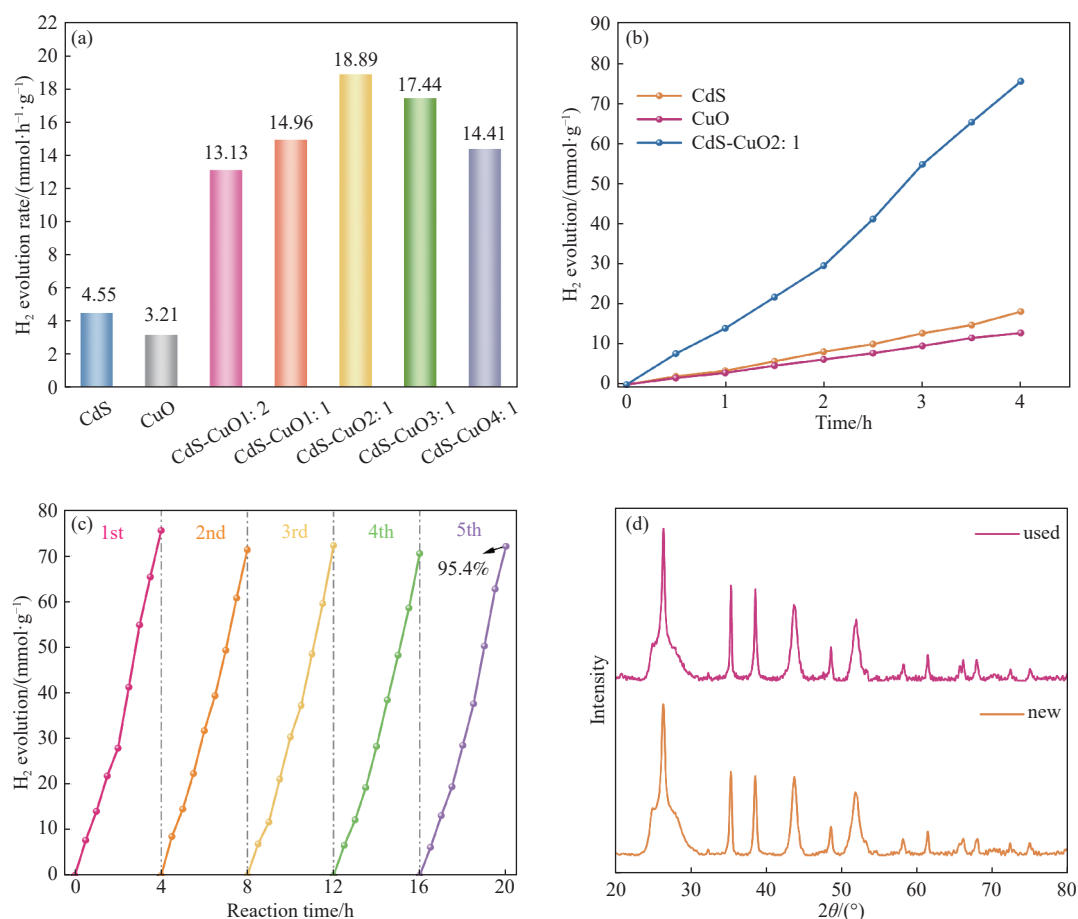


Fig. 3 (a) Photocatalytic H_2 evolution rates for the CdS, CuO and CdS-CuO samples; (b) Comparison of the photocatalytic H_2 evolution rates for CdS, CuO and CdS-CuO2:1; (c) Cycling photocatalytic H_2 evolution tests of the CdS-CuO2:1 photocatalyst; (d) XRD patterns of fresh and used CdS-CuO2:1

The characterizations of the spent catalysts, including XRD, SEM and XPS were also carried out to examine the structural integrity of the used CdS-CuO₂:1 in detail. The XRD and SEM patterns before and after PHE (Figure 3(d) and S3) also reveal no prominent change compared with those of the fresh catalysts. Meanwhile, XPS (Figure S4, Supporting Information) also confirms that the chemical structure of sample CdS-CuO₂:1 is well preserved. In conclusion, the analyses above demonstrate that this S-scheme heterojunction catalyst exhibits excellent stability and superb photo-corrosion resistance.

2.3 S-scheme heterojunction band structure

To understand the surface electron transportation properties of the catalysts, surface photovoltage (SPV) is employed. SPV signal arises when the photoinduced electron-hole pairs are separated in space, and a stronger photovoltage signal implies better charge transfer ability of the photocatalyst. Whereas the negative photovoltage signal elucidates photogenerated electrons that migrate towards the surface^[47–50]. The S-scheme heterojunctions are well known to be high-efficiency on the charge transfer. Hence, the photocatalytic mechanism of as-prepared heterojunctions was further investigated through SPV (Figure 4(a)). As suggested in Figure 4(a), an inversed photovoltage signal is observed for CdS-CuO₂:1, demonstrating the existence of

an interfacial electric field, whereby the photoinduced charge carriers can be separated rapidly and efficiently^[53–56]. The strong signal centered ca. 475 nm also indicates a much higher photogenerated electron transfer efficiency towards the interface than that of pure CdS, which determines a greatly improved PHE capability. Combined with the XPS results, the successful fabrication of S-scheme heterojunctions with CdS and CuO can be ultimately ascertained.

The optical properties and band structures are detected via UV-vis DRS and valence band X-ray photoelectron spectroscopy (VB-XPS) spectra. The UV-vis DRS spectra in Figure 4(b) reveals that the pristine CdS presents strong visible light response with the absorption edge at ~540 nm, while CuO shows a wide absorption band from the ultraviolet region to the visible region with the absorption edge at 840 nm. Hence, the absorption edge of CdS-CuO₂:1 catalyst is red-shifted compared with that of CdS, and further extends into the visible light region as expected, which results in better light absorption. Figure 4(c) illustrates the Tauc's bandgap plots that are transformed from the UV-vis DRS measurements. The energy bandgaps (E_g) of CdS, CuO and CdS-CuO₂:1 are evaluated to be 2.06, 1.61 and 1.73 eV, respectively (Figure 4(c) and S5). It has been well demonstrated that the band gap accounts for a major factor affecting the PHE activities. A wide band gap can provide a high light absorption intensity, but the absorption range is limited.

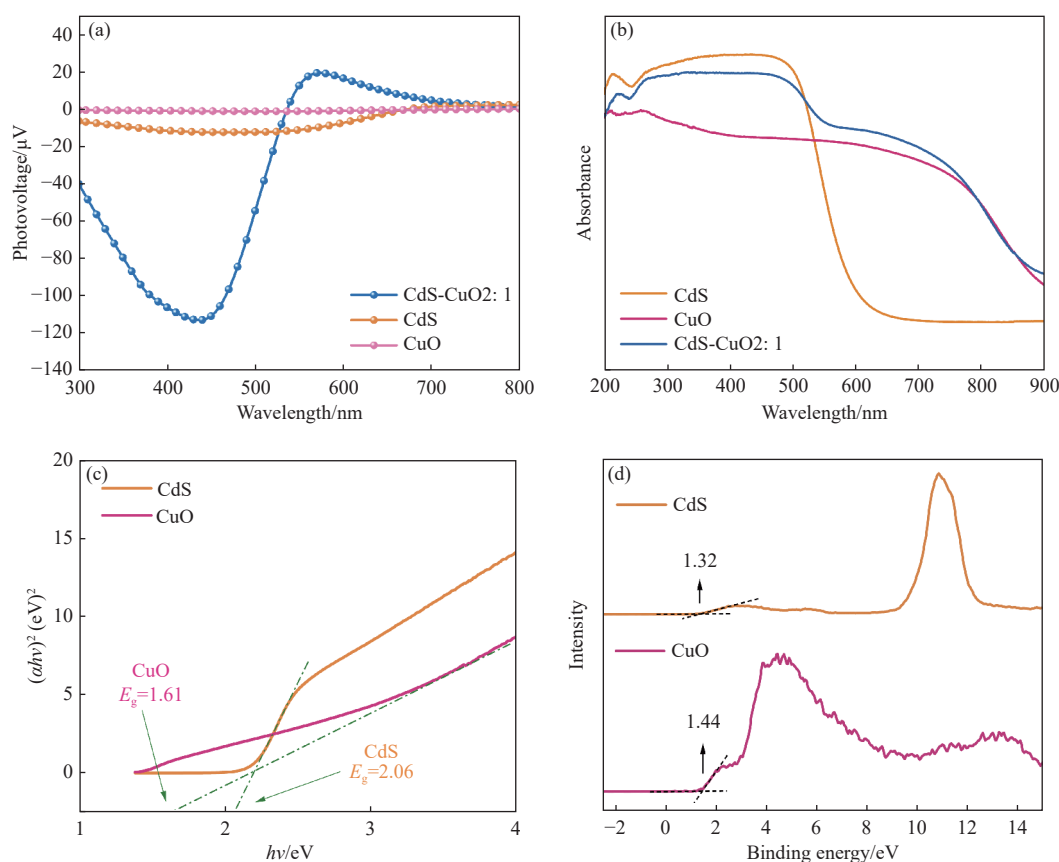


Fig. 4 Photochemical properties of the catalysts: (a) SPV spectra of CdS, CuO and CdS-CuO₂:1; (b) UV-vis DRS spectra of samples; (c) Tauc's energy bandgap of CdS and CuO; (d) VB XPS spectra of CdS and CuO

Conversely, a narrow band gap sacrifices the light absorption intensity to realize a wide light absorption range^[57–58]. Therefore, the compromised E_g of CdS-CuO2:1 is favorable to the light absorption, as well as the generation of photoinduced carriers. The specific valence band positions are determined through VB XPS spectra (Figure 4(d)). The VB top positions (E_{VB}) of CdS and CuO, are located at 1.32 and 1.44 eV versus the normal hydrogen electrode (NHE), respectively. Thus, their conduction band potentials (E_{CB}) can be estimated to be -0.74 and -0.17 eV according to the equation of $E_g = E_{VB} - E_{CB}$. Base on previous reports, the CB and VB of oxidation-side semiconductor in the S-scheme heterojunctions should be lower than those of the reduction-side photocatalyst to facilitate the formation of a directional driving force for the photogenerated electron-hole pairs^[4,59]. Hence, the coordination of band structures between CdS and CuO are energetically favorable for the construction of S-scheme heterojunction as estimated^[23,33,40,44].

EPR was carried out to validate the charge transfer mechanism of this S-scheme heterojunction, and further analysis the electric potentials of available e^- and h^+ . DMPO was utilized as radical capture reagent of superoxide radical ($\cdot O_2^-$) and hydroxyl radical ($\cdot OH$), which respectively represents the reducibility and oxidizing ability. As shown in Figure 5(a) and (b), no signal of DMPO- $\cdot O_2^-$ (1:1:1:1 peak intensity) and DMPO- $\cdot OH$ (1:2:2:1 peak intensity) can be found in dark (dark, 0 min), indicating that there is

almost no valid e^- or h^+ are produced. After irradiation for 2 min, the signal of DMPO- $\cdot O_2^-$ was readily detected in pristine CdS, while no signal could be found in pristine CuO, which can be attributed to the more positive E_{CB} of CuO than that of O_2/O_2^- (-0.33 eV vs. NHE). As for $\cdot OH$, even though the production amount over both pristine catalysts are relatively weak, one can find CuO performs slightly better than CdS, indicating that the former can produce more h^+ . By contrast, the signals of both $\cdot O_2^-$ and $\cdot OH$ over CdS-CuO2:1 are much stronger, suggesting its powerful charge transfer efficiency for the attractive PHE performance. Assuming that the CdS-CuO catalyst is a type II heterojunction, there will be a contradiction that the photogenerated e^- in E_{CB} of CuO is not able to support the formation of $\cdot O_2^-$ radicals dominated by the potential of the O_2/O_2^- . Instead, it is more explicable that the photogenerated e^- is accumulated on the CB of CdS (the highest reduction potential), while the photogenerated h^+ transfers to the VB of the CuO (the highest oxidation potential), which agrees well with the features of S-scheme heterojunctions.

TPR and EIS results are depicted in Figure 5(c) and (d) to identify the efficiencies of charge separation and transfer. Similarly, CdS-CuO2:1 presents the smallest semicircle and higher photo-current density compared to the two counterparts of single component, which implies a lower potential barrier for the photo-generated carrier separation and transfer at the S-scheme heterojunction interface^[60–61].

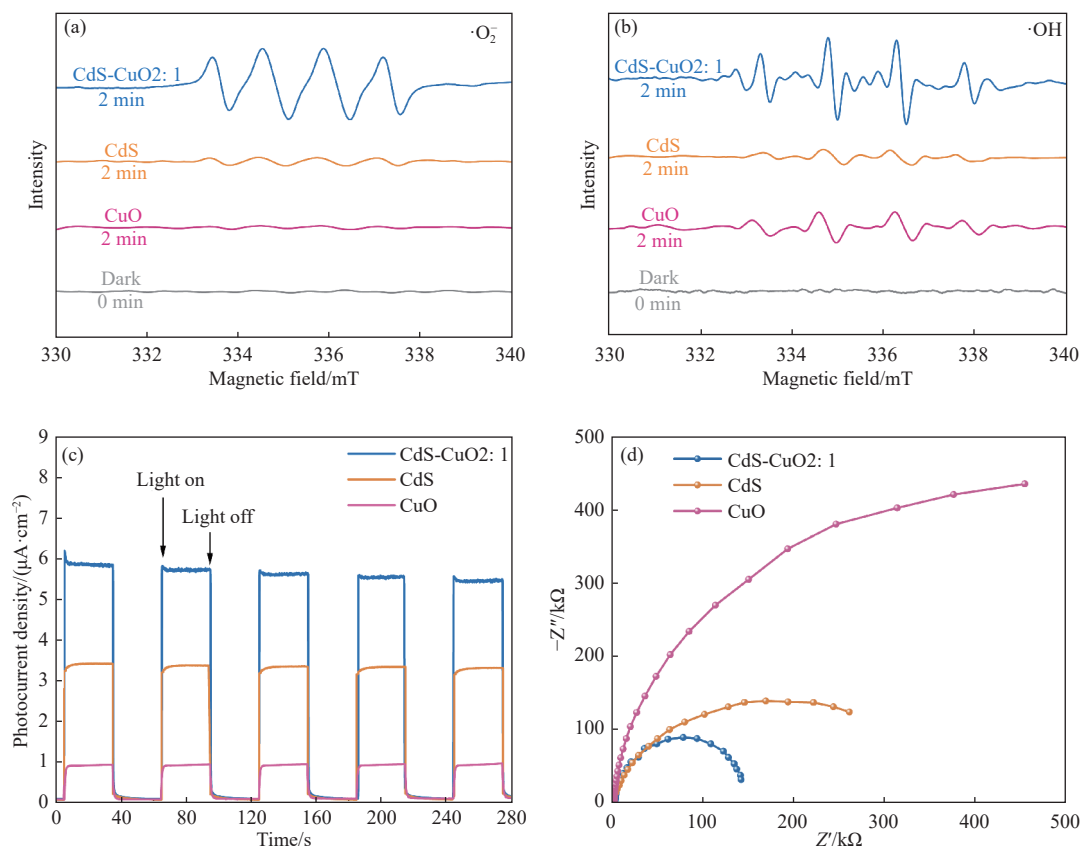


Fig. 5 (a) 5,5-dimethyl-1-pyrroline N-oxide (DMPO)- $\cdot O_2^-$ EPR; (b) DMPO- $\cdot OH$ EPR; (c) transient photocurrent response; (d) EIS Nyquist plots spectra of CdS, CuO and CdS-CuO2:1

2.4 DFT calculations

DFT calculations based on the Materials Studio is considered as an effective approach for unveiling the detailed mechanisms during PHE^[62]. Firstly, the models are established and verified to ensure the accuracy of the whole simulation^[63–65]. Figure 6(a) and (b) display the bandgap of CdS and CuO, which are calculated to be 2.26 and 1.642 eV respectively, and well coincided with the aforementioned experimental results. Meanwhile, both of them exhibit direct-bandgap semiconductor features, consistent with previous literature^[57–59]. Since the accuracy of models are verified, density of states (DOS) for CdS and CuO can be further calculated as shown in Figure 6(d) and (e). Clearly, the conduction band minimum (CBM) of CdS mainly consists of the *p* orbitals of S, while the valence-band maximum (VBM) is composed of the *d* orbitals of Cd and the *p* orbitals of S. The CBM of CuO is mainly contributed by the *s* orbitals of O, while its VBM is originated from the *d* orbitals of Cu and the *s* and *p* orbitals of O. Figure 6(c) provides the energy band structures of the CdS-CuO catalyst. The bandgap is calculated to be 1.748 eV, which matches well with the experimental results (1.73 eV). From the profiles of CdS-CuO heterojunction in Figure 6(f), it is observed that the O 2*s* orbitals comprise the majority of the VBM, while the Cd 3*d* mainly contributes to the CBM of the heterojunction. Hence, it could be concluded that the e^- from the CB of CuO transfers to CdS while the h^+ from the VB of CdS transfers to the CuO, which is consistent with the conclusions drawn by EPR (Figure 5(a) and (b)). In addition, more dense band distribution near the Fermi level can be found in the heterojunction than those of the single semiconductors, evidencing the formation of hybridized orbitals^[44,66–68]. This hybridization causes bonding resonances near Fermi levels in CdS-CuO heterojunction

and facilitates the electrons moving easily through the interface of the heterojunction, thus giving rise to high-efficiency electron transfer in CdS-CuO. This enhancement serves as another major factor to improve the photocatalytic activity, which is in complement to the band structure results (Figure 2) and the SPV characterizations (Figure 4(a)).

2.5 Charge transfer mechanism

As evidenced previously, an IEF was generated at the interface by combining two semiconductors with different E_f ^[4,30,44]. The work function (Φ), defined as the energy difference between the vacuum and Fermi levels, can precisely evaluate the electron transfer capacity within heterojunctions^[44,69–70]. It can be obtained via the formula $\Phi = E_{vac} - E_f$, where E_{vac} and E_f represent the energy of vacuum level (assumed as 0 eV) and Fermi level^[44,71]. Figure 7(a) reveals the work function of CdS (5.42 eV) and CuO (7.02 eV). The difference of E_f between CdS and CuO (1.6 eV) permits a powerful driven force for the electron transfer from CdS to CuO, and thus generates an IEF pointing from CdS to CuO. To further analyze the electron transport properties based on the band structures of the CdS-CuO heterojunction, the EDD located at the interface was simulated and shown in Figure 7(b). Obviously, the electron cloud around CuO region (yellow) is much more enriched than that in the CdS region (blue), indicating the electron transferring from CdS to CuO in the composite^[72]. An asymmetric charge distribution is formed at the interfacial region. Electron depletion and accumulation separately occur in CdS and CuO, which are in good agreement with the results obtained from the XPS experiments as discussed above (Figure 2), confirming the formation of IEF between CdS and CuO.

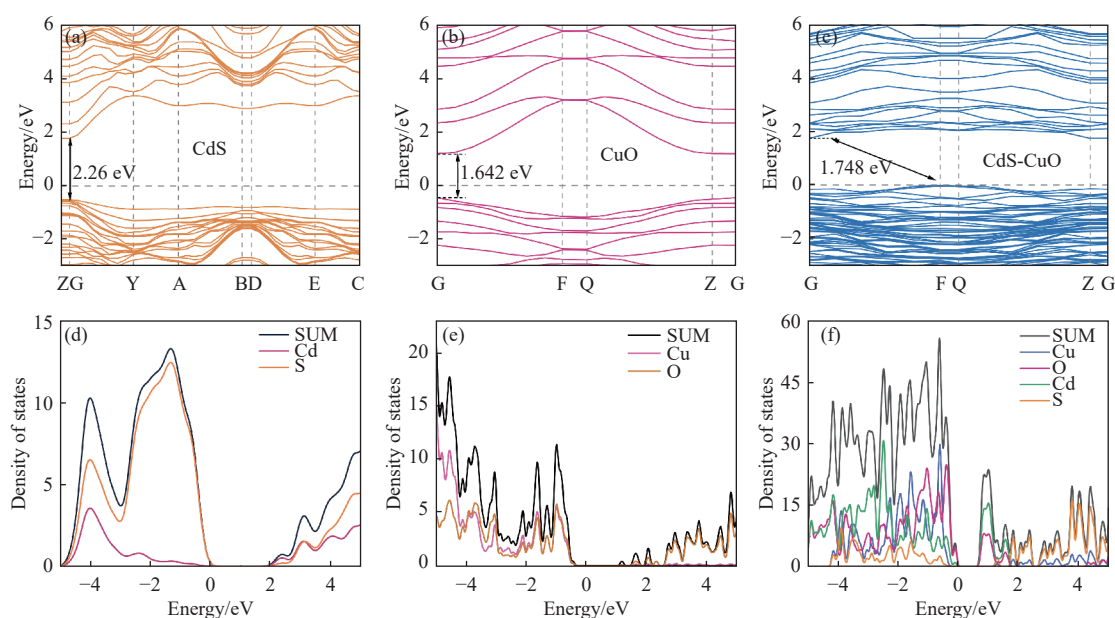


Fig. 6 Calculated band structures of (a) CdS, (b) CuO and (c) CdS-CuO heterostructure; Calculated DOS of (d) CdS, (e) CuO and (f) CdS-CuO heterostructure

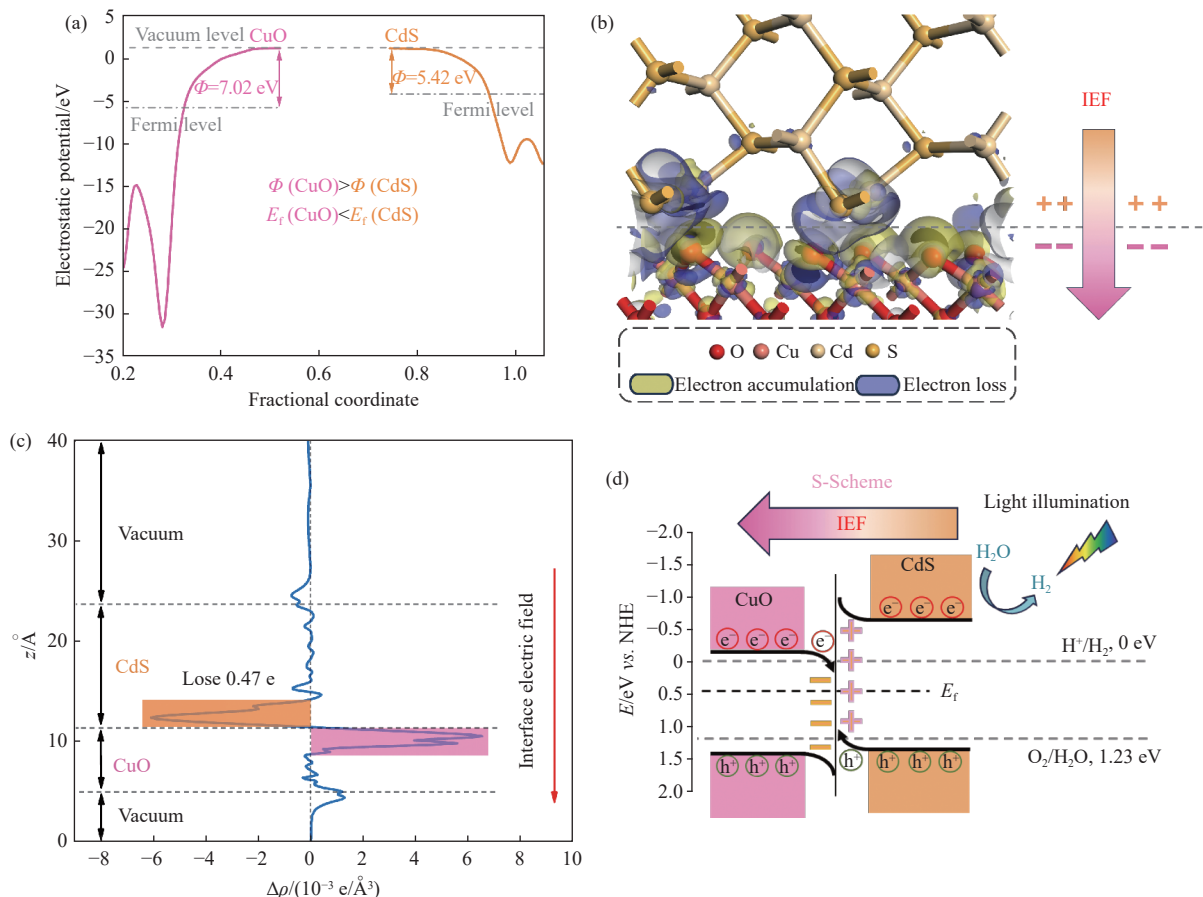


Fig. 7 (a) Calculated average potential profile along the z axis of CdS and CuO; (b) Electron density difference between CdS and CuO heterostructure; (c) Planar-averaged electron density difference $\Delta\rho(z)$ for CdS-CuO along z axis and Schematic for internal interfacial electric field; (d) Schematic for S-scheme heterojunction between CdS and CuO

Moreover, to visualize the charge transfer between CdS and CuO, Figure 7(c) presents the electron transfer curve along the z -direction of the vacuum layer, which can directly reflect the change of the charge density at the heterojunction interface. The accumulation and the depletion of electrons are intuitively exhibited by positive and negative values. Obviously, 0.47 e is transferred from CdS to CuO after the construction of heterojunction, owing to their different work functions^[4,45,51]. By virtue of the noticeable electron transmission, the CuO region becomes nucleophilic (Figure 7(b) yellow region), while the CdS region is electrophilic (Figure 7(b) blue region). Thus, the result further validates the occurrence of charge transfer between CdS and CuO, as well as the existence of the interfacial electric field. This, in turn, leads to a remarkable efficiency in the transfer of photogenerated electrons to the surface of CdS during the photocatalytic reaction.^[33–34,73–74]

In this case, the charge transfer mechanism is well unraveled and coincides with the above experimental and calculation results. The excellent photocatalytic performance of this CdS-CuO composite relies on the formation of S-scheme heterojunction. The overall reaction mechanism is proposed, as depicted in Figure 7(d). At the interface, electrons transfer to the CdS from CuO after the combination and generated an IEF pointing from CdS to

CuO. Under the action of Coulombic attraction, the VB of CdS at the interface bends upward, and the CB of CuO bends upward. This enables the photogenerated electrons and photogenerated holes, to be effectively separated and transferred to the surface of CdS and the surface of CuO, which have higher reduction and oxidation potentials. As a result, highly efficient photocatalytic hydrogen evolution is achieved.

3 Conclusion

In summary, the metal sulfide/oxide, CdS and CuO, were utilized to construct heterojunctions for PHE. A series of S-scheme heterojunctions have been successfully designed and fabricated through simple physical combination method. By adjusting the proportion of CdS and CuO, these two semiconductors were uniformly and intimately assembled to generate the heterojunctions, which exhibit greatly improved PHE efficiency (maximum 18.89 mmol/(h·g), 4.15 times higher than that of CdS). Via the results of XRD, HRTEM and XPS, the existence of electron transfer between CdS and CuO is explicitly confirmed. Comprehensive characterizations, including UV-vis DRS, TPR and SPV, demonstrate that the built-in field locates

between the highest occupied molecular orbital of CdS and the valence band (VB) of CuO, symbolizing the successful fabrication of the S-scheme heterojunction. With the aid of EPR analyses, the charge transfer mechanism is further discussed. The energy band structures and electron density difference calculations based on the DFT confirm that the enrichment and directional transfer of photoexcited e^- and h^+ between CdS and CuO are induced by the IEF, which further contributes to the efficient PHE rate and high stability of the as-prepared photocatalysts. This work replenishes the photo-catalysis mechanism of S-scheme heterojunctions and explores the design of efficient and stable PHE photocatalysts.

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Declaration of Competing Interest

The authors declare no conflict of interest.

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CdS-CuO 异质结的 S 型传输机制增强光催化析氢效率

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摘要: 光催化析氢催化剂的效率和稳定性在很大程度上受异质结内电荷转移的影响。在本研究中, CuO 作为一种典型的具有宽光谱吸收范围的半导体, 作为电子受体与 CdS 结合, 构建了 S-scheme 异质结, 其最佳配比 (CdS-CuO₂:1) 产氢效率高达 18.89 mmol/(g·h), 是纯 CdS 的 4.15 倍, 纯 CuO 的 5.88 倍。通过 X 射线光电子能谱 (XPS) 及紫外可见漫反射吸收光谱证明了符合 S 型能带结构排布, 并且表面光电压 (SPV) 和电子顺磁共振 (EPR) 表明 CdS-CuO₂:1 在光照下光生电子转移至还原电位更高的 CdS 的导带, 光生空穴转移至氧化电位更高的 CuO 的价带, 符合 S 型异质结电荷转移机制。通过电荷差分密度模拟计算了 CdS-CuO 异质结界面处的电荷分布发现, 其在界面处形成了由 CdS 指向 CuO 的界面电场。在界面电场的作用下, CdS-CuO 复合 S 型异质结的光生载流子分离及迁移效率得到提升, 进而提升光催化产氢效率。本研究为设计具有高光利用率的 S 型异质结提供了一种新的策略, 旨在实现高效的绿色能源生产。

关键词: 光催化析氢; CdS-CuO s 型异质结; 电子定向传输; 界面电场; DFT 计算

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