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Article

An effective CdS/Ti-Fe₂O₃ heterojunction photoanode: Analyzing Z-scheme charge-transfer mechanism for enhanced photoelectrochemical water-oxidation activity

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ABSTRACT

Z-scheme photocatalytic system has been regarded as a popular field of research in photoelectrochemical (PEC) water splitting. Among the many obstacles facing a Z-scheme photocatalytic system, the analysis methods of interfacial Z-scheme charge transfer still remain a significant challenge. Hence, in this study, CdS/Ti-Fe₂O₃ heterojunction photoanodes are elaborately designed to explore the charge-transfer behavior in PEC water splitting. In this study, photophysical measurements, including the Kelvin probe measurement, surface photovoltage spectroscopy (SPV), and transient photovoltage spectroscopy (TPV), are used to monitor the migration behavior of photogenerated charges at the interface electric field of CdS/Ti-Fe₂O₃ Z-scheme heterojunction photoanodes. The Kelvin probe and SPV measurements demonstrate that CdS/Ti-Fe₂O₃ interfacial driving force favors the rapid transfer of photoexcited electrons to CdS. The double-beam strategy based on TPV indicates that more electrons of Ti-Fe₂O₃ are combined with the holes of CdS owing to the intensive interface electric field. The results of these measurements successfully prove the Z-scheme migration mechanism of CdS/Ti-Fe₂O₃ photoanodes. Benefiting from the desirable charge transfer at the interface electric field, CdS/Ti-Fe₂O₃ photoanodes exhibit superior photocatalytic oxygen evolution reaction performance compared with that of pure Ti-Fe₂O₃. The photocurrent density of the 25CdS/Ti-Fe₂O₃ photoanode reaches 1.94 mA/cm² at 1.23 V versus reversible hydrogen electrode without excess cocatalyst, and it is two times higher than that of pure Ti-Fe₂O₃ photoanode. Therefore, an outstanding strategy is provided in this study to prove the Z-scheme charge-transfer mechanism of photocatalytic systems in PEC water splitting.

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1. Introduction

Photoelectrochemical (PEC) water splitting has been regarded as an effective means of solving the energy crisis. Typically, the efficiency of PEC water splitting is limited by the oxygen evolution reaction (OER), because the water oxidation re-

action is a challenging four-proton/four-electron process [1,2]. Therefore, exploration of eminent photoanodes is an effective means of improving the PEC efficiency. However, a single photoanode yields a low photocatalytic performance, which cannot meet the needs of commercial applications. Therefore, construction of heterojunction photoanodes in photocatalytic sys-

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tems has been viewed as a promising strategy to further improve the photocatalytic efficiency [3]. Recently, the Z-scheme photocatalytic system with its Z-scheme heterojunction photoanode has garnered the interest of researchers. This is because the Z-scheme photocatalytic system can enhance the separation efficiency of photogenerated charge by allowing the excited electrons of photosystem II (PSII) to recombine with the holes of photosystem I, leading to the accumulation of additional holes on the surface of PSII for the OER in water splitting [4,5]. In the last few years, Z-scheme photocatalytic systems have been constructed by applying noble-metal mediators (such as Pt, Ag, and Au) and graphene in the field of water splitting [6,7], such as $\text{TiO}_2\text{-Au-CdS}$ [8], $\text{rGO/InVO}_4\text{/Fe}_2\text{O}_3$ [9], and $\text{WO}_3\text{/Au/CdS}$ [10]. However, noble-metal mediators absorb part of the visible light, accounting for the reduced light absorption of semiconductor photocatalysts. Therefore, to overcome this shortcoming, direct Z-scheme systems without the noble-metal mediators have received widespread interest [3]. Various direct Z-scheme photocatalysts, such as $\text{WO}_3\text{/n-Si}$ [11], $\text{ZnIn}_2\text{S}_4\text{/VS}_2$ [12], ZnO-WO_{3-x} [13], and $\text{TiO}_2\text{/Cu}_2\text{O}$ [14], have been reported in recent years. Unfortunately, the low efficiency of PEC water splitting limits their further application [1,15]. Consequently, it is necessary to design direct Z-scheme photoanodes with a high efficiency for PEC water splitting.

Among various photoanode materials, hematite ($\alpha\text{-Fe}_2\text{O}_3$) has been regarded as an ideal candidate in PEC water splitting for the photocatalytic OER process [16–18], owing to its suitable energy-band structure, topping stability in an alkaline solution, and theoretical solar-to-hydrogen efficiency of 15.8% [19–23]. Nevertheless, its shortcomings, such as short hole diffusion length and severe bulk recombination, can result in a low efficiency of photocatalytic OER. Furthermore, CdS with its narrow band gap (2.4 eV) is also considered as an excellent photocatalyst for hydrogen production through solar water splitting [24–26]. Examples of CdS-based photocatalysts are 2D-2D CdS/ Ni_2SP composites [27], 2D-2D CdS/ Cu_7S_4 layered heterojunctions [28], and $\text{MoS}_2\text{/CdS}$ heterojunctions [29]. However, the photo-corrosion phenomenon accounts for their instability in PEC water splitting. Therefore, the construction of the heterojunction by combining CdS and $\alpha\text{-Fe}_2\text{O}_3$ has increased widespread attention [30,31]. This combination could not only decrease the bulk recombination of Fe_2O_3 , but also avoid photo-corrosion of CdS in PEC water splitting; hence, it is highly desirable to develop robust $\text{Ti-Fe}_2\text{O}_3$ -based Z-scheme heterojunction photoanodes for PEC applications.

Typically, it is a challenge to prove the Z-scheme mechanism in heterojunctions. In recent years, several methods have been proposed to prove the Z-scheme mechanism, such as radical species trapping test, photo-deposition, and X-ray photoelectron spectroscopy (XPS) analysis. The radical species trapping test has captured the attention of several researchers [32–34]. For instance, the $\cdot\text{OH}$ radical trapping test was effectively applied to confirm the accumulation of photogenerated holes on semiconductors with high or low oxidation potential [35]. In addition, photo-deposition of metal nanoparticles was applied to directly confirm the reduction sites of the photocatalytic system, providing information regarding the Z-scheme me-

chanical migration pathway of photogenerated carriers [36]. Moreover, XPS characterization was extensively applied to ascertain the changes in the electronic density on the different surfaces of a photocatalyst through exploring the shift in the binding energies [37]. These methods successfully proved the Z-scheme heterojunction mechanism in different directions. However, there are very few reports on the Z-scheme migration behavior of photo-carriers at the interface electric field. According to our previous studies, photovoltaic technology can be used as an alternative method to explore the behavior of interfacial electron transfer [38,39]. Thus, it is necessary to prove the Z-scheme charge-transfer mechanism of CdS/ $\text{Ti-Fe}_2\text{O}_3$ heterojunctions through photovoltaic technology.

Therefore, in this study, CdS/ $\text{Ti-Fe}_2\text{O}_3$ heterojunction photoanodes are constructed to explore the charge-transfer behavior at the interface electric field. The Z-scheme charge-transfer mechanism of CdS/ $\text{Ti-Fe}_2\text{O}_3$ is fully demonstrated through the work function (WF), surface photovoltage spectroscopy (SPV), and transient photovoltage spectroscopy (TPV) measurements. It is worth noting that an in-depth study regarding the transmission path of carriers at the interface electric fields of CdS/ $\text{Ti-Fe}_2\text{O}_3$ is different from previous methods [40,41]. The results completely proved that the transfer path of the photo-generated holes of CdS/ $\text{Ti-Fe}_2\text{O}_3$ is from CdS to $\text{Ti-Fe}_2\text{O}_3$ at the interface, and the electrons of $\text{Ti-Fe}_2\text{O}_3$ recombine with the holes of CdS, accounting for the migration of additional holes to the $\text{Ti-Fe}_2\text{O}_3$ surface for PEC water splitting. Therefore, CdS/ $\text{Ti-Fe}_2\text{O}_3$ Z-scheme heterojunction photoanodes exhibit superior PEC performance than pure $\text{Ti-Fe}_2\text{O}_3$ photoanodes. Furthermore, these findings demonstrate that the construction of CdS/ $\text{Ti-Fe}_2\text{O}_3$ heterojunction photoanodes with the desirable orientations of the built-in electric field can facilitate a valid strategy to enhance PEC water splitting.

2. Experimental

2.1. Synthesis of CdS

The CdS nanoparticles were deposited onto a fluorine-doped tin oxide (FTO) glass (Nippon Sheet Glass) substrate (1 cm $\times$ 2.5 cm) through chemical bath deposition (CBD) according to previous reports, but with some modifications [42]. The FTO glass was sonicated for 20 min in deionized water, ethanol, acetone, ethylacetate, and ethanol successively before placing it into a Teflon-lined autoclave. The CBD solution was prepared by mixing 0.5 M KOH, 0.02 M $\text{CdCl}_2\cdot 2.5\text{H}_2\text{O}$, 1.5 M NH_4NO_3 , and 0.2 M $\text{CH}_4\text{N}_2\text{S}$ and stirring for 30 min. Subsequently, the transparent FTO, with the conductive side facing down, was placed obliquely in the CBD solution, and the mixture was kept in a 80 °C water bath for different durations (5, 25, and 50 min) to obtain the best photoanode. Finally, the FTO with CdS was washed with double-distilled water and dried in ambient air.

2.2. Synthesis of CdS/ $\text{Ti-Fe}_2\text{O}_3$

The $\text{Ti-Fe}_2\text{O}_3$ nanorod arrays were synthesized on CdS/FTO

through a hydrothermal method reported previously [43]. The precursor solution was prepared by dissolving 0.15 M iron chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), 1 M sodium nitrate (NaNO_3), and 1 mL 0.05% titanium tetrachloride (TiCl_4) ethanol solution (volume percentage) in the aqueous solution. Next, the FTO/CdS, with its conductive side facing down the Teflon-lined autoclave, was immersed in the abovementioned solution. Subsequently, the autoclave was transferred to an oven for 12 h, which was pre-adjusted to 100 °C. The synthesized FTO/CdS/Ti- Fe_2O_3 was annealed at 550 °C for 2 h under an argon atmosphere. According to the durations for the CBD of CdS (5, 25, and 50 min), the samples were denoted as 5CdS/Ti- Fe_2O_3 , 25CdS/Ti- Fe_2O_3 , and 50CdS/Ti- Fe_2O_3 , respectively. Ti- Fe_2O_3 was prepared using the same method.

2.3. Characterizations

X-ray diffraction (XRD; D/MAX2250) was used to characterize the phase structure of the samples in the 2θ range from 20° to 80° at a scan rate of 10°/min. The morphology and elemental composition of the samples were characterized through a field emission scanning electron microscopy (SEM; Hitachi Company) and high-resolution transmission electron microscopy (HRTEM; FEI Tecnai G2 F20). The chemical state of the elements was evaluated through XPS using the C 1s peak as a correction. The ultraviolet-visible (UV-vis) absorption spectrum of the samples was obtained for the range of 300–800 nm using an UV-vis-near infrared spectrophotometer (Shimadzu UV-3600). The separation and kinetic behaviors of photogenerated charge carriers were studied with the aid of lock-in-based SPV and TPV measurements according to our previous study [38,41]. The WF measurement was conducted using a Kelvin probe instrument (SKP 5050, KP Technology Ltd, UK).

2.4. PEC Measurements

All PEC measurements were performed using a 300-W xenon lamp (Micro Solar 300 Perfect Light) equipped with simulated AM 1.5 G illumination (100 mW/cm²) on the photoanode side with the help of an electrochemical station (CHI 660E) in a standard three-electrode configuration, which consisted of the prepared photoanodes, Pt, and Ag/AgCl as the working, counter, and reference electrodes, respectively. The applied potential versus Ag/AgCl was translated into potential versus reversible hydrogen electrode (RHE) based on the Nernst equation, as expressed in Eq. (1):

$$E_{\text{RHE}} = E^{\circ}_{\text{Ag/AgCl}} + 0.059\text{pH} + E^{\circ}_{\text{Ag/AgCl}} \quad (1)$$

The electrolyte in our PEC measurements was 1 M KOH (pH = 13.8) unless otherwise specified, and the active area was 0.283 cm². The current vs potential curve was obtained through linear sweep voltammetry at a scan rate of 10 mV/s. The electrochemical impedance spectroscopy (EIS) was measured with a frequency range of 10⁵–0.05 Hz to ascertain the charge transport of the photoanodes. Applied bias photon to current efficiency (ABPE) was calculated using Eq. (2):

$$\text{ABPE} = (J_{\text{light}} - J_{\text{dark}}) \times (1.23 - V_{\text{RHE}}) / P_{\text{light}} \quad (2)$$

where J_{light} and J_{dark} are the current densities of the synthesized photoanodes under illumination and in dark, respectively, V_{RHE} is the applied potential versus RHE, and P_{light} is the incident light intensity (100 mW/cm²). The accumulated charge densities of the CdS/Ti- Fe_2O_3 film were obtained by integrating the transient photocurrent density at different potential values of 0.8–1.6 V vs. RHE. The injection efficiency of the photoanode was obtained by employing 0.5 M H_2O_2 as a hole scavenger in 1 M KOH electrolyte; the oxidation of H_2O_2 is thermodynamically and kinetically more favorable than water. The injection efficiency (η_{inj}) was determined using Eq. (3):

$$\eta_{\text{inj}} = J_{\text{H}_2\text{O}} / J_{\text{H}_2\text{O}_2} \quad (3)$$

where $J_{\text{H}_2\text{O}}$ and $J_{\text{H}_2\text{O}_2}$ are the photocurrent density for PEC H_2O oxidation and PEC H_2O_2 oxidation, respectively.

3. Result and discussion

3.1. Characterization

XRD was used to determine the crystal structure of the obtained photoanode (Fig. S1(a)). It is evident that all diffraction peaks of CdS/Ti- Fe_2O_3 could be indexed to Ti- Fe_2O_3 (PDF#33-0664) and FTO. However, no clear diffraction peaks of CdS could be observed. This may be because of the relatively weak diffraction peak intensity of CdS, which could not be detected by XRD measurement. Hence, the XRD of CdS powder prepared by the same method was carried out to certify the crystalline structure of CdS (PDF#10-0454) (Fig. S1(b)). In addition, the morphology of Ti- Fe_2O_3 and CdS/Ti- Fe_2O_3 was characterized by SEM and TEM, respectively. Fig. 1(a) shows that the pure Ti- Fe_2O_3 nanorods with diameters of approximately 30 nm are in vertical alignment with the FTO substrate. In addition, the surface and dimension of 25CdS/Ti- Fe_2O_3 have no changes compared with the pure Ti- Fe_2O_3 , as shown in Fig.

Fig. 1. Top-view SEM images of Ti- Fe_2O_3 (a) and 25CdS/Ti- Fe_2O_3 (b); (c) HRTEM image of 25CdS/Ti- Fe_2O_3 ; (d) EDS elemental mapping of Fe, O, Cd, and S in 25CdS/Ti- Fe_2O_3 .

Fig. 2. XPS spectra of Fe 2p (a) and O 1s (b) from 25CdS/Ti-Fe₂O₃.

1(b). The pristine CdS exhibits a nanoparticle structure with a diameter of approximately 80 nm (Fig. S2). The HRTEM image of 25CdS/Ti-Fe₂O₃ displays an interplanar spacing of 0.22 nm, which is indexed to the (113) plane of Ti-Fe₂O₃ [44]. Another interplanar spacing of 0.17 nm obtained from the inner nano-rods corresponds to the (200) plane of CdS (Fig. 1(c)). The results of HRTEM demonstrate that the CdS/Ti-Fe₂O₃ heterojunction photoanode was successfully synthesized. Furthermore, energy-dispersive X-ray spectroscopy (EDS) elemental mapping illustrates the existence of a uniform distribution of Fe, O, Cd, and S elements in 25CdS/Ti-Fe₂O₃, as shown in Fig. 1(d).

The XPS analysis was used to further determine the valence and chemical composition of 25CdS/Ti-Fe₂O₃. The survey spectrum demonstrates the coexistence of Fe, O, and Ti elements. Fig. 2(a) shows three peaks at 710.20, 723.75, and 718.21 eV in the Fe 2p XPS spectrum, which correspond to Fe 2p_{3/2}, Fe 2p_{1/2}, and Fe³⁺, respectively [21]. The O 1s spectrum in Fig. 2(b) shows that the two peaks at 530.58 and 529.08 eV, identify the existence of O element in the form of oxide (O²⁻) [44]. The survey spectrum in Fig. S3(a) demonstrates the coexistence of Fe, O, Ti elements in 25CdS/Ti-Fe₂O₃. Fig. S3(b) demonstrates that the peak of Ti 2p at 457.2 eV is assigned to Ti⁴⁺ in Ti-Fe₂O₃. However, the S and Cd elements could not be detected owing to the complete coverage of Ti-Fe₂O₃.

3.2. Separation and transfer of photogenerated charge carriers

of CdS/Ti-Fe₂O₃

The UV/Vis diffuse reflection absorption spectra of pure Ti-Fe₂O₃ and CdS/Ti-Fe₂O₃ film is shown in Fig. S4(a). There is no clear change for CdS/Ti-Fe₂O₃ compared with the pure Ti-Fe₂O₃ in the absorption edge. To more accurately determine whether the load CdS influences the band gap of Ti-Fe₂O₃, the band gaps obtained by Tauc's plots of the absorption curves are shown in Fig. S4(b). The band gaps were 2.12, 2.12, 2.11, and 2.08 eV for Ti-Fe₂O₃, 5CdS/Ti-Fe₂O₃, 25CdS/Ti-Fe₂O₃, and 50CdS/Ti-Fe₂O₃, respectively. Based on the above analysis, we can conclude that there is no apparent change in the absorption edge for CdS/Ti-Fe₂O₃ and the pure Ti-Fe₂O₃. Therefore, light absorption is not the main reason for the enhancing catalytic performance.

SPV and TPV measurements (Introduction of instruments in support information) were performed to explore the separation efficiency of the photoanodes [45]. According to our previous report, the SPV and TPV signals could be used to analyze the surface charge behavior of photoanodes when illuminated from the FTO electrode side [20,45]. Moreover, the positive signal represents that the holes transfer to the surface and negative signal represents the migration of electrons to the surface. Fig. 3(a) shows the SPV spectra of CdS/Ti-Fe₂O₃ heterojunction films with front side illumination (the monochromatic light irradiated from the FTO electrode side). In this way,

Fig. 3. (a) SPV signal of Ti-Fe₂O₃ and CdS/Ti-Fe₂O₃ photoanodes. The inset shows the schematic of SPV measurements. (b) TPV signal of Ti-Fe₂O₃ and CdS/Ti-Fe₂O₃ photoanodes. The inset shows the schematic of TPV measurements.

most photons are absorbed by the Ti-Fe₂O₃ layer, and the photoinduced charge carriers are separated by the effect of the interfacial electric field. For CdS/Ti-Fe₂O₃, the SPV spectrum shows a positive response for all the response range, which indicates that photoinduced holes transfer to the irradiation side under the action of the interfacial electric field. Concurrently, photoinduced electrons accumulate at the CdS layer [46,47]. In addition, Fig. 3(b) shows the conventional TPV signal of the Ti-Fe₂O₃ and CdS/Ti-Fe₂O₃ electrodes under 532-nm laser pulse. Evidently, 25CdS/Ti-Fe₂O₃ has the strongest positive signal, meaning the highest separation efficiency compared with that of other samples. This result is consistent with the SPV results. Therefore, the built-in electric field at the CdS/Ti-Fe₂O₃ interface favors the photoexcited electron transfer to CdS.

3.3. Z-scheme charge-transfer mechanism

We assumed that CdS/Ti-Fe₂O₃ formed Z-scheme heterojunction photoanodes. In this Z-scheme system, electrons on Ti-Fe₂O₃ with lower conduction band potential combined with the holes on CdS with higher valence band potential, which could lead to the accumulation of additional holes in the surface of Ti-Fe₂O₃ for the OER in water splitting. Based on this assumption, we investigated the built-in electric field at the CdS/Ti-Fe₂O₃ interface, and the driving force at the interface

electric field was explored through the WF measurement. The WF (Φ) of the samples was tested through the Kelvin probe technique, which indirectly reveals the contact potential difference (CPD) between the samples and the Au probe. The WF values of CdS and Ti-Fe₂O₃ are calculated by the following Eq. (4):

$$\Phi_{\text{sample}} = \Phi_{\text{Au}} + e\text{CPD} \quad (\Phi_{\text{Au}} = 4.8 \text{ eV}) \quad (4)$$

As shown in Fig. 4(a), the CPD values of Ti-Fe₂O₃ and CdS are 110 and -320 mV, respectively. Therefore, the WF values of CdS and Ti-Fe₂O₃ are 4.48 and 4.91 eV, respectively, based on Eq. (4). These data indicate that the Fermi level of CdS is higher than that of Ti-Fe₂O₃. Hence, CdS could form an upward bend, whereas Ti-Fe₂O₃ could form a downward bend when they contact, which is beneficial for the electrons transfer from Ti-Fe₂O₃ to CdS. Clearly, it is reasonable to assume that the holes of CdS combine with the electrons of Ti-Fe₂O₃, leading to additional holes of Ti-Fe₂O₃ migrating to the surface for PEC water splitting. Hence, the interfacial electron transfer process of CdS/Ti-Fe₂O₃ may obey the Z-scheme charge-transfer mechanism.

To further ascertain the Z-scheme charge-transfer mechanism of CdS/Ti-Fe₂O₃, the interfacial charge-transfer behavior of CdS/Ti-Fe₂O₃ could also be studied using photovoltaic technology. According to our previous reports, the SPV and TPV signals can explain the charge-transfer process under the interface electric field when the sample is illuminated from the

Fig. 4. (a) WF mapping measurements of Ti-Fe₂O₃ and CdS; (b) SPV of Ti-Fe₂O₃ and 25CdS/Ti-Fe₂O₃; (c) TPV of Ti-Fe₂O₃ and 25CdS/Ti-Fe₂O₃; (d) SPV of Ti-Fe₂O₃ and Ti-Fe₂O₃/25CdS.

FTO substrate side [39,45]. Fig. 4(b) shows the SPV spectra of CdS/Ti-Fe₂O₃ heterojunction films with back side illumination (the monochromatic light irradiated from FTO substrate side). In this way, most photons are absorbed by the CdS layer, and the photoinduced charge carriers are separated by the effect of the interfacial electric field. For CdS/Ti-Fe₂O₃, the SPV spectrum shows a negative response for all the response range, which indicates that photoinduced electrons transfer to the irradiation side driven by the interfacial electric field. At the same time, photoinduced holes accumulate at the Ti-Fe₂O₃ layer to participate in the oxidation of water. In addition, Fig. 4(c) shows the TPV spectra of CdS/Ti-Fe₂O₃ heterojunction films from the back side under 532-nm laser pulse illumination. Compared with Ti-Fe₂O₃, the reduced positive signal indicates that more electrons have migrated to the illuminated side (CdS side) in a short time, and the increasing photovoltage signal can be seen for the CdS/Ti-Fe₂O₃ electrode in a short time, which implies that the CdS/Ti-Fe₂O₃ photoanode generates a smaller Schottky barrier under the influence of CdS during the electron transmission process, indicating a smoother electron transfer process. Based on the above analysis, additional CdS electrons migrate to the FTO substrate side, and additional holes migrate to the Ti-Fe₂O₃ side, so the CdS holes and Ti-Fe₂O₃ electrons could recombine by the effect of the interfacial electric field. Therefore, the results of SPV and TPV indicate that the electron transfer occurs from Ti-Fe₂O₃ to CdS driven by the formation of the interface electric field, which may follow the Z-scheme electron transfer mechanism.

Furthermore, for a comprehensive understanding of the Z-scheme charge-transfer mechanism of 25CdS/Ti-Fe₂O₃, other composites consisting of Ti-Fe₂O₃/CdS were prepared by exchanging the deposition order of Ti-Fe₂O₃ and CdS. Briefly, a Ti-Fe₂O₃ film was first synthesized by a simple hydrothermal reaction to obtain Ti-Fe₂O₃/FTO. After, the Ti-Fe₂O₃/CdS film was prepared by deposition of CdS on Ti-Fe₂O₃/FTO using the CBD method for different times (5, 25, and 50 min). In Fig. 4(d), the positive signal of the Ti-Fe₂O₃/25CdS is weakened compared with pure 25CdS when the sample is illuminated from the FTO electrode side through the SPV measurement. This

may be owing to additional CdS holes combining with electrons of Ti-Fe₂O₃, leading to the reduced number of holes on the surface of CdS. In Fig. S5, the positive signal of the Ti-Fe₂O₃/25CdS is weakened compared with that of pure 25CdS when the sample is illuminated from the FTO electrode side through the TPV measurement; this is consistent with the results from SPV. In addition, the results for Ti-Fe₂O₃/5CdS and Ti-Fe₂O₃/50CdS show the same tendency of Ti-Fe₂O₃/25CdS, as shown in Fig. S6. Therefore, the behavior of the electron transfer from Ti-Fe₂O₃ to CdS has been further confirmed.

To further prove the Z-scheme charge-transfer behavior of Ti-Fe₂O₃/CdS under an internal electric field, a double-beam strategy based on TPV measurements was adopted [8]. For the test, the sample was illuminated from the FTO electrode side with 532-nm pulsed laser, whereas a 405-nm laser illuminated the sample from the FTO substrate side, thereby further increasing the depletion width of CdS at the interface and strengthening the interface electric field under the double-beam. As shown in Fig. 5(a), the TPV signal observed when the sample is illuminated by the double-beam decreases when compared to that of the sample illuminated by the single beam (532-nm pulsed laser). This could be attributed to the additional electrons of Ti-Fe₂O₃ recombining with the holes of CdS under the internal electric field, resulting in a reduction of CdS holes. In addition, to further define the Z-scheme charge-transfer behavior, another strategy based on TPV was employed. Succinctly, the Ti-Fe₂O₃/25CdS sample was illuminated from the FTO substrate side with a 532-nm pulsed laser, whereas another 405-nm laser illuminated Ti-Fe₂O₃/25CdS from the FTO electrode side. As depicted in Fig. 5(b), the decreasing TPV signal of the sample when illuminated by the double-beam is also observed, because the combination of the electrons of Ti-Fe₂O₃ and the holes of CdS can lead to a reduction of Ti-Fe₂O₃ electrons. These results are consistent with the abovementioned results. Therefore, the Z-scheme charge-transfer mechanism of CdS/Ti-Fe₂O₃ was further confirmed, demonstrating that the behavior of interfacial electron transfer of CdS/Ti-Fe₂O₃ follows the Z-scheme electron-transfer mechanism.

Fig. 5. (a) TPV signal of Ti-Fe₂O₃/25CdS sample with FTO substrate side under 405-nm laser irradiation and FTO electrode side under 532-nm laser illumination; (b) TPV signal of Ti-Fe₂O₃/25CdS sample with FTO electrode side under 405-nm laser illumination and FTO substrate side under 532-nm laser illumination.

Scheme 1. Schematic band diagram of CdS/Ti-Fe₂O₃.

The schematic band diagram of 25CdS/Ti-Fe₂O₃ based on Z-scheme charge-transfer mechanism is illustrated in Scheme 1. Here, when CdS and Ti-Fe₂O₃ contact to form the Z-scheme heterojunction, the CdS could form an upward bend, whereas Ti-Fe₂O₃ could form a downward bend. As 25CdS/Ti-Fe₂O₃ is illuminated, the electrons on Ti-Fe₂O₃ with lower conduction band potential will combine with the holes on CdS with higher valence band potential, rather than combining with the conduction band of the CdS by overcoming the barrier. Thus, the charge-transfer efficiency of Ti-Fe₂O₃ could be improved by introducing CdS, which further leads to more holes transferring to the Ti-Fe₂O₃ surface for PEC water splitting.

3.4. PEC performance of CdS/Ti-Fe₂O₃ electrodes

To further verify that CdS/Ti-Fe₂O₃ Z-scheme heterojunction photoanodes could improve the separation efficiency of photo-generated charges, current density-potential curves under AM 1.5G illumination were explored. Fig. 6(a) shows the current density-potential curves of Ti-Fe₂O₃ and CdS/Ti-Fe₂O₃ photoanodes. It is evident that CdS/Ti-Fe₂O₃ has outstanding PEC performance compared with the pure Ti-Fe₂O₃. 25CdS/Ti-Fe₂O₃ exhibits the highest photocurrent density of 1.94 mA/cm² at 1.23 V vs. RHE, which is twice as high as that of the pure Ti-Fe₂O₃. In addition, Fig. 6(b) also shows that the ABPE value of 25CdS/Ti-Fe₂O₃ is 0.09% at 1.12 V vs. RHE is 2.25 times higher than that of Ti-Fe₂O₃. The excellent photocurrent density at 1.23 V vs. RHE and the higher ABPE value indicate that without co-catalyst addition, the improvement of

charge separation efficiency is the main factor leading to the outstanding PEC performance. In other words, owing to the effective separation and transport of interface charge, it is likely that more holes transfer to the Ti-Fe₂O₃ surface for PEC water splitting.

As we know, the reaction for PEC water splitting entails several critical factors, including light absorption, transport of the photogenerated charge carriers, and charge transfer at the solid-liquid interface for water splitting reaction. Compared with CdS/Ti-Fe₂O₃ and pure Ti-Fe₂O₃, there are no clear changes in light absorption. (Fig. S4) Therefore, the excellent photocurrent density at 1.23 V vs. RHE and the higher ABPE value of 25CdS/Ti-Fe₂O₃ without the addition of co-catalyst could be mainly attributed to the improvement of charge separation efficiency, and it also is the main factor for the outstanding PEC performance.

In addition, the injection efficiency and accumulation charge densities of the CdS/Ti-Fe₂O₃ Z-scheme heterojunction photoanode were applied to explore the charge transfer between Ti-Fe₂O₃ and the electrolyte. Fig. 7(a) shows enhanced injection efficiencies of CdS/Ti-Fe₂O₃ compared with the pure Ti-Fe₂O₃, meaning that more holes migrate to the surface of Ti-Fe₂O₃ for water splitting reaction, which agrees with the results from the separation efficiency measurements. Furthermore, the accumulated charge density of 25CdS/Ti-Fe₂O₃ decreased compared with pure Ti-Fe₂O₃ (Fig. 7(b)), suggesting the accumulation of more holes on the surface of Ti-Fe₂O₃ for PEC water splitting. The superior performance of the photoanode is further confirmed by measuring the incident photon to current efficiency (IPCE). Fig. 7(c) shows that the 25CdS/Ti-Fe₂O₃ heterojunction photoanode leads to intensive IPCE values in the wavelength range of 370–570 nm. More importantly, 25CdS/Ti-Fe₂O₃ can maintain approximately 95% of the initial photocurrent density at 1.23 V vs. RHE after 2 h photostability measurement in 1 M KOH, as shown in Fig. 7(d). These results indicate that the formation of the CdS/Ti-Fe₂O₃ Z-scheme heterojunction photoanode could improve the PEC performance and separation efficiency of photo-generated charges.

Furthermore, the EIS Nyquist plots are used to further analyze the interfacial charge-transfer kinetics of the Z-scheme CdS/Ti-Fe₂O₃ heterojunction photoanodes. The equivalent cir-

Fig. 6. (a) Current density-potential curves of Ti-Fe₂O₃ and CdS/Ti-Fe₂O₃; (b) ABPE of Ti-Fe₂O₃ and CdS/Ti-Fe₂O₃.

Fig. 7. (a) Injection efficiencies of Ti-Fe₂O₃ and CdS/Ti-Fe₂O₃ photoanodes; (b) Charge-accumulation densities of Ti-Fe₂O₃ and CdS/Ti-Fe₂O₃ photoanodes; (c) IPCEs at 1.23 V vs. RHE; (d) PEC stability test of the 25CdS/Ti-Fe₂O₃ photoanode at 1.23 V vs. RHE.

circuit diagram (inset of Fig. 8) is used to fit the EIS data and the specific data are presented in Table S1. Here, R_1 is related to the charge-transfer resistance in bulk photoanodes, whereas R_2 corresponds to transport resistance at the interface of photoanode and electrolyte [49,50]. The 25CdS/Ti-Fe₂O₃ displays the smallest R_1 among other modified electrodes (Fig. 8), indicating the lowest charge-transport resistance and the highest charge-transfer efficiency in the bulk. According to the fitted results in Table S1, CdS/Ti-Fe₂O₃ photoanodes, particularly 25CdS/Ti-Fe₂O₃, exhibit a decreased transfer resistance (R_2) at the Ti-Fe₂O₃ and electrolyte interface. These results indicate

that the reduced interface charge-transport resistance of CdS and Ti-Fe₂O₃ is beneficial for improving the interfacial charge-transfer kinetics and optimize the PEC performance.

4. Conclusions

Z-scheme CdS/Ti-Fe₂O₃ heterojunction photoanodes for PEC water splitting were fabricated onto an FTO substrate. The Z-scheme charge-transfer mechanism of CdS/Ti-Fe₂O₃ was successfully explored through Kelvin probe, SPV, and TPV measurements. Our results confirmed that the built-in electric field at the CdS/Ti-Fe₂O₃ interface favors the transfer of photo-excited electrons to CdS. Hence, the electrons of Ti-Fe₂O₃ recombined with the holes of CdS, promoting the transfer of additional holes to the surface of Ti-Fe₂O₃. Therefore, CdS/Ti-Fe₂O₃ heterojunction photoanodes exhibited outstanding PEC performance in water splitting, particularly, the photocurrent of the 25CdS/Ti-Fe₂O₃ photoanode reached 1.94 mA/cm² at 1.23 V vs. RHE. The improved PEC performance could be attributed to the excellent separation efficiency at the interfacial electric field. Ultimately, our study could also provide an effective method for verifying the Z-scheme charge-transfer mechanism.

Conflict of interest

The authors declare no conflict of interest.

Fig. 8. Nyquist plots of Ti-Fe₂O₃ and CdS/Ti-Fe₂O₃ photoanode at 1.1 V vs. RHE under AM 1.5G illumination (inset: equivalent circuit diagram).

Graphical Abstract

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**An effective CdS/Ti-Fe₂O₃ heterojunction photoanode:
Analyzing Z-scheme charge-transfer mechanism for enhanced
photoelectrochemical water-oxidation activity**

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As Ti-Fe₂O₃ and CdS make contact to form the Z-scheme heterojunction, the electrons of Ti-Fe₂O₃ recombine with the holes of CdS at the internal electric field, leading to more holes transferring to the Ti-Fe₂O₃ surface.

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高效的CdS/Ti-Fe₂O₃异质结光阳极：研究Z型电荷迁移机制增强光 电催化水氧化活性

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摘要: 近年来以Z型机制为转移的光催化体系成微光电化学分解水领域的研究热点。相比较传统的异质结, Z型异质结能够保留具有高氧化能力与高还原能力的位点, 从而提高光电化学效率。其中, 证明电荷的Z型迁移机制成为研究人员努力的方向, 比较有效的证明方法包括自由基捕获、XPS分析和检测还原位点等。对于Z型异质结, 界面电场处电荷的迁移行为是至关重要的, 但目前常用的证明手段对界面电场处电荷的迁移行为研究还比较少。因此, 本文精心设计了CdS/Ti-Fe₂O₃异质结光阳极来探索光电化学分解水中的电荷转移行为。采用开尔文探针测试、表面光电压谱测试和瞬态光电压谱测试等光物理测试手段监测CdS/Ti-Fe₂O₃ Z型异质结光阳极界面电场中光生电荷的迁移行为。其中, 开尔文探针和表面光电压测量表明, CdS/Ti-Fe₂O₃界面驱动力有利于激发电子快速迁移至CdS; 由于Z型异质结是一个双光子的过程, 因此在瞬态光电压的过程中采取了双光束策略, 即用不同波长的光分别从两个半导体侧进行照光, 以充分发挥内层CdS的电子传输层的作用。结果表明, 在双光束照射下界面电场增强, 使得更多Ti-Fe₂O₃电子与CdS空穴结合, 使得更多Ti-Fe₂O₃电子与CdS空穴结合, 更多的空穴迁移到Ti-Fe₂O₃的表面去参与反应, 充分证明了CdS/Ti-Fe₂O₃光阳极的Z型迁移机制。基于界面电场有效的电荷迁移与分离的分析, 对Z型异质结光阳极进行了光电化学的测试, 与单纯Ti-Fe₂O₃光阳极相比, CdS/Ti-Fe₂O₃光阳极表现出优异的光电化学性能。其中, 25CdS/Ti-Fe₂O₃光阳极的光电流密度在1.23V (相对于标准氢电极)达到1.94 mA/cm², 比单纯Ti-Fe₂O₃光电流高出两倍。阻抗测试结果表明, CdS/Ti-Fe₂O₃光阳极能够减小电荷传输阻力, 从而加快电荷分离效率, 这也间接证明了Z型光阳极的成功构筑, 因此, 本文提供了一个有效且新颖的手段来证明光电化学分解水中光催化系统的Z型电荷转移机制。

关键词: CdS/Ti-Fe₂O₃; Z型; 电荷迁移; 界面电场; 异质结光阳极

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