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Enhanced visible light catalytic activity of MoS₂/TiO₂/Ti photocathode by hybrid-junction

Chaoqun Cheng^a, Guohua Liu^b, Kang Du^a, Gang Li^c, Wendong Zhang^c, Simone Sanna^d, Yunzhong Chen^d, Nini Pryds^d and Kaiying Wang^{a,*}

^aDepartment of MicroSystems, University College of Southeast Norway, Horten 3184, Norway

^bState Key Laboratory of Alternate Electrical Power System with Renewable Energy Sources, North China Electric Power University, Beijing 102206, China

^cMicro and Nano System Research Center, Key Lab of Advanced Transducers and Intelligent Control System (Ministry of Education) & College of Information Engineering, Taiyuan University of Technology, Taiyuan, 030024, China.

^dDepartment of energy conversion and storage, Technical University of Denmark, Risø Campus, 4000 Roskilde, Denmark

Corresponding Author

*E-mail: Kaiying.Wang@usn.no

Graphical Abstract

Highlights

- MoS₂/TiO₂/Ti photocathode was facile fabricated with visible light responsivity.
- Enhanced catalytic activity under visible light illumination was achieved.
- The enhancement was due to improved charge separation, transfer and transport.
- A proper charge-carrier dynamics of hybrid-junction was proposed.

Abstract:

In photoelectrochemical (PEC) water splitting systems, crucial obstacles limiting their performance are poor charge carrier dynamics and high recombination rate of photoexcited electron hole pairs. Here, we report that this issue can be alleviated by engineering a hybrid-junction that is composed of homo- and hetero- junctions. This strategy is performed by facile hand-spraying MoS₂ over the surface of a anatase/rutile homo-junction TiO₂ film on the Ti

substrate to further form a hybrid-junction photocathode. By applying this photocathode into PEC reactor, enhanced catalytic activity is achieved under visible light (AM1.5 illumination of 300 W/m²) with hydrogen evolution reaction (HER) potential of -114 mV versus reversible hydrogen electrode (RHE) at 10 mA/cm² and long-term stability of more than 10 times improvement comparing to ordinary electrode without the introduction of hybrid-junction. The hybrid-junction that effectively regulates charge separation and transfer pathways is proven to be responsible for the enhanced activity. As a novel exploration, this hybrid-junction system comprising of low-cost, efficient charge separation and transfer, and visible light responsivity offers a new path for relative materials to boost their PEC performance.

KEYWORDS:

hybrid-junction, water splitting, titanium dioxide, Z-scheme, molybdenum disulfide

1. Introduction

Photoelectrochemical (PEC) water splitting system harvesting sunlight to drive uphill water splitting reactions has been the focus of attention due to its potential of converting sunlight into chemical fuels in a cost-economical and sustainable way ^[1-4]. In the past decades excellent advancement has been achieved, specially the metal oxide semiconductor has been invested greatly due to their intrinsic nature of the d orbital states, earth-abundance and superior PEC performance ^[5-8]. However, their PEC performance to the practical commercialization is still subjected to the limitations of poor charge-carrier dynamics and high recombination rate issues under the solar illumination ^[9,10]. To solve these issues, some efforts have been made to pursue reliable strategies in particular the search for hybrid systems ^[3,11-13].

Hetero- and homo-junctions are two distinctive approaches used in the hybrid systems^[14,15]. The designing of hetero-junction is a well-established approach as it holds great potential to overcome the drawbacks of serious charge recombination and limited visible-light utilization^[16], typically involving building an advanced two-step (Z-scheme) system. The Z-scheme system composed of two semiconductors with desired band gaps and energy positions ensure that the separated electrons and holes transport only in opposite directions toward surface for preferred reactions, minimizing deleterious recombination and undesirable side reactions^[17, 18]. Z-scheme construction can not only regulate charge transfer pathways but also increase the sunlight utilization through the series connected two semiconducting materials with narrow bandgap absorbing visible light^[19,20]. As an example, there have been reports that Z-scheme hetero-junction of MoS₂/TiO₂ with CdS quantum dots can effectively improve the catalytic activities under the visible light irradiation as the result of beneficial charge interaction in the interface^[21]. Recent studies have also demonstrated that the excellent catalytic activity in the heterojunctions of MoS₂/TiO₂ is related to the strong interaction between the MoS₂ and TiO₂^[22-27].

On the other hand, the construction of homo-junction (phase-junction) is an alternative configuration access to charge separation because the formation of homo-junction between two distinct phases can adjust the transport of the charge carriers along the inter-phases band alignment^[9]. For example, it has been reported that surficial phase-junction between the nanoparticles of anatase and rutile TiO₂ can enhance the water splitting activities^[28]. The basic mechanism is that the surficial anatase/rutile phase junctions can guide the electrons or holes transferred between band structures of rutile and anatase TiO₂, thereby facilitating separation of electron-hole pairs and catalytic activities^[28-30].

Although configuring hetero-junction or homo-junction is well explored, the potentials of integrating hybrid-junction comprising of hetero-junction and homo-junction into a single photoelectrode is still lack of investigation, especially in terms of the impact on charge carrier dynamics. In the heterogeneous system, the doping of foreign elements ^[31-33] was explored to provide multi-channel paths for improving the charge-carrier dynamics. In this study, we propose a facile strategy of building hybrid-junction to improve the catalytic activity of photocathode under visible light. We demonstrate that integration of homo-junction and hetero-junction on the bulk metal substrate as a simple but effective strategy could effectively fast the performance of charge separation, transfer and transportation dynamics at the interface and reduce charge carrier recombination in the bulk and at the surface.

We fabricated hybrid-junction of MoS₂/TiO₂ by hetero-coupling MoS₂ and homo-junction (mixed-phases) TiO₂ on the substrate of Ti foil. The hybrid-junction MoS₂/TiO₂ exhibits high activities under a visible light irradiation (AM 1.5G illumination of 300 W/m²) with hydrogen evolution reaction (HER) potential of -114 mV versus reversible hydrogen electrode (RHE) at 10 mA/cm², as well as long-term stability for more than 12 hours at -0.3 V vs RHE while comparing to about 1 hour without the introduction of hybrid-junction under same measurement conditions, more than 10 times improvement. The homo-junction TiO₂ thin layer on the substrate of Ti was synthesized through simple one-step thermal annealing process, different from traditional synthesis using hydrothermal or sol-gel methods ^[34-36]. The characterization on the HER activities suggest the homo-junction TiO₂ on the substrate of Ti could facilitate charge separation and transportation under the visible light illumination. After the hetero-coupling with MoS₂ constructed as hybrid-junction system, this cathode composite of MoS₂/TiO₂ on the substrate Ti exhibit higher activity and stability during the HER. The underlying charge transfer analysis

elucidated that the hybrid-junction of Z-scheme hetero-junction and homo-junction plays important roles in the excellent performance.

2. Experimental section

2.1. Materials

Commercially Molybdenum disulfide (MoS_2) microflakes liquid-spraying was purchased from CRC Industries Americas Group. Titanium foils (Ti foils, 30 mm $\times$ 14 mm $\times$ 0.5 mm, 99.8 % purity) were cut out from Ti sheet, which was purchased from Baoji Titanium Industry Co., LTD. Ethanol, acetone, isopropanol and deionized water were obtained from Sigma-Aldrich without further purification.

2.2. Preparation of homo-junction TiO_2 and $\text{MoS}_2/\text{TiO}_2$ composite electrodes

The fabrication consists of oxidation, spraying and annealing processes. Initially, Ti foils were cleaned by immersing the foils into the acetone rinsed by ultrasonic bath and subsequently dried in flowing nitrogen gas. After the initial cleaning step, Ti foils were oxidized at 400, 500 and 600 °C for 2 hours with oxygen gas continually flowing through the quartz tube furnace to generate a thin layer of homo-junction TiO_2 on the surface of the Ti foil (Figure S1). Following the oxidation step, commercial lubricating MoS_2 spray (CRC Industries) was applied to the TiO_2/Ti , followed by baking at 100 °C in the oven with ambient atmosphere for 10 hours to ensure that all the solvent is evaporated. In the last annealing process, the pristine $\text{MoS}_2/\text{TiO}_2/\text{Ti}$ foils were annealed at 500 °C for 1, 2, and 3 hours, respectively in Nitrogen atmosphere under ambient pressure and cooled to the room temperature.

2.3. Physical Characterization

Surface morphology of as-prepared samples was examined by field emission scanning electron microscopy (FESEM) (Hitachi, SU 8230) equipped with energy-dispersive X-ray spectrum (EDS)

and electron backscatter diffraction (EBSD) microstructural-crystallographic characterization. Atomic force microscopy (AFM, Parker XE 200) was used to visualize surface the topography of samples on the nanometer scale. UV-Vis light absorption spectra of the as-prepared samples were obtained using a SHIMADZU, UV-2600 spectrophotometer equipped with an integrated sphere assembly using diffuse reflection method. BaSO₄ was used as a reference to measure all samples in the wavelength range of 250 - 800 nm with a slit width of 1 nm. X-ray diffraction (XRD) patterns were collected on a Bruker D8-Advance diffractometer using Cu K α radiation ($\lambda = 1.5405 \text{ \AA}$) in a range of 2-80° at a scan rate of 5°/min. Photoluminescence (PL) spectra were performed in the FS5 Spectrofluorometer of Edinburgh Instruments by focusing the laser radiation centered at 400 nm from an Xeon lamp onto the samples.

2.4. Photoelectrochemical Measurement

PEC/Electrochemical measurements with/without simulated solar light illumination were performed and evaluated in a standard PEC three electrodes setup which is connected to electrochemical workstation (Zahner Elektrik IM6). The incident light was filtered through AM 1.5G solar simulator over an adjustable 500 W Xeon lamp (AM 1.5G, 300 W/m²). The as-prepared composites, platinum gauze and Ag/AgCl with saturated KCl solution were used as working, counter and reference electrodes. In the text, the measured potentials *vs.* Ag/AgCl were all changed to the RHE scale based on the Nernst equation: $E_{\text{RHE}} = E_{\text{Ag}}/E_{\text{AgCl}} + \text{pH} * 0.059 + 0.1976$. All the current density reported in the work were calibrated using IR compensation, where the R (resistivity) was estimated by electrochemical impedance spectroscopy (EIS) with a frequency ranging from 10 Hz to 1 M Hz.

Linear scanning voltammetry measurements were carried out in 0.5 M H₂SO₄ at a constant scan rate of 20 mV/s over the potential range of -0.6 - 0 V (vs RHE). A long-term stability test for

MoS₂/TiO₂ and MoS₂/Ti were conducted by an extended electrolysis (15 hours) under dark or light conditions at a constant reduction potential of -0.3 V vs RHE. EIS test were carried out at open-circuit potential by applying an AC potential with amplitude of 50 mV during the frequency range of 4×10^5 to 10^{-3} Hz in 0.5 M H₂SO₄ with/without the AM 1.5G illumination (300 W/m²). Mott-Schottky plots were obtained at frequencies of 5, 10 and 15 kHz and amplitude of 10 mV in 0.5 M H₂SO₄ solution under the dark or light conditions. In addition, current density-voltage (J-V) characteristic in an anodic direction was acquired at a scan rate of 20 mV/s. The measurements were carried out in a solution of Na₂SO₄ (pH 6.8) and subsequently in another solution of 1 M KOH (pH 13).

3. Results and discussion

3.1. Homo-junction TiO₂ on the substrate of Ti

Homo-junction TiO₂ was synthesized on the surface of Ti foil using simple one-step annealing process, as presented in the experimental section. The presence of homo-junction (mixed-phases) TiO₂ on the surface of Ti foil after the annealing process was determined by X-ray diffraction (XRD) and electron backscatter diffraction (EBSD). Figure 1a shows the XRD patterns of TiO₂ at temperature ranging from 400 °C to 600 °C, in which both anatase or rutile TiO₂ could be observed (Figure S2). Figure 1b presents the EBSD mapping, clearly showing the mixed-phases orientation mapping on the surface with assorted colors.

Figure 1c shows the UV-Vis absorption spectra, indicating a strong resonant visible light absorption peak around 480 nm at 500 °C [37-40]. Figure 1d further shows the UV-vis absorption spectra, in which the absorption edge wavelength of material moves to the infrared light area in the direction of longer wavelength as the processing temperature increases gradually, confirming the dependence of resonance absorption wavelength on the microscopic changes of surficial

mixed-phases TiO₂ induced by the elevated thermal treatment in the temperature range (Figure S4) [37, 41].

Figure 2 show *J-V* plots of proton reduction with/without AM 1.5G illumination and corresponding Tafel slope values. Figures 2a-c show *J-V* curves measured in dark and light respectively. As seen from these figures, TiO₂/Ti (400 °C) and TiO₂/Ti (500 °C) exhibit better reduction activities under the light condition, while TiO₂/Ti (600 °C) itself shows a poor reduction current under light, even worse than that in dark. This difference is consistent with the differential absorption spectra in the Figure 1c. For the TiO₂/Ti (500 °C), an overpotential of 216 mV at 10 mV/cm² was achieved under the application of light, almost 50% improvement comparing to the 403 mV under the dark condition, suggesting that TiO₂/Ti (500) has better PEC activities in the visible light range. Figure 2d presents the Tafel slope for the TiO₂/Ti under the dark and light, in which the TiO₂/Ti (500 °C) has a lower Tafel slope value of 159 mV/decade, and thus was better activity than the others. Since the Tafel slope value is close to the Volmer reaction regime (120 mV/decade) [42,43], the rate-limiting step here is the electrochemical adsorption step due to a limited amount of surface active sites.

3.2. Hybrid-junction MoS₂/TiO₂/Ti electrode

The investigation suggests that the homo-junction TiO₂ on the substrate of Ti has favourable charge transfer features under the visible light illumination but is restricted by the deficient surface sites which could increase the rate of interfacial charge transport. To eliminate the deficit, the homo-junction TiO₂ was covered by hand-spraying thin layer of commercial MoS₂, forming a functional complementary hetero-junction system. In addition to the merits of containing no precious metals and earth abundance, MoS₂ with large amount of edges could also offer enough active sites for HER activities [7,44]. The commercial MoS₂ nanoflakes liquid-spraying received our

attention due to the universal of this method enabling easy-fabricating hetero-junction system. Figure 3(a) shows the facile and cost-efficient processes for fabricating the novel hybrid-junction $\text{MoS}_2/\text{TiO}_2$. All the prepared samples at different processes are noted respectively as Ti (**A**), homo-junction TiO_2/Ti (**B**), pristine $\text{MoS}_2/\text{TiO}_2/\text{Ti}$ (**C**) and annealed $\text{MoS}_2/\text{TiO}_2/\text{Ti}$ (1h/2h/3h) (**D/E/F**).

Figure 3(b) shows SEM top-view images of the TiO_2 (sample **B**), pristine $\text{MoS}_2/\text{TiO}_2/\text{Ti}$ (noted as $\text{MoS}_2/\text{TiO}_2$, sample **C**) and annealed $\text{MoS}_2/\text{TiO}_2/\text{Ti}$ ($\text{MoS}_2/\text{TiO}_2$, sample **D**, **E** and **F**). The morphology of the materials TiO_2 on the surface is shown in Figure 3 (b)-**B**. The as-received (without thermal treatment) pristine MoS_2 shows rough and irregular surface morphology. Upon annealing at 500 °C in the nitrogen atmosphere, much more dense structure with small pores on the surface is observed in the sample **E**, mainly due to the thermal treatment which crystalizes the surficial MoS_2 microflakes ^[43]. Favouring the specific surface area, these top-porous networks offer more edge sites allowing for HER reactions ^[45]. Furthermore, the thin layer of continuous network structure on the surface provides an accessible tunnel for light penetrating to the inner part of TiO_2 . After longer annealing time, the undersigned damage to the surface structure could be observed as the potholes in the surface of sample **F**. Figure S6 show the energy dispersive X-ray spectroscopy (EDS) mapping, confirming that the Ti, O, Mo, and S species existed in the multi-layered film composites. To verify the thickness of MoS_2 and the MoS_2 wrapped on the surface of particles, a cross-sectional FESEM analysis was conducted (Figure S7a, b). The FESEM images show distinct wrapping of MoS_2 , with measured thickness of 1.30 μm (MoS_2 pristine) and 400 nm (MoS_2 2h). Element-specific analysis was performed by the dedicated Line-scan EDS along the direction of bottom to surface (Figure 1c), indicating existence of the material of MoS_2 . The morphology of MoS_2 wrapped on the surface of particles was further confirmed by AFM surface topology (Figure S7d).

Figure 3(c) shows the XRD patterns of five as-prepared hybrid-junction samples. Before spraying MoS₂, the peaks of (112) and (204) facets of anatase TiO₂ and (111) facet of rutile TiO₂ could be observed in Figure 3(c)-B (Anatase PDF 00-021-1272; Rutile PDF 00-021-1276). After annealing, the diffraction characteristic peaks of TiO₂ are still observed in the patterns of MoS₂/TiO₂ composites with grown crystallite size and strength after the thermal treatment. The peaks centered at 26° and 28.7° can be assigned to (101) facet of anatase TiO₂ and (110) facet of rutile TiO₂ (Anatase PDF 00-021-1272; Rutile PDF 00-021-1276). For MoS₂, the detected signals located at 29.5°, 44.6° and 60.5° are assigned to (004), (006) and (110) (MoS₂ PDF 01-087-2416) respectively with increased crystallinity along with increasing annealing temperature [46]. The crystal phase information on the TiO₂ and MoS₂ suggests the hetero-junction composite consisting of MoS₂ and mixed-phases TiO₂ based homo-junction.

The HER activities of MoS₂/TiO₂ were measured and compared with that of the MoS₂/Ti. Figure 4a presents photo-current of the obtained dark-current and photo-current (Figure S8(a-c)), in which the MoS₂/TiO₂ (500 °C 2h) exhibited higher photo-current during the HER under the light irradiation than the rest, and excellent HER activities with overpotential of -114 mV at 10 mA/cm². The improved overpotential is much lower than that of latest reports, such as 0D(MoS₂)/2D(g-C₃N₄) heterojunctions (about -450 mV at 2 mA/cm²) [18], a-MoS_x@MPA colloidal nanodots (about -270 mV at 5 mA/cm²) [47] and high-percentage 1T-phase MoS₂ nanodots (about -180 mV at 10 mA/cm²) [48]. It is even comparable to that of MoS₂ with multifunctional active sites (around -100 mV at 10 mA/cm² in 1.0 M aqueous KOH) [49]. To examine the role of homo-junction TiO₂ in the hetero-junction, the HER activities of MoS₂/Ti without introducing homo-junction TiO₂ was also measured. Figure S8d shows the current density under the dark and light condition during the HER for the MoS₂/Ti. The current density under the light is almost overlapped with the current density

under the dark, indicating a poor visible light utilization. Thus, the homo-junction TiO_2 plays a crucial role on promoting the HER activities of $\text{MoS}_2/\text{TiO}_2$ after thermal treatment. Figure 4b presents the Tafel slope for the $\text{MoS}_2/\text{TiO}_2$ (500 °C 2h), with a value of 99 mV/decade under the light, much lower than the Tafel slope value 159 mV/decade of TiO_2/Ti shown in the Figure 2d. The Tafel slope value is much closer to the Heyrovsky reaction regime (40 mV/decade), therefore the rate-limiting step is changing from the electrochemical adsorption step to the desorption step due to the covered MoS_2 [43]. In addition, in contrast to the HER activities of singular TiO_2 (TiO_2/Ti , Figure 2c) and MoS_2 (MoS_2/Ti , Figure S8d), the hetero-junction of $\text{MoS}_2/\text{TiO}_2$ exhibits lower overpotential and higher current under the light, suggesting that the hetero-junction interface between the homo-junction TiO_2 and MoS_2 also contributed to the charge separation and transfer, and then hastened the reaction kinetics.

A long-time stability test for $\text{MoS}_2/\text{TiO}_2$ (500 °C 2h) was also carried out. Figure 4c shows the current density measured during an extended electrolysis (15 hours) under the light at constant potential of -0.3 V (vs RHE), in which only 5% current density decay was observed after 12-hours continuous test under the light for the $\text{MoS}_2/\text{TiO}_2$ (500 °C 2h). For comparison, Figure 4d and Figure 4e present the stability test for both $\text{MoS}_2/\text{TiO}_2$ without illumination and MoS_2/Ti with illumination. Almost 30% current decay was obtained for the MoS_2/Ti under the light, demonstrating a faster degradation rate than that of $\text{MoS}_2/\text{TiO}_2$ with/without illumination.

Figure 4f further shows the HER polarization curves before and after 10 hours stability test for the $\text{MoS}_2/\text{TiO}_2$ with/without the light, in which the current curve under the dark after 10 hours stability measurement displays similar and repeatable features as the initial test before stability test. While a larger deviation in the current was observed under the light condition, indicating that the stability under the light is slightly weaker than that under the dark. We attribute the reason for the

stability difference between the dark and the light to the photoinduced corrosion process on the edge sites or defect sites of the MoS₂ under the light exposure^[50], because the faster and stronger reactions happened during the HER under the light. EIS was used to examine the impedance difference. Figure S9 shows the EIS plots, in which a smaller semicircle of the arc line was exhibited for the MoS₂/TiO₂ (500 °C 2h) under the light comparing to that under the dark, indicating better interfacial charge-transfer kinetics^[43,44]. Meanwhile, a concave arc-line representing intense diffusion of ions of the interface between electrolyte and electrode was observed for the MoS₂/Ti under the light^[51,52], suggesting poor charge-transfer property which is in agreement with a weak PEC activities. It should be noted that the high stability of the hybrid-junction of MoS₂/TiO₂ is comparable to other reported junctions such as MoS₂/TiO₂, nanojunction of (001) Facets MoS₂/Anatase TiO₂ (cyclic H₂ production for 9 hours)^[53], heterojunction of MoS₂/anatase TiO₂ (recycle degradation of MB for 5 hours)^[4], and MoS₂/TiO₂ Edge-On Heterostructure (12 hours recycling photocatalytic H₂ evolution with intermittent evacuation)^[26].

3.3. Discussion

Figure S10 a,b shows the UV-Vis absorption spectra of TiO₂ and MoS₂ respectively, in which the absorption edges of TiO₂ and MoS₂ were found to be 760 and 990 nm respectively, corresponding to the direct band gap energy (E_g) of 1.63 eV and 1.25 eV derived from Beer–Lambert law^[37] as shown in the Figure S10c. The narrower bandgap energy of homo-junction TiO₂ compare with the pure anatase phase (3.20 eV) and rutile phase of TiO₂ (3.03 eV)^[54] could be attributed to the monolithic homo-junction TiO₂. To further understand the band positions, Figure S11 presents the Mott-Schottky plots of the TiO₂ and the MoS₂/TiO₂ (500 °C 2 h) (the inset in Figure S11), in which the positive slopes of Mott-Schottky indicate n-type TiO₂ and MoS₂⁵⁵. The labeled flat-band potentials are pointing at the difference between Fermi levels and water-

oxidation potentials. We assumed that the Fermi levels were close to the conduction band, ignoring the slight difference between the Fermi levels and conduction band which has no effect on the analytical conclusion. Based on this, we propose an energy diagram of charge-carrier generation, separation and migration processes for the hybrid-junction $\text{MoS}_2/\text{TiO}_2$ on the Ti substrate as illustrated in Figure 5. The detailed Z-scheme mechanism are illustrated in the Figure S12 and explained as follows.

In general, the $\text{MoS}_2/\text{TiO}_2$ composite shall be working as typical staggered gap (type II) heterojunction under usual double paths of charge transferring^[56-59]. Guided by the matched bending band between the MoS_2 and TiO_2 , an inner potential difference induced electric field would be created. The electrons from the conduction band (CB) of MoS_2 could transfer to the CB of TiO_2 ; in the meantime, the holes would tend to transfer from the valance band (VB) of TiO_2 to the VB of MoS_2 . Given the fact that the CB potential of homo-junction TiO_2 is more positive than the standard proton reduction potential of $\text{H}_2/\text{H}_2\text{O}$ (0.00 V Vs NHE), thereby protons cannot be thermodynamically reduced to hydrogen. Similarly, since the VB potential of MoS_2 is more negative than that of $\text{O}_2/\text{H}_2\text{O}$ (1.23 V Vs NHE), thus the oxygen evolution reaction is prohibited. However, enhanced HER activities and stability were achieved in the work. Therefore, it is proposed that a direct Z-scheme catalytic mechanism is established. Under the mechanism, the built-in static electric field would guide the electrons from the CB of homo-junction TiO_2 transferring to the interface to combine with the active holes from the VB of MoS_2 , thus preventing the electrons in the CB of homo-junction TiO_2 from the strong reducibility and the holes in the VB of MoS_2 from the oxidizability. Thus, an enhanced HER activities could be achieved on the hybrid-junction of $\text{MoS}_2/\text{TiO}_2$.^[60]

For the hetero-junction of $\text{MoS}_2/\text{TiO}_2$, to further ascertain that the underneath homo-junction TiO_2 on the substrate of Ti still has resonant visible light responsivity during the HER, we applied the linear sweeps (J - V) in anodic direction as shown in Figure S13 under the dark. The oxygen evolution reactions (OER) was observed as gas bubbles in the electrolytes. Note that, once the gas bubbles were generated out of the surface, the surficial MoS_2 would delaminate from the surface due to the fact that the OER just taking place on the active sites of inner TiO_2 . Once irradiated by light, the observed delamination process became much more severe so that deteriorating of MoS_2 flakes was observed. The reason could be due to the TiO_2 harvesting light energy resulted in the accelerated OER. These findings confirm that the ions and visible light can interacting with the underneath TiO_2 , possibly owing to surficial porous MoS_2 . Therefore, the underneath homo-junction TiO_2 on the substrate of Ti could absorb the visible light and convert the light energy during the catalytic reactions.

The interface between the TiO_2 and Ti in the hetero-junction of $\text{MoS}_2/\text{TiO}_2/\text{Ti}$ also plays an important effect on the overall charge carriers transfer and separation while restraining the recombination which resulted in the photoluminescence (PL) signal. Thus, PL emission spectra were recorded (Figure S14) to probe the behavior of the interface. Comparing to the PL intensity of Ti substrate, much weaker intensity of MoS_2/Ti , TiO_2/Ti and $\text{MoS}_2/\text{TiO}_2/\text{Ti}$ were obtained, suggesting the surficial decoration with MoS_2 , TiO_2 , or $\text{MoS}_2/\text{TiO}_2$ could depress the recombination effectively^[61]. This confirms the interface is in favor of the charge separation and transfer between the TiO_2 and Ti during the HER under the light.

In brief, the homo-junction on the substrate of Ti and Z-scheme hetero-junction play multiple roles during the whole HER. First, the homo-junction TiO_2 with narrow band gap can not only utilize visible light energy to excite the electrons from the VB to CB, but also acquire the hot

electrons transferred at the interface of quasi-core-shell TiO_2/Ti [37-40]. The homo-junction forms an inter-phase junction to afford the band bending, and then favoring the excited electrons toward the hetero-junction interface. Second, the Z-scheme hetero-junction transports the electrons to the VB of MoS_2 , where the electrons are then excited to the CB by the sunlight energy, further participating into the HER on the active sites of MoS_2 . Furthermore, the Z-scheme connection provides excellent protection on the MoS_2 through directing the photo-excited holes in the VB of MoS_2 toward the hetero-junction interface space meeting with the electrons from the CB of TiO_2 , preventing the MoS_2 from the photo-excited holes induced corrosion and therefore imparting a higher stability to the system [62]. In turn, the upper MoS_2 layer also acts as protective material for the underneath TiO_2 . The low cost of Ti and MoS_2 with simply fabrication processes makes them favorable to demonstrate our hybrid-junction scheme. The optimization for the processes and manipulation should result in better HER performance and enhanced the visible light utilization, like modifying the thickness of MoS_2 [63-65].

Conclusions

Novel hybrid-junction $\text{MoS}_2/\text{TiO}_2/\text{Ti}$ photocathode was fabricated by a facile process that combines thermal oxidation and hand-spraying. This hybrid-junction photocathode under visible light exhibited improved HER activities, in which the overpotential required to obtain 10 mA cm^{-2} was reduced to -114 mV, as well as long-term stability was achieved for over more than 12 hours at -0.3 V Vs RHE while in comparison the cathode without the introduction of hybrid-junction only persisted about 1 hour under the same conditions. The associated homo-junction and Z-scheme hetero-junction were attributed to the enhanced charge carrier dynamics and reduced recombination, therefore improved HER activities under the light. Synthesized by simple one-step

thermal oxidation process, the homo-junction TiO_2 on the substrate of Ti with plasmonic resonances and charge separation ability is supposed to have more wide range of application capability in sunlight energy-conversion systems. The concept of hybrid-junction provides a cost-economical strategy to regulate the charge carrier separation, transfer and transportation dynamics of photoelectrodes and catalysts that do hold poor characteristic under given working environment for practical solar water splitting.

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REFERENCES

- [1] O. Khaselev, A monolithic photovoltaic-photoelectrochemical device for hydrogen production via water splitting, *Science*, 280 (1998) 425-427.
- [2] Y. Tachibana, L. Vayssieres, J.R. Durrant, Artificial photosynthesis for solar water-splitting, *Nat. Photonics*, 6 (2012) 511-518.
- [3] D.M. Fabian, S. Hu, N. Singh, F.A. Houle, T. Hisatomi, K. Domen, F.E. Osterloh, S. Ardo, Particle suspension reactors and materials for solar-driven water splitting, *Energy Environ. Sci.*, 8 (2015) 2825-2850.
- [4] A. Landman, H. Dotan, G.E. Shter, M. Wullenkord, A. Houaijia, A. Maljusch, G.S. Grader, A. Rothschild, Photoelectrochemical water splitting in separate oxygen and hydrogen cells, *Nat. Mater.*, 16 (2017) 646-651.
- [5] R.M. Navarro, M.C. Alvarez-Galván, J.A. Villoria de la Mano, S.M. Al-Zahrani, J.L.G. Fierro, A framework for visible-light water splitting, *Energy Environ. Sci.*, 3 (2010) 1865.
- [6] J.H. Montoya, L.C. Seitz, P. Chakthranont, A. Vojvodic, T.F. Jaramillo, J.K. Norskov, Materials for solar fuels and chemicals, *Nat. Mater.*, 16 (2016) 70-81.
- [7] I. Roger, M.A. Shipman, M.D. Symes, Earth-abundant catalysts for electrochemical and photoelectrochemical water splitting, *Nat. Rev. Chem.*, 1 (2017) 0003.
- [8] L. Zhou, H. Zhang, H. Sun, S. Liu, M.O. Tade, S. Wang, W. Jin, Recent advances in non-metal modification of graphitic carbon nitride for photocatalysis: a historic review, *Catal. Sci. Technol.*, 6 (2016) 7002-7023.
- [9] F.F. Abdi, L. Han, A.H. Smets, M. Zeman, B. Dam, R. van de Krol, Efficient solar water splitting by enhanced charge separation in a bismuth vanadate-silicon tandem photoelectrode, *Nat. Commun.*, 4 (2013) 2195. Khaselev

- [10] K.T. Fountaine, H.J. Lewerenz, H.A. Atwater, Efficiency limits for photoelectrochemical water-splitting, *Nat. Commun.*, 7 (2016) 13706.
- [11] H.M. Chen, C.K. Chen, R.S. Liu, L. Zhang, J. Zhang, D.P. Wilkinson, Nano-architecture and material designs for water splitting photoelectrodes, *Chem. Soc. Rev.*, 41 (2012) 5654-5671.
- [12] S.Y. Reece, J.A. Hamel, K. Sung, T.D. Jarvi, A.J. Esswein, J.J. Pijpers, D.G. Nocera, Wireless solar water splitting using silicon-based semiconductors and earth-abundant catalysts, *Science*, 334 (2011) 645-648.
- [13] J. Luo, J.H. Im, M.T. Mayer, M. Schreier, M.K. Nazeeruddin, N.G. Park, S.D. Tilley, H.J. Fan, M. Gratzel, Water photolysis at 12.3% efficiency via perovskite photovoltaics and Earth-abundant catalysts, *Science*, 345 (2014) 1593-1596.
- [14] X. Li, J. Yu, J. Low, Y. Fang, J. Xiao, X. Chen, Engineering heterogeneous semiconductors for solar water splitting, *J. Mater. Chem. A*, 3 (2015) 2485-2534.
- [15] L. Yuan, C. Han, M.-Q. Yang, Y.-J. Xu, Photocatalytic water splitting for solar hydrogen generation: fundamentals and recent advancements, *Int. Rev. Phys. Chem.*, 35 (2016) 1-36.
- [16] H. Wang, L. Zhang, Z. Chen, J. Hu, S. Li, Z. Wang, J. Liu, X. Wang, Semiconductor heterojunction photocatalysts: design, construction, and photocatalytic performances, *Chem. Soc. Rev.*, 43 (2014) 5234-5244.
- [17] G. Liu, K. Du, S. Haussener, K. Wang, Charge transport in two-photon semiconducting structures for solar fuels, *ChemSusChem*, 9 (2016) 2878-2904.

- [18] Y. Liu, H. Zhang, J. Ke, J. Zhang, W. Tian, X. Xu, X. Duan, H. Sun, M. O Tade, S. Wang, 0D (MoS₂)/2D (g-C₃N₄) heterojunctions in Z-scheme for enhanced photocatalytic and electrochemical hydrogen evolution, *Appl. Catal., B.*, 228 (2018) 64-74.
- [19] R. Abe, Recent progress on photocatalytic and photoelectrochemical water splitting under visible light irradiation, *J. Photoch. Photobio. C*, 11 (2010) 179-209.
- [20] T. Hisatomi, J. Kubota, K. Domen, Recent advances in semiconductors for photocatalytic and photoelectrochemical water splitting, *Chem. Soc. Rev.*, 43 (2014) 7520-7535.
- [21] R. Raja, P. Sudhagar, A. Devadoss, C. Terashima, L.K. Shrestha, K. Nakata, R. Jayavel, K. Ariga, A. Fujishima, Pt-free solar driven photoelectrochemical hydrogen fuel generation using 1T MoS₂ co-catalyst assembled CdS QDs/TiO₂ photoelectrode, *Chem Commun (Camb)*, 51 (2015) 522-525.
- [22] Y. Pi, Z. Li, D. Xu, J. Liu, Y. Li, F. Zhang, G. Zhang, W. Peng, X. Fan, 1T-Phase MoS₂ Nanosheets on TiO₂ nanorod arrays: 3D photoanode with extraordinary catalytic performance, *ACS Sustain. Chem. Eng.*, 5 (2017) 5175-5182.
- [23] X. Zhu, X. Liang, X. Fan, X. Su, Fabrication of flower-like MoS₂/TiO₂ hybrid as an anode material for lithium ion batteries, *RSC Adv.*, 7 (2017) 38119-38124.
- [24] J. Zhang, L. Zhang, W. Yu, F. Jiang, E. Zhang, H. Wang, Z. Kong, J. Xi, Z. Ji, Novel dual heterojunction between MoS₂ and anatase TiO₂ with coexposed {101} and {001} facets, *J. Am. Ceram. Soc.*, 100 (2017) 5274-5285.
- [25] B. Chen, Y. Meng, J. Sha, C. Zhong, W. Hu, N. Zhao, Preparation of MoS₂/TiO₂ based nanocomposites for photocatalysis and rechargeable batteries: progress, challenges, and perspective, *Nanoscale*, 10 (2017) 34-68.

- [26] H. He, J. Lin, W. Fu, X. Wang, H. Wang, Q. Zeng, Q. Gu, Y. Li, C. Yan, B.K. Tay, C. Xue, X. Hu, S.T. Pantelides, W. Zhou, Z. Liu, MoS₂/TiO₂ Edge-on heterostructure for efficient photocatalytic hydrogen evolution, *Adv. Energy Mater.*, 6 (2016) 1600464.
- [27] L. Guo, Z. Yang, K. Marcus, Z. Li, B. Luo, L. Zhou, X. Wang, Y. Du, Y. Yang, MoS₂/TiO₂ heterostructures as nonmetal plasmonic photocatalysts for highly efficient hydrogen evolution, *Energy Environ. Sci.*, 11 (2018) 106-114.
- [28] W.K. Wang, J.J. Chen, X. Zhang, Y.X. Huang, W.W. Li, H.Q. Yu, Self-induced synthesis of phase-junction TiO₂ with a tailored rutile to anatase ratio below phase transition temperature, *Sci. Rep.*, 6 (2016) 20491.
- [29] A. Li, Z. Wang, H. Yin, S. Wang, P. Yan, B. Huang, X. Wang, R. Li, X. Zong, H. Han, C. Li, Understanding the anatase–rutile phase junction in charge separation and transfer in a TiO₂ electrode for photoelectrochemical water splitting, *Chem. Sci.*, 7 (2016) 6076-6082.
- [30] Y. Zhao, N. Hoivik, K. Wang, Recent advance on engineering titanium dioxide nanotubes for photochemical and photoelectrochemical water splitting, *Nano Energy*, 30 (2016) 728-744.
- [31] F.F. Abdi, L. Han, A.H. Smets, M. Zeman, B. Dam, R. van de Krol, Efficient solar water splitting by enhanced charge separation in a bismuth vanadate-silicon tandem photoelectrode, *Nat. Commun.*, 4 (2013) 2195.
- [32] N. Wang, M. Liu, H. Tan, J. Liang, Q. Zhang, C. Wei, Y. Zhao, E.H. Sargent, X. Zhang, Compound homojunction: heterojunction reduces bulk and interface recombination in ZnO photoanodes for water splitting, *Small*, 13 (2017).

- [33] Z. Zhang, Y. Huang, K. Liu, L. Guo, Q. Yuan, B. Dong, Multichannel-improved charge-carrier dynamics in well-designed hetero-nanostructural plasmonic photocatalysts toward highly efficient solar-to-fuels conversion, *Adv. Mater.*, 27 (2015) 5906-5914.
- [34] Y.H. Tseng, C.S. Kuo, C.H. Huang, Y.Y. Li, P.W. Chou, C.L. Cheng, M.S. Wong, Visible-light-responsive nano-TiO₂ with mixed crystal lattice and its photocatalytic activity, *Nanotechnology*, 17 (2006) 2490-2497.
- [35] M.A. Mohamed, W.N. Wan Salleh, J. Jaafar, N. Yusof, Preparation and photocatalytic activity of mixed phase anatase/rutile TiO₂ nanoparticles for phenol degradation, *Jurnal Teknologi*, 70 (2014).
- [36] S. Yeniyol, I. Mutlu, Z. He, B. Yuksel, R.J. Boylan, M. Urgan, Z.C. Karabuda, C. Basegmez, J.L. Ricci, Photocatalytical antibacterial activity of mixed-phase TiO₂ Nanocomposite thin films against *Aggregatibacter actinomycetemcomitans*, *BioMed research international*, 2015 (2015) 705871.
- [37] R. Jiang, B. Li, C. Fang, J. Wang, Metal/Semiconductor hybrid nanostructures for plasmon-enhanced applications, *Adv. Mater.*, 26 (2014) 5274-5309.
- [38] Y. Pihosh, I. Turkevych, K. Mawatari, N. Fukuda, R. Ohta, M. Tosa, K. Shimamura, E.G. Villora, T. Kitamori, Ubiquitous element approach to plasmonic enhanced photocatalytic water splitting: the case of Ti@TiO₂ core-shell nanostructure, *Nanotechnology*, 25 (2014) 315402.
- [39] G. Liu, K. Du, J. Xu, G. Chen, M. Gu, C. Yang, K. Wang, H. Jakobsen, Plasmon-dominated photoelectrodes for solar water splitting, *J. Mater. Chem. A*, 5 (2017) 4233-4253.

- [40] S. Tan, A. Argondizzo, J. Ren, L. Liu, J. Zhao, H. Petek, Plasmonic coupling at a metal/semiconductor interface, *Nat. Photonics*, 11 (2017) 806-812.
- [41] M.W. Knight, N.S. King, L. Liu, H.O. Everitt, P. Nordlander, N.J. Halas, Aluminum for plasmonics, *ACS nano*, 8 (2014) 834-840.
- [42] N.T. Thomas, K. Nobe, Kinetics of the hydrogen evolution reaction on titanium, *J. Electrochem. Soc.*, 117 (1970) 622.
- [43] D. Kiriya, P. Lobaccaro, H.Y. Nyein, P. Taheri, M. Hettick, H. Shiraki, C.M. Sutter-Fella, P. Zhao, W. Gao, R. Maboudian, J.W. Ager, A. Javey, General thermal texturization process of MoS₂ for efficient electrocatalytic hydrogen evolution reaction, *Nano Lett.*, 16 (2016) 4047-4053.
- [44] X. Zou, Y. Zhang, Noble metal-free hydrogen evolution catalysts for water splitting, *Chem. Soc. Rev.*, 44 (2015) 5148-5180.
- [45] J. Kibsgaard, Z. Chen, B.N. Reinecke, T.F. Jaramillo, Engineering the surface structure of MoS₂ to preferentially expose active edge sites for electrocatalysis, *Nat. Mater.*, 11 (2012) 963-969.
- [46] X. Hai, W. Zhou, K. Chang, H. Pang, H. Liu, L. Shi, F. Ichihara, J. Ye, Engineering the crystallinity of MoS₂ monolayers for highly efficient solar hydrogen production, *J. Mater. Chem. A*, 5 (2017) 8591-8598.
- [47] K. Chang, H. Pang, X. Hai, G. Zhao, H. Zhang, L. Shi, F. Ichihara, J. Ye, Ultra-small freestanding amorphous molybdenum sulfide colloidal nanodots for highly efficient photocatalytic hydrogen evolution reaction, *Appl. Catal., B.*, 232 (2018) 446-453.
- [48] C. Tan, Z. Luo, A. Chaturvedi, Y. Cai, Y. Du, Y. Gong, Y. Huang, Z. Lai, X. Zhang, L. Zheng, X. Qi, M.H. Goh, J. Wang, S. Han, X.J. Wu, L. Gu, C. Kloc, H. Zhang, Preparation

- of high-percentage 1T-phase transition metal dichalcogenide nanodots for electrochemical hydrogen evolution, *Adv. Mater.*, 30 (2018).
- [49] M.A.R. Anjum, H.Y. Jeong, M.H. Lee, H.S. Shin, J.S. Lee, Efficient hydrogen evolution reaction catalysis in alkaline media by all-in-one MoS₂ with multifunctional active sites, *Adv. Mater.*, 30 (2018) e1707105.
- [50] E. Parzinger, B. Miller, B. Blaschke, J.A. Garrido, J.W. Ager, A. Holleitner, U. Wurstbauer, Photocatalytic stability of single- and few-layer MoS(2), *ACS nano*, 9 (2015) 11302-11309.
- [51] T. Lopes, L. Andrade, H.A. Ribeiro, A. Mendes, Characterization of photoelectrochemical cells for water splitting by electrochemical impedance spectroscopy, *Int. J. Hydrogen Energy*, 35 (2010) 11601-11608.
- [52] M.I.D.-G.a.R. Gómez, Investigating water splitting with CaFe₂O₄ photocathodes by electrochemical impedance spectroscopy, *ACS Appl. Mater. Interfaces*, 8 (2016) 11.
- [53] Y.-J. Yuan, Z.-J. Ye, H.-W. Lu, B. Hu, Y.-H. Li, D.-Q. Chen, J.-S. Zhong, Z.-T. Yu, Z.-G. Zou, Constructing anatase TiO₂ nanosheets with exposed (001) facets/layered MoS₂ two-dimensional nanojunctions for enhanced solar hydrogen generation, *ACS Catal.*, 6 (2015) 532-541.
- [54] D.O. Scanlon, C.W. Dunnill, J. Buckeridge, S.A. Shevlin, A.J. Logsdail, S.M. Woodley, C.R. Catlow, M.J. Powell, R.G. Palgrave, I.P. Parkin, G.W. Watson, T.W. Keal, P. Sherwood, A. Walsh, A.A. Sokol, Band alignment of rutile and anatase TiO(2), *Nat. Mater.*, 12 (2013) 798-801.
- [55] N. Baram, Y. Ein-Eli, Electrochemical impedance spectroscopy of porous TiO₂ for photocatalytic applications, *J. Phys. Chem. C*, 114 (2010) 9781-9790.

- [56] L. Cao, R. Wang, D. Wang, X. Li, H. Jia, MoS₂ -hybridized TiO₂ nanosheets with exposed {001} facets to enhance the visible-light photocatalytic activity, *Mater. Lett.*, 160 (2015) 286-290.
- [57] J. Tao, J. Chai, L. Guan, J. Pan, S. Wang, Effect of interfacial coupling on photocatalytic performance of large scale MoS₂/TiO₂ hetero-thin films, *Appl. Phys. Lett.*, 106 (2015) 081602.
- [58] D. Wang, Y. Xu, F. Sun, Q. Zhang, P. Wang, X. Wang, Enhanced photocatalytic activity of TiO₂ under sunlight by MoS₂ nanodots modification, *Appl. Surf. Sci.*, 377 (2016) 221-227.
- [59] X. Liu, Z. Xing, Y. Zhang, Z. Li, X. Wu, S. Tan, X. Yu, Q. Zhu, W. Zhou, Fabrication of 3D flower-like black N-TiO_{2-x} @MoS₂ for unprecedented-high visible-light-driven photocatalytic performance, *Appl. Catal. B: Environ.*, 201 (2017) 119-127.
- [60] Z. Jiang, W. Wan, H. Li, S. Yuan, H. Zhao, P.K. Wong, A hierarchical Z-scheme alpha-FeO₃/g-C₃N₄ hybrid for enhanced photocatalytic CO₂ reduction, *Adv. Mater.*, (2018).
- [61] X. Yang, H. Huang, B. Jin, J. Luo, X. Zhou, Facile synthesis of MoS₂/B-TiO₂ nanosheets with exposed {001} facets and enhanced visible-light-driven photocatalytic H₂ production activity, *RSC Adv.*, 6 (2016) 107075-107080.
- [62] Y. Yang, Y. Ling, G. Wang, T. Liu, F. Wang, T. Zhai, Y. Tong, Y. Li, Photohole Induced Corrosion of Titanium Dioxide: Mechanism and Solutions, *Nano Lett.*, 15 (2015) 7051-7057.
- [63] D. McAteer, Z. Gholamvand, N. McEvoy, A. Harvey, E. O'Malley, G.S. Duesberg, J.N. Coleman, Thickness dependence and percolation scaling of hydrogen production rate in

MoS₂ nanosheet and nanosheet-carbon nanotube composite catalytic electrodes, ACS Nano, 10 (2016) 672-683.

[64] Y. Zhang, H. Li, H. Wang, H. Xie, R. Liu, S.L. Zhang, Z.J. Qiu, Thickness considerations of two-dimensional layered semiconductors for transistor applications, Sci. Rep., 6 (2016) 29615.

[65] A. Sohn, H. Moon, J. Kim, M. Seo, K.-A. Min, S.W. Lee, S. Yoon, S. Hong, D.-W. Kim, Band alignment at Au/MoS₂ contacts: thickness dependence of exfoliated flakes, J. Phys. Chem. C, 121 (2017) 22517-22522.

Figures (color):

Figure 1. a). XRD patterns of the as-prepared samples. b) Orientation map of mixed-phases TiO₂ marked with assorted colors using EBSD microstructural crystallographic technology. More parameters refer to Figure S3 (Table S1, S2 and S3). (c) Ultraviolet-visible (UV-Vis) absorption spectrums of all samples TiO₂/Ti after 2 hours annealing process at respective 400, 500 and 600 °C. (d) UV-Vis absorption spectra of a group of TiO₂/Ti samples after 2 hours of annealing under varied temperature with distinct visible light absorption bandwidth.

Figure 2. (a-c) Room-temperature *J-V* curves of the TiO₂/Ti measured in 0.5 M H₂SO₄ under respective dark and light with AM 1.5G illumination (300 W/m²). (d) Tafel plots corresponding to the HER polarization curves and related data for the samples.

Figure 3. (a). Schematic fabrication processes of all samples. Five kinds of samples involved in the experiments: Ti foil (sample **A**), TiO₂/Ti (sample **B**), pristine MoS₂/TiO₂/Ti (sample **C**), and annealed MoS₂/TiO₂/Ti in nitrogen atmosphere at temperatures of 500 °C (1h/2h/3h) (sample **D/E/F**). The corresponding SEM images (b) and X-Ray diffraction patterns (c) of the as-received samples.

Figure 4. (a) Polarization curves for the composites of MoS₂/Ti, measured in 0.5 M H₂SO₄ at a scanning rate of 20 mV/S under the light. (b) The corresponding Tafel plots and related data for the MoS₂/Ti (500 °C 2h). The long-term stability test for (c) the MoS₂/Ti (500 °C 2h), (d) MoS₂/TiO₂ under the dark and (e) MoS₂/Ti under the light, respectively, during the HER at -0.3 V vs RHE for 15 hours. (f) The HER polarization curves of the MoS₂/Ti (500 °C 2h) measured before and after the 10 hours stability test at 20 mV/S. The figure of 500 in the figures all refers to the temperature of 500 °C.

Figure 5. Energy diagram of charge-carrier generation, separation and transportation processes for the hybrid-junction MoS₂/TiO₂ on the Ti substrate. (1) Plasmons assisted charge-carrier injection; (2) band-gap enabled excitation of charge-carrier; (3) Z-scheme mechanism of charge-carrier transportation.