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All-Solid-State Z-Scheme Photocatalyst with Carbon Nanotubes as an Electron Mediator for Hydrogen Evolution under Simulated Solar Light

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Abstract
In this contribution, the effectiveness of tailor-made multi-walled carbon nanotubes (MWCNTs) as a solid-state electron mediator for facilitating Z-schematic water splitting is demonstrated. An anisotropic Zn$_{0.5}$Cd$_{0.5}$S-MWCNT-TiO$_2$ ternary core-shell nanocomposites fabricated by a facile coating and hydrothermal route renders a much higher photocatalytic activity than the corresponding single- and two-component systems, revealing MWCNTs can shuttle photogenerated electrons from PS II (TiO$_2$) to PS I (Zn$_{0.5}$Cd$_{0.5}$S). This unique type of vectorial electron transfer between the two photosystems imparts an efficient spatial charge isolation and endows suitable relative band positions with strong redox ability to the Z-scheme system. Consequently, the simulated solar-light-driven (AM 1.5) photocatalytic H$_2$ evolution rate of the as-prepared Zn$_{0.5}$Cd$_{0.5}$S-MWCNT-TiO$_2$ photocatalyst (21.9 µmol h$^{-1}$) is ca. 4.5- and 2.8-fold enhancement over pristine Zn$_{0.5}$Cd$_{0.5}$S and MWCNT-Zn$_{0.5}$Cd$_{0.5}$S samples, respectively. The structural and chemical properties of the typical photocatalysts were characterized using X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), high resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS), photoluminescence (PL) and ultraviolet-visible diffuse spectroscopy (UV-Vis). Besides, electrochemical characterizations (transient photocurrent, Nyquist and Mott-Schottky measurements) were performed to depict the ascendency of the Z-scheme system. Based on the outcomes of the experiment, a plausible charge transfer mechanism for the Z-schematic Zn$_{0.5}$Cd$_{0.5}$S-MWCNT-TiO$_2$ system was postulated.

Keywords
Carbon nanotubes, z-scheme, water splitting, photocatalyst, hydrogen

1. Introduction
Inspired by natural photosynthesis, biomimetic artificial Z-scheme photocatalytic water splitting achieves efficient hydrogen production through the synergistic actions of two isolated photosystems and an electron transporter ingeniously arranged in a nano-platform [1]. The most commonly employed ionic electron mediators, for instance IO$_3^-$/I$^-$ and Fe$^{3+}$/Fe$^{2+}$ redox couples, are competent in shuttling photogenerated electrons from an O$_2$-evolving photocatalyst (PS II) to a H$_2$-evolving photocatalyst (PS I) [2, 3]. However, the redox pair aided Z-scheme system often suffers from inevitable drawbacks such as backward reaction and shielding effect which impede the forward redox reaction [4]. With respect to this issue, a transition of electron relay to a redox pair-free solid-state mediating system is indispensable. Hitherto, there has been an incessant endeavor, in a larger fraction, constructing all-solid-state Z-scheme system with metallic electron mediator [5, 6]. The three-component CdS-Au-TiO$_2$ utilize Au as a metallic electron shuttle to suppress the recombination of carriers, achieving a photocatalytic H$_2$ yield of 3.2 µmol h$^{-1}$ under full range light illumination [7]. Even so, the efficiency of precedent Z-scheme photocatalytic water reduction studies is still much lower than the requirement for commercialization of hydrogen production (QE = 30%) [8]. A proof-of-principle demonstration on Z-scheme system speculates that interparticle electron transfer between the two photosystems is the rate-determining step [9]. Thus, the photocatalytic performance is inextricably linked to the interparticulate electron mediator and, as a result, a serious devotion for developing an effective electron relaying medium to realize a highly competent Z-scheme system is imperative.

The versatile tailoring and excellent intrinsic properties of nanocarbon material, for instance carbon nanotubes, is worth noting as a potential solid-state electron mediator. As is known, multi-walled carbon nanotubes (MWCNTs) possess a very low defect density and, in this regard, they exhibit superior electrical conductivity and stability [10]. Previous studies on Fermi level equilibration of carbon nanotube composites highlight the mediating role of carbonaceous materials in accepting and storing electrons (1 electron per 32 carbon atoms) upon photoexcitation and release them to an electron acceptor, achieving a charge equilibrium with the circumjacent medium [11]. Although MWCNTs show compelling electron transfer ability, the challenge in constructing a highly compatible nanocarbon-mediated Z-scheme system remains in attaining a thermodynamic equilibrium between the electron accepting and donating capabilities of the relaying mediator [12]. As a result, an intimate contact interface between photocatalysts and mediator is of paramount significance to provide a low-resistance pathway for continuous vectorial electron flow from PS II to PS I.
Herein, we report a fine-tuned MWCNT-mediated Z-scheme system using $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ and TiO$_2$ as the H$_2$- and O$_2$-evolving photocatalysts, respectively. The site-selective $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$-MWCNT-TiO$_2$ ternary nanocomposites can efficiently suppress charge recombination and promote water reduction, achieving a H$_2$ evolution rate of 21.9 µmol h$^{-1}$ despite its dopant-free structure. The intimate contact between the photocatalysts and MWCNTs allows the photogenerated electrons from TiO$_2$ to be readily recombine with the photogenerated holes from $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ through a low contact resistance interface, namely Ohmic contact [4, 13]. To the best of our knowledge, this is the first ever reported Z-scheme system using MWCNTs as an interparticulate mediator to interface H$_2$- and O$_2$-evolving photocatalysts.

2. Experimental

2.1. Materials

Pristine MWCNTs with measured carbon content of ca. 70% used in this study were produced from methane decomposition over Co-Mo/MgO catalyst using a rotary reactor. For the acid treatment of MWCNTs, sulfuric acid (95-97%, Friendemann Schmidt Chemical) and nitric acid (69%, Friendemann Schmidt Chemical) were used. Titanium (IV) butoxide (97%, Sigma Aldrich), Zn(NO$_3$)$_2$.6H$_2$O (98%, Sigma Aldrich), Cd(NO$_3$)$_2$.4H$_2$O (98%, Sigma Aldrich), thiourea (≥99%, Sigma Aldrich), NaOH (98%, Sigma Aldrich), ethanol (Grade AR 96%, Friendemann Schmidt Chemical) and acetone (Grade AR ≥99.5%, Friendemann Schmidt Chemical) were used as received without further purification for the fabrication of the ternary nanocomposites.

2.2. Acid treatment of MWCNTs

First and foremost, pristine MWCNTs were acid-treated to introduce hydrophilic behaviour on the tube surface via the formation of carboxyl groups in the meantime removing metal catalyst impurities from the previous MWCNTs production. In brief, 0.5 g of pristine MWCNTs were stirred and heated continuously under reflux at 100 ºC in a 120 mL mixture containing sulfuric acid (5 M) and nitric acid (5 M) with the volume ratio of 3:1 for 3 h. Subsequently, the mixture was filtered and washed repeatedly with DI water to achieve neutral pH. The functionalization of MWCNTs was verified by Raman analysis in which the degree of graphitization ($I_G/I_D$) was found to reduce from 1.07 of pristine MWCNTs to 0.84 of acid-treated MWCNTs, ascertain the generation of defects on the tube surface (Fig. S1 in
the Supporting Information). Detailed acid treatment procedures can be obtained from the earlier publications by our research group [14].

2.3. Preparation of TiO$_2$ nanoparticles and MWCNT-TiO$_2$ nanocomposites

Pristine TiO$_2$ nanoparticles were synthesized through the hydrolysis of titanium (IV) butoxide (TBOT) as the titanium precursor. Briefly, 2.05 mL of TBOT was dissolved in 10 mL of ethanol by stirring for 15 min. The pre-dissolved TBOT solution was then added dropwise into a mixture of ethanol and DI water (20 mL: 1 mL) under stirring with ice bath for 1 h. The powder was then retrieved using vacuum filtration and washed with ethanol and DI water.

MWCNT-TiO$_2$ nanocomposites were prepared from a simple coating approach according to our previous reports with slight modification [15, 16]. Typically, 0.24 g of acid-treated MWCNTs along with 20 mL ethanol and 1 mL DI water were stirred and sonicated for 15 min, respectively. Afterwards, the solution was added dropwise with TBOT (2.05 mL) pre-dissolved in ethanol (10 mL) and stirred under ice bath for 1 h. The powder was then collected using vacuum filtration and washed with ethanol and DI water.

2.4. Preparation of Zn$_{0.5}$Cd$_{0.5}$S nanoparticles and MWCNT-Zn$_{0.5}$Cd$_{0.5}$S nanocomposites

Pristine Zn$_{0.5}$Cd$_{0.5}$S nanoparticles were synthesized by a hydrothermal method. In brief, 5 mmol of Zn(NO$_3$)$_2$.6H$_2$O (1.487 g) and 5 mmol of Cd(NO$_3$)$_2$.4H$_2$O (1.542 g) were added into 5 mL of DI water and stirred for 15 min. The solution was then added into a 90 mL mixture of ethanol and DI water (2:1) under stirring for 30 min. Later on, the mixture was added with 10 mL of 6 M NaOH and stirred for another 30 min. Successively, 5 mmol of thiourea (1.52 g) was added into the solution and further stirred for 1 h before transferring into a Teflon-lined stainless steel autoclave and subjected to hydrothermal process at 180 °C for 12 h. Subsequently, the solution was allowed to cool into room temperature and the precipitates were obtained by centrifugation. The as-obtained powder was then washed repeatedly with ethanol and acetone.

MWCNT-Zn$_{0.5}$Cd$_{0.5}$S nanocomposites were also prepared under similar conditions except that 0.24 g of acid-treated MWCNTs were initially dispersed in the 90 mL ethanol and DI water mixture by stirring and sonication for 15 min each before the solution containing Zn(NO$_3$)$_2$.6H$_2$O and Cd(NO$_3$)$_2$.4H$_2$O was added.

2.5. Preparation of Zn$_{0.5}$Cd$_{0.5}$S-MWCNT-TiO$_2$ ternary nanocomposites
Z-schematic Zn_{0.5}Cd_{0.5}S-MWCNT-TiO_{2} sample was synthesized via a two-step coating and co-precipitation-hydrothermal strategy. In the first step, MWCNTs was coated with TiO_{2} through in-situ hydrolysis of titanium butoxide (TBOT) as the titanium precursor. The coating of MWCNT-TiO_{2} was aforementioned in Section 2.3. In the second step, the as-fabricated MWCNT-TiO_{2} nanocomposites were grafted with Zn^{2+}, Cd^{2+} and organic S precursors before subjected into hydrothermal process to form Zn_{0.5}Cd_{0.5}S nanoislands on the MWCNTs framework. Typically, the as-prepared MWCNT-TiO_{2} nanocomposites were dispersed in 90 mL DI water and ethanol mixture in the volume ratio of 2:1. The solution was then added with 5 mmol Zn(NO_{3})_{2}.6H_{2}O and Cd(NO_{3})_{2}.4H_{2}O pre-dissolved in 5 mL DI water and stirred for 30 min. Afterwards, 10 mL of 6 M NaOH was added into the solution as a precipitating agent and further stirred for another 30 min. Then, 5 mmol of thiourea was then added slowly into the solution and stirred for 1 h before subjected to hydrothermal process at 180 °C for 12 h. Consecutively, the solution was centrifuged and the precipitates were washed with ethanol and acetone. The as-obtained powder was then dried in oven to collect a resulting product of Zn_{0.5}Cd_{0.5}S-MWCNT-TiO_{2} ternary hybrids. In this context, the mass ratio of PS I and II was controlled at 1:1 (g/g). The whole synthesis protocol of the nanocomposites is illustrated in Fig. 1. For comparison, Zn_{0.5}Cd_{0.5}S-TiO_{2} binary nanocomposites without MWCNTs as mediator were prepared by mechanical mixing of Zn_{0.5}Cd_{0.5}S and TiO_{2} samples with equal mass ratio.
2.6. Materials characterization

The crystallographic properties of the as-obtained powder was investigated using X-ray diffraction (XRD) analysis on a Bruker D8 Discover X-ray diffractometer with Ni-filtered Cu Kα radiation (λ = 1.54056 Å) at a scan rate of 0.02° s⁻¹ with 2θ ranging from 20 to 90°. The surface morphology and elemental composition were examined using a Hitachi SU8010 field emission scanning electron microscopy (FESEM) with energy-dispersive X-ray (EDX) spectroscopy. High resolution TEM (HRTEM) images were obtained using a JEOL JEM-2100F microscope operated at 200 kV. Optical properties of the samples were analysed using a Cary 100 UV-Vis spectrophotometer (Agilent) equipped with an integrated sphere and BaSO₄ was employed as a reflectance standard. Meanwhile, Raman spectrum was recorded on a Horiba LabRAM HR Evolution micro-Raman spectrometer with laser excitation of 514 nm. Photoluminescence (PL) emission spectra were obtained using a fluorescence spectrometer (Perkin Elmer, LS55) at room temperature. Lastly, X-ray photoelectron spectroscopy (XPS) measurements were carried out by a scanning X-ray microprobe PHI Quantera II (Ulvac-PHI, INC.) with monochromatic Al-Kα (hv = 1486.6 eV) X-ray source. Prior to deconvolution, all binding energies were referenced to adventitious carbon signal (C 1s peak) at 284.6 eV.

2.7. Electrochemical analysis

The electrochemical characterizations (transient photocurrent, Nyquist and Mott-Schottky measurements) were carried out with a basic Autolab PGSTAT302N applied potentiostat unit using a conventional three-electrode quartz cell containing a working electrode, Pt counter electrode and Ag/AgCl saturated with 3 M KCl as reference electrode. The working electrode was prepared by drop-casting of the typical samples in ethanol suspension (1 mg/mL) on a fluorine-doped tin oxide (FTO) substrate with an electroactive area fixed at 1 cm². The measurements were performed using an aqueous 0.5 M Na₂SO₄ solution as electrolyte and the working electrode was illuminated with a lamp-to-sample distance of 5 cm. The transient
photocurrent responses were recorded at a bias voltage of 10 mV under intermittent simulated solar light. During the PEC measurement, the amplitude and frequency of AC potential were set as 0.6 V and 100 Hz, respectively.

2.8. Evaluation of photocatalytic activities

The photocatalytic H\textsubscript{2} evolution was carried out in a Pyrex side-irradiated vessel with a continuous N\textsubscript{2} flow at atmospheric pressure. Each photocatalyst (0.03 g) was dispersed in 120 mL aqueous mixture of Na\textsubscript{2}S (0.1 M) and Na\textsubscript{2}SO\textsubscript{3} (0.1 M) under vigorous stirring. Prior to the photocatalytic activity, the reaction system was purged with N\textsubscript{2} gas at a flow rate of 50 mL/min for 30 min to ensure complete air evacuation. A 500 W Xe arc lamp (CHF-XM-500W) equipped with an optical filter (AM 1.5) was used as a simulated solar light source. Spectrum of the light source is given in Fig. S2 in the Supporting Information. Upon the onset of irradiation, the photocatalytic H\textsubscript{2} evolution was conducted with a constant N\textsubscript{2} flow rate of 5 mL/min. The gas sampling port of the system is directly connected to a gas chromatography (Agilent 7890A, TCD, Ar carrier gas) for measuring the product gas online (auto-sampling time of 1 h interval).

3. Results and discussion

Z-schematic Zn\textsubscript{0.5}Cd\textsubscript{0.5}S-MWCNT-TiO\textsubscript{2} nanoarchitectures were prepared via a two-step coating and co-precipitation-hydrothermal strategy using functionalized MWCNTs as the hybridization template. Typically, acid-treated MWCNTs were firstly coated with TiO\textsubscript{2} to form nanocarbon hybrids decorated with TiO\textsubscript{2} nanoislands (Fig. S3 in the Supporting Information). The as-fabricated MWCNT-TiO\textsubscript{2} nanocomposites were subsequently grafted with Zn\textsuperscript{2+}, Cd\textsuperscript{2+} and organic S precursors before subjected into hydrothermal process. With the addition of NaOH as a precipitating agent, it was found to reduce the heterogeneous nucleation rate and suppress aggregation of Zn\textsubscript{0.5}Cd\textsubscript{0.5}S [17]. Thus, strongly coupled
Zn$_{0.5}$Cd$_{0.5}$S nanoparticles were in-situ generated on the MWCNT-TiO$_2$ nanocomposites, resulting the formation of a ternary core-shell nanostructure. For comparison, pristine TiO$_2$, Zn$_{0.5}$Cd$_{0.5}$S, MWCNT-TiO$_2$ and MWCNT-Zn$_{0.5}$Cd$_{0.5}$S were prepared to render the ascendancy of the Z-scheme system. Detailed procedures of materials preparation is aforementioned in the Experimental Section. XRD patterns of the as-synthesized Zn$_{0.5}$Cd$_{0.5}$S-MWCNT-TiO$_2$ as well as the corresponding pristine Zn$_{0.5}$Cd$_{0.5}$S and TiO$_2$ samples are depicted in Fig. 2. Typical characteristic diffraction peaks of hexagonal wurtzite structured Zn$_{0.5}$Cd$_{0.5}$S (denoted with ▼) and anatase phase of hexagonal TiO$_2$ with dominant (101) facet (denoted with ○) were present in the Z-scheme sample, indicating the formation of PS I and II on the MWCNTs framework [17-19]. No distinctive characteristics peak of MWCNTs was observed owing to the overlapping of main diffraction peaks of MWCNTs and anatase TiO$_2$ (101) which are relatively close, i.e. 2θ = 25.2 and 26.0°, respectively [14].
Fig. 2. XRD pattern of (a) acid-treated MWCNTs, (b) bare TiO₂, (c) bare Zn₀.₅Cd₀.₅S, and (d) Zn₀.₅Cd₀.₅S-MWCNT-TiO₂ nanocomposites.

The photocatalytic water reduction performance of the Z-scheme system was investigated using an aqueous mixture of Na₂S and Na₂SO₃ as hole scavenger under simulated solar light illumination. No activity was found in the dark and H₂ gas evolution commenced with the onset of irradiation. As observed from Table 1, no considerable H₂ gas was detected when the photocatalytic reaction of TiO₂ alone was conducted, either with or without the presence of MWCNTs (entries 1 and 2). This is ascribed to the low conduction band potential of TiO₂ which has a proximal energy level as the standard potential of hydrogen production, H⁺/H₂. The deficiency in potential negativity of bottom conduction band (BCB) places a thermodynamic constraint for the water reduction reaction on TiO₂ surface and impedes the photocatalytic H₂ production [4]. Contrastingly, Zn₀.₅Cd₀.₅S (entry 3) and MWCNT-Zn₀.₅Cd₀.₅S (entry 4) samples which possess a more negative or analogously higher BCB potential than H⁺/H₂, evolved H₂ gas at a steady rate of 4.9 and 7.8 µmol h⁻¹, respectively. However, both samples exhibited minimal H₂ activities due to flash recombination of charge carriers. Time courses of H₂ evolution on Z-schematic Zn₀.₅Cd₀.₅S-MWCNT-TiO₂ sample (entry 5) yielded a substantial improvement in the gas production, leading to ca. 4.5- and 2.8-fold enhancement over pristine Zn₀.₅Cd₀.₅S and MWCNT-Zn₀.₅Cd₀.₅S photocatalysts (Fig. 3). The habitation of TiO₂ on MWCNT-Zn₀.₅Cd₀.₅S structure could supply photogenerated electrons to recombine with the photogenerated holes in Zn₀.₅Cd₀.₅S which eventually reduce bulk electron-hole recombination and prolong the lifetime of photogenerated electrons in Zn₀.₅Cd₀.₅S. Control experiment of H₂ production on Zn₀.₅Cd₀.₅S-TiO₂ sample was conducted to attest the role of MWCNTs in driving H₂ evolution (entry 6). The augmentation in photocatalytic activity of Z-schematic Zn₀.₅Cd₀.₅S-MWCNT-TiO₂ eminently manifests the concomitant effects of the two photocatalysts with MWCNTs as electron mediator to achieve an exceptional water reduction performance. Besides, it is worth noting that Z-schematic Zn₀.₅Cd₀.₅S-MWCNT-TiO₂ demonstrated high photostability in which the sample preserved a reactivity of 90.2 % after three consecutive photocatalytic reactions (18 h) under same experimental conditions (Fig. S4 in the Supporting Information).

Table 1. H₂ production via photocatalytic water splitting of typical photocatalysts under simulated solar light irradiation.

<table>
<thead>
<tr>
<th>Entry</th>
<th>H₂-photocatalyst</th>
<th>Electron mediator</th>
<th>O₂-photocatalyst</th>
<th>H₂ evolution rates</th>
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<tr>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Material</td>
<td></td>
<td></td>
<td>[μmol h⁻¹] [a]</td>
</tr>
<tr>
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<tr>
<td>1</td>
<td>-</td>
<td>-</td>
<td>TiO₂</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
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<td>-</td>
<td>TiO₂</td>
<td>12.3</td>
</tr>
</tbody>
</table>

[a] Reaction conditions: 30 mg photocatalyst; 120 mL aqueous mixture of Na₂S (0.1 M) and Na₂SO₃ (0.1 M); Pyrex side-irradiated cell; 500 W Xe lamp (AM 1.5); 6 h reaction time.

Fig. 3. Time courses of H₂ evolution for (a) Zn₀.₅Cd₀.₅S, (b) Zn₀.₅Cd₀.₅S-TiO₂, (c) MWCNT-Zn₀.₅Cd₀.₅S, and (d) Zn₀.₅Cd₀.₅S-MWCNT-TiO₂ nanocomposites. Reaction conditions: 30 mg photocatalyst; 120 mL aqueous mixture of Na₂S (0.1 M) and Na₂SO₃ (0.1 M); Pyrex side-irradiated cell; 500 W Xe lamp (AM 1.5); 6 h reaction time.

To corroborate the promotion effect of the MWCNT-mediated Z-scheme system, the surface morphology and microstructure of the as-obtained Zn₀.₅Cd₀.₅S-MWCNT-TiO₂ sample was firstly characterized by FESEM and HRTEM. Fig. 4a delineates a fairly uniform deposition of TiO₂ and Zn₀.₅Cd₀.₅S nanoparticles over the surface of MWCNTs with minimum agglomeration. It can be visualized that both photocatalysts were distributed
separately on the MWCNTs scaffold, forming a shell composed of TiO$_2$ and Zn$_{0.5}$Cd$_{0.5}$S nanoislands that is wrapped up along the tube wall of MWCNTs (Fig. 4b). The HRTEM images also imply the existence of abundant and intimate interfacial contact between the photocatalysts and MWCNTs. As depicted in Fig. 4c, the overlapping of three different lattice fringes indicates the formation of interactive heterojunctions in the ternary Z-scheme hybrids with an orientation relationship of Zn$_{0.5}$Cd$_{0.5}$S (101) || MWCNTs (002) || TiO$_2$ (101) nanostructure. The lattice spacing measurements of 0.32, 0.33 and 0.35 nm were corresponded to Zn$_{0.5}$Cd$_{0.5}$S, MWCNTs and TiO$_2$, respectively (Fig. 4d) [17, 18]. The presence of elements was further verified by the EDX results (Fig. S5 in the Supporting Information).

Fig. 4f postulates a plausible charge transfer mechanism for the MWCNT-mediated Z-scheme system in photocatalytic H$_2$ production. Upon light irradiation, delocalization of charges were induced in both Zn$_{0.5}$Cd$_{0.5}$S (PS I) and TiO$_2$ (PS II) photocatalysts. With the incorporation of MWCNTs as a solid-state electron mediator, photogenerated electrons from the conduction band of TiO$_2$ are migrated and recombined with the photogenerated holes from the valence band of Zn$_{0.5}$Cd$_{0.5}$S through Ohmic contact. This profile of electron flow could maximize the isolation of carriers, thus leaving photogenerated electrons in Zn$_{0.5}$Cd$_{0.5}$S and holes in TiO$_2$ to perform the corresponding water reduction and oxidation, respectively. The vectorial electron transfer of TiO$_2$ → MWCNTs → Zn$_{0.5}$Cd$_{0.5}$S in the Z-scheme system is feasible since the driving force for reverse electron flow is hindered by two factors. In the first aspect, photogenerated electrons from TiO$_2$ can only be transferred to MWCNTs due to limitation of BCB potential for water reduction reaction. The second one divulges that photogenerated electrons from Zn$_{0.5}$Cd$_{0.5}$S can be dictated in two potential ways: transferred to MWCNTs and reduction of water. However, the latter is more likely to occur since vast surface area of the photocatalyst is adsorbed with water while only minority of it is in contact with the mediator. In this context, the opposite direction of electron flow from Zn$_{0.5}$Cd$_{0.5}$S to MWCNTs and TiO$_2$ is a minor pathway, strongly suggesting that majority of the electrons (Zn$_{0.5}$Cd$_{0.5}$S) would be used for the water reduction reaction. Therefore, an artificial Z-scheme system should be viable using a combination of Zn$_{0.5}$Cd$_{0.5}$S and TiO$_2$ with MWCNTs mediator as disclosed in Fig. 4e.
**Fig. 4.** (a) Representative FESEM image of Zn$_{0.5}$Cd$_{0.5}$S-MWCNT-TiO$_2$. HRTEM images showing (b) MWCNTs uncoated and coated with TiO$_2$ and Zn$_{0.5}$Cd$_{0.5}$S, (c) heterojunctions of the ternary hybrids, and (d) enlarged image of selected heterojunctions showing lattice spacing in Zn$_{0.5}$Cd$_{0.5}$S-MWCNT-TiO$_2$. (e) Schematic model of Zn$_{0.5}$Cd$_{0.5}$S-MWCNT-TiO$_2$ nanocomposites. (f) Proposed electron/hole transfer mechanism for MWCNT-mediated Z-scheme system.

In this work, the intimate contact interface of photocatalyst/MWCNT was driven by the strong interaction between surface oxygen-containing functional groups on MWCNTs and the charge nature of the precursors of photocatalysts. This “in-situ” approach of composites synthesis promotes strongly coupling of semiconductor/MWCNT which allows efficient interparticle electron transfer in the Z-scheme system. In order to provide an insight on the interfacial interaction of the Z-schematic Zn$_{0.5}$Cd$_{0.5}$S-MWCNT-TiO$_2$ sample, the chemical
states of pristine Zn$_{0.5}$Cd$_{0.5}$S and the typical Zn$_{0.5}$Cd$_{0.5}$S-MWCNT-TiO$_{2}$ samples were investigated using X-ray photoelectron spectroscopy (XPS). Fig. 5A shows the full XPS survey scan of both Zn$_{0.5}$Cd$_{0.5}$S and Zn$_{0.5}$Cd$_{0.5}$S-MWCNT-TiO$_{2}$ samples, revealing the presence of Zn, Cd, S, Ti and C as the major elements in Zn$_{0.5}$Cd$_{0.5}$S-MWCNT-TiO$_{2}$. Besides, there are absence of Ti peaks and a relatively low C 1s peak for the pristine Zn$_{0.5}$Cd$_{0.5}$S sample. Fig. 5B shows the high resolution Zn 2p XPS spectra in which the two peaks at 1023.1 and 1046.0 eV could be attributed to Zn 2p$_{3/2}$ and Zn 2p$_{1/2}$, respectively. High resolution XPS spectra of Cd 3d (Fig. 5C) demonstrates the presence of Cd 3d$_{5/2}$ (406.4 eV) and Cd3d$_{3/2}$ (413.1 eV) peaks in both Zn$_{0.5}$Cd$_{0.5}$S and Zn$_{0.5}$Cd$_{0.5}$S-MWCNT-TiO$_{2}$ samples, which is synonymous to Cd$^{2+}$ in CdS [20]. Besides, Fig. 5D exhibits the high resolution XPS spectra of S 2s in which the peak is observed at binding energy of 226.6 eV. In contrast, a shift in binding energies of Zn 2p, Cd 3d and S 2s of Zn$_{0.5}$Cd$_{0.5}$S-MWCNT-TiO$_{2}$ sample to a higher value as compared to pristine Zn$_{0.5}$Cd$_{0.5}$S sample strongly indicate the presence of interfacial interaction between Zn$_{0.5}$Cd$_{0.5}$S and MWCNTs [21, 22]. In addition, to ascertain the deoxygenation of functionalized MWCNTs after coupled with Zn$_{0.5}$Cd$_{0.5}$S (PS I) and TiO$_{2}$ (PS II) in the Z-scheme system, the XPS spectrum of C 1s of Zn$_{0.5}$Cd$_{0.5}$S-MWCNT-TiO$_{2}$ sample is compared with the functionalized MWCNTs. With respect to C 1s spectrum of functionalized MWCNTs as delineated in Fig. 5E, six peaks at 284.8, 285.1, 286.6, 287.9, 289.9 and 292.2 eV are fitted which associated with C-C/ C=C, defects, C-O, C=O, carboxyl and π-π* transitions [23]. As a stark contrast with the peaks present in the Z-scheme sample (Fig. 5F), a relatively lower C-C/ C=C peak and higher defects and oxygen-bounded carbon peaks indicated the sufficient oxidation of functionalized MWCNTs (Fig. 5E). The diminish in the oxygen-bounded carbon peaks and a relatively higher C-C/ C=C peak in Zn$_{0.5}$Cd$_{0.5}$S-MWCNT-TiO$_{2}$ sample suggested the efficient deoxygenation of functional groups on MWCNTs, leading to a strong evidence for the presence of interfacial interaction between photocatalysts and MWCNTs [24].
Fig. 5. (A) Full XPS spectra of $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ and $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$-MWCNT-TiO$_2$. (B) Zn 2p XPS spectra. (C) Cd 3d XPS spectra. (D) S 2s XPS spectra. (E) C 1s XPS spectra of functionalized MWCNTs. (F) C 1s XPS spectra of $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$-MWCNT-TiO$_2$.

To elucidate the charge transport properties of the typical samples, electrochemical impedance spectroscopy (EIS) Nyquist plots were analyzed to insight the charge transfer resistance and separation efficiency of carriers [25]. According to Fig. 6A, the smaller arc radius of $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$-MWCNT-TiO$_2$ Z-scheme sample reflects its accelerated charge transfer rate with a lower interfacial layer resistance. Besides, the Z-scheme sample shows a more depressed semicircle under light irradiation, which is attributed to the photo-induced improvement in conductivity, as concordant with the properties of semiconducting materials (Fig. 6B). Thus, Z-scheme sample exemplifies a more favourable $\text{H}_2$ evolution kinetics, revealing the facilitated couriers isolation through the vectorial electron transfer. On top of that, the electron relay in Z-scheme system is a facile transport, originating from the excellent electron mediating ability of MWCNTs with low defect density.
Fig. 6. (A) Nyquist impedance plot for (a) TiO$_2$, (b) MWCNT-TiO$_2$, (c) Zn$_{0.5}$Cd$_{0.5}$S, (d) MWCNT-Zn$_{0.5}$Cd$_{0.5}$S, and (e) Zn$_{0.5}$Cd$_{0.5}$S-MWCNT-TiO$_2$ nanocomposites under irradiation. (B) Nyquist impedance plots for Zn$_{0.5}$Cd$_{0.5}$S-MWCNT-TiO$_2$ nanocomposites in light and dark conditions.

Photocurrent formation with an onset potential under light irradiation is a direct reflection of the photocatalytic performance. Fig. 7 displays the transient photocurrent responses of the samples at a bias voltage of 10 mV under intermittent simulated solar irradiation. Z-schematic Zn$_{0.5}$Cd$_{0.5}$S-MWCNT-TiO$_2$ sample delineates a stark improvement of photocurrent density over the single- and two-component samples, leading to ca. 3.7- and 1.9-fold enhancement over pristine Zn$_{0.5}$Cd$_{0.5}$S and MWCNT-Zn$_{0.5}$Cd$_{0.5}$S photocatalysts. It is strongly entrenched that the reasoning of photocurrent generation is attributed to the diffusion of excitons to the back contact and the simultaneous uptake of photogenerated holes by the electrolyte which is a hole scavenger [26] Thus, the former indicates that with the incorporation of MWCNTs as a mediator to interface both PS I and II, it can promote effective electron-hole pairs separation and prolong the lifetime of photogenerated charge carriers in PS I and II respectively. Besides, PL measurements were conducted to determine the charge recombination and transfer behaviour of the samples (Fig. S6 in the Supporting Information). PL intensity is a direct measurement of electron-hole pairs recombination, in which a higher peak reflects a faster recombination of carriers. As delineated in Fig. S6, the PL intensities were observed in the order of Zn$_{0.5}$Cd$_{0.5}$S > Zn$_{0.5}$Cd$_{0.5}$S-MWCNT-TiO$_2$ > MWCNT-Zn$_{0.5}$Cd$_{0.5}$S. The weakening of emission intensity of Z-schematic Zn$_{0.5}$Cd$_{0.5}$S-
MWCNT-TiO$_2$ sample as compared to the single-component Zn$_{0.5}$Cd$_{0.5}$S sample was attributed to the reduction in bulk electron-hole recombination and the increase in lifetime of photogenerated charge carriers. However, the PL intensity of the two-component MWCNT-Zn$_{0.5}$Cd$_{0.5}$S sample was found to be lower than the Z-scheme sample. This can be ascribed to the recombination of electrons from TiO$_2$ and holes from Zn$_{0.5}$Cd$_{0.5}$S in former through Ohmic contact in the MWCNTs mediator for Z-schematic system. This contributed to the higher PL intensity of Z-scheme sample as compared to two-component system in the same time exemplify the plausible charge isolation in two different photosystems.

![Graph](image)

**Fig. 7.** Transient photocurrent responses of (a) TiO$_2$, (b) MWCNT-TiO$_2$, (c) Zn$_{0.5}$Cd$_{0.5}$S, (d) MWCNT-Zn$_{0.5}$Cd$_{0.5}$S, and (e) Zn$_{0.5}$Cd$_{0.5}$S-MWCNT-TiO$_2$ nanocomposites at a bias voltage of 10 mV under intermittent simulated solar light irradiation.
Band gap characterizations of the Z-scheme sample are of utmost important in determining their relative band positions (PS I and II) to attest the thermodynamic feasibility of the two-step photocatalytic water splitting. UV-Vis DRS of Zn$_{0.5}$Cd$_{0.5}$S (PS I) and TiO$_2$ (PS II) are presented in Fig. 8A with absorption edges at ca. 540 and 400 nm. Two shoulders which corresponded to the absorbance of PS I and II are observed in the absorption profile of the Z-scheme sample as depicted in the inset of Fig. 8A. According to the Kubelka-Munk (KM) function, the band gaps of PS I and II are estimated to be 2.20 and 3.05 eV, respectively (Fig. 8B). Besides, the flat-band potentials of PS I and II were fitted to be -1.38 and -0.43 V versus NHE from the Mott-Schottky plots in Fig. 8C. Working in conjugation with their band gaps, an estimated band-structure diagram of Z-schematic Zn$_{0.5}$Cd$_{0.5}$S-MWCNT-TiO$_2$ system is then proposed in Fig. 8D. The calculated work function of MWCNTs is -4.3 eV vs. vacuum (0.14 eV vs. NHE), which is judiciously arranged between the CB of TiO$_2$ and VB of Zn$_{0.5}$Cd$_{0.5}$S [27]. Thus, this Z-scheme system can allow the vectorial electron transfer and demonstrates the strong reduction ability of Zn$_{0.5}$Cd$_{0.5}$S and strong oxidizing ability of TiO$_2$, with their relative band positions (CB of PS I and VB of PS II) which are sufficiently to govern the excellent redox reaction.
Fig. 8. Band gap characterizations of Zn$_{0.5}$Cd$_{0.5}$S-MWCNT-TiO$_2$ nanocomposites: (A) UV-Vis DRS of (a) TiO$_2$ and (b) Zn$_{0.5}$Cd$_{0.5}$S (inset show one peak and two shoulders observed in Zn$_{0.5}$Cd$_{0.5}$S-MWCNT-TiO$_2$ samples which corresponding to light absorption of PS I and II). (B) Plot of transformed KM function vs $h\nu$ for (a) TiO$_2$ and (b) Zn$_{0.5}$Cd$_{0.5}$S. (C) Mott-Schottky plots of TiO$_2$ and Zn$_{0.5}$Cd$_{0.5}$S. Frequency: 100 Hz. (D) Estimated relative band positions of Zn$_{0.5}$Cd$_{0.5}$S-MWCNT-TiO$_2$ nanocomposite.
4. Conclusions

In summary, we have successfully devised an artificial Z-scheme system using MWCNTs as a solid-state electron mediator in realizing highly efficient photocatalytic H\textsubscript{2} production. The combination of Zn\textsubscript{0.5}Cd\textsubscript{0.5}S-MWCNT-TiO\textsubscript{2} system enables the strong reducibility of PS I and the strong oxidizability of PS II to be ingeniously accomplished in one nanospace, achieving a H\textsubscript{2} evolution rate of 21.9 µmol h\textsuperscript{-1}. The massive 4.5- and 2.8-fold improvement in the photocatalytic H\textsubscript{2} production over pristine Zn\textsubscript{0.5}Cd\textsubscript{0.5}S and MWCNT-Zn\textsubscript{0.5}Cd\textsubscript{0.5}S samples was mainly attributed to the enhanced spatial charge isolation with the photogenerated electrons and holes being accommodated in PS I and II, respectively. As aforementioned, this is the first ever reported Z-scheme water splitting system which employs MWCNTs as an interparticulate electron relay to shuttle the vectorial electron transfer from PS II to PS I. As a whole, our findings highlight the potential of MWCNTs as a new intriguing graphitic carbon material in designing all-solid-state Z-scheme system and pave a future way in developing high-efficiency devises for photocatalytic H\textsubscript{2} production.

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References


Graphical Abstract
Highlights:

- All-solid-state Z-scheme system mediated by MWCNTs is proposed.
- The unique vectorial electron transfer imparts efficient spatial charge isolation.
- Electrons are isolated in Zn$_{0.5}$Cd$_{0.5}$S and holes in TiO$_2$ with strong redox ability.
- The presence of MWCNTs as electron mediator enhances the H$_2$ evolution rate.