## Enhanced photocatalytic hydrogen evolution by prolonging the lifetime of carriers in ZnO/CdS heterostructures<sup>†</sup>

Xuewen Wang, ‡<sup>a</sup> Gang Liu, ‡<sup>a</sup> Zhi-Gang Chen,<sup>b</sup> Feng Li,<sup>a</sup> Lianzhou Wang,<sup>b</sup> Gao Qing Lu\*<sup>b</sup> and Hui-Ming Cheng\*<sup>a</sup>

Received (in Cambridge, UK) 6th March 2009, Accepted 1st April 2009 First published as an Advance Article on the web 6th May 2009 DOI: 10.1039/b904668b

Coupled ZnO/CdS heterostructures based on the Z-scheme mechanism are demonstrated to be highly active photocatalysts for  $H_2$  evolution under simulated solar light irradiation due to the greatly prolonged lifetime of photoexcited carriers.

The search for highly active photocatalysts for water splitting under solar light irradiation has been a challenging yet very important research topic due to the growing environmental concerns and increasing energy demand. In addition to singlephase photocatalysts for water splitting,<sup>1-5</sup> integration of two or more desirable semiconductor systems<sup>6-10</sup> based on the Z-scheme mimicking the natural photosynthesis process in plants<sup>7,8</sup> or the traditional electron transfer process,<sup>9,10</sup> where photoexcited electrons can flow from one semiconductor with a higher conduction band minimum (CBM) to the other with a lower CBM, is of great importance in better realizing water splitting under solar irradiation. Compared to single-phase photocatalysts, which usually have less flexibility in changing their electronic structure by doping and low separation efficiency of photoexcited charge carriers, the hybrid or integrated multi-semiconductor systems possess significant advantages of promoting the separation of electron-hole pairs and keeping reduction and oxidation reactions at two different reaction sites.

Based on the Z-scheme where two separate semiconductors are suspended in a reaction solution containing indispensable redox mediators, many successful examples have been developed in recent years, such as the semiconductor pairs of  $RuO_2/WO_3$ ,<sup>11</sup> Pt-WO\_3/Pt-SrTiO\_3 (Cr-Ta-doped),<sup>12</sup> Pt-SrTiO\_3/Rh-BiVO\_4,<sup>13</sup> rutile/anatase TiO\_2,<sup>14</sup> RuO\_2-TaON/Pt-TaON,<sup>15</sup> Pt-CaTaO\_2N/WO\_3<sup>16</sup> together with their redox mediators Fe<sup>2+</sup>/Fe<sup>3+</sup>, I<sup>-</sup>/IO<sup>3-</sup> and Br<sup>-</sup>/BrO<sup>3-</sup>. The advantages of these systems lie in the availability of the higher CBM of one semiconductor and the lower valence band maximum (VBM) of the other in water splitting reactions. However,

these reactions suffer from competing oxidation/reduction carriers in solutions, which reduce the reaction efficiency. On the other hand, two intimately contacted semiconductor systems without the assistance of redox mediators, such as the reported CdS/TiO<sub>2</sub><sup>7</sup> and Cr-In<sub>2</sub>O<sub>3</sub>/Cr-Ba<sub>2</sub>In<sub>2</sub>O<sub>3</sub>,<sup>10</sup> can be effective in promoting the separation of carriers by transferring the photoexcited electrons in the higher CBM to the lower CBM, which could result in lowered reduction power of transferred electrons and then the impairment of the capability for hydrogen generation. According to the above results and analysis, it is therefore considered that if some excited electrons in one semiconductor with a lower CBM could recombine with the holes in the other with a higher VBM in two contacted semiconductors (Fig. 1) more powerful excited electrons and holes can be retained on different counterparts. According to an early investigation by Spanhel et al.,<sup>17</sup> it was found that the photoexcited electron injection efficiency from CdS into ZnO was much less efficient than that from CdS into TiO<sub>2</sub>. We also noted that the ZnO/CdS coupling unit is widely used in PN junction solar cells due to its excellent carrier transport at the interface.<sup>18,19</sup> Therefore, it may be an effective system to realize the desirable reverse carrier transfer and hence to possess a favorable photocatalytic water splitting capability. In this work, we clearly demonstrate the synergistic effects of coupled ZnO/CdS heterostructures on photocatalytic water splitting by the Z-scheme, which contribute to a ca. 14 and 40 times enhancement in hydrogen evolution compared to the sole CdS and ZnO under the same simulated solar light irradiation.

ZnO/CdS heterostructures were prepared by a wet chemistry method. 0.02 M  $NH_3{\cdot}H_2O$  solution was dropwise added into a 20 mL aqueous solution containing 20 mmol



Fig. 1 Schematic of band structures in the Z-scheme mechanism in  $\rm ZnO/CdS$  heterostructures.

<sup>&</sup>lt;sup>a</sup> Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, 72 Wenhua Road, Shenyang 110016, P. R. China. E-mail: cheng@imr.ac.cn; Fax: +86 24 23903126; Tel: +86 24 23971611

<sup>&</sup>lt;sup>b</sup> ARC Centre of Excellence for Functional Nanomaterials, School of Engineering and Australian Institute of Bioengineering and Nanotechnology, The University of Queensland, Qld. 4072, Australia. E-mail: maxlu@uq.edu.au; Fax: +61 7 33656074; Tel: +61 7 33653735

<sup>†</sup> Electronic supplementary information (ESI) available: XRD patterns, TEM images, XPS spectra, and photocurrent spectra. See DOI: 10.1039/b904668b

<sup>‡</sup> These authors contributed equally to this work.



**Fig. 2** UV-visible absorption spectra of ZnO,  $(ZnO)_x/(CdS)_y$  heterostructures (where x and y denote the molar ratios of Zn and Cd precursors in preparing the ZnO/CdS heterostructures), and CdS.

Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O at room temperature. When the pH value of the solution reached 7, the white Zn(OH)<sub>2</sub> was precipitated and then was washed with de-ionized water three times. After that, 2–36 mmol CdCl<sub>2</sub>·2.5H<sub>2</sub>O was dissolved into a 30 mL aqueous solution containing all the above white Zn(OH)<sub>2</sub> precipitate. Afterwards, a 0.2 M Na<sub>2</sub>S solution was added dropwise into the suspension until pH = 7. The final precipitate was washed three times and dried at 60 °C for 24 h in air, resulting in ZnO/CdS heterostructure samples.

The XRD patterns of ZnO/CdS heterostructures with different molar ratios of ZnO to CdS are given in Fig. S1.<sup>†</sup> All the diffraction peaks can be indexed to hexagonal ZnO (space group: *P63mc*) and CdS (space group: *P63mc*) phases. Compared to the sharp peaks of the ZnO phase, the much broader diffraction peaks of the CdS phase suggest its relatively small particle size. The Brunauer–Emmett–Teller (BET) specific surface area of the ZnO/CdS heterostructures was *ca.* 90 m<sup>2</sup> g<sup>-1</sup>. The optical absorption spectra of these samples (Fig. 2) indicate that the absorption edge can be drastically extended to around 550 nm upon the addition of a small portion of CdS ((ZnO)<sub>1</sub>/(CdS)<sub>0.1</sub>). An increase in the CdS ratio led to further shifts in the absorption edge to be closer to that of pure CdS.

Photoelectrochemical results (Fig. S2<sup>+</sup>) of the photoanodes with CdS, ZnO and a typical ZnO/CdS heterostructure (i.e.,  $(ZnO)_1/(CdS)_{0,2}$ ) show that the generated photocurrent with the CdS photoanode is 1.2 µA despite of its long light absorption edge up to ca. 600 nm. However, the photocurrent from the ZnO photoanode with its light absorption range less than 400 nm was much larger, around 100 µA. This remarkable difference in generating photocurrent is closely related to the different VBMs of CdS and ZnO. To a large extent, the lower VBM of ZnO by 0.5 eV than that of CdS enables more efficient transfer of holes in the interface between ZnO and electrolyte, consequently reducing the recombination probability of electrons and holes. As expected, the photocurrent of the (ZnO)<sub>1</sub>/(CdS)<sub>0.2</sub> photoanode was drastically enhanced to 350 µA, around 291 and 3.5 times that of pure CdS and ZnO photoanodes, respectively. This obvious synergistic effect can be attributed to the significantly suppressed recombination of charge carriers in the heterostructures, being a primary evidence of the success of our new heterogeneous photocatalyst design.



**Fig. 3** (a)  $H_2$  evolution of ZnO,  $(ZnO)_x/(CdS)_y$  heterostructures and CdS, where *x* and *y* denote the molar ratios of Zn and Cd precursors; (b)  $H_2$  evolution of the  $(ZnO)_1/(CdS)_{0.2}$  heterostructure with different content of loaded Pt. Measurement conditions: 0.2 g sample, 300 mL aqueous solution containing 0.1 M Na<sub>2</sub>S and 0.1 M Na<sub>2</sub>SO<sub>3</sub>, and light source: 300 W Xe lamp.

H<sub>2</sub> evolution measurements from photocatalytic water splitting using the ZnO/CdS heterostructures were conducted (Fig. 3a). The measurements were carried out in an aqueous solution containing  $SO_3^{2-}$  and  $S^{2-}$  ions as sacrificial reagents under the simulated solar light irradiation. The ZnO/CdS heterostructures exhibit a much higher ability for H<sub>2</sub> evolution than that of the sole CdS or ZnO. In particular,  $(ZnO)_1/(CdS)_{0,2}$  demonstrates the highest H<sub>2</sub> evolution rate of 1805 µmol h<sup>-1</sup> g<sup>-1</sup> among different ZnO/CdS heterostructures, which is 14 and 40 times that of the reference CdS and ZnO photocatalysts prepared by parallel synthesis routes. H<sub>2</sub> evolution from ZnO/CdS heterostructures gradually decreases with the increasing CdS molar ratios though their absorption edges are further extended. This is possibly due to the decreased oxidation reaction sites on the ZnO surface by post-deposited CdS.

 $H_2$  evolution of the  $(ZnO)_1/(CdS)_{0.2}$  heterostructure with different contents of Pt co-catalyst was further investigated and is shown in Fig. 3b. The  $H_2$  evolution rate of the  $(ZnO)_1/(CdS)_{0.2}$  heterostructure was significantly enhanced by loading Pt. The optimal loading content of Pt was found to be 1 wt%, which gives the highest  $H_2$  evolution (3870 µmol h<sup>-1</sup> g<sup>-1</sup>) and is twice that of the  $(ZnO)_1/(CdS)_{0.2}$ alone. It is known that Pt particles loaded on photocatalysts can trap excited electrons and act as  $H_2$  evolution sites.<sup>6,20,21</sup> These results clearly demonstrate that the Pt-loaded  $(ZnO)_1/(CdS)_{0.2}$  heterostructure is an excellent photocatalysts for water splitting. The average photonic conversion efficiency within 300 ~ 600 nm is estimated to be 3.2%.



**Fig. 4** Fluorescence emission decay spectra of the  $(ZnO)_1/(CdS)_{0.2}$  heterostructure, ZnO and CdS monitored at 575 nm by timecorrelated single photon counting. The powder samples in a quartz cell were excited by the 340 nm laser in air at room temperature. The inset is the comparison of H<sub>2</sub> evolution from ZnO, CdS and  $(ZnO)_1/(CdS)_{0.2}$  heterostructure.

To better understand the synergistic effects of coupled ZnO/CdS heterostructures on hydrogen evolution, we investigated their decay behavior of photoexcited carriers. Fig. 4 shows the time-resolved fluorescence emission decay spectra of ZnO, CdS and  $(ZnO)_1/(CdS)_{0.2}$  heterostructure monitored at 575 nm. Clearly, in contrast to the nearly overlapped fast decay curves of ZnO and CdS, the decay kinetics of the  $(ZnO)_1/(CdS)_{0.2}$  heterostructure is strikingly slow. In detail, the decay lifetime of carriers in sole ZnO and CdS is *ca*. 60 ns, while the decay lifetime of carriers in the  $(ZnO)_1/(CdS)_{0.2}$  heterostructure is greatly prolonged to 220 ns. This indicates that the transfer of photoexcited electrons and holes between ZnO and CdS must exist, which can retard the recombination probability of electron and hole pairs and thus improve its photoactivity as shown in Fig. 3.

The realization of such synergistic effects in the ZnO/CdS heterostructure requires two key conditions. One is the intimate contact between ZnO and CdS phases. In a reference experiment, a mixture of ZnO and CdS by mechanical milling with the same ratio as that in the  $(ZnO)_1/(CdS)_{0,2}$  heterostructure demonstrates no obvious improvement in hydrogen evolution compared to ZnO and CdS. Transmission electron microscope (TEM) imaging (Fig. S3<sup>†</sup>) reveals that the primary particles in several nanometres have intimate interfaces. X-Ray photoelectron (XPS) spectroscopy (Fig. S4<sup>†</sup>) further confirms the strong phase interaction by the binding energy shift of  $Zn 2p_{3/2}$ , Cd  $3d_{5/2}$ , O 1s and S 2p in the  $(ZnO)_1/(CdS)_{0,2}$  heterostructure in contrast to the pure ZnO and CdS. The important role of intimate contact between different phases in facilitating the transfer of carriers from one phase to the other is also evidenced in anatase-rutile mixed TiO2.<sup>22</sup> The other is the indispensable availability of a small portion of UV light to realize the synergistic effects of the integrated (ZnO)1/(CdS)0.2 heterostructure. The photoexcitation of wide bandgap ZnO (3.2 eV) in the heterostructures requires UV light. Upon the simulated solar light irradiation, electrons in the valence bands of CdS and ZnO can be excited so that the possible carrier transfer between them can occur, which is responsible for the greatly prolonged decay lifetime of carriers in the  $(ZnO)_1/(CdS)_{0.2}$  heterostructure.

However, it should be pointed out that after the recombination of a conduction band electron from ZnO with a valence band hole from CdS, the conduction band electron transfer from CdS to the conduction band of ZnO and the valence band hole transfer from ZnO to the valence band of CdS might exist but the probability can be very low due to the competitive equilibrium from surface redox reactions  $(2h^+ + SO_3^{2-} + O^{2-} \rightarrow SO_4^{2-}; 2e^- + 2H^+ \rightarrow H_2).$ 

In summary, ZnO/CdS heterostructures based on the Z-scheme mechanism are demonstrated to be highly active photocatalysts for H<sub>2</sub> evolution under simulated solar light irradiation. Particularly, H<sub>2</sub> evolution with 1 wt% Pt-loaded  $(ZnO)_1/(CdS)_{0.2}$  reaches 3870 µmol h<sup>-1</sup> g<sup>-1</sup>. The prolonged lifetime of photoexcited carriers in the coupled heterostructures is responsible for the enhanced hydrogen evolution. Therefore, the Z-scheme mechanism occurring within two intimately contacted semiconductors is successfully demonstrated in designing heterogeneous photocatalysts for water splitting.

The work was supported by the Major Basic Research Program, Ministry of Science and Technology China (No. 2009CB220001) and the Australian Research Council under its Centers of Excellence Program.

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