

# Effects of the preparation method of the ternary CdS/TiO<sub>2</sub>/Pt hybrid photocatalysts on visible light-induced hydrogen production†

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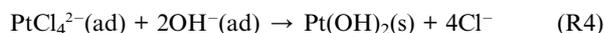
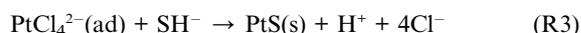
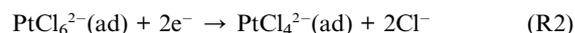
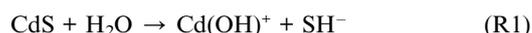
A variety of combinations of CdS, TiO<sub>2</sub>, and Pt in preparing the hybrid catalysts were studied for hydrogen production under visible light ( $\lambda > 420$  nm) irradiation. The preparation method sensitively influenced the activity of the ternary hybrid catalysts. The formation of the potential gradient at the interface between CdS and TiO<sub>2</sub> is necessary in achieving the efficient charge separation and transfer and how the platinum as a cocatalyst is loaded onto the CdS/TiO<sub>2</sub> hybrid catalysts determines the overall hydrogen production efficiency. The common method of photoplatinization of CdS/TiO<sub>2</sub> hybrid [Pt-(CdS/TiO<sub>2</sub>)] was much less efficient than the present method in which Pt was photodeposited on bare TiO<sub>2</sub>, which was followed by the deposition of CdS [CdS/(Pt-TiO<sub>2</sub>)]. The CdS/(Pt-TiO<sub>2</sub>) has the hydrogen production rate ranging  $(6-9) \times 10^{-3}$  mol h<sup>-1</sup> g<sup>-1</sup>, which is higher by a factor of 3–30 than that of Pt-(CdS/TiO<sub>2</sub>). The photocatalytic activity of the ternary hybrid catalysts was extremely sensitive to where the platinum is loaded. The photoactivity of the hybrid catalyst was also assessed in terms of the photocurrent collected by the methyl viologen electron shuttle in the catalyst suspension. CdS/(Pt-TiO<sub>2</sub>) generated higher photocurrents than Pt-(CdS/TiO<sub>2</sub>) by a factor of 2–7. The extreme sensitivity of the preparation method to the hydrogen production activity should be taken into account when hybrid photocatalysts are designed and prepared.

## Introduction

Hydrogen has received growing attention as a medium of solar energy storage and transfer.<sup>1</sup> By contrast to conventional fossil fuels, hydrogen is environmentally clean (*i.e.*, no carbon footprint) and has higher energy capacity per weight than alcohols. One of the ideal ways to produce hydrogen from renewable sources is to utilize solar energy for the water splitting reaction. As a mean to achieve this goal, semiconductor photocatalysts have been extensively studied. In particular, a variety of visible light-active photocatalysts<sup>2–6</sup> including CdS<sup>7–13</sup> have been studied.

In terms of the band gap magnitude and the position of band edges, CdS is ideally suited for photocatalytic water splitting but it is not effective at all unless suitable electron donors (EDs) are present. Therefore, the CdS-based photocatalytic system can be applied to producing hydrogen from water containing electron donors (*e.g.*, wastewaters). The photocatalytic efficiency of CdS is substantially influenced by various factors such as crystallinity,<sup>9</sup> surface area,<sup>10</sup> surface etching,<sup>11,14,15</sup> pH and related properties (*e.g.*, flat band potential, surface charge),<sup>16–20</sup> ED and solvent (*e.g.*, alcohols, sulfide, sulfite),<sup>10,18,21,22</sup> cocatalyst (*e.g.*, Pt, Ni),<sup>10,14,15,20–27</sup> support materials (*e.g.*, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, ZnO, ZnS, zeolite, KNbO<sub>3</sub>),<sup>22,28–31</sup> *etc.* For hydrogen production,

CdS particles are usually platinized either by physical mixing with Pt particles (*e.g.*, Pt black, Pt sol) or by photoplatinization. It is interesting to note that the reported effects of platinization are very diverse. For example, Reber and Rusek reported that platinized CdS (Pt-CdS) obtained by the photodeposition showed an enhanced hydrogen production rate of 300 mL/h at 1.5 wt% loading of Pt,<sup>10</sup> whereas Serpone *et al.* observed that the enhancement of hydrogen production by platinization was almost negligible.<sup>23</sup> Although photoplatinization is expected to make a better contact at the Pt/CdS interface than physical mixing, the former was reportedly much less effective than the latter for the photocatalytic degradation of lactic acid.<sup>32</sup> The surface chemistry of CdS usually interferes with the photochemical reduction of Pt ion (Pt<sup>4+</sup>) as follows:<sup>20</sup>



In acidic environment, PtS is deposited on the surface of CdS (R3) whereas Pt(OH)<sub>2</sub> is deposited at high pH (R4). These unwanted Pt species usually lower the efficiency, and thus subsequent heat treatment (>400 °C) is essentially required to convert PtS or Pt(OH)<sub>2</sub> to metallic Pt (Pt<sup>0</sup>).

An alternative method to improve the photoefficiency of CdS is hybridization with metal oxides like TiO<sub>2</sub> (*i.e.*, CdS/TiO<sub>2</sub>). Recently this hybrid photocatalyst has been highlighted as a material that mimics natural photosynthesis.<sup>33</sup> TiO<sub>2</sub> plays

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dual roles in the hybrid: it supports CdS and prevents aggregation of CdS, and enhances the charge separation by forming a potential gradient at the interface of CdS and TiO<sub>2</sub>. The rate of photoinduced electron transfer at CdS increases tenfold in the presence of TiO<sub>2</sub>,<sup>34,35</sup> which increases the photocatalytic efficiency.<sup>36</sup> However, the photoplatinized CdS/TiO<sub>2</sub> (Pt-CdS/TiO<sub>2</sub>) exhibited disappointingly low efficiency.<sup>29</sup> Alternatively, CdS can be physically mixed with platinized TiO<sub>2</sub> (CdS + Pt-TiO<sub>2</sub>). However, the activities of the physically mixed CdS + Pt-TiO<sub>2</sub> that were reported in the literature are inconsistent. It enhanced hydrogen production compared to plain CdS,<sup>25</sup> but sometimes lowered the efficiency by 8 times.<sup>23</sup>

We report a comparative study on the hybridization of CdS, TiO<sub>2</sub>, and Pt in terms of hydrogen production and photocurrent generation under visible light ( $\lambda > 420$  nm). It was found that changing the order of hybridization in the preparation step significantly altered the efficiency for both hydrogen production and photocurrent generation. CdS prepared on Pt-TiO<sub>2</sub> particles (CdS/Pt-TiO<sub>2</sub>) produced hydrogen at the milli-molar level, which is far more efficient than any other CdS/TiO<sub>2</sub> hybrid photocatalysts (*e.g.*, photoplatinized CdS/TiO<sub>2</sub>, physical mixing of CdS and Pt-TiO<sub>2</sub>, *etc.*) that have been reported in the literature. Direct contact of CdS on TiO<sub>2</sub> particles makes the electron transfer from CdS to TiO<sub>2</sub> efficient, and depositing Pt only on the TiO<sub>2</sub> surface seems to be critical in maximizing the overall efficiency.

## Experimental

### Materials and reagents

**CdS.** A solution of sodium sulfide (Na<sub>2</sub>S) was added dropwise to cadmium acetate solution (Cd(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O) with a molar ratio of 1 : 1, stirred for 1 h, filtered with 0.45  $\mu$ m PTFE (Millipore), washed with distilled water, and dried overnight at 60 °C after collection.

**CdS/TiO<sub>2</sub>.** The above CdS preparation was carried out in an aqueous suspension of TiO<sub>2</sub> (Degussa P25). TiO<sub>2</sub>, a mixture of anatase and rutile (8 : 2), has a BET surface area of *ca.* 50 m<sup>2</sup> g<sup>-1</sup> and its primary particle size is *ca.* 27 nm for anatase and *ca.* 16 nm for rutile. The weight ratio of CdS to TiO<sub>2</sub> is approximately 1.7.

**CdS/sgTiO<sub>2</sub>.** The synthetic procedure of sol-gel TiO<sub>2</sub> (sgTiO<sub>2</sub>) is described elsewhere.<sup>37</sup> 50 mL of the sgTiO<sub>2</sub> solution (1.24 g/L), 1 mL cadmium acetate solution (1 M) and 1 mL sodium sulfide solution (1 M) were mixed and diluted with distilled water to 285 mL, which was subsequently filtered and collected. The final weight ratio of CdS to sgTiO<sub>2</sub> is approximately 2.

**Pt-CdS, Pt-TiO<sub>2</sub>, Pt-sgTiO<sub>2</sub>.** The platinization of CdS followed a typical photodeposition method.<sup>10,11,24–26,29</sup> The as-prepared CdS suspension (0.5 g/L) with 10 mM Na<sub>2</sub>S, 10 mM Na<sub>2</sub>SO<sub>3</sub>, 0.1 mM H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (Aldrich), and 1 M methanol was irradiated with a 200 W Hg lamp for 45 min and collected. For the platinized TiO<sub>2</sub> (Pt-TiO<sub>2</sub>), 0.5 g/L TiO<sub>2</sub> (Degussa P25) or 0.22 g/L sgTiO<sub>2</sub> suspension with 0.1 mM H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O and 1 M methanol was irradiated and collected.

**Pt-(CdS/TiO<sub>2</sub>), Pt-(CdS/sgTiO<sub>2</sub>).** Three different methods (A, B, C) were employed for the preparation of Pt-(CdS/TiO<sub>2</sub>). (A) The as-prepared CdS/TiO<sub>2</sub> (0.25 g) was suspended in 0.5 L solution containing H<sub>2</sub>PtCl<sub>6</sub> (0.1 mM), methanol (1 M), Na<sub>2</sub>S (10 mM), and Na<sub>2</sub>SO<sub>3</sub> (10 mM), which was irradiated for 45 min using a 300 W Hg lamp. (B) Acetic acid (20 mL) as an electron donor (ED) was used instead of the mixture in method A (methanol + Na<sub>2</sub>S + Na<sub>2</sub>SO<sub>3</sub>). The other details are identical to those of method A. (C) The as-prepared CdS/TiO<sub>2</sub> (0.05 g) was suspended in 0.1 L solution containing H<sub>2</sub>PtCl<sub>6</sub> (0.1 mM), acetic acid (4 mL), Na<sub>2</sub>S (10 mM), and Na<sub>2</sub>SO<sub>3</sub> (10 mM), and irradiated for 4 h with visible light ( $>420$  nm) using a 450 W Xe arc lamp. For Pt-(CdS/sgTiO<sub>2</sub>), the as-prepared CdS/sgTiO<sub>2</sub> suspension (0.22 g/L) in the presence of methanol (1 M) and H<sub>2</sub>PtCl<sub>6</sub> (0.1 mM) was irradiated with a 300 W Hg lamp for 45 min and recovered as powder.

**CdS/(Pt-TiO<sub>2</sub>), CdS/(Pt-sgTiO<sub>2</sub>).** CdS was prepared in the presence of Pt-TiO<sub>2</sub> or Pt-sgTiO<sub>2</sub> particles.

**sgTiO<sub>2</sub>/(Pt-CdS).** sgTiO<sub>2</sub> was synthesized in the presence of Pt-CdS.

**Pt<sub>sol</sub>.** Colloidal platinum was prepared by following the literature method.<sup>38</sup>

The above photocatalyst particles were analyzed by field emission transmission electron microscopy (FE-TEM, JEM-20110F) and field emission scanning electron microscopy (FE-SEM, LEO 1550 VP).

### Hydrogen production and photocurrent measurement

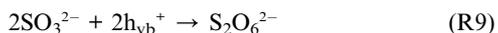
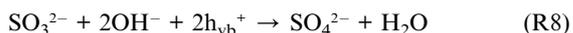
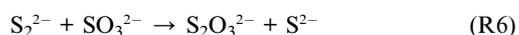
The hydrogen production was achieved under visible light irradiation in an aqueous solution (25 mL) containing 0.5 g/L photocatalyst, Na<sub>2</sub>S (4 or 40 mM), and Na<sub>2</sub>SO<sub>4</sub> (4 or 40 mM). A 450 W Xe arc lamp was used as a light source. Light passed through a 10 cm IR water filter and a cutoff filter ( $\lambda > 420$  nm), and then the filtered light was focused onto the reactor. Prior to light illumination, nitrogen was purged for 30 min. During irradiation, the headspace gas (*ca.* 10 mL) of the reactor was intermittently sampled and analyzed for H<sub>2</sub> using a gas chromatograph (Agilent) equipped with a thermal conductivity detector and a 5 Å molecular sieve column. Light intensity was measured by chemical actinometry using (*E*)- $\alpha$ -(2,5-dimethyl-3-furylethylidene) (isopropylidene)succinic anhydride (Aberchrome 540).<sup>39</sup> The typical incident light intensity was measured to be about  $2 \times 10^{-3}$  einstein L<sup>-1</sup> min<sup>-1</sup> in the wavelength range 420–550 nm.

Photocurrents were collected on an inert working electrode (Pt) immersed in an aqueous suspension of photocatalyst (0.5 g/L, 0.95 N NaOH) using methyl viologen (MV<sup>2+</sup>, 0.5 mM) as an electron shuttle as described elsewhere.<sup>40–42</sup> A saturated calomel electrode (SCE) and a graphite rod were used as a reference and a counter electrode, respectively. For the collection of MV<sup>2+</sup>-mediated photocurrent, the working electrode was held at  $-0.4$  V *vs.* SCE. Before and during irradiation, nitrogen gas was continuously purged, and a 300 W Xe arc lamp was used for visible light irradiation ( $\lambda > 420$  nm).

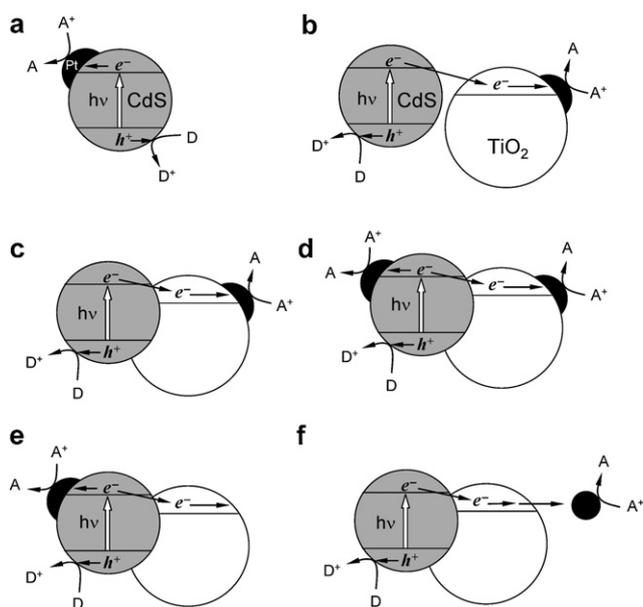
## Results and discussion

### Photocatalytic hydrogen production on hybrid catalysts

The hybrid photocatalysts tested in this study are illustratively compared in Scheme 1 and the measured activities for hydrogen production are summarized in Table 1. The CdS particles prepared by hydrolysis precipitation bear a reddish yellow color. As the concentration of CdS increases, the size of CdS particle grows. The dried and re-collected CdS powder exhibits broad and weak XRD peaks at  $2\theta = 28, 44,$  and  $52^\circ$ , which is a typical pattern of cubic CdS. No heat treatment was carried out. The as-prepared CdS aggregates are in the size range 1 to  $3\ \mu\text{m}$  (Fig. 1) and produced hydrogen at the rate of  $1.6 \times 10^{-4}\ \text{mol h}^{-1}\ \text{g}^{-1}$  in the presence of mixed ED (sulfide + sulfite) under visible light irradiation. This mixed ED was found to be better than either sulfide alone or sulfite alone for hydrogen production because sulfides are regenerated through the reaction of disulfide ( $\text{S}_2^{2-}$ ) and sulfite as follows:<sup>10</sup>



The photoactivity of the synthesized CdS is a little higher than that of Aldrich CdS (Table 1). The platinization of CdS (Scheme 1a) did not improve the activity; the rate of hydrogen

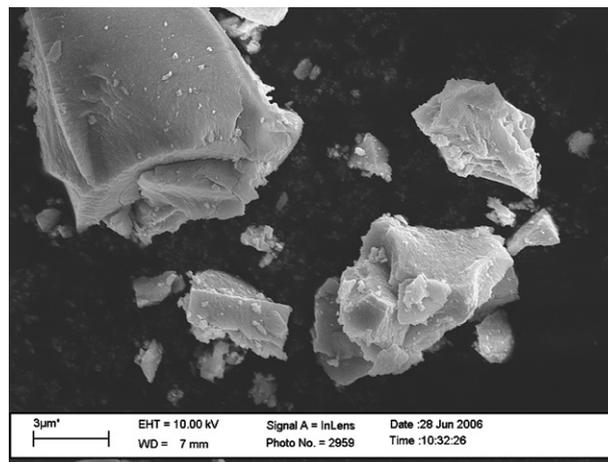


**Scheme 1** Illustrative diagrams of the electron transfers in the hybrid photocatalysts. (a) Pt-CdS; (b) CdS + Pt-TiO<sub>2</sub> (physically mixed); (c) CdS/(Pt-TiO<sub>2</sub>); (d) Pt-(CdS/TiO<sub>2</sub>); (e) sgTiO<sub>2</sub>/(Pt-CdS); (f) CdS/TiO<sub>2</sub> + Pt sol.

**Table 1** Hydrogen production rates of various hybrid photocatalysts under visible light

Photocatalyst <sup>a</sup>	H <sub>2</sub> production ( $\times 10^{-3}\ \text{mol h}^{-1}\ \text{g}^{-1}$ ) <sup>b</sup>	
	40 mM (ED) <sup>c</sup>	4 mM (ED) <sup>c</sup>
T1a CdS	0.17	—
T1b CdS (Aldrich)	0.88	—
T2 CdS + TiO <sub>2</sub>	0.26	—
T3 CdS/TiO <sub>2</sub>	0.32	—
T4 Pt-CdS	0.26	0.16
T5a Pt-CdS + TiO <sub>2</sub>	0.42	0.12
T5b Pt-CdS + sgTiO <sub>2</sub>	0.45	0.08
T6a CdS + Pt-TiO <sub>2</sub>	1.05	0.73
T6b CdS + Pt-sgTiO <sub>2</sub>	1.60	0.38
T7a Pt-(CdS/TiO <sub>2</sub> ) A	0.77	0.30
T7b Pt-(CdS/TiO <sub>2</sub> ) B	1.06	0.24
T7c Pt-(CdS/TiO <sub>2</sub> ) C	2.42	0.20
T7d Pt-(CdS/sgTiO <sub>2</sub> )	2.42	0.85
T8 Pt <sub>sol</sub> + (CdS/TiO <sub>2</sub> )	2.06	1.21
T9a CdS/(Pt-TiO <sub>2</sub> )	6.72	8.8
T9b CdS/(Pt-sgTiO <sub>2</sub> )	2.67	2.69
T10 sgTiO <sub>2</sub> /(Pt-CdS)	0.25	0.88

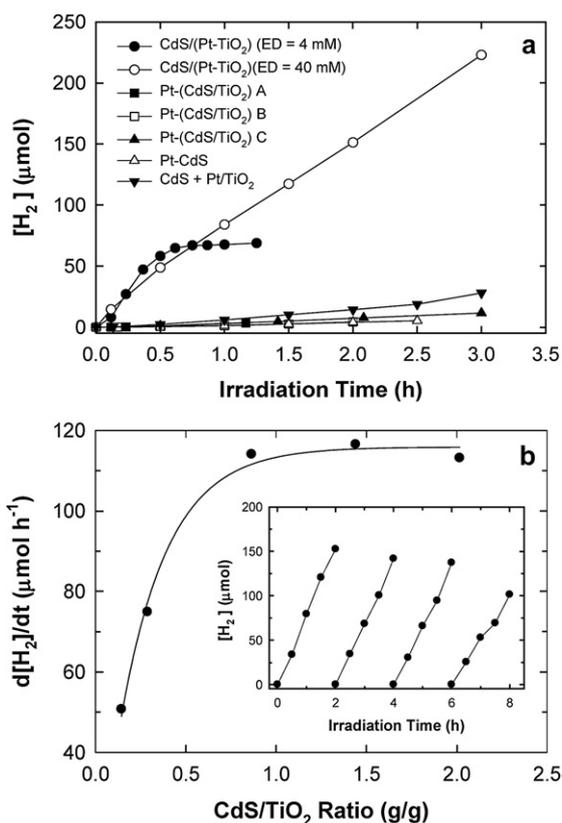
<sup>a</sup> [CdS]/[TiO<sub>2</sub>] (g/g)  $\approx 1.7$ ; [CdS]/[sgTiO<sub>2</sub>] (g/g)  $\approx 2$ ; Pt<sub>sol</sub> = 3 mL added (typical amount of Pt = 0.3 wt%). “+” means physical mixing. <sup>b</sup> Average rate after 3 h irradiation ( $\lambda > 420\ \text{nm}$ ). [photocatalyst] = 0.5 g/L; solution volume = 25 mL; head-space volume = 10 mL. Light intensity was measured to be around  $2 \times 10^{-3}\ \text{einstein/min/L}$ . <sup>c</sup> Each Na<sub>2</sub>S and Na<sub>2</sub>SO<sub>3</sub>.



**Fig. 1** SEM image of the as-prepared CdS particles.

production remains as low as  $(1.6\text{--}2.4) \times 10^{-4}\ \text{mol h}^{-1}\ \text{g}^{-1}$  (Fig. 2a), which is comparable to the literature value.<sup>25,43</sup>

The hybridization of CdS with TiO<sub>2</sub> was performed in various ways to enhance the rate of hydrogen production because the potential gradient at the interface of TiO<sub>2</sub>/CdS enhances the efficiency of charge separation.<sup>34,35</sup> The photoactivity of CdS and Pt-CdS, which were physically mixed with or directly deposited onto TiO<sub>2</sub> particles, was improved. It is interesting to note that the physical mixture of CdS and Pt-TiO<sub>2</sub> (CdS + Pt-TiO<sub>2</sub>) shows higher photoactivity than that of Pt-CdS + TiO<sub>2</sub> (T5 vs. T6). (The sign “+” means physical mixing throughout the text.) This indicates that the hydrogen formation on the surface of Pt is more favored on the TiO<sub>2</sub> side. This is consistent with the



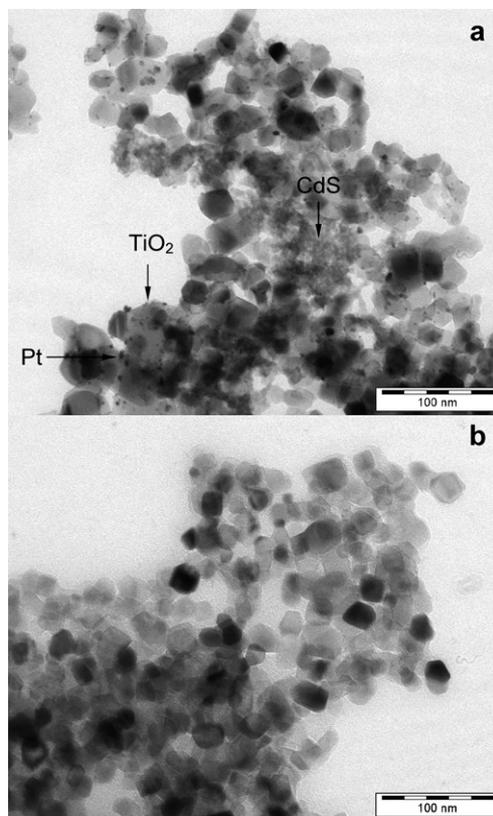
**Fig. 2** (a) Effects of different hybridization of CdS/TiO<sub>2</sub>/Pt on the hydrogen production. [photocatalyst] = 0.5 g/L (25 mL); [Na<sub>2</sub>S] = [Na<sub>2</sub>SO<sub>3</sub>] = 4 or 40 mM; nitrogen purged for 30 min prior to visible light ( $\lambda > 420$  nm) irradiation. (b) The rate of hydrogen production depending on the amount of CdS in the CdS/Pt-TiO<sub>2</sub>. [Na<sub>2</sub>S] = [Na<sub>2</sub>SO<sub>3</sub>] = 4 mM; other details identical to those of (a). Inset shows repeated hydrogen production in CdS/(Pt-TiO<sub>2</sub>) suspension with 40 mM Na<sub>2</sub>S and 40 mM Na<sub>2</sub>SO<sub>3</sub>.

fact that the conduction band (CB) edge potential of TiO<sub>2</sub> ( $E_{CB} = -0.43$  V vs. NHE at pH 10) is more positive than that of CdS ( $E_{CB} = -0.75$  V vs. NHE) with creating the potential gradient at the CdS/TiO<sub>2</sub> interface. The CB electrons generated on CdS transfer to TiO<sub>2</sub> CB through the potential gradient. Another reason for the lower activity of (Pt-CdS + TiO<sub>2</sub>) might be related to the fact that the Pt speciation on CdS could be different from that on TiO<sub>2</sub>. It has been reported that platinum ions (Pt<sup>IV</sup>) at the CdS surface are transformed into Pt<sup>II</sup>S or Pt<sup>II</sup>(OH)<sub>2</sub> in the process of photoplatinization (R2–R4), and thus subsequent heat treatment (>400 °C) was required to obtain active Pt<sup>0</sup>.<sup>14</sup> On the other hand, the platinum ions could be converted to metallic Pt<sup>0</sup> on the TiO<sub>2</sub> surface without further heat treatment.<sup>44,45</sup>

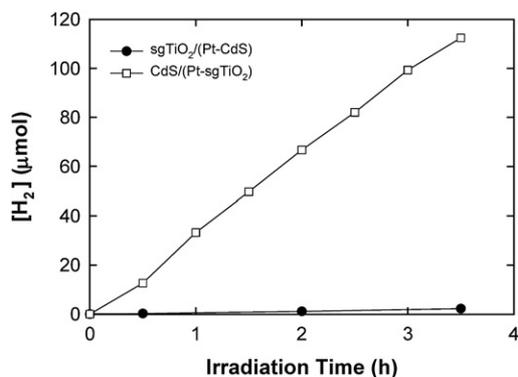
To improve the interfacial contact between CdS and TiO<sub>2</sub>, CdS was prepared in a suspension of TiO<sub>2</sub> particles and then platinum was deposited on the surface of the CdS/TiO<sub>2</sub> hybrid through three different methods (A, B, and C) (Scheme 1d). Methods A and B are frequently found in the literature<sup>10,11,24–26,29</sup> and method C is a modification of method B. However, Fig. 2a shows that all three hybrids produced a small amount of hydrogen (*ca.*  $2.4 \times 10^{-4}$  mol h<sup>-1</sup> g<sup>-1</sup>) with ED (4 mM Na<sub>2</sub>S + 4 mM Na<sub>2</sub>SO<sub>3</sub>), which is not much better than Pt-CdS (Scheme 1a). High ED

concentration (40 mM Na<sub>2</sub>S + 40 mM Na<sub>2</sub>SO<sub>3</sub>) slightly increased the rate of hydrogen production. On the other hand, CdS/(Pt-TiO<sub>2</sub>) (Scheme 1c), which was obtained *via* the photoplatinization of TiO<sub>2</sub> and the subsequent preparation of CdS on the as-prepared Pt-TiO<sub>2</sub>, showed the highest rate of hydrogen production of *ca.*  $6.7 \times 10^{-3}$  mol h<sup>-1</sup> g<sup>-1</sup> (corresponding to an apparent quantum efficiency of 4.5%) with [ED] = 40 mM. The initial rate of hydrogen production depended on the amount of CdS loaded on Pt-TiO<sub>2</sub>, and reached a plateau around [CdS] = 3 mM (where the weight ratio of CdS to TiO<sub>2</sub> is around 1.7) (Fig. 2b). CdS/(Pt-TiO<sub>2</sub>) was quite stable for repeated cycles of hydrogen production as long as ED was present (*see* Fig. 2b inset). The TEM images show the clear difference between CdS/(Pt-TiO<sub>2</sub>) and the conventional Pt-(CdS/TiO<sub>2</sub>) catalysts. On CdS/(Pt-TiO<sub>2</sub>) particles (Fig. 3a), discrete Pt nanoparticles with the size of 3–5 nm are clearly seen whereas they are not observed on Pt-(CdS/TiO<sub>2</sub>) (Fig. 3b). The deposited platinum seems to be uniformly distributed over the entire hybrid in the latter catalyst. Therefore, the vectorial electron transfer of CdS → TiO<sub>2</sub> → Pt is well defined in CdS/(Pt-TiO<sub>2</sub>) with enhanced charge separation but such unidirectional electron transfer and efficient charge separation is not favored with Pt-(CdS/TiO<sub>2</sub>) because the active Pt sites coexist in both CdS and TiO<sub>2</sub> phases.

Instead of using commercial TiO<sub>2</sub> particles (Degussa P25), TiO<sub>2</sub> nanoparticles prepared *via* sol-gel (sgTiO<sub>2</sub>) were hybridized with CdS and Pt. sgTiO<sub>2</sub> is usually better than P25 for hydrogen production (T6a vs. T6b; T7a–c vs. T7d) except in one case (T9a vs. T9b). It should be noted that the rate of hydrogen production in CdS/(Pt-sgTiO<sub>2</sub>) is far higher than in sgTiO<sub>2</sub>/(Pt-CdS) by



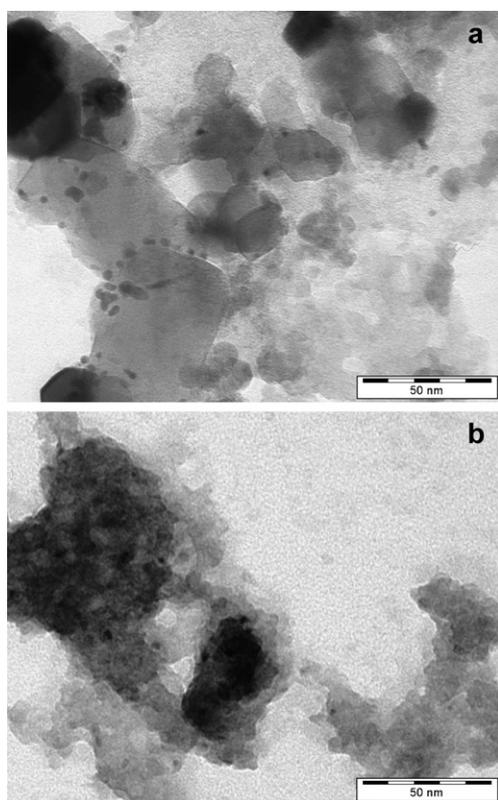
**Fig. 3** TEM images of (a) CdS/(Pt-TiO<sub>2</sub>) and (b) Pt-(CdS/TiO<sub>2</sub>) C.



**Fig. 4** Hydrogen production with sgTiO<sub>2</sub>/(Pt-CdS) and CdS/(Pt-sgTiO<sub>2</sub>) under visible light. [Na<sub>2</sub>S] = [Na<sub>2</sub>SO<sub>3</sub>] = 40 mM; other details identical to those of Fig. 2(a).

a factor of 10 (see Fig. 4 and T9b vs. T10). The TEM images of both hybrids are compared in Fig. 5. This confirms that the vectorial electron transfer of CdS → TiO<sub>2</sub> → Pt is critical in maximizing the hydrogen production in this ternary hybrid catalyst.

Finally, Pt sol was separately prepared and mixed with CdS/TiO<sub>2</sub> hybrid particles (Pt<sub>sol</sub> + (CdS/TiO<sub>2</sub>), Scheme 1f), which was compared with Pt-(CdS/TiO<sub>2</sub>) (Scheme 1d). Contrary to the expectation that the photodeposited Pt should be more efficient than the physically loaded Pt because of the better interfacial contact with the base semiconductor, the hydrogen production was generally higher with Pt<sub>sol</sub> + (CdS/TiO<sub>2</sub>). An



**Fig. 5** TEM images of (a) CdS/(Pt-sgTiO<sub>2</sub>) and (b) sgTiO<sub>2</sub>/(Pt-CdS).

explanation for the lower activity of Pt-(CdS/TiO<sub>2</sub>) might be either that CdS deposited on TiO<sub>2</sub> underwent photocorrosion during the photoreductive conversion of PtCl<sub>6</sub><sup>2-</sup> or that the major photodeposited Pt species is PtS or Pt(OH)<sub>2</sub> as we discussed above. Pt/TiO<sub>2</sub> or Pt sol alone did not produce any hydrogen under the same experimental conditions. A typical absorption spectrum of Pt/TiO<sub>2</sub> has a broad background in the visible light region, which is a characteristic optical property of Pt metal/TiO<sub>2</sub> composites,<sup>46</sup> but it usually has no visible light photocatalytic activity.

### Photocurrent generation

The photoelectrochemical characteristics of the hybrid catalysts were also compared. The visible light-induced photocurrents can be indirectly collected in the catalyst suspensions *via* an electron shuttle to an inert Pt electrode (Scheme 2).<sup>40,42</sup> Methyl viologen (MV<sup>2+</sup>) was used as the electron shuttle and no external electron donor was added. Under these conditions, the MV<sup>2+</sup>-mediated currents come directly from the CB electrons while the VB holes are consumed by water oxidation. It has been reported that CdS could produce oxygen from water in the presence of an electron scavenger under visible light irradiation (R10).<sup>47</sup>

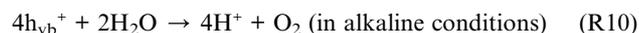
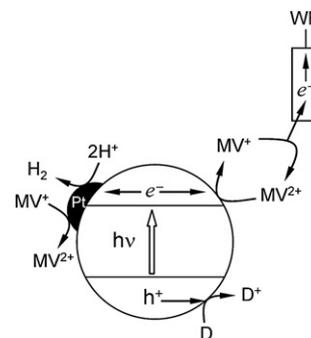
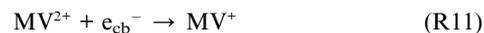
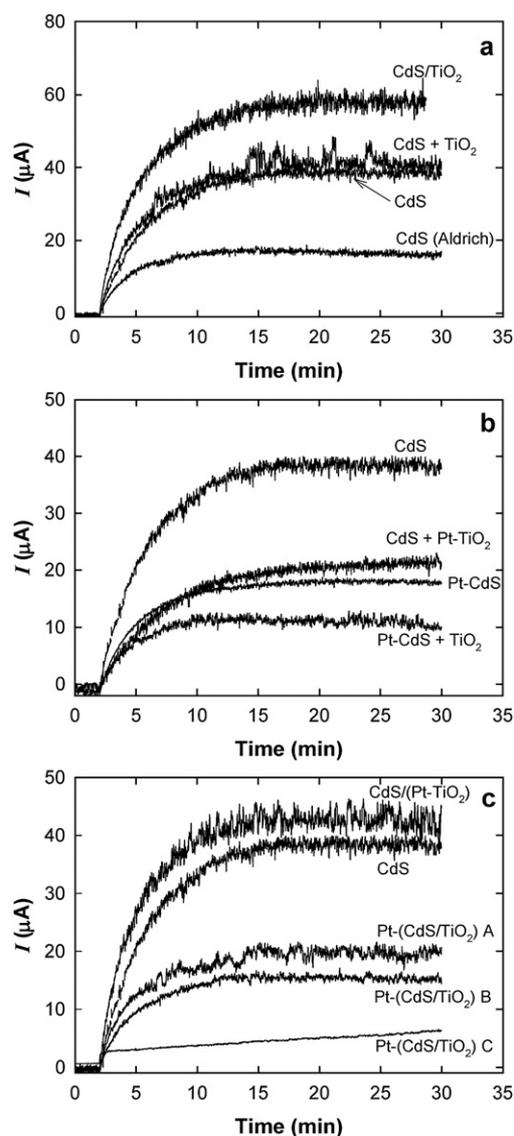


Fig. 6a compares the photocurrents collected in the suspensions of CdS, CdS + TiO<sub>2</sub>, and CdS/TiO<sub>2</sub> without platinum loading on their surfaces. The synthesized CdS is more efficient than Aldrich CdS by a factor of two. Physically mixed (CdS + TiO<sub>2</sub>) is no better than synthesized CdS. However, CdS/TiO<sub>2</sub> shows 50% higher photocurrent than synthesized CdS, which is consistent with the case of hydrogen production. This indicates that the electron transfer and separation would be enhanced by the potential gradient at the interface of CdS and TiO<sub>2</sub> with generating higher photocurrent and hydrogen.

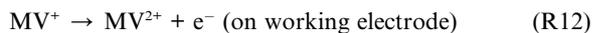
The presence of Pt makes the photocurrent generation mechanism more complicated since Pt improves the charge separation with facilitating the electron transfer whereas MV<sup>+</sup> can be reoxidized to MV<sup>2+</sup> with producing hydrogen on Pt (R11–R13).



**Scheme 2** Electron shuttle (MV<sup>2+</sup>)-mediated photocurrent collection on a Pt working electrode (WE) immersed in visible light-irradiated photocatalyst suspension.



**Fig. 6** Time profiles of MV<sup>2+</sup>-mediated photocurrents generated in hybrid catalyst suspensions. [photocatalyst] = 0.0180 g/36 mL; [MV<sup>2+</sup>] = 0.5 mM; 0.95 N NaOH; measured under  $-0.4$  V vs. SCE; N<sub>2</sub> purged for 1 h prior to and continually during visible light ( $>420$  nm) irradiation. No electron donor added.



Such back reactions of electron relay on the surface of Pt have been frequently reported.<sup>40,42</sup> Accordingly, Fig. 6 shows that platinization of CdS lowered the photocurrent generation significantly in both single (CdS vs. Pt-CdS) and physically mixed (CdS + TiO<sub>2</sub> vs. Pt-CdS + TiO<sub>2</sub>) systems. The platinization of TiO<sub>2</sub> in CdS + TiO<sub>2</sub> suspension also decreased the photocurrent by half whereas it enhanced the hydrogen production. Comparing Pt-CdS + TiO<sub>2</sub> and CdS + Pt-TiO<sub>2</sub>, the photocurrent generation is higher in the latter than the former, which is consistent with the hydrogen generation efficiency. That is, in both photocurrent collection and hydrogen production, the preferable

sites of Pt should be on the TiO<sub>2</sub> side to maximize the electron transfer efficiency. The effect of platinization is more prominent in Fig. 6c. All three hybrids prepared by methods A, B, and C are less efficient than the synthesized CdS despite their higher activity in hydrogen production. This indicates that the back reaction of MV<sup>+</sup> (R13) is efficient on Pt-(CdS/TiO<sub>2</sub>). On the other hand, CdS/(Pt-TiO<sub>2</sub>) hybrid is far more efficient than Pt-(CdS/TiO<sub>2</sub>) in both photocurrent generation and hydrogen production. The efficiency of back reaction R13 seems to be similar between CdS/(Pt-TiO<sub>2</sub>) and Pt-(CdS/TiO<sub>2</sub>) catalysts. In such cases, the photocurrent collection efficiency correlates with the hydrogen production efficiency.

## Conclusions

One of the key factors of high-efficiency hybrid photocatalysts for hydrogen production is to achieve efficient charge transfer. This study clearly demonstrates that the charge transfer is sensitively and greatly affected by how the hybrid is organized. Direct particle-to-particle contact of CdS and TiO<sub>2</sub> is basically required to achieve a potential gradient and the Pt particle should be located on the TiO<sub>2</sub> particle surface to have the vectorial electron transfer of CdS → TiO<sub>2</sub> → Pt. The conventional platinization of CdS/TiO<sub>2</sub> causes multi-directional electron transfer throughout the hybrid, inevitably lowering charge transfer efficiency. A variety of structure-based approaches for the high-efficiency hybrid photocatalysts have been studied and thus these results will be considered guideline on their hybridization.

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