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Spatial separation of dual-cocatalysts on onedimensional semiconductors for photocatalytic hydrogen production[†]

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Light-driven hydrogen production using semiconductor photocatalysts has gained much interest owing to their ability to store sunlight in the form of portable chemical fuel. The spatial separation of dual-cocatalysts onto different surfaces has been considered as a useful strategy for fabricating dynamic particulate photocatalysts to hinder charge recombination and reverse reactions. Herein, using onedimensional (1D) semiconductors, CdSe nanorods as an example, we experimentally demonstrated that photogenerated electrons and holes can be effectively separated along different directions of a 1D semiconductor. Following this phenomenon, the reduction cocatalyst Pt and oxidation cocatalyst PdS were spatially deposited on different sites via an in situ photodeposition process, which drastically enhanced the photocatalytic activity for hydrogen production to more than 20 times, thus exhibiting an extremely high apparent quantum efficiency (AQE) of \sim 45% at 420 nm. Further studies using photoluminescence spectroscopy indicated that the spatially separated dual-cocatalysts efficiently captured the photogenerated electrons and holes migrating to the surface, which greatly decreased the recombination of charge carriers and consequently led to superior photocatalytic performances. Our work provides an effective strategy for the rational construction of highly efficient photocatalyst systems based on (quasi) 1D semiconductors for artificial solar energy conversion.

1 Introduction

With the constant depletion of fossil fuels and their impact on the environment, the conversion of solar energy into

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environmentally friendly and renewable H2 fuels has received considerable attention in the past few decades.¹ Photocatalytic water splitting offers a clean, sustainable and cost-effective pathway for hydrogen fuel production and is being considered as the "holy grail" of chemical science.²⁻⁵ In a typical photocatalytic process, photocatalysts absorb incident light to generate electrons and holes, which are separated and transferred to the surface for redox reactions.6 The recombination of photogenerated charges and the inhibition of reverse reaction are challenging issues in photocatalysis.7 Dual cocatalysts, i.e. reductive and oxidative cocatalysts, can improve the spatial charge separation efficiency through quick trapping of photogenerated holes by oxidative cocatalysts and withdrawing of electrons by reductive cocatalysts.8-13 The rational construction of dual-cocatalysts on different sites so that the reduction and oxidation reactions can be separated in space, which has proven to be crucial in inhibiting the charge recombination and reverse reaction, leads to a remarkable enhancement in the photocatalytic activities.^{11,14-16} One dimensional (1D) nanostructures have drawn considerable attention owing to their intrinsic optical, structural, and electronic properties.¹⁷⁻²¹ Generally, a 1D nanostructure is constructed with a high aspect ratio with at least one of the dimensions as 1-100 nm, irrespective of whether it is rod-, wire-, belt- or tube-shaped.²²⁻²⁴ A 1D nanostructure provides a unique transit for charge transport along the long axis of the 1D structure and decouples the direction of charge carrier collection, which is favourable for the separation of electronhole pairs. Moreover, the tips of nanorods are usually correlated with specific exposed facets of a single crystal,25-27 which helps in selectively loading reduction cocatalysts (such as platinum and gold)28-31 at the tip and oxidation cocatalysts such as CoO at the lateral facets. Light-driven H₂ production by using semiconductor nanocrystal heterostructures has gained much interest owing to the ability to rationally improve their activity by tailoring their composition, morphology, and size.10,29,30,32,33 However, there are few reports focusing on the spatial separation of different cocatalysts on well-defined 1D nanostructured semiconductors for photocatalytic water splitting.

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Herein, aiming for the rational designing of dual-cocatalysts on 1D nanostructure semiconductors, visible-light-responsive CdSe nanorods were chosen as examples. Using an in situ photo-reduction and photo-oxidation deposition as the probe reaction, we demonstrated that photogenerated electrons and holes of CdSe nanorods were separated both parallelly and perpendicularly to the nanorod under visible-light irradiation. The selective deposition of Pt and PdS nanoparticles, which act as reduction and oxidation cocatalysts, respectively, was successfully fabricated at different positions of CdSe nanorods. Surprisingly, the spatially separated dual-cocatalyst (Pt and PdS) system showed a remarkable enhancement in photocatalytic hydrogen production under visible light, which is more than 20 times higher than that of bare nanorods and exhibited an extremely high apparent quantum efficiency (AQE) of \sim 45% at 420 nm. Characterizations using photoluminescence spectroscopy indicate that the spatially separated dual-cocatalysts efficiently captured photogenerated charge carriers, which greatly inhibited charge recombination and consequently led to superior photocatalytic performances.

2 Results and discussion

1D nanostructured semiconductors have been recognized to exhibit unique properties for charge separation along the axis of the 1D structure and decoupling the direction of charge carrier collection.³⁴ As photogenerated electrons and holes possess differences in properties such as diffusion lengths, charge mobility and effective mass, they induce unique behaviours for the separation of electrons and holes once excited under light irradiation. Fig. 1 shows the proposed schematic description of the preferential separation of electron-hole pairs in a typical 1D nanostructured semiconductor. Due to their different natures, the photogenerated electrons and holes in 1D semiconductors are possibly separated and transferred in different directions, e.g., parallel or perpendicular to the 1D structure regardless of rod or wire morphology, such that the electrons and holes are spatially separated along different surfaces (sites) for the corresponding redox reactions. CdSe is a representative semiconductor with a wide light absorption range (bandgap of \sim 1.7 eV), which exhibits a wide range of electrical and optical properties that depend sensitively on both size and shape, thus



Fig. 1 Scheme of spatial separation of photogenerated charge carries on one-dimensional semiconductors after light illumination.

intriguing the interests of fields including microelectronics and optics.³⁵⁻³⁷ Serving as a prototype material, CdSe nanorods were synthesized using a hot-injection method similar to the reported process with an inconsequential modification.³⁸ The crystallinity of CdSe nanorods was confirmed from the X-ray diffraction pattern, which showed well-aligned and strong diffraction peaks indexed to the wurtzite structure (Fig. S1†), and its light absorption range reached more than ~650 nm (Fig. S2†).

As shown in Fig. 2a and S3,[†] the as-prepared CdSe nanorods displayed a well-defined rod-like morphology with lengths of \sim 2–3 µm and diameters of \sim 15–20 nm. To identify the photogenerated charge distribution on CdSe nanorods, in situ photoreduction and photo-oxidation depositions were introduced as probing reactions to determine the transmittance of photogenerated electrons and holes. In our experiment, we chose the photo-reduction deposition of Pt and photo-oxidation deposition of CoO_x nanoparticles as probe reactions. As shown in Fig. 2b and c, we found that almost all the Pt nanoparticles with sizes of \sim 2–6 nm were selectively deposited on the tip of CdSe nanorods using H₂PtCl₆ as the precursor, indicating that the photogenerated electrons were transmitted along the nanorod and moved to the tip of the CdSe nanorods. Furthermore, after the photo-oxidation deposition of CoO_x using $Co(NO_3)_2$ as the precursor in the presence of NaIO₃ as the sacrificial reagent, we found that most of the CoO_x nanoparticles attached themselves to the lateral surface of nanorods, revealing the fact that photogenerated holes of CdSe were separated perpendicular to the rod, which is complementary from the sites for the photoreduction deposition of Pt nanoparticles (Fig. 2d and e). Such differentiated deposition sites for Pt and CoO_x were further confirmed by simultaneously depositing both Pt and CoO_x on CdSe nanorods (Fig. 2f). The chemical states of the deposited Pt and CoO_x were characterized by X-ray photoelectron spectroscopy (XPS), and the metallic state for Pt and mixed metal oxide nanoparticles of Co3O4 and Co2O3 was obtained (Fig. S4 and S5^{\dagger}), demonstrating that the products of Pt and CoO_x were formed via photo-reduction and photo-oxidation deposition, respectively. The above results clearly indicate that the photogenerated electrons and holes are indeed spatially separated on the tip and lateral facets of CdSe nanorods. As Pt is an efficient reduction cocatalyst and PdS is proved as the best oxidation cocatalyst in most of the sulphide and selenide semiconductors, we tried to use PdS nanoparticles as oxidative cocatalysts. The PdS nanoparticles were synthesized by injecting a certain amount of PdCl₂ solution in situ into the photocatalytic reaction suspension containing Na2S-Na2SO3 solution, which was sonicated and stirred vigorously for half an hour followed by the addition of CdSe photocatalyst. A localized intrinsic electric field was induced upon photoexcitation on the surface of CdSe, which directed the electrons lengthwise and holes perpendicular to the rod as demonstrated in the case of Pt-CoO_x/CdSe. It has also been reported that PdS nanoparticles could be deposited on the surface of semiconductors through a photo-induced process using PdCl₂ as a precursor combined with an aqueous solution of S^{2-.39} Following the above process, we fabricated PdS nanoparticles on the surface of CdSe and found that almost



Fig. 2 TEM images of CdSe nanorods after an *in situ* photodeposition of noble metals and metal oxides. (a) CdSe nanorods; (b and c) CdSe nanorods after the photo-reduction deposition of Pt nanoparticles, denoted as Pt/CdSe; (d and e) CdSe nanorods after the photo-oxidation deposition of CoO_x nanoparticles, denoted as $CoO_x/CdSe$; (f) CdSe nanorods after simultaneous deposition of both Pt and CoO_x nanoparticles, denoted as $Pt-CoO_x/CdSe$; (g) photo-induced deposition of PdS on CdSe nanorods, denoted as PdS/CdSe; (h and i) dual-deposition of Pt and PdS on CdSe nanorods, denoted as Pt-PdS/CdSe; and (j) schematic description of CdSe nanorods after depositing with different species.

all the PdS nanoparticles appeared only on the lateral facets of CdSe nanorods (Fig. 2g). The chemical states of PdS were also analysed from the XPS spectra (Fig. S6[†]). The dual deposition of Pt and PdS was further verified to be spatially separated on the tip and lateral facets of CdSe nanorods, as shown in Fig. 2h and i. This implies that the construction of Pt and PdS on the electron-accumulating and hole-accumulating sites of CdSe nanorods was successfully achieved. The deposited Pt and PdS nanoparticles on the different surfaces of CdSe nanorods were further validated using high-resolution TEM (HRTEM) characterization (Fig. S7[†]) and elemental mapping (Fig. S8[†]). To know well about the redox deposition sites, Fig. 2j gives a schematic description to show the deposition sites for the abovementioned cocatalysts on CdSe nanorods. Based on the results, we can draw a conclusion that the photogenerated electrons and holes of CdSe nanorods are separated and transferred parallelly and perpendicularly to the rod due to the intrinsic electric field induced by photoexcitation, resulting in the spatial separation of electrons and holes. This further verified the scheme for the 1D nanostructured semiconductor that was predicted in Fig. 1.

To recognize the effect of spatial charge separation on CdSe nanorods, the photocatalytic performance of photocatalysts deposited with Pt and PdS, acting as active sites for reduction and oxidation reactions, were evaluated. The photocatalytic performance in terms of photocatalytic hydrogen production in the presence of Na₂S-Na₂SO₃ solution under visible light was determined for various CdSe-based photocatalysts such as CdSe, Pt/CdSe, PdS/CdSe and Pt-PdS/CdSe. As shown in Fig. 3a, bare CdSe exhibited negligible photocatalytic activity for hydrogen production without any cocatalysts. After depositing Pt as a cocatalyst, we found that the photocatalytic hydrogen production activity was remarkably enhanced, which was about 3 times higher than that for bare CdSe, as Pt is a well-known reduction cocatalyst. A comparable result was achieved when PdS nanoparticles were deposited on the CdSe nanorod as PdS is reported to be an efficient cocatalyst for the oxidation of S²⁻ ions.40 Interestingly, when both Pt and PdS were selectively deposited on different sites of the CdSe nanorod simultaneously (denoted Pt-PdS/CdSe), as shown in Fig. 3a and b, the rate of photocatalytic H₂ production drastically increased and reached 5300 μ mol h⁻¹ g⁻¹, which was more than 20 times higher than that of bare CdSe and nearly 10 times higher than those of Pt/CdSe and PdS/CdSe. The apparent quantum efficiency (AQE) for photocatalytic hydrogen production on the Pt-PdS/CdSe photocatalyst was measured to be \sim 45% at 420 nm. As far as we know, it is one of the highest AQEs for CdSe-based photocatalysts reported so far. The dual-deposition of Pt and



Fig. 3 (a and b) Photocatalytic H₂ evolution and apparent quantum yield under visible light irradiation over CdSe, Pt/CdSe, PdS/CdSe and Pt–PdS/CdSe; (c and d) photoluminescence emission spectra and quenching percentage of CdSe after depositing different cocatalysts. Reaction condition: catalyst, 100 mg; 0.1 M Na₂S–Na₂SO₃ aqueous solution (100 mL); light source: Xe lamp (300 W) with an optical filter (λ > 420 nm); the amount of cocatalyst was fixed to 0.5% for both Pt and PdS.

 CoO_x was also found to exhibit a similar synergistic effect as that of Pt-PdS/CdSe although the total activity was lower, as shown in Fig. S9.† The results clearly demonstrate that the superior photocatalytic properties can only be obtained when the reduction cocatalyst and oxidation cocatalyst are spatially separated on different sites of the semiconductors. To investigate why an extremely high photocatalytic activity is only achieved when dual-cocatalysts are spatially separated on CdSe nanorods, photoluminescence (PL) emission spectra were obtained to monitor the photoexcited energy/electron transfer and recombination processes of CdSe-based photocatalysts. Fig. 3c shows the comparison of photoluminescence spectra of CdSe, Pt/CdSe, PdS/CdSe, and Pt-PdS/CdSe samples. The bare CdSe displays an intense emission band centred at ~675 nm, which is ascribed to its band-edge emission. The fluorescence intensities were drastically quenched by loading Pt and PdS cocatalysts and even further by co-loading both Pt and PdS on CdSe nanorods. These results suggested that Pt and PdS cocatalysts efficiently captured the photogenerated electrons and holes once they migrated to the surface, which effectively reduced the probability of charge recombination. It should be noted that the Schottky junction at the interface of Pt (PdS)/CdSe nanorods can provide a driving force for the spatial separation of

photogenerated charges, which will reduce the charge recombination. Comparably, Fig. 3d shows the quenching efficiency of the fluorescence intensity of CdSe nanorods after loading with different cocatalysts, which was calculated from the fluorescence intensities in Fig. 3c. It is surprisingly found that the trend of quenching efficiency of fluorescence intensity with different cocatalysts is in good agreement with their photocatalytic hydrogen production activities. Predominantly, for Pt-PdS/CdSe, more than 95% fluorescence intensity was found to be quenched after depositing Pt and PdS that were spatially separated on CdSe nanorods. As confirmed by the photoluminescence spectra, Pt-PdS/CdSe exhibited the highest quenching efficiency, indicating that a rapid flow of photogenerated electrons migrated to Pt nanoparticles located at the tip of CdSe nanorods, and photogenerated holes were quickly extracted by PdS located on the lateral surface with light irradiation. Therefore, we can postulate that the superior photocatalytic performance of Pt-PdS/CdSe photocatalyst is essentially owing to the effective prohibition of recombination processes by spatially separated cocatalysts on different sites. In this case, Pt nanoparticles are responsible for transferring the photogenerated electrons while the oxidative cocatalysts PdS are responsible for the effective removal of photogenerated

holes.^{41,42} Therefore, we stress that the superior photocatalytic activity is due to the unique one-dimensional nanostructure on which the dual-cocatalysts are spatially separated, which decreases the probability of charge recombination and improves the charge separation efficiency. The stability of the synthesized sample of Pt–PdS/CdSe (NRs) is assessed by conducting the reaction for 16 h with the H₂ generation amount in every four hours being measured. No plausible deactivation is perceived in the consecutive three cycles (Fig. S10†), confirming the extraordinary stability of the Pt–PdS/CdSe (NRs) photocatalyst.

Comparably, the dual-cocatalysts were randomly loaded on CdSe nanorods through a traditional impregnation method without any selectivity. Fig. 4a shows the TEM image of Pt and PdS deposited on CdSe nanorods *via* an impregnation method, and along with this we have synthesized CdSe nanoparticles using a similar hot-injection method at the same temperature using CdSe nanorods. We can see that all the Pt and PdS nanoparticles were randomly distributed on the surface of CdSe nanorods and nanoparticles (Fig. S11†). The corresponding photocatalytic activity of CdSe nanorods with a random distribution of dual-cocatalysts is found to be lower by more than an order of magnitude than that of CdSe nanorods with spatially separated Pt and PdS on different sites (Fig. 4b). The photocatalytic activities of samples with different sizes have been compared by normalization in terms of the exposed surface of the cocatalysts.¹¹ The results indicate that the drastic difference in the activity among the samples is primarily owing to the spatial separation of photogenerated charges instead of the variation in sizes caused by different methods for cocatalyst deposition (Fig. S12[†]).

To recognize the merits of spatial charge separation on 1D semiconductors, we employed CdSe nanoparticles instead of CdSe nanorods and evaluated their photocatalytic activity under the same conditions for comparison (Fig. 4c). The photocatalytic H₂ evolution of CdSe nanoparticles is observed to be much inferior to that of CdSe nanorods at 5300 μ mol h⁻¹ g⁻¹ and 1280 μ mol h⁻¹ g⁻¹ for nanorods and nanoparticles, respectively (Fig. 4d). It should be emphasized that the surface areas of CdSe nanoparticles are more than an order of magnitude than those of CdSe nanorods. If the photocatalytic activities were normalized with respect to surface area, the difference in photocatalytic performances between nanoparticles and nanorods would be further enlarged. The apparent quantum yield of Pt–PdS/CdSe nanoparticles was measured to be ~15%, which was much lower than that of nanorods, possibly due to



Fig. 4 (a) TEM image of CdSe nanorods with random deposition of Pt and PdS by the impregnation method; (b) comparative H₂ production of CdSe nanorods with selective deposition and random deposition of dual-cocatalysts; (c) TEM image of CdSe nanoparticles prepared under the similar conditions; (d) comparative H₂ production of CdSe nanorods (NRs) and nanoparticles (NPs), S.D. means selective deposition and R.D. means random deposition: catalyst, 100 mg; $0.1 \text{ M Na}_2\text{S}-\text{Na}_2\text{SO}_3$ aqueous solution (100 mL); light source: Xe lamp (300 W) with an optical filter (λ > 420 nm).



Fig. 5 TEM images of CdSe nanorods with controlling different lengths of rods, (a) small rod (SR) $\sim 2-3 \mu$ m, (b) medium rod (MR) $\sim 300-400$ nm, (c) large rod (LR) ~ 20 nm; (d) time course of photocatalytic H₂ generation by CdSe with different rod lengths in the presence of optimized amount of Pt and PdS; (e) photocatalytic H₂ production performances and apparent quantum yield by different nanocrystals; (f) the relation between the aspect ratio length/diameter (*L/D*) of CdSe nanorods. Reaction conditions: catalyst, 100 mg; 0.1 M Na₂S–Na₂SO₃ aqueous solution (100 mL); light source: Xe lamp (300 W) with an optical filter ($\lambda > 420$ nm).

the poor charge separation in nanoparticles as confirmed by the photoluminescence emission spectra in Fig. S13.[†] From the results obtained, it is expected that CdSe nanoparticles show phonon blockage for their energetic electrons during a photoexcitation process. Nevertheless, the photoexcited electrons in semiconductor nanoparticles relax very quickly compared to those in nanorods, which decreases the lifetime of photogenerated carriers in CdSe nanoparticles. Our results also revealed that the photogenerated charges can be efficiently separated on the 1D nanostructures compared with nanoparticles. The unique property of spatial charge separation on 1D semiconductors will have a promising potential application in photocatalysis.

As the spatial charge separation is dependent on the geometrical structure of the nanorod, we synthesized different CdSe nanocrystals with varied rod lengths to investigate the effect of length/diameter ratio on spatial charge separation. TEM images in Fig. 5a–c show that the average length of the assynthesized CdSe nanorods were tuned from ~20 nm to 300 nm, even to more than 2 μ m. We found that the photocatalytic activities over CdSe nanorods increased with an increasing rod length, *i.e.*, longer nanorods exhibited better photocatalytic activities. It can be proposed that the increase in the *L/D* ratio can optimize the intrinsic properties for spatial charge separation of the nanorods, which further results in different photocatalytic performances. The separation and recombination rates of photo-excited charges of the H₂ evolution system are also investigated using photoluminescence (PL)

measurements under an excitation wavelength of 630 nm (Fig. S14†). The PL quenching principally reflects an inhibited recombination rate of charge carriers, which can greatly enhance H_2 production by increasing the length of nanorods. The increase in the lifetime of trapped holes for longer nanorods may be attributed to the larger volume available to the electrons to remain separated from the hole. Further studies on the intrinsic mechanism of the relationship between the L/D ratio and photocatalytic activity are being pursued.

The above results indicate that the separation of dualcocatalysts on CdSe nanorod plays a key role in enhancing the



Fig. 6 Scheme of the proposed mechanism for photocatalytic hydrogen production on one-dimensional CdSe nanorods with spatial separation of dual-cocatalysts.

spatial charge separation and photocatalytic hydrogen generation activity. Fig. 6 shows a schematic description of the spatial charge separation process on the CdSe nanorod. Upon light irradiation on CdSe nanorods, the photogenerated electronhole pair separated and transferred to the surface and then the electrons were quickly trapped by Pt nanoparticles, which facilitated the catalytic reduction of protons to hydrogen, while the holes migrated to the side surface of the nanorod trapped by PdS. The quick trapping of electrons and holes by dualcocatalysts also increases the charge separation and prohibits charge recombination. Therefore, both the unique spatial charge separation for nanorods and the spatial distribution of dual-cocatalysts contribute to the superior photocatalytic activity in our experiment.

Conclusion

In summary, we have reported that photogenerated electrons and holes can be effectively separated along different directions of one-dimensional CdSe nanorods. The reduction cocatalyst Pt and the oxidation cocatalyst PdS were spatially deposited on different sites via an in situ photodeposition process, which drastically increased the photocatalytic activity for hydrogen production to more than 20 times, giving an apparent quantum efficiency (AQE) of ~45% at 420 nm. Characterizations including photoluminescence spectroscopy indicated that the spatially separated dual-cocatalysts could efficiently capture photogenerated electrons or holes, which decreased the recombination inside the CdSe nanorods and consequently led to superior photocatalytic performances. This work not only shows an informative approach for designing highly efficient photocatalyst systems for artificial photosynthesis but also reports the inhibition of charge recombination on 1D semiconductor photocatalysts, thus opening a new avenue for the application of 1D materials in solar energy conversion and related fields.

Conflicts of interest

There are no conflicts to declare.

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