Aggregation-Enhanced Photocatalytic H₂ Evolution Activity of Photosensitizing Cadmium Selenide Quantum Dots and Platinum Colloidal Catalysts

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ABSTRACT¹

We have synthesized CdSe (cadmium selenide) quantum dots (QDs) with three different surface-passivating ligands: 3-mercaptopropionic acid (MPA), 4-mercaptobenzoic acid (MBA), and 4-mercaptomethylbenzoic acid (MMBA). Although all the QDs possessed similar diameters and thiol-based ligands, the MPA-passivated QD exhibited the highest photocatalytic H₂ evolution activity in the presence of a polyvinylpyrrolidone-protected Pt (Pt-PVP) colloidal catalyst. Moreover, dynamic light scattering and zeta potential measurements clearly indicated a significant difference in their dispersibility in water. Thus, CdSe-MPA, having the sterically smallest thiol ligand, displayed the largest negative zeta potential and the best dispersibility owing to the presence of negatively charged carboxylate groups on the QD surface. This was sufficient for the QD to disperse as single particles. In contrast, the bulkier MMBA ligand covered the surface of the CdSe QD with a smaller number of ligand moieties, resulting in a smaller zeta potential and the formation of large aggregates (~126 nm in diameter). In the presence of a Pt-PVP colloid as the hydrogen evolution catalyst, CdSe-MPA formed large aggregates (~1.6 μ m in diameter) with the Pt-PVP colloid by electrostatic interactions. Conversely, CdSe-MMBA did not form such large aggregates with the Pt-PVP colloid. Since the emission of the CdSe QD was effectively quenched in the presence of the Pt-PVP colloid, we concluded that CdSe-MPA exhibits the highest photocatalytic hydrogen evolution activity with the Pt-PVP colloidal catalyst because the electron transfer efficiency from the photosensitizing CdSe QD to the Pt-PVP colloidal catalyst is enhanced by the formation of aggregates.

¹ **Abbreviations:** DHLA, dihydrolipoic acid; DLS, dynamic light scattering; HER, H₂ evolution reaction; MBA, 4-mercaptobenzoic acid; MEO, 2-mercaptoethanol; MMBA, 4-mercaptomethylbenzoic acid; MPA, 3-mercaptopropionic acid; Pt-PVP, polyvinylpyrrolidone-protected Pt; QD, quantum dot; TOF, turn over frequency; TON, turn over number; TOPO, tri-*n*-octylphosphine oxide; VB, valence band.

Keywords: Photocatalyst, Hydrogen, Artificial photosynthesis, Quantum dot, Aggregation

1. INTRODUCTION

In recent years, the photocatalytic water splitting reaction has been regarded as a promising solution for global energy issues [1–11]. Quantum dots (QDs) have attracted much attention because their band-gap energy may be controlled by the tailoring of their particle size (quantum confinement effect) [12–17]. By taking advantage of this characteristic, QDs have been extensively studied for solar cell [18,19], photodetector [20,21], luminescence diode [22,23], and photosensitizer [24–35] applications.

Among the various QDs, CdSe (cadmium selenide) QDs are attractive visible-light-driven photosensitizers for water reduction because of their suitable redox potentials and tunable visible light absorption (quantum confinement effect). Several studies on CdSe-QD-based photocatalytic hydrogen evolution systems have been reported to date [36–46]. In most of these studies, simple alkyl thiols with carboxyl or hydroxyl groups at different terminals of the molecule [for example, 3-mercaptopropionic acid (MPA) and 2-mercaptoethanol (MEO)] have been widely used as surface ligands to enable good QD dispersion in water media. For example, Osterloh et al. reported [39] the photocatalytic H₂ production of a system containing MEO-covered CdSe QDs as the photosensitizer and Na₂SO₃ as the sacrificial electron donor. They discovered that in situ generated Cd⁰ acts as the catalyst for H₂ production. Wu et al. reported [37] a similar photocatalytic H₂ evolution reaction (HER). This team used MPA as the surface passivating ligand of the CdSe QDs, NiCl₂ as the precursor of the catalyst, and 2-isopropanol as the sacrificial electron donor. In this case, the in situ-generated Ni-CdS layer on the CdSe QD plays

an important role in photocatalytic H₂ production. Eisenberg et al. also reported [36] that the active H₂-evolving catalyst in photocatalytic HER driven by CdSe QDs covered by dihydrolipoic acid (DHLLA), in the presence of a NiCl₂ precatalyst and sacrificial electron-donating ascorbic acid, was a molecular Ni-DHLLA species. These recent examples indicate the promising photosensitizing ability of CdSe QDs for solar H₂ production. However, further studies are required, especially on the design of the surface passivating ligands, to improve the photocatalytic activity. Notably, the aforementioned studies employed similar thiolate-based ligands, but different active catalysts. The electronic state of a CdSe QD strongly depends on the surface ligand [47–49]. Thus, the surface passivating ligand on the CdSe QD in a photocatalytic HER plays several key roles in the stabilization and solubilization of the QD as well as in the photoinduced electron transfer pathway and/or formation of the active catalyst.

Herein, we report photocatalytic **activity for HER** of photosensitizing CdSe QDs capped by three different thiol ligands (Scheme 1) to elucidate the role of the surface ligand. These ligands are the widely used MPA ligand, 4-mercaptobenzoic acid (MBA; comprises a surface-passivating thiol group at the para-position to the water-solubilizing carboxyl group), and 4-mercaptomethylbenzoic acid (MMBA; comprises a surface-passivating thiol group at the para-position and a methyl group between the thiol and phenyl groups). In this work, we used a polyvinylpyrrolidone-protected Pt colloid (Pt-PVP) as the H₂ evolution catalyst to compare the photosensitizing efficiency of the three CdSe QDs and clarify the role of the surface passivating ligand in the photoinduced electron transfer pathway. We demonstrate that in spite of their similar thiolate-based ligands, MPA-capped CdSe QDs exhibit higher photocatalytic **activity for** HER in the presence of a Pt-PVP than either MBA- or MMBA-capped CdSe QDs. Dynamic light scattering (DLS) measurements clearly indicate that one of the key factors for higher

photocatalytic activity for HER is the formation of aggregates composed of CdSe QDs and Pt-PVP colloids.

Scheme 1. Chemical structures of the surface passivating ligands used in this study: 3-mercaptopropionic acid (MPA), 4-mercaptobenzoic acid (MBA), and 4-mercaptomethylbenzoic acid (MMBA).

2. EXPERIMENTAL SECTION

2.1 Materials

All manipulations were conducted under N₂ using standard Schlenk techniques unless otherwise indicated. All commercially available starting materials [Cd(AcO)₂·*n*H₂O, Se, tetradecylphosphonic acid, hexadecylamine, tri-*n*-octylphosphine oxide (TOPO), tri-*n*-octylphosphine, MPA, MBA, and tetramethylammonium hydroxide] were used as received, and solvents were used without any purification. TOPO- [50] and MPA-passivated CdSe QD and Pt-PVP [51] nanoparticles, as well as MMBA [52,53] were prepared according to literature. The averaged diameter of Pt-PVP colloid was estimated to be 3.1 nm by the peak fitting of powder X-ray diffraction pattern using Scherrer equation.

2.2 Synthesis of CdSe-MBA and CdSe-MMBA

MBA and MMBA-passivated CdSe QDs were synthesized according to literature [54], with slight modifications, as follows: a mixture of 500 μL hexane solution of CdSe-TOPO (200 nmol

of the nanoparticles) and 8 mL of methanol was placed in a two-necked flask and degassed by N₂ bubbling for 5 min. Next, MBA (0.3238 g, 2.2 mmol)/MMBA (0.3700 g, 2.2 mmol) was dissolved in 1.5 mL of 10% aqueous tetramethylammonium hydroxide solution and 8 mL methanol in a separate flask, degassed by N₂ bubbling for 5 min, and transferred to the two-necked flask containing the first mixture. The mixed solution was refluxed at 65 °C overnight and protected from light. Ethyl acetate (20 mL) was added to the reaction solution. The solution was then centrifuged and CdSe-MBA/CdSe-MMBA was collected as a precipitate. After removing the supernatant, the precipitate was dispersed in H₂O (2 mL) containing two drops of 10% tetramethylammonium hydroxide solution.

2.3 Measurements

UV-Vis absorption and emission spectra were recorded on a Shimadzu MultiSpec-1500 spectrophotometer and a JASCO FP-6600 spectrofluorometer, respectively, using a 1 cm path length quartz cell. Powder X-ray diffraction patterns were recorded on a Bruker D8 Advance diffractometer equipped with a graphite monochromator using Cu-K α radiation and a one-dimensional LinxEye detector. DLS and the zeta potentials were measured on an OTSUKA ELSZ-100SCI analyzer; glass and standard cell units were used for zeta potential measurements. The pH of the solutions was controlled by adding sodium hydroxide aqueous solution and dilute hydrochloric acid. Transmittance electron microscopy was recorded on a JEOL 2010 FASTEM (200kV).

2.4 Photocatalytic Hydrogen Evolution

Samples were prepared in 40 mL vials and protected from light before use. A 2.7 μ M Pt-PVP colloid, 4.0 μ M CdSe-QDs (CdSe-MBA or CdSe-MPA), and 0.5 M ascorbic acid in H₂O were

added to form a total volume of 4.5 mL. The pH of the solution was adjusted by the addition of aqueous 2 M HCl or 2 M NaOH solution. The samples were sealed with an airtight cap equipped with two rubber septa and then degassed by N₂ bubbling for 1 h. The samples were irradiated from below the vials with OP6-5310HP2 visible light LEDs ($\lambda = 525$ nm, Opt-Device Laboratory Ltd). The light power of each LED was set to 40 mW and measured with a COHERENT FieldMaxII-TO laser power meter. During the photoreaction, the samples were stirred using a stirrer tip. The gas in the top-space of the vials was collected using a HAMILTON Microlab 600 auto-dispenser and injected to an Agilent 490 MicroGC gas chromatograph to measure the amount of hydrogen evolved.

3. RESULTS AND DISCUSSION

3.1 Absorption and emission properties of CdSe QDs

Figure 1 illustrates UV-Vis absorption and emission spectra of the afforded QDs in the solution state. The particle size of CdSe QDs can be estimated from the first exciton peak [55]. The CdSe-TOPO, CdSe-MBA, CdSe-MPA, and CdSe-MMBA QDs exhibited a first exciton peak at almost the same wavelength (Table 1), indicating that the particle sizes of these QDs are almost independent of the surface passivating ligand. Powder X-ray diffraction measurements for these QDs revealed that all four have a zinc blend structure and their particle diameters were estimated (Scherrer's equation) to be almost constant (2.6 ± 0.2 nm, Figure S1 in the supplementary information) which is also consistent to the size of CdSe-TOPO estimated by transmission electron microscopic (TEM) analysis (see Figure S2). This indicates that the surface ligand exchange reactions between TOPO and the three different thiols have little effect on the particle size. The small (compared to that of CdSe-TOPO) red shifts of the first exciton peak

observed for CdSe-MBA, CdSe-MPA, and CdSe-MMBA are not attributed to the change in particle size but to the differences in the electronic state of the surface ligands. Several groups reported that the thiol ligands form stronger coordination bonds on the surface of the CdSe QDs than TOPO. This leads to a smaller quantum confinement effect [56–58]. Thus, the small red shifts observed for CdSe-MPA, CdSe-MBA, and CdSe-MMBA are attributed to the same reaction mechanism as that of the thiol-passivated CdSe QDs reported in literature.

Figure 1. UV-Vis absorption (dotted lines) and emission (solid lines) spectra of CdSe-TOPO in *n*-hexane, CdSe-MBA, CdSe-MPA, and CdSe-MMBA in basic water; $\lambda_{\text{ex}} = 400$ nm.

Table 1. Absorption and emission peaks for the afforded CdSe QDs.

CdSe QDs	Absorption / nm	Emission / nm
CdSe-TOPO	518.4	543.4
CdSe-MBA	528.7	n.d.
CdSe-MPA	523.6	541.2, 680.8
CdSe-MMBA	525.0	546.2, 687.6

CdSe QDs are strong emitters, and their luminescence quantum yields strongly depend on the surface ligand. Strong band-edge fluorescence was observed at 543 nm for CdSe-TOPO, whereas the three thiolate-passivated CdSe QDs only exhibited weak band-edge emissions (Figure 1). The thiol-based surface ligands were reported to trap holes generated in the valence band (VB) of the CdSe QDs and quench photoluminescence. This is due to the higher HOMO orbital of the thiols when compared to the VB of the CdSe QDs [59,60]. In addition, the efficiency of hole trapping by the thiol ligands depends on the electronic state of the thiol; aromatic thiols tend to trap holes more effectively than aliphatic thiols because the hole in the VB can be delocalized not only on the thiolate group, but also in the aromatic ring [61]. In the case of MMBA, it would be difficult to transfer the hole generated on the VB of CdSe QD to the aromatic ring of MMBA. This is because the methylene spacer interrupts the delocalization of the hole in the aromatic ring. However, a small amount of charge separation still occurs through **tunneling** effects of the aromatic ring π -electrons [62]. Thus, CdSe-MBA exhibits the weakest band-edge emission, following CdSe-MMBA and CdSe-MPA, respectively.

Notably, the thiolate-passivated QDs displayed another weak and broad emission band at ~680 nm that can be attributed to deep trap emission. Kamat et al. reported that Se-vacant sites are

formed on the surface of the CdSe QDs when an MPA surface ligand is added to the system [62–64]. This results in emission from a deeply trapped state. The MPA-passivated CdSe QDs clearly display a lower-energy broad emission assignable to the deep trap emission from the Se-vacant site at 680 nm (Figure 1). The CdSe-MMBA QD also exhibits a similar emission spectrum. In contrast, CdSe-MBA did not exhibit any emission in this range, suggesting that the electron transfer quenching by the MBA ligand is more effective than that of the other two ligands. These results clearly indicate that changing the surface ligand from TOPO to thiolates does not affect the particle size of the CdSe QDs. The emission behavior of these QDs strongly depends on the electronic nature of the ligand, even among similar thiol derivatives.

3.2 Photocatalytic hydrogen evolution

Figure 2 illustrates the results of the photoinduced HERs driven by the photosensitizing CdSe QD and the Pt-PVP colloidal catalyst in aqueous solution (pH = 6). The reaction solutions comprise 0.5 M ascorbic acid as the sacrificial electron donor (the wavelength of irradiated light = 525 nm). The determined turn over number (TON) and turn over frequency (TOF) for each solution are summarized in Table 2. The TON and TOF values decrease in the order: CdSe-MPA > CdSe-MBA > CdSe-MMBA, despite the fact that the CdSe QDs have almost comparable particle diameters and first exciton energies. Thus, since the Pt-PVP nanoparticles were the same as those used in the hydrogen evolving catalyst, the large difference in evolved H₂ should originate from differences in the CdSe QDs. After light irradiation for 15 hours, orange precipitates were formed in all three reaction solutions, implying the these three CdSe QDs are not stable enough to maintain the photocatalytic activity for long-time irradiation, probably because of the more labile nature of monothiolate ligand than the other ligands with several thiolate groups [38, 46].

Figure 2. Photocatalytic hydrogen evolution reactions (HERs) from aqueous solutions (pH 6) comprising 4 μ M CdSe-MBA (black circles), CdSe-MPA (red triangles), or CdSe-MMBA (blue squares) as the photosensitizer, ascorbic acid (0.5 M) as the sacrificial electron donor, and Pt-PVP (12 nM) as the hydrogen evolution catalyst; light irradiation at 525 nm.

Table 2. Turnover numbers (TON) and maximum turnover frequencies (maxTOF) of photocatalytic hydrogen evolution reactions (HERs) driven by photosensitizing CdSe QDs and a Pt-PVP colloid.

QD	TON ^a	maxTOF / h
CdSe-MPA	34211	3902
CdSe-MBA	15318	1953
CdSe-MMBA	5356	715

^aTurn over numbers per amount of CdSe QD nanoparticles calculated from the amount of hydrogen evolved after irradiation for 15 h.

To clarify why the photocatalytic activity strongly depends on the surface passivating ligand of the CdSe QD, the dispersibility of the QDs in water was investigated by DLS. Figure 3 displays the distribution of the particle diameters of the three thiolate-passivated CdSe QDs. Notably, the estimated particle diameters of these three QDs are remarkably different, even in the absence of the Pt-PVP colloidal catalyst. The average diameters were estimated by DLS as ~2.0 nm for CdSe-MPA, 51.2 nm for CdSe-MBA, and 126 nm for CdSe-MMBA (in water, pH = 6, Table 3). This significant difference in particle size is attributed to the difference in the dispersibility of the three CdSe QDs. This is confirmed by the UV-vis absorption spectra (Figure 1) that clearly indicate that the particle diameters of all three CdSe QDs are comparable. The electrostatic interactions between the particles are crucial for the dispersibility of the particles in water, i.e., highly charged particles are well dispersed in water because of the electrostatic repulsion between them. The pKa values of the COOH group in MBA and MMBA should therefore be lower than that of MPA [64] because the COOH groups of the former two ligands are directly attached to the electron-withdrawing phenyl ring, while that of the latter ligand is attached to the electron-donating alkyl group. Thus, in an aqueous solution with pH 6, MMBA and MBA should become more deprotonated than MPA. As a result, the surface of CdSe-MBA and CdSe-MMBA could display a more negative charge. However, CdSe-MPA exhibited better dispersibility in an aqueous solution (pH 6) because it depended on the bulkiness of the surface passivating ligand (molecular volume: MPA = 86.07 Å³, MBA = 122.73 Å³, MMBA = 140.05 Å³). This hypothesis is also supported by the pH dependence of the average particle sizes of CdSe-MPA and CdSe-MBA; the large aggregates (over 1000 nm) were observed at pH = 5 for CdSe-MBA, but the aggregation occurred at lower pH (pH = 4) for CdSe-MPA (see Figure S3). When these surface passivating ligands covered same-sized QDs, the number of MBA or

MMBA moieties was less than that of MPA because both MBA and MMBA are bulkier than MPA. In addition, the methylene group between the thiolate and phenyl groups of MMBA ligand would increase the actual molecular volume due to the free rotation along the C-C bonds at the methylene group. Thus, a reduction in surface negative charge density (a property that requires good dispersibility) was observed, while the dispersibility of both MBA and MMBA became worse. These observations were supported by the zeta (ζ) potential values where CdSe-MPA displayed the largest negative charge followed by CdSe-MBA and CdSe-MMBA, respectively (pH 6 aqueous solution, Table 3). Moreover, after the Pt-PVP colloid (12 nM) was added to the CdSe QD-dispersed solution, the average size of CdSe-MPA and CdSe-MBA increased to 1645 nm and 461 nm, respectively, while a negligible decrease in the size of CdSe-MMBA was observed. Considering that Pt-PVP has a zeta potential of +2.6 mV, we concluded that the increasing average size of CdSe-MPA and CdSe-MBA, following the addition of the Pt-PVP colloid, was due to aggregate formation between Pt-PVP and CdSe-MPA/CdSe-MBA by electrostatic interactions between the negatively charged CdSe QD and the positively charged Pt-PVP colloid. This is supported by the plots in Figure 3 that illustrate that the addition of a PVP polymer without a Pt colloid did not alter the average size (measured by DLS) of the CdSe QD. Moreover, the addition of Pt-PVP caused a positive shift in the zeta potentials of both CdSe-MPA and CdSe-MBA (Table 3). Conversely, the addition of the Pt-PVP colloid did not affect the average size of CdSe-MMBA. This occurs for two main reasons, namely, the negative charge of CdSe-MMBA is smaller than those of both CdSe-MPA and CdSe-MBA, and CdSe-MMBA already undergoes aggregation in the absence of Pt-PVP.

Figure 3. Particle diameter distributions estimated by dynamic light scattering (DLS) of CdSe-MPA (top), CdSe-MBA (middle), and CdSe-MMBA (bottom), dispersed in water (pH = 6) before (black) and after addition of a Pt-PVP colloidal solution (red) or PVP polymer (blue, 4.95 mM as the monomer unit). The particle concentrations of the CdSe QD and Pt-PVP colloid are 4.0 μ M and 12.0 nM, respectively.

Table 3. Average particle diameter and zeta potential of CdSe QDs in the dispersed aqueous solution.

	aqueous solution (pH 6)		+ 12 nM Pt-PVP colloid ^a	
	Average diameter / nm	ζ potential / mV	Average diameter / nm	ζ potential / mV
CdSe-MPA	2.0	−38.37 mV	1645	−13.94 mV
CdSe-MBA	51.2	−29.79 mV	461	−19.39 mV
CdSe-MMBA	126	−20.59 mV	107	−17.39 mV

^a ζ potential of Pt-PVP colloid in aqueous solution (pH = 6) was +2.66 mV.

A luminescence quenching experiment was conducted to clarify the effect of the aggregation of CdSe-MPA and the Pt-PVP colloid on the photophysical properties of the CdSe QD. Figure 4 illustrates the changes in the luminescence spectrum of CdSe-MPA caused by the addition of the Pt-PVP colloid, or ascorbic acid, as the luminescence quencher. As discussed above, CdSe-MPA exhibits a sharp band-edge emission at 524 nm and a broad emission originating from the surface Se-defect at 680 nm. Interestingly, both the emission derived from the Se-defect and the band-edge fluorescence completely disappear after the addition of the Pt-PVP colloid. Notably, the concentration of the colloid was only one-tenth of that used in the photocatalytic HER. The formation of aggregates composed of CdSe-MPA and Pt-PVP colloids was confirmed by DLS measurements even in more diluted concentrations of the Pt-PVP colloid (Figure S4). These results clearly indicate that the luminescence of the CdSe QD was effectively quenched in the aggregate comprising the Pt-PVP colloid. This is probably due to electron transfer from the photoexcited CdSe QD to the Pt-PVP colloidal catalyst (oxidative quenching mechanism). The complete quenching of the emission from Se-defect site by Pt-PVP colloid was also observed at

the different pH conditions (pH = 5, 6 and 8, see Figure S5). On the other hand, although similar emission quenching was observed in the presence of ascorbic acid as the sacrificial electron donor, the quenching efficiency was found to be less than that of the Pt-PVP colloid. The intensity of broad Se-defect emission decreased by 30% in the presence of an ascorbic acid quencher (20 mM), and it was almost completely quenched in the presence of a much more concentrated (0.4 M) ascorbic acid solution. Notably, the band-edge emission of CdSe-MPA was still observed in the 0.4 M ascorbic acid solution whereas it was completely quenched in the presence of the 12 nM Pt-PVP colloid. Taking into consideration that the concentrations of the Pt-PVP colloidal catalyst and sacrificial electron-donating ascorbic acid in the photocatalytic HERs were 12 nM and 0.5 M, respectively, we propose two photoinduced electron transfer mechanisms. In the first mechanism, the photoexcited CdSe-MPA donates the excited electron to the Pt-PVP colloidal catalyst. The oxidized CdSe-MPA is then regenerated by electron transfer from ascorbic acid (sacrificial electron donor). The second mechanism is the inverse process. Thus, the photoexcited CdSe-MPA first receives an electron from the ascorbic acid, after which, the one-electron-reduced CdSe donates an electron to the Pt-PVP colloidal catalyst. Since CdSe-MPA forms aggregates with the Pt-PVP colloid, the former mechanism would be dominant for the CdSe-MPA directly attached to Pt-PVP colloid, whereas the latter process would be more dominant for the CdSe-MPA present near the surface of the aggregate. This occurs because of easier access to the ascorbic acid in the aqueous solution. We also confirmed that the Se-defect emission of CdSe-MMBA was completely quenched in the presence of the Pt-PVP colloid (1.2 nM, one-tenth of the concentration of the photocatalytic HER, Figure S6). This suggests that an electron transfer pathway similar to that of CdSe-MPA would contribute toward the

photocatalytic HER and the difference of molecular length of the surface passivating ligands MMBA and MPA would not affect significantly on the emission quenching efficiency.

Figure 4. Emission spectra of CdSe-MPA (black, 1.4 μM), in the presence of 1.2 nM Pt-PVP colloid (red), and 0.02 M (blue) or 0.4 M ascorbic acid (green). The peaks indicated by the asterisk are attributed to Raman scattering of the water solvent; $\lambda_{\text{ex}} = 500 \text{ nm}$.

Considering the above-mentioned results, we henceforth discuss the dependence of photocatalytic H_2 evolution activity, driven by a CdSe QD as the photosensitizer and a Pt-PVP colloidal catalyst, on the surface passivating ligand. As mentioned above, the photocatalytic activity for HER increases in the order: CdSe-MMBA < CdSe-MBA < CdSe-MPA (Figure 2). Among the three CdSe QDs, CdSe-MPA exhibited the best dispersibility in water. Moreover, a broad lower-energy emission originating from the Se-defect site was clearly observed. In the presence of Pt-PVP colloids, CdSe-MPA forms large aggregates (composite of the CdSe QD and

Pt colloid) with a diameter of $\sim 1.6 \mu\text{m}$ [Scheme 2(a)]. Moreover, both emissions originate from the band-edge transition state and the Se-defect sites are completely quenched. This suggests that the electron transfer from the CdSe QD to the Pt-PVP colloid occurs effectively *via* the Se-defect level as shown in Scheme 2(c). Although the formation of aggregates would reduce the active surface area of the Pt-PVP colloidal catalyst, such negative effect on the catalytic performance could be cancelled by the improvement of efficiency of photoinduced electron transfer. In contrast, in the case of CdSe-MMBA, comprising ligands with phenyl and methylene groups between the carboxylic acid and thiol groups, large aggregates formed even in the absence of the Pt-PVP colloid [Scheme 2(b)]. This probably occurs because the surface of the CdSe QD is covered by a smaller number of the bulkier MMBA ligands (compared to MPA), resulting in less dispersibility of the CdSe QD in water. These large aggregates are thought to suppress the formation of aggregates with the Pt-PVP colloidal catalyst as suggested by DLS measurements (see Table 3), implying that the lower efficiency of photoinduced electron transfer from the CdSe QD to Pt-PVP colloidal catalyst than the other two. In the case of CdSe-MBA, the Se-defect emission that contributes to the electron transfer from the CdSe QD to the Pt colloidal catalyst was negligible. Furthermore, the photocatalytic activity for HER was higher than that of CdSe-MMBA, suggesting that the formation of aggregates composed of a CdSe QD and the Pt-PVP colloid would significantly improve the electron transfer efficiency from the CdSe QD to the Pt-PVP colloid. Thus, the surface passivating ligand plays an important role not only in the stabilization of the CdSe QD, but also in the electron transfer pathway from the photosensitizing CdSe QD to the hydrogen evolving catalyst.

Scheme 2. Schematic representations of the aggregates of photosensitizing (a) CdSe-MPA or (b) CdSe-MMBA before (left) and after (right) the addition of the Pt-PVP colloid catalyst. (c) Schematic energy diagram of photocatalytic HER driven by CdSe-MPA and Pt-PVP colloidal catalyst. The values corresponding to the positions of conduction band (CB) minimum, valence band (VB) maximum, and the redox potential of ascorbic acid (AA) are referred from the references [24, 65, 66, and 67].

4. CONCLUSIONS

In this study, a photocatalytic HER driven by photosensitizing CdSe QDs and using PVP-polymer-protected colloidal Pt as the H_2 evolving catalyst has been examined. Although the three CdSe QDs are passivated by similar thiol-based surface passivating ligands (MPA, MBA, or MMBA), they exhibit very different emission behavior. Consequently, CdSe-MPA and CdSe-MMBA exhibit deep trap emissions, probably derived from the surface Se-vacant sites. Conversely, such emissions were negligible in CdSe-MBA. This was due to effective hole

trapping by the aromatic thiol group. In the presence of a Pt-PVP colloidal catalyst, CdSe-MPA exhibited higher activity for photocatalytic hydrogen production when compared to CdSe-MBA and CdSe-MMBA. DLS measurements clearly indicate that the dispersibility of the CdSe QDs in aqueous media is improved in the order: CdSe-MMBA < CdSe-MBA < CdSe-MPA, probably due to less steric bulkiness of the surface passivating ligand. In addition, we concluded that the formation of aggregates, composed of CdSe QDs and the Pt colloidal catalyst, plays a crucial role in the photoinduced electron transfer between the photosensitizing CdSe QD and the hydrogen evolving Pt catalyst. Zeta potential measurements indicate that the well-dispersed CdSe-MPA effectively forms aggregates with the Pt colloidal catalyst because of the electrostatic interactions between the negatively charged CdSe QD and the positively charged Pt-PVP colloid. Thus, CdSe-MPA exhibits the highest photocatalytic activity among the three CdSe QDs. The results clearly indicate the importance of the surface passivating ligand; the ligand affects the photophysical properties of CdSe QD as well as the interactions between the photosensitizing CdSe QD and the H₂ evolving catalyst that dominates the photoinduced electron transfer efficiency between them. Further study on the interaction between the CdSe QDs and molecular H₂ evolving catalysts is now in progress.

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REFERENCES

- [1] A. Fujishima, K. Honda, Electrochemical Photolysis of Water at a Semiconductor Electrode, *Nature* 238 (1972) 37-38.
- [2] N. S. Lewis, D. G. Nocera, Powering the planet: Chemical challenges in solar energy utilization, *Proc. Natl. Acad. Sci.* 103 (2006) 15729-15735.
- [3] A. Kudo, Y. Miseki, Heterogeneous photocatalyst materials for water splitting, *Chem. Soc. Rev.* 38 (2009) 253-278.
- [4] S. Berardi, S. Drouet, L. Francàs, C. G.-Suriñach, M. Guttentag, C. Richmond, T. Stoll and A. Lobet, Molecular artificial photosynthesis, *Chem. Soc. Rev.* 43 (2014) 7501.
- [5] P. Du, R. Eisenberg, Catalysts made of earth-abundant elements (Co, Ni, Fe) for water splitting: Recent progress and future challenges, *Energy Environ. Sci.* 5 (2012) 6012-6021.
- [6] K. Sakai, H. Ozawa, Homogeneous catalysis of platinum(II) complexes in photochemical hydrogen production from water, *Coord. Chem. Rev.* 251 (2007) 2753-2766.
- [7] A. J. Esswein, D. G. Nocera, Hydrogen Production by Molecular Photocatalysis, *Chem. Rev.* 107 (2007) 4022-4047.
- [8] S. Fukuzumi, Y. Yamada, T. Suenobu, K. Ohkubo, H. Kotani, Catalytic mechanisms of hydrogen evolution with homogeneous and heterogeneous catalysts, *Energy Environ. Sci.* 4 (2011) 2754-2766.

- [9] V. S. Thoi, Y. Sun, J. R. Long, C. J. Chang, Complexes of earth-abundant metals for catalytic electrochemical hydrogen generation under aqueous conditions, *Chem. Soc. Rev.* 42 (2013) 2388-2400.
- [10] W. T. Eckenhoff, R. Eisenberg, Molecular systems for light driven hydrogen production, *Dalton Trans.* 41 (2012) 13004-13021.
- [11] M. Wang, L. Chen, L. Sun, Recent progress in electrochemical hydrogen production with earth-abundant metal complexes as catalysts, *Energy Environ. Sci.* 5 (2012) 6763-6778.
- [12] J. Jasieniak, M. Califano, S. E. Watkins, Size-Dependent Valence and Conduction Band-Edge Energies of Semiconductor Nanocrystals, *ACS Nano*, 5 (2011) 5888-5902.
- [13] M. A. Holmes, T. K. Townesnd, F E. Osterloh, *Chem. Commun.* 48 (2012) 371-373.
- [14] A. P. Alivisatos, Semiconductor Clusters, Nanocrystals, and Quantum Dots, *Science* 271 (1996) 933-937.
- [15] W. W. Yu, L. Qu, W. Guo, X. Peng, Experimental Determination of the Extinction Coefficient of CdTe, CdSe, and CdS Nanocrystals, *Chem. Mater.* 15 (2003) 2854-2860.
- [16] L. E. Brus, A simple model for the ionization potential, electron affinity, and aqueous redox potentials of small semiconductor crystallites, *J. Chem. Phys.* 79 (1983) 5566-5571.
- [17] L. E. Brus, Electron-electron and electron-hole interactions in small semiconductor crystallites: The size dependence of the lowest excited electronic state, *J. Chem. Phys.* 80 (1984) 4403-4409.

- [18] K. Meng, P. K. Surolia, O. Byrne, K. R. Thampi, Quantum dot and quantum dot-dye co-sensitized solar cells containing organic thiolate-disulfide redox electrolyte, *Journal of Power Sources* 275 (2015) 681-687.
- [19] I. Gur, N. A. Fromer, M. L. Geier, A. P. Alivisatos, Air-Stable All-Inorganic Nanocrystal Solar Cells Processed from Solution, *Science* 310 (2005) 310, 462.
- [20] G. Gu, N. Mojaverian, J. Vaillancourt, X. Lu, Surface plasmonic resonance induced near-field vectors and their contribution to quantum dot infrared photodetector enhancement, *J. Phys. D: Appl. Phys.* 47 (2014) 435106.
- [21] G. Konstantatos, I. Howard, A. Fischer, S. Hoogland, J. Clifford, E. Klem, L. Levina, E. H. Sargent, Ultrasensitive solution-cast quantum dot photodetectors, *Nature* 442 (2006) 180-183.
- [22] J.-Y. Kim, A. R. bin M. Yusoff, J. Jang, Quantum-Dot Light-Emitting Diode Featuring Polymeric Metal Oxide Anode Buffer Layer, *IEEE J. Quantum Electron* 21 (2015) 1900206.
- [23] S. Coe, W.-K. Woo, M. Bawendi, V. Bulović, Electroluminescence from single monolayers of nanocrystals in molecular organic devices, *Nature* 420 (2002) 800-803.
- [24] J. Huang, K. L. Mulfort, P. Du, L.X. Chen, Photodriven Charge Separation Dynamics in CdSe/ZnS Core/Shell Quantum Dot/Cobaloxime Hybrid for Efficient Hydrogen Production, *J. Am. Chem. Soc.* 134 (2012) 16472-16475.
- [25] Z. Fang, Y. Wang, J. Song, Y. Sun, J. Zhou, R. Xu, H. Duan, Immobilizing CdS quantum dots and dendritic Pt nanocrystals on thiolated graphene nanosheets toward highly efficient photocatalytic H₂ evolution, *Nanoscale* 5 (2013) 9830-9838.

- [26] T. Nann, S. K. Ibrahim, P.-M. Woi, S. Xu, J. Ziegler C. J. Pickett, Water Splitting by Visible Light: A Nanophotocathode for Hydrogen Production, *Angew. Chem. Int. Ed.* 49 (2010) 1574-1577.
- [27] K. A. Brown, S. Dayal, X. Ai, G. Rumbles and P. W. King, Controlled Assembly of Hydrogenase-CdTe Nanocrystal Hybrids for Solar Hydrogen Production, *J. Am. Chem. Soc.* 132 (2010) 9672-9680.
- [28] E. Khon, K. Lambrigh, R. S. Khnayzer, P. Moroz, D. Perera, E. Butaeva, S. Lambrigh, F. N. Castellano, M. Zamkov, Improving the Catalytic Activity of Semiconductor Nanocrystals through Selective Domain Etching, *Nano Lett.* 13 (2013) 2016-2023.
- [29] P. Wang, J. Zhang, H. He, X. Xu, Y. Jin, The important role of surface ligand on CdSe/CdS core/shell nanocrystals in affecting the efficiency of H₂ photogeneration from water, *Nanoscale* 7 (2015) 5767-5775.
- [30] C. G.-Suriñach, J. Albero, T. Stoll, J. Fortage, M.-N. Collomb, A. Deronzier, E. Palomares A. Lobet, Efficient and Limiting Reactions in Aqueous Light-Induced Hydrogen Evolution Systems using Molecular Catalysts and Quantum Dots, *J. Am. Chem. Soc.* 136 (2014) 7655-7661.
- [31] H. Zhu, N. Song, H. Lv, C. L. Hill T. Lian, Near Unity Quantum Yield of Light-Driven Redox Mediator Reduction and Efficient H₂ Generation Using Colloidal Nanorod Heterostructures, *J. Am. Chem. Soc.* 134 (2012) 11701-11708.
- [32] T. O'Connor, M. S. Panov, A. Mereshchenko, A. N. Tarnovsky, R. Lorek, D. Perera, G. Diederich, S. Lambricht, P. Moroz, M. Zamkov, The Effect of the Charge-Separating Interface

on Exciton Dynamics in Photocatalytic Colloidal Heteronanocrystals, ACS Nano 6 (2012) 8156-8165.

[33] Z.-J. Li, X.-B. Li, J.-J. Wang, S. Yu, C.-B. Li, C.-H. Tung, L.-Z. Wu, A robust “artificial catalyst” in situ formed from CdTe QDs and inorganic cobalt salts for photocatalytic hydrogen evolution, Energy Environ. Sci. 6 (2013) 465-469.

[34] K. Wu, Z. Chen, H. Lv, H. Zhu, C. L. Hill, T. Lian, Hole Removal Rate Limits Photodriven H₂ Generation Efficiency in CdS-Pt and CdSe/CdS-Pt Semiconductor Nanorod–Metal Tip Heterostructures, J. Am. Chem. Soc. 136 (2014) 7708-7716.

[35] Z.-J. Li, X.-B. Fan, X.-B. Li, J.-X. Li, C. Ye, J.-J. Wang, S. Yu, C.-B. Li, Y.-J. Gao, Q.-Y. Meng, C.-H. Tung, L.-Z. Wu, Visible Light Catalysis-Assisted Assembly of Ni₀-QD Hollow Nanospheres in Situ via Hydrogen Bubbles, J. Am. Chem. Soc. 136 (2014) 8261-8268.

[36] Z. Han, F. Qiu, R. Eisenberg, P. L. Holland and T. D. Krauss, Robust Photogeneration of H₂ in Water Using Semiconductor Nanocrystals and a Nickel Catalyst, Science 338 (2012) 1321-1324.

[37] Z.-J. Li, J.-J. Wang, X.-B. Li, X.-B. Fan, Q.-Y. Meng, K. Feng, B. Chen, C.-H. Tung, L.-Z. Wu, An Exceptional Artificial Photocatalyst, Ni₀-CdSe/CdS Core/Shell Hybrid, Made In Situ from CdSe Quantum Dots and Nickel Salts for Efficient Hydrogen Evolution, Adv. Mater. 25 (2013) 6613-6618.

[38] A Das, Z. Han, M. G. Haghighi, R. Eisenberg, Photogeneration of hydrogen from water using CdSe nanocrystals demonstrating the importance of surface exchange, Proc. Natl. Acad. Sci. 110 (2013) 16716-16723.

- [39] J. Zhao, M. A. Holmes, F. E. Osterloh, Quantum Confinement Controls Photocatalysis: A Free Energy Analysis for Photocatalytic Proton Reduction at CdSe Nanocrystals, *ACS Nano* 7 (2013) 4316-4325.
- [40] C.-B. Li, Z.-J. Li, S. Yu, G.-X. Wang, F. Wang, Q.-Y. Meng, B. Chen, K. Feng, C.-H. Tung, L.-Z. Wu, Interface-directed assembly of a simple precursor of [FeFe]-H₂ase mimics on CdSe QDs for photosynthetic hydrogen evolution in water, *Energy Environ. Sci.* 6 (2013) 2597-2602.
- [41] X.-B. Li, Z.-J. Li, Y.-J. Gao, Q.-Y. Meng, S. Yu, R. G. Weiss, C.-H. Tung, L.-Z. Wu, Mechanistic Insights into the Interface-Directed Transformation of Thiols into Disulfides and Molecular Hydrogen by Visible-Light Irradiation of Quantum Dots, *Angew. Chem. Int. Ed.* 53 (2014) 2085-2089.
- [42] Z. Han, R. Eisenberg, Fuel from Water: The Photochemical Generation of Hydrogen from Water, *Acc. Chem. Res.* 47 (2014) 2537-2544.
- [43] J.-J. Wang, Z.-J. Li, X.-B. Li, X.-B. Fan, Q.-Y. Meng, S. Yu, C.-B. Li, J.-X. Li, C.-H. Tung, L.-Z. Wu, Photocatalytic Hydrogen Evolution from Glycerol and Water over Nickel-Hybrid Cadmium Sulfide Quantum Dots under Visible-Light Irradiation, *ChemSusChem* 7 (2014) 1468-1475.
- [44] L.-Z. Wu, B. Chen, Z.-J. Li, C.-H. Tung, Enhancement of the Efficiency of Photocatalytic Reduction of Protons to Hydrogen via Molecular Assembly, *Acc. Chem. Res.* 47 (2014) 2177-2185.

- [45] J.-X. Jian, C. Ye, X.-Z. Wang, M. Wen, Z.-J. Li, X.-B. Li, B. Chen, C.-H. Tung, L.-Z. Wu, Comparison of H₂ photogeneration by [FeFe]-hydrogenase mimics with CdSe QDs and Ru(bpy)₃Cl₂ in aqueous solution, *Energy Environ. Sci.* 9 (2016) 2083-2089.
- [46] H. Lv, T. P. A. Ruberu, V. E. Fleischauer, W. W. Brennessel, M. L. Neidig, R. Eisenberg, Catalytic Light-Driven Generation of Hydrogen from Water by Iron Dithiolene Complexes, *J. Am. Chem. Soc.* 118 (2016) 138, 11654-11663.
- [47] K. E. Knowles, D. B. Tice, E. A. McArthur, G. C. Solomon, E. A. Weiss, Chemical Control of the Photoluminescence of CdSe Quantum Dot-Organic Complexes with a Series of Para-Substituted Aniline Ligands, *J. Am. Chem. Soc.* 132 (2010) 1041-1050.
- [48] Y. Liang, J. E. Thorne, B. A. Parkinson, Controlling the Electronic Coupling between CdSe Quantum Dots and Thiol Capping Ligands via pH and Ligand Selection, *Langmuir* 38 (2012) 11072-11077.
- [49] P. R. Brown, D. Kim, R. R. Lunt, N. Zhao, M. G. Bawendi, J. C. Grossman, V. Bulović, Energy Level Modification in Lead Sulfide Quantum Dot Thin Films through Ligand Exchange, *ACS Nano* 8 (2014) 5863-5872.
- [50] X. Wang, X. Ren, K. Kahen, M. A. Hahn, M. Rajeswaran, S. M.-Zacher, J. Silcox, G. E. Cragg, A. L. Efros, T. D. Krauss, Non-blinking semiconductor nanocrystals, *Nature* 459 (2009) 686-689.
- [51] T. Teranishi, M. Hosoe, T. Tanaka, M. Miyake, Size Control of Monodispersed Pt Nanoparticles and Their 2D Organization by Electrophoretic Deposition, *J. Phys. Chem. B* 103 (1999) 3818-3827.

- [52] Z.-Q. Yu, X.-M. Xu, C.-Y. Hong, D.-C. Wu, Y.-Z. You, A Responsive Hyperbranched Polymer Not Only Can Self-Immolate but Also Can Self-Cross-Link, *Macromolecules* 47 (2014) 4136-4143.
- [53] M. C. Schuster, D. A. Mann, T. J. Buchholz, K. M. Johnson, W. D. Thomas, L. L. Kiessling, Parallel Synthesis of Glycomimetic Libraries: Targeting a C-Type Lectin, *Org. Lett.* 5 (2003) 1407-1410.
- [54] W. W. Yu, L. Qu, W. Guo, X. Peng, Experimental Determination of the Extinction Coefficient of CdTe, CdSe, and CdS Nanocrystals, *Chem. Mater.* 15 (2003) 2854-2860.
- [55] J. Aldana, N. Lavelle, Y. Wang, X. Peng, Size-Dependent Dissociation pH of Thiolate Ligands from Cadmium Chalcogenide Nanocrystals, *J. Am. Chem. Soc.* 127 (2005) 2496-2504.
- [56] R. Koole, P. Schapotschnikow, C. de M. Dongená, T. J. H. Vlugt, A. Meijerink, *ACS Nano* 2 (2008) 1703-1714.
- [57] Y. Liang, J. E. Thorne, B. A. Parkinson, Controlling the Electronic Coupling between CdSe Quantum Dots and Thiol Capping Ligands via pH and Ligand Selection, *Langmuir* 28 (2012) 11072-11077.
- [58] S. F. Wuister, C. de M. Dongená, A. Meijerink, Influence of Thiol Capping on the Exciton Luminescence and Decay Kinetics of CdTe and CdSe Quantum Dots, *J. Phys. Chem. B* 108 (2004) 17393-17397.
- [59] J. Aldana, Y. A. Wang, X. Peng, Photochemical Instability of CdSe Nanocrystals Coated by Hydrophilic Thiols, *J. Am. Chem. Soc.* 123 (2001) 8844-8850.

- [60] I-S. Liu, H.-H. Lo, C.-T. Chien, Y.-Y. Lin, C.-W. Chen, Y.-F. Chen, W.-F. Su, S.-C. Liou, Enhancing photoluminescence quenching and photoelectric properties of CdSe quantum dots with hole accepting ligands, *J. Mater. Chem.* 18 (2008) 675-682.
- [61] J. J. Ramsden, M. Grätzel, Photoluminescence of Small Cadmium Sulphide Particles, *J. Chem. Soc. Faraday Trans. 1* 80 (1984) 919-933.
- [62] C. F. Landes, M. Braun, M. A. E.-Sayed, On the Nanoparticle to Molecular Size Transition: Fluorescence Quenching Studies, *J. Phys. Chem. B* 105 (2001) 10554-10558.
- [63] D. R. Baker, P. V. Kamat, Tuning the Emission of CdSe Quantum Dots by Controlled Trap Enhancement, *Langmuir* 26 (2010) 11272-11276.
- [64] R. J. Irving, L. Nelander, I. Wadso, Thermodynamics of the Ionization of Some Thiols in Aqueous Solution, *Acta Chem. Scand.* 18 (1964) 769-787.
- [65] L. E. Brus, A simple model for the ionization potential, electron affinity, and aqueous redox potentials of small semiconductor crystallites, *J. Chem. Phys.* 79 (1983) 5566-5571.
- [66] L. E. Brus, Electron-electron and electron-hole interaction in small semiconductor crystallites: The size dependence of the lowest excited electron state, *J. Chem. Phys.* 80 (1984) 4403-4409.
- [67] T. Matsui, Y. Kitagawa, M. Okumura, Y. Shigeta, Accurate Standard Hydrogen Electrode Potential and Applications to the Redox Potentials of Vitamin C and NAD/NADH, *J. Phys. Chem. A* 119 (2015) 369-376.