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Highly Efficient Photocatalytic CO₂-to-CO Conversion Catalyzed by a Surface Ligand-Removed and Cd-Rich CdSe Quantum Dots

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Abstract: A surface ligand-removed and Cd-rich CdSe quantum dots as a sole photocatalyst exhibits exceptional activity on CO₂-to-CO conversion. The CO production rate up to 789 mmol g⁻¹ h⁻¹ was achieved in TEA/DMF mixture solution under visible light irradiation. Mechanism studies revealed that improving Cd/Se stoichiometric ratio and exposing more active surface Cd atom significantly enhance activity of CdSe QDs on CO₂ photoreduction.

The conversion of carbon dioxide (CO₂) to solar fuels is one of basic half-reactions in artificial photosynthesis (AP).^[1-3] However, the inertness of molecular CO₂ and multi-products characteristic of CO₂ reduction result in low efficiency and selectivity of photocatalytic CO₂ reduction.^[4] In comparison to its sister halfreaction, photocatalytic hydrogen production, the rates and efficiencies of photocatalytic CO₂ reduction in documented systems are much lower. The development of catalyst/photocatalyst of CO2 reduction with high catalytic rate and selectivity is therefore very necessary.

Nano-semiconductor quantum dots (QDs) of cadmium chalcogenides,^[5-9] such as CdSe and CdTe QDs, of tunable absorption, multi-electron excitation, and facile preparation had being widely used as photosensitizer (PS) for H₂ production since the pioneering works described in 2010s.^[10-14] Recently, studies of using QDs as PS in combination with various cocatalysts, such as molecular catalyst^[15-18] or inorganic heterogeneous catalyst,^[19-21] for photocatalytic CO₂ reduction are blooming. In these systems, QDs functions as a light harvester to adsorb photons and thus delivers excited electrons to cocatalyst; the reduced cocatalyst is the real place for CO₂ transformation.^[19] In such system, the efficiency of interfacial electron transfer between QDs and cocatalyst always determines the overall efficiency of the system. The reported

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Figure1. (a) Schematic diagram of preparation of LRCR-CdSe QDs. (b) FT-IR spectra of MPA-CdSe-2 and CdSe-2 QDs. (c) TGA data for MPA-CdSe-2 and CdSe-2. (d) Surface zeta potential of MPA-CdSe-2 and CdSe-2 QDs. (e) XRD spectra of MPA-CdSe-2 and CdSe-2 QDs before and after photocatalysis. (f) TEM images of MPA-CdSe-2. HTEM image of CdSe-2 QDs before (g) and after (h) irradiation.

systems containing QDs suffer from low efficiency and selectivity for CO_2 -to-CO conversion.^[19]

Quantum dots themselves as a photocatalyst have potential ability of mediating photoredox reactions on their surface.^[22-29] The coordination unsaturated metals at QDs' surface enable to act as an active center to bind substrate and then carry out catalytic conversion with the assistance of the photoexcited electrons and holes.^[22-25] Yanagida previously suggested that surface Cd atom in CdS nanocrystallites as the active site enables to bind CO_2 .^[23, 24] Recently, Frei also revealed that surface Cd atom in MPA-CdSe QDs (MPA = 3-mercapto-propionic acid) chemically adsorbs CO_2 to form Cd-C₂O₄⁻ adduct.^[25] These studies revealed that surface Cd atom of QDs is essential to its photoactivity on CO_2 reduction. We wonder whether the photoactivity of CO_2 reduction would be much improved if more Cd atoms are exposed at the surface of CdSe QDs.

Herein, we report a *Ligand-Removed and Cd-Rich CdSe QDs* (**LRCR-CdSe** QDs) as a photocatalyst boosts CO₂-to-CO conversion in TEA/DMF mixture under visible light irradiation with exceptional activity and selectivity. Benefiting from improving Cd/Se stoichiometric ratio of CdSe QDs and stripping

organic ligands from CdSe QDs' surface, more surface Cd atoms are exposed as active sites of CO₂ reduction. At the optimal condition, the **LRCR-CdSe** (CdSe-4) QDs as a sole photocatalyst enabled to produce 217 µmol CO and with a high selectivity up to 95% at a low concentration (0.005 mg mL⁻¹) under visible light irradiation; the corresponding initial rate of CO production and the apparent quantum yield achieve up to 789 mmol h⁻¹ g⁻¹ and 51.4 ± 1.1%, respectively.

The LRCR-CdSe QDs was prepared by using MPA-CdSe QDs as a precursor, which was synthesized according to literatures' methods.^[12, 30] The Cd/Se ratio of CdSe QDs is tuned by putting different feeding ratio of cadmium and selenium precursors, CdCl₂ and Na₂SeSO₃, in synthesis.^[30] The MPA ligand can be easily removed by adding HCI (37% aqueous solution) into MPA-CdSe QDs aqueous solution at pH 4.0 (Figure 1a and SI). By using this manipulation, we prepared a series of ligand-removed CdSe QDs with different Cd/Se stoichiometric ratios, which are labeled as CdSe-1, CdSe-2, CdSe-3, and CdSe-4, respectively. Inductively coupled plasmaatomic emission spectrometry (ICP-AES) analysis showed that n_{Cd/Se} ratio of these four CdSe QDs is 1.57, 3.07, 4.63, and 6.53. respectively. The atomic surface composition of these four QDs analyzed by XPS showed that the percentage of surface Cd atom of these four CdSe QDs is 41.45% for CdSe-1, 43.26% for CdSd-2, 53,52% for CdSe-3, and 51,70% for CdSe-4, while the surface Se decreased as 20.71% for CdSe-1, 11.68% for CdSe-2, 11.20% for CdSe-3, and 7.38% for CdSe-4. These results indicate the successful control of surface Cd/Se ratio in this series of CdSe QDs.

By using CdSe-2 as a model, the FT-IR comparison spectra (Figure 1b) demonstrates that the characteristic peaks of MPA ligand in MPA-CdSe-2 at 1566 cm⁻¹ (C=O of COO⁻) and 670 cm⁻ ¹ (C-S bond) disappeared after ligand stripping treatments.^[31, 32] Thermogravimetric analysis (TGA) of MPA-CdSe-2 and CdSe-2 under N₂ atmosphere demonstrated that MPA-CdSe-2 shows an obvious mass reduction in the heating temperature range of 250 - 375 °C in comparison to CdSe-2 (Figure 1c), which is the mass loss of organic ligand.[33] Surface zeta potential of CdSe-2 decreases from -58.6 mV before ligand stripping to -0.79 mV (Figure 1d). These results demonstrate that most of MPA ligand was successfully removed from CdSe QDs. As shown in Figure 1e, the XRD spectra of MPA-CdSe-2 (black line) and CdSe-2 (red line) showed the same pattern of three characteristic peaks at ca.25.16°, 42.07°, and 49.64°, which are assigning to the lattice planes of (111), (220), and (311) of CdSe (JCPDS Card No. 19-0191), respectively.^[34] This is indicative that the structure of CdSe core doesn't damage after the ligand stripping operation. TEM image in Figure 1f shows that MPA-CdSe-2 are monodispersed particles. In contrast, CdSe-2 (Figure 1g) were aggregated due to high surface energy of QDs after ligand stripping.^[35] In high resolution TEM (HTEM) image (Figure 1g, inset), the lattice stripes of CdSe-2 can be recognized. Above findings demonstrated that surface ligand stripping results in aggregation between CdSe QDs, however, the core structure of CdSe particles is kept.

The photoactivity of the CdSe QDs on CO₂ reduction was firstly evaluated by using MPA-CdSe-2 and **CdSe-2** with a standard concentration of 0.2 mg mL⁻¹ in CO₂-saturated DMF solution by using trimethylamine (TEA) as an electron donor



Figure 2. (a) Photocatalytic CO₂ reduction by using CdSe QDs (0.2 mg mL⁻¹) with different Cd/Se ratios and MPA-CdSe-2, [QDs] = 0.2 mg mL⁻¹. (b) Mass spectra of isotope experiments. (c) long-time photocatalytic CO₂ reduction by using **CdSe-4** (0.005 mg mL⁻¹); inset: the CO production selectivity of the long-time photocatalysis. (d) Transient photocurrent response to on-off illumination of CdSe QDs with different Cd/Se ratios (Xe lamp, $\lambda > 400$ nm).

(v(DMF)/v(TEA) = 4/1, total volume = 5.00 mL). As shown in Figure 2a, after 20 hours of irradiation under blue LED lamp $(\lambda_{max} = 450 \text{ nm})$, the **CdSe-2** system produced 354 µmol CO and only 37 µmol H₂ as a by-product; no formate and methane were found in the system. The CO production efficiency based on QDs and selectivity are 354 mmol g⁻¹ and 90.5%, respectively. However, the amount of CO and H₂ production from MPA-CdSe-2 system is only 128 and 11 μ mol (Selectivity_{CO} = 91.1%), respectively. A ca. 2.8 times improvement on CO production was obtained by stripping of MPA ligand from CdSe QDs. Control experiments revealed that CdSe QDs, TEA, and visible light irradiation are necessary for efficient CO production, because no CO or H₂ were detected in the absence of QDs or TEA, or setting the system in dark. The **CdSe-2** in N₂-saturated DMF produced only 126 µmol H₂; isotope experiment operated in ¹³CO₂ atmosphere further demonstrated that ¹³CO is the only carbon-based reduction product (Figure 2b). These results indicate CO₂ is the only source of CO production. By decreasing the concentration of CdSe-2 from 0.2 mg mL⁻¹ to 0.005 mg mL⁻¹, the CO production efficiency increased from 354 mmol g⁻¹ to 2787 mmol g⁻¹ (SI, Figure S6); almost 8 times improvement was obtained, indicating the significant concentration effect of QDs.

It was found that Cd/Se ratio of CdSe QDs affect much on CO production activity. As the Cd/Se ratio of CdSe increasing from **CdSe-1** ($n_{Cd/Se} = 1.57$) to **CdSe-3** ($n_{Cd/Se} = 4.63$), the amount of CO production increases from 15.4 µmol to 1386 µ mol at the same condition (Figure 2a). By using **CdSe-4** ($n_{Cd/Se} = 6.53$) as a photocatalyst, the CO production efficiency slightly increases to 1422 µmol, which is *ca.* a 92 times improvement in comparison to **CdSe-1**. Except **CdSe-1** with a CO selectivity of only 53.8%, the other three QDs, **CdSe-2**, **CdSe-3**, and **CdSe-4**, kept CO selectivity in the range of 90.5 - 96.4%.

Based on above findings, we performed a long-time photocatalysis at the optimal condition by using CdSe-4 as a photocatalyst with a low concentration of 0.005 mg mL⁻¹. As

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Figure 3. (a) and (b) XPS spectra of CdSe-2 before and after photocatalysis. (c) Schematic diagram of CB and VB positions, sizes of CdSe QDs with different CdSe ratios. (d) Decay kinetics at 440 nm of CdSe-2 in N₂- (red line) and CO₂-saturated (black line) DMF solution (excitation wavelength = 350 nm).

shown in Figure 2c, the system continuously produced CO in the whole 120 hours of irradiation. At the end of photocatalysis, the system produced 217 µmol CO with a CO selectivity of 95%. The average CO production rate is 72.2 mmol g⁻¹ h⁻¹ based on QDs. An exceptional fast CO production rate of 789 mmol g⁻¹ h⁻¹ was obtained in the initial 5 hours of irradiation (SI, Table S7).^[19] During the long time photocatalysis, the system kept high CO selectivity in the range of 93.8-96.7% (Figure 2c, inset). The apparent quantum yield (AQY) of CO production was also estimated as 51.4 ± 1.1 % by using **CdSe-4** at the same condition (SI, Table S1).

To investigate the inactivation of the photocatalyst, XRD, HTEM and XPS measurements of CdSe QDs (**CdSe-2**) samples before and after 120 hours of photocatalysis were applied. No obvious change of morphology and aggregation state of QDs were observed after photocatalysis in comparison to that of before photocatalysis (Figure 1g and 1h). After photocatalysis, the lattice pattern and shape of QDs are still identifiable (SI, Figure S4). The diameter of QDs increases slightly from 2.18 nm to 2.36 nm (SI, Table S2). XRD spectra of QDs before and after photocatalysis (Figure 1e) also shows the same diffractions pattern. These evidences indicate that the core structure of CdSe QDs doesn't damage in the course of photocatalysis.

The photoredox reactions operate on the surface of QDs. The coordination unsaturated surface Cd^{2+} atom is the active site.^[23-25] The surface state of QDs was therefore examined by XPS analysis. As shown in Figure 3a, Cd *3d* spectrum of **CdSe-2** before photocatalysis shows two distinct peaks of *3d*_{3/2} at 411.82eV and *3d*_{5/2} at 405.08 eV.^[30] Each of *3d* signal is composed of bulk Cd and surface Cd.^[30, 36] After photocatalysis, two Cd *3d* peaks turn broad and positively shift, while a new contribution at 404.67 eV in *3d*_{5/2} peak and 411.45 eV in *3d*_{3/2} emerged. This new contribution is attributed to Cd-O species.^[37, 38] Figure 3b shows Se *3d* peaks before and after photocatalysis. Obviously, except the main peak of Se *3d*, a new peak of

oxidized Se species at 58.60 eV is emerged after photocatalysis.^[39, 40] These evidences indicate that surface oxidation occurs in the course of photocatalysis. The loss of surface Cd is also detected. The surface Cd/Se ratio decrease from 3.70 before photocatalysis to 2.41 after photocatalysis. Above evidences demonstrate that surface environment of CdSe QDs changes after photocatalysis. The inactivation reasons of the photocatalyst are attributed to partially surface oxidation and loss of surface Cd atom during long-time photocatalysis.

Previous studies had been revealed that lowering surface Se ratio suppresses the possibility of non-radiative recombination of photogenerated hole-electron pairs in CdSe QDs,^[36, 41, 42] which is beneficial to photocatalysis. The on-off switching behavior of photocurrent (Figure 2d) of these four CdSe QDs show that all of four QDs gave transient photocurrent response (SI, Figure S17). The photocurrent density exhibits significant dependence on Cd/Se ratio of CdSe QDs. The photocurrent density increased as the Cd/Se ratio of QDs increasing, indicating more photogenerated carriers produced in CdSe QDs with higher Cd/Se ratio. This is also consistent with the results of photocatalytic CO production.

Frei et al. revealed that surface Cd in CdSe QDs chemically adsorbs CO₂ to form Cd-C₂O₄⁻ adduct.^[25] It was found that a constant reductive peak at -0.82 V vs. SCE emerged under CO2 atmosphere in cyclic voltammogram measurement of using CdSe QDs with different Cd/Se ratios (SI, Figure S16). However, no obvious peak was observed under N₂ atmosphere at the same condition. We therefore assign this peak to the reduction of Cd-C₂O₄⁻ adduct.^[23, 25] According to Tauc plot (Figure S8) and Mott-Schottky measurements (Figure S9), the flat band positions, approximate to the conduction band (CB) position, of these four QDs are shown in Figure 3c. As the Cd/Se ratio increasing, the E_{CB} position negatively shift from -0.84 V for CdSe-1 to -0.99 V for CdSe-4. According to Rehm-Weller equation, the free energy change of photoinduced electron transfer (PET) from conduction band of QDs to surface Cd-C₂O₄⁻ adduct is thermodynamically feasible. The driven force of the PET process increases as the Cd/Se ratio increasing. Time-resolved transient absorption (TA) of CdSe-2 in N2 or CO2-saturated DMF was further investigated. As shown in Figure 3d, after excitation of a N₂-saturanted DMF solution containing CdSe-2 by 350 nm femtosecond laser, the TA spectra of CdSe-2 QDs show a bleach of 1s exciton band



Scheme 1. The schematic diagram of photoinduced electron transfer in photocatalysis.

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at 460 nm (SI, Figure S12).^[43-46] The bleach recovery kinetics can be fitted by three exponential decays of lifetime 5.8, 51.0, and 1201 ps. By excitation of the same solution saturated by CO₂ (SI, Figure S13), all three lifetimes of 1s excitation decreases to 1.8, 20.0, and 587 ps (Figure 3d and Table S6), indicating the short-lived 1s electrons under CO₂ atmosphere. We attributed this bleach quenching to the electron transfer from conduction bond of CdSe QDs to Cd-C₂O₄⁻ adduct.^[25] It was also found that the long lifetime τ_3 of QDs decrease to 682 ps in the presence of TEA (Table S6 and Figure S15). This can be attributed to the hole consumption by TEA under irradiation.^[47, 48]

Based on above results, a plausible mechanism of the system can be proposed (Scheme 1). Under visible light irradiation, the CdSe QDs is excited to generate electrons on conduction band and holes on valence band. In one hand, the electrons on CB transfer to surface adsorbed Cd-C₂O₄⁻ species to fulfill CO₂-to-CO conversion. In another hand, the holes on VB of QDs are consumed by TEA: the oxidized TEA subsequently releases protons as a source of hydrogen production in the system.^[49] The ultra-fast CO production of this system is benefited from following advantages. First, more surface Cd atoms are exposed via surface manipulation of improving surface Cd/Se ratio and stripping organic ligands, which exposes more active sites on the surface of the photocatalyst.[23-Second, more photogenerated carriers is achieved by improving Cd/Se ratio of CdSe QDs; this means a higher concentration of photogenerated electrons participates surface catalysis. Third, higher conduction band of QDs is obtained through improving Cd/Se ratio, which leads to larger driven force of PET from QDs to Cd-C₂O₄⁻ adduct.

In conclusion, benefiting from surface manipulation of CdSe, improving Cd/Se stoichiometric ratio and stripping of surface ligand, the photocatalytic activity on CO₂-to-CO conversion of CdSe QDs was dramatically improved. An exceptional fast photocatalytic CO production rate of 789 mmol g⁻¹ h⁻¹ was obtained by using the **LRCR-CdSe** (CdSe-4) QDs as a photocatalyst without any cocatalyst. Our results demonstrate that the surface environment and stoichiometry of CdSe QDs are critical important to its activity on CO₂ photoreduction. Surface oxidation and loss of surface Cd during long-time photocatalysis lead to inactivation of CdSe QDs.

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A surface ligand-removed and Cdrich CdSe quantum dots as a sole photocatalyst exhibits exceptional activity on CO₂-to-CO conversion.



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Highly Efficient Photocatalytic CO₂to-CO Conversion Catalyzed by a Surface Ligand-Removed and Cd-Rich CdSe Quantum Dots