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# Efficient and Selective CO<sub>2</sub> Reduction Integrated with Organic Synthesis by Solar Energy



Solar-driven  $CO_2$  photoreduction is attractive to produce usable fuels and valueadded chemicals. However, conventional strategies suffer from low activity and/or expense of sacrificial reagents. Here, the first example of  $CO_2$  reduction to CO integrated with an oxidative organic synthesis of 1-phenylethanol to pinacols under solar light is reported. This strategy, making full utilization of photogenerated electrons and holes in redox reactions, provides the exact answer toward cost-effective  $CO_2$  photoreduction.



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### HIGHLIGHTS

Exceptional activity and selectivity of CO<sub>2</sub>-to-CO conversion is realized by QDs

CO<sub>2</sub> reduction is firstly integrated with oxidative organic synthesis by solar energy

Full utilization of photogenerated electrons and holes in redox reactions is achieved

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# Efficient and Selective CO<sub>2</sub> Reduction Integrated with Organic Synthesis by Solar Energy

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### SUMMARY

Solar-driven catalytic CO<sub>2</sub> reduction is attractive to produce usable fuels and value-added chemicals. However, conventional strategies suffer from low activity and/or expense of sacrificial reagents. Here, we describe the first example of CO<sub>2</sub> reduction integrated with the oxidative organic synthesis by solar energy. With visible-light irradiation, CdSe/CdS quantum dots (QDs) enable photocatalytic conversion of CO<sub>2</sub> to CO with an exciting rate of ~412.8 mmol g<sup>-1</sup> h<sup>-1</sup> and a high selectivity of > 96% in the presence of triethylamine. More importantly, CO<sub>2</sub>-to-CO conversion proceeds smoothly when integrated with oxidative coupling of 1-phenylethanol to evolve pinacol. 1-Phenylethanol with electron-donating groups at the *p*-position of aryl ring, for example, is converted to corresponding pinacols with excellent yields up to 98%. The released protons and electrons of oxidative half-reaction are used for CO<sub>2</sub> reduction. Apparently, this strategy provides the exact answer toward cost-effective CO<sub>2</sub> photoreduction and opens a new horizon for efficient solar-to-fuel conversion.

### INTRODUCTION

Catalytic reduction of CO<sub>2</sub> into usable fuels and value-added chemicals by solar energy has emerged as a crucial energy-storage pathway to address greenhouse effect and energy crisis.<sup>1-6</sup> Tremendous efforts have been devoted to converting CO<sub>2</sub> into corresponding gaseous products (for example, CO,  $CH_4$ , and  $C_2H_4$ )<sup>7-9</sup> and liquid products (for example, HCOOH, CH<sub>3</sub>OH, and C<sub>2</sub>H<sub>5</sub>OH).<sup>10-12</sup> A carbon neutral cycle of coupling CO<sub>2</sub> reduction and water (H<sub>2</sub>O) oxidation together is regarded as a dream reaction to store solar energy in chemical bonds of CO<sub>2</sub> reduction products and  $O_2$  gas.<sup>13</sup> Up to date, various types of semiconductor materials (for example, CdSe, <sup>14</sup> TiO<sub>2</sub>, <sup>15,16</sup> InVO<sub>4</sub>, <sup>17</sup> BiOBr, <sup>18</sup> and ZnIn<sub>2</sub>S<sub>4</sub><sup>19</sup>) are capable of driving multielectron CO<sub>2</sub> reduction (usually to CO or CH<sub>4</sub>) by employing H<sub>2</sub>O as the proton and electron donor. However, the kinetically sluggish oxidation half-reaction ( $2H_2O \rightarrow 4e^- +$  $4H^{+} + O_{2}$ ) makes these photosystems limited by low activity and poor durability. On the contrary, CO<sub>2</sub> photoreduction at the expense of sacrificial reagents (for example, ascorbic acid,<sup>20</sup> sodium sulfite  $(Na_2SO_3)$ ,<sup>21</sup> triethanolamine (TEOA)<sup>22-24</sup> and N, N, N', N'-tetramethyl-p-phenylenediamine (TMPD)<sup>25</sup>) as the hole scavengers shows accessibility toward effective  $CO_2$  conversion. Unfortunately, such a strategy is not economically feasible and wastes the oxidizing power of photogenerated holes. It is highly desirable to utilize these excited holes to drive meaningful chemical reactions. In recent years, the examples of H<sub>2</sub> photogeneration coupled with oxidative organic synthesis have been reported to simultaneously produce solar fuel (H<sub>2</sub>)

### **The Bigger Picture**

CO<sub>2</sub> reduction to fuels driven by solar energy has great importance for climate and energy issues. However, the low activity under visible light and the waste of sacrificial reagents of traditional photocatalysis limit its practical application. Here, CO<sub>2</sub> photoreduction is firstly integrated with oxidative organic synthesis to simultaneously produce solar fuels and valueadded chemicals by solar energy, which provides the exact answer for cost-effective CO<sub>2</sub> photoreduction and opens a new horizon for efficient solar-to-fuel conversion. Owing to its extremely high activity and costeffective nature, this strategy shows great potentials in solardriven CO<sub>2</sub> conversion on a large scale in the near future.

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and value-added organic chemicals.<sup>26–29</sup> However, to the best of our knowledge, a solar-light-driven system that effectively integrates  $CO_2$  photoreduction with oxidative organic synthesis has yet to be demonstrated.<sup>30–32</sup>

Here, we firstly report semiconductor QDs photocatalyzed CO<sub>2</sub> reduction integrated with oxidative organic transformation under visible light (Scheme 1), thus enabling the full utilization of excited electrons and holes to simultaneously produce gas product of CO and liquid product of value-added chemical (pinacol). Pinacol emerges as the important structural motifs in natural products and pharmaceutical intermediates.<sup>33</sup> Synthesis of pinacol mainly focuses on reductive dimerization of aldehydes and/or ketones in the aid of co-reductants (for example, low-valent metals of Cu, Zn, and Mg).<sup>34,35</sup> Recent interest in visible-light mediated coupling of alcohols has become an effective pathway to evolve pinacol.<sup>36-38</sup> Our initial experiments indicate that CdSe/CdS QDs can catalyze CO2-to-CO conversion under visible-light irradiation ( $\lambda$  = 450 nm) with an exciting rate of ~412.8 mmol g<sup>-1</sup> h<sup>-1</sup> and a high selectivity of >96% in the presence of triethylamine (TEA). More importantly, photocatalytic CO<sub>2</sub>-to-CO conversion proceeds smoothly and effectively when integrated with the oxidative C-C coupling of 1-phenylethanol derivatives to corresponding pinacols, not ketones, with yields as high as >98%. This strategy provides the exact answer for solar driven catalytic CO<sub>2</sub> reduction and opens a new horizon for efficient solar-to-fuel conversion owing to its extremely high activity and cost-effective nature.

### RESULTS

### Visible-Light-Driven CO<sub>2</sub> Reduction Using Semiconductor QDs

Due to their adjustable band positions, excellent light-harvesting properties, and abundant surface sites, semiconductor QDs consisting of II-VI elements were chosen as the photocatalysts (see preparation procedures in Supplemental Experimental Procedures and corresponding characterization details in Figures S1 and S2).<sup>39</sup> The initial experiments of photocatalytic CO<sub>2</sub> reduction using semiconductor QDs were performed in the presence of sacrificial reagent (triethylamine; TEA) in organic solvent of dimethylformamide (DMF). DMF was employed as the solvent for two reasons: (1) the excellent solubility of CO<sub>2</sub> gas, and (2) the strong coordination of DMF at surface Cd suppressing proton adsorption and reduction.<sup>40</sup> Surprisingly, CdSe/CdS QDs were able to effectively reduce CO<sub>2</sub> to CO with a rate of 318.9  $\pm$  5.8 mmol g<sup>-1</sup> h<sup>-1</sup>, which was much higher than those of CdSe, CdS and the physical

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### Figure 1. Photocatalytic CO<sub>2</sub> Reduction in the Presence of Sacrificial Reagents

(A) The rate of photocatalytic  $CO_2$  reduction reaction using different semiconductor QDs as the photocatalysts.

(B) Photocatalytic CO<sub>2</sub> reduction of CdSe QDs modified with different atomic thickness of CdS shell under the same conditions.

(C) Long-time photocatalytic  $CO_2$  reduction experiment using CdSe/CdS QDs as photocatalysts and TEA as electron donor under Xe lamp irradiation (300 mW with 400 nm filter).

(D) The generation of  $CO_2$  reduction products as a function of time with solar simulator (AM1.5G) as the light source by using CdSe/CdS QDs as photocatalysts.

(E) GC-MS chromatogram of gas products obtained by photocatalytic reaction under a <sup>13</sup>CO<sub>2</sub> atmosphere with different irradiation time.

(F) Growth kinetics of  $^{13}$ CO and the corresponding decay kinetics of  $^{13}$ CO<sub>2</sub> along with 450 nm LEDs irradiation obtained from GC quantization. The error bars represent the relative deviation of three independent experiments.

mixture of CdSe and CdS QDs under the same conditions (room temperature; 450 nm LEDs) (Figure 1A). <sup>1</sup>H NMR and ion chromatography revealed that no liquid products (e.g., CH<sub>3</sub>OH, HCOOH) were produced. That is to say, H<sub>2</sub> gas is the only by-product of CO<sub>2</sub> photoreduction. According to following equation ( $\eta = n(CO)/[n(CO) + n(H_2)] \times 100\%$ ), the selectivity of CO<sub>2</sub>-to-CO catalyzed by CdSe/CdS QDs was above 94%.

As the thickness of CdS shell greatly influences the light harvesting and charge separation of the heterostructured QDs,<sup>41</sup> the influence of CdS shell thickness on CO<sub>2</sub> photoreduction is investigated. According to our previous reports,<sup>42,43</sup> CdSe QDs (~2.0 nm) covered with different shell thickness of CdS were successfully synthesized in aqueous solution using a successive ion layer adsorption and reaction (SILAR) approach. Obviously, introduction of CdS shell onto CdSe core significantly changed the activity of CO<sub>2</sub> photoreduction (Figure 1B). Due to the high selectivity and activity of CO evolution, CdSe/CdS QDs with ~3 atomic layers of CdS were taken as the photocatalysts afterwards. Under the optimal conditions, the system produced CO with an exceptional rate of ~412.8 mmol g<sup>-1</sup> h<sup>-1</sup> and a selectivity of >96% under visible light (Figure S3). Taking monochromatic LEDs as the light source ( $\lambda = 450$  nm, 60 mW cm<sup>-2</sup>, and 1.0 cm<sup>2</sup>), the apparent quantum yield

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(AQY) of CO evolution was determined as high as 32.7%, see details in Figure S4. Compared with typical QDs based photocatalytic CO<sub>2</sub> reduction systems, the present photosystem exhibited much higher activity and/or selectivity in the absence of any external cocatalysts (Table S1). Furthermore, CdSe/CdS QDs also demonstrated excellent stability toward CO<sub>2</sub> photoreduction. As shown in Figure 1C, both activity and selectivity of CO production were well preserved after 6 recycling experiments. Excitingly, this system could effectively convert CO<sub>2</sub> to CO with an average rate of ~63.1 mmol g<sup>-1</sup> h<sup>-1</sup> and a selectivity of >97% under the irradiation of AM1.5 (Figure 1D), indicating its great potential applications in conversion solar energy into chemical fuels on a large scale.

In order to reveal the origin of evolved H<sub>2</sub>, deuterium substituted DMF (d<sub>7</sub>-DMF) was used as the solvent of CO<sub>2</sub> photoreduction. Gas chromatography (GC) analysis confirmed that H<sub>2</sub>, instead of D<sub>2</sub>, was detected. This result indicated that sacrificial reagent (TEA) here worked as both electron and proton donor. To further validate the origin of CO from CO<sub>2</sub> reduction, an isotopic experiment using  $^{13}CO_2$  as reactant was carried out, and the obtained gaseous products were analyzed by gas chromatography-mass spectrometry (GC-MS). As shown in Figure 1E, the signals at m/z = 29 and m/z = 45 were observed, which could be assigned to the photogenerated <sup>13</sup>CO and the residual <sup>13</sup>CO<sub>2</sub>, respectively. This result qualitatively confirmed the produced CO originated from  $CO_2$ . As signal at m/z = 17 was not observed, further confirming that the system did not produce CH<sub>4</sub> from CO<sub>2</sub> photoreduction (Figure S5). Furthermore, the growth kinetics of <sup>13</sup>CO and the corresponding decay kinetics of <sup>13</sup>CO<sub>2</sub> during the photocatalytic process were monitored. It clearly showed the continuous decrease of <sup>13</sup>CO<sub>2</sub> along with the increase of corresponding  $^{13}$ CO with the reaction proceeding, and  $^{13}$ CO<sub>2</sub> was quantitatively converted to  $^{13}$ CO after 12 h visible-light irradiation (Figure 1F). These results clearly indicated that CO was originated from CO<sub>2</sub> photoreduction.

## Solar-Light-Driven CO<sub>2</sub> Reduction Integrated with Oxidative Organic Synthesis

Compared with photocatalytic CO<sub>2</sub> reduction in the aid of sacrificial reagents (e.g., TEA, ascorbic acid), CO<sub>2</sub> photoreduction coupled with desired organic synthesis is more challenging and meaningful. On the basis of above results, here, we realized efficient and selective CO<sub>2</sub> photoreduction integrated with an oxidative organic synthesis of pinacol through oxidative C-C coupling reaction by solar energy for the first time. Taking colloidal semiconductor QDs as the photocatalysts, the photogenerated holes initiated the oxidative coupling of 1-phenylethanol to pinacol (see details in <sup>1</sup>H NMR, <sup>13</sup>C NMR and mass spectrum of the oxidative product in Figures S6 and S7), while the released protons of the oxidative half-reaction participated in CO<sub>2</sub> photoreduction. This protocol shows considerable advantages in full utilization of solar energy as two useful products, solar fuel (CO) and value-added chemical (pinacol), are obtained simultaneously. Furthermore, the reduction product (CO) and oxidation product (pinacol) are spontaneously separated in the gaseous phase and solution, respectively.

Detailed experiments revealed that CdSe/CdS QDs showed higher activity of CO production and better pinacol yield than those of CdSe or CdS QDs under the same conditions (Table 1). The conversion was also greatly influenced by the shell thickness of CdS from 0 to 7 atomic layers. When the shell thickness of CdS was 3 atomic layers, the system demonstrated the highest activity of CO evolution (27.63 mmol  $g^{-1}$  h<sup>-1</sup>) with a selectivity of ~94%. Meanwhile, the production of oxidation product of pinacol also showed a climax rate (26.5 mmol  $g^{-1}$  h<sup>-1</sup>) with a

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	c	$CO_2 + 2$ $R$ $CO + H_2O$ $R$ $CO + H_2O$ $R$ $R$ $CO + H_2O$							
QDs	–R	Shell Thickness (N) <sup>a</sup>	Gas Products (mmol g <sup>-1</sup> h <sup>-1</sup> ) <sup>b</sup>		CO Selectivity (%) <sup>c</sup>	Liquid Products (mmol $g^{-1} h^{-1}$ )		Pinacol Yield (%) <sup>d</sup>	e <sup>-</sup> /h <sup>+e</sup>
			H <sub>2</sub>	со		Acetop- henone	Pina- col		
CdSe	-H	0	1.59	22.85	93.5	1.77	21.2	60.4	1.06
CdS	-H	0	2.29	7.46	76.5	1.32	9.40	24.6	0.91
CdSe/CdS	-H	1	1.30	22.41	94.5	1.06	20.6	53.5	1.09
CdSe/CdS	-H	3	1.55	27.63	94.7	1.18	26.5	74.0	1.05
CdSe/CdS	-H	5	1.05	7.57	87.8	1.01	8.3	20.9	0.93
CdSe/CdS	-H	7	1.10	7.90	87.8	0.93	8.2	21.0	0.99
CdSe/CdS <sup>f</sup>	-H	3	1.03	6.71	86.7	0.34	6.4	18.2	1.15
CdSe/CdS	-CH <sub>3</sub>	3	0.32	7.13	95.7	-	7.17	92.2 <sup>9</sup>	1.04
CdSe/CdS	-OCH <sub>3</sub>	3	0.46	8.34	94.8	-	8.01	98.7 <sup>h</sup>	1.10
CdSe/CdS	-NO <sub>2</sub>	3	-	-	-	-	-	-	-

#### Table 1. Visible-Light-Driven CO<sub>2</sub> Reduction Integrated with Pinacol Coupling Reaction

Reaction conditions: 2.9 mg QDs were dispersed in 5.0 mL DMF. Then, 1-phenylethanol (0.5 mmol) and Na<sub>2</sub>CO<sub>3</sub> (0.5 mmol) were added into the solution. The solution was bubbled with CO<sub>2</sub> for 30 min and was irradiated with blue LEDs ( $\lambda$  = 450 nm) for 2.0 h at room temperature.

<sup>a</sup>Atomic layers of CdS on CdSe QDs core, which was calculated on the amounts of Cd and S precursors consumed.

 $^{\rm b}{\rm Generation}$  rates of CO and  ${\rm H}_2$  were determined by GC with CH\_4 as internal standard.

 $^{\rm c}$ Selectivity of CO was calculated according to equation of n(CO)/[n(CO) + n(H2)]  $\times$  100%.

<sup>d</sup>The produced pinacol was determined using <sup>1</sup>H NMR analysis with diphenyl carbinol as an internal standard. The yield was calculated using the equation of 2n(pinacol) /n(1-phenylethanol)<sub>Consumed</sub> × 100%, d.r. value was determined by <sup>1</sup>H NMR analysis of the unpurified reaction mixture to be 1.5:1.

<sup>e</sup>The ratio of electrons and holes consumed in redox reactions was calculated by following equation:  $e^{-h^+} = [2 \times n(H2) + 2 \times n(CO)]/[2 \times n(acetophenone) + 2 \times n(pinacol)].$ 

<sup>f</sup>The system was irradiated under AM1.5 for 4.0 h.

 $^{g}$ Yield of pinacol after 10.0 h irradiation, d.r.=1.3:1.

<sup>h</sup>Yield of pinacol after 10.0 h irradiation, d.r.=1.2:1.

yield of ~74%. Control experiments implied that, in the absence of visible light, 1-phenylethanol, or  $CO_2$ , the reaction would not proceed at all (Figure S8). Under the optimal conditions, the conversion could also occur smoothly to evolve CO and pinacol simultaneously under the irradiation of AM1.5, indicating its potential application in solar energy conversion. In addition, the tendency of AQY of pinacol generation matched well with the UV-vis absorption spectrum of CdSe/CdS QDs (Figure S9), confirming that QDs worked as the active photocatalysts of this conversion. It should also be noted that the ratio of consumed excited electrons and holes were quite close to 1.0, indicating the good balance between redox reactions.

To obtain direct evidences on the reaction, the concentration-time curves of reactant and products were monitored every 15 min by gas chromatography with FID detector (SHIMADZU, GC-2010plus) and <sup>1</sup>H NMR. As shown in Figure S10, the concentration of 1-phenylethanol gradually decreased while the C-C coupling product of pinacol apparently increased. Notably, acetophenone always kept at an extremely low concentration compared with that of pinacol during the whole process of light irradiation. Meanwhile, the evolved amount of oxidative product (pinacol) well matched with that of reductive product (CO), indicating that acetophenone was only a by-product in our system. In addition, the generation of CO was inhibited when small amount of ketone was added to reaction system (Figure S11), further indicating that the produced acetophenone was not intermediate but a by-product.

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The detailed reaction mechanism will be discussed below. Further investigation indicated that the introduction of electron-donating groups on aryl ring significantly enhanced the yields of corresponding pinacols. For example, 1-phenylethanol with methoxyl group (-OCH<sub>3</sub>) at the *p*-position could give an exceptional yield of pinacol production (>98%). On the contrary, the electron-withdrawing group (for example, -NO<sub>2</sub>) significantly declined the yield (see details in Table 1 and corresponding characterizations in Figures S12–S15).

#### DISCUSSION

#### Mechanisms of Photocatalytic CO<sub>2</sub> Reduction and C-C Coupling

According to our previous results,  $^{43}$  the conduction bands (E<sub>CB</sub>) of CdSe QDs and CdSe/CdS QDs are about -1.60 and -1.40 V versus normal hydrogen electrode (NHE), the reduction of free CO<sub>2</sub> to the one-electron reduction intermediates of anion radical is thermodynamically unfavorable for the extremely negative reduction potential (CO<sub>2</sub> +  $e^- \rightarrow CO_2^{-}$ ,  $E^0_{Redox} = -1.90$  V versus NHE).<sup>44</sup> The adsorption and activation of CO<sub>2</sub> molecules on QD surface would be the first step of the whole process. Spectroscopic results provided evidences on the binding of CO<sub>2</sub> molecules on QD surface. The emission intensity of CdSe QDs in solution significantly enhanced while the UV-vis adsorption spectrum showed negligible change under CO<sub>2</sub> atmosphere (Figures 2A and S16). The enhanced emission was due to the adsorption of CO<sub>2</sub> on QD surface, thus inhibiting the annihilation of excited electron-hole pairs at trap states. In order to confirm this point, density functional theory (DFT) calculations were carried out on the (111) facet of CdSe, see details in Experimental Procedures. It revealed that the perfect (111) facet of CdSe was not beneficial for  $CO_2$ adsorption, while CO<sub>2</sub> was energetically favorable to adsorb at the Se-vacancy on CdSe surface (Figure 2B). This result matched well with the enhanced emission intensity of QDs in the presence of CO2. Adsorption configuration of CO2 on CdSe surface was optimized without any symmetry constraint. CO2 molecule adsorbed at the Se-vacancy via the Cd-O and Cd-C interaction with an adsorption energy of -0.96 eV. The adsorbed CO<sub>2</sub> was greatly distorted from linear to bended configuration with an O1-C-O2 bond angle of 118°. Besides, both C-O1 and C-O2 bonds were stretched from 1.171 to 1.248 and 1.312 Å, respectively. The reduced O1-C-O2 angle and elongated C-O bonds indicated that the adsorbed CO2 was highly activated. We also investigated the adsorption and activation of  $CO_2$ on CdS shell. As shown in Figure S17, sulfur vacancy of CdS shell played a very similar role in CO<sub>2</sub> activation to enable the bended molecular configuration and the elongated C-O bonds.

X-ray photoelectron spectroscopy (XPS) surface analysis revealed that the stoichiometry ratio of surface Cd to Se was ~3.6, indicating the Cd-rich surface of CdSe QDs used here (Figure S18; Table S2). To directly confirm the presence of Sevacancy, the powder electron paramagnetic resonance (EPR) was performed. As shown in Figure S19, the EPR signal centered at g = 2.0040 well matched with the reported singly charged anion vacancies of semiconductor QDs.<sup>45</sup> As it is challenging to directly measure the exact reductive potential of the absorbed CO<sub>2</sub> species at anion vacancy, CdSe QDs with different sizes were used for photocatalysis to gain indirect thermodynamic evidences on CO<sub>2</sub> reduction (Figure 2C). Under visible light, the activity of CO<sub>2</sub>-to-CO conversion decreased with increasing the size of CdSe QDs from 2.0 to 4.5 nm, which was a result of the declined E<sub>CB</sub> potential of CdSe QDs from -1.60 to -1.05 V versus NHE.<sup>46</sup> When the size of QDs was larger than 2.8 nm, trace amount of CO was produced. Thus, the reductive potential of the adsorbed CO<sub>2</sub> species was estimated to be ca. -1.33 V versus NHE, which

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#### Figure 2. Insights into QDs Photocatalyzed CO<sub>2</sub> Reduction

(A) Photoluminescent emission of CdSe QDs solution before and after bubbling with  $CO_2$  gas for 20 min.

(B) The interaction between CO<sub>2</sub> molecules and CdSe (111) facet with and without Se-vacancy (the orange, yellow, gray, and red balls represent Cd, Se, C, and O atoms, respectively).

(C) The variation of band-position alignment (upper panel) and activity of CO<sub>2</sub> photoreduction (nether panel) of CdSe with different diameter.

(D) Full potential energy for the adsorption and dissociation of  $CO_2$  via proton-coupled electron transfer to generate CO on cubic CdSe or CdS (111) facet (gray, red, white, buff, and yellow atoms represent C, O, H, Cd and Se (S) atoms, respectively).

The error bars represent the relative deviation of three independent experiments.

was more positive than  $E_{CB}$  of CdSe and CdSe/CdS QDs used here, thereby indicating the feasibility of photo-driven CO<sub>2</sub> reduction on QD surface.

The elementary steps of CO<sub>2</sub> reduction on QD surface were further revealed by DFT calculations. As shown in Figure 2D, CO2 could be converted to CO through the following steps: (1) firstly, the adsorbed CO2\* molecules on surface generate COOH\* intermediates through a proton-coupled electron transfer process; (2) secondly, the COOH\* intermediate was further reduced and dissociated to produce OH\* and CO\* intermediates, and (3) finally, OH\* combined with a proton to produce  $H_2O$  and CO<sup>\*</sup> detached from the surface to generate the product of CO. During this process, the adsorption energy of COOH\* was -2.4 eV, which made it highly difficult to detach from QD surface. This was the reason why no HCOOH was detected in our system. Desorption of CO\* was endothermic by 0.625 eV with a barrier of 1.389 eV. However, the adsorption energy of CO was only -0.46 eV, the smallest among CO<sub>2</sub>, COOH, and CO. Therefore, CO was the sole carbon-based product here. We found that the second step of COOH\* protonation needed to overcome an energy barrier of 2.425 eV, which was regarded as the rate-determining step of the whole process. Interestingly, the reaction showed much lower energy barriers of CO<sub>2</sub> adsorption and COOH\* reduction (0.097 and 1.773 eV) on CdS than those obtained on CdSe

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#### Figure 3. Mechanisms of Photo-Induced Oxidative Coupling of 1-Phenylethanol to Pinacol

(A) Comparison of bond cleavage energy of  $C_{\alpha}$ -H,  $C_{\beta}$ -H and O-H bonds of 1-phenylethanol.

(B) EPR spectrum of argon (Ar) saturated acetonitrile solution of DMPO and CdSe/CdS QDs (1) with and (2) without the addition of 1-phenylethanol upon 10 s visible-light irradiation ( $\lambda$  = 450 nm).

(C) Full potential energy for 1-phenylethanol deprotonation on CdSe and CdS (111) facet with Se/S-vacancy by DFT calculations, respectively.

(0.470 and 2.425 eV). Furthermore, light response and charge separation efficiencies of CdSe QDs could also be significantly enhanced by introducing a certain amount of CdS shell to form the quasi type-II structure (Figures S20 and S21). Based on the aforementioned advantages, the process of CO<sub>2</sub> photoreduction on CdSe/CdS QDs was thermodynamically and kinetically promoted.

The selective oxidative coupling of 1-phenylethanol to produce pinacol was also investigated. DFT calculations were firstly performed to explore the bond cleavage energy of  $C_{\alpha}$ -H,  $C_{\beta}$ -H, and O-H bonds to the corresponding radicals. Compared with  $C_{\beta}$ -H and O-H bonds, the  $C_{\alpha}$ -H bond showed the lowest bond cleavage energy ( $\sim$ 58 kcal mol<sup>-1</sup>) to give corresponding carbon-centered radical (Figure 3A), indicating the better feasibility of  $C_{\alpha}$ -H bond break under the same conditions. DFT results also indicated that 1-phenylethanol vertically adsorbed atop the anion vacancies of CdSe or CdS via the substituent group while aryl ring was far away from the surface (see details in Figure S22). Moreover, it is reported that the oxidation potential of  $C_{\alpha}-H$  bond was about +1.10 V versus NHE,  $^{47}$  which was more negative than the valence band ( $E_{VB}$ ) position of CdSe/CdS QDs (+1.15 V versus NHE). Thus, the photogenerated holes could sufficiently oxidize  $C_{\alpha}$ -H bond to produce carbon radical. Control experiments indicated that the addition of a small amount of radical scavenger 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) into the reaction system would inhibit the production of neither CO nor pinacol, indicating the reaction proceeded via radical intermediates. Thereafter, in situ EPR studies using 5,5dimethyl-1-pyrroline N-oxide (DMPO) as radical scavenger revealed the formation of C radical in the absence of CO<sub>2</sub> as the coupling constants ( $a_N = 14.9$ ,  $a_H = 22.1$ ) of the signal (Figure 3B) were consistent with reported values of C radical,<sup>28</sup> and the molecular weight equaled to the adduct of DMPO and  $C_{\alpha}$  radical (Figure S23).

Based on the above results, a tentative reaction mechanism of the oxidative half-reaction was proposed. The excited QDs were reductively quenched by the surface bound 1-phenylethanols, thereby producing carbon-centered radicals, which coupled to produce corresponding pinacols on the surface of QDs. As pinacol presented much lower binding strength on QDs than those of 1-phenylethanol and intermediates (see details in Table S3), the produced pinacol molecules were released

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into the solvent and then additional 1-phenylethanols from the solution bound to the active sites to complete the reaction cycle. The mechanism of surface reaction presented here is quite different from our previous report of oxidizing alcohols to carbonyl compounds in solution through a radical relay process.<sup>48</sup> Notably, the energy barrier of  $C_{\alpha}$ -H cleavage at S-vacancy of CdS (2.268 eV) was much lower than that at Se-vacancy of CdSe (3.470 eV) (Figure 3C). This might be one of the reasons for the significantly enhanced selectivity of pinacol production after introducing suitable thickness of CdS shell on CdSe QDs. The introduction of CdS shell simultaneously promoted CO<sub>2</sub> reduction and  $C_{\alpha}$ -H activation. As a result, the selectivity of CO evolution and the yield of pinacol production coupled with organic transformation was provided in Figure S24.

### **EXPERIMENTAL PROCEDURES**

### Solar-Light-Driven CO<sub>2</sub> Reduction with Sacrificial Reagents<sup>49</sup>

First of all, 1.0 mL synthesized QDs solution was precipitated by adding excessive amount of isopropanol. Subsequently, it was re-dispersed in 5.0 mL DMF, resulting QDs DMF solution (c =  $1.1 \times 10^{-5}$  mol/L). Then, 1.0 mL TEA was added to 5 mL QDs DMF solution. The solution was degassed by bubbling CO<sub>2</sub> for 30 min to ensure the dissolution of enough CO<sub>2</sub> and 600 µL ultrapure CH<sub>4</sub> was injected into the system to work as the internal standard for quantitative GC analysis. Finally, the system was irradiated under 450 nm LEDs (130 mW cm<sup>-2</sup>) at room temperature.

### Solar-Light-Driven CO<sub>2</sub> Reduction Integrated with Pinacol Synthesis<sup>50</sup>

First of all, 1.0 mL synthesized QDs solution was precipitated by adding excessive amount of isopropanol. Subsequently, it was re-dispersed in 5.0 mL DMF, resulting QDs DMF solution (c =  $1.1 \times 10^{-5}$  mol/L). Then, 60 µL (0.5 mmol) 1-phenylethanol was added to 5 mL QDs DMF solution. 53 mg (0.5 mmol) Na<sub>2</sub>CO<sub>3</sub> was employed as the basic additive. The solution was degassed by bubbling CO<sub>2</sub> for 30 min to ensure the dissolution of enough CO<sub>2</sub> and 600 µL ultrapure CH<sub>4</sub> was injected into the system to work as the internal standard for quantitative GC analysis. Finally, the system was irradiated under 450 nm LEDs (130 mW cm<sup>-2</sup>) at room temperature.

#### **Quantification of Gas and Liquid Products**

The generated gas in the reaction headspace for photocatalytic experiments were quantified by a gas chromatograph (GC, *Shimadzu GC2014CAFC/APC*) equipped with a thermal conductivity detector and a 5 Å molecular sieves GC column, argon as a carrier gas. GC analysis revealed the production of CO and H<sub>2</sub>. Thus, CH<sub>4</sub> was chosen as the internal standard for quantitative GC analysis. Under the experimental condition, the response factors of CO/CH<sub>4</sub> and H<sub>2</sub>/CH<sub>4</sub> for GC analysis were about 0.39 and 4.08, respectively, which were established by calibration with known amounts of CO, H<sub>2</sub> and CH<sub>4</sub>, and determined before and after measurements. On the other hand, the produced liquid products were monitored by <sup>1</sup>H NMR, <sup>13</sup>C NMR analysis (*Avance-400*) and liquid chromatograph-mass spectra (LC-MS, *Q-Exactive*), revealing the major generation of pinacol. For further quantification analysis, 0.1 mmol benzhydrol was added into CDCl<sub>3</sub> solution as the internal standard. Error bars on CO, H<sub>2</sub>, and pinacol were calculated from at least three independent experiments.

### **DFT Calculations**

Taking CdSe (111) facet as an example, the first-principles calculations were performed by the pseudopotential<sup>51</sup> methods implemented in the package<sup>52</sup> based

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on the DFT. A 400 eV plane wave basis set the cutoff, and the cutoff energy was used throughout our calculations. The convergence thresholds between optimization cycles for energy change and maximum force were set as 5.0 imes10<sup>-6</sup> eV/atom and 0.03 eV/Å, respectively. The Monkhorst-Pack grids<sup>53</sup> of  $2 \times 2 \times 1$  k-points were used for the (111) surface of cubic CdSe. Based on the optimized reactant and product structures, the transition state (TS) searches were performed using complete LST-QST methods<sup>54</sup> so as to determine accurate activation barriers of the reaction. In the work, we constructed stoichiometric slabs of 12.96 Å  $\times$  12.96 Å  $\times$  11.46 Å (eight atomic layers) with a vacuum thickness of 15 Å to model the (111) surface of CdSe. In all calculations, the atoms in the bottom layers were fixed, but the atoms in the two topmost layers, as well as C, O, and H atoms, were allowed to relax. The geometry structure of the isolated CO<sub>2</sub> molecule was optimized using a supercell of 15 Å  $\times$  15 Å  $\times$  15 Å. The calculated C-O bond length and bond angle (O-C-O) were 1.171 Å and 180.0°, which were in good agreement with the experimental values.<sup>55</sup> After optimization, the electron density of states (DOS) and Mulliken charge analysis<sup>56</sup> were performed.

Taking  $CO_2$  as an example, the adsorption energy was defined as:

$$Eads = E_{(CO_2 + slab)} - [E_{CO_2} + E_{slab}],$$

where the first term is the total energy of the slab with the adsorbed  $CO_2$  molecule on the surface, the second term is the total energy of isolated  $CO_2$  molecule, and the third term is the total energy of the bare slab of the surface (perfect or Se-vacancy slab). For CO, the similar calculated method is used. According to the above definitions, a negative  $E_{ads}$  value corresponds to an exothermic adsorption, and the more negative the  $E_{ads}$ , the stronger the adsorption.

### SUPPLEMENTAL INFORMATION

Supplemental Information can be found online at https://doi.org/10.1016/j.chempr. 2019.06.019.

### ACKNOWLEDGMENTS

We are grateful for financial support from the Ministry of Science and Technology of China (2017YFA0206903), the National Science Foundation of China (21861132004 and 21603248), the Strategic Priority Research Program of the Chinese Academy of Science (XDB17000000), Key Research Program of Frontier Science of the Chinese Academy of Sciences (QYZDY-SSW-JSC029), the Youth Innovation Promotion Association of Chinese Academy of Sciences (2018031), and K.C. Wong Education Foundation, China. We specially thank Prof. Qing Zhang at Dalian Institute of Chemical Physics (CAS) for GC-MS measurements.

### **AUTHOR CONTRIBUTIONS**

X.-B.L. and L.-Z.W. conceived and designed the research and wrote the manuscript. Q.G. carried out all experiments and analyzed the data. C.-H.T. helped to analyze data and write the paper. F.L. performed the DFT calculations under the supervision of Z.-S.L., and Y.-J.G., M.-Y.H., Y.W., S.-G.X., X.-Y.G., and Q.-C.G. helped to synthesize semiconductor QDs and perform some of the photocatalytic experiments.

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### **DECLARATION OF INTERESTS**

L.-Z.W., X.-B.L., Y.-J.G., M.-Y.H., and Z.-J.L. have a patent: CN. Pat, 201510083816.X. L.-Z.W., Q.G., X.-B.L., and S.-G.X. have a patent: CN. Pat, 201910383837.1.

Received: March 15, 2019 Revised: April 6, 2019 Accepted: June 24, 2019 Published: July 23, 2019

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