

## Preview

# Solar-Powered Artificial Photosynthesis Coupled with Organic Synthesis

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**The introduction of sacrificial agents in artificial photosynthesis greatly boosts the charge separation, resulting in high activity. However, this causes environmental and economic issues. In this issue of *Chem*, Wu, Li, and co-workers have demonstrated a selective photocatalytic CO<sub>2</sub> reduction coupled with oxidative organic synthesis by semiconductor quantum dots (QDs).**

The rapid consumption of fossil fuels poses a great challenge toward energy shortage and drastic climate change.<sup>1</sup> Solar energy, as a clean and sustainable alternative, provides abundant renewable energy source. The solar-driven CO<sub>2</sub> reduction to fuel by mimicking green plants is a promising strategy to harvest this inexhaustible energy resource and maintain the natural carbon balance. Unfortunately, the artificial photosynthesis composed of CO<sub>2</sub> reduction and water oxidation is far from achieving a practical level because of its kinetically sluggish O<sub>2</sub>-evolving half reaction.<sup>2</sup> Moreover, the evolution of O<sub>2</sub> gives low economic value, and it is possible to produce explosive mixtures with the generated gaseous reduction products (for example, CO and CH<sub>4</sub>). To achieve efficient CO<sub>2</sub> photo-reduction, researchers usually adopt different reductants (such as sodium sulfite, triethanolamine, triethylamine, etc.) as sacrificial agents. However, this definitely goes against the original intention for its environmentally unfriendly feature, economic unfeasibility, and waste of oxidizing power.

To make the best of solar energy and achieve maximum output, several reports have already offered accessible references. By replacing the water

oxidation with value-added organic transformation, it opens a new horizon to overcome the drawbacks of water oxidation and, meanwhile, provides additional economic value from the products. In recent reports, different organic oxidative transformations, including methanol, thiol, and benzylamine oxidative coupling, benzene C–H amination and hydroxylation, as well as furfural alcohol selective oxidation, have been employed to be integrated with photocatalytic H<sub>2</sub> generation.<sup>3–6</sup> The generated reduction product (H<sub>2</sub>) and organic products, as different phases, are naturally separated, avoiding the formation of explosive mixture and additional cost for separation. However, it remains blank to integrate CO<sub>2</sub> photoreduction with organic oxidative transformation driven by solar energy, featuring high activity and selectivity for overall reactions.

In this issue of *Chem*, Wu, Li, and co-workers have reported the first example of solar-driven CO<sub>2</sub> photoreduction together with value-added oxidative synthesis of pinacol from 1-phenylethanol (Figure 1A).<sup>7</sup> The catalysts adopted are CdSe QDs (~2.0 nm) covered with different shell thicknesses of CdS, in a core-shell nanostructure, rationally fabricated by the approach of a successive ion layer adsorption and reaction

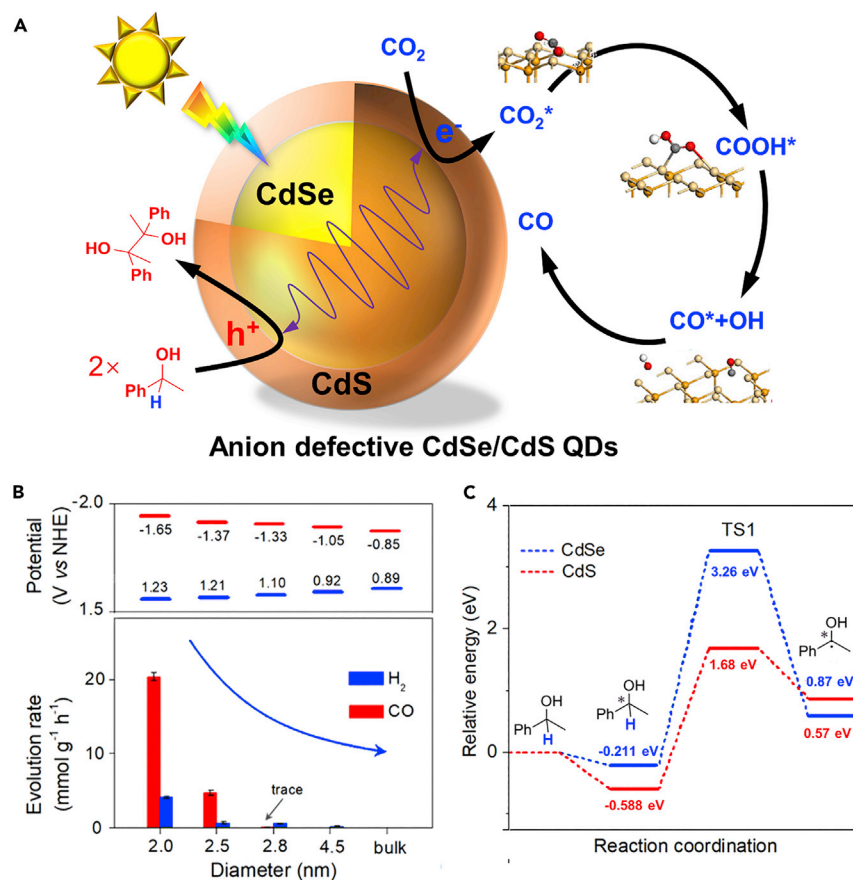
(SILAR) in aqueous solution. According to the X-ray photoelectron spectroscopy (XPS) and electron paramagnetic resonance (EPR) data, the surface of these catalysts is proved to be anion defective, which provides sufficient trapping sites for favorable CO<sub>2</sub> adsorption and activation.<sup>8</sup> The CdSe QDs coated with three layered CdS shells achieve excellent photocatalytic CO<sub>2</sub> reduction to CO in the present of sacrificial agent (trimethylamine), reaching 412.8 mmol·g<sup>-1</sup>·h<sup>-1</sup> (apparent quantum yield of 32.7% at 450 nm) with a selectivity of >96% for at least 6 runs. Even under the simulated solar light (AM1.5), the catalytic system can give a sound CO production rate of 63.1 mmol·g<sup>-1</sup>·h<sup>-1</sup> (CO selectivity: >97%). This superb activity gives strong hint that, the replacement of sacrificial reagent consumption with organic oxidative transformation would be meaningful and feasible, though organic substrates generally present inferior electron-donating ability to the common sacrificial agents.

Pinacol, being recognized as important structural motifs in natural products and pharmaceutical intermediates, can be synthesized by dimerization of aldehydes and/or ketones with the assistance of co-reductants or alcohol coupling under light irradiation.<sup>9,10</sup> With that consideration, the authors replace the consumption of sacrificial agents with pinacol synthesis, affording an activity of CO<sub>2</sub> photoreduction up to 27.63 mmol·g<sup>-1</sup>·h<sup>-1</sup> (CO selectivity: ~94%) and pinacol production rate of

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**Figure 1. Schematic Illustration Showing Photocatalytic  $CO_2$  Reduction Coupled with Organic Synthesis**

(A) Solar-driven photocatalytic  $CO_2$  reduction integrated with 1-phenylethanol oxidative coupling to pinacol by semiconductor QDs.

(B) The size-dependent variation of the band position (top) and related  $CO_2$  photoreduction activities (bottom) of CdSe QDs in different diameters.

(C) The energy diagrams by DFT calculations for pinacol synthesis on CdSe or CdS (111) facet with Se- or S-vacancy, respectively.<sup>7</sup>

$26.5 \text{ mmol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$  with a yield of 74%. The calculated ratio of the consumed photogenerated electrons and holes are very close to 1.0, reflecting the ideal balance between the redox reactions. Control experiments unambiguously show that visible light, 1-phenylethanol and  $CO_2$  are all indispensable to efficiently complete the overall conversion. Decoration of the catalytic substrate on aryl ring with electron-donating groups (such as  $-CH_3$  and  $-OCH_3$ ) results in enhanced yields of >92% to the corresponding pinacols. Strikingly, this integrated system proceeds smoothly to simultaneously produce  $CO$  and pinacol under the simu-

lated solar light (AM1.5) irradiation, indicating the potential for practical application.

The detailed mechanism on the integrated photocatalytic  $CO_2$  reduction and oxidative C–C coupling has been meticulously explored by multiple tools. The enhanced charge separation and promoted  $CO_2$  photoreduction on CdSe–CdS QDs can be mainly ascribed to (1) the formation of quasi type-II structure by introducing some CdS shells, (2) the optimized size of the QDs gives proper band-position alignment for  $CO_2$  reduction (Figure 1B), and (3) the surface anion vacancy can

serve as energetically favorable trapping sites for  $CO_2$  adsorption and activation. Particularly, the energy barriers, required for  $CO_2$  adsorption and  $COOH^*$  protonation (rate-determining step), are apparently lower on CdS surface than those on CdSe on the basis of the DFT calculation, demonstrating the necessity of CdS shell. Not limited to the reductive reaction, the S-vacancy of CdS surface possesses greatly lower energy barrier for the  $C_{\alpha}$ -H cleavage than Se-vacancy of CdSe, which is believed to be responsible for the much-enhanced selectivity of pinacol production after CdS shell introduction (Figure 1C).

In conclusion, in this issue of *Chem*, the authors provide an elegant example of efficient photocatalytic  $CO_2$  reduction integrated with pinacol synthesis, simultaneously producing solar fuels and value-added chemicals, over semiconductor QDs, even by solar light. With this encouraging work, more efforts and progress are highly expected on the artificial photosynthesis with the full use of photogenerated electrons and holes in near future.

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## Preview

# Placing Functionality Where You Want: The Allure of Sequence Control

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**In this issue of *Chem*, Xia and coworkers employ user-friendly ring-opening metathesis polymerization (ROMP) and cyclopropene monomers (CPEs) to achieve multiple single additions of CPEs along a polymer backbone. This simple yet powerful strategy greatly expands the scope of sequence-controlled materials and allows key questions to be addressed.**

The synthesis of sequence-controlled and sequence-defined macromolecules is an emerging challenge in polymer science. Driven by the desire to have a degree of structural control that is traditionally found only with proteins and other biological systems, the promise of sequence-controlled macromolecules has drawn considerable attention.<sup>1</sup> Coupled with the structural control over the position of multiple repeat units along a polymer chain is the potential for accessing unique properties and applications, again typically only found in biomaterials. As a result, the development of procedures for preparing sequence-controlled and sequence-defined macromolecules from readily available monomers would enable new directions in fields ranging from polymer physics to mate-

rials science and nanotechnology.<sup>2</sup> During the last decade, significant effort has focused attention on key issues such as the importance of precise sequence control versus sequence dispersity, scalability of user-friendly procedures, and the overarching question for this emerging field—what benefits and new properties emerge from sequence control in synthetic systems.<sup>3</sup>

To illustrate recent synthetic advances toward scalable, sequence-defined materials, several approaches involving termination with a specific, non-propagating monomer and then transformation of this chain end back to an active, propagating unit have been examined. For example, allyl alcohol was used as a chain-end capping agent during

atom-transfer radical polymerization (ATRP), followed by oxidation and esterification to “reactivate” the chain end.<sup>4</sup> In a similar fashion, an addition-cleavage-regeneration cycle can be realized through dynamic bonds by connecting a radical-generating site with an alkene chain end as described by Sawamoto and coworkers.<sup>5</sup> While successful for controlling a limited number of monomer insertions, multiple purification steps are necessary, decreasing the applicability of these strategies for high-molecular-weight polymers and true single-monomer insertions.

Increased sequence regulation with near-single-monomer precision can be attained using specific comonomer pairs that copolymerize in an alternating manner. In these systems, cross-propagation is favored over homo-propagation with electron-rich monomers (e.g., styrene or indene) and electron-poor monomers (e.g., maleimide) copolymerizing to give an AB-repeating sequence. By exploiting living polymerizations and multiple monomer additions, Lutz and coworkers have shown that controlled

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