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 CO2 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.1 Solar energy, as a clean and sustainable alternative, provides abundant renewable energy source. The solar-driven CO2 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 CO2 reduction and water oxidation is far from achieving a practical level because of its kinetically sluggish O2-evolving half reaction.2 Moreover, the evolution of O2 gives low economic value, and it is possible to produce explosive mixtures with the generated gaseous reduction products (for example, CO and CH4). To achieve efficient CO2 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 H2 generation.3–6 The generated reduction product (H2) 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 CO2 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 CO2 photoreduction together with value-added oxidative synthesis of pinacol from 1-phenylethanol (Figure 1A).7 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 CO2 adsorption and activation.8 The CdSe QDs coated with three layered CdS shells achieve excellent photocatalytic CO2 reduction to CO in the present of sacrificial agent (trimethylamine), reaching 412.8 mmol·g⁻¹·h⁻¹ (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⁻¹·h⁻¹ (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.9,10 With that consideration, the authors replace the consumption of sacrificial agents with pinacol synthesis, affording an activity of CO2 photoreduction up to 27.63 mmol·g⁻¹·h⁻¹ (CO selectivity: ~94%) and pinacol production rate of 2.0 nm).

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26.5 mmol·g⁻¹·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 CO₂ are all indispensable to efficiently complete the overall conversion. Decoration of the catalytic substrate on aryl ring with electron-donating groups (such as CH₃ and OCH₃) results in enhanced yields of >92% to the corresponding pinacols. Strikingly, this integrated system proceeds smoothly to simultaneously produce CO and pinacol under the simulated solar light (AM1.5) irradiation, indicating the potential for practical application.

The detailed mechanism on the integrated photocatalytic CO₂ reduction and oxidative C–C coupling has been meticulously explored by multiple tools. The enhanced charge separation and promoted CO₂ 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 CO₂ reduction (Figure 1B), and (3) the surface anion vacancy can serve as energetically favorable trapping sites for CO₂ adsorption and activation. Particularly, the energy barriers, required for CO₂ 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 C₆H₆ 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).
achieve multiple single additions of CPEs along a polymer backbone. This simple metathesis polymerization (ROMP) and cyclopropene monomers (CPEs) to attention. Coupled with the structural molecules has drawn considerable promise of sequence-controlled macromolecules and other biological systems, the that is traditionally found only with pro-...