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Si Nanowires as Photoelectrodes for Carbon Dioxide Fixation

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Natural photosynthesis harvests the energy in solar light to power chemical reactions and uses CO₂ as the carbon source. Because light as an energy source is free and abundant, chemical reactions similar to photosynthesis have major fundamental and practical implications.^[1–2] Indeed, significant efforts have been attracted to this research goal. The majority of attention for photochemical reactions that transform CO₂ have focused primarily on conversion into *fuels*.^[3–4] How to learn from photosynthesis and devise reaction routes for the synthesis of useful organic compounds receives relatively underwhelmed considerations.^[5] Drawing inspiration from the mechanisms found in dark reactions of photosynthesis and using p-type Si nanowires as a photocathode, here we show that highly specific reactions can be readily carried out to produce α -hydroxy acids by photoreduction of aromatic ketones, followed by CO₂ fixation. Powered by solar light, this reaction is in close resemblance to natural photosynthesis, and different from its electrochemical analogues. The carboxylation products of two of the substrates examined in this communication serve as precursors to nonsteroidal anti inflammatory drugs (NSAID), ibuprofen and naproxen.^[6]

In nature, photosynthesis is carried out in two distinct stages: light and dark reactions. During the light promoted stage, the energy in photons is harvested and stored in chemicals such as NADPH (nicotinamide adenine dinucleotide phosphate) and ATP (adenosine-5'-triphosphate) are subsequently used to sequester carbon dioxide for the synthesis of complex sugar monomers. At the heart of the Calvin cycle (dark reactions) is the conversion of ribulose-1,5-bis-phosphate (RuBP) into an intermediate β -keto-acid (Scheme 1), which ultimately fragments to 3-phosphoglycerate (3PG), the core building block for sugars.^[7] By not directly reducing CO₂, this process avoids producing C in a variety of oxidation states and gains a critical advantage of high selectivity.^[8] This chemistry inspires us to propose a strategy to perform carboxylation reactions using light as a direct energy source and CO₂ as a carbon source. As shown in Schemes 1 and 2, our reaction route is in close resemblance to natural photosynthesis but different from existing approaches that seek to directly photoreduce CO₂. It solves a critical challenge of poor selectivity inherent to the direct photoreduction of CO₂ due to the nature of the multielectron transfer processes. Our strategy has the potential to meet the selectivity requirement necessary for more complex synthetic targets than fuels, opening up doors to a wide range of light-powered chemical reactions^[9–12] that have not been previously studied.

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Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.

We used Si nanowires (SiNWs) as the light-harvesting electrode because they have been shown to be efficient in converting solar energy into electrical forms, easy to make, and remarkably stable under reductive conditions.^[13-17] To examine their suitability for organic synthesis, we first conducted a reaction that has been previously performed electrochemically, the formation of benzoic acid through CO₂ fixation by benzophenone.^[18-19] The key difference of the result reported here is that light serves as an important source of energy input. Our goal for this initial set of experiments was to determine whether the energy levels of Si are aligned for reduction of benzophenone to the radical anion, the key step in the carboxylation reaction. We would then apply this knowledge to the CO₂ photofixation with ketone-based substrates. Information important to our considerations includes the electrochemical potential of the solution (determined by the Tafel technique in dark as -0.12 V; all potentials were relative to Ag/AgI/T⁻ reference, which was 0.60 V more positive than SCE, saturated calomel electrode) and the Fermi level of Si (measured by the Mott-Schottky plot as 0.74 V, see supporting information). From this information and the known doping levels of Si (10¹⁵ cm⁻³ B-doped; ρ : 10-20 ω -cm), we constructed the energetics of the benzophenone system as shown in Figure 1. Under equilibrium conditions, a large degree of band bending (0.86 V in magnitude) on the surface creates a substantial depletion layer where photogenerated charges can be separated with high efficiencies when illuminated. This understanding was indeed consistent with the photoelectrochemical (PEC) measurements (Figure 2). Both p-type and n-type SiNWs with different doping levels were investigated, and moderately doped p-type SiNWs were found to be the most suitable photocathodes (see supporting information).

Several additional characteristics of the PEC data are noteworthy. First, in the absence of light, no photocurrent was detected for applied potentials up to -2.4 V, nor did we obtain any carboxylation products (Figure 2a). In contrast, when illuminated, a high saturation current density is measured at relatively low negative applied potentials (31.1 mA/cm² at -1.20 V, Figure 2). These results support that the reaction as shown in Schemes 1 & 2 is indeed powered by light. Control experiments where SiNWs were replaced by Pt only measured 2.00 mA/cm² under identical applied potential and illumination conditions. The current level also approaches what is theoretically possible by Si (43.0 mA/cm²) under the same lighting conditions,^[20-21] further highlighting the feasibility of using the system for high-efficiency PEC operations. Important to this discussion, the saturation current density scales with illumination intensity in a linear fashion, supporting that the charge separation mechanism agrees with that proposed in Figure 1, and that charge collection is effective. Third, the sharp turn-on of the photocurrent density (a slope of 70.1 mA cm⁻² V⁻¹ was measured in the linear region between -1.00 and -1.20 V) was comparable to that measured on Si in the more extensively studied CoCp₂/CoCp₂⁺ system,^[22] where charge transfer resistance from Si to the electrolyte is known to be low, as well as that of Pt (a slope of 72.0 mA cm⁻² V⁻¹ between -1.15 and -1.50 V). The comparison indicates illuminated Si is a suitable candidate for aromatic ketone reduction. Indeed, under typical operation conditions (-1.20 V, 100 mW/cm² AM 1.5 illumination), benzophenone is carboxylated at a faradic efficiency of 94% and in >98% isolated yield of the α -hydroxy acid product (Figure 2c). We note that in order to avoid direct reduction of CO₂, which would alter the proposed reaction mechanism and produce undesired by-products, it is important to limit the operating potentials at or above -1.2 V. Additional control experiments also suggest that the reaction proceeds by a 2-step single-electron transfer process (supporting information).^[23-24] Dimerization of the starting material as well as reduction to the secondary alcohol is often observed in electrochemical coupling of ketones with carbon dioxide but is absent in our experiments as confirmed by analysis of the crude photoelectrochemical reaction mixture by ¹H NMR. This result is consistent with the high isolated yield.^[25] Lastly, we note that as the anode, Al is oxidized to produce Al³⁺ (Scheme 2) and dissolved in the reaction medium.^[24]

Further analysis of the benzophenone carboxylation reaction showed that SiNWs exhibit a less negative turn-on (-0.52 V at >1 mA/cm²) than planar Si (-0.63 V) but lower saturation current density (32.1 mA/cm² vs. 34.4 mA/cm², Figure 2a). It has been reported that the high surface area of nanostructures such as SiNWs may result in increased charge recombination at the semiconductor/solution interface, leading to reduced saturation current densities without considering light trapping mechanisms.^[16, 26-27] However, the recombination mechanism would also predict reduced open-circuit potentials, implying a more negative turn-on voltage should be measured on SiNWs than on planar Si. To account for the apparent discrepancies, we suggest that the observed trend is indicative of improved charge transfer kinetics on SiNWs. That is, the multifaceted nature of SiNWs favors charge transfer from Si to benzophenone, resulting in lower overpotentials. Our hypothesis is supported by control experiments where the turn-on voltages were compared with the length of SiNWs (L varying between 0 and 10 μ m). Within a limited range ($0 < L \leq 6$ μ m), the turn-on voltage changes with the surface roughening factor monotonically; the recombination-induced open-circuit reduction dominates for longer SiNWs ($L > 6$ μ m), and more negative turn-on voltages were measured (supporting information). Similar effect has been observed on SiNWs-based water splitting reactions previously,^[28-29] although more details about the reasons remain unclear to the best of our knowledge.

For practical applications, the stability of the photoelectrodes against photo corrosion and other mechanisms that may degrade their performance such as oxidation is an important concern. For the reported process, the SiNWs are operating under reductive conditions, so we considered oxidation of SiNWs less likely and instead focused our attention on assessing the stability. Recycling of the photoelectrode made of SiNWs up to four times showed no measurable differences in the PEC performance (Figure 3). Importantly, the rate, yield, and selectivity were reproduced over each successive experiment, consistent with the fact that SiNWs remain intact over the course of the reaction (> 34 h). If we assume every Si surface atom as an active site, a peak turn-over frequency (TOF) of 25.8 s⁻¹ is estimated (see supporting information for more details).

To demonstrate the synthetic utility of the reaction we applied the methodology to 2-acetyl-6-methoxynaphthalene and 4-isobutylacetophenone, which are precursors for the anti-inflammatory drugs naproxen and ibuprofen.^[19, 24] We observed consistently high yield and selectivity for both new substrates (Figure 4); furthermore, the performance is comparable to what has been reported by electrochemical carboxylation techniques where electricity was the only source of energy input and graphite or mercury were the electrodes (see supporting information for a detailed comparison). We emphasize that the photoelectrochemical syntheses reported here were carried out at potentials up to 670 mV less negative than what has been reported using electrochemical approaches, the difference provided by solar light. Our strategy showed that solar light photon energies can indeed be harnessed to promote the synthesis at lower applied potential.^[30]

In conclusion, we demonstrated a chemical reaction that is powered by light, the most abundant energy source on the surface of earth, and uses CO₂, an inexpensive and readily available source of carbon. Significantly, these reactions produce organic targets that can be readily used to synthesize NSAIDs such as ibuprofen and naproxen. Although the energy harvesting aspect of natural photosynthesis has been widely exploited in reactions such as H₂O splitting or CO₂ reduction for fuel production, how to learn from nature and use the harvested photo energy for complex molecule synthesis is an underdeveloped area. One of the most important merits offered by the reported reaction strategy is the ease with which electron exchange (donation for photocathode or withdrawal for photoanode) takes place between the photoelectrode and the organic substrates. It has the potential to greatly broaden the scope of photosynthesis. While in the present proof of concept demonstration an

additional electrochemical potential is still necessary, the energy input from the harvested light plays a critically important role. As such, our approach represents a step forward in the use of light to power complex organic molecule syntheses.

Experimental Section

Photoelectrode fabrication

The preparation of SiNWs was reported previously.^[31] Once prepared, the substrates containing SiNWs were immersed in HF (aqueous, 5 %) for 2 min and then dried in a stream of N₂. Al (300 nm) was then sputtered onto the backside of the substrates by radio frequency magnetron sputtering (AJA International, Orion 8, MA, USA). They were then annealed in Ar (flow rate: 5000 standard cubic centimeter per minute, SCCM) at 450 °C for 5 min. Afterward, tinned Cu wires were fixed to the Al film by Ag epoxy (SPI supplies, PA, USA). Lastly, non-conductive hysol epoxy (Loctite, OH, USA) was used to seal the entire substrates except the regions where SiNWs resided.

Photoelectrochemical Synthesis

To a flame-dried, three-neck, 25-mL round-bottom flask equipped with magnetic stir bar was added tetrabutylammonium bromide (0.644 g, 2.00 mmol), benzophenone (0.22 M benzophenone in acetonitrile; 2.00 mL, 80.0 mg, 0.439 mmol) and acetonitrile (18 mL) in a dry box. One of the following was placed in each neck of the round-bottom flask: Si NWs working electrode, aluminum counter electrode, Ag/AgI/I⁻ reference electrode. The reaction vessel was brought out of the dry box and CO₂ was bubbled through the solution with an oil bubbler outlet. A constant potential of -1.2 V was applied to the reaction mixture and reaction current was monitored during the synthesis time. Light was shined onto the reaction with vigorous stirring overnight. Without illumination, the reaction current was negligible.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.

Energetics of using p-type SiNWs for benzophenone reduction. Under equilibrium conditions in the dark, a substantial band bending (0.86 V in magnitude) forms, providing a basis for efficient charge separation. When illuminated, the separated charges create a built-in field to help power the benzilic acid formation by carboxylation.

Figure 2.

Photoelectrochemical characteristics of benzilic acid formation by p-type SiNWs. (a) Compared with Pt and planar Si substrate, p-type SiNWs exhibit less negative turn-on voltages. Data obtained under 100 mW/cm² AM 1.5G illumination. (b) Photocurrent density vs. voltage plots under different illumination conditions. A cross sectional view of the electrode is shown in the inset; scale bar: 1 μm. (c) Light powered carboxylation of benzophenone.

Figure 3.

Stability of Si NW photoelectrodes. No significant difference is observed for four consecutive runs under identical operating conditions. Y axis: electron mole per starting material mole. Reaction yields as determined by ^1H NMR: 1st run, >98%; 2nd run 97%; 3rd run, 98%; 4th run, >98%.

Figure 4.
Summary of selectivity and isolated yield for NSAID precursors.

Carbon dioxide fixation in Calvin Cycle

Scheme 1.

Comparison of the key carboxylation steps in natural photosynthesis and those in this communication

Scheme 2.

Proposed mechanism of the light-driven carboxylation reactions