DOI: 10.1002/anie.201202569

VIP **CO_2 Photochemistry**

Silicon Nanowires as Photoelectrodes for Carbon Dioxide Fixation**

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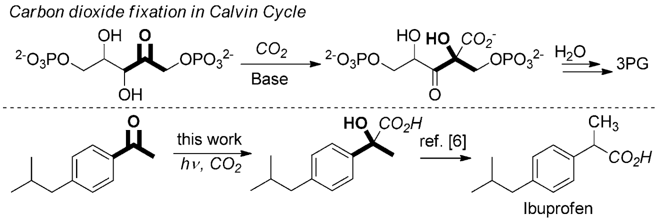
Natural photosynthesis harvests the energy in solar light to power chemical reactions and uses CO_2 as the carbon source. Because light as an energy source is free and abundant, chemical reactions similar to photosynthesis have major fundamental and practical implications.[1,2] Indeed, significant efforts have been attracted to this research goal. The majority of attention for photochemical reactions that transform CO_2 has 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 surprisingly little consideration.[5] Drawing inspiration from the mechanisms found in dark reactions of photosynthesis and using p-type Si nanowires as a photocathode, herein we show that highly specific reactions can be readily carried out to produce α-hydroxy acids by the photoreduction of aromatic ketones, and subsequent CO_2 fixation. Powered by solar light, this reaction closely resembles natural photosynthesis, and is different from its electrochemical analogues. The carboxylation products of two of the substrates examined 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′-tiphosphate), which 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 CO_2, this process avoids producing C in a variety of oxidation states and gains a critical advantage of high selectivity.[8] This chemistry inspired us to propose a strategy to perform carboxylation reactions using light as a direct energy source and CO_2 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 CO_2. It solves a critical challenge of poor selectivity inherent to the direct photoreduction of CO_2 which arises from the nature of the multielectron transfer processes. Our strategy has the potential to meet the selectivity requirement necessary for synthetic targets more complex than fuels, opening doors to a wide range of light-powered chemical reactions[9–12] that have not been studied to date.



Scheme 1. The key carboxylation steps in natural photosynthesis and those reported herein.

We used Si nanowires (SiNWs) as the light-harvesting electrode because they are efficient in converting solar energy into electrical energy, 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 benzilic acid through CO_2 fixation by benzophenone.[18,19] The key difference of the result reported herein 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 correctly aligned for the reduction of benzophenone to the radical anion, the key step in the carboxylation reaction. We would then apply this knowledge to the CO_2 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 are relative to $Ag/AgI/I^-$ reference, which was 0.60 V more positive than the saturated calomel electrode; SCE) 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 ($10^{15}\,cm^{-3}$ 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

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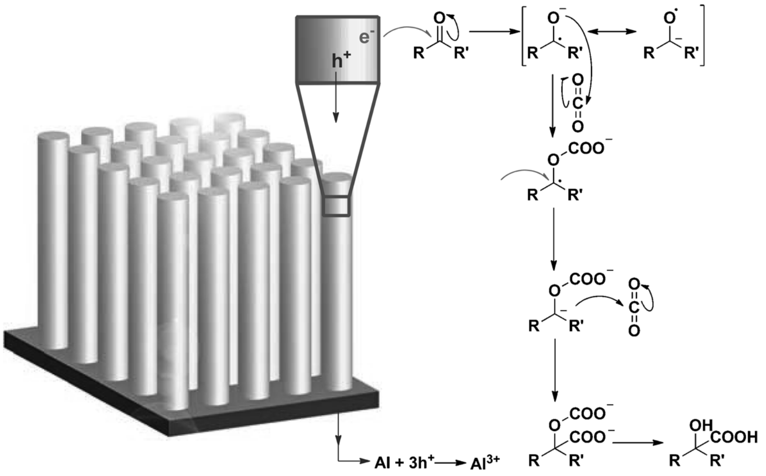
[**] We thank S. Shepard and M. Miao for their technical assistance. Financial support is provided by NSF (DMR 105576 to D.W.) and in part by NIGMS (R01GM087581 to K.L.T.). Mass spectrometry instrumentation at Boston College is supported by funding from the NSF (DBI-0619576).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201202569.



Scheme 2. Proposed mechanism of the light-driven carboxylation reactions; h^+ = hole.

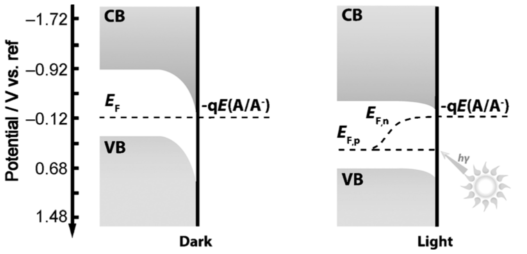


Figure 1. Energetics of using p-type SiNWs for benzophenone reduction. Under equilibrium conditions in the dark, a substantial band bending (0.86 V in magnitude) forms, providing a basis for efficient charge separation. When illuminated, the separated charges create a build-in field to help power the benzilic acid formation by carboxylation. CB = conduction band, VB = valence band, E_F = Fermi level, $E_{F,p}$ = quasi Fermi level of holes, $E_{F,n}$ = quasi Fermi level of electrons, $-qE(A/A^-)$ = reduction potential of benzophenone.

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. 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 ($31.1\ \mathrm{mA\,cm^{-2}}$ at −1.20 V, Figure 2). These results suggest that the reaction as shown in Scheme 1 and Scheme 2 is indeed powered by light. Control experiments where SiNWs were replaced by Pt only gave $2.00\ \mathrm{mA\,cm^{-2}}$ under identical applied potential and illumination conditions. The current level also approaches what is theoretically possible by Si ($43.0\ \mathrm{mA\,cm^{-2}}$) 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. The sharp turn-on of the photocurrent density (a slope of $70.1\ \mathrm{mA\,cm^{-2}\,V^{-1}}$ 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 $[\mathrm{CoCp_2}]^{+/0}$ (Cp = C_5H_5) system,[22] in which charge-transfer resistance from Si to the electrolyte is low, as well as that of Pt (a slope of $72.0\ \mathrm{mA\,cm^{-2}\,V^{-1}}$ 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, $100\ \mathrm{mW\,cm^{-2}}$ AM 1.5 illumination), benzophenone is carboxylated at a faradic efficiency of 94 % and in over 98 % yield of isolated α-hydroxy acid product (**2a**; Figure 2c). We note that to avoid direct reduction of CO_2, which would alter the proposed reaction mechanism and produce undesired by-products, it is important to limit the operating potentials at or more positive than −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 ^{1}H NMR spectroscopy. This result is consistent with the high yield of isolated product.[25] Lastly, we note that the anode, Al is oxidized to produce Al^{3+} (Scheme 2) and dissolves in the reaction medium.[24]

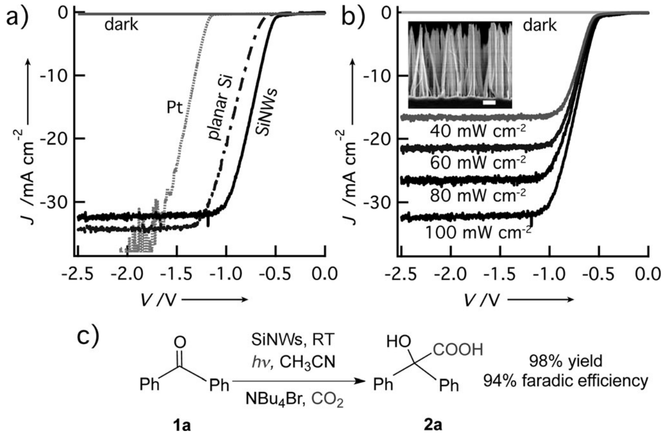


Figure 2. Photoelectrochemical characteristics of benzilic acid formation by p-type SiNWs. a) Compared with Pt and planar Si substrates, p-type SiNWs have less-negative turn-on voltages. Data obtained under 100 mWcm^2 AM 1.5 G illumination. b) Photocurrent density versus voltage plots under different illumination conditions. Inset: A cross sectional SEM view of the electrode; scale bar: 1 μm. c) Light-powered carboxylation of benzophenone.

Further analysis of the benzophenone carboxylation reaction showed that SiNWs exhibit a less-negative turn-on voltage (-0.52 V at >1 mA cm^{-2}) than planar Si (-0.63 V) but lower saturation current density (32.1 mA cm^{-2} vs. 34.4 mA cm^{-2}, Figure 2 a). 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 in which the turn-on voltages were compared with the length of SiNWs (L varying between 0 and 10 μm). Within a limited range ($0 < L \leq 6 \mu m$), the turn-on voltage changes with the surface roughening factor monotonically; the recombination-induced open-circuit potential reduction dominates for longer SiNWs ($L > 6$ μm), and more-negative turn-on voltages were measured (Supporting Information). A similar effect has also been observed in SiNWs-based water-splitting reactions,[28,29] although more details about the reasons remain, to our knowledge, unclear.

For practical applications, the stability of the photoelectrodes against photocorrosion 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 SiNWs remaining intact over the course of the reaction (over 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).

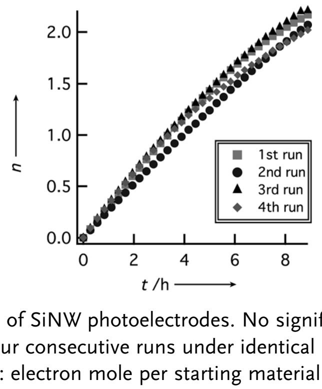
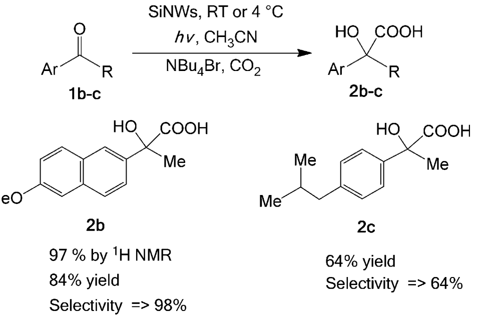


Figure 3. Stability of SiNW photoelectrodes. No significant difference is observed for four consecutive runs under identical operating conditions. y axis: electron mole per starting material mole. Reaction yields as determined by ^{1}H NMR spectroscopy: 1st run, over 98%; 2nd run 97%; 3rd run, 98%; 4th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

To demonstrate the synthetic utility of the reaction we applied the method to 2-acetyl-6-methoxynaphthalene and 4-isobutylacetophenone, which are precursors for the anti-flammatory drugs naproxen and ibuprofen.[19,24] We observed consistently high yields and selectivities for both substrates (Figure 4); furthermore, the performance is comparable to that reported for 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 herein were carried out at potentials up to 670 mV less-negative than those reported using electrochemical approaches, the difference being provided by solar light. Our strategy showed that solar-light photon energies can indeed be harnessed to promote the synthesis at lower applied potentials.[30]



97 % by ^{1}H NMR
84% yield
Selectivity => 98%

64% yield
Selectivity => 64%

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

In conclusion, we demonstrated a chemical reaction that is powered by light, the most abundant energy source on the surface of earth, and uses CO_2, 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 H_2O splitting or CO_2 reduction, for fuel production, learning from nature and using the harvested photoenergy for complex-molecule synthesis is an underdeveloped area. One of the most important merits offered by the 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 artificial 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 critical role. As such, our approach is 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 N_2. 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: In a dry box 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) were added to a flame-dried, three-neck, 25 mL round-bottom flask equipped with magnetic stir bar. One of the following was placed in each neck of the round-bottom flask: SiNWs working electrode, aluminum counter electrode, $Ag/AgI/I^-$ reference electrode. The reaction vessel was brought out of the dry box and CO_2 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 which was vigorously stirred overnight. Without illumination, the reaction current was negligible.

Received: April 2, 2012

Keywords: aromatic ketones · carboxylation · CO_2 fixation · photosynthesis · Si nanowires

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