Tuning redox potentials of CO₂ reduction catalysts for carbon photofixation by Si nanowires

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Si nanowires (SiNWs) are shown to absorb visible light to reduce Ni catalysts into Ni⁰ compounds, enabling alkyne carboxylation reactions with CO₂ as a carbon feedstock. The reduced Ni catalysts are effective in CO₂ fixation through a 4-octyne carboxylation reaction. The reduction potentials of the Ni catalysts can be tuned from –1.35 to –0.51 V (vs. saturated calomel electrode) by altering the binding ligands. The results shed light on the nature of charge transfer from SiNWs to the catalyst for this new class of photocatalytic reactions. By controlling the CO₂ reduction potential of the catalysts with carefully ligand designs, it will bring more opportunities and options to realize the highly selective, effective and sustainable CO₂ reduction in the future.

Converting water or carbon dioxide into fuel through artificial photosynthesis by semiconductors is an attractive strategy to harvest solar energy [1–4]. Analogous to natural photosynthesis, this process requires semiconductors with suitable bandgaps to efficiently capture solar irradiation and convert it into useful forms of energy for storage in chemical bonds. Water splitting or CO₂ reduction catalysts are often necessary to improve the overall efficiency and product selectivity [4–10]. While significant work has been performed in solar water splitting for hydrogen generation, development in CO₂ photofixation is lagging behind due to slow kinetics, high overpotentials, and extremely poor selectivity [11–13]. Given that a hydrogen storage, redistribution and utilization infrastructure is by and large absent, it is of great importance to develop CO₂ photoreduction systems that can produce products to readily utilize existing infrastructures. Toward this direction, Barton *et al.* [14] demonstrated pyridine as a catalyst on p-type GaP to photoreduce carbon dioxide to methanol, with a Faradaic efficiency as high as 96%. Kumar *et al.* [15] reported CO₂ selective reduction to CO using a hydrogen terminated p-Si/Re(bipy-Bu⁺)(CO)₃Cl molecular catalysts junction with 600 mV photovoltage. CO₂ was also shown to be photoreduced to formate on p-InP/ruthenium com-

plex polymer junction by Chardon-Noblat *et al.* [16]. The Faradic efficiency was measured at 63% in aqueous solutions. These results are encouraging because they show that catalysts can not only increase the efficiency when converting solar energy into chemical energy, but also increase the product selectivity by limiting the reaction pathway, especially for CO₂ photoreduction. Concurrently, our group has demonstrated that high product selectivity can be achieved by avoiding directly passing electrons to carbon in CO₂ [17,18]. Instead, when a reactive intermediate is activated by light-driven reactions, it binds with and reduces CO₂ in a highly specific manner. Our approach is inspired by dark reactions in natural photosynthesis. We have shown that the reactive intermediate can be a substrate or a metal catalyst (Scheme 1), the latter of which promises a broader scope of reactions. Building upon our previous success, herein we report that the redox potentials of the intermediate can be readily tuned to match the reducing power of the Si nanowire photocathode.

Controlling redox potentials of catalysts is important because how they align with the energetics of the photoelectrode determines the ease or difficulty of charge transfer at the electrode/catalyst interface. For instance, for reduction reactions, the redox potential of the catalyst needs to be more negative than the Fermi level of the semiconductor to allow for the flow of electrons from semiconductor to catalyst. Additionally, the overpotential of the charge transfer from semiconductor to catalyst should be sufficiently small. All these considerations add extra challenges to find suitable semiconductor/catalyst pairs for practical CO₂ reduction. The semiconductors are limited by the following requirement in a high efficient photoelectrochemical cells: 1) suitable band gap to absorb large portion of solar light; 2) high-quantum efficiency of light to electron conversion; 3) long charge diffusion length of the bulk material to reduce charge recombination; 4) earth abundance for low cost at large scales. Only a handful of semiconductors meet these

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requirements, with Si being the most prominent example. Since the energetics of the photoelectrode (such as the band edge positions and Fermi levels) are often fixed, tuning the redox potential of the catalysts is an imperative task that needs significant research attention.

In this work, we address these issues by focusing on tuning the redox potential of Ni catalysts through the exchange of ligands. We began with Ni(bpy)₃(BF₄)₂ (bpy=2,2'-bipyridine, catalyst 1) as a model catalyst for the carboxylation of 4-octyne using CO₂ as a C1 source, which has previously been shown on carbon fiber [19]. As a symmetric alkyne, 4-octyne presents advantages of minimized products stereoisomers and simplifies product analysis, although we see no reasons why similar other alkynes cannot be studied for the systems we report here. Silicon nanowires (SiNWs) are used as the photocathode to reduce the Ni catalysts. This work demonstrates the ability to tune the redox potential of a system simply by changing ligands on a catalyst, allowing for the selection of an appropriate catalyst/semiconductor pair.

The proposed mechanism for the carboxylation is shown in Scheme 1. Ni(II)L₂ (L=ligand) receives photo-generated electrons from SiNWs under light illumination, and is reduced to Ni(0)L₂, the active catalyst in the reaction cycle. Ni(0)L₂ then couples with substrates, CO₂ and 4-octyne, forming an intermediate nickelacycle complex. With the help of the Al³⁺ ions generated at the anode by the holes from valence band of SiNWs, the carboxylate is released, regenerating Ni catalyst in the form of Ni(II)L₂. The catalytic cycle is maintained as long as SiNWs continuously reduce Ni(II)L₂ with the assistance of light.

The electrochemical properties of this reaction were investigated to determine the effects of applying different ligands to the Ni metal center. This was done with cyclic voltammetry (CV) scans, which are commonly used to in-

vestigate the electrochemical properties of metal complex redox reactions. All experiments were carried out at room temperature under 1 atm pressure of CO₂.

In the CV measurements, Pt or SiNW electrodes were employed as a cathode, high purity aluminum was used as an anode, and the reference electrode was a saturated calomel electrode (SCE). The Ni catalyst 1 reduction peak on SiNWs with light irradiation is distinct (Fig. 1). In the absence of CO₂ and 4-octyne, symmetric CV peaks are obtained. This suggests that the redox pair Ni(II)(bpy)₂/Ni(0)(bpy)₂ has good reversibility. The reduction peak position is the most relevant information gained from this data, as it offers a direct measure on how much potential is required to reduce the Ni catalyst. Compared to a conductive but non-photoeffective Pt cathode, the reduction peak position is shifted about 450 mV on SiNWs in light. This positive shift of reduction potential is due to photovoltage produced by SiNWs. It means Ni catalyst can be reduced more easily with SiNWs due to the solar light contribution. It is worth mentioning that the dark current on SiNWs is close to 0 mA cm⁻² (about 3 orders smaller than light current), implying that all the current on SiNWs comes from solar light irradiation.

We then compared the results of our model catalyst with derivatives employing ligands alternative to 2,2'-bipyridine (Scheme 2). It is shown that the introduction of electron withdrawing or electron donating groups can shift the redox potential of metal complexes [20]. Overall, five additional Ni catalysts were synthesized (from catalyst 2 to catalyst 6, with ligands of bathophenanthroline, 4,5-diazafluoren-9-one, 4,4'-dinitro-2,2'-bipyridine, 4,4'-di-tert-butyl-2,2'-bipyridine, 4,4'-dimethyl-2,2'-bipyridine, respectively).

We see that, similar to our model catalyst, it is easier to reduce these catalysts on SiNWs relative to Pt due to

Scheme 1 Reaction mechanism of light promoted nickel catalyzing carboxylation of alkynes on SiNWs.

Figure 1 CV of catalyst 1 on Pt and SiNWs under the conditions of: 5 mM Ni catalyst and 0.1 M Bu₄NBr in acetonitrile with N₂ as a protection gas.

Scheme 2 Library of Ni catalysts used for CO₂ photofixation through alkyne carboxylation reaction.

the gained photovoltage. Looking at the effects of adding different substituents to the bipyridine ligand backbone, however, we see a marked change in the redox potential. Looking at the application of electron withdrawing groups, such as in catalyst 4, we see a much more positive reduction peak position, at -0.51 V compared to that of catalyst 1 at -1.25 V (on Pt, see Fig. 2). Conversely, we see a relative negative shift in the reduction peak position with the introduction of electron donating groups, such as in catalyst 5. This result agrees with our expectation, as the addition of electron withdrawing groups allows for a less electron rich metal center, and therefore a more easily reduced one. Similarly, a more electron rich metal center is less easily reduced. These effects demonstrate the ability to take advantage of the use of different ligands in order to obtain a desired reduction potential in a catalytic system.

In addition to the intrinsic reduction peak position of the catalysts, the respective reduction in the presence of substrate (CO₂ and 4-octyne) binding was also investigated, which presents the real artificial photosynthesis condition. When substrates are present in solution, they bind to the

Ni(0) active catalyst species, and as a result the oxidation peak will be suppressed (see Supplementary information, Fig. S1). However, our primary focus is on the reduction peak and how it compares to the reduction peak without substrate. Reduction peak positions on a Pt electrode do not display a substantial difference with or without substrate binding in most catalysts. An exception to this is seen in catalyst 4. The primary difference with this catalyst is the strongly electron withdrawing NO₂ groups. This makes the nickel species without substrates easy to reduce. The species formed in the presence of substrates may not be as electron poor, and is therefore not as easily reduced as the original species, which is represented in the more negative potential required to reduce the species in the presence of substrates. Again, with SiNWs as the photocathode, the reduction peak potentials consistently show ca. 400 to 450 mV shifts in a positive direction relative to those on Pt electrodes due to the energy gain from solar light. The detailed reduction peak positions of each catalyst on both Pt and SiNWs are summarized in Table S1.

The alkyne carboxylation reaction on Ni catalysts requires good chemical stability and electrochemical stability of both catalyst and SiNWs in the reaction solution. Catalyst 4 exhibits relatively poor stability during long-term test due to the high reactivity of its ligands. Catalyst 2 is protected by bulky ligands, making it difficult to couple with alkyne molecules or CO₂ or both. Other than these two, other catalysts (catalysts 3, 5 and 6) feature comparable CV results. Catalyst 6 is chosen here to compare with those by the original Ni catalyst (catalyst 1). Stability experiments were completed on SiNWs in the presence of catalyst 6, CO₂ and 4-octyne. The CV curve of the SiNWs has good reproducibility (10 continuous CV scans overlap well, see Fig. 3a), suggesting that the stability of both SiNWs and the Ni catalyst are well maintained under these experimental conditions. Most of the catalysts in Fig. 2 have similar CV stabilities (except catalyst 4).

Long-term reactions were also completed with catalyst 6, CO₂ and 4-octyne in acetonitrile. The SiNWs were applied with constant potential (-0.90 V vs. SCE), and the electrode showed no extensive photocurrent decay for more than 20 h (Fig. 3b). The small decrease in the current is due to the formation of the [4-octyne-catalyst-CO₂] intermediate compounds [18]. The dissociation of these intermediates requires multivalent cations generated on the anode, whose supply is limited by the ionic mobility of the organic salt. The slow dissociation of the [4-octyne-catalyst-CO₂] intermediates leads to undesired build-up that gradually reduces the current densities in long-term stability test. The final products were determined by UV-vis ab-

Figure 2 Reduction peak potentials of Ni catalysts. All the solutions contain 5 mM Ni catalyst and 0.1 M tetrabutylammonium bromide in acetonitrile. For the conditions with substrate binding, 0.05 M 4-octyne was added with CO_2 gas bubbling. SiNWs are illuminated with a 100 mW cm^{-2} Xenon lamp.

Figure 3 (a) CV stability of catalyst 6 on SiNWs. SiNWs were illuminated with a 100 mW cm^{-2} Xenon lamp. (b) Long-term experiment on SiNWs under light with constant applied potential shows very stable photocurrent. The solutions contain 5 mM Ni catalyst and 0.1 M tetrabutylammonium bromide in acetonitrile. 0.05 M 4-octyne was slowly added by a syringe pump with CO_2 gas bubbling.

sorption and mass spectrometry. The Faradic efficiency of this reaction was calculated to be 79% for catalyst 4. Control experiments with catalyst 4 on Au electrode yielded a Faradaic efficiency of 80%. The results agree well with the results obtained on catalyst 1 (81%) [18]. The difference in

the catalyst structures does not appear to induce measurable changes to the Faradic efficiencies, even though the changes are sufficient to tune the reduction potentials of the catalysts.

In conclusion, we tuned the reduction potentials of Ni

catalysts over a range of 0.86 V simply by changing the ligands on the catalyst. With SiNWs as the electrode, we consistently observed 400–450 mV photovoltage. The photogenerated electrons can continuously inject into the Ni catalysts from the SiNWs for more than 20 h. The redox potentials of catalysts for CO₂ reduction were readily tuned by altering the ligands. More electron withdrawing ligands help stabilize metal centers, making the catalyst more easily reduced at comparably higher potentials. Correspondingly, the CO₂ reduction capability by SiNWs becomes easier. Although the work was carried out on systems without covalent bonding, similar results are expected from systems containing immobilized catalysts because the underlying principles are comparable. Highly electron-withdrawing ligands (e.g., catalyst 4), however, introduces additional challenges of poor stabilities. Issues of similar nature require additional research. Nevertheless, we hope this work will inspire people to use ligand effects as a viable design control in manipulating energetic structures to study the application of catalysts on semiconductors.

EXPERIMENTAL SECTION

Ni catalysts were prepared by the addition of Ni(BF₄)₂·6H₂O and the appropriate ligand in a 1:3 ratio in ethanol for 1 h [21]. The resultant precipitate was washed with ether and dried overnight under reduced pressure. All ligands were obtained commercially, with the exception of ligand 3, which was prepared according to literature [21].

Electroless etched SiNWs were prepared following a reported method [22]. A p-type Si (100) substrate (Wafertec, 10¹⁵ cm⁻³, B-doped; 10–20 Ω cm) was cleaned with acetone, methanol, and isopropanol sequentially and then oxidized in H₂O₂/H₂SO₄ 1:3 at 90°C for 10 min to remove heavy metals and organic species. The cleaned substrate was immersed in an HF/AgNO₃ aqueous solution (4.6 M HF and 0.02 M AgNO₃) for 30 min at 50°C to produce SiNWs. Electrode fabrication was done after Al post-treatment to form Ohmic contact as detailed in our previous work [17].

Photoelectrochemical experiments were performed on a CHI 609D Potentiostat. A three-electrode configuration was used, in which Pt or SiNW electrodes were used as the working electrode, a piece of high-purity Al foil (99.9995%, Alfa Aesar, USA) served as the counter electrode, and a SCE was used as the reference electrode. The electrolyte solution was composed of 5 mM Ni catalyst and 0.1 M tetrabutyl ammonium bromide (TBAB) (> 99.0%, Sigma-Aldrich, USA) in 20 mL acetonitrile. CO₂ (Airgas, USA; flow rate: 120 sccm) was continuously bubbled through the solution. A 150 W Xenon lamp (model 71228, Newport, USA)

equipped with an AM 1.5G filter and illumination intensity calibrated to be 100 mW cm⁻² was used as the light source. The scan rates of CV curves were 50 mV s⁻¹. The resultant product was analyzed by NMR and mass spectrometry.

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Author contributions Liu R, Tan KL and Wang D designed the project and the experiments. Liu R and Stephani C performed the experiments. Liu R and Wang D analyzed the results and wrote the paper.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

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中文摘要 硅纳米线在吸收光之后还原催化剂镍离子,从而引发以二氧化碳为碳原料的炔烃羧基化反应. 镍催化剂的还原态产物在这一固碳反应中能够非常高效地将4-辛炔羧酸化. 配位体的给电子基团和吸电子基团的能力不同,将会影响催化剂的氧化还原电位. 还原电位由于构成镍催化剂的配位体不同,控制在−1.35到−0.51 V(相对于甘汞电极电位)之间. 这种新的光催化反应本质上是利用了硅纳米线在光照时产生的光电子从半导体界面转移到催化剂的现象,通过改变催化剂的配位体实现控制催化剂的还原电位. 此方法为实现设计可持续性高效的二氧化碳还原反应提供了更多的选择.