

Solid-State Charge-Based Device for Control of Catalytic Carbon Monoxide Oxidation on Platinum Nanofilms Using External Bias and Light

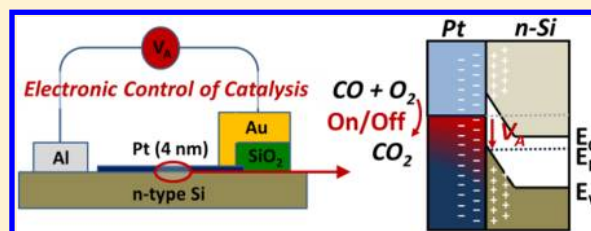
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S Supporting Information

ABSTRACT: Using a Pt/Si catalytic nanodiode, we externally control the rate of CO oxidation on a Pt nanofilm. The catalytic reaction can be turned on and off by alternating between bias states of the device. Additionally, the reaction rate is sensitive to photocurrent induced by visible light. The effects of both bias and light show that negative charge on the Pt increases catalytic activity, while positive charge on the Pt decreases catalytic activity for CO oxidation.

KEYWORDS: Catalysis, solid-state device, nanodiode, strong metal–support interactions, and photochemistry



The development of more efficient catalysts depends on the ability to control electronic interactions for the selective enhancement of desired reaction pathways.^{1–3} Driving catalytic chemistry with a charge flow already forms the basis of electrochemistry, photochemistry, and acid–base catalysis.^{4–9} However, an unexplored approach to charge-mediated catalysis is to use a solid-state device to externally control the catalyst electronic structure with an applied bias or a photoinduced current. In this work, we demonstrate the viability of using a Pt/Si nanodiode to control the rate of CO oxidation.

Many industrial catalysts consist of metal nanoparticles dispersed on a porous support. Because the support is often chemically inert without the metal, the metal is usually considered the active catalyst. However, numerous studies have demonstrated that the electronic properties of the support play a major role in determining the activity and selectivity of the metal/support system.^{10–15} This complex interaction between a metal and its support has been widely studied and is commonly called the strong metal–support interaction (SMSI).^{16–20} We are interested in SMSI because these interactions often give rise to highly active and selective reaction pathways.^{3,21}

SMSI affects a wide range of catalytic reactions, including CO and CO₂ hydrogenation,^{19–21} CO oxidation,^{1,22–24} selective hydrogenation,^{25–27} and selective partial oxidation reactions.^{2,28–30} We have recently demonstrated that for CO oxidation and methanol oxidation, the Pt/TiO₂ interaction is controlled by electron transfer from the TiO₂, which can be modified by chemical doping.^{24,30}

The ability to control the electric field and charge flow at a metal/support interface using a solid-state charge-based device would provide nonthermal, electronic control of a catalytic reaction.^{31–34} From SMSI studies, it is clear that charge flow at the metal/support interface has a major influence on the rate

and selectivity of a catalytic reaction. If this approach is viable, solid-state device technology could soon find major applications in the field of catalysis for tunable control of selective surface chemistry.

The goal of activating nonthermal chemical processes electronically using a solid-state device is an active area of research, and attempts to drive nonthermal surface chemistry have focused primarily on using a tunneling junction to emit hot electrons into a metal thin film.^{31,35–41} When the thickness of the metal thin film is less than the mean free path of the hot electron, it is assumed that the electron reaches the surface before scattering to low energy electron hole pairs and subsequent lattice vibrations (a process that occurs in ~1 ps).⁴² Several studies have demonstrated the ability of these hot electron emitters to induce a chemical reaction involving a single preadsorbed monolayer of reactant.^{35–37} However, no reports have been made that demonstrate the ability to electronically activate a catalyst operating in steady state turnover by directly measuring the product yield.

We have previously reported the production of hot electron flow during CO oxidation using a catalytic nanodiode.^{43,44} In that work, a catalytic reaction was used to drive a current flow across a nanodiode. We demonstrate in this paper that the opposite is also possible. Using a catalytic nanodiode, an externally applied bias and a photoinduced current flow are used to control the rate of the catalytic reaction. We find that applying a negative charge to the Pt increases the reaction rate, while a flux of photoinduced positive charges to the Pt

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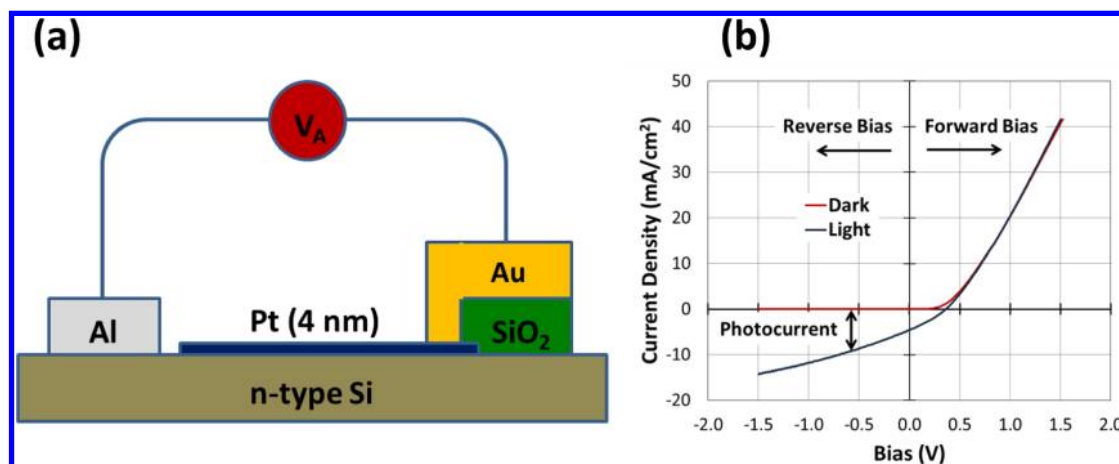


Figure 1. (a) Schematic of the catalytic nanodiode. The rectifying interface is made by depositing Pt (4 nm) on n-type Si. An Al pad (100 nm) makes ohmic contact to the Si, and an Au pad (100 nm) makes contact to the Pt. A layer of SiO₂ (150 nm) insulates the Au pad from the Si substrate. The 4 nm Pt layer is thin enough to transmit visible light, so the device is also a photodiode. (b) *I*–*V* curves of the catalytic nanodiode in the dark (red curve) and during illumination with visible light (blue curve) at room temperature. As seen in the dark curve, forward bias induces a flow of electrons from the Si substrate to the Pt. Reverse bias does not induce a current flow, but a field is generated at the Pt/Si interface. The difference between the blue and red curves represents the photocurrent which increases with reverse bias. The light source is a halogen lamp emitting 60 mW/cm² with a spectral profile similar to the solar spectrum.

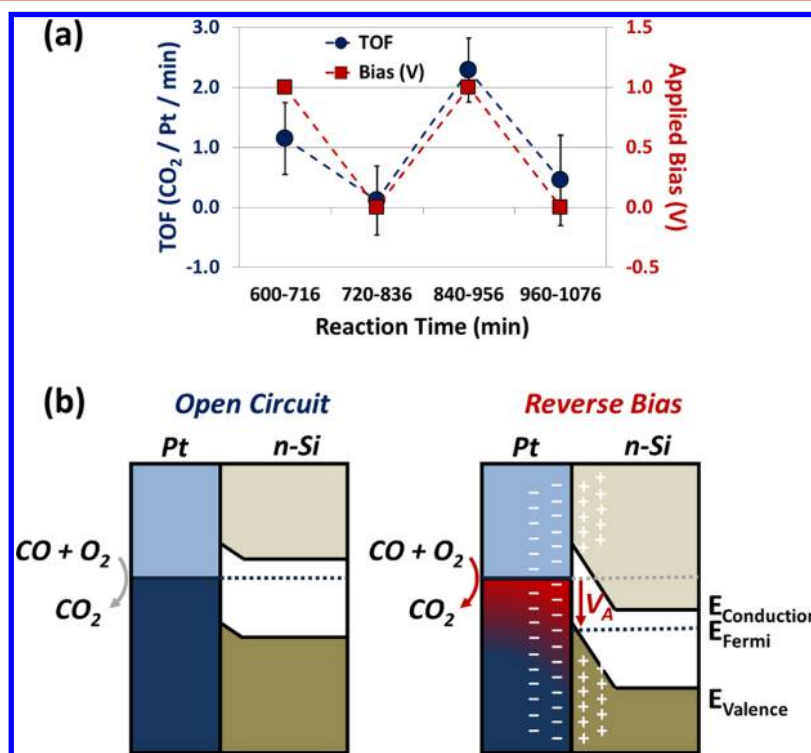


Figure 2. (a) Effect of bias on the catalytic activity of the nanodiode for CO oxidation. Red squares show the reverse bias that was externally applied to the device during CO oxidation. Blue circles show the corresponding turnover frequencies. TOF is given as the number of CO₂ molecules produced per Pt site per minute. The error bars represent 95% confidence intervals for the TOF measurements. The device was cycled between 1 V reverse bias and open circuit (i.e., no applied bias). As shown, the TOF strongly depends on the bias state of the device, and the activity could be turned on and off by switching between reverse bias and no bias, respectively. (b) Band diagrams of the nanodiode in open circuit and during reverse bias. During reverse bias, positive charge builds up on the Si and negative charge builds up on the Pt. This increases band bending in the Si and results in a high electric field at the Pt/Si interface. It appears that the negative charge on the Pt enhances catalytic activity.

decreases the reaction rate. In both cases, the rate change is reversible under conditions of steady state turnover.

The catalytic nanodiode was fabricated by depositing Pt onto n-type Si. The Pt served as the catalyst, and a Schottky barrier formed at the Pt/Si interface. The Pt film was 4 nm thick. We found this was thin enough to transmit visible light, so the

device was also an efficient photodiode showing power conversion efficiency (PCE) of 1.5% and a spectrally averaged incident photon to current conversion efficiency (IPCE) of 15%. Figure 1A shows the device architecture; Figure 1B shows the current–voltage (*I*–*V*) curves of the device in the dark and during illumination by a halogen lamp (~60 mW/cm²) at room

temperature. The spectral profile of the lamp closely followed the solar spectrum (see Supporting Information Figure S1).

Figure 2A shows the effect of applied bias on the catalytic activity of the device for CO oxidation. The experiment was performed in 40 Torr CO and 100 Torr O₂ at 443 K. Exposing the device to reaction conditions for approximately 10 h serves as a pretreatment necessary to observe a rate enhancement by bias. During the pretreatment, the device that is initially active in open circuit (i.e., no applied bias) deactivates as a result of Pt oxidation. Previous work has shown that the activity of the oxidized nanofilm can be reactivated by heating to 523 K in CO to reduce the Pt catalyst.²⁴ However, we find that although the oxidized Pt nanofilm is not active in open circuit, it responds to an applied bias. Following the pretreatment, we find that the catalyst activity can be enhanced by applying a reverse bias across the device. As shown in Figure 2A, this effect is reversible, so that the reaction rate can be turned on and off simply by switching the applied bias. In the experiment shown, a 1 V reverse bias is used to enhance the catalytic reaction rate, and the device is switched back and forth between an applied bias and an open circuit (i.e., no applied bias) state corresponding to high catalyst activity and no activity, respectively. This effect was observed under steady-state turnover conditions for approximately 8 h.

We attempted to perform similar experiments to observe how the magnitude of applied bias affects the catalyst activity. For example, we may assume that applying a 0.5 V bias rather than a 1 V bias would result in a smaller rate enhancement, while a 2 V bias would yield a greater rate enhancement. The major challenge of this experiment is that the bias effect is sensitive to the oxidation state of the Pt nanofilm that is changing during reaction, and we find that the rate enhancement is more sensitive to the oxidation state of the catalyst than it is to the magnitude of the applied bias. Consequently, we could not quantify the magnitude of rate enhancement as a function of applied bias in a way that is statistically significant.

The direction of the applied bias is important because of the rectifying nature of the diode. A forward bias induces a current flow, and we find that under conditions of high current flow induced by a forward bias, the device is unstable in reaction. However, because of the Schottky barrier between the Pt and n-type Si, a reverse bias does not induce a current flow. Rather an electric field is generated at the Pt/Si interface with a negative charge build-up on the Pt and a positive charge build-up on the Si as shown in Figure 2B. It appears that the negative charge on the Pt enhances catalytic activity. Our studies of hot electron flow during CO oxidation using a Pt/TiO₂ catalytic nanodiode could be explained by density functional theory showing that the reaction proceeds via a negatively charged CO₂⁻ transition state.⁴⁵ This finding implicates the important role of negatively charged reaction intermediates leading to a correlation of turnover rates with electron flow.^{43,44} Accordingly, it is not surprising that generating negatively charged intermediates by external bias leads to an enhancement of the turnover rate.

We also explored the possibility of using visible light to control the reaction rate by generating a photocurrent across the device. Figure 3A shows the reaction rate for CO oxidation on the catalytic device first in the dark, then under illumination, then in the dark again. Figure 3A also shows the corresponding photocurrent measurements made during the reaction. The results show that the photocurrent decreases the reaction rate by a factor of ~3. As with the bias, this effect is reversible, and the rate increases again when the light is turned off.

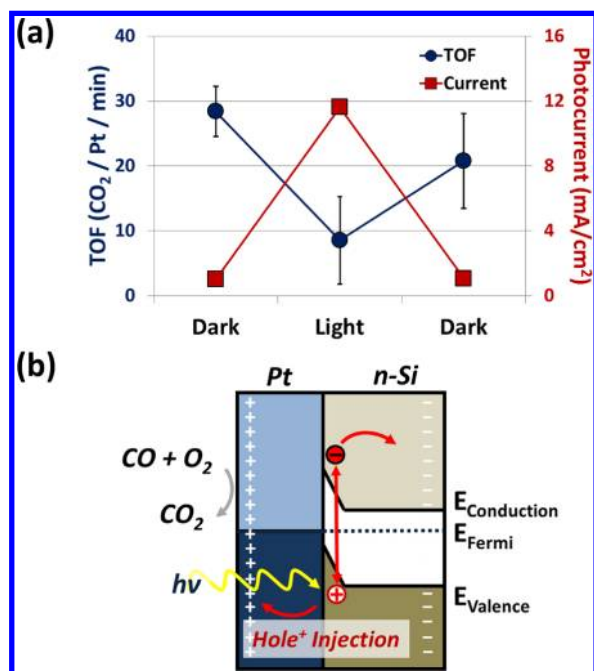


Figure 3. (a) Effect of photocurrent on the catalytic activity of the nanodiode for CO oxidation. Red squares show the current flow across the device in the dark and during illumination under reaction conditions. Blue circles show the corresponding TOF. The error bars represent 95% confidence intervals for the TOF measurements. During this experiment, the reverse bias was kept fixed at 0.6 V. As shown, the photocurrent reversibly decreases the reaction rate by a factor of ~3. (b) Band diagram of the device showing the mechanism of photocurrent generation. The 4 nm Pt film is thin enough to transmit visible that is absorbed in the Si, generating electron–hole pairs. Because of the interface potential, the holes move across the Pt/Si interface resulting in a flow of positive charge to the Pt surface.

The photochemistry experiment was performed in 8 Torr CO and 20 Torr O₂ at 423 K. During this experiment, the reverse bias was kept fixed at 0.6 V. The role of the bias was to increase the reaction rate as well as the efficiency of photocurrent generation that scales with reverse bias. It is important to note that prior to the reaction, the device was subjected to an oxidizing pretreatment at 473 K. We found that the oxidizing pretreatment greatly increased the reaction rate at reverse bias (the same as in the above case showing a turnover rate increase by external bias without light), and this pretreatment was necessary to observe an effect by light on the reaction rate. Again, this implicates the important role of Pt oxidation in observing an effect of charge flow on the catalytic reaction rate.

The mechanism of photocurrent flux is generation of an electron–hole pair in the Si followed by hole injection to the Pt as shown in Figure 3B. Accordingly, photocurrent represents a flux of positive charge to the Pt catalyst and negative charge to the Si support. By bias we showed that a negative charge on the Pt increases the reaction rate; now we show that a flux of positive charge to the Pt decreases the reaction rate.

We found that the chemical changes of the device under reaction conditions played an important role in determining both the bias effect and the photon effect. The bias effect shown in Figure 2A was reversible for about 8 h prior to losing control of the device. The photon effect shown in Figure 3A was shorter, lasting for only about 1 h. However, in both cases, the device was effective long enough to control the chemistry

for at least several hundred turnover events per active site. There appears to be a window in the oxidation state of Pt that shows a dramatic effect by bias and light on the catalytic activity for CO oxidation. At a lower oxidation state of the Pt nanofilm, the device is less sensitive to the applied bias and the photocurrent flux, while at a higher oxidation state, the catalytic activity is too low to measure. In both the bias and the light experiments, the device pretreatments were empirically optimized to yield the greatest effect by bias and light, and a detailed description of device hysteresis is included in Supporting Information.

This work demonstrates direct control of catalytic CO oxidation using a catalytic nanodiode. This is the first time that a charge-based device has been shown to provide external control of a surface catalytic reaction as determined by measuring the product yield, and this was achieved using both applied bias and visible light. On the basis of these results, we believe that charge-based device technology will be further developed for catalytic applications in energy conversion and selective chemistry.

Methods. To fabricate the catalytic Schottky diode, Pt was deposited on n-type Si (100) by electron beam evaporation. The n-type Si substrate was phosphorus doped to achieve a conductivity of 1–10 Ω cm. The Pt film was 4 nm thick as measured by quartz crystal microbalance. The chamber base pressure for electron beam deposition was $>1 \times 10^{-5}$ Torr. No etching of the Si native oxide was performed. We found that the native oxide did not act as a significant tunneling barrier to charge flow. This was verified by two observations: (1) linear ohmic contact to the n-Si with Al metal and (2) high photocurrent efficiency showing easy charge flow between the n-Si substrate and the Pt active area.

Using a shadow mask, the Pt was deposited as a 4 \times 6 mm rectangle that served as the device active area. An aluminum (Al) pad provided ohmic contact to the n-type Si, and a gold (Au) pad provided contact to the Pt active area. Both the Al and Au contact pads were 100 nm thick. A layer of SiO₂ (150 nm) insulated the Au pad from the Si substrate. These Al, Au, and SiO₂ layers were each deposited by electron beam evaporation using shadow masks.

A halogen lamp was used to illuminate the catalytic diode through a sapphire window on the reaction chamber. Lamp power was 1.35 W, the numerical aperture was 0.3, and the distance from the lamp to the diode was 8 cm. This resulted in approximately 60 mW/cm² of radiation over the active area of the diode. The spectral profile of the lamp closely followed the solar spectrum.

A batch mode reactor with a boron nitride substrate heater was used to determine activity of the catalytic diode for CO oxidation. A 2:5 ratio of CO to O₂ was used in the chamber in a background of He. A metal bellows circulation pump provided gas mixing. Reactions were performed at several temperatures between 423 and 443 K as measured by a type-K thermocouple. CO₂ production was monitored as a function of time using a gas chromatograph with a thermal conductivity detector.

Electrical connections were made between the contact pads of the device and BNC feedthroughs on the chamber using Au wire. Depending on the activity of the catalytic diode for a given reaction condition, up to three diodes were connected in parallel to increase the catalytic device area. A Keithley 2400 Sourcemeter was used to control the electrical bias across the device, measure photocurrent, and obtain *I*–*V* curves of the device during reaction.

Reaction rates are reported in turnover frequency (TOF) as CO₂ molecules produced per Pt site per minute. All error bars represent the 95% confidence interval based on the rate of CO₂ production normalized to the estimated number of Pt sites. The number of Pt sites was estimated by assuming a uniform (111) surface structure over the entire catalyst area. Although this calculation is approximate, it provides a consistent normalization to the catalyst area and yields a reasonable estimate of the absolute TOF.

■ ASSOCIATED CONTENT

Supporting Information

Spectral profile of halogen lamp and device stability and hysteresis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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