

# Hot-Electron-Mediated Surface Chemistry: Toward Electronic Control of Catalytic Activity

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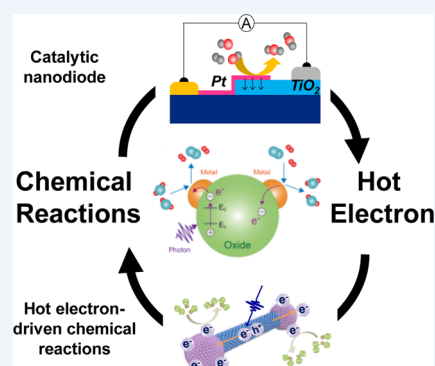
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**CONSPECTUS:** Energy dissipation at surfaces and interfaces is mediated by excitation of elementary processes, including phonons and electronic excitation, once external energy is deposited to the surface during exothermic chemical processes. Nonadiabatic electronic excitation in exothermic catalytic reactions results in the flow of energetic electrons with an energy of 1–3 eV when chemical energy is converted to electron flow on a short (femtosecond) time scale before atomic vibration adiabatically dissipates the energy (in picoseconds). These energetic electrons that are not in thermal equilibrium with the metal atoms are called “hot electrons”. The detection of hot electron flow under atomic or molecular processes and understanding its role in chemical reactions have been major topics in surface chemistry. Recent studies have demonstrated electronic excitation produced during atomic or molecular processes on surfaces, and the influence of hot electrons on atomic and molecular processes.

We outline research efforts aimed at identification of the intrinsic relation between the flow of hot electrons and catalytic reactions. We show various strategies for detection and use of hot electrons generated by the energy dissipation processes in surface chemical reactions and photon absorption. A Schottky barrier localized at the metal–oxide interface of either catalytic nanodiodes or hybrid nanocatalysts allows hot electrons to irreversibly transport through the interface. We show that the chemicurrent, composed of hot electrons excited by the surface reaction of CO oxidation or hydrogen oxidation, correlates well with the turnover rate measured separately by gas chromatography. Furthermore, we show that hot electron flows generated on a gold thin film by photon absorption (or internal photoemission) can be amplified by localized surface plasmon resonance. The influence of hot charge carriers on the chemistry at the metal–oxide interface are discussed for the cases of Au, Ag, and Pt nanoparticles on oxide supports and Pt–CdSe–Pt nanodumbbells. We show that the accumulation or depletion of hot electrons on metal nanoparticles, in turn, can also influence catalytic reactions. Mechanisms suggested for hot-electron-induced chemical reactions on a photoexcited plasmonic metal are discussed. We propose that the manipulation of the flow of hot electrons by changing the electrical characteristics of metal–oxide and metal–semiconductor interfaces can give rise to the intriguing capability of tuning the catalytic activity of hybrid nanocatalysts.



## 1. INTRODUCTION

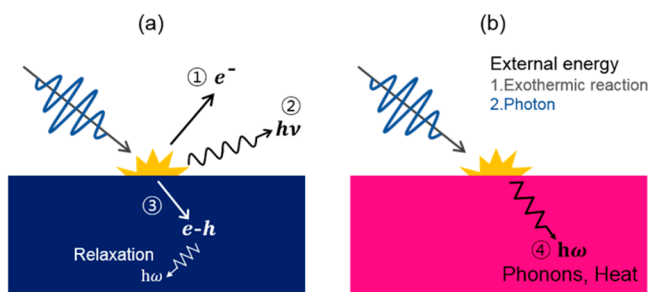
Investigating charge and energy transfer during the elementary steps of surface reactions is crucial for understanding heterogeneous catalysis.<sup>1–3</sup> Once external energy is deposited onto the metal surface (i.e., during mechanical interactions, exothermic reactions, or absorption of photons in general), energy dissipation is mediated by excitation of elementary processes, including adiabatic atomic vibration (phonons) and nonadiabatic electronic excitation, as shown in Figure 1.<sup>2</sup> Because of the historic lack of appropriate experimental methods, quantification of nonadiabatic energy transfer during molecular interactions on metals was not really possible. Direct detection of hot electrons was challenging because of their fast thermalization by means of electron–electron scattering and electron–phonon coupling. In turn, exoelectrons and chemiluminescence were observed only in rare cases, such as highly

exothermic reactions on metals with a low work function<sup>4,5</sup> (Figure 1a), and thus were considered something rather bizarre. Consequently, relaxation of catalytic systems has been mostly evaluated using the adiabatic approximation, which greatly simplifies the picture of the process by assuming that metal electrons adapt immediately to nuclear motion. Thus, any electronic excitation was neglected (Figure 1b).<sup>2,4,6</sup>

However, recent progress in manufacturing metal–semiconductor (MS) nanodiodes with a characteristic size comparable to the mean free path of hot electrons has made it possible to obtain direct evidence of nonadiabatic charge transfer during surface reactions.<sup>2,7,8</sup> A key element of these nanodiodes is a Schottky barrier that acts as a filter allowing hot

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**Figure 1.** Schematic representation of (a) nonadiabatic and (b) adiabatic energy transfer on the metal surface following the deposition of external energy. Both exothermic reactions and photons can be origins for external-energy-stimulated excitation of (1) exoelectrons, (2) luminescence, (3) electron–hole pairs (nonadiabatic), and (4) phonons through adiabatic pathways.

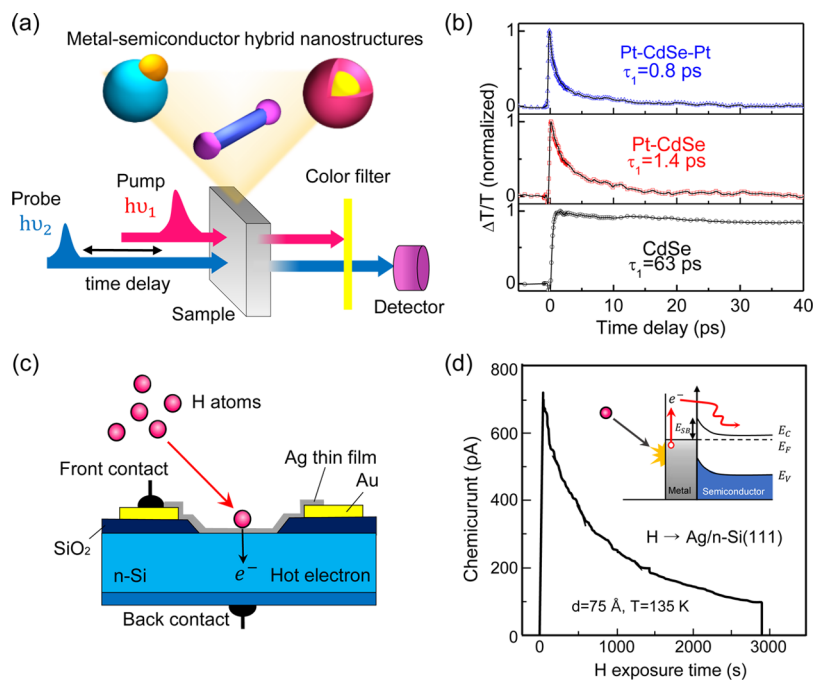
electrons with a certain energy to pass across the MS interface. In addition, the Schottky barrier can serve as an efficient separator of hot electrons and holes, thus preventing recombination of these excited charge carriers, which is especially important for photocatalytic reactions. To date, catalytic systems where nonadiabatic electronic excitation could play notable or even dominant roles in energy dissipation have been discussed in a series of studies.<sup>1–11</sup> These include various catalytic and photocatalytic reactions at gas–metal or liquid–metal interfaces, where nonadiabatic excitation occurs on a femtosecond time scale before the chemical or photon energy is adiabatically dissipated by phonons in picoseconds. Considering these findings, a growing number of studies suggest the use of nonadiabatic charge transfer to alter the performance of composite catalysts. Being a long-standing issue in catalysis, this

idea is based on the pioneering studies done by Schwab and Koller,<sup>12</sup> and Solymosi,<sup>13</sup> who discovered a significant change in the activity of metal catalysts when there was contact between a metal and an oxide support. Called a “strong metal–support interaction” (SMSI), this phenomenon could be attributed to the formation of a Schottky barrier at the metal–oxide interface and the following transport of electrons across the barrier.<sup>14–17</sup> We emphasize the particular importance of experiments aimed at direct detection of nonadiabatic electronic excitation during surface reactions for an atomic-level understanding of the surface chemistry in general and, in particular, for creation of catalysts with tunable performance. Given the high complexity of chemical interactions on metal surfaces, existing theoretical models often have to deal with various arbitrarily chosen parameters, which in turn, lead to opposing estimates of the importance of charge transfer in surface reactions.<sup>2,18–21</sup>

In this Account, we consider the basic aspects of studies aimed at developing methods for changing the performance of composite catalysts by controlling the transfer of hot charge carriers. We first outline various schemes to detect hot electrons that are generated during surface chemical processes and give an overview of the related complexities. Furthermore, we show recent results of hot-electron-driven chemistry that were mediated by surface plasmon resonance. We discuss the relation between surface plasmons, hot electron flows, and possible mechanisms for hot-electron-driven reactions.

## 2. DETECTION OF HOT ELECTRONS WITH SPATIAL AND TEMPORAL RESOLUTION

Further progress toward a microscopic understanding of nonadiabatic energy transfer during surface reactions has been



**Figure 2.** (a) General representation of metal–semiconductor hybrid nanostructures and scheme of the two-color pump–probe transmission measurements. The first pump pulse of the laser ( $h\nu_1$ ) initiates the dynamics of interest (e.g., hot electron generation) followed by the second probe pulse ( $h\nu_2$ ) that tracks its temporal change in the energy distribution of electrons as a function of the delay time ( $\Delta t$ ) between the pulses. (b) Time-resolved transmission spectra for CdSe, Pt–CdSe, and Pt–CdSe–Pt nanostructures as a function of the pump–probe delay. (c) Scheme of the cross section of the Ag/n-Si Schottky nanodiode. (d) Chemicurrent measured during H exposure on the Ag/n-Si nanodiode. Adapted with permission from ref 2. Copyright (2002) Elsevier.

achieved by direct detection of hot electrons with two experimental approaches: one is employing femtosecond laser pulses for observation of the excitation with sufficient time (temporal) resolution (Figure 2a,b),<sup>22–25</sup> and the other is introducing an energy barrier at the metal–oxide interface for irreversible flow of the hot electrons (Figure 2c,d).<sup>2,26</sup>

Ultrafast time-resolved pump–probe spectroscopy is a powerful technique to monitor the electronic structure and dynamics of excited electrons in different systems by measuring different transient signals in real time. Using this pump–probe technique, several research groups have intensively studied hot electron dynamics on metal and semiconductor surfaces as well as charge transfer between adsorbate and substrate since the 1990s.<sup>22–25</sup> As the fields of metal–semiconductor hybrid nanocatalysts have grown, due to their ultrafast charge transfer, the desire to probe electronic dynamics has also been extended to this area. The representatives of hybrid nanostructures, considered recently as promising catalysts, are shown in Figure 2a: metal-attached semiconductor nanodots,<sup>27</sup> metal-tipped semiconductor nanorods,<sup>28</sup> and core/shell nanoparticles.<sup>29</sup> To demonstrate charge separation across the MS interface in various hybrid nanocatalysts, two-color pump–probe transmission measurements are normally used in which temporal changes in the optical transmission or absorption are monitored in real time (Figure 2a). Recently, we conducted this measurement with one-tipped Pt–CdSe nanorods and bare CdSe nanorods as well as Pt–CdSe–Pt nanodumbbells.<sup>28</sup> Figure 2b shows transient decays of the relative optical transmittance ( $\Delta T/T$ ) obtained in each case. When probing the transmission signals with the wavelength adjusted to near the band gap of the CdSe nanorods, an abrupt increase in transmittance appears in all structures at  $\Delta t = 0$ , which is attributed to the carrier state filling in the band edge of the CdSe nanorods. After this increase, the signals decay again due to electron–hole recombination and carrier trapping at defects. Therefore, the lifetime of excited electron–hole pairs can be accounted for by fitting the decay curves to a biexponential model.<sup>30</sup> It is interesting to note that the lifetimes of excited electron–hole pairs in Pt–CdSe–Pt nanodumbbells ( $\tau_1 = 0.8$  ps) and Pt–CdSe nanorods ( $\tau_1 = 1.4$  ps) are much shorter than CdSe nanorods ( $\tau_1 = 63$  ps), thus indicating ultrafast electron injection from the CdSe into the Pt. We will discuss the strong correlation between the ultrafast transport of hot electrons and the enhancement of catalytic activity in Part 5.

Similar to the case of light absorption, exothermic reactions catalyzed on metals can generate hot electrons and holes. These hot charge carriers can be directly detected as an electric signal, called chemicurrent, if the metal is deposited on a semiconducting substrate so as to form a Schottky barrier. This concept was first applied by Nienhaus et al.<sup>31</sup> to observe the generation of hot electrons and holes during chemisorption of monatomic gas particles on the Ag/n-Si nanodiodes, as shown in Figure 2c. When the metal thickness is less than the mean free path of the hot charge carriers (typically, tens of nanometers for hot electrons with 1 eV of excess energy), the chemically excited electrons and holes can travel ballistically through the metal film and reach the MS interface. Furthermore, hot charge carriers with a sufficient amount of excess energy and polarity (electrons for n-type and holes for p-type diodes) may traverse the Schottky barrier, leading to chemicurrent (Figure 2d). Thus, detection of hot carriers occurs due to their spatial separation by the potential energy barrier at the MS interface.

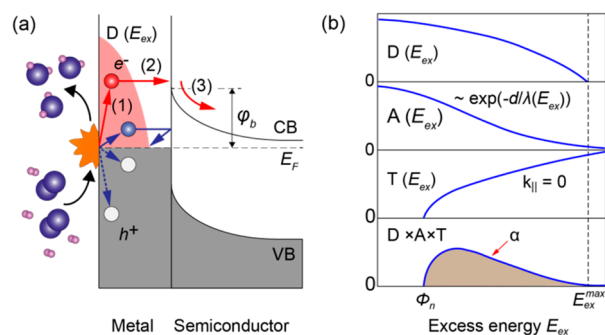
### 3. NATURE OF HOT ELECTRONS GENERATED BY EXOTHERMIC CHEMICAL PROCESSES

Dissipation of the excess kinetic energy of gas particle sticking to the surface of a metal catalyst is a prerequisite for this particle to further participate in a surface reaction. In many cases, however, the mass ratio of the incident particle to that of the metal atom is so small that energy transfer via phonon excitation is not sufficient. Thus, alternative pathways are often considered, such as nonadiabatic electronic excitation. Indeed, from a theoretical point of view, the continuum of low-lying excited electronic states that exist in metals can be seen as an effective absorber of the excess energy.<sup>2,4,7,8</sup> This, in turn, may serve as the basis for surface chemistry with electronic control of the catalytic activity.<sup>1,3</sup> However, an in-depth experimental study of chemical energy dissipation via nonadiabatic electronic excitation is still required.

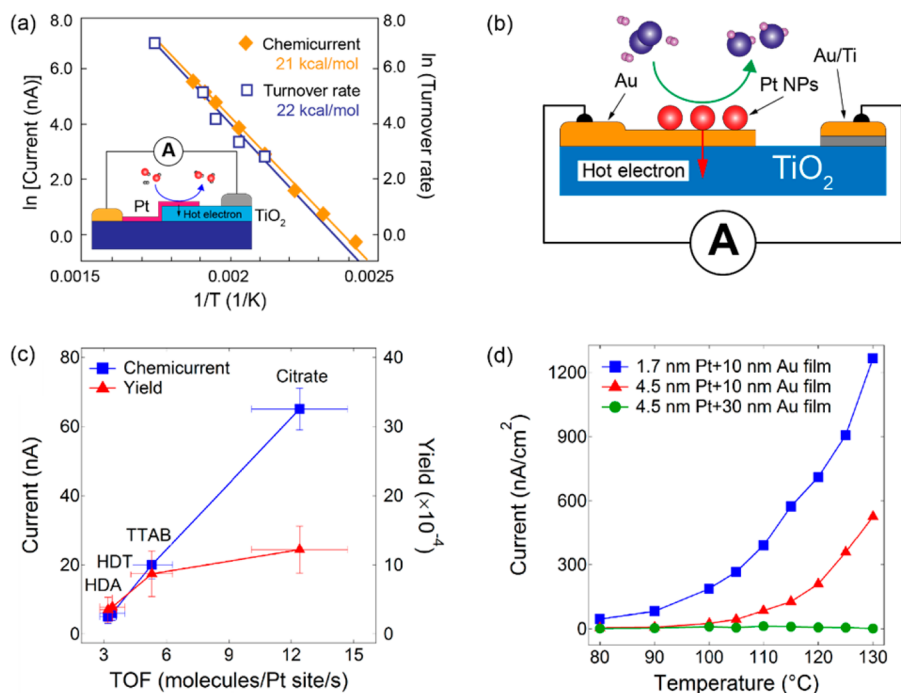
Chemicurrent experiments offer a reliable and easy-to-implement method to study nonadiabaticity in surface chemical interactions. Recently, experiments of this type, with the use of catalytic nanodiodes and simple chemical interactions (e.g., adsorption of monatomic gas particles), allowed for development of a theoretical basis for describing transfer of hot electrons in metal–semiconductor heterostructures induced by chemical reactions. In particular, it was shown that the chemicurrent is proportional to the reaction rate, which is the number of surface events,  $N(t)$ , per second. Thus, the time-dependent chemicurrent can be written as<sup>2,32,33</sup>

$$I_{\text{ch}}(t) = \alpha q A \frac{dN(t)}{dt} \quad (1)$$

where  $\alpha$  is the chemicurrent yield,  $q$  is the elementary charge,  $A$  is the active area of the nanodiode, and  $dN(t)/dt$  is the reaction rate. The physical meaning of  $\alpha$  is the number of hot electrons detected by the nanodiode per one molecule of product formed in the surface reaction. The commonly accepted analytical expression for the chemicurrent yield is based on the so-called three-step model suggested by Nienhaus.<sup>2</sup> According to this model, the creation of chemicurrent is considered to be three subsequent and independent processes, namely: (1) generation of hot electrons by a reaction, (2) ballistic transport through the metal film, and (3) transmission of hot electrons across the



**Figure 3.** (a) Schematic layout and energy-band diagram of a chemicurrent experiment using a Schottky diode. The following steps are shown: (1) excitation of hot charge carriers, (2) ballistic transport, and (3) transmission of hot electrons across the Schottky barrier. (b) Different contributions to the chemicurrent according to eq 2. The area beneath the product  $DAT$  corresponds to the chemicurrent yield. Adapted with permission from ref 2. Copyright (2002) Elsevier.



**Figure 4.** (a) Arrhenius plots of chemicurrent and turnover rate measured on a Pt/TiO<sub>2</sub> nanodiode. Inset shows the structure of the Pt/TiO<sub>2</sub> nanodiode. (b) Schematic of the Pt NPs/Au/TiO<sub>2</sub> nanodiode. (c) Chemicurrent and chemicurrent yield, measured at 240 °C, from Au/TiO<sub>2</sub> nanodiodes decorated with Pt NPs under various capping layers of tetradecyltrimethylammonium bromide (TTAB), hexadecylamine (HDA), hexadecylthiol (HDT), and citrate. (d) Temperature dependence of the chemicurrent, measured on Au/TiO<sub>2</sub> nanodiodes with various sizes of Pt NPs and thicknesses of Au film.

Schottky barrier (see Figure 3a). As a result, the chemicurrent yield is expressed by<sup>2</sup>

$$\alpha = \int_0^{\infty} D(E_{\text{ex}}) A(E_{\text{ex}}) T(E_{\text{ex}}) dE_{\text{ex}} \quad (2)$$

where  $D(E_{\text{ex}})$  is the distribution of hot electrons with excess energy  $E_{\text{ex}} = |E - E_{\text{F}}|$ ,  $A(E_{\text{ex}})$  is the attenuation in a metal film, and  $T(E_{\text{ex}})$  is the transmission probability across the Schottky barrier. Equations similar to eqs 1 and 2 can also be written for the case of chemically excited hot holes.<sup>2</sup> To date, measured values of the chemicurrent yield are in the range of  $10^{-7}$ – $10^{-2}$  electrons per molecule of product,<sup>2,7,8,32</sup> which is clear evidence that the amount of energy dissipated via nonadiabatic electronic excitation is larger than what has commonly been expected.

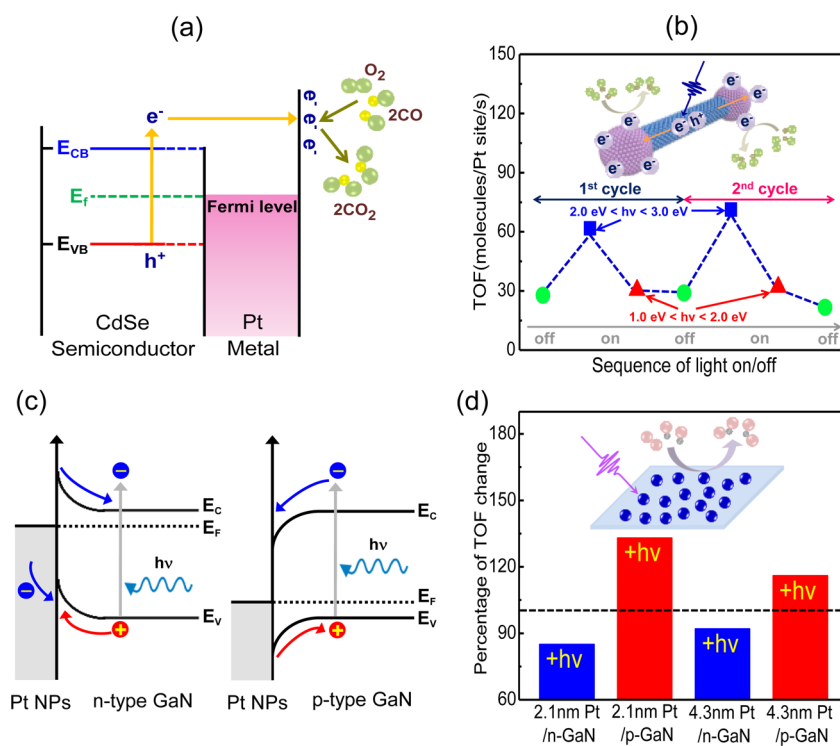
Whereas the attenuation of hot electrons in a metal film,  $A(E_{\text{ex}})$ , and the probability of their transmission across the Schottky barrier,  $T(E_{\text{ex}})$ , are well investigated (e.g., studies using ballistic electron emission spectroscopy (BEEM)<sup>34</sup>), the energy distribution of the chemically excited electrons,  $D(E_{\text{ex}})$ , remains speculative.<sup>2,35</sup> Several mechanisms are proposed to make an assessment of the energy distribution of electrons excited in surface reactions. It was considered that a model function,  $D(E_{\text{ex}})$ , for the case of adsorption of atomic gases on metals, had a maximum value close to the Fermi energy with a following rapid decrease to zero when the excess energy was equal to the adsorption energy (see the upper panel in Figure 3b).<sup>2</sup> The middle panels of Figure 4b display other contributors to the chemicurrent, according to eq 2. The area under the curve,  $DAT$ , shown in the lower panel in Figure 3b, represents the value for the chemicurrent yield. The energy distribution of the chemicurrent yield has a maximum at an energy slightly greater than the Schottky barrier height, which is characteristic

for the function  $D(E_{\text{ex}})$  that decreases as the excess energy increases.

#### 4. DETECTION AND UTILIZATION OF CHEMICAL-REACTION-INDUCED HOT ELECTRONS: COMPLEXITIES RELATED TO HOT ELECTRON DETECTION

After experiments with atomic gases, the concept of catalytic nanodiodes, for detection of chemically induced hot charge carriers was successfully tested for various catalytic systems and reactions showing the applicability of the three-step model to describe the chemicurrent generated in catalytic reactions.<sup>8,26,36,37</sup> Furthermore, the need to operate at high temperatures and gas pressures, which is a prerequisite for catalytic reactions, unveiled the necessity to account for some secondary effects that accompany the generation of chemicurrent and influence its value. These include, for example, the thermoelectric effect that occurs due to temperature gradients in nanodiodes when catalytic reactions take place on their surface.<sup>8,38,39</sup>

The original analysis of hot electrons using nanodiodes was first applied to practical heterogeneous catalytic systems in 2005.<sup>26,40</sup> The first attempt was to measure the chemicurrent under catalytic CO oxidation on Pt, which follows several reaction steps: adsorption of CO and O<sub>2</sub>, dissociation of O<sub>2</sub>, and formation of CO<sub>2</sub> product. It is well-known that CO<sub>2</sub> formation over Pt is highly exothermic, releasing a total of 2.9 eV. A quantitative correlation between hot electrons and catalytic activity obtained from turnover rate results was verified in Figure 4a. The activation energies of CO oxidation extracted from Arrhenius plots of both chemicurrent and turnover rate measurements are 21 and 22 kcal/mol, respectively. The well-matched values imply that the number of hot electrons



**Figure 5.** (a) Energetic band alignment representing the flow of hot electrons generated on Pt–CdSe–Pt nanodumbbells under light irradiation and their participation in CO oxidation. (b) Catalytic activity of the nanodumbbells without light, with light having high photon energy, and with light having low photon energy measured at 553 K. (c) Energetic band alignment of the Pt/GaN model systems showing two plausible routes for hot carrier flows according to the doping type of the GaN substrates. (d) Percentage change of TOF for 2.1 and 4.3 nm Pt/GaN during light irradiation.

generated during the reaction is directly related to the number of product molecules; furthermore, hot electrons are a key parameter for determining catalytic activity and selectivity on the catalyst surface. A series of studies have since been implemented extensively in various catalytic reactions with different Schottky diodes that have clarified energy transfer via hot electron generation on catalysts.<sup>8,37,40–44</sup>

Most catalysts are complex systems that consist of metal nanoparticles (NPs), typically 1–10 nm in size, dispersed on a support.<sup>3,7,44,45</sup> To study the transfer of charge carriers across the metal NP–support interface in such systems, Park et al.<sup>44</sup> demonstrated a modified nanodiode, shown in Figure 4b. Here, Pt colloid NPs of a certain size are deposited on a 2.5 nm-thick Au film. The Au film, in turn, is supported on  $TiO_2$ . To record the chemi-current, the  $TiO_2$  substrate is equipped with a Ti/Au ohmic contact. The thin Au film, placed between the Pt NPs and the  $TiO_2$  substrate, created an electrical connection between the Pt NPs and the external circuit where the chemi-current was measured. Experiments with Pt NPs/Au/ $TiO_2$  nanodiodes unveiled intensive flows of hot electrons, generated on Pt NPs during CO oxidation, across the potential barrier formed at the Au/ $TiO_2$  interface (see Figure 4c). As shown, the chemi-current is proportional to the turnover rate, which agrees well with eq 1. Given a value for the reaction rate, this corresponds to a chemi-current yield on the order of  $10^{-4}$  electrons/ $CO_2$  at 240 °C, which is comparable to measurements performed using thin-film Pt/ $TiO_2$  and Pt/GaN nanodiodes.<sup>8</sup> The last fact can be seen as evidence of the high efficiency of hot electron transport across the Pt NPs/Au/ $TiO_2$  interface. Another interesting feature of chemi-current was discovered when Pt NPs with different capping layers were deposited on Au/ $TiO_2$  nanodiodes.<sup>44</sup> We also verified the

crucial role of attenuation of the hot electron flow in Pt NPs on the overall magnitude of the chemi-current.<sup>7</sup> Figure 4d shows the chemi-current measured at different temperatures from Au/ $TiO_2$  nanodiodes decorated with Pt NPs of various sizes during hydrogen oxidation. A clear tendency of the chemi-current to rapidly decrease with increasing Pt NP size is seen across the entire temperature range. Recently, chemi-current studies on a catalytic nanodiode that contains a layer of porous titanium oxide were demonstrated by Schierbaum et al.<sup>46</sup> and Karpov et al.<sup>47,48</sup> The key feature of Pt/porous  $TiO_2$  nanodiodes is a very large chemi-current (up to tens of  $\mu A$ ), due to a high surface area that increases the activity of heterogeneous catalysts.<sup>3,45</sup>

## 5. MICROSCOPIC MECHANISM OF HOT-ELECTRON- AND SURFACE-PLASMON-INDUCED CHEMISTRY: PHENOMENA AND INTERPRETATION

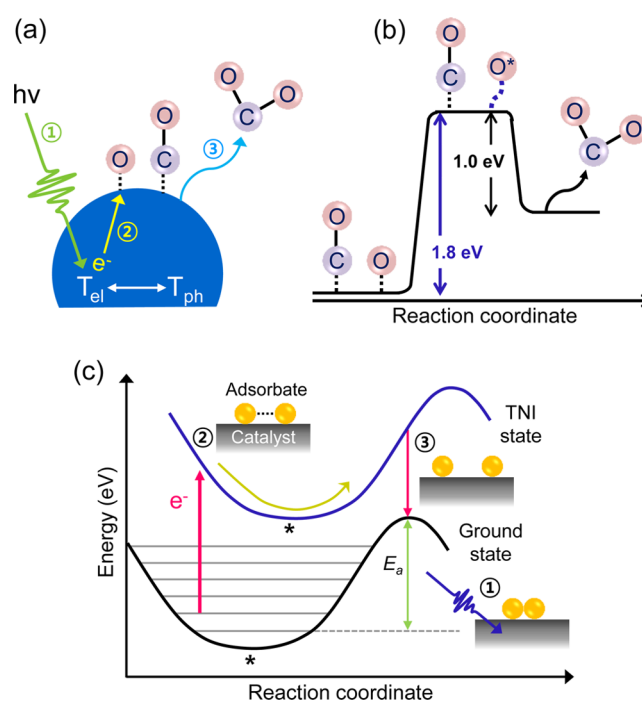
The fascinating findings that hot electrons influence chemical reaction processes at atomic or molecular levels have significantly increased attention for it, creating new technical terminology of so-called “hot-electron-driven chemistry” in the field of heterogeneous catalysis.<sup>11,49–51</sup> This concept was pioneered by the earlier work by Ertl et al.<sup>9</sup> and has now been extensively developed by many research groups, thus concurrently opening up the need for elaborately designed catalysts that couple light energy into chemical reactions.<sup>52</sup> Of representative groups using surface plasmon resonance (SPR), one of the key elements that mediate energy conversion, both the Linic and Halas groups have demonstrated that SPR excitation of plasmonic metallic nanostructures is an efficient source of hot electrons and it drives various catalytic oxidation reactions at lower temperatures.<sup>53,54</sup> Our group also succeeded in monitoring hot electron dynamics in the presence of

localized surface plasmons of metal nanostructures.<sup>43,55</sup> Furthermore, recent studies have focused on controlling the chemistry to describe specific pathways for selectivity control in catalysis on metal nanoparticles as well as driving the chemistry itself. Christopher et al. found that direct photoexcitation of adsorbate–metal bonds with a targeted wavelength and at optimal system temperatures enables selective catalytic reactions, which is difficult to achieve using thermal energy.<sup>56,57</sup> Ke et al. identified plasmon-induced control of catalytic selectivity by manipulating the wavelength of visible light irradiation.<sup>58</sup>

As additional key elements, we investigated the role of hot carriers generated on diverse nanohybrid nanostructures—consisting of a MS junction (Schottky barrier)—during a surface chemical reaction<sup>28,59</sup> As shown in the band alignment in Figure 5a and schematic drawing inset in Figure 5b, hot electrons in both-sided Pt-tipped Pt–CdSe–Pt nanodumbbells are generated in the CdSe nanorods upon light absorption; they can then be injected into the Pt nanoparticles, resulting in a change in the catalytic activity for CO oxidation.<sup>28</sup> Figure 5b shows the influence of photon energy on the catalytic enhancement of the nanodumbbells, which indicates that hot electrons are generated when irradiated with light having a photon energy above the bandgap energy of the CdSe nanorods, and that the hot electrons promote CO oxidation at the surface of the Pt metal. The hot electron effect was examined in other types of MS contact that consist of two-dimensional Pt NPs arrays on n- or p-type GaN substrates, as shown in the inset of Figure 5d.<sup>59</sup> With the given energetic alignment of Figure 5c, the recombination of electrons from the Pt NPs with holes from the n-type GaN semiconductor under illumination is expected. Likewise, electron transfer to the Pt NPs is expected for the p-type GaN supports. Figure 5d shows the percentage change of turnover frequency of the Pt/GaN catalysts according to the size of the Pt NPs and the doping type of the GaN substrates, indicating that the type of hot carrier influences the catalytic activity.

As described above, it is clear that hot electrons participate in chemical reactions occurring at the metal surface, although we still lack a microscopic understanding of the mechanism which may probably open new reaction pathways apart from thermal reactions. Surface femtochemistry provides a significant chance to follow ultrafast reaction dynamics driven by hot-electron-mediated reaction pathways. Ertl and others, pioneers in this field, have devoted much time to demonstrate these electronic excitation processes at metal surfaces.<sup>9,60,61</sup> For this reason, we adopted their idea as a solution for explaining our results induced by hot electrons, as shown in the scheme of Figure 6a. At thermal equilibrium,  $T_{el}$  is equal to  $T_{ph}$  due to electron–photon coupling with a characteristic time scale of  $\sim$  ps. This situation is broken simultaneously with light irradiation, and hot electrons generated through electron–electron scattering are transferred to the metal–O bond, facilitating the activation of oxygen requiring higher energy than CO desorption and promoting the formation of CO<sub>2</sub> as the product (Figure 6b). In other words, hot electrons can drive chemical processes never allowed in a thermally excited system where only CO desorption occurs.

Figure 6c shows another feasible mechanism involving desorption induced by electronic transitions from electron scattering via adsorbate–substrate resonance using one-dimensional potential energy curves. This mechanism is explained as follows: First, when the adsorbate is irradiated with light on a

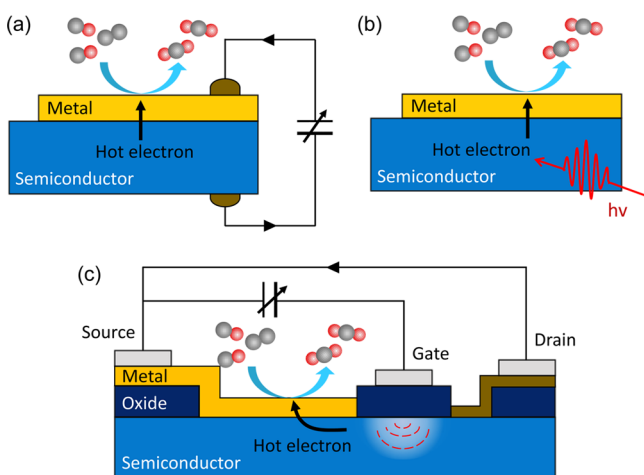


**Figure 6.** Schematic diagram illustrating a hot-electron-induced chemical reaction. (a,b) Generation of hot electrons on a metal surface under femtosecond laser excitation and role of hot electrons during CO oxidation. (c) Proposed mechanism for a hot-electron-induced chemical reaction on a photoexcited plasmonic metal. Panel (b) adapted with permission from ref 9. Copyright (1999) Science. Panel (c) adapted with permission from ref 62. Copyright (2011) Nature Publishing Group.

ground-state potential energy surface, a transient negative ion (TNI ( $\delta^-$ )) that rapidly reacts on the metal surface is produced. Second, the adsorbate travels on the TNI potential energy surface, gaining kinetic energy along the reaction coordinate. Third, the electron decays back to the metal Fermi level after a short lifetime,  $\tau$ , and the adsorbate returns to the ground-state potential energy surface with increased vibrational energy.<sup>62</sup>

## 6. CONCLUSION

This Account has focused on research efforts on the physical, electronic, and chemical properties of metal–oxide interfaces and their influence on catalytic activity with the aim of “*electronic control of surface reactions*”. The intrinsic relation between catalytic activity and generated hot electron flux indicates the intriguing possibility for tailoring chemical reactions via manipulating hot electron flows across metal–oxide interfaces. Figure 7 shows the various schemes for controlling chemical reactions by (a) applying a bias voltage between the two electrodes in a nanodiode, (b) light illumination and the creation of electron–hole pairs, and (c) a catalytic actuator with configurations of source, drain, and gate capable of tuning the electric field in the pathway of the hot electrons. The subject of “*electronic control of surface reactions*” is a key issue for bridging the materials gap and will continue to be an active research area in heterogeneous catalysis. Generation and detection of hot electron flows with several different schemes were shown. The strong correlation between hot electron generation and turnover rates of catalyzed reactions was shown for several catalysts and reactions. The



**Figure 7.** Scheme for utilization of hot electrons to change the catalytic activity via (a) changing the bias voltage of the metal–semiconductor nanodiodes, (b) light illumination, and (c) changing the gate bias of the three terminal devices.

impact of hot electrons and surface plasmons on catalytic surface reactions and their mechanisms were discussed for the cases of Au, Ag, and Pt nanoparticles supported on oxide substrates. The nature and theoretic descriptions of hot electrons during exothermic chemical reactions were also discussed.

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### Notes

The authors declare no competing financial interest.

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**Jeong Young Park** is currently a group leader at the Center for Nanomaterials and Chemical Reactions, Institute for Basic Science, and an associate professor at the Graduate School of EEWS, KAIST, Republic of Korea. He received his Ph.D. from Seoul National University in 1999. After spending 3 years at the University of Maryland as a postdoctoral associate, he joined the Lawrence Berkeley National Laboratory where he worked as a staff scientist. His research focuses on surface phenomena covering energy dissipation and conversion at surfaces, nanotribology, catalysis, and hot electron transport through metal–oxide interfaces. He has published 130 peer-reviewed articles and book chapters in the fields of surface science and catalysis.

**Sun Mi Kim** received her Ph.D. from the Graduate School of EEWS Graduate School at KAIST (2014). Before she joined KAIST as a Ph.D. candidate in 2010, she was a researcher at the Korea Atomic Energy Research Institute from 2007 to 2009 and is currently a Postdoctoral Fellow at the Institute for Basic Science. Her research interests focus on developing new hybrid nanocatalysts and hot-electron-driven chemical reactions on two-dimensional model catalysis.

**Hyosun Lee** received her Master's Degree from the EEWS Graduate School at KAIST (2014), and she is currently pursuing a Ph.D. in the group of Prof. Jeong Young Park. Her main research interest is mechanistically understanding chemically induced hot electron flows on supported metal catalysis on catalytic nanodiodes.

**Ievgen I. Nedrygailov** received his Ph.D. from the University of Duisburg-Essen in 2014. He is currently a research fellow at the Center for Nanomaterials and Chemical Reactions, Institute for Basic Science. His research interests include electronic excitation and surface chemistry on metal–semiconductor heterostructures and measurement of hot electron flows at liquid–solid interfaces.

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## REFERENCES

- (1) Kim, S. M.; Lee, H.; Park, J. Y. Charge transport in metal-oxide interfaces: genesis and detection of hot electron flow and its role in heterogeneous catalysis. *Catal. Lett.* **2015**, *145*, 299–308.
- (2) Nienhaus, H. Electronic excitations by chemical reactions on metal surfaces. *Surf. Sci. Rep.* **2002**, *45*, 1–78.
- (3) Somorjai, G. A.; Frei, H.; Park, J. Y. Advancing the frontiers in nanocatalysis, biointerfaces, and renewable energy conversion by innovations of surface techniques. *J. Am. Chem. Soc.* **2009**, *131*, 16589–16605.
- (4) Greber, T. Charge-transfer induced particle emission in gas surface reactions. *Surf. Sci. Rep.* **1997**, *28*, 1–64.
- (5) Kasemo, B.; Walldén, L. Photon and electron emission during halogen adsorption on sodium. *Surf. Sci.* **1975**, *53*, 393–407.
- (6) Wodtke, A. M.; Matsiev, D.; Auerbach, D. J. Energy transfer and chemical dynamics at solid surfaces: The special role of charge transfer. *Prog. Surf. Sci.* **2008**, *83*, 167–214.
- (7) Lee, H.; Nedrygailov, I. I.; Lee, C.; Somorjai, G. A.; Park, J. Y. Chemical reaction-induced hot electron flows on Pt colloid nanoparticles under hydrogen oxidation: Impact of nanoparticle size. *Angew. Chem., Int. Ed.* **2015**, *54*, 2340–2344.
- (8) Park, J. Y.; Renzas, J. R.; Hsu, B. B.; Somorjai, G. A. Interfacial and chemical properties of Pt/TiO<sub>2</sub>, Pd/TiO<sub>2</sub>, and Pt/GaN catalytic nanodiodes influencing hot electron flow. *J. Phys. Chem. C* **2007**, *111*, 15331–15336.
- (9) Bonn, M.; Funk, S.; Hess, C.; Denzler, D. N.; Stampfl, C.; Scheffler, M.; Wolf, M.; Ertl, G. Phonon-versus electron-mediated desorption and oxidation of CO on Ru (0001). *Science* **1999**, *285*, 1042–1045.
- (10) Frischkorn, C.; Wolf, M. Femtochemistry at metal surfaces: Nonadiabatic reaction dynamics. *Chem. Rev.* **2006**, *106*, 4207–4233.
- (11) Shen, T. C.; Wang, C.; Abeln, G. C.; Tucker, J. R.; Lyding, J. W.; Avouris, P.; Walkup, R. E. Atomic-scale desorption through electronic and vibrational-excitation mechanisms. *Science* **1995**, *268*, 1590–1592.
- (12) Schwab, G.-M.; Koller, K. Combined action of metal and semiconductor catalysts. *J. Am. Chem. Soc.* **1968**, *90*, 3078–3080.
- (13) Solymosi, F. Importance of the electric properties of supports in the carrier effect. *Catal. Rev.: Sci. Eng.* **1968**, *1*, 233–255.
- (14) Tauster, S. J. Strong metal-support interactions. *Acc. Chem. Res.* **1987**, *20*, 389–394.
- (15) Liu, X.; Liu, M.-H.; Luo, Y.-C.; Mou, C.-Y.; Lin, S. D.; Cheng, H.; Chen, J.-M.; Lee, J.-F.; Lin, T.-S. Strong metal-support interactions between gold nanoparticles and ZnO nanorods in CO oxidation. *J. Am. Chem. Soc.* **2012**, *134*, 10251–10258.
- (16) Spencer, M. S. Models of strong metal-support interactions (SMSI) in Pt on TiO<sub>2</sub> catalysts. *J. Catal.* **1985**, *93*, 216–223.
- (17) Willinger, M. G.; Zhang, W.; Bondarchuk, O.; Shaikhutdinov, S.; Freund, H.-J.; Schlögl, R. A case of strong metal-support interactions: Combining advanced microscopy and model systems to elucidate the atomic structure of interfaces. *Angew. Chem., Int. Ed.* **2014**, *53*, 5998–6001.
- (18) Behler, J.; Reuter, K.; Scheffler, M. Nonadiabatic effects in the dissociation of oxygen molecules at the Al(111) surface. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2008**, *77*, 115421.
- (19) Goikoetxea, I.; Beltran, J.; Meyer, J.; Juaristi, J. I.; Alducin, M.; Reuter, K. Non-adiabatic effects during the dissociative adsorption of

O<sub>2</sub> at Ag(111)? A first-principles divide and conquer study. *New J. Phys.* **2012**, *14*, 013050.

(20) Meyer, J.; Reuter, K. Electron-hole pairs during the adsorption dynamics of O<sub>2</sub> on Pd(100): exciting or not? *New J. Phys.* **2011**, *13*, 085010.

(21) Pavanello, M.; Auerbach, D. J.; Wodtke, A. M.; Blanco-Rey, M.; Alducin, M.; Kroes, G. J. Adiabatic energy loss in hyperthermal H atom collisions with Cu and Au: A basis for testing the importance of nonadiabatic energy loss. *J. Phys. Chem. Lett.* **2013**, *4*, 3735–3740.

(22) Bokor, J. Ultrafast dynamics at semiconductor and metal surfaces. *Science* **1989**, *246*, 1130–1134.

(23) Haight, R. Electron dynamics at surfaces. *Surf. Sci. Rep.* **1995**, *21*, 275–325.

(24) Hertel, T.; Knoesel, E.; Wolf, M.; Ertl, G. Ultrafast electron dynamics at Cu (111): Response of an electron gas to optical excitation. *Phys. Rev. Lett.* **1996**, *76*, 535–538.

(25) Petek, H.; Ogawa, S. Femtosecond time-resolved two-photon photoemission studies of electron dynamics in metals. *Prog. Surf. Sci.* **1997**, *56*, 239–310.

(26) Ji, X.; Zupero, A.; Gidwani, J. M.; Somorjai, G. A. Electron flow generated by gas phase exothermic catalytic reactions using a platinum-gallium nitride nanodiode. *J. Am. Chem. Soc.* **2005**, *127*, 5792–5793.

(27) Du, L.; Furube, A.; Hara, K.; Katoh, R.; Tachiya, M. Ultrafast plasmon induced electron injection mechanism in gold–TiO<sub>2</sub> nanoparticle system. *J. Photochem. Photobiol., C* **2013**, *15*, 21–30.

(28) Kim, S. M.; Lee, S. J.; Kim, S. H.; Kwon, S.; Yee, K. J.; Song, H.; Somorjai, G. A.; Park, J. Y. Hot carrier-driven catalytic reactions on Pt–CdSe–Pt nanodumbbells and Pt/GaN under light irradiation. *Nano Lett.* **2013**, *13*, 1352–1358.

(29) Zhang, N.; Liu, S.; Xu, Y.-J. Recent progress on metal core@ semiconductor shell nanocomposites as a promising type of photocatalyst. *Nanoscale* **2012**, *4*, 2227–2238.

(30) Klimov, V.; McBranch, D.; Leatherdale, C.; Bawendi, M. Electron and hole relaxation pathways in semiconductor quantum dots. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1999**, *60*, 13740–13749.

(31) Nienhaus, H.; Bergh, H.; Gergen, B.; Majumdar, A.; Weinberg, W.; McFarland, E. Electron-hole pair creation at Ag and Cu surfaces by adsorption of atomic hydrogen and deuterium. *Phys. Rev. Lett.* **1999**, *82*, 446–449.

(32) Gergen, B.; Nienhaus, H.; Weinberg, W. H.; McFarland, E. W. Chemically induced electronic excitations at metal surfaces. *Science* **2001**, *294*, 2521–2523.

(33) Nienhaus, H.; Bergh, H. S.; Gergen, B.; Majumdar, A.; Weinberg, W. H.; McFarland, E. W. Direct detection of electron-hole pairs generated by chemical reactions on metal surfaces. *Surf. Sci.* **2000**, *445*, 335–342.

(34) Prietsch, M. Ballistic-electron emission microscopy (BEEM): Studies of metal/semiconductor interfaces with nanometer resolution. *Phys. Rep.* **1995**, *253*, 163–233.

(35) Schindler, B.; Diesing, D.; Hasselbrink, E. Electronic excitations induced by hydrogen surface chemical reactions on gold. *J. Chem. Phys.* **2011**, *134*, 034705.

(36) Dasari, S. K.; Hashemian, M. A.; Mohan, J.; Karpov, E. G. A Nonthermal chemisorption effect of hydrogen adsorption on Pt/SiC planar nanostructures at normal ambient conditions. *Chem. Phys. Lett.* **2012**, *553*, 47–50.

(37) Hervier, A.; Renzas, J. R.; Park, J. Y.; Somorjai, G. A. Hydrogen oxidation-driven hot electron flow detected by catalytic nanodiodes. *Nano Lett.* **2009**, *9*, 3930–3933.

(38) Creighton, J. R.; Coltrin, M. E. Origin of reaction-induced current in Pt/GaN catalytic nanodiodes. *J. Phys. Chem. C* **2012**, *116*, 1139–1144.

(39) Nedrygailov, I. I.; Karpov, E. G.; Hasselbrink, E.; Diesing, D. On the significance of thermoelectric and thermionic emission currents induced by chemical reactions catalyzed on nanofilm metal-semiconductor heterostructures. *J. Vac. Sci. Technol., A* **2013**, *31*, 021101.

(40) Park, J. Y.; Somorjai, G. A. The catalytic nanodiode: detecting continuous electron flow at oxide–metal interfaces generated by a gas–phase exothermic reaction. *ChemPhysChem* **2006**, *7*, 1409–1413.

(41) Park, J. Y.; Somorjai, G. A. Energy conversion from catalytic reaction to hot electron current with metal-semiconductor Schottky nanodiodes. *J. Vac. Sci. Technol. B* **2006**, *24*, 1967–1971.

(42) Renzas, J. R.; Somorjai, G. A. Rh thin-film nanocatalysts as chemical sensors—The hot electron effect. *J. Phys. Chem. C* **2010**, *114*, 17660–17664.

(43) Lee, H.; Lee, Y. K.; Hwang, E.; Park, J. Y. Enhanced surface plasmon effect of Ag/TiO<sub>2</sub> nanodiodes on internal photoemission. *J. Phys. Chem. C* **2014**, *118*, S650–S656.

(44) Park, J. Y.; Lee, H.; Renzas, J. R.; Zhang, Y.; Somorjai, G. A. Probing hot electron flow generated on Pt nanoparticles with Au/TiO<sub>2</sub> Schottky diodes during catalytic CO oxidation. *Nano Lett.* **2008**, *8*, 2388–2392.

(45) Sauer, J.; Freund, H.-J. Models in catalysis. *Catal. Lett.* **2015**, *145*, 109–125.

(46) Schierbaum, K.; El Achhab, M. Generation of an electromotive force by hydrogen-to-water oxidation with Pt-coated oxidized titanium foils. *Phys. Status Solidi A* **2011**, *208*, 2796–2802.

(47) Hashemian, M. A.; Palacios, E.; Nedrygailov, I. I.; Diesing, D.; Karpov, E. G. Thermal properties of the stationary current in mesoporous Pt/TiO<sub>2</sub> structures in an oxyhydrogen atmosphere. *ACS Appl. Mater. Interfaces* **2013**, *5*, 12375–12379.

(48) Karpov, E. G.; Hashemian, M. A.; Dasari, S. K. Chemistry-driven signal transduction in a mesoporous Pt/TiO<sub>2</sub> system. *J. Phys. Chem. C* **2013**, *117*, 15632–15638.

(49) Fomin, E.; Tatarkhanov, M.; Mitsui, T.; Rose, M.; Ogletree, D. F.; Salmeron, M. Vibrationally assisted diffusion of H<sub>2</sub>O and D<sub>2</sub>O on Pd(111). *Surf. Sci.* **2006**, *600*, 542–546.

(50) Henzl, J.; Mehlhorn, M.; Gawronski, H.; Rieder, K. H.; Morgenstern, K. Reversible cis-trans isomerization of a single azobenzene molecule. *Angew. Chem., Int. Ed.* **2006**, *45*, 603–606.

(51) Hung, W. H.; Aykol, M.; Valley, D.; Hou, W. B.; Cronin, S. B. Plasmon resonant enhancement of carbon monoxide catalysis. *Nano Lett.* **2010**, *10*, 1314–1318.

(52) Linic, S.; Christopher, P.; Xin, H. L.; Marimuthu, A. Catalytic and photocatalytic transformations on metal nanoparticles with targeted geometric and plasmonic properties. *Acc. Chem. Res.* **2013**, *46*, 1890–1899.

(53) Christopher, P.; Xin, H. L.; Linic, S. Visible-light-enhanced catalytic oxidation reactions on plasmonic silver nanostructures. *Nat. Chem.* **2011**, *3*, 467–472.

(54) Mukherjee, S.; Libisch, F.; Large, N.; Neumann, O.; Brown, L. V.; Cheng, J.; Lassiter, J. B.; Carter, E. A.; Nordlander, P.; Halas, N. J. Hot electrons do the impossible: Plasmon-induced dissociation of H<sub>2</sub> on Au. *Nano Lett.* **2013**, *13*, 240–247.

(55) Lee, Y. K.; Jung, C. H.; Park, J.; Seo, H.; Somorjai, G. A.; Park, J. Y. Surface plasmon-driven hot electron flow probed with metal-semiconductor nanodiodes. *Nano Lett.* **2011**, *11*, 4251–4255.

(56) Avanesian, T.; Christopher, P. Adsorbate specificity in hot electron driven photochemistry on catalytic metal surfaces. *J. Phys. Chem. C* **2014**, *118*, 28017–28031.

(57) Kale, M. J.; Avanesian, T.; Xin, H. L.; Yan, J.; Christopher, P. Controlling catalytic selectivity on metal nanoparticles by direct photoexcitation of adsorbate-metal bonds. *Nano Lett.* **2014**, *14*, S405–S412.

(58) Ke, X. B.; Sarina, S.; Zhao, J.; Zhang, X. G.; Chang, J.; Zhu, H. Y. Tuning the reduction power of supported gold nanoparticle photocatalysts for selective reductions by manipulating the wavelength of visible light irradiation. *Chem. Commun.* **2012**, *48*, 3509–3511.

(59) Kim, S. M.; Park, D.; Yuk, Y.; Kim, S. H.; Park, J. Y. Influence of hot carriers on catalytic reaction; Pt nanoparticles on GaN substrates under light irradiation. *Faraday Discuss.* **2013**, *162*, 355–364.

(60) Denzler, D. N.; Frischkorn, C.; Wolf, M.; Ertl, G. Surface femtochemistry: Associative desorption of hydrogen from Ru(001) induced by electronic excitations. *J. Phys. Chem. B* **2004**, *108*, 14503–14510.



(61) Hess, C.; Funk, S.; Bonn, M.; Denzler, D. N.; Wolf, M.; Ertl, G. Femtosecond dynamics of chemical reactions at surfaces. *Appl. Phys. A: Mater. Sci. Process.* **2000**, *71*, 477–483.

(62) Linic, S.; Christopher, P.; Ingram, D. B. Plasmonic-metal nanostructures for efficient conversion of solar to chemical energy. *Nat. Mater.* **2011**, *10*, 911–921.