In Situ Investigation of Ultrafast Dynamics of Hot Electron-Driven Photocatalysis in Plasmon-Resonant Grating Structures

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Read Online Cite This: J. Am. Chem. Soc. 2022, 144, 3517-3526 ACCESS III Metrics & More Article Recommendations s Supporting Information ABSTRACT: Understanding the relaxation and injection dynam-ics of hot electrons is crucial to utilizing them in photocatalytic In Air 6 Probe (mu) 4 applications. While most studies have focused on hot carrier Time Delay dynamics at metal/semiconductor interfaces, we study the in situ **Relative Shift** 2 Pump dynamics of direct hot electron injection from metal to adsorbates. 0 -2 Here, we report a hot electron-driven hydrogen evolution reaction (HER) by exciting the localized surface plasmon resonance -6 (LSPR) in Au grating photoelectrodes. In situ ultrafast transient 8 absorption (TA) measurements show a depletion peak resulting 1.0 1.5 2.0 Time (ps) 2.5 3.0 Detector from hot electrons. When the sample is immersed in solution under -1 V applied potential, the extracted electron-phonon

interaction time decreases from 0.94 to 0.67 ps because of additional energy dissipation channels. The LSPR TA signal is redshifted with delay time because of charge transfer and subsequent change in the dielectric constant of nearby solution. Plateau-like photocurrent peaks appear when exciting a 266 nm linewidth grating with p-polarized (on resonance) light, accompanied by a similar profile in the measured absorptance. Double peaks in the photocurrent measurement are observed when irradiating a 300 nm linewidth grating. The enhancement factor (i.e., reaction rate) is 15.6× between p-polarized and s-polarized light for the 300 nm linewidth grating and 4.4× for the 266 nm linewidth grating. Finite-difference time domain (FDTD) simulations show two resonant modes for both grating structures, corresponding to dipolar LSPR modes at the metal/fused silica and metal/water interfaces. To our knowledge, this is the first work in which LSPR-induced hot electron-driven photochemistry and in situ photoexcited carrier dynamics are studied on the same plasmon resonance structure with and without adsorbates.

INTRODUCTION

Since the mid 2000s, many researchers have tried improving the photocatalytic performance of metal surfaces and metal/ semiconductor interfaces by exploiting the localized surface plasmon resonance (LSPR), $^{1-7}$ in which the coherent oscillation of free electrons is coupled strongly to electromagnetic fields from incident light.⁸⁻¹⁵ Early studies focused on photothermal effects.^{16,17} Later, LSPR-induced local electric field enhancement was established as an important mechanism in enhancing many photochemical and photoelectrochemical processes.^{18,19} Under LSPR, the absorption cross-section of a metallic nanoparticle (NP) can be 3-5 orders of magnitude higher compared to that of a typical dye-sensitized molecule.²⁰ Using this approach, Liu et al. reported a 66-fold enhancement in the reaction rate by adding Au nanoparticles (NPs) on a catalytic TiO₂ substrate under 633 nm light irradiation. Electromagnetic simulations showed that the highly improved photocatalytic activity is caused by the electric field concentration at AuNP/TiO₂ interfaces.¹⁸ Christopher et al. also showed that by introducing optically active Ag nanostructures onto TiO2 photocatalysts in the methylene blue decomposition reaction, the conversion efficiency of incident photons into e^-/h^+ pairs in TiO₂ was highly increased. They also found that the size and shape of Ag nanostructures have strong effects on the photocatalytic performance of TiO₂.²¹

More recently, hot electron-driven photocatalysis and electrophotocatalysis have drawn considerable interest.^{22–30} Here, nonthermalized hot carriers are induced through nonradiative dephasing (i.e., damping) of plasmon resonance and used to drive high activation energy barrier chemical reactions, such as hydrogen dissociation.^{9,23,31–37} These plasmon-induced hot electrons can be excited near metal surfaces and subsequently transferred to the lowest unoccupied molecular orbitals (LUMOs) of adsorbates.^{9,23} Alternatively, this charge transfer can occur through energy-state hybridization between metal surfaces and adsorbates, leaving hot

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The first demonstration of a chemical reaction driven by hot electrons was the charge-transfer resonance study of paminothiophenol (p-ATP) adsorbed on Ag nanoparticles through the surface-enhanced Raman scattering (SERS) phenomenon in 1994.40 After that, various photochemical reactions driven by LSPR-generated hot electrons have been demonstrated, such as water splitting,^{33,34} CO₂ reduction,⁴¹ and chemical decomposition.^{35,36,42} Mukherjee et al. showcased hot electron-induced H₂ dissociation on Au nanoparticles with visible light irradiation on SiO₂ and TiO₂ substrates. In these studies, hot electrons transfer into H₂ antibonding orbitals, followed by returning to their ground states with elongated bond lengths, ultimately resulting in complete dissociation.^{35,36} Recently, Sytwu et al. discovered new nucleation sites for the phase transformation of palladium hydride, which are activated by LSPR-induced hot spots.⁴³

The timescales of LSPR-induced hot carrier generation and relaxation have been theoretically calculated and experimentally studied.^{9,33,34,44–49} Upon LSPR excitation, the generation of nonthermal hot electrons and holes near metal surfaces occurs from nonradiative LSPR dephasing (within 20 fs), as shown in Figure 1a, which is followed by internal thermal-



Figure 1. (a) LSPR-induced hot electrons and holes are initially extended over a nonthermal distribution and (b) quickly thermalized to a hot Fermi–Dirac distribution (red profile) through electron–electron scattering in 50 fs and subsequently to a room-temperature Fermi–Dirac distribution (blue profile) through electron–phonon scattering within 1 to 10 ps.

ization through electron–electron scattering (Figure 1b). Electron–electron interaction time varies from tens of fs to several hundred fs, depending on the individual nanostructure as well as the optical excitation wavelength and intensity.^{50,51} During and after thermalization, electrons dissipate energy to the nearby lattice through electron–phonon scattering within 1 to 10 ps.^{9,34} Finally, heat is further distributed to the environment through phonon–phonon scattering (100 ps to 10 ns). However, in the presence of adsorbates, chemical interface damping (direct electron transfer) and chemical interface scattering (indirect electron transfer) provide two

additional channels for hot carrier energy dissipation, which are both expected to decrease hot carrier relaxation time.²³

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In the work presented here, in situ transient absorption (TA) measurements are performed under both dry conditions and in solution to compare the hot carrier excitation and relaxation processes with and without adsorbates on the same grating nanostructure photoelectrode. While there are previous studies focusing on ultrafast hot carrier dynamics on plasmonic nanostructures, most of these either focus on colloidal nanoparticles or metal/semiconductor interfaces instead of electrochemically tunable purely metallic surfaces.^{52–59} Within the plasmonics and photocatalysis research communities, it is important to quantify the effect of adsorbates on the electronphonon interaction times during plasmon-induced hot carrier excitation while driving reactions. However, because hot carrier dynamics depend on the metal composition, nanostructure morphology, irradiation wavelength, and intensity, the extracted electron-phonon interaction times vary widely from group to group, making it difficult to compare relaxation time constants between different studies. $^{60-62}$ As such, a direct comparative study on the same plasmonic nanostructure with and without adsorbates is still lacking. To our knowledge, our results are the first to quantitatively examine the effect of adsorbates on hot carrier dynamics in metallic nanostructured photoelectrodes. Another focus in this work is on different spectral shifts observed in TA measurements, which were not studied in our previous research.³⁴ Blue shifting with delay time in air results from the cooling of hot electrons and redshifting with delay time in solution is attributed to charge transfer during the reaction and subsequent change of the dielectric constant at the nearby environment. For many researchers in the community, this red-shifting trend can be used as a quick assessment of whether there is charge transfer. Previously, we drove HER through hot electrons induced by surface plasmon polaritons (SPPs) on continuous film gratings and studied the effect of different incident wavelengths on reaction rates.²⁵ Here, we present different reaction rates of HER utilizing hot carriers originating from the LSPR instead of SPPs. In addition, we focus on different grating linewidths instead of irradiation wavelengths. Finite-difference time domain (FDTD) simulations are used to study the local electric field intensity distribution (i.e., $|E|^2/|E_0|^2$) near the surface of the metal lines on and off resonance. To our knowledge, this is the first work in which in situ photoexcited carrier dynamics and LSPR-induced hot electron-driven photochemistry are studied on the same plasmon resonance structure with and without adsorbates.

EXPERIMENTAL METHODS

Figure 2 shows a scanning electron microscope (SEM) image and a schematic diagram of the grating structure, as well as the photoelectrochemical measurement setup. Here, a periodic array of 50 nm thick Au metal lines with different widths are patterned by photolithography (ASML Holding) and reactive ion etching with a 500 nm pitch on the top of BK-7 fused silica substrates. Copper wires are attached by silver paint (SPI Supplies Inc.) to establish electrical contact for photocurrent measurements using a three-terminal potentiostat (Gamry Inc.). As-fabricated grating is connected to the working electrode with Ag/AgCl (3 M NaCl) as the reference electrode and a Pt wire (BASI Inc.) as the counter electrode. Applied potentials of -0.3 V vs normal hydrogen electrode (NHE) in a 0.5 M Na₂SO₄ (anhydrous ACS, VWR) solution are used to assist in the hydrogen evolution reaction (HER). In order to detect the relatively small photocurrents produced by the nonthermalized, short-lived hot



Figure 2. (a) SEM image of Au grating with 500 nm period and 266 nm metal linewidth. Schematic diagrams of (b) TA measurement, (c) hot electron-driven photocatalytic water-splitting process, and (c) angle-dependent photocurrent measurement setup.

electrons, the incident light (633 nm) is modulated using an optical chopper (Stanford Research System SR-540) at a frequency of 200 Hz, and a lock-in amplifier (Stanford Research System SR-830) is used to measure the signal from the potentiostat (current monitor port) at the specific frequency of the chopper, as shown in Figure 2d.^{19,32,63,64} The grating sample is mount on a motorized rotational stage (Thorlabs, Inc.) in order to sweep the incident angle during photoelectrochemical current measurements, and a half waveplate is used to adjust the polarization direction of the incident light in order to tune on and off the resonance while keeping all the other parameters of the measurement constant.

To probe the ultrafast dynamics of hot electrons during photoelectrochemical hydrogen evolution, in situ TA measurements are conducted. Here, a 680 nm pump and a broadband 400-670 nm probe femtosecond lasers are used in the experiment at the normal incident angle, and both pump and probe pulses are generated using a 1 kHz Ti:sapphire amplifier (Legend Elite HE+, Coherent). Pump pulses are generated using a doubling stage of the optical parametric amplifier (OPA) (OPerA Solo, Coherent) output and modulated at 250 Hz. The broadband white light probe is generated by focusing the Ti:sapphire onto a CaF₂ crystal and modulated using an optical chopper at 500 Hz. A balanced detection scheme is employed to eliminate noise due to fluctuations in the probe spectrum. The probe signal is detected using a charge-coupled device (CCD) camera (Princeton Instruments Pixis) passing through a spectrometer (Horiba iHR320) with a 320 mm focal length and a 150 g/mm grating. The focal spot diameters for the pump and probe are 140 and 180 μ m, respectively. The TA signals are taken as the difference between the absorption of the probe pulse before and after the pump with a certain time delay, which is shown in Figure 2b.

The angle-dependent absorptance and electric field intensity profiles are calculated using the FDTD method (Lumerical Inc.).^{32,65} Au metal lines (50 nm thick) with a period of 500 nm and different linewidths of 266 and 300 nm deposited on the top of fused silica substrates are created with a surrounding environment refractive index of 1.33 (for the aqueous environment). A mesh size of 0.5 nm is used, and a plane wave source is placed above the grating with various incident angles from 0° to 20° and different polarization

directions. Bloch boundary conditions are applied at the sides of the grating, and the direction perpendicular to the grating surface is defined by perfectly matched layer boundary conditions. Power monitors above and below the grating surface are used to capture the reflected and transmitted light for calculating the absorptance. Another power monitor is placed normal to the grating substrate to simulate the field intensity distribution near the surface of metal lines. Spurious effects of total internally reflected light from the bottom surface of the glass substrate are excluded.

RESULTS AND DISCUSSION

In our pump-probe femtosecond pulsed laser system, we selectively pump electrons in the metal, and then, the broadband probes their relaxation back to equilibrium in both wavelength and time.³⁴ The measured signal is the change in absorbance of the probe pulse before and after pump excitation (i.e., $\Delta A = A_{after} - A_{before}$). Figure 3a shows twodimensional (2D) map of the time evolution of in situ TA measurement of a 266 nm linewidth Au grating with a 500 nm period. The sample is immersed in a 0.5 M Na₂SO₄ solution under an applied voltage of -1 V in a two-terminal home-built electrochemical cell with transparent CaF₂ side windows. Figure 3 b shows the TA mapping of the same sample in dry conditions without any water adsorbate. Figure 3c, d presents the horizontal cuts of the measured TA mapping at various time delays for samples in solution and in air, respectively. Pump pulses with 680 nm wavelength excite electrons with energies of up to 1.82 eV below the Fermi level in the Au 6 s band to states above the Fermi level with maximum energy equal to 1.82 eV, leaving hot holes generated. The 680 nm wavelength is selected to be lower than the Au interband transitions (around 2.4 eV) so that the pulse does not disturb the electron energy distribution in the lower Au d band. On the other hand, the 400-670 nm broadband probe pulse covers both interband transitions and LSPR wavelengths. The



Figure 3. TA measurements for Au grating with 266 nm metal line width and 500 nm period (a) in solution and (b) in the air environment with the p-polarized probe pulse. Selected broadband TA spectra of different delay times between the pump and probe (c) in solution and (d) in air condition, respectively. (e) Time evolution of normalized ΔA at 631 and 549 nm for Au grating in solution and in air, respectively. The solid lines are fitted curves based on a monoexponential decay convoluted with 100 fs FWHM Gaussian pump pulse. (f) Relative shift of the plasmon-resonant bleaching peaks in TA spectra as delay time increases.

positive absorption peak shown in Figure 3a around 500 nm is caused by excess interband transitions excited by the probe pulse from the Au 5d band to the 6s band associated with pulse-induced hot holes. In TA measurements on the same sample in air (shown in Figure 3b), the positive modulated signal at 500 nm does not shift with the changing environment, which further confirms its origin from interband transitions.

In contrast, the depletion peak (i.e., less absorption) around 630 nm shown in Figure 3a is caused by LSPR-induced hot electrons from the p-polarized probe pulse. The electric field direction in the probe pulse is perpendicular to the grating lines so that the transverse dipolar resonance mode is excited. However, the LSPR signal for the grating in air (Figure 3b) shifts from 630 to 550 nm because of the different dielectric constant of the environment, which changes from 1.33 (aqueous) to 1 (air). When the probe pulse is s-polarized, there is no depletion peak because no LSPR-generated hot electrons are involved, as shown in Figure S1. After pump laser irradiation, the heating of electrons will cause the probe generated LSPR absorbance signal to be broadened and decrease in intensity, thus creating a dip around 630 nm.^{34,39}

imaginary (ϵ_2) parts of the metal dielectric function, resulting from the pump disturbance. The pump excitation changes the electron distribution based on Fermi-Dirac statistics at higher electronic temperatures, which results in the changes in the dielectric function.⁶⁶ This broadening also corresponds to a faster plasmon oscillation dephasing time. At higher temperatures, more electrons occupy higher energy states, which leads to higher electron scattering rate and increased damping of the plasmon oscillation.⁶⁷ The measured UV-vis transmittance spectrum of one of our 266 nm linewidth Au gratings is shown in Figure S2. Here, the dip observed near 560 nm corresponds to the LSPR, which appears as a depletion peak in TA measurements shown in Figure 3b, d. In addition, the decrease in transmittance for wavelengths below 500 nm observed in Figure S2 is due to interband transitions, which is detected as a positive modulation in the TA measurements (Figure 3b, d).

To quantify and compare the electron-phonon interaction time constants τ_{ep} in air and in solution, we use a simple twotemperature model (TTM), in which electrons with temperature T_e exchange energy with the lattice at temperature T_1 .^{51,68-70} After pump excitation, a broad non-Fermi distribution with electron energies up to the pump photon energy above the Fermi level is created. Energy is redistributed within electrons through electron–electron interactions, leading to a hot Fermi distribution with a definite temperature $T_{\rm e}$. Because the electron–electron interaction time constant is faster than the pump pulse used in our system, we only consider the process after this initial thermalization of electrons is completed. As soon as the electron temperature is well established and assuming electron–electron and phonon–phonon interactions are quick enough to maintain the local temperature of each subsystem, the temperature time evolution can be modeled through the following two coupled differential equations:

$$C_{\rm e}(T_{\rm e})\frac{\partial T_{\rm e}}{\partial t} = \nabla(\kappa\nabla T_{\rm e}) - G(T_{\rm e} - T_{\rm l}) + H(z, t)$$
(1)

$$C_{\rm l} \frac{\partial T_{\rm l}}{\partial t} = G(T_{\rm e} - T_{\rm l})$$
⁽²⁾

where C_{e} and C_{l} are heat capacities of electrons and lattices, respectively, κ stands for the electronic thermal conductivity describing the heat transferred away from the laser spot, G is the electron-phonon coupling constant, and H(z, t) defines the spatial and temporal evolution of the exciting pump energy source. Because the thickness of grating lines studied in this work is only 50 nm thick and 266 nm wide, the initial excitation is homogeneous over the thickness of the sample, and heat diffusion effects are neglected. Ce usually depends on the electronic temperature, but for small changes in temperature, it can be treated as a constant. The increase in the temperature of electrons changes their occupation states near the Fermi level, leading to the absorption modification near the plasmon bleach band and consequently affects the metal dielectric function. When $\Delta T_{\rm e}$ is small, it leads to a linear change in ϵ_1 and ϵ_2 . The optical properties such as changes in absorbance (ΔA), as shown in Figure 3a, b, can be treated as linear combinations of $\Delta \epsilon_1$ and $\Delta \epsilon_2$, which are used to monitor the temperature dynamics and are predicted to decay exponentially based on eqs 1 and 2. Under the assumption of instantaneous thermalization of the electron gas and neglecting heat diffusion as we mentioned previously, the impulse response function in our system has the following form:

$$S(t) = u(t)(e^{-t/\tau_{\rm ep}} + \alpha)$$
(3)

where u(t) is a Heaviside step function, and α accounts for a finite increase in local electron-phonon temperature compared to the initial temperature. α is expected to decay exponentially with the time constant on the order of 100 ps mainly through phonon-phonon interactions.⁵¹ In our system, only signals in the first several ps are collected, so it can be assumed to be a constant.

In order to extract τ_{ep} from our measurements, we did the vertical cut of the TA mapping shown in Figure 3a, b, and the cutting wavelengths are selected for the plasmon bleaching bands to show the highest sensitivity. Figure 3e shows the time evolutions of normalized ΔA at 631 and 549 nm for the 266 nm Au gratings in solution under -1 V potential and in air, respectively. The collected signals are fitted with a mono-exponential decay convoluted with a Gaussian pulse with the full width at half maximum (FWHM) of 100 fs, which corresponds to the finite time duration of the pump pulse. The fitted τ_{ep} for gratings in air is 0.94 ps, which agrees well with the previous reports.^{51,60–62,66} Groeneveld et al. showed from

0.25 to 1 ps electron-phonon relaxation time in Au and Ag thin films when inducing surface plasmon polariton resonance.⁶⁰ Schoenlein et al. reported 2-3 ps relaxation time in Au metal through transient reflectivity measurements, which is on the same order of magnitude as we report here.⁶² However, $au_{
m ep}$ decreases from 0.94 to 0.67 ps when the sample is immersed in 0.5 M Na₂SO₄ solution under -1 V applied potential. This decrease in τ_{ep} clearly indicates extra relaxation channels for the dissipation of electron energy other than electron-phonon interactions. There are two extra relaxation channels. In one channel, after LSPR excitation, the dephasing of the LSPR directly populates electrons from the metal surface to water adsorbates (i.e., chemical interface damping), so the temperature of hot electrons after internal thermalization is less than that of the sample in air. This leads to a smaller temperature difference between electron and phonon subsystems and faster au_{ep} , as observed in Figure 3e. Wu et al. first observed chemical interface damping in cadmium selenide nanorods with gold tips in 2015.⁵⁹ In their study, the quantum efficiency of this process is larger than 24%, which is independent of excitation photon energy over a 1 eV range. In the other channel, after LSPR dephasing and a hot Fermi-Dirac electron distribution is established, the electron subsystem not only transfers energy to the phonon subsystem but also dissipates energy into water adsorbates through hot electron injection (i.e., chemical interface scattering) and drives HER under the applied potential, resulting in faster τ_{ep} .²³

Another feature of this LSPR-related depletion peak is that it is redshifted by 8 nm as the time delay between the pump and pulse is increased from 0.4 to 3 ps (Figure 3c, f). As hot electrons generated by the pump are transferred from the metal surface to adsorbed water molecules' LUMO states, the effective dielectric constant of the water environment is decreased. The decrease in the effective environmental dielectric constant increases the restoring force of free electrons on metal surfaces, leading to the observed increase in the LSPR resonance frequency.^{71–73} This is why we observe shorter wavelength depletion peaks when the delay time is small. As the delay time increases from 0.4 to 3 ps, there is less charge transfer as hot electrons relax back to their original ground states through electron-phonon coupling, which results in a redshift of the depletion peak. There are two mechanisms, as we previously mentioned, which cause charge transfer from the Au electrode to water adsorbates. One mechanism is direct charge transfer (i.e., chemical interface damping), in which higher energy electrons are generated directly in the LUMO states of the surrounding adsorbates, leaving holes in the Au electrode. The other mechanism is indirect charge transfer (i.e., chemical interface scattering). The hot electrons are first generated in the Au photocathode and then migrate into water LUMO states driven by the applied external electric field. In contrast, Figure 3b, d shows TA signals for the same grating structure in air without any applied voltage. Here, the interband transition signal appears at the same wavelength near 500 nm because the interband transitions correspond to the intrinsic properties of Au and do not depend on the surrounding environment or the geometry of the grating. Figure 3f shows the relative shift produced by the plasmon-resonant absorption plotted as a function of time. Here, we can see more clearly the blueshift with delay time in air, which is due to the cooling of the electrons. Yeshchenko et al. studied the temperature dependence of the LSPR in gold



Figure 4. (a) Measured AC photoelectrochemical current, (b) measured and calculated absorptance plotted as a function of the incident angle for the 266 nm linewidth grating. Electric field intensity distributions near the grating surface at incident angles of (c) 4.0° , (d) 8.3° , and (e) 9.3° for p-polarized 633 nm irradiation.



Figure 5. (a) Measured AC photocurrent and calculated absorptance plotted as a function of incident angle for the 300 nm linewidth grating. Electric field intensity profile near the grating surface at (b) 7.5°, (c) 8.5°, and (d) 10.5° for p-polarized 633 nm light.

nanoparticles and found a quasi-linear monotonic blueshift of the LSPR wavelength when the sample temperature decreases from 1000 to 20 °C.⁷⁴ They attributed this trend mainly to the thermal expansion of the nanoparticles. In our work, as the time delay increases from 0.4 to 3 ps, the electron temperature decreases because of electron–phonon scattering, leading to shorter LSPR wavelengths. In summary, a redshift with delay time is observed for Au gratings in solution under -1 V potential, originating from charge transfer, while a blueshift is observed for the same sample in air because of the decrease in the electron temperature.

Figure 4a shows the AC photoelectrochemical current measurement of the Au grating with a 266 nm linewidth and 500 nm period under 633 nm light irradiation. For p-polarized light (electric field perpendicular to the grating lines), LSPR is induced when the incident light angle is between 3.6° and 9° with respect to the grating surface normal. Hot electrons generated from LSPR dephasing are transferred to the LUMO

states of water molecules adsorbed on the metal surfaces through chemical interface damping (i.e., direct electron transfer) or chemical interface scattering (i.e., indirect electron transfer),²³ thus driving the HER ($2H_2O + 2e^- \rightarrow H_2 +$ 20H⁻), as indicated in Figure 2c. Here, no plasmon-resonant hot electrons are generated when the incident light is spolarized (electric field parallel to the grating lines). The photocurrent generated from s-polarized light is mainly caused by interband transitions and is $4.4 \times$ smaller than the photocurrent observed when irradiated with p-polarized light on resonance. That is, the enhancement factor in the reaction rates between p and s polarization is 4.4×. The experimentally measured absorptance shown in Figure 4b also exhibits a similar angle-dependent profile for p-polarized light, as seen in the photocurrent measurement. The FDTD simulated absorptance spectrum shown in Figure 4b exhibits resonant features spanning a range of angles from 4.0° to 9.3° , similar to these observed experimentally. However, the dip around 8.3° is too sharp to be measured experimentally because of the inhomogeneity of the device morphology, leading to a plateaulike profile in the measured photocurrent and absorptance. The simulated electric field intensity distributions (i.e., $|E|^2/|E_0|^2$) at 4.0° , 8.3° , and 9.3° are shown in Figure 4c-e, respectively, and two different dipolar resonance modes are observed. One mode corresponds to the field confinement on metal surfaces near the water environment (Figure 4c) and the other results from a resonant mode with field confinement adjacent to the fused silica substrate (Figure 4e). Sherry et al. reported a similar phenomenon for silver nanocubes on the fused silica substrate.⁷² In their work, when the nanocube is far away from the substrate, the scattering spectra only have one peak associated with the dipolar LSPR mode, and as the nanocube approaches the substrate, this single peak begins to split into two peaks. This is because the underlying fused silica substrate breaks the symmetry of the Au metal line structure and causes an anisotropic dipole oscillation.⁷³

Figure 5a shows the photocurrent measurement as well as simulated absorptance with respect to the incident angle of the Au grating with a 300 nm linewidth and 500 nm period. The simulated absorptance spectrum in Figure 5a shows double peaks feature at 7.5° and 10.5° with p-polarized light corresponding to different dipolar LSPR modes. When the incident light is s-polarized, neither photocurrent nor absorptance shows angle dependence. The electric field intensity profiles at 7.5°, 8.5°, and 10.5° for p-polarized light are shown in Figure 5b-d, respectively. The dip in simulated absorptance shown in Figure 5a is not as sharp as that for 266 nm linewidth grating, and the measured photocurrent in Figure 5a shows the double-peak profile. A higher enhancement factor $(15.6\times)$ of reaction rates is observed when the incident light angle is at 6.7°, which corresponds to the upper surface dipolar LSPR mode and higher absorptance. When light is irradiated at 8.4° , the enhancement factor is somewhat lower (9.5×) because of lower absorptance, and there are fewer adsorbed water molecules in regions where the hot electrons are generated.

CONCLUSIONS

In conclusion, in situ TA measurements probe the dynamics of these hot carriers with both in solution and in air. The extracted τ_{ep} decreases from 0.94 to 0.67 ps when the Au grating is immersed in 0.5 M Na₂SO₄ solution under an applied potential of -1 V, which is mainly due to extra energy

dissipation channels between the metal surface and water adsorbates. The LSPR-induced depletion peak observed in the TA spectra is redshifted with time in solution caused by charge transfer and blueshifted under air, resulting from hot electron cooling. In addition, s and p-polarized angle-dependent photocurrent measurements on 500 nm period Au gratings with different linewidths are conducted to differentiate current driven by hot electrons from interband transitions. A doublepeak profile with an enhancement factor of 15.6×, as well as plateau-like photocurrent profiles with an enhancement factor of 4.4× are observed for 300 nm and 266 nm linewidth gratings, respectively. FDTD simulations show two peaks in the absorptance spectra for both gratings, corresponding to different dipolar LSPR modes near and far away from the grating/substrate interfaces.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c12069.

Transient absorption spectra of 266 nm linewidth Au grating when the probe is s-polarized; measured UV-vis spectrum of 266 nm linewidth Au grating in air (PDF)

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Notes

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