SUPPORTING INFORMATION

High Quantum Efficiency Hot Electron Electrochemistry

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Figure S1a shows a schematic of the current flow map in our device. It notes the measured currents ($I_{\text{Solution}}$, $I_{\text{Au}}$, $I_{\text{Si}}$) and the internal currents components in the device. Specifically, we note that there are 4 components we need to consider: (i) the diode current between Si and gold, (ii) the thermal electron reduction current between the solution and gold, (iii) the hot electron reduction current between the solution and gold, and finally (iv) the direct silicon injection current from the silicon into the solution. Our measurement setup uses two working electrodes to simultaneously apply bias between the gold/silicon and gold/solution. Thus, we have two sets of counter electrodes (CE 1 & CE 2), working electrodes (WE 1 & WE 2), and reference electrodes (RE 1 & RE 2). In a potentiostat, current flows between the working electrode and the counter electrode, while the reference electrode is used to set the voltage\(^1\). To apply voltage between the gold and solution, we connect WE 1 to the gold, CE 1 to a platinum wire in the solution, and RE 1 to an Ag/AgCl as the reference electrode also in the solution. To simultaneously apply voltage between the gold and silicon, we connect the silicon to WE 2, the gold to RE 2, and the platinum wire to CE 2. This allows us to control the voltage of these two junctions (Au/Si and Au/Solution) independently. $I_{WE1}$ and $I_{WE2}$ represent working electrode current in channel 1 and 2. $I_{CE1}$ and $I_{CE2}$ indicate

**Figure S1.** Current flow across the device and measurement set up. a, The directions of all the current components. b, The schematic of measurement system connections.
counter electrode current in channel 1 and 2, which are connected in series to a Keithly Multimeter to measure the solution current more precisely. Supplementary Figure S16 shows the accurate overlap between the currents measured from the potentiostat and the multimeter.

**Three terminal current measurement**

Three different currents were measured to investigate the behavior of the MIS hot electron device using the described measurement setup. The Si current and the Au current were measured through the potentiostat and the solution current was measured using the digital multimeter (Figure S1.). The relationships between the different current components are as shown below:

\[
I_{WE1} = I_{Au} = -I_{CE1} \tag{1}
\]
\[
I_{Au} = I_{Au-Solution} - I_{Au-Si} \tag{2}
\]
\[
I_{Au-Solution} = I_{Hot electron} + I_{Thermal electron} \tag{3}
\]
\[
I_{WE2} = I_{Si} = -I_{CE2} \tag{3}
\]
\[
I_{Si} = I_{Au-Si} + I_{Direct Injection} \tag{4}
\]
\[
I_{Solution} = I_{CE1} + I_{CE2} = -(I_{Au-Solution} - I_{Au-Si}) - (I_{Au-Si} + I_{Direct Injection}) = -I_{Au-Solution} - I_{Direct Injection} = -(I_{Hot electron} + I_{Thermal electron} + I_{Direct Injection}) \tag{5}
\]

Equations (1) and (3) represent the working electrodes connected to Au and Si, respectively. The counter electrode current will be the negative value of working electrode since it has an opposite direction to the working electrode in the closed potentiostat system. Equation (2) shows that the measured gold current represents the hydrogen reduction current minus the diode current. We claim that the hydrogen reduction current at the Au surface is composed of hot electrons and thermal electrons. Equation (4) shows the components of Si current. Nominally, the Si current should be the same whether the diode is in solution or out of solution, and is represented by the diode current, \( I_{Au-Si} \). However, our experiments show that there is an increase in the measured silicon current without a commensurate increase in the gold current, suggesting that there are some conditions under which electrons are directly injected into the solution from the silicon. This also
contribute to the Si current, which is what is described in equation 4. Finally, we can get the total current by adding the current from both counter electrodes, shown in equation 5. When we add the two together, we see that the measured counter electrode current, $I_{\text{Solution}}$, will be composed of three different components, $I_{\text{Hot electron}}$, $I_{\text{Thermal electron}}$, and $I_{\text{Direct Injection}}$.

**S2. Modification of voltage sources in measurement system**

1. **Measurement system control test setup – Supply $V_{\text{Au-Si}}$ with the voltage source**

   In order to confirm that the measured results were not a circuit level effect, we used a 2-terminal voltage source/multimeter to bias the Au/Si diode while keeping the Au/Solution potentiostat connection. Figure S2a shows the measurement setup. Figure S2b-d shows the accurate fitting between the potentiostat and the voltage supplier of solution current at fixed $V_{\text{Au-Si}}$.

   **Figure S2.** Accurate fitting between the potentiostat and the voltage supplier of solution current at fixed $V_{\text{Au-Si}}$. a, Measurement setup, b-d, Redox current density in $V_{\text{Au-Si}} = 0.5V, 1.0V$, and $1.5V$.
comparison results using the voltage source plus a single potentiostat channel versus using two potentiostat channels simultaneously. These results are nearly identical and show that this could not explain the results.

2. Measurement system control test setup – Supply both $V_{Au-Si}$ and $V_{Au-Solution}$ with two voltage sources

We also just used two voltage sources, one to bias the Au/Platinum and one to bias the Au/Si. While this is a 2 terminal solution measurement with a thin Pt wire, we wanted to ensure that some change was seen, to eliminate the complex circuitry of the potentiostat. Since there is no

Figure S3. Effect of $V_{Au-Si}$ without using the potentiostat system. a, Measurement setup, b, Solution current density in different fixed $V_{Au-Si}$ across $V_{Au-Pt}$ and c, log scale of b. solution current at fixed $V_{Au-Solution}$. a, -0.2V, b, -0.4V and c, -0.5V of $V_{Au-Solution}$.
Ag/AgCl reference electrode, the voltage drop across the electrolyte to the Pt counter electrode limits the effect. However, the results show that as we increase the $V_{Au-Si}$, it clearly affects the solution current.

3. Measurement system control test setup—Supply $V_{Au-Si}$ with battery

![Figure S4. Comparison between the potentiostat and a 1.5V battery connected to Au-Si junction. a, Measurement setup, b, Solution current comparison in different biasing condition, c, log scale of b.](image-url)
Lastly, we also tested the biasing the $V_{Au-Si}$ by using a 1.5V battery. The results do not exactly overlap with the 1.5V applied using the potentiostat, however, this is due to the actual voltage supplied by the battery not being exactly 1.5V.

S3. Control Samples – Lateral Resistance and Pinholes in Gold Film

In order to ensure that lateral resistivity of the thin gold film (Figure S5a), or pinholes in the gold film (Figure S5b) were not the cause of the observed effect, we carried out two sets of control measurements and simulations. The first set of measurements was done to identify how much voltage drop we might expect laterally across the gold film due to the current flow in the electrode. The second, was a control sample with thick gold and lithographically defined holes in the gold to simulate the effect of pinholes in a controlled fashion. Both of these effects will be influenced by the surface roughness of the electrode, resistance of the gold electrode, and shape of contact.\(^2\),\(^3\).

First, we evaporated 12 nm and 100 nm gold films onto a 6nm Al$_2$O$_3$ deposited with an atomic layer deposition (ALD) on Si/SiO$_2$ handle substrate. By using a thick SiO$_2$ layer of 2 \(\mu\)m, we ensured that the Au was electrically isolated from the underlying Si. Next, we evaporated 4 bar electrodes using of 100 nm silver through a shadow mask. We used the outer two bars to inject current and the inner two bars to measure the voltage drop. Figure 6a and 6b show the measured voltages on the two inner bars. The actual voltage drop across those two bars is then the subtraction of the two lines shown in each graph. We carried these measurements out on both 100 nm thick and 12 nm thick gold. From the measurements we were able to extract resistivity and sheet resistance, as shown in Table 1. Importantly we got similar resistivity values for both 12 nm and 100 nm thick films, but with about a 10x difference in sheet resistance, which is expected. Using this data, we could then carry out a
The full 3-D simulation of the diode with the gold contact using the resistivity measured experimentally. By doing so, we could then identify what kind of voltage variation we could expect across our gold film during diode operation.

To minimize the voltage distribution across the film, a silver paste rectangular ring shape contact was used, as shown in the inset of Figure S7a. We then carried out a dry I-V measurement, and carried out a 3-D TCAD Sentaurus simulation to match the simulation. Figure S7a shows the overlap between our measured J-V curve and simulated J-V curve. We can see that the characteristics are highly similar. Since we had already measured the resistivity of different thickness of gold as shown in Figure S6 and Table S1, we simply used that value as an input parameter for Sentaurus simulations. The important feature of these Sentaurus simulations is that the current density from the device is accurate, and the size of the device simulated in Sentaurus matched the real world size. Therefore, allows us to get a realistic map of the voltage drop expected across the gold surface. Figure S7b shows a heat map of the potentials extracted from the Sentaurus simulation for the potential in the gold laterally. This result was extracted at a

<table>
<thead>
<tr>
<th>Thickness</th>
<th>R</th>
<th>Rs</th>
<th>$\rho$</th>
</tr>
</thead>
<tbody>
<tr>
<td>12nm</td>
<td>5.5Ω</td>
<td>24.9</td>
<td>$298\times10^{-9}\Omega\cdot m$</td>
</tr>
<tr>
<td>100nm</td>
<td>0.59Ω</td>
<td>2.67</td>
<td>$267\times10^{-9}\Omega\cdot m$</td>
</tr>
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**Table S1.** Sheet Resistance ($R_s$) and Conductivity can be derived from measurement. Both ~12nm and ~100nm Au films show similar conductivity values.

**Figure S6.** Four-probe measurement of **a**, ~12nm Au film on SiO$_2$ and **b**, ~100nm Au film on SiO$_2$. Both films were measured with 1mm spacing between four probes.
voltage which resulted in a current density of 10 mA/cm$^2$ results of the electrostatic potential distribution on the thin gold surface from ring contact to center of the thin film. From the heatmap of voltage distribution, we see that the difference of the highest electrostatic potential (0.3609V) to the lowest point (0.3547V) is 0.0062V. Thus, we estimated that we get ~6 mV of lateral voltage drop for every 10 mA/cm$^2$ flowing through the device. Since we worked between 0-30 mA/cm$^2$, we expect the overall lateral voltage drop to be negligible for the magnitude of the effect we see here.

Controlling the surface roughness of thin Au film is also important, as there can be pinholes that form in the gold, which will both increase resistivity, and cause the solution to contact the Si/Al$_2$O$_3$, neither of which is desirable here. To minimize this, we carry out our gold film evaporation using a thermal evaporator with the substrate held at ~90K. This low temperature minimized mobility of the deposited gold atoms and enables highly smooth surfaces. Figure S8

**Figure S7.** a, Fitting results of experiment and simulation diode curves. b, Sentaurus electrostatic potential simulation with the silver ring contact modeled device

**Figure S8.** AFM analysis of the 12nm Au film. 12nm Au film evaporated with cryogenic temperatures. The RMS roughness for this film was measured to be 0.71 nm from the AFM.
shows AFM measurements of the cryo evaporated 12 nm Au film. The RMS roughness extracted from this AFM measurement is 0.71 nm, which is extremely smooth.

However, to test the effect of pinholes in the gold film, we fabricated a device which has a 100 nm thick Au film with lithographically defined holes with 1 μm radius and a 30 μm pitch. These holes are meant to simulate the effect of pinholes in our gold film. In Figure S9, we show the redox measurements for applied diode biases of 0V, 1V, and 2V. Importantly we see minimal shift in the resulting electrochemical J-V curves. This result shows that the magnitude of the observed behavior cannot come purely from current being directly injected into the solution from Si.

S4. Metal-Semiconductor Hot Electron and Control Devices

In addition to the study of the lateral resistivity and pinholes, we created several metal semiconductor devices to study this effect. Specifically, we create (i) thin gold/n-Si devices which mirrored our MIS devices, but without the insulator layer, (ii) thick gold/n-Si devices, and (iii) thin gold/n++-Si devices, where a heavily doped silicon wafer was used. Figure S10 shows the results from these devices. First, Figure S10a shows the cartoon band diagram for the thin Au/moderately doped Si device, and the corresponding measurements are shown in Figure S10d. We see that a similar effect as previously observed for the MIS structure is observed. Next, Figure S10b shows the cartoon band diagram for thick Au/moderately doped Si, and Figure S10e shows the corresponding electrochemical measurements. As we see from the curves, there is essentially no effect. Finally, Figure S10c shows the cartoon band diagram for thin gold/heavily doped Si. In this device, since the electrons are injected at the Fermi level of the gold, it is not expected that there will be any observed effect. Figure S10f shows the electrochemical current vs voltage curves for
The heavily doped gold device, again showing minimal effect. Thus, of the three samples, the only device which showed a significant effect was the sample with thin gold and moderately doped Si. For the thick gold device, we expect that the majority of the injected hot electrons will have lost their energy by the time they reach the surface, so there is not going to be a significant population of hot electrons. For the heavily doped Si device, the Schottky barrier width in the silicon will be very small, which will cause electrons to directly tunnel into the gold, so even though the gold film is thin, the injected electrons will not be hot.

**Figure S10. Control devices band diagram and measurements.** a, Band diagram of MS device with ~12nm Au, b, with ~100nm Au and c, with heavily doped Si emitter. d, Solution current result from device ‘a’, as injected current to base increased, it shows hot electron effect. e, from device ‘b’, showing no hot electron effect due to thick Au region, and f, from device ‘c’, no hot electrons generated from emitter region, due to narrow barrier.
**S5. Device Stability measurement in different conditions**

![Graphs showing device stability measurement](image)

**Figure S11. Device stability measurement in before/after electrochemistry experiment.** a, linear scale of device current measurement before and after HER measurement. Note that measurements were carried out about 1 year apart. Strongly indicating stability of device. b, log scale of a. c, Redox current measured in fixed voltage condition for 1-hour.

Stability tests were conducted to show our device is stable in a 0.5M H₂SO₄ solution under measurement conditions. Figure S11a and b shows the comparison between diode I-V curves before and after the electrochemical measurements were carried out in linear scale (Figure S11a) and log scale (Figure S11b). The initial device current was measured before any electrochemical measurement inside a 0.5M H₂SO₄ solution. After the electrochemical experiments included in this paper were carried out, we remeasured the diode J-V characteristics again. It should be noted that between the initial fabrication of the device, and the “post-electrochemical measurement”, about 1 year elapsed. Additionally, a large number of measurements were carried out. As we see from Figure S11a,b, there is almost no change in the device behavior. We use this data to show that the MIS device is stable. Additionally, Figure S11c shows the device electrochemical current when it is biased to $V_{Au-Si}$=1 V and $V_{Au-Solution}$=-0.8 V for 1 hour. While we see an initial drop, the current is overall stable. The initial drop is attributed to some fraction of the surface being covered by bubbles due to the HER.
S5.1 Current Stability measurement in different conditions

![Figure S12](image)

Figure S12. Current stability measurement in different conditions along the time. Silicon, Au, and Solution current at **a**, $V_{Au-Si} = 1.0V$, $V_{Au-Solution} = -0.2V$, **b**, $V_{Au-Si} = 2.0V$, $V_{Au-Solution} = -0.2V$, **c**, $V_{Au-Si} = 1.0V$, $V_{Au-Solution} = -0.4V$, and **d**, $V_{Au-Si} = 2.0V$, $V_{Au-Solution} = -0.4V$. 

[108x138] $V_{Au-Si}$ $V_{Au-Solution}$

[285x159] $V_{Au-Si}$ $V_{Au-Solution}$
S6. Device Quantum Efficiency

In this study, we present the device quantum efficiency to characterize how many hot electrons can be extracted from the device. Quantum efficiency was calculated by dividing the hot electron current density in solution ($J_{\text{Hot Electron}}$) current to the current density injected to the Au region from the silicon/gold bias. Figure S14a shows the quantum efficiency of the device along

Figure S13. Three component currents in fixed $V_{\text{Au-Solution}}$ at a, 0V, b, -0.2V, c, -0.4V, and d, -0.8V.
the solution voltage. It indicates that when $V_{Au-Solution}$ increases, the quantum efficiency increases tremendously. It is noteworthy that at $V_{Au-Si} = 2.0V$ and $V_{Au-Solution} = -1.5V$ point, quantum efficiency reaches to ~85% and appears to saturate. Figure S14b shows the quantum efficiency of device as a function of the diode bias, $V_{Au-Si}$. It shows that at a fixed $V_{Au-Solution}$ bias, higher $V_{Au-Si}$ improves the quantum efficiency.

![Figure S14](image-url)

**Figure S14. Quantum Efficiency of Device in different conditions.** a, Quantum Efficiency vs $V_{Au-Solution}$ in different fixed $V_{Au-Si}$ values., b, Quantum Efficiency vs $V_{Au-Si}$ in different fixed $V_{Au-Solution}$ values.
Analysis of series resistance of back contact of diode

Figure S15. Ohmic behavior of the back contact of device. The contact is one of the significant factors in device measurement. To reduce the current loss in the contact region, Ag was introduced as a contact material to n-type Si. Ag, which has work function ~4.7eV forms the ohmic contact with n-type Si. We can see that in higher voltage regime, the resistivity starts to increase due to the series resistivity. This behavior of back contact affects the device measurement results.
S8. Ensuring accuracy between potentiostat and multimeter measurements

One challenge with the potentiostat is the relatively low resolution for the current measurement. To enable measurements to lower current levels, we used an external multimeter connected in series to the platinum electrode. Here, we show that for the high current measurements, the measured currents are nearly identical for both the potentiostat and the multimeter. By using the two channels of the potentiostat, we can measure two different currents ($I_{Si}$ and $I_{Au}$) and $I_{Solution}$ can be determined by adding two currents. Since $I_{Si} + I_{Au} + I_{Solution} = 0$, we can always know the solution current from the measurements of the Si and Au currents. However, the limited resolution of the potentiostat limits the minimum current we can measure. We connected the multimeter between the potentiostat and counter electrode to measure the Redox current more precisely when chemical reactions happen. Figure S18 shows accurately overlapped solution current measured with the multimeter and the potentiostat, respectively.

![Figure S16. Accurate fitting between the potentiostat and the digital multimeter of solution current at fixed $V_{Au-Solution}$.](image)

Figure S16. Accurate fitting between the potentiostat and the digital multimeter of solution current at fixed $V_{Au-Solution}$. **a**, -0.2V, **b**, -0.4V and **c**, -0.5V of $V_{Au-Solution}$. 
S9. Measurement in different pH medium

To show that our effects are not only coming from the acid medium, we measured the sample in a neutral solution (pH = 7, 0.1M K₂SO₄). Figure S17 shows the solution current

**Figure S17.** HER in D.I water condition. **a,** $I$-$V$ measurement of solution current of linear scale and **b,** log scale measured in different fixed $V_{Au-Si}$ values. **c,** $I$-$V$ measurement of solution current of linear scale and **d,** log scale measured in different fixed $V_{Au-Solution}$ values.
measured with the same bias condition in the acid (pH = 0, 0.5M H₂SO₄) medium. We show that for this, we also observe a similar change in current as a function of applied bias. However, we note that it is dramatically smaller. The increase in current is from ~ 0.1mA/cm² to ~0.75mA/cm² as we modify the bias conditions. Our interpretation of these results center on the idea that the lower [H⁺] concentration is responsible for a lower injection rate of hot electrons from the gold into the solution, dramatically reducing the overall efficiency.

**S10. Bubbling at device surface**

In Figure S18 we show two images, Figure S18a shows the device with both the Au-Solution and Au-Si are biased to 0V. This gives us no current or hydrogen generation. Next, while keeping the Au-Solution voltage at 0V, we turn on only the Au-Si voltage to 2V. At this point we see bubbling that as the device turns on, we see bubble generation. At this bias condition, the solution current is ~0.1-1 mA/cm².

![Image of bubbling at device surface](image)

**Figure S18. Gas formation at different biasing conditions.** **a**, No reaction happens at non-biased condition for both Au-Solution and Au-Si. **b**, Hydrogen generation happens at 2.0V Au-Si biased condition without biasing Au-Solution voltage.

**S11. Monte Carlo Simulation**

**S11.1 Monte Carlo simulation of the nonequilibrium carrier dynamics of gold**

The dynamics of electrons injected into gold from silicon has been treated with the aid of an open-source 2D ensemble Monte Carlo (MC) simulator, Archimedes⁵. We have modified the code to incorporate the scattering mechanisms relevant to gold. We have considered a rectangular region
of gold with a width of 12 nm and a length of 300 nm. The shorter dimension corresponds to the transport direction of the injected electrons. We have considered a parabolic dispersion relationship for gold with an effective mass equal to that of free electrons. Since our simulation takes only two dimensions into account, it is necessary to properly normalize the data with respect to thermal electrons vs injected electrons. To do so, we initialize the simulation with 1 million particles, which corresponds to a 3-D sample with a volume of $300 \times 12 \times 4.7 \, \text{nm}^3$, considering the gold carrier density of $5.9 \times 10^{28} \, \text{m}^{-3}$ for the conduction band. This depth factor then allows us to properly normalize the effect of the injected electrons with the thermal electrons.

**S11.2 Initial equilibrium carrier distribution**

We begin the simulation by initializing the equilibrium carrier distribution of gold according to the temperature of the lattice (300K) and the density of states (DOS) of gold. The DOS used for gold in this simulation has been extracted from the work of Ladstadter et. al, who used first-principles based calculations to obtain the DOS. We only consider the conduction band of gold where the Fermi level of gold lies 5.5 eV above the bottom of the conduction band.

**S11.3 Scattering mechanisms**

There are two major scattering mechanisms that affect the carrier dynamics of gold: (1) electron-electron scattering and (2) electron-acoustic phonon scattering. Gold has no optical phonon branch since it has only one atom per unit cell.

**S11.4 Electron-electron scattering**

Electron-electron scattering rate in gold has been calculated using Fermi’s golden rule that is given by

$$\frac{1}{\tau_{\text{ee}}} = \frac{2\pi}{\hbar} \sum_{(k_1,k_2),(k_3,k_4)} |M(k_1,k_2,k_3,k_4)|^2 (1 - f(k_3)(1 - f(k_4)) \delta_E$$

Here, $\frac{1}{\tau_{\text{ee}}}$ is the electron-electron scattering rate, $M(k_1,k_2,k_3,k_4)$ is the matrix element for the transition between the initial state $|k_1,k_2\rangle$ to the final state $|k_3,k_4\rangle$, $f(k)$ is the Fermi-Dirac distribution, and $\delta_E$ stands for the energy conservation. The matrix element for electron-electron scattering in gold is given by

$$M(k_1,k_2,k_3,k_4) = \frac{e^2}{\epsilon(q)|q|^2 + q_{TF}^2} \delta_{q_{k_1-k_3}} \delta_{q_{k_4-k_2}}$$
Where \( q = k_1 - k_3 = k_4 - k_2 \) is the change in wavevector, \( q_{TF} \) is the Thomas-Fermi screening momentum \( (q_{TF}^2 = \frac{3N_0e^2}{2\epsilon_0E_F}) \) where \( N_0 = 5.9 \times 10^{28} \text{ m}^{-3} \) is the carrier density in gold, \( E_F = 5.5 \text{ eV} \) is the Fermi level, \( \epsilon(q) \) is the screened dielectric function \( (\epsilon(q) = \epsilon_0(1 + \frac{q_{TF}^2q^2}{\epsilon_0}) ) \), and the delta functions stand for the momentum conservation. Since we consider scattering due to coulombic interaction between two electrons, we randomly choose an electron from the Fermi sea which acts as a scattering partner for the electron that is being simulated before every scattering event. The conduction electrons in gold are predominantly from 6sp orbital and they have a vanishing matrix element while scattering with d-band electrons\(^6,11\). Therefore, we excluded the d-band electrons while choosing the partner electrons. The inclusion of \((1 - f(k_3))(1 - f(k_4))\) term ensures that an electron cannot scatter into a state that is already occupied hence satisfying the Pauli blocking principle. We dynamically track the energy resolved distribution of the electrons to take Pauli blocking into consideration. Then we numerically calculate the scattering rate prior to every scattering event. Using a free parameter, we have fit the electron-electron scattering rates to that calculated by Ladstadter et. al\(^6\) as shown in Figure S19. Ladstadter et. al\(^6\) used first principles calculation approach to calculate the rates from the complete electronic band structure of gold.

S11.5 Electron-acoustic phonon scattering

We have extracted the electron-acoustic phonon scattering rates from the work of Lugovskoy et. al\(^10\) as shown in figure 5(a) of the main text. These scattering rates were calculated using a pseudopotential approach considering the phonon dispersion relationship as well as the band structure of gold calculated in a first principles approach.
S11.6 Calculation of final states

In order to calculate the final states after each electron-electron scattering event, we have considered both the energy and momentum conservation laws. Let the initial wavevectors of the two electrons be \((k_{x1}, k_{y1}), (k_{x2}, k_{y2})\) and the final wavevectors be \((k_{x3}, k_{y3}), (k_{x4}, k_{y4})\). Then the energy conservation requires 
\[
(k_{x1})^2 + (k_{y1})^2 + (k_{x2})^2 + (k_{y2})^2 = (k_{x3})^2 + (k_{y3})^2 + (k_{x4})^2 + (k_{y4})^2
\]
whereas momentum conservation requires 
\[
k_{x1} + k_{x2} = k_{x3} + k_{x4} \quad \text{and} \quad k_{y1} + k_{y2} = k_{y3} + k_{y4}
\]
13,14. If we do not have any further information, there are an infinite number of solutions for the unknowns \((k_{x3}, k_{y3})\) and \((k_{x4}, k_{y4})\). However, if we fix the energy of one final state hence automatically fixing the energy of the other final state, the solution becomes unique. Therefore, we check the energies of all the available final states and randomly choose the energy of one final state. This is equivalent to choosing the values of both \((k_{x3})^2 + (k_{y3})^2\) and \((k_{x4})^2 + (k_{y4})^2\). With these new information, it is possible to find unique solutions for \((k_{x3}, k_{y3})\) and \((k_{x4}, k_{y4})\). After analytically solving the equations mentioned above, we update the wavevectors of both electrons accordingly.

On the other hand, the phonon band structure of gold requires the acoustic phonon energy to be between 0~3 meV12, 13. For electron-acoustic phonon scattering, we randomly choose an energy between 0~3 meV for the phonon. Then we randomly assign the wavevectors of the final state so that the energy of the final state equals the sum (difference) of the energy of the initial state and the phonon for absorption (emission) of phonon.

S11.7 Dynamic calculation of the electronic temperature

A thermalized distribution of electrons can be associated with an equivalent electronic temperature following the Fermi-Dirac distribution
\[
f = \frac{1}{e^{(E-E_F)/k_BT}+1}
\]
Here, \(k_B\) is the Boltzmann constant, \(T\) is the electronic temperature, and \(E_F\) is the Fermi level.

From this equation, we can write
\[
\frac{df}{dE} = -\frac{f^2}{k_BT}e^{(E-E_F)/k_BT}.
\]
At \(E = E_F\), \(f = 0.5\) and 
\[
\frac{df}{dE} = \frac{(0.5)^2}{k_BT}e^{E_F/k_BT} = -0.25\frac{E_F}{k_BT}.
\]
Therefore, \(\frac{df}{dE}\) vs \(\frac{1}{T}\) plot will have a minima at \(E = E_F\) from which we can easily determine the electronic temperature, \(T\). We dynamically calculate the distribution and pass it through a smoothing function so that the noise around the minima is greatly reduced. Then, we calculate the electronic temperature by identifying the minima of the distribution at the Fermi level.
Monte Carlo simulation results - Attempt rates of hot electrons

To study the effects of the injected electrons, we have simulated for a situation where we inject 1 electron into gold every 5 fs whereas we start the simulation with 1 million electrons. The injected electrons either transfer the energy to other electrons via e-e scattering or to the lattice via phonon scattering. While going through these scattering processes, it travels inside gold with a group velocity $v = \sqrt{\frac{2E}{m}}$. As a result, these electrons bounce back and forth between the walls of the gold region in the transport direction (12 nm apart). Here, we use the analog of the attempt rate in tunneling theory to normalize the effect of the injected electrons to the thermal electrons. Thus, in this formalism, each time an electron reflects off the gold solution interface, it attempts to tunnel into the solution to drive the redox reaction. However, the actual probability of tunneling into the solution is related to the specific redox reaction, the concentration of the reactant as the surface etc. The number of reflections per unit time correspond to the attempt rate of the hot electrons which essentially gives us a quantitative understanding of how frequently the hot electrons are attempting to interact with the gold-electrolyte interface. With that in mind, we calculated the energy-resolved attempt rates of the hot electrons in gold for different injection energies as shown in Figure S20a. The thermal electrons get accelerated when they gain energy from the injected electrons.

![Energy resolved attempt rates](image)

**Figure S20:** a, Energy resolved attempt rates calculated at different electron injection energies b, match between the electronic temperature profile calculated by Jiang et. al. from pump-probe experiment and our MC simulations.
electrons and they tend to hit the gold-electrolyte interface more compared to the case where no electron is injected. The injected electrons help populate the higher energy states and these states also contribute to the total attempts. Some fraction of the injected electrons interacts with the gold-solution interface without significant scattering, giving rise to a peak in the attempt rate at the injection energy.

**S11.9 Calculation of the attempt rates**

During the simulation, the $i^{th}$ electron has a momentum $(k_{xi}, k_{yi})$ and we have set the x-direction as the transport direction. A positive (negative) value of $k_{xi}$ means the electron would move to the $+x$ ($-x$) direction. We consider that there is no electric field present inside gold and hence the change in position of the electron is decided by the equation, $m_0 \frac{dx}{dt} = \hbar k_{xi}$ where $dx$ is the change in position in x-direction after a time $dt$, and $m_0$ is the effective mass of an electron in gold which we have assumed to be equal to the free electron mass as stated earlier. At the device transport boundary ($x=12$ nm), we set a boundary condition such that if the final position of an electron at a certain time were to exceed the boundary ($x_{final} = 12 + x_0$ nm), the electron would be elastically reflected ($x_{final} = 12 - x_0$ nm). Then we obtain the energy resolved attempt rates by registering the total number of attempts at hitting the boundary at different energies with an energy bin size of 0.01 eV. In the steady state, the energy resolved attempt rates for the thermal electrons follow the profile of the actual number of electrons available at each energy, hence follow the $D(E)f(E)$ profile. At energies higher than the Fermi level, the Fermi-Dirac distribution, $f(E)$ falls exponentially and so does $D(E)f(E)$. Since we simulate a finite number of electrons, the simulation itself cannot capture such small numbers. Therefore, we extrapolate the energy resolved attempt rates by fitting it to the numerically calculated $C \times D(E)f(E)$ profile where $C$ is a constant. For the simulations that include the injection of hot electrons, we calculate the energy resolved attempt rates in the same way. However, since we use a much higher injection current density during the simulation compared to the real device, we need to normalize these rates to the injection current density of the real device to get a quantitative understanding of the attempt rates. The energy resolved attempt rate profile for hot electron injection has two components: (1) attempts due to thermal electrons that follow the $D(E)f(E)$ profile and (2) attempts due to the hot electrons. We subtract the thermal component from the overall energy resolved attempt rates and
that gives us the attempts due to the hot electrons only. We assume that the energy resolved attempt rates due to the hot electrons is linearly related to the injection current density and therefore we linearly scale the rates to the real injection current density. Since the number of thermal electrons is much larger than the injected electrons, we can assume that the change in attempts due to the thermal electrons is negligible as a function of injection current density. Following this assumption, we sum the scaled energy resolved attempt rates due to hot electrons with the \( C \times D(E) f(E) \) profile calculated before and this sum gives us the overall energy resolved attempt rates for hot electron injection normalized to the real injection current density.

**S11.10 Normalization of the attempt rates**

In the real device, the injected current density is in the order of \( \sim 10^2 \, \text{Am}^{-2} \). However, such a small injection current density would require us to simulate for several microseconds if we want to build a good statistics of simulation results. Since the scattering processes have a lifetime in the order of \( \sim 0.1 \, \text{fs} \), it would take a very long time to perform those simulations if we want to capture the effects of the scattering events on the transport of the injected electrons which is not computationally feasible. Therefore, we perform the simulations with a relatively high injection rate of 0.2 electrons/\( \text{fs} \) which corresponds to an injection current density of \( 2.26 \times 10^{10} \, \text{Am}^{-2} \) where the cross-section area of the device is \( 300 \times 4.7 \, \text{nm}^2 \) (12 nm being the transport length). To get a quantitative understanding of the simulation results, we need to normalize the attempt rates to an injection current density that we observe in the real device (\( \sim 260 \, \text{Am}^{-2} \)). This can be achieved by dividing the attempt rates by the ratio \( \frac{2.26 \times 10^{10}}{260} = 8.71 \times 10^7 \). Since we calculate the attempt rates within an energy bin of 0.1 eV, the energy resolved attempt rates also need to be normalized to the quantized energy bin size. This will give us the attempt rates in the units \# attempts/(eV-\( \text{fs} \)). Finally, we normalize this attempt rate to the cross-section area of the simulated device (\( 300 \times 4.7 \, \text{nm}^2 \)) which gives us the attempt rates in the units of \# attempts/(eV-\( \text{fs}-\text{cm}^2 \)). The normalized attempt rates obtained using this procedure have been shown in Figures 5c and 5d of the main text.

**S11.11 Reproducing published results with Monte Carlo simulations**

To verify the accuracy of our phonon scattering rates, we have tried to reproduce the experimental pump probe spectroscopy results for gold from the work of Jiang et. al\(^{14, 15}\). They have showed that a 140 fs pump pulse of 1053 nm center wavelength with a fluence of 0.05 J/cm\(^2\) can increase the electronic temperature up to \( \sim 3250 \, \text{K} \) and the excited distribution cools down to the lattice temperature within \( \sim 10 \, \text{ps} \). In order to reproduce the results, we start the simulation with an
elevated temperature 3250 K and let it run for 20 ps. As shown in Figure S20b, the excited population cools down to the lattice temperature within 10.24 ps and then the cooling stops as expected. This agreement between the experimental data and our MC simulation results confirms that our phonon scattering rates are accurate enough to explain the underlying dynamics of the nonequilibrium electrons of gold.

References