Supplementary Materials

I. DETAILS OF THE APPARATUS

The cathode (sample) can be plugged into the flat ring cathode stage (outer diameter 50 mm) from the rear. The inserted depth is adjustable such that the sample surface is flush with the surface of the cathode stage. A quartz glass coated with 8 nm gold (for electrical conduction) is used as the anode with a round hole of 2.5 mm diameter in its center where an ultra-fine hexagonal 1000 mesh microscope grid is pasted with ultra-high vacuum (UHV) compatible silver loaded epoxy. The quartz anode is adhered on the hat-shaped metallic anode holder with the same epoxy. The anode is parallel to the cathode, and the distance between their opposite surfaces is 5 mm. A scintillator (Ce: GAGG) screen is located at a distance of 250 mm from the grid. The cathode is connected to a high negative power supply of -5 kV while the anode, grid, and scintillator screen are grounded. This geometric design will provide a uniform electric field around the medial axis of the apparatus between the anode and cathode, and the electric field in the space of the anode to the scintillator is almost zero. All these assemblies are arranged in an UHV chamber, and the pressure during the whole measurement is of the order of $10^{-8}$ Pa. The ultrashort laser pulses are generated from a wavelength tunable Ti: sapphire infrared laser and 3rd harmonic generator system operating at 80 MHz repetition rate. Passing through a vacuum viewport and the coated glass, the laser beam can be focused onto the sample at several discrete incidence angles. When the cathode is irradiated by the laser, it emits not only electrons but also fluorescence. By receiving the fluorescence with a CCD camera, we monitor the size and intensity distribution of the laser spot and thus the electron beam. The laser power is adjusted with UV fused silica reflective neutral density filters. The photocurrent can be obtained by measuring the current from the cathode to the ground with a high precision source meter (Keithley 6487) applying a -500 V potential on the cathode instead of the high - 5 kV voltage. And a photocurrent of equal to 12.8 pA corresponds only 1 electron per pulse averagely. The quantum efficiency (QE) of the photocathode can be calculated by recording the laser power and photocurrent synchronously. Photoelectrons emitted from the sample will be accelerated in the uniform electric field between the cathode and anode in parabolic trajectories. More than half (about 57%) of the electrons will pass through the grid and drift along straight lines in the field free range then come across the scintillator where they are imaged and recorded by a monochrome CCD camera (QImaging Retiga R6).

II. OBTAINMENT OF THE EFFECTIVE WORK FUNCTION

According to Fowler’s theory,$^{3,4}$ for the photon energies $\hbar \omega$ near the work function $\phi$, the quantum efficiency $QE$ of the cathode satisfies the following expression

$$\ln \left( \frac{QE}{T_e^2} \right) = b + \ln \left[ f \left( \frac{\hbar \omega - \phi}{k_B T_e} \right) \right],$$

(S1)
where $T_e$ is the electron temperature (approximately equal to 300 K), $b$ is a constant independent of temperature and photon energy, $k_B$ is Boltzmann’s constant. The function $f(x)$ is expressed as

$$f(x) = \begin{cases} e^x - \frac{e^{2x}}{4} + \frac{e^{3x}}{9} - \ldots & x \leq 0 \\ \frac{\pi^2}{6} + \frac{x^2}{2} - \left( e^{-x} - \frac{e^{-2x}}{4} + \frac{e^{-3x}}{9} - \ldots \right) & x \geq 0 \end{cases}$$

We measured the quantum efficiency of the cathode for every higher photon energy at which the photocurrent density depends linearly on the laser intensity. Then the work function of the cathode was found to be 4.112 eV by fitting these $QE$ data with Eq. (S1) (FIG. S1). In addition, when the $QE$ was measured, the electric field on the cathode surface was 0.1 MV/m. Considering the Schottky reduction of the work function of 0.012eV, the work function of the cathode is 4.12 eV. And the electric field on the cathode surface of 1 MV/m during the emittance measurement reduced the effective work function to 4.09 eV.

![FIG. S1. Fowler fit](image)

FIG. S1. Fowler fit. The electron temperature was assumed to be 300 K. The work function of the cathode was found to be 4.112 eV. Considering the Schottky reduction of the work function of 0.012eV, the work function of the cathode is 4.12 eV

### III. TWO MAIN ERROR SOURCES

The equation used to calculate the transverse momentum of electrons (Eq. (3) in main text) is based on the assumption that the electrons are emitted from a single point and the grid does not affect their transverse momentum. However, the laser spot then the electron emission region is not a geometric point, and the mesh elements defocus the electron beam as electrostatic lenses. Therefore, the position of an electron on the screen is the summation of the initial position, the transverse displacement and the deviation caused by the grid.

For ideal single point emission case, the probability density distribution of $x$ displacement on the screen is noted as $s(x)$, and satisfies the normalization condition
\[ \int s(x)dx = 1. \]  
(S3)

The mean squared displacement can be calculated by
\[ \langle x^2 \rangle = \int x^2 s(x)dx. \]  
(S4)

Additionally, we assume that the electron emission is isotropic in the surface of the cathode, so \( s(x) \) is an even function,
\[ s(-x) = s(x). \]  
(S5)

For actual measurement, the probability density distribution of \( x \) displacement on the screen is noted as \( c(x_c) \), where \( x_c \) is the displacement where the electron is emitted, \( x_c \in [x_{c_{\text{min}}}, x_{c_{\text{max}}}] \). Assuming the probability density distribution of deviation on the screen caused by the grid is \( h(x_H) \), where \( x_H \) is deviation on the screen caused by the grid, \( x_H \in [x_{H_{\text{min}}}, x_{H_{\text{max}}}] \). Both \( c(x_c) \) and \( h(x_H) \) satisfy the normalization conditions like Eq. (S3).

Considering the finite laser spot size and the defocus of the anode grid, the probability density distribution of \( x \) displacement on the screen is expressed as

\[ s_{\text{clH}}(x) = \int_{x_{c_{\text{min}}}}^{x_{c_{\text{max}}}} \int_{x_{H_{\text{min}}}}^{x_{H_{\text{max}}}} dx_c dx_H s(x - x_c - x_H) c(x_c) h(x_H). \]  
(S6)

The measured mean squared displacement is written as

\[ \langle x^2 \rangle_{\text{clH}} = \int x^2 s_{\text{clH}}(x)dx \]
\[ = \int_{x_{c_{\text{min}}} + x_{H_{\text{min}}}}^{x_{c_{\text{max}}} + x_{H_{\text{max}}}} dx \int_{x_{c_{\text{min}}} + x_{H_{\text{min}}}}^{x_{c_{\text{max}}} + x_{H_{\text{max}}}} dx_c \int_{x_{H_{\text{min}}}}^{x_{H_{\text{max}}}} dx_H x^2 s(x - x_c - x_H) c(x_c) h(x_H). \]  
(S7)

We write the item \( x^2 \) in the integrand as
\[ x^2 = (x - x_c - x_H)^2 + 2(x_c + x_H)(x - x_c - x_H) + (x_c + x_H)^2. \]  
(S8)

Substituting Eq. (S8) into Eq. (S7), using Eq.(S3) - (S5) and considering the normalization conditions of \( c(x_c) \) and \( h(x_H) \), one obtains the following for the measured mean squared displacement:

\[ \langle x^2 \rangle_{\text{clH}} = \langle x^2 \rangle + \langle x_c^2 \rangle + \langle x_H^2 \rangle + 2\langle x_c \rangle\langle x_H \rangle. \]  
(S9)

If we further assume the deviation caused by the grid is isotropic, then \( h(x_H) \) is an even function and we obtain the following:

\[ \langle x^2 \rangle_{\text{clH}} = \langle x^2 \rangle + \langle x_c^2 \rangle + \langle x_H^2 \rangle. \]  
(S10)
Therefore, the finite laser spot size and the defocus of the anode grid add the mean squared displacement on the cathode and the mean squared deviation caused by the grid in the mean squared displacement on the screen.

The laser spot size should be adjusted small enough so that the increase of the emittance caused by the finite laser spot size is negligible. In the experiment, the laser beam was focused to about 100 μm FWHM ensured that the increase of measured emittance was less than 0.5%. According to Davisson's electron-lens formula, the position of the electrons on the screen will deviate

\[ x_d = \frac{d}{4g} x_e \]  

from the ideal position. \( x_e \) is the distance between its trajectory and the axis of the mesh when the electron passed through the grid anode. \( d \) and \( g \) are the distances from the grid to the scintillator screen and cathode, respectively. For the hexagonal grid used in our apparatus, the maximum value of \( x_e \) is 11 μm corresponding to a displacement deviation of 137 μm. Assuming that the displacement of electrons shift to 137 μm in two opposite directions, which is obviously overestimated, the measured emittance value will be about 2% higher than the actual value.

IV. NUMERICAL CALCULATION OF THE ELECTRON TEMPERATURE

In order to rule out the effect of laser heating on emittance increase, we calculated the electron and lattice temperature illuminated with ultrashort laser pulse at the emitting surface using the 1D two-temperature model. Electrons and lattice are treated as two separate thermal subsystems that interact via an electron-phonon scattering term. If the effect of electron thermal conductivity is ignored, the electron temperature \( T_e \) and lattice temperature \( T_l \) as functions of time \( t \) are described by the differential equation set

\[
\begin{align*}
C_e(T_e) \frac{dT_e}{dt} &= -g_e(T_e - T_l) + P_d(t) \\
C_l(T_l) \frac{dT_l}{dt} &= g_e(T_e - T_l)
\end{align*}
\]

where \( C_e(T_e) \) and \( C_l(T_l) \) are the electron and lattice heat capacity per unit volume, \( g_e \) is the electron-phonon coupling constant, \( P_d(t) \) is the absorbed laser power density. Both of \( C_e(T_e) \) and \( C_l(T_l) \) are functions of the corresponding subsystem temperature. We use the approximation that the electronic heat capacity varies linearly with the electronic temperature, \( C_e = \gamma T_e \). And the lattice heat capacity is calculated using the Debye model. For sech\(^2\)-shaped pulses, the absorbed laser power density is expressed as

\[ P_d(t) = \frac{1-R_p}{d_p} I_p \text{sech}^2\left(\frac{t-t_0}{\tau}\right), \]

\[ \text{(S13)} \]
where $R_e$ is the reflection coefficient, $I_p$ is the peak intensity of the laser pulse, $d_p$ is the effective penetration depth of the laser energy, $\tau$ is the duration parameter, and $t_0 = 5\tau$. For a 100 fs (FWHM) pulse duration, $\tau$ is equal to 57 fs. $I_p$ is taken as 3.22 MW/cm², corresponding to the upper limit of peak intensity during the emittance measurement. The other parameters are obtained from Ref. 7 and references therein, TABLE I.

TABLE I. Parameters used to compute the electron and lattice temperatures shown in FIG. S2.⁷

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$g_e$: electron-phonon coupling constant</td>
<td>$10^{17}$ W/(m³ K)</td>
</tr>
<tr>
<td>$R_e$: reflection coefficient</td>
<td>0.34</td>
</tr>
<tr>
<td>$d_p$: effective penetration depth</td>
<td>83 nm</td>
</tr>
<tr>
<td>$\Theta_D$: Debye temperature of copper</td>
<td>343 K</td>
</tr>
<tr>
<td>$\gamma$: electronic constant of heat capacity</td>
<td>96.6 J/(m³ K²)</td>
</tr>
</tbody>
</table>

FIG. S2. Electron and lattice temperature at the emitting surface under the two-temperature model. The effect of electron thermal conductivity is ignored. The peak intensity of the laser pulse is taken as 3.22 MW/cm², corresponding to the upper limit of peak intensity during the emittance measurement.

The calculated electron and lattice temperatures as a function of time are shown in FIG. S2. The electron temperature rises only when the laser pulse arrives, and then drops rapidly toward the lattice temperature. The peak value of the electron temperature is only about 1 K higher than the room temperature, and the effect on the electron emission is negligible.
V. EXPLANATION ABOUT THE FITTED SLOPES

The emitted current density $J$ of multiphoton photoemission can be written as a sum of the currents for each n-photon emission $J_n$, \(^8\)

$$J = \sum_n J_n = \sum_n \sigma_n I^n, \quad (S14)$$

where the sum is over all possible values of $n$, $\sigma_n$ is the generalized n-photon ionization cross section, $I$ is the incident laser intensity. Writing \(\log_{10} J = J_{\log}\) and \(\log_{10} I = I_{\log}\), we get

$$10^{J_{\log}} = \sum_n \sigma_n 10^{nI_{\log}}. \quad (S15)$$

Taking the derivative of both sides of the equation with respect to $I_{\log}$ and simplifying the expression, we obtain

$$\frac{dJ_{\log}}{dI_{\log}} = \frac{\sum_n n\sigma_n I^n}{\sum_n \sigma_n I^n}. \quad (S16)$$

With a single-valued $n$, the right side of Eq. (S16) becomes $n$. That is to say, for pure n-photon photoemission, $J$ and $I$ can be plotted as a straight line of slope $n$ in the logarithmic coordinate. When $n$ takes two or more values, corresponding to a mixed photoemission process, \(dJ_{\log}/dI_{\log}\) is a function of $I$, which means there is a nonlinear relationship between $J$ and $I$ in the logarithmic coordinate. Therefore, a non-integral slope obtained from linear fit in the logarithmic coordinate indicates mixed photoemission process. And the slope is only the mean of \(dJ_{\log}/dI_{\log}\) in some sense.

Assuming the possible values of $n$ to be 1 and 2, Eq. (S16) can be simplified as

$$\frac{dJ_{\log}}{dI_{\log}} = \frac{\sigma_1 I + 2\sigma_2 I^2}{\sigma_1 I + \sigma_2 I^2} = 2 - \frac{J_1}{J}, \quad (S17)$$

where $J_1/J$ is the ratio of the n-photon photoemission current to the total photocurrent. As a consequence, for a mixed photoemission process containing only single and two-photon photoemission, the larger the derivative $dJ_{\log}/dI_{\log}$ and hence the fitted slope are, the smaller the proportion of single-photon photoemission current becomes.

\(^1\)See http://www.tedpella.com/grids_html/gilder.htm#anchor1736005 for more information about the grid; accessed 22 February 2018.
2Jan Bok, Ondřej Lalinský, MartinHanuš, ZuzanaOnderišinová, JakubKelar, and MiroslavKučera, Ultramicroscopy 163 (2016) 1.


