Supporting Information: Observation of Plasmon Energy Gain for Emitted Secondary Electron in Vacuo

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Supplemental Figures

Figure S1: (a), (b) Top and side views of optimized atomic structures of an Au(111) surface and Au(111)-graphene. The yellow and green balls represent Au and C atoms. The optimized distance between the Au(111) surface and graphene is 3.4 Å. (c), (d) The respective planar average electrostatic potentials of the Au(111) surface and Au(111)-graphene along the perpendicular (z) direction of the surface plane. WF$_{Au}$ and WF$_{Gra}$ denote the work functions of Au(111) and graphene, respectively. $E_F$ is the Fermi energy level. (e), (f) The respective planar average electrostatic potentials of Au(111) surface and Au(111)-graphene in the vacuum regions, near the Au(111) and Au(111)-graphene surfaces. The half atomic radius of Au and C atoms are 0.72 and 0.385 Å, respectively.
Figure S2: (a) An SEM image of a polycrystalline Au sample; (b) Misorientation-axis distributions in the normal direction (ND) of the polycrystalline Au sample. Electron backscatter diffraction (EBSD) maps for (c) ND, (d) rolling direction (RD), (e) transverse direction (TD); (f) EBSD image quality map (EBSD-Q) of the same region of the sample in which the image quality value is measured for each diffraction pattern obtained during an EBSD scan to a grayer color scale.
Figure S3: (a) SE spectra, and (b) derivative spectra, obtained from 16 independent groups of measurements in the energy range from 0 to 20 eV with an energy step of 0.1 eV at bright bare Au grains as shown in Supplementary Figure 3b with incident electron energies of 10 keV (black) and 15 keV (red). The standard deviations for the 16 group measurements are presented as error bars. The corresponding raw spectra measured from 16 different selected measurement points for (c), SE spectra, and (d), derivative spectra, are plotted together as lines of the same color in the electron energy of 1–3.5 eV.
Figure S4: (a) A 32×32 pixelated SEM image of the polycrystalline Au sample renormalized from Figure S2a; (b) A 32×32 pixelated image of the misorientation angle along the Au(111) direction in the normal direction (ND) of the same region of the polycrystalline Au sample renormalized from the EBSD image in the normal direction (EBSD-NDND), Figure S2c; (c) A 32×32 pixelated EBSD image quality map (EBSD-Q) of the same region of the polycrystalline Au sample renormalized from Figure S2f. Four SE spectra measured at bright Au grains and dark Au grains are marked by grey and black arrows, respectively. The plasmon gain intensity (peak-to-peak intensity) determined from Figure S3d as a function of (d) SEM intensity in the SEM image, (e) disorientation angle in the EBSD-ND and (f) quality value in the EBSD-Q.
Figure S5: (a) SEM image of few-layer graphene sheets on a polycrystalline Au film. The regions with a bare Au film labelled SEM1 is presented in (b), regions with six- and eleven-layer graphene labelled SEM2 is presented in (c), and regions with four- and fourteen-layer graphene labelled SEM3 is presented in (d). The number of layers in the graphene was estimated in cross-sectional AFM. The incident beam positions in the eight groups of measurements are also presented in the SEM image for measurements performed on: bright bare Au grains ($J_B$)—pink diagonal crosses, dark bare Au grains ($J_D$)—yellow crosses, four-layer graphene (SEM1) and six-layer graphene (SEM2) on bright Au grains—red diagonal crosses, four- and six-layer graphene on dark Au grains—blue crosses, eleven-layer graphene (SEM2) and fourteen-layer graphene (SEM1) on bright Au grains—red diagonal open crosses and eleven- and fourteen-layer graphene on dark Au grains—blue open crosses, respectively.
Figure S6: (a) SE spectra and (b) derivative spectra obtained from eight independent groups of measurements related to the bright Au grains ($J_B$) and dark Au grains ($J_D$) in the energy range from 0 to 10 eV with 0.1 eV energy steps for bare Au film (0 L), and four-, six-, eleven- and fourteen-layer graphene on an Au substrate with an incident electron energy of 10 keV. Error bars represent the standard deviations for the eight group measurements at intervals of 0.1 eV. For the different numbers of graphene layers, the corresponding raw spectra measured from 8 different selected measurement points for (c) SE spectra, and (d) derivative spectra, are plotted together as lines of the same color in the electron energy range of 1–3 eV.
Figure S7: (a) Difference spectra determined for bare Au film (0 L), and four-, six-, eleven- and fourteen-layer graphene on an Au substrate in the energy range from 0 to 20 eV in steps of 0.1 eV with an incident electron energy of 10 keV. Each spectrum is averaged from 64 possible difference spectra calculated from all eight measurements for each type of selected measurement points. Error bars represent one standard deviation; (b) For the different layer number of graphene, the difference spectra plotted in the electron energy range of 1–3 eV.
Supplementary Note 1: First-principles calculations.

First-principles calculations of the total energy were performed within the framework of density functional theory (DFT) [1,2] as implemented in the Quantum Espresso code [3]. Projector-augmented wave pseudopotentials were used to describe the electron–ion interaction [4]. The valence wave functions and the augmented charge density were expanded using a plane-wave basis set with cutoff energies of 60 and 540 Ry, respectively. We used the van der Waals corrected density functional [5] for the exchange-correlation energy to describe the weak binding between Au(111) surface and graphene accurately.

We used a slab model in which the Au thin film was simulated as a seven-layer Au(111) surface. The Au(111) thin film with $\sqrt{3} \times \sqrt{3}$ lateral periodicity was coated with a graphene monolayer with $2 \times 2$ lateral periodicity, in which the lateral lattice parameters of graphene are fixed to the optimized lattice parameter of the Au(111) surface of 2.928 Å. All atoms were fully optimized until the remaining force acting on each atom was less than 0.0001 Ry/Bohr. The Brillouin-zone integration was sampled by the Monkhorst–Pack (MP) scheme [6] with $42 \times 42 \times 1$ k-point grids in the self-consistent field calculations for optimization structures and energy band structures. All calculations were performed on the Numerical Materials Simulator supercomputer at the National Institute for Materials Science (NIMS).
Supplementary Note 2: SE spectra measurement.

Au sample preparation: Au layers (200 nm) were evaporated at rates of 0.2 nm s\(^{-1}\) on Si(100) substrates with Ti buffer layers (5 nm) pre-evaporated at rates of 0.05 nm s\(^{-1}\) by electron-beam evaporation (RDEB-1206K, R-DEC Co. Ltd., Ibaraki, Japan) with a chamber pressure of \(\sim 1.0 \times 10^{-5} \) Pa. After evaporation, the samples were annealed by rapid thermal annealing (QHC-P410, Ulvac-Riko Inc., Kanagawa, Japan) under an N\(_2\) atmosphere at 300 °C for 30 s.

Graphene fabrication: Graphene flakes were produced on the Au substrates by mechanical exfoliation by mechanical exfoliation. The number of graphene layers was estimated by atomic force microscopy (AFM) and further confirmed by Raman spectroscopy.

SE spectra measurement: SE spectra were measured at room temperature with a scanning Auger electron spectrometer (SAM650, Ulvac-Phi, Kanagawa, Japan) with a cylindrical mirror analyzer. The take-off angle of the instrument was 42.3\(\pm\)6°. The incident electron beam current for these raw spectra was about 0.87 nA, as calibrated with a Faraday cup before the measurements. Sixteen groups of SE spectra were measured on the bare Au surface with an incident electron energy of 10 and 15 keV, respectively. Eight groups of SE spectra were measured on each graphene sheets with an incident electron energy of 10 keV. Each group contained two SE spectra measured at bright and dark regions (~490 nm\(^2\)), respectively, on the bare Au substrate or similar neighboring regions covered by graphene sheets. Short-term repeated measurements for multiple cycles were used to minimize the influences from the stability of the instrument changing over time.

Supplementary Note 3: Calculation of differential inelastic scattering cross-section

The inelastic scattering probability is governed by the bulk dielectric function \(\varepsilon(q,\omega)\) of the solid in a dielectric response theory. The experimental values of the optical dielectric function
\( \varepsilon(\omega) \) taken from a database [7] were employed to model the dielectric function \( \varepsilon(q,\omega) \). An extrapolation from the optical limit to other momentum transfers was made according to Ritchie and Howie’s scheme [8], i.e., the energy loss function \( \text{Im}[-1/\varepsilon(q,\omega)] \) is approximately extended from an optical energy loss function \( \text{Im}[-1/\varepsilon(\omega)] \): a bulk energy loss function is first decomposed into \( N \) terms of the Drude-Lindhard model energy loss function:

\[
\text{Im}\left\{ \frac{-1}{\varepsilon(q = 0, \omega)} \right\} = \sum_{i=1}^{N} a_i \frac{\gamma_i \omega \omega_{pi}^2}{(\omega^2 + \omega_{pi}^2)^2 + \gamma_i^2 \omega^2},
\]

where the \( 3N \) parameters, \( a_i, \omega_{pi} \) and \( \gamma_i \) are, respectively, the oscillator strength which can be negative, energy, and width of the \( i \)th oscillator. The parameters are then determined from the experimental optical energy loss function of Au [7] using a fitting procedure.

Based on the determined dielectric function \( \varepsilon(q,\omega) \), according to a specular surface reflection model, the potential is determined by the external charge and its mirror image charge and the fictitious surface charges fixed by the boundary conditions [9] using the standard quantum mechanics framework [10–12]. By solving Poisson’s equation, the Fourier components of the potentials in the media can be obtained for cases where the charge is in the vacuum \((z > 0)\) or inside the solid \((z < 0)\), and for the point \( z' \) of the induced potential in the vacuum \((z' > 0)\) or inside the solid \((z' < 0)\), respectively; specifically,

\[
\Phi(q,\omega) = \begin{cases} 
\frac{4\pi}{q^2} \left[ 2 \cos(q_z z) + \rho^+_S(q_{||},\omega) \right] & z > 0, z' > 0 \\
\frac{4\pi}{q^2} \rho^+_S(q_{||},\omega) & z > 0, z' < 0 \\
\frac{4\pi}{q^2} \rho^-_S(q_{||},\omega) & z < 0, z' > 0 \\
\frac{4\pi}{q^2} \left[ 2 \cos(q_z z) + \rho^-_S(q_{||},\omega) \right] & z > 0, z' > 0 
\end{cases}
\]
where the surface charges, determined by matching conditions for incident and emission instances at the surface, are respectively

\[
\begin{align*}
\rho^+(\mathbf{q}, \omega) &= -2\varepsilon_s(\mathbf{q}, \omega) e^{-q_1 z} \\
\rho^-(\mathbf{q}, \omega) &= -2\varepsilon_s(\mathbf{q}, \omega) \frac{q_1}{\pi} \int_{-\infty}^{+\infty} \cos(q_{1z}) \frac{dq_{1\perp}}{q^2 \varepsilon(\mathbf{q}, \omega)}
\end{align*}
\]

(3)

The surface dielectric function is defined by

\[
\varepsilon_s^{-1}(\mathbf{q}, \omega) = 1 + \frac{q_1}{\pi} \int_{-\infty}^{+\infty} \frac{dq_{1\perp}}{q^2 \varepsilon(\mathbf{q}, \omega)},
\]

(4)

however, the corresponding induced potentials are then obtained after removing the potential of the external charge.

\[
\Phi(z > 0, z' > 0) = \frac{2\pi}{q_1} e^{-q_1 z} \left\{ \varepsilon(q', \mathbf{q}, \omega) \frac{q_1}{\pi} \int_{-\infty}^{+\infty} e^{i q_{1z}} \frac{dq_{1\perp}}{q^2 \varepsilon(\mathbf{q}, \omega)} \right\},
\]

(5)

\[
\Phi(z > 0, z' < 0) = \frac{2\pi}{q_1} e^{-q_1 z} \left\{ \varepsilon(q', \mathbf{q}, \omega) \frac{q_1}{\pi} \int_{-\infty}^{+\infty} e^{i q_{1z}} \frac{dq_{1\perp}}{q^2 \varepsilon(\mathbf{q}, \omega)} \right\},
\]

(6)

\[
\Phi(z < 0, z' > 0) = \frac{2\pi}{q_1} e^{-q_1 z} \left\{ \varepsilon(q', \mathbf{q}, \omega) \frac{q_1}{\pi} \int_{-\infty}^{+\infty} e^{i q_{1z}} \frac{dq_{1\perp}}{q^2 \varepsilon(\mathbf{q}, \omega)} \right\},
\]

(7)

\[
\Phi(z < 0, z' < 0) = \int_{-\infty}^{+\infty} e^{i q_{1z}} \left\{ 2e^{-i q_{1z}} \left( \frac{1}{\varepsilon(\mathbf{q}, \omega)} - 1 \right) \frac{1}{q^2} + 2e^{i q_{1z}} \frac{1}{q^2 \varepsilon(\mathbf{q}, \omega)} \right\} dq_{1\perp}
\]

(8)

In the time-ordered formalism, the RPA self-energy of a system inhomogeneous in the \( z \)-direction is obtained from
\[ \Sigma(z' | q_{\parallel}, \omega) = \frac{i}{\delta \pi^2} \int \Phi\left(z' | q_{\parallel}', \omega\right) G_S\left(z' | q_{\parallel} - q_{\parallel}', \omega - \omega'\right) dq_{\parallel}' d\omega', \quad (9) \]

where \( G_S \) is a surface Green’s function, which can be constructed from a bulk free-electron Green’s function. After integrating over \( q_{\parallel} \), the corresponding differential self-energy inhomogeneous in the \( z \)-direction for various conditions of position and the direction of the moving electrons is provided as follows:

\[ \Sigma(z | \omega) = \begin{cases} 
\Sigma_i(z | \omega) & z > 0, v_\perp < 0 \\
\Sigma_b(\omega) + \Sigma_i(z | \omega) + \Sigma_s(z | \omega) + \Sigma_{i,s}(z | \omega) & z < 0, v_\perp < 0 \\
\Sigma_i(z | \omega) + \Sigma_s(z | \omega) & z > 0, v_\perp > 0 \\
\Sigma_b(\omega) + \Sigma_i(z | \omega) + \Sigma_s(z | \omega) & z < 0, v_\perp > 0 
\end{cases} \quad (10) \]

where \( \Sigma_b \), \( \Sigma_i(z | \omega) \), \( \Sigma_s(z | \omega) \), and \( \Sigma_{i,s}(z | \omega) \) are the position independent bulk term, the image charge term, the surface charge term, and the interference term between the image charge and the surface charges. When an electron is in the vacuum region, \( \Sigma_i(z | \omega) \) is the classical self-energy for an electron incident onto and escaping from the surface, and the extra term \( \Sigma_{i,s}(z | \omega) \) contains the contribution from both the image charge and the surface charges. Here \( v_\perp \) is the vertical component of the velocity vector; the vertical distance \( z \) measured from the surface is positive in a vacuum and negative in a solid. The differential inelastic scattering cross-section (DISCS) can be obtained from the imaginary part of the differential self-energy,

\[ \sigma_{in}(\omega | E, \alpha, z) = -\frac{2}{\nu} \text{Im} \{ \Sigma(\omega | \alpha, z) \}, \quad (11) \]

where \( E = \nu^2/2 \) is the electron kinetic energy, and \( \alpha \) the angle between the velocity vector and surface normal.
REFERENCES


