Supporting Information

Engineering Perovskite Bandgap for Control of Hot-Electron Dynamics in Plasmonic Nanodiodes

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Figure S1. (a) Absorbance and photoluminescence (PL) spectra of the perovskite films with various Br fractions. (b-d) Optical bandgaps of the perovskites with (b) Br 0%, (c) Br 20%, and (d) Br 40% determined from Tauc plots.



Figure S2. (a) Low binding energy region and (b) high binding energy region of UPS spectra of the perovskites with various Br fractions. (c) Energy levels of the perovskites with Br 0%, Br 20%, and Br 40%.

Before the measurement, the photoelectron binding energy was calibrated using the Fermi edge of a sputtered Au film. The work function (Φ s) and the valence band maximum (VBM) were calculated using the following equations:

High binding energy $\operatorname{cutoff} = hv - \Phi s$ Low binding energy $\operatorname{cutoff} = E_F - VBM$ where hv is the energy source (21.22 eV) and E_F is the Fermi energy level (set at 0 eV). The cutoff binding energies are determined by measuring the intercept between a line fit to the background and a line fit to the steepest part of the cutoff.



Figure S3. STEM-EDS elemental mapping images for (a) Cs, (b) Pb, (c) Br, (d) I, (e) Au, (f) Ti, and (g) O.



Figures S4. The surface SEM images of (a) the bare plasmonic Au/TiO₂, (b) the Br 0%/plasmonic Au/TiO₂, and (c) the Br 20%/plasmonic Au/TiO₂.



Figure S5. (a) Thicknesses of the plasmonic Au layer and the perovskite films with various Br fractions. (b) Short-circuit photocurrents measured on the perovskite-modified plasmonic Au nanodiodes.



Figure S6. Plots of I-V curves (open symbol) and fits (solid line) from the thermionic emission model of the bare plasmonic Au and the perovskite modified plasmonic Au nanodiodes measured under (a) dark condition and (b) light illumination.



Figure S7. Schematic illustration showing the various hot-electron flow pathways.



Figure S8. (a) Absorbance spectra of perovskite/plasmonic Au/TiO_2 structures and (b) zoomed-in view of the absorbance spectra from highlighted region of the full spectra.



Figure S9. Thicknesses of the perovskite thin films with Br 20% for various precursor concentrations.



Figure S10. Transient absorption spectra measured on (a) bare plasmonic Au/TiO₂ and (b) ${\rm TiO}_2$.



Figure S11. Kinetic analysis of transient absorption data obtained from Br 0%/plasmonic Au/TiO₂ (a) Time-dependent population changes of each decay constant. (b) Species-associated difference spectrum for each decay constant. (c) Experimentally measured TA spectra (top panel), theoretically calculated TA spectra acquired by multiplying population changes with species-associated difference spectrum (middle panel), and residual between experimental TA spectra and theoretical TA spectra (bottom panel).



Figure S12. Kinetic analysis of transient absorption data obtained from Br 20%/plasmonic Au/TiO₂ (a) Time-dependent population changes of each decay constant. (b) Species-associated difference spectrum for each decay constant. (c) Experimentally measured TA spectra (top panel), theoretically calculated TA spectra acquired by multiplying population changes with species-associated difference spectrum (middle panel), and residual between experimental TA spectra and theoretical TA spectra (bottom panel).



Figure S13. Kinetic analysis of transient absorption data obtained from Br 40%/plasmonic Au/TiO₂ (a) Time-dependent population changes of each decay constant. (b) Species-associated difference spectrum for each decay constant. (c) Experimentally measured TA spectra (top panel), theoretically calculated TA spectra acquired by multiplying population changes with species-associated difference spectrum (middle panel), and residual between experimental TA spectra and theoretical TA spectra (bottom panel).



Figure S14. XRD patterns of perovskite films of Br 20% and Br 40%.



Figure S15. Pseudo-color TA spectra (left panel) and DAS (right panel) for (a) Br 0%/TiO₂,(b) Br 20%/TiO₂, and (c) Br 40%/TiO₂.

Dark	Plasmonic Au	Br 0%/plas. Au	Br 20%/plas. Au	Br 40%/plas. Au
η	1.39	1.19	1.13	1.16
E _{SB} (eV)	0.83	0.93	0.92	0.92

Table S1. Summarized values of ideality factor (η) and Schottky barrier height (E_{SB}) obtained from fitting the *I-V* curves measured under dark conditions to the thermionic emission model

Table S2. Summarized values of ideality factor (η) and Schottky barrier height (E_{SB}) obtained from fitting the *I-V* curves measured under illumination to the thermionic emission model

Light	Plasmonic Au	Br 0%/plas. Au	Br 20%/plas. Au	Br 40%/plas. Au
η	1.39	1.1	0.99	1.04
E _{SB} (eV)	0.83	0.97	0.97	0.97

Table S3. Summarized fit parameters for multi-exponential decay of the perovskite/ TiO_2 structures with three various Br fractions

	$ au_1$ (ps)	$ au_2$ (ps)	$ au_3$ (ps)	$ au_4$ (ps)
Br 0%/ TiO ₂	1.31 ± 0.02	7.53 ± 0.08	49.56 ± 2.33	>2000
Br 20%/ TiO ₂	1.12 ± 0.02	8.56 ± 0.10	92.99 ± 5.00	>2000
Br 40%/ TiO ₂	0.63 ± 0.01	8.86 ± 0.09	138.67 ± 7.73	>2000

Supplementary Note 1. Estimation of the pump fluence.

The pump fluence (j) can be calculated as the following equation:

$$j = \frac{E}{A}$$
 Equation (S1)

where *E* is the energy per pulse, and *A* is the beam area. The energy per pulse (*E*) was measured to be 70 nJ (pulse repetition rate = 1 kHz). Considering that the beam spot diameter is 400 μ m, the area of the beam spot (*A*) is calculated as 1.256×10^{-3} cm². Therefore, the pump fluence (*j*) is estimated to be 55.7 μ J cm⁻².

Supplementary Note 2. Estimation of the carrier density.

The carrier density (n_0) can be calculated by the following equation,

$$n_0 = n \times \alpha$$
 Equation (S2)

where *n* is the number of photons per area, and α is the absorption coefficient of perovskite at the pump wavelength (420 nm). The number of photons per area (*n*) can be expressed as the following equation.^[1-2]

$$j = nh(C/\lambda)$$
 Equation (S3)

where *j* is the pump fluence, *h* is the Planck constant, *C* is the speed of light, and λ is the pump wavelength. Therefore, the number of photons per area (*n*) is estimated to be 1.18×10^{14} cm⁻². In the case of the absorption coefficient of perovskite (α), it is approximated to $\approx 10^5$ cm⁻¹, given the organic-inorganic hybrid perovskite excited at 420 nm.^[3] Accordingly, the carrier density (n_0) can be calculated as 1.18×10^{19} cm⁻³.

Supplementary Note 3. Validation of global analysis model.

In this study, we employed global analysis rather than probing specific wavelengths to obtain decay components. This approach was chosen because spectral changes over time may involve multiple relaxation mechanisms for a given probe wavelength. To validate our methodology for analyzing TA spectra, we conducted the kinetic analysis, where the theoretical TA spectra can be estimated using the proposed decay time components, as depicted in Figures S11, S12, and S13, by using the kinetic model including various hot-carrier mechanisms we proposed based on global analysis. (Figure 6a)

The kinetic analysis method, described in the previous TA study,^[4] allows us to track the time-dependent population changes of each intermediates using the kinetic model we employed to assign the origins of decay time components, represented as a matrix **C**, which is a concentration matrix. (Figures S11a, S12a, and S12c) The intermediate species included initially excited hot electrons (Franck–Condon state, FC state), trapped hot-electrons at defect states (Trap), thermalized hot electrons into CB2 (CB2), and hot electrons relaxed to the ground state (Ground state). In all three PVSK samples, we observed that as the population of initial hot electrons decreased, the population of trapped species increased, followed by an increase in population of CB2 species. Subsequently, as the population of CB2 species decreased, the ground state population increased. This sequence of population changes over time ranges well with the times scale of each hot-electron relaxation mechanism obtained through global analysis, where trap-assisted relaxation occurs first, followed by hot-electron relaxation to CB2, and Auger recombination occurs last.

Subsequently, we derived species-associated difference spectrum (SADS) of each intermediate, represented as matrix \mathbf{E} , where the columns contain coefficients for the time-

dependent concentrations. (Figures S11b, S12b, and S13b) This enabled us to estimate the theoretical TA spectrum (A_{fitted}) at a given λ and t by conducting a linear combination of multiplying **E** and **C**. Once **C** is specified by a kinetic model with a certain set of variable kinetic parameters, such as rate coefficients, **E** can be optimized by minimizing the discrepancy between the experimentally measured TA spectra (A) and theoretical TA spectra ($A_{fitted} = EC$), using the fmincon function in the Optimization Toolbox package of MATLAB.

Last, by optimizing the matrix **E**, we obtained the optimized theoretical TA spectra. (middle panel of Figures S11c, S12c, and S13c) These theoretical TA spectra were compared with the experimental TA spectra of plasmonic Au/TiO_2 modified with PVSK with various ratios. The calculated TA spectra closely align with the measured TA spectra, demonstrating featureless and relatively small residuals (**A** - **A**fitted). In this regard, we believe the close match between the theoretical TA spectra calculated using the kinetic model from the global analysis and the measured TA spectra supports the validity of our model.

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