Supplementary Information

Electrochemical modulation of plasmon-induced charge separation behaviour at Au-TiO\textsubscript{2} photocathodes
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Fig. S1 Band diagram for the ITO/TiO\textsubscript{2} contact.

Fig. S2 (a) Typical AFM image, (b) SEM image and (c) histogram of the AuNP diameter evaluated from the data in (a) for the ITO/TiO\textsubscript{2}/AuNP photoanode.

Fig. S3 (a) Transmittance, (b) absorption and (c) reflectance spectra of Electrodes A–E.
Fig. S4 AFM images of Electrodes A–E before TiO$_2$ coating.

Fig. S5 Short-circuit photocurrent responses of Electrode A (ITO/AuNP/TiO$_2$) and electrodes without AuNPs and/or TiO$_2$. The peak IPCE for Electrode A is $\sim 1.7 \times 10^{-4}\%$.

Fig. S6 Plots of ln$I$ vs. $V$ ($V = |E_{Apl} - E_{OC}|$) based on the data in Fig. 4b for Electrodes A–E (symbols). The straight lines are fitted to those plots on the basis of the thermionic emission equation (eq. 1 in the main text) and the following values: $A^* = 120$ A cm$^{-2}$ K$^{-2}$ for free electrons, $T = 300$ K, $\Phi = 0.91, 0.99, 0.93, 0.94$ and 0.89 eV, $k_B = 1.381 \times 10^{-23}$ cm$^2$ kg s$^{-2}$ K$^{-1}$, $e = 1.602 \times 10^{-19}$ A s and $\eta = 3.7, 4.8, 5.4, 6.8$ and 42.8 for Electrodes A, B, C, D and E, respectively.

Reference