Supporting information

Reactive Reach of Plasmonic Hot Holes through Molecular Barriers

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1. Experimental Section

1.1 Materials

Fluorine-doped tin oxide (FTO) glass coated with a 10 nm amorphous TiO_2 layer was used as substrate by NSG-Pilkington (United Kingdom). Gold (99.99%) pellets for evaporation by Metalor (Sweden). The remaining chemicals, namely alkanethiols compounds (1-butanethiol, 1-octanethiol, 1-dodecanethiol, and 1-hexadecathiol), NaBr, ethanol, and isopropanol (analytical grade) were purchased from Sigma-Aldrich and used without further purification. All solvents were degassed with N_2 prior to use.

1.2 Preparation of photoelectrodes

1.2.1 Preparation of Au NPs on Substrates

The plasmonic electrodes employed in this study are based on an energy-filter concept reported previously.[1] Briefly, a uniform and pinhole-free ~10 nm amorphous TiO_2 layer was deposited onto fluorine-doped tin oxide (FTO) glass, forming an ultrathin insulating barrier between the transparent collector and the plasmonic nanostructure. This interfacial layer acts as an energetic filter with a step-like transmission profile,[2] enabling the extraction of hot electrons above a threshold of ~0.5-0.6 eV (consistent with the TiO_2 work function of 4.4-4.5 eV) while effectively blocking low-energy carriers and hot holes. Such selective filtering prolongs the lifetimes and energetics of hot holes within the Au nanoparticles, thereby increasing their availability for catalytic processes.

Au NPs were then fabricated directly on the TiO_2-coated FTO (FTO/TiO_2) substrates by physical vapor deposition of a 2 nm Au film, followed by thermal annealing at 723 K for 30 min. This procedure produced a dense distribution of spherical Au NPs with diameters in the range of 10-20 nm (average ~15 nm), exhibiting a localized surface plasmon resonance (LSPR) band centered around 610 nm.[3] Structural and optical characterizations of these electrodes, as well as full fabrication details, have been reported previously.[3]

1.2.2 Surface Functionalization and Poisoning

For in situ functionalization, the Au NP substrates were immersed in a sealed photoelectrochemical cell filled with N_2-purged ethanol containing the target alkanethiol (10 mM). The substrates were exposed to the thiol solution for 24 h, enabling the formation of

self-assembled monolayers. After functionalization, the electrodes were rinsed thoroughly with ethanol to remove physiosorbed molecules.

To selectively poison catalytic surface sites, a 1 mM NaBr solution in absolute ethanol was used. The Au NP electrodes were exposed to this solution for 15 min, followed by rinsing with ethanol to eliminate excess bromide.

1.3 Standard characterization

UV-Vis absorption spectra were recorded on a Cary 5000 spectrophotometer to confirm LSPR. SEM was performed using a Zeiss Merlin microscope (Myfab, Ångström Laboratory). The acceleration voltage was 5 or 10 kV, and the working distance was between 5-7 mm. X-ray photoelectron spectroscopy (XPS, Al Kα source) was performed using a PHI Quantera II instrument, with spectra charge-corrected to the C 1s peak at 284.6 eV.

1.4 Photoelectrochemical Measurements

Electrochemical experiments were carried out in a 1.5 mL quartz cell (Redox.me) using a three-electrode configuration, with the FTO/TiO_2/Au NP electrode as the working electrode, Ag/Ag^+ (non-aqueous) as the reference, and a Pt wire as the counter electrode. A 1.6 mM KNO_3 solution in ethanol served as the electrolyte. Chronoamperometry was performed under 635 nm laser illumination (132 mW/cm^2), modulated in 2 s ON/OFF cycles. The illuminated electrode area was 0.95 cm^2, corresponding to ~15% optical absorption of the incident laser power by the semitransparent plasmonic films. Current transients were recorded with a PalmSens4 potentiostat and analyzed using with Python scrips.

1.5 Electrochemical Impedance Spectroscopy (EIS)

EIS measurements were performed using a PalmSens4 potentiostat. All experiments were conducted in an aqueous solution of 1.6 mM KCl**,** which served as the supporting electrolyte. The impedance spectra were recorded at an open circuit potential (or at a DC bias of 0 V vs. Ag/AgCl Ref) by applying a sinusoidal AC perturbation of 10 mV (0.01 V). The frequency range scanned was from 50000 to 0.01 Hz. All measurements were carried out at room temperature.

2. Additional data

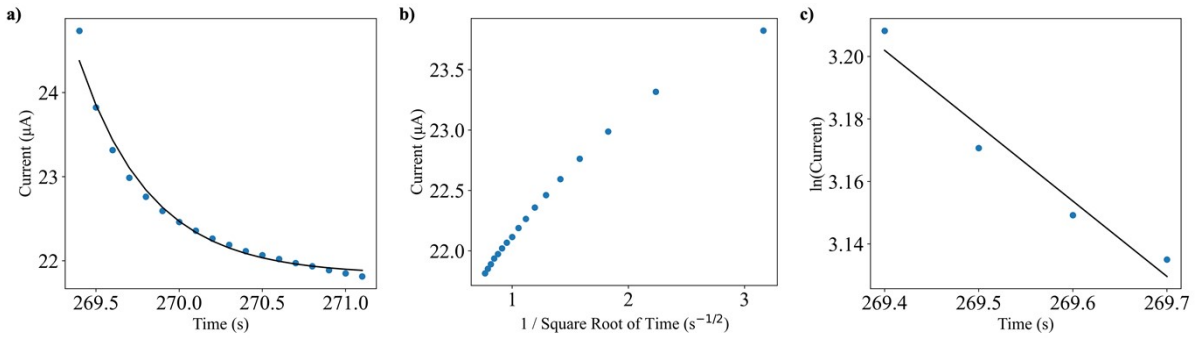

Figure S1: Workflow for determining the hole-transfer rate. (a) The photocurrent decay after illumination is fitted with an exponential function to identify the usable portion of the decay; (b) the data is then fitted with the Cottrell model to define the time interval in which the decay is not influenced by diffusion; and (c) a linear fit of the diffusion-independent data is applied using the adapted Chidsey methodology.

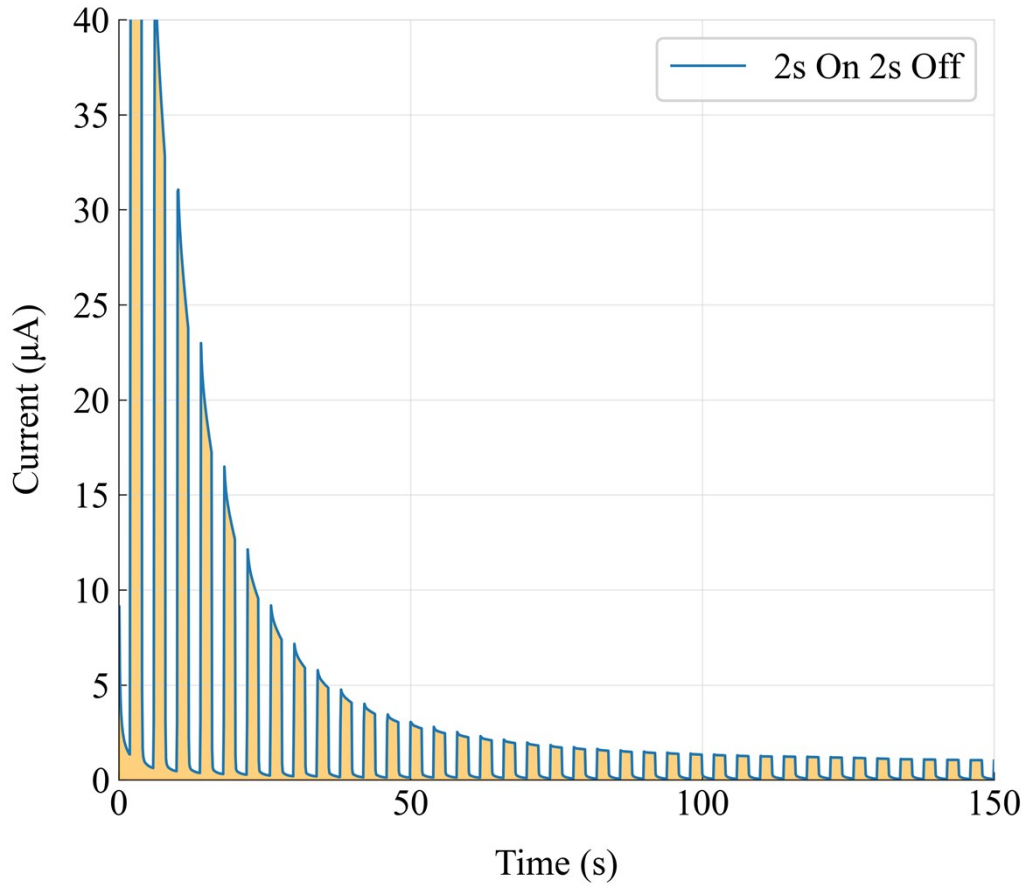

Figure S2: Effect of adding 1 mM NaBr to the electrolyte on the photocurrent during ethanol oxidation using pristine Au nanoparticles on FTO/TiO_2.

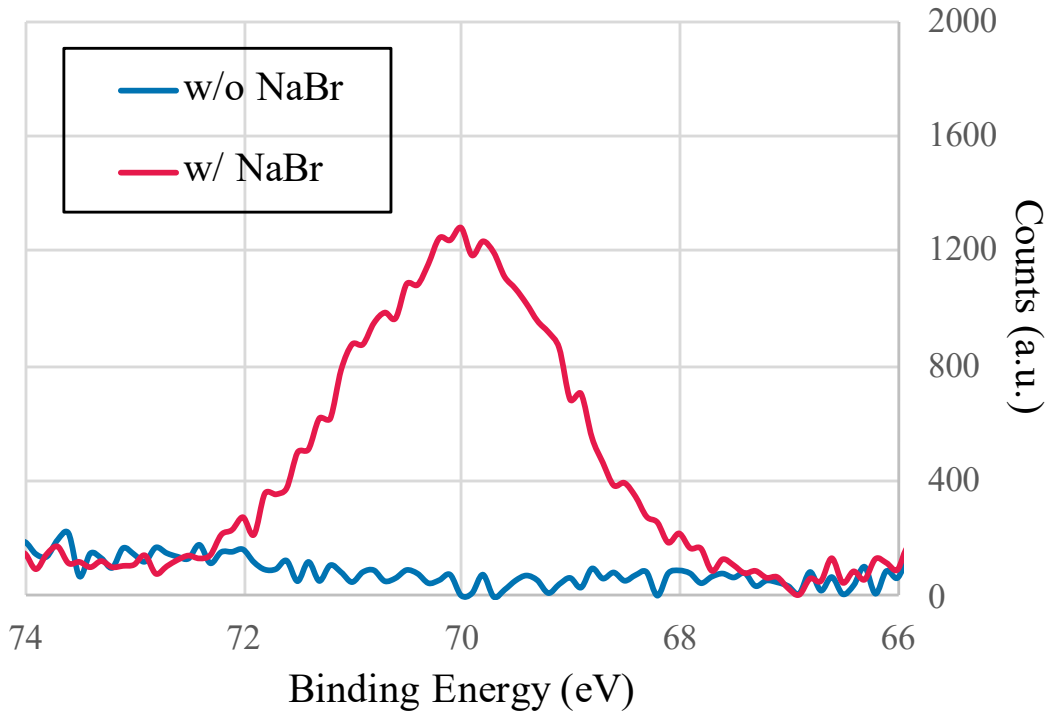

Figure S3: Br 3*d* XPS spectra showing the effect of poisoning the electrode with addition of 1 mM NaBr (w/) and without addition of 1 mM NaBr (w/o).

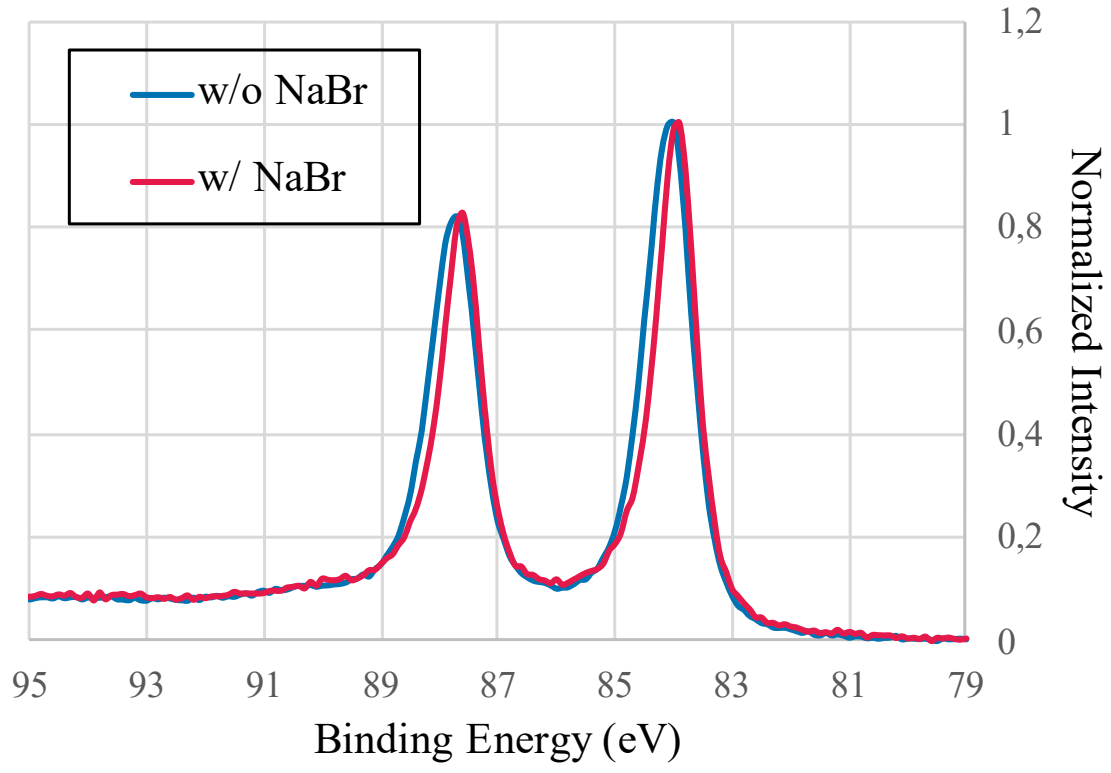

Figure S4: Au 4*f* XPS spectra showing the effect of poisoning the electrode with addition of 1 mM NaBr (w/) and without addition of 1 M NaBr (w/o).

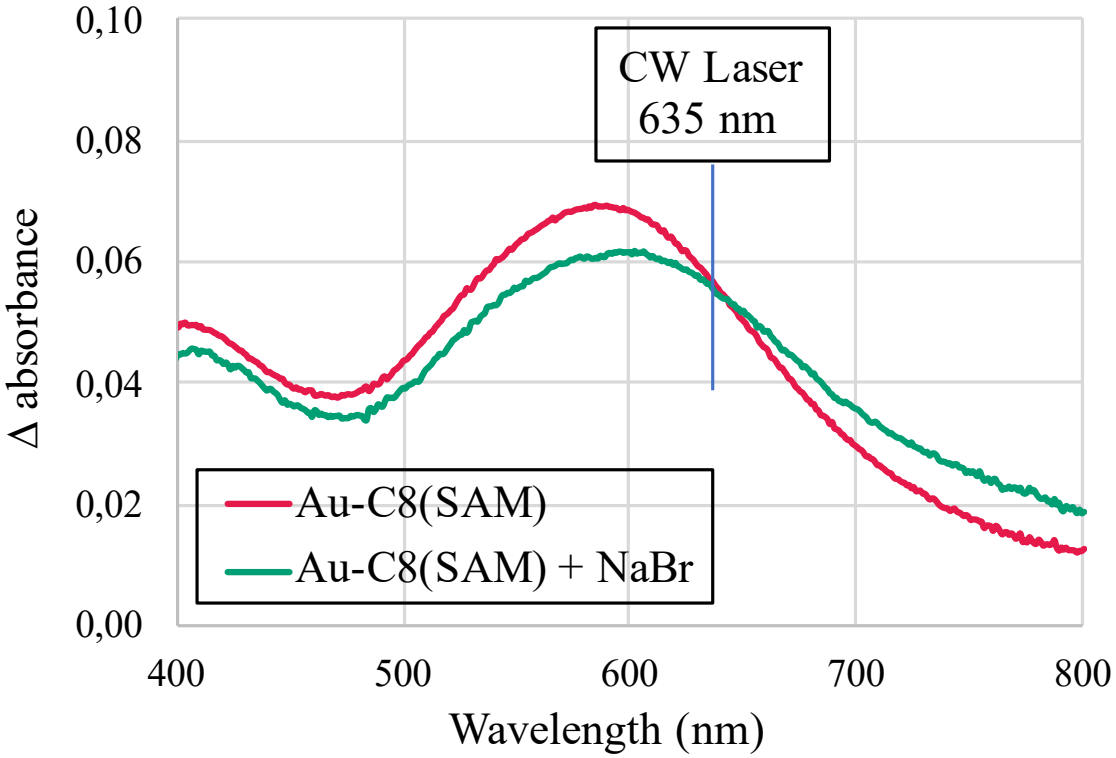

Figure S5: UV-Vis spectra showing the effect of poisoning the electrode with additions of 1 mM NaBr on the Au LSPR band.

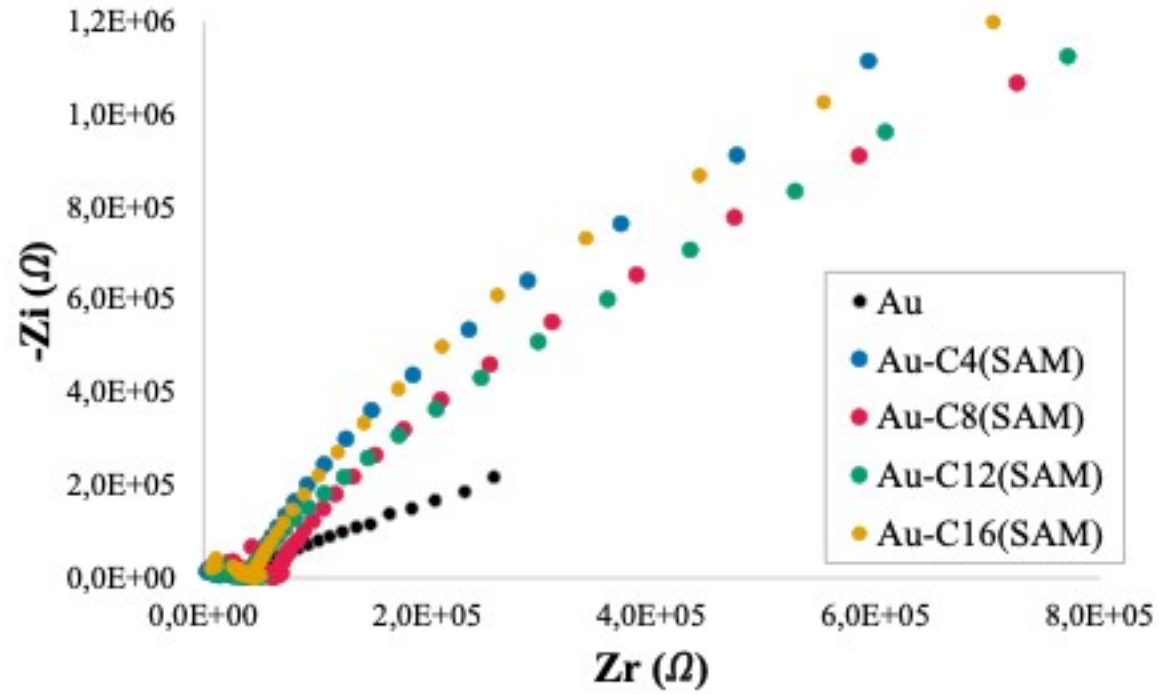

Figure S6: EIS spectra demonstrating the influence of alkanethiol chain length in SAMs on the electrochemical behaviour of Au NPs electrodes.

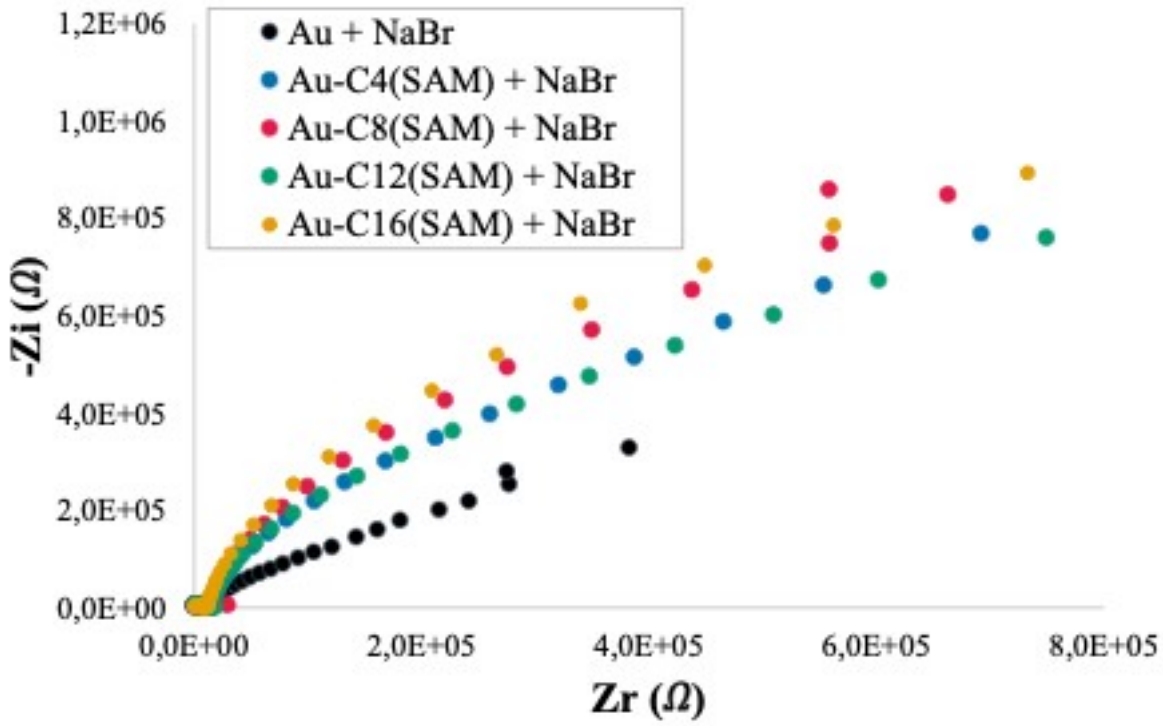

Figure S7: EIS spectra demonstrating the effect of NaBr poisoning on SAM-modified Au NP electrodes.

References:

1 P. Sekar, R. Bericat-Vadell, Y. Patehebieke, P. Bröqvist, C.-J. Wallentin, M. Görlin, J. Sá, *Nano Lett.* 2024, **24**, 8619-8625.

2 J. Fast, U. Aeberhard, S. P. Bremmer, H. Linke. *Appl. Phys. Rev.* 2021, **8**, 021309.

3 R. Bericat-Vadell, J. Sá. *Small Struct.* 2025, 2500185.