Supplemental Information for

Hot plasmonic electron-driven catalytic reaction on patterned metal-insulator-metal nanostructures

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Fig. S1 (a) TEM image and (b) size distribution histogram for 4.3 nm Pt nanoparticles prepared using the one-pot polyol reduction method.



Fig. S2 Photographs of the catalytic batch reactor that was used for the CO oxidation experiments.



Fig. S3 The geometrical parameters of the nanopatterned metal islands: (a–c) width, (d–f) height, and (g–i) taper angle distribution histogram of the Al, Ag, and Au nanoislands.





Fig. S4 (a) Transmission electron microscopy (TEM) images, (b) scanning transmission electron microscopy and high-angle annular dark field (STEM-HAADF) images, and (c) energy-dispersive X-ray spectroscopy (EDS) elemental maps of the Pt/2 nm TiO_2/Al nanostructures.



Fig. S5 (a) TEM images, (b) STEM-HAADF images, and (c) EDS elemental maps of the Pt/2 nm Al_2O_3/Al nanostructures.





Fig. S6 (a) TEM images, (b) STEM-HAADF images, and (c) EDS elemental maps of the Pt/2 nm Al_2O_3/Au nanostructures.



Fig. S7 (a) Spectral profile of the halogen lamp used during light irradiation and (b) UV–Vis absorbance spectra of each MIM nanostructure having nanopatterned Al, Ag, or Au as the plasmonic metals and Al_2O_3 as the insulating layer.

Finite-difference time-domain (FDTD) simulations

Optical simulations were performed using the finite-difference time-domain (FDTD) method in three spatial dimensions. All the simulations were periodic in the x- and y-directions, while the perfectly matched layer (PML) was used in the z-directions. Incident radiation was a plane wave from 300 to 1000 nm with a mesh size of 1 nm.



Fig. S8 Cross-sectional view of the model MIM nanostructure (*i.e.* $Pt/Al_2O_3/Au$) for the FDTD simulation.



Fig. S9 The electric field distributions for the top of the various MIM nanostructures calculated from the FDTD simulation. Scale bar is 30 nm.



Fig. S10 The absorption spectrum for the various MIM nanostructures calculated from the FDTD simulation.



Fig. S11 Average electric field intensity around the MIM nanostructure depending on the bottom metal: (a) Pt/Al₂O₃/Ag, (b) Pt/Al₂O₃/Au, and (c) Pt/Al₂O₃/Al, calculated using FDTD simulations.



Fig. S12 X-ray photoelectron spectroscopy (XPS) analysis of the MIM nanostructures.



Fig. S13 XPS analysis of the MIM nanostructures.



Fig. S14 The absorption spectrum depending on the thickness of the insulator layer calculated from the FDTD simulation for $Pt/Al_2O_3/Ag$ and $Pt/Al_2O_3/Au$.