Supplementary material for: Dynamical evolution of the Schottky barrier as a determinant contribution to electron-hole pair stabilization and photocatalysis of plasmon-induced hot carriers

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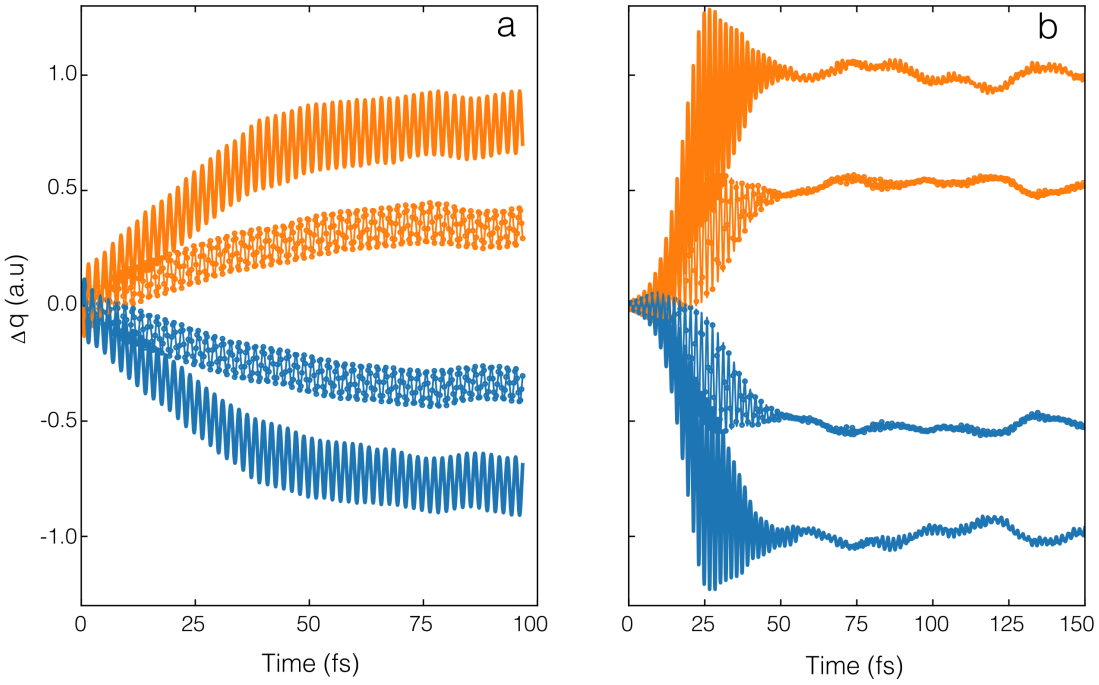


Figure S1: Panels a and b present the charge evolution (Δq) of Au NP (orange) and [TiO_2 + CO] (blue), compared to the ground state, as a function of time for a continuum and a pulsed laser respectively. Positive/negative values of Δq stand for electron loss/accumulation. continuum line and dotted line for simulations with and without the CO molecules, respectively.

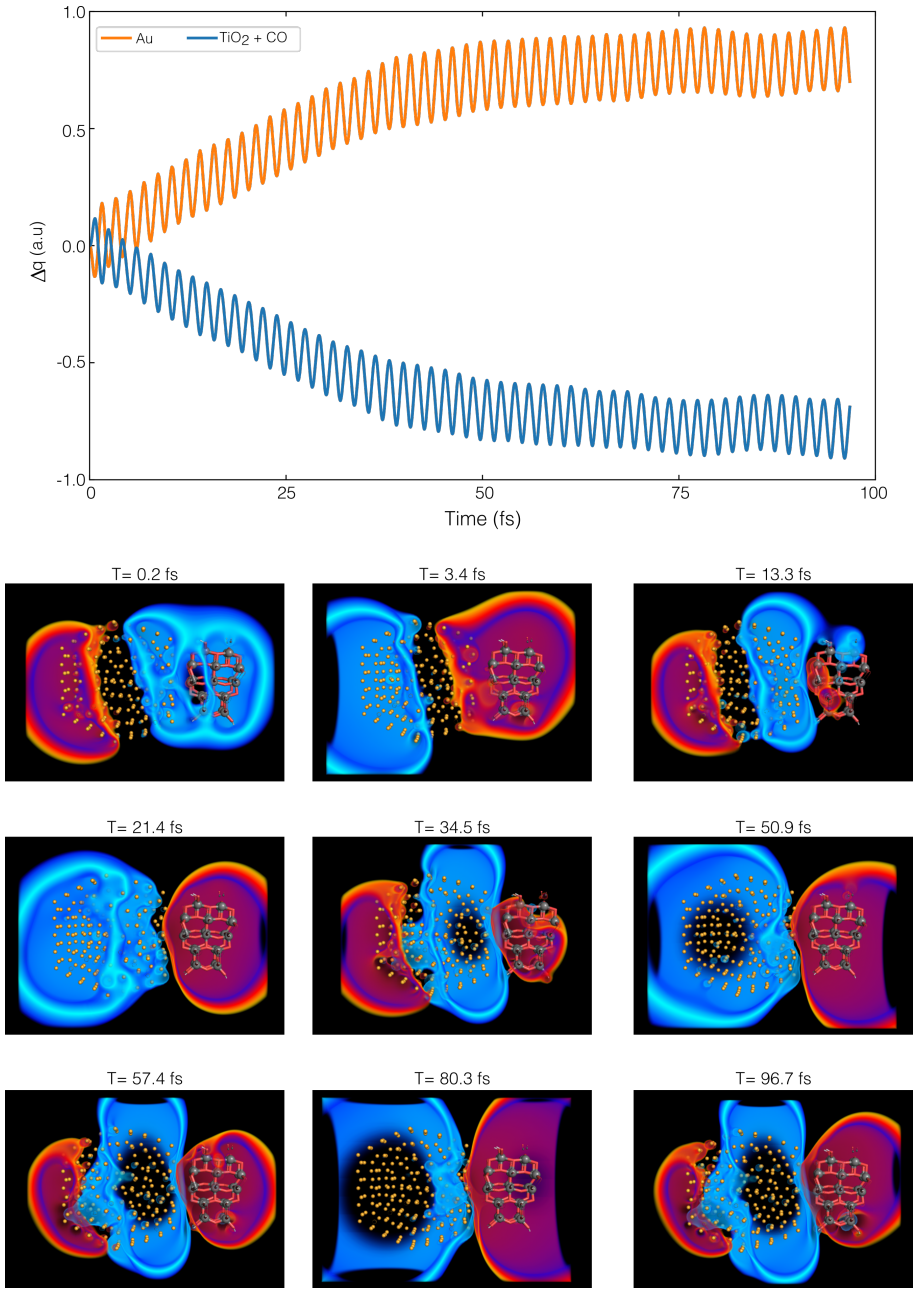


Figure S2: Up: charge evolution (Δq) of Au NP (orange) and [TiO_2 + CO] (blue), compared to the ground state, as a function of time for a continuum laser. Down: Developed electrostatic potential respect to the ground state $\Delta V = V_t - V_{t=0}$ dynamically rising a potential barrier. Slice of the 3d volume rendering centered at the interparticle axes. Blue tones depict $\Delta V > 0$ while violet to yellow scale encodes $\Delta V < 0$.

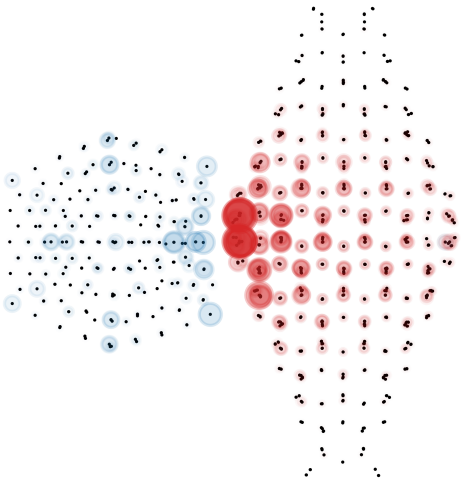


Figure S3: $x - z$ projection of the atomic charge modification (Δq). For each atom, Δq is represented by a circle, the size and opacity of the circle increases as Δq does. To allow differentiating the bulk and the out-layer atoms, an anatase TiO_2 particle with 852 atoms was used.

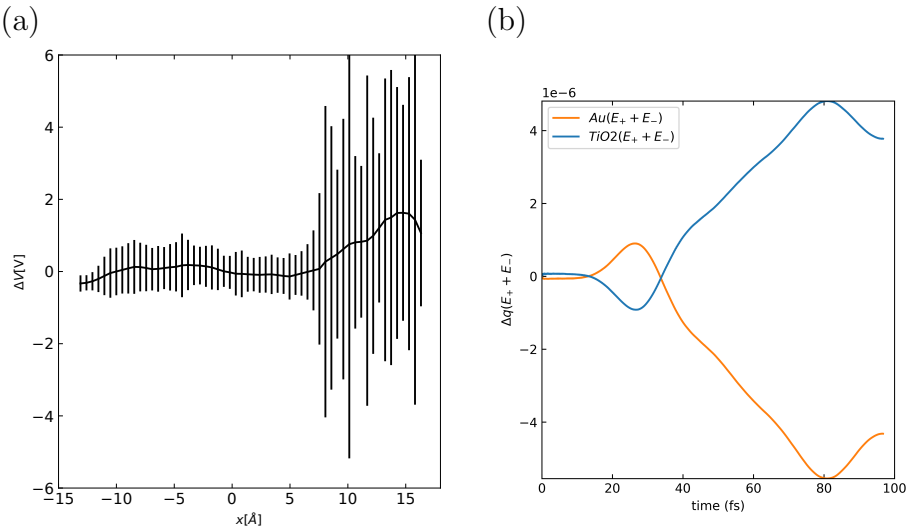


Figure S4: **(a)** presents ΔV along x axes at the ground state. The error bar represents the standard deviation of ΔV in the $y - z$ plane. **(b)** Charge rectification obtained when an electric field, polarized in the positive or negative x direction (E_+ and E_-, respectively), is applied to the system at the ground state. Orange and blue lines for Au NP and [TiO_2 + CO] particles, respectively. Note that a negative/positive value of $[\Delta q(E_+ + E_-)]$ indicates that electrons flow preferentially in the negative/positive x direction.

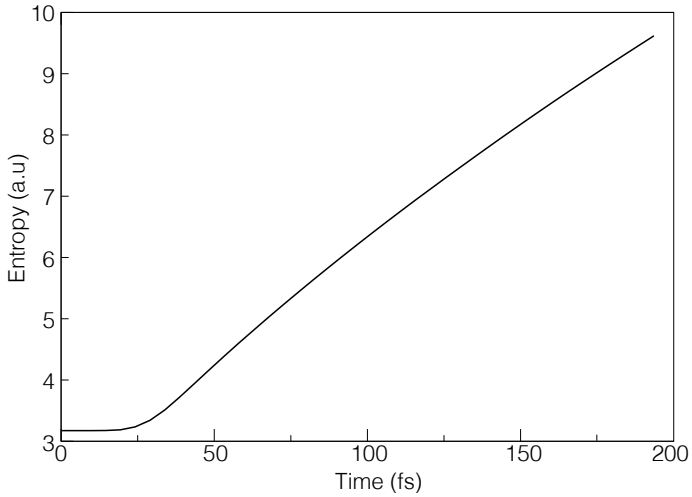


Figure S5: Electronic entropy evolution during the dynamics triggered by a laser pulse.

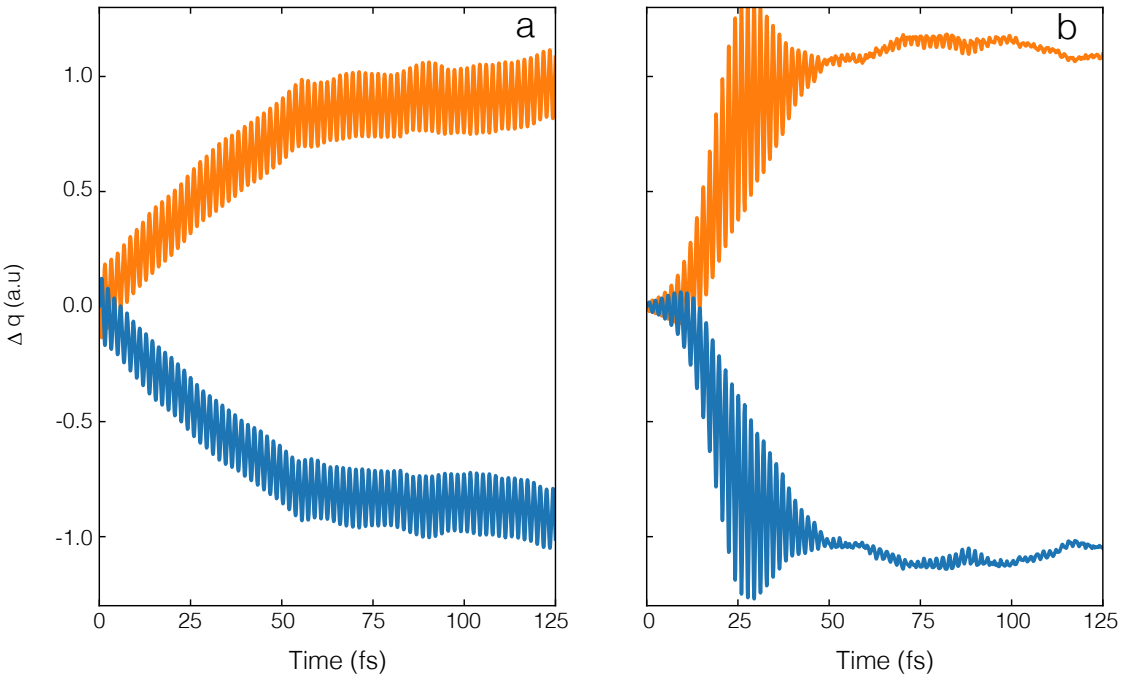


Figure S6: Panels a and b present the charge evolution (Δq) of Au NP (orange) and [TiO_2 + CO] (blue), compared to the ground state, as a function of time for a continuum and a pulsed laser, respectively. In these simulations the electron and ion dynamics were coupled. Positive/negative values of Δq stand for electron loos/accumulation.

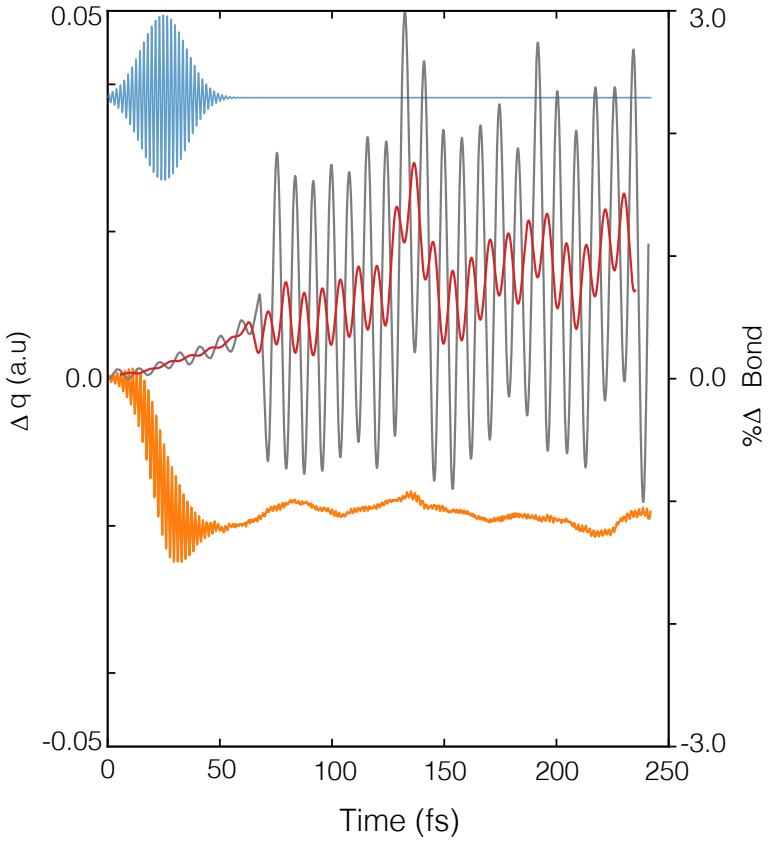


Figure S7: Hot carriers catalytic effect described by coupled electron-ion dynamics. The [Au-TiO_2-H_2] cluster was irradiated by a laser pulse. Orange and gray lines present the Δq for the H_2 molecules and the change of the H-H bond distance as a percentage of the ground state distance, respectively.

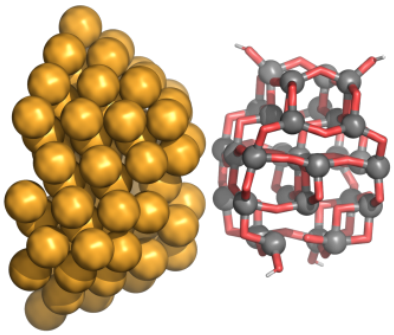


Figure S8: The model structure employed to compare the DFTB parameterization Vs. DFT simulations. This structure was generated using half of a 147 atom icosahedral Au NP and the TiO_2 NP. For the structural optimization, the Au atoms at the cut plane were held fixed. The binding energy difference between the Au and TiO_2 NP computed for the structure optimized at the DFT and the DFTB levels was $\sim$6% while the Au-Ti bond distance difference for the atoms at the interface was $\sim$1%

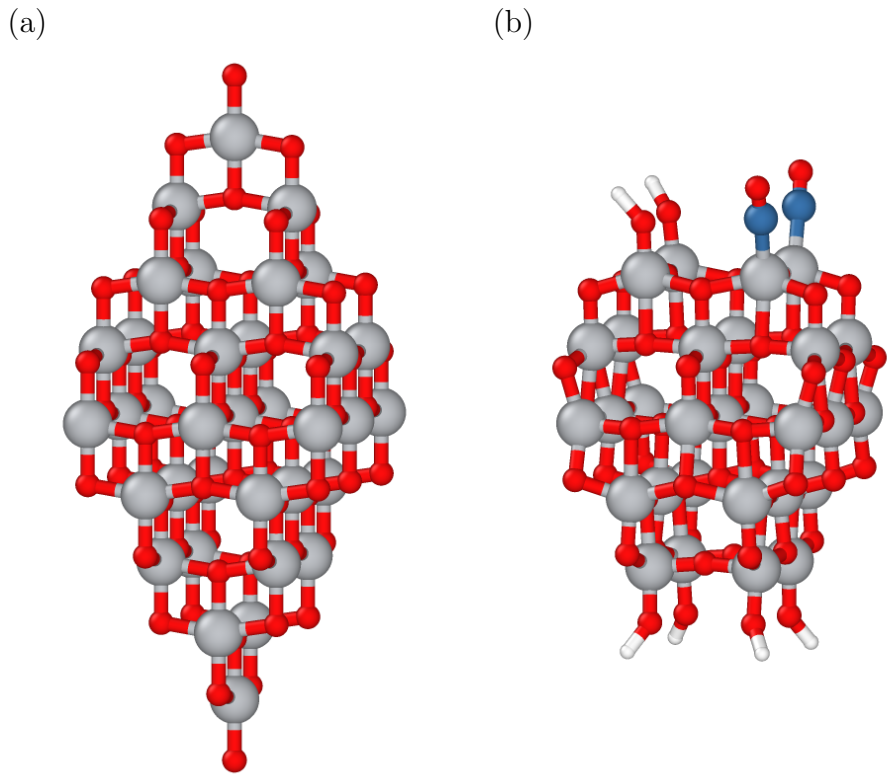
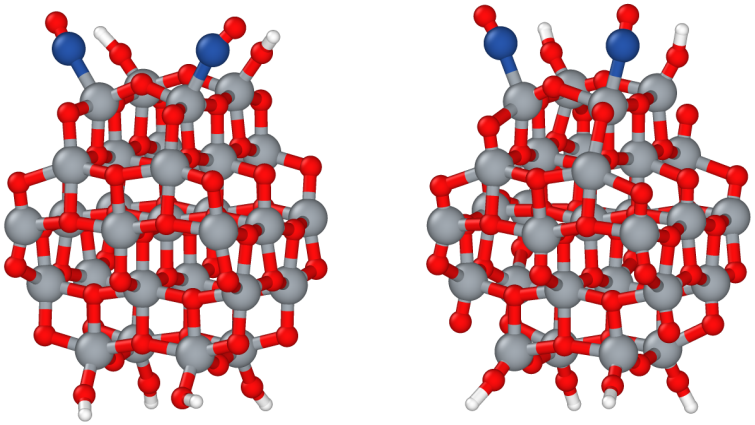


Figure S9: **(a)** Anatase TiO_2 nanoparticle constructed with the Wulff approach, resulting in a bipyramid with eight (101) facets. **(b)** Former nanoparticle after truncation and addition of H atoms to passivate the O dangling bonds, and the adsorption of two CO molecules. Gray, red, white and blue particles correspond to Ti, O, H and C atoms, respectively.

(a)



(b)

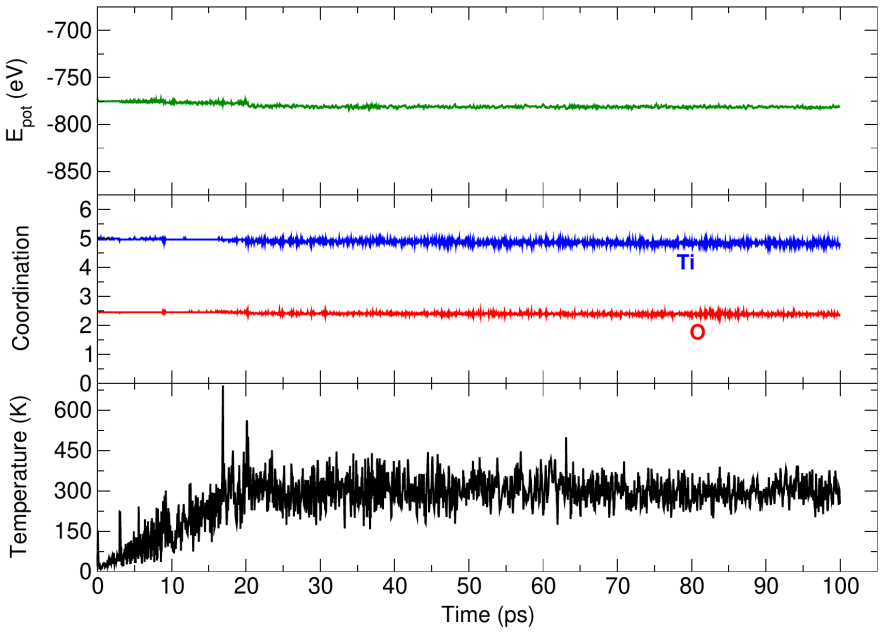


Figure S10: **(a)** Snapshots of the TiO_2 nanoparticle at 20 ps (left) and 100 ps of the molecular dynamic simulation. Same atomic coloring as mentioned above is used. No reconstruction are observed, the nanoparticle integrity remains unaffected during the simulation. **(b)** Temperature, average coordination and potential energy of the molecular dynamic simulation. Nor the energy, neither the coordination of O and Ti atoms change significantly during the simulation.