

Supporting Information for

**Control of Charge Carrier Relaxation at Au/WSe₂ Interface by Ti and TiO₂ Adhesion Layers:
Ab Initio Quantum Dynamics**

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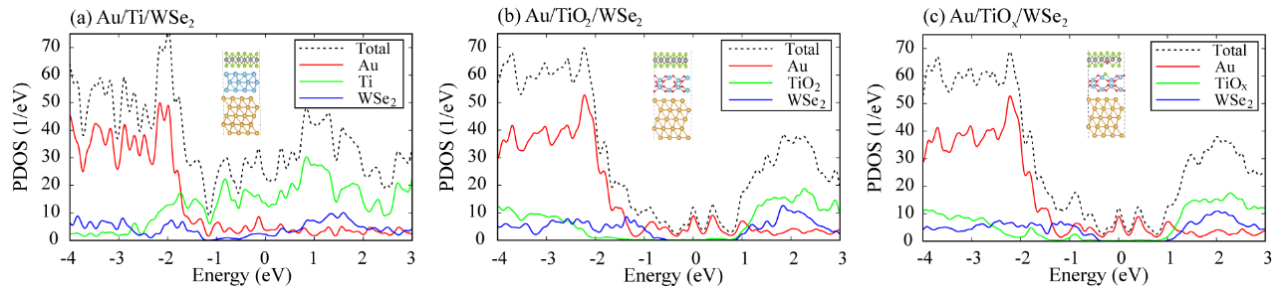


Figure S1. Atom-projected DOS for thicker Ti, TiO₂ or TiO_x layers in **(a)** Au/Ti/WSe₂, **(b)** Au/TiO₂/WSe₂, and **(c)** Au/TiO_x/WSe₂ at 0 K. The insets show the atomic structures. The DOS of the thicker Ti, TiO₂ and TiO_x layers are similar to the DOS shown in Figure 2.

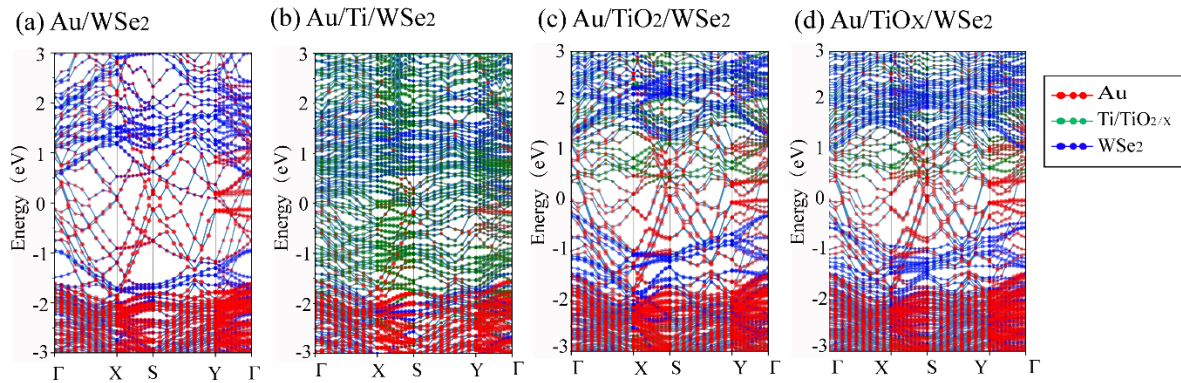


Figure S2. Electronic band structure of **(a)** Au/WSe₂, **(b)** Au/Ti/WSe₂, **(c)** Au/TiO₂/WSe₂ and **(d)** Au/TiO_x/WSe₂ along high symmetry directions of the Brillouin zone. All the calculations are obtained using the PBE functional. The Fermi level for all systems is set to 0.

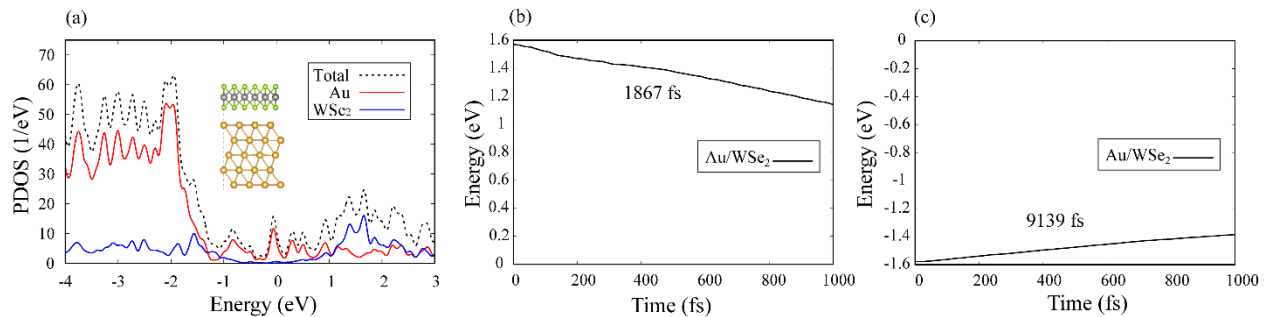


Figure S3. **(a)** Atom-projected DOS in the Au/WSe₂ system. The insert shows the atomic structure. Evolution of **(b)** electron and **(c)** hole energies in the Au/WSe₂ system.

Table S1. Distances between adjacent layers at 300 K. All the distances are calculated from center of one layer to the center of the other layer. The values reported here are averaged over the entire MD trajectory.

| | Distance from Au to adhesion layer Ti/TiO ₂ /TiO _x (Å) | Distance from adhesion layer Ti/TiO ₂ /TiO _x to WSe ₂ (Å) |
|---------------------------------------|--|--|
| Au/Ti/WSe ₂ | 2.238 | 2.311 |
| Au/TiO ₂ /WSe ₂ | 2.324 | 2.504 |
| Au/TiO _x /WSe ₂ | 2.342 | 2.576 |

THEORY AND METHODS

A. Time-Domain Density Functional Theory (TDDFT)

Within the Kohn-Sham (KS) representation of DFT,^{1,2} the electron density, $\rho(\mathbf{r}, t)$, is described as a sum of densities of time-dependent (TD) single particle KS orbitals, denoted by $\varphi_n(\mathbf{r}, t)$, occupied by N_e electrons:

$$\rho(\mathbf{r}, t) = \sum_{i=1}^{N_e} |\varphi_i(\mathbf{r}, t)|^2 \quad (\text{S1})$$

The evolution of the electron density is determined by applying the TD variational principle to the KS energy, which gives the following equations of motion (EOM):

$$i\hbar \frac{\partial \varphi_i(\mathbf{r}, t)}{\partial t} = H(\mathbf{r}, \mathbf{R}, t) \varphi_i(\mathbf{r}, t) \quad (\text{S2})$$

Here, \mathbf{r} and \mathbf{R} are the electronic and nuclear coordinates, respectively. These time-dependent Kohn-Sham (TDKS) equations are coupled because of the dependence of the Hamiltonian, H , on the overall electron density. The TDKS equations are then solved by expanding the TDKS orbitals $\varphi_n(\mathbf{r}, t)$ in the adiabatic KS basis, $\tilde{\varphi}_k(\mathbf{r}; \mathbf{R})$, obtained from the time-independent ground state DFT calculation,

$$\varphi_i(\mathbf{r}, t) = \sum_{j=1}^{N_e} c_{ij}(t) |\tilde{\varphi}_i(\mathbf{r}; \mathbf{R})\rangle \quad (\text{S3})$$

Using the above expression, equation S2 transforms into a set of differential EOM for the expansion coefficients:

$$i\hbar \frac{\partial c_{ij}(t)}{\partial t} = \sum_{k=1}^{N_e} c_{ik}(t) (\varepsilon_k \delta_{jk} + \mathbf{d}_{jk}) \quad (\text{S4})$$

where ε_k corresponds to the energy of the adiabatic KS state k , and \mathbf{d}_{jk} is the non-adiabatic coupling (NAC) between adiabatic states j and k . The latter arises due to the dependence of the adiabatic KS orbitals on the nuclear coordinates, \mathbf{R} and, therefore, describes electron-phonon interaction. It is calculated numerically as the overlap between wave functions j and k at sequential time steps as follows:

$$\mathbf{d}_{jk} = -i\hbar \langle \tilde{\varphi}_j(\mathbf{r}; \mathbf{R}) | \nabla_{\mathbf{R}} | \tilde{\varphi}_k(\mathbf{r}; \mathbf{R}) \rangle \cdot \dot{\mathbf{R}} = -i\hbar \langle \tilde{\varphi}_j(\mathbf{r}; \mathbf{R}) | \frac{\partial}{\partial t} | \tilde{\varphi}_k(\mathbf{r}; \mathbf{R}) \rangle \quad (\text{S5})$$

Nuclear trajectories of the ground electronic state are used to sample initial conditions to create ensemble averages for subsequent simulations of the excited state dynamics

B. Fewest Switches Surface Hopping (FSSH)

The ultrafast electron and hole relaxation processes are modeled using FSSH, which is the most widely used NA molecular dynamics (MD) technique.³⁻⁶ FSSH can be viewed as a master equation, with non-perturbative time-dependent transition rates between states arising from solution of the TD Schrödinger equation.

The method minimizes the number of surface hops by prescribing a probability for hopping between electronic states that is based on population fluxes instead of the populations themselves. The dependence of the transition probabilities on the atomic coordinates creates a correlation between the nuclear and electronic dynamics. The NAC and the wave function amplitudes are used as input to determine the FSSH probability. The time-dependent probability of hopping between states i and j within the time interval Δt is equal to

$$dP_{ij} = \left(\frac{-2\text{Re}(a_{ij}^* d_{ij})}{a_{ii}} \right) dt \quad (\text{S6})$$

where $a_{ij} = c_i c_j^*$. In cases where dP_{ij} is negative, the hopping probability is set to zero because, by construction, a hop from state i to state j can take place only when the occupation of state j increases and the occupation of state i decreases. This feature of the algorithm achieves “fewest switches” by minimizing the number of hops. A uniform random number between 0 and 1 is generated every time step and compared to the probability to decide whether a hop will take

place or not. A hop is rejected if the kinetic energy available to the nuclei along the direction of the NA coupling is insufficient to accommodate an increase in the electronic energy. If the hop occurs, the nuclear velocity is rescaled to conserve the total electron-nuclear energy.

The classical path approximation (CPA) to FSSH assumes that the nuclear dynamics are weakly dependent on the electronic evolution, for instance, as compared to thermally induced nuclear fluctuations.⁷ The CPA approximation allows significant computational savings since the time-dependent potential that drives multiple FSSH realizations of the NA dynamics of the electronic subsystem can be obtained from a single MD trajectory. The velocity rescaling plus hop rejection feature of the original FSSH is replaced by multiplying the FSSH probability for transitions upward in energy by the Boltzmann factor. This maintains the condition of detailed balance and achieves thermodynamic equilibrium in the long-time limit.

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