

**Supporting information for:**

**Novel Excitonic Solar Cells in Phosphorene-TiO<sub>2</sub>**

**Heterostructures with Extraordinary Charge**

**Separation Efficiency**

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## Methods

We used the ab Initio nonadiabatic molecular dynamics method<sup>S1,S2</sup> to calculate the interfacial photoinduced electron transfer dynamics. In this method, the coupled electron-ion dynamics was described by surface hopping formalisms.<sup>S3-S5</sup> The photoinduced electron state is expressed based on the basis of adiabatic Kohn-Sham (KS) orbitals via the time-independent DFT calculation for the current ionic configuration  $R$  at each molecular dynamics step, and is evolved in real time. The electron transfer (ET) at a given time can be characterized by the amount (or the fraction) of the PE electron remaining at the phosphorene layers,

$$E(t) = 1 - \sum_{i,j} c_i^* c_j \int \phi_i^*(r, R(t)) \phi_j(r, R(t)) dr \quad (1)$$

where  $i$  and  $j$  are summed over all relevant KS orbitals,  $c_i$  and  $c_j$  are expansion coefficients of PE state,  $\phi_i$  and  $\phi_j$  are the adiabatic KS orbitals, and the integration is taken over the volume of the sensitizer. Taking the time derivative of eq 1, we obtain two contributions,

$$\frac{d}{dt} ET(t) = - \sum_{i,j} \left\{ \frac{c_i^* c_j}{dt} \int \phi_i^*(r, R(t)) \phi_j(r, R(t)) dr + c_i^* c_j \frac{d \int_{dye} \phi_i^*(r, R(t)) \phi_j(r, R(t)) dr}{dt} \right\} \quad (2)$$

The first term represents the nonadiabatic ET, corresponding to the variation in the adiabatic occupied states. The second term indicates the adiabatic contribution, corresponding to the changes in the adiabatic states. In our cases, the PE electron remains in the same KS orbitals while still evolved in space, leading to ET. The sum of nonadiabatic ET, adiabatic ET, as well as the initial ET at  $t = 0$  gives rise to the total ET.<sup>S2,S6,S7</sup>

## Absorbance calculations

The imaginary part of the dielectric tensor  $\epsilon_2(\omega)$  as a function of photon frequency  $\omega$  is relevant for interband optical transitions. Starting from  $\epsilon_2(\omega)$ , the monolayer absorbance

$A(\omega)$  of phosphorene layers, defined as the fraction of photons of energy  $E = \hbar\omega$  absorbed by the monolayer, is obtained using an approximation<sup>S8,S9</sup> as follows:

$$A(\omega) = \frac{\omega}{c} \epsilon_2(\omega) \Delta z \quad (3)$$

here  $c$  is the speed of light, and  $\Delta z$  is the size of the simulation cell in the layer-normal direction. This formula can be seen as a Taylor expansion for small thickness  $\Delta z$  of the absorbance  $A = 1 - e^{-\alpha \Delta z}$  for a flat layer of a bulk material with thickness  $\Delta z$  and absorption coefficient  $\alpha = \frac{\epsilon_2 \omega}{cn}$ , with refractive index  $n = 1$  due to the presence of vacuum in the simulation cell. Equivalently, it can be seen as deriving from the polarizability per unit area, or from the optical conductivity of the monolayer.

## Simulation details

A  $2 \times 2$  supercell of single phosphorene layer containing 16 phosphorus atoms is used to match a  $3 \times 1$  six atomic layer stoichiometric  $\text{TiO}_2(110)$  surface slab containing 12 Ti and 24 atoms with three bottom layers fixed at bulk position in a supercell ( $8.877 \times 6.497 \times 26 \text{ \AA}^3$ ). First-principles calculations based on the density functional theory (DFT) were carried out using the Vienna *ab initio* Simulation Package (VASP).<sup>S10</sup> The exchange correlation interaction was treated within the generalized gradient approximation (GGA),<sup>S11</sup> which is parametrized by the Perdew, Burke, and Ernzerhof (PBE).<sup>S12</sup> The plane-wave basis set with a kinetic energy cutoff of 400 eV is used. All the atoms in the unit cell are fully relaxed until the force on each atom is less than 0.01 eV/ $\text{\AA}$ . The on-site Coulomb correction to GGA (GGA + U)<sup>S13</sup> have been carried out. Parameters U and J are chosen to be 6.0 and 0.5 eV ( $U_{eff} = U - J = 5.5 \text{ eV}$ ), which is more reasonable, as reported in a previous study.<sup>S14</sup> In the structural relaxation and the stationary self-consistent-field calculation, a k-point grid with 0.02  $\text{\AA}^{-1}$  spacing is adopted and a 0.01  $\text{\AA}^{-1}$  k-grid for the calculations of density of states (DOS) and optical properties is used. The PBE approach is well-known to have an

inaccurate description of the dispersion force and thus a poor estimation of the interlayer distance. Here all the structures are relaxed by using the optimized Becke88 van der Waals (optB88-vdW) functional.<sup>S15</sup>

Since DFT methods often underestimate the band gap and wrongly describe the CBM and VBM of  $\text{TiO}_2(110)$  surface, the screened exchange hybrid density functional by Heyd-Scuseria-Ernzerhof (HSE06)<sup>S16,S17</sup> was adopted. It is well-known that many-body interactions play an important role in the absorption spectrum in the low-dimensional system because of the reduced charge screening and the enhanced electron-electron correlation. Therefore, the GW calculations will be performed without self-consistency in the Green's function and the screened Coulomb interaction ( $G_0W_0$  approximation) in combination with the random phase approximation (RPA) or Bethe-Salpeter equation (BSE) calculations to calculate the optical absorption spectra with or without electron-hole (e-h) interactions, as implemented in BerkelyGW package.<sup>S18,S19</sup>

After relaxing the geometry at 0 K, we used velocity recalling to bring the temperature of the hybrid phosphorene-/ $\text{TiO}_2$  system to 300 K, similar to system at room temperature. We then performed a 2ps adiabatic molecular dynamics (MD) simulation in the microcanonical ensemble with a 1 fs atomic time-step. To determine interfacial electron transfer dynamics, 300 short MD trajectories, each containing 300 fs simulation for electron injection and 150 fs for charge recombination, were included in the ensemble average, so as to efficiently capture the stochastic nature of the coupled electron-ion dynamics.

The adiabatic state energies and nonadiabatic couplings were calculated for each step of the MD run. The slab used for simulations was doubled from static calculations, containing six atomic layer of  $\text{TiO}_2$  with 24 Ti atoms and 48 O atoms. The above phosphorene layer contains 32 phosphorus atoms. In the doped systems, we replaced one phosphorus atom by Al or Cl atom with a doping concentration of 3.1 %, which is twice smaller than than in the static calculations and can be easier realized in future experiments.

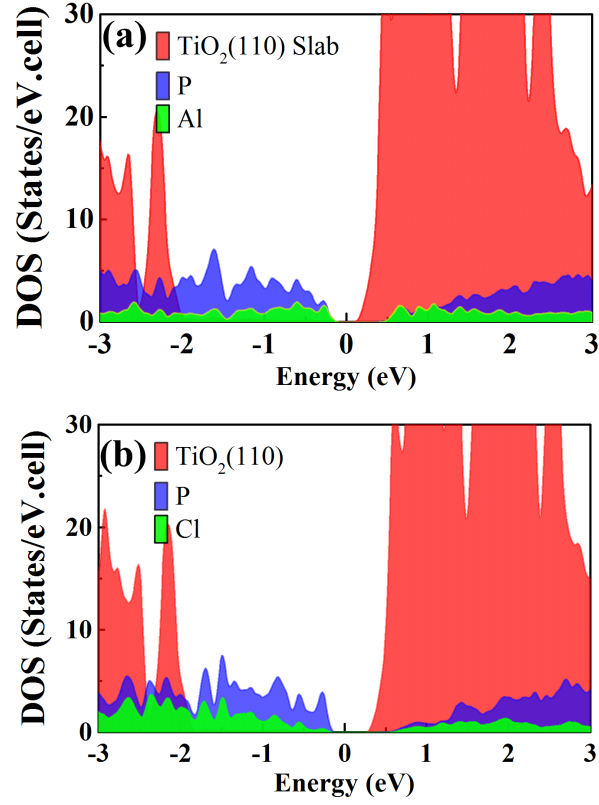


Figure S1: Density of states (DOS) for (a) Al@1L-BP/TiO<sub>2</sub> interface and (b) Cl@1L-BP/TiO<sub>2</sub> interface, respectively. The Fermi level is set to zero. The DOS shows phosphorene states dominates the states above the top of the valence band (VB).

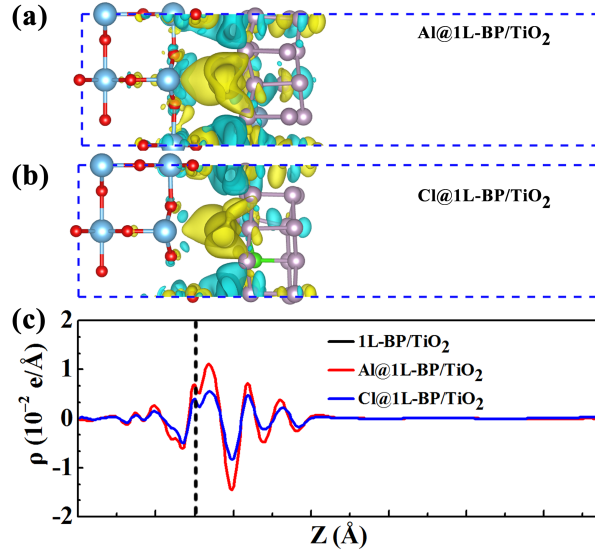


Figure S2: Charge density differences for (a) Al@1L-BP/TiO<sub>2</sub>, and (b) Cl@1L-BP/TiO<sub>2</sub>, respectively. The yellow region represents charge accumulation, and the cyan region indicates charge depletion; the isosurface value is  $0.0004 \text{ e}/\text{\AA}^3$ . (c) Plane-averaged differential charge density  $\Delta\rho(z)$  for three heterostructures, 1L-BP/TiO<sub>2</sub>, Al- and Cl@1L-BP/TiO<sub>2</sub> as a function of position in the  $z$ -direction. The vertical dash line shows the location of the top layer of the TiO<sub>2</sub>(110) surface.

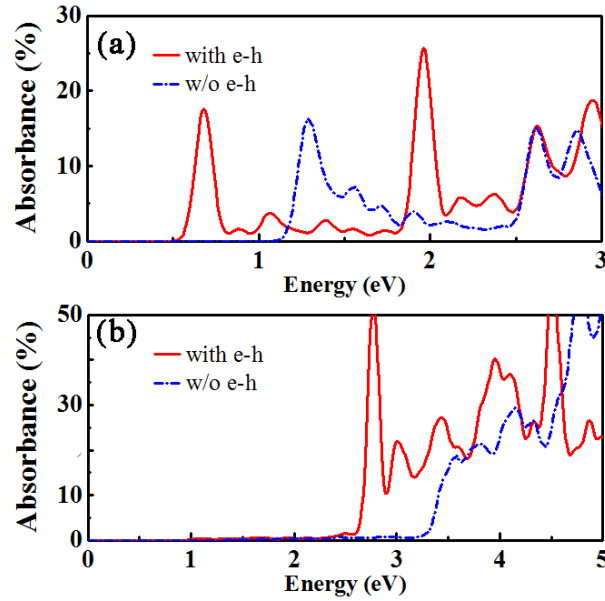


Figure S3: Absorbance spectra of bilayer black phosphorus for the incident light polarized along the (a) armchair and (b) zigzag direction, respectively. The single-particle optical absorption without electron-hole (e-h) interaction (blue) and with e-h interaction (red), based on GW + RPA and GW + BSE levels.

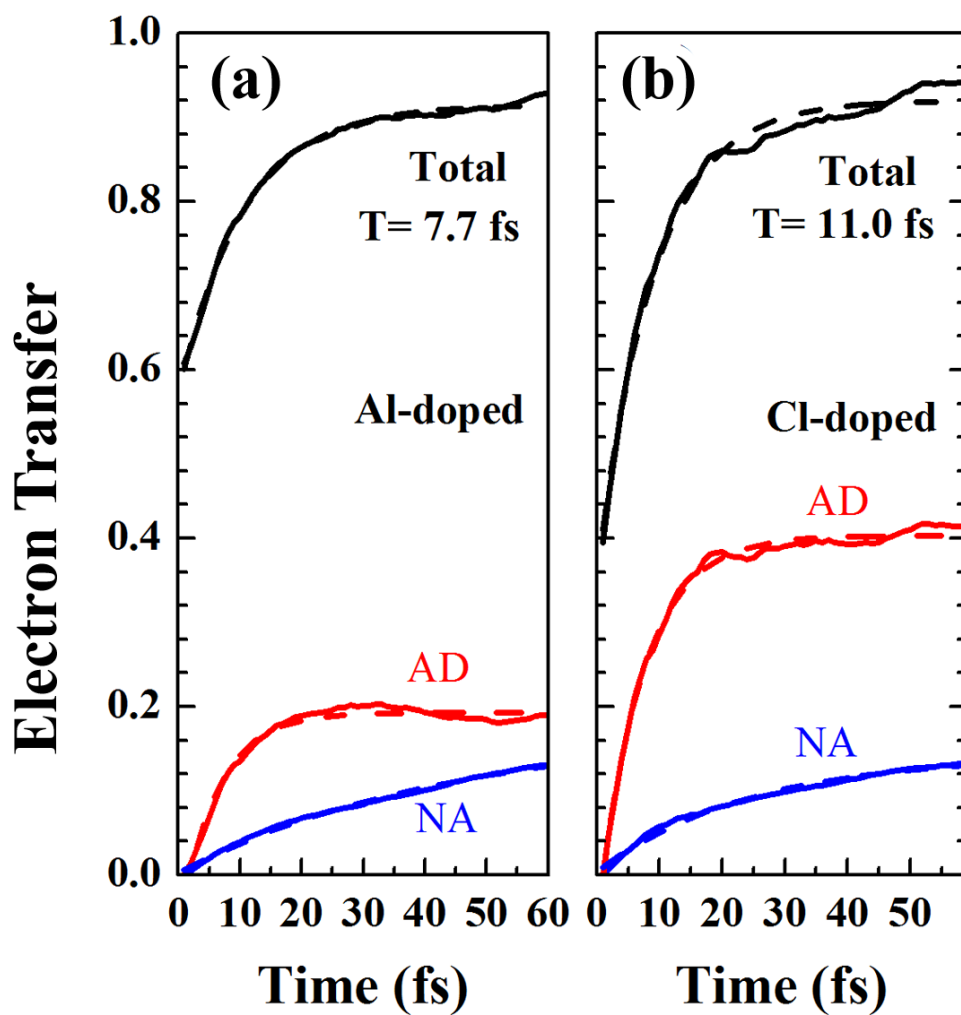


Figure S4: Average electron transfer dynamics of photoexcited states for (a) Al@1L-BP/TiO<sub>2</sub>, (b) Cl@1L-BP/TiO<sub>2</sub>. The solid black, solid red and solid blue lines represent the total adiabatic and nonadiabatic electron transfer. The total, adiabatic (AD) and nonadiabatic (NA) ET are indicated by the black solid, red solid and blue solid lines, respectively. The dashed lines show the exponential fits of each lines.

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