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High-efficient photogenerated electron transfer at black phosphorus / indium selenide heterostructure interface from ultrafast dynamics

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Nonadiabatic molecular dynamics with time-domain density functional theory

We applied *ab initio* nonadiabatic molecular dynamics (NAMD) implemented within time domain density functional theory (TD-DFT) in the Kohn-Sham (KS) framework to model the photogenerated electron dynamics. The Runge-Gross theorem asserts that all observables are determined with the knowledge of the one-body electron density. TD-DFT in the Kohn-Sham approach maps an interacting many-body system onto a system of noninteracting particles where the electron density of the latter equals to the former. The time-dependent charge density of the interacting system can thus be obtained from the time-dependent KS orbitals, $\psi_p(r,t)$ as:

$$\rho(r,t) = \sum_{p=1}^{N_e} |\psi_p(r,t)|^2 \tag{1}$$

The evolution of the electron density is determined by the TD variational principle, leading to a set of single-electron equations for the evolution of the KS orbitals:

$$i\hbar \frac{\partial \psi_p(r,t)}{\partial t} = H(r;R)\psi_p(r,t); p = 1,2,...,N_e \tag{2}$$

By expanding the time-dependent KS orbitals in the adiabatic KS orbital basis,

$\phi_p(r;R)$, which is calculated with time-independent DFT from the geometry in the adibatic MD as shown below,

$$\psi_p(r,t) = \sum_k c_k(t)\phi_k(r;R) \tag{3}$$

By inserting Eq. 3 into Eq. 2, one can obtain equations for the expanding coefficients:

$$i\hbar\frac{\partial}{\partial t}c_j(t) = \sum_k c_k(t)(\varepsilon_k\delta_{jk} + d_{jk}) \tag{4}$$

Where ε_k is the energy of the adiabatic state *k*, and d_{jk} is the non-adiabatic couplings between the basis *j* and *k*.

The extent of photogenerated electron transfer between BP and InSe is computed by integrating the projected electron density on BP (it is similar to integrate the projected electron density on InSe).

$$\int_{BP}\rho_{PE}(r,t)dr = \int_{BP}|\psi_{PE}((r),t)|^2 dr = \sum_{i,j} c_i^*(t)c_j(t)\int_{BP}\phi_i^*(r,R(t))\phi_j(r,R(t))dr \tag{5}$$

Taking the time-derivative of Eq. 5 gives the expression for adiabatic (AD) and non-adiabatic (NA) contributions to charge transfer:

$$\frac{d\int_{BP}\rho_{PE}(r,t)dr}{dt} = \sum_{i,j}\left\{\frac{d(c_i^*c_j)}{dt}\int_{BP}\phi_i^*\phi_j dr + c_i^*c_j\frac{\int_{BP}\phi_i^*\phi_j dr}{dt}\right\} \tag{6}$$

The change in the charge density described by the first term on the right-hand side of Eq. 6 is due to change of state occupations of the adiabatic KS states, which we refer to as nonadiabatic transfer term. On the other hand, the second term causes change of charge density by change of localization of the KS adiabatic states, hence the name adiabatic transfer. The contribution to the total charge transfer was obtained by further integrating the two terms on the right-hand side of Eq. 6.

The calculation of binding energy

In order to determine the interaction between BP and InSe layers, the binding energy between BP and InSe layers can be calculated by $E_b=[E_{BP/InSe} -(E_{BP}+E_{InSe})]/n$, where n represents the number of atoms, and $E_{BP/InSe}$, E_{BP} and E_{InSe} are the total energies of BP/InSe vdW heterostructure, the individual BP and InSe layers, respectively.

The calculation of optical property

The imaginary part of dielectric matrix $\varepsilon_{\alpha\beta}^{(2)}(\omega)$ is determined from the following equation: [1]

$$\varepsilon_{\alpha\beta}^{(2)}(\omega)=\frac{4\pi^2e^2}{\Omega}\lim_{q\to 0}\frac{1}{q^2}\sum_{c,v,\mathbf{k}}2w_{\mathbf{k}}\delta(\varepsilon_{c\mathbf{k}}-\varepsilon_{v\mathbf{k}}-\omega)\times\left\langle u_{c\mathbf{k}+e_\alpha\mathbf{q}}\,|\,u_{v\mathbf{k}}\right\rangle\left\langle u_{c\mathbf{k}+e_\beta\mathbf{q}}\,|\,u_{v\mathbf{k}}\right\rangle^{*} \qquad (7)$$

Where Ω is the volume of the primitive cell, q is the electron momentum operator, c and v are the conduction and valence band states, respectively, $\omega_{\mathbf{k}}$ is the **k** point weight, $\varepsilon_{c\mathbf{k}}$, $\varepsilon_{v\mathbf{k}}$ and $u_{c\mathbf{k}+e_\alpha\mathbf{q}}$, $u_{c\mathbf{k}+e_\beta\mathbf{q}}$ are the eigenvalues and wave-functions at the **k** point, respectively,

[1] M. Gajdoš, K. Hummer, G. Kresse, J. Furthmüller and F. Bechstedt, Phys. Rev. B ***73***, 045112 (2006).

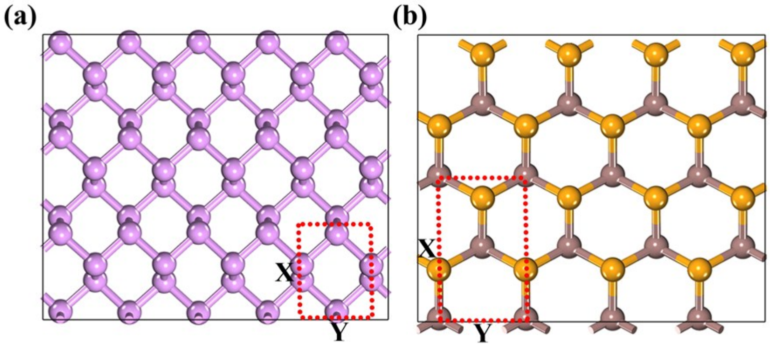

Figure S1. Structure of (a) BP and (b) InSe. The shape of rectangular unit cell is plotted using red dotted line.

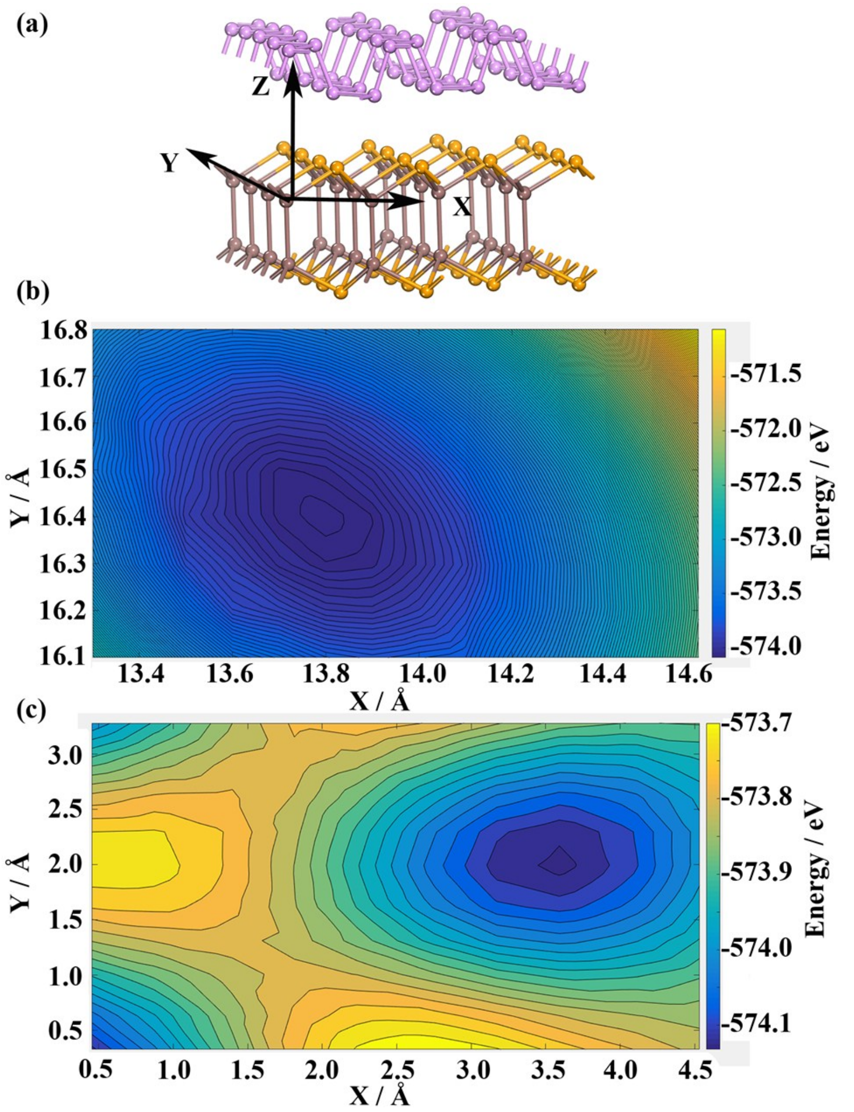

Figure S2. (a) Lattice structure of BP/InSe vdW heterostructure from side view. (b) Total energy of BP/InSe vdW heterostructure as a function of the lattice parameters. (c) Total energy of BP/InSe vdW heterostructure as a function of the stacking form. The schematic of interlayer displacement in which the bottom InSe layer stands still and top BP layer is moved in x and y direction.

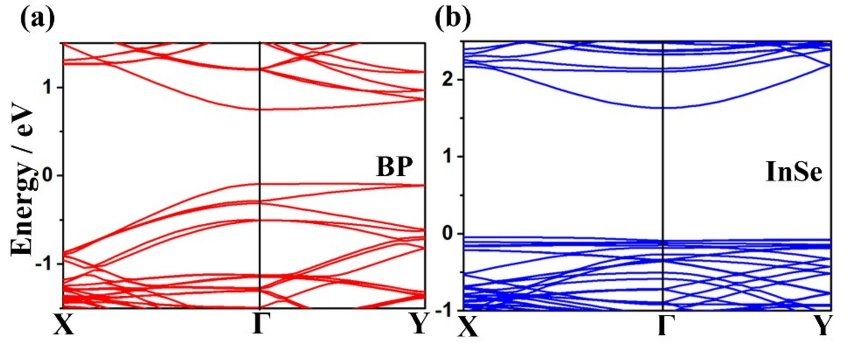

Figure S3. Band structures of (a) BP and (b) InSe. The Fermi level is set as zero.

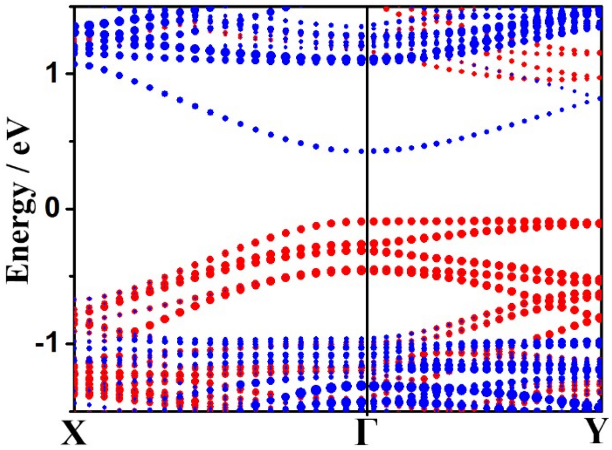

Figure S4. Band structures of BP/InSe heterostructure where red and blue lines record the contributions of BP and InSe layer, respectively. The Fermi level is set as zero.

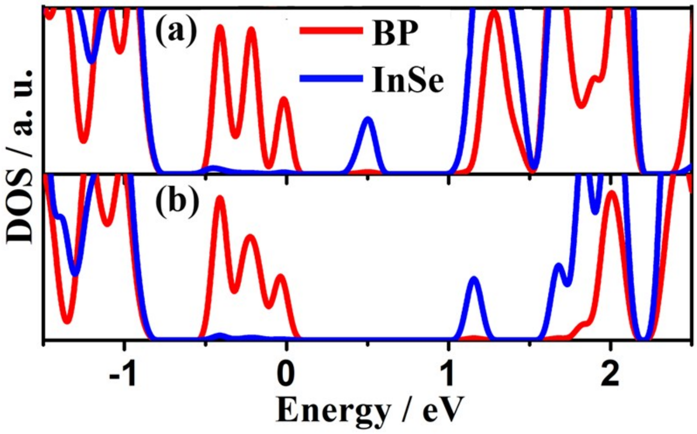

Figure S5. Density of states (DOS) of BP/InSe vdW heterostructure, where red and blue lines record the contributions of BP and InSe layer, respectively. The DOS obtained by (a) PBE functional and (b) HSE06 functional.

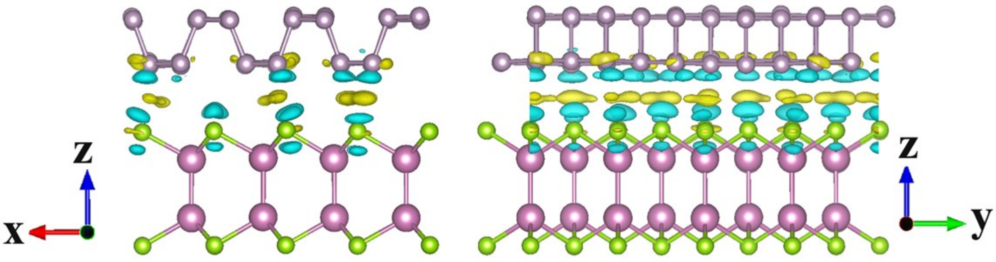

Figure S6. Charge density difference of BP/InSe vdW heterostructure. The yellow and blue color isosurfaces correspond to the accumulation and depletion of electrons. The isovalue is 5×10^{-4} e/Bohr^3. $\Delta\rho = \rho_{BP/InSe} - \rho_{BP} - \rho_{InSe}$, where $\rho_{BP/InSe}$, ρ_{BP} and ρ_{InSe} are the charge densities of BP/InSe heterostructure, BP and InSe isolated layer, respectively.