Supporting Information

Low-energy Interlayer Phonon Assisted Carriers Recombination in Z-Scheme van der Waals Heterostructures for Photocatalysis

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Computational details

The DFT simulations were performed based on the Vienna ab initio simulation package (VASP) package.\textsuperscript{1, 2} The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof form (PBE) was adopted to treat the electronic exchange-correlation energy. Both the projector augmented (PAW) functions and HSE06 functions were used to calculate the band structure and optical properties. All atomic structures were fully relaxed until energies and forces were
coverage to $10^{-6}$ eV and $1 \times 10^{-4}$ eV/Å respectively with a cutoff energy of 500 eV in the plane-wave expansion. The vdW interaction was also considered by the empirical DFT-D3 method. The unit cells of the TMD and WSi$_2$N$_4$ were optimized at first by using a $15 \times 15 \times 1$ Monkhorst-Pack k-mesh. Then, the Brillouin zone integration was sampled using the $3 \times 3 \times 1$ k-points mesh for structure optimization and a denser $5 \times 5 \times 1$ k-points mesh for electronic properties calculation for the heterostructures. A vacuum layer of 15 Å was added in the z direction to avoid the impact of pseudo images. The harmonic interaction force constants (2nd) and phonon dispersion spectrum were determined using the density-functional perturbation theory (DFPT) scheme by the Phonopy package.\(^3\)

**Calculation details for NAMD.** After the structure optimization at 0 K, the $4 \times 4 \times 1$ supercells were adopted for the WSi$_2$N$_4$ monolayer and WSi$_2$N$_4$/TMD heterostructures to suppress artificially introduced “phonon bottleneck”. Due to the big system and high computational load, only the phonon modes at the $\Gamma$ point were considered for both heterostructures. All systems were equilibrated through repeated velocity rescaling for 5 ps at 300 K, and another 5 ps adiabatic molecular dynamic trajectories were generated within the subsequent microcanonical ab initio molecular dynamics using a time step of 1 fs. The molecular dynamics were performed at $\Gamma$ point. The nonadiabatic molecular dynamics (NAMD) calculations were performed by using the semi-classical decoherence induced surface hopping (DISH) approach implemented in PYXAID code.\(^4\) The decoherence effects were considered through the semi-classical DISH scheme which describes the interactions between the quantum nuclei and electronic subsystem. In order to mimic the charge dynamic on a long-time scale, the obtained nonadiabatic Hamiltonians were involved in an iteration process. The first 1000 geometries were selected as the initial conditions, and 2000 sampling numbers for each initial structure to realize the statistical average. Baring mind a similar band structure and orbital composition obtained by the PBE and HSE06 levels, a scissor operator is applicable within the NAMD simulation to compensate the band gap lowering. The scissor operators of 0.45 eV and 0.3 eV were applied for the MoS$_2$/WSi$_2$N$_4$ and MoSe$_2$/WSi$_2$N$_4$ heterostructures, respectively to match the HSE06 derived band gap.

**Calculation details for HER and OER.** Considering the longer carrier lifetime and more suitable band alignment of the WSi$_2$N$_4$/MoS$_2$ heterostructure, the same $4 \times 4 \times 1$ WSi$_2$N$_4$/MoS$_2$ supercell
was used for exploring the thermodynamics of the HER and OER processes, which take place at the WSi$_2$N$_4$ and MoS$_2$ side, respectively. Additional vacancy models were constructed through substituting one N or S atom by one vacancy on the surface. The Gibbs free energy, $\Delta G$, under standard condition is defined as:

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S - n_e - U_{RHE}$$

(1)

where $\Delta E$ is the total energy change obtained from DFT calculation; $\Delta E_{ZPE}$ is the change in zero-point energy derived from the vibrational frequency; $\Delta S$ is the difference in entropy; $n$ is the number of proton/e$^-$ pairs consumed within a certain step; and $U_{RHE}$ is the contribution from external potential. The OER process involves four elementary oxidation steps and expressed as:

$$\ast + H_2O \rightarrow \ast OH + H^+ + e^-$$

(2)

$$\ast OH \rightarrow \ast O + H^+ + e^-$$

(3)

$$\ast O + H_2O \rightarrow \ast OO + H^+ + e^-$$

(4)

$$\ast OO \rightarrow \ast + O_2 + H^+ + e^-$$

(5)

where the $\ast$ represents the active site on the pristine catalysts surface, and the $\ast OH$, $\ast O$, and $\ast OO$ denote the radial adsorbed on the surface. Meanwhile, the HER process can be decomposed into two one-electron steps, as follow:

$$\ast + H^+ + e^- \rightarrow \ast H$$

(6)

$$\ast H + H^+ + e^- \rightarrow \ast + H_2$$

(7)

**HER and OER catalytic activity of WSi$_2$N$_4$/MoS$_2$.** The catalytic activities for the HER and OER of the WSi$_2$N$_4$/MoS$_2$ heterostructure are investigated by the Gibbs free energy. The nitrogen vacancy (V$_N$) and selfie vacancy (V$_S$) contained surfaces are also considered for the HER and OER processes, respectively, as the single atom vacancy is a common method to enhance the catalytic ability. In Figure S8a, $\Delta G_{H\ast}$ for the pristine WSi$_2$N$_4$/MoS$_2$ of 0.17 eV is even smaller than that of 0.36 eV in V$_N$ contained surface. Under a bias external potential of 0.4 V, the HER
catalytic occurs on the WSi$_2$N$_4$/MoS$_2$ surface spontaneously. For the OER process, the free energy evolution in the WSi$_2$N$_4$/MoS$_2$ is an uphill process at 0 V. Meanwhile, these elementary steps become spontaneously in the V$_S$ contained surface at an equilibrium potential of 1.23 V. In summary, the constructed Z-scheme WSi$_2$N$_4$/MoS$_2$ heterostructure is an applicable photocatalyst for water splitting.

**Figure S1.** (a) Honeycomb like crystal structures of the WSi$_2$N$_4$ from (b) top and (c) side view.

**Figure S2.** Phonon dispersion of WSi$_2$N$_4$ based on a 4×4×1 supercell.
Figure S3. Element projected band structures of the WSi$_2$N$_4$/MoS$_2$ and WSi$_2$N$_4$/MoSe$_2$ heterostructures from the PBE calculations.

Figure S4. Partial density of states (PDOS) of the (a) WSi$_2$N$_4$/MoS$_2$ and (b) WSi$_2$N$_4$/MoSe$_2$ heterostructures from the PBE calculations.
Figure S5. Evolution of the total energy of the heterostructures WSi$_2$N$_4$/MoS$_2$ (a) and WSi$_2$N$_4$/MoSe$_2$ (b) within the last 2.5 ps during the NVE AIMD equilibrium process. The inserted pictures are the snapshots of the heterostructures at 5.0 ps.

Figure S6. Evolution of the band gap of the heterostructures WSi$_2$N$_4$/MoS$_2$ and WSi$_2$N$_4$/MoSe$_2$ within the NAMD simulation. The band gap is rescaled by the scissor operators with the HSE06 results as the reference.
Figure S7. Related phonon modes for charge recombination in the (a) WSi$_2$N$_4$/MoS$_2$ and (b) WSi$_2$N$_4$/MoSe$_2$ heterostructures.

Figure S8. Electron-hole recombination through interlayer ($CBM_{TMD} - VBM_{WSi_2N_4}$) and innerlayer ($CBM_{TMD} - VBM_{TMD}$) channels in the (a) WSi$_2$N$_4$/MoS$_2$ and (b) WSi$_2$N$_4$/MoSe$_2$ heterostructures.
Figure S9. The Gibbs free energy profiles of the (a) HER and (b) OER on the WSi$_2$N$_4$/MoS$_2$ heterostructure.

Table S1. Hot electron relaxation time of each orbital.

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<th>Orbital</th>
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References