Supplementary Materials

Unveiling ultrafast carrier dynamics in photocatalytic 2-D heterostructures: Insights from first-principles and nonadiabatic molecular dynamics†

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Text S1 The calculations details of NAMD.

For the calculation of excited state dynamics of photogenerated carriers, the quantum decoherence-induced surface hopping (DISH) method under the classical path approximation was used for NAMD calculations. Based on the optimized geometric structure at 0 K, the velocity rescaling method was used to increase the system temperature to 300 K, then 5 ps trajectories are sampled under the NVE ensemble, the last 2000 trajectories are selected, and the corresponding wave functions are generated. NAMD results are averaged over 100 different initial structures in the trajectory.

Text S2 Calculation of Gibbs free energy.

The HER proceeds via a two-electronic reaction step, represented by Eqs. 1-2, where $*$ denotes the reactive site on the GaN/SnS_2 heterostructure.

$$* + H^+ + e^- \rightarrow H* \tag{1}$$

$$*H + H^+ + e^- \rightarrow H_2 + * \tag{2}$$

The OER proceeds via a four-electronic reaction step, represented by Eqs. 3-6, where $OH*$, $O*$, and $OOH*$ denote the intermediates in the process of reaction, respectively.

$$* + H_2O \rightarrow *OH + H^+ + e^- \tag{3}$$

$$*OH \rightarrow *O + H^+ + e^- \tag{4}$$

$$*O + H_2O \rightarrow *OOH + H^+ + e^- \tag{5}$$

$$*OOH \rightarrow * + O_2 + H_2 + e^- \tag{6}$$

The activity of the reaction is determined by the changes of Gibbs free energy (ΔG) of the intermediates in the HER and OER, as defined by Nørskov:[39]

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S + \Delta G_{pH} + \Delta G_U \tag{7}$$

here, ΔE represents the adsorption energy of the reaction intermediates calculated by DFT, ΔE_{ZPE} and $T\Delta S$ are the zero-point energy and entropy of the intermediates, respectively. The influence of pH and external potential on ΔG is reflected by ΔG_{pH} and ΔG_U, with $\Delta G_{pH} = -kT\ln(10) \times pH$ and $\Delta G_U = -eU$, where U is the electrode potential relative to the standard hydrogen electrode (SHE) potential.

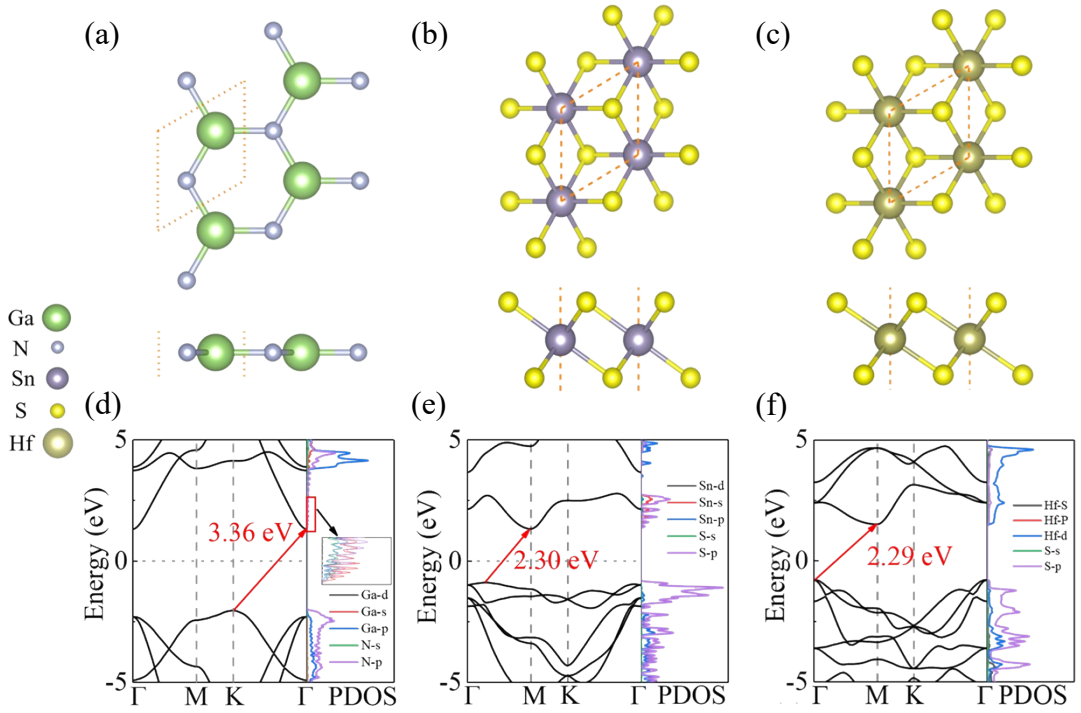

Fig. S1. The optimized geometrical structures of (a) GaN, (b) SnS_2, and (c) HfS_2 monolayers. (d-f) The band structures and PDOS of monolayers.

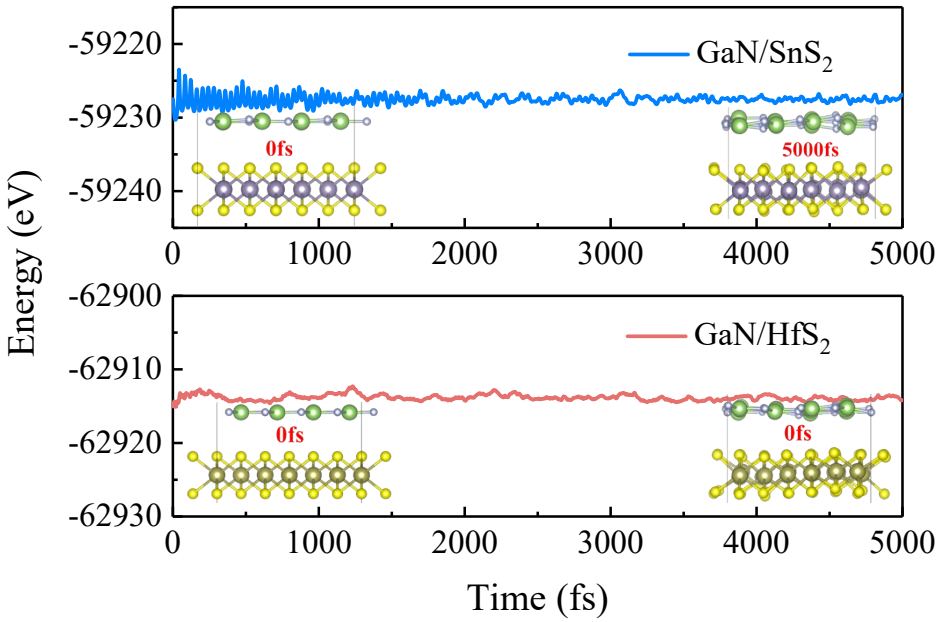

Fig. S2. Changes in energy of GaN/SnS_2 and GaN/HfS_2 heterostructures during a 5 ps AIMD simulation at 300K. Insets display the initial and final structures of heterostructures during simulation.

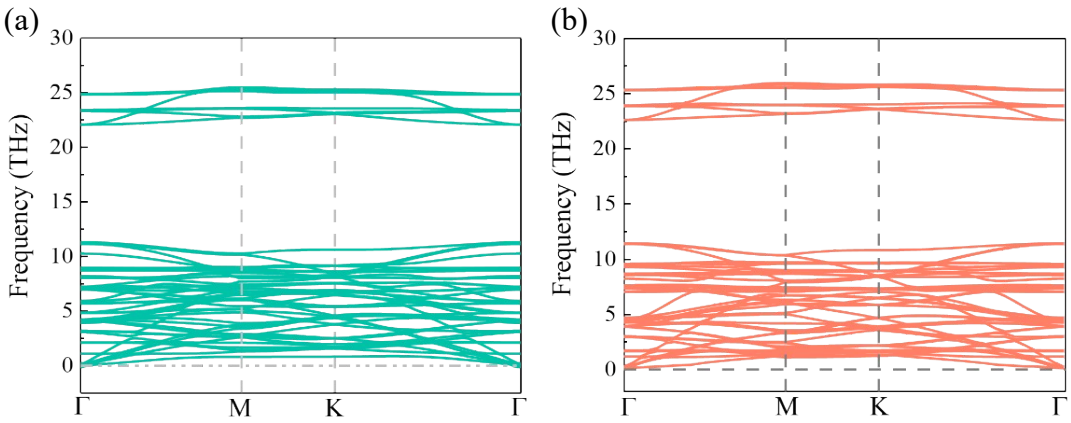

Fig. S3. Phonon dispersion spectra of (a) GaN/SnS_2 and (b) GaN/HfS_2 heterostructures.

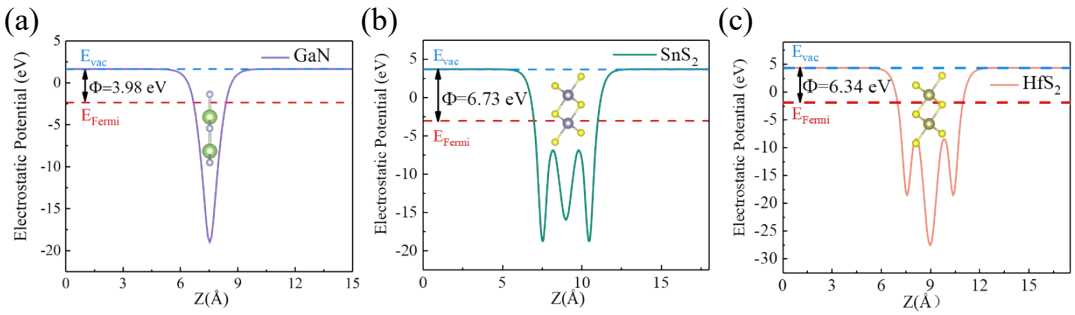

Fig. S4. Electrostatic potential of monolayers: (a) GaN, (b) SnS_2, and (c) HfS_2.

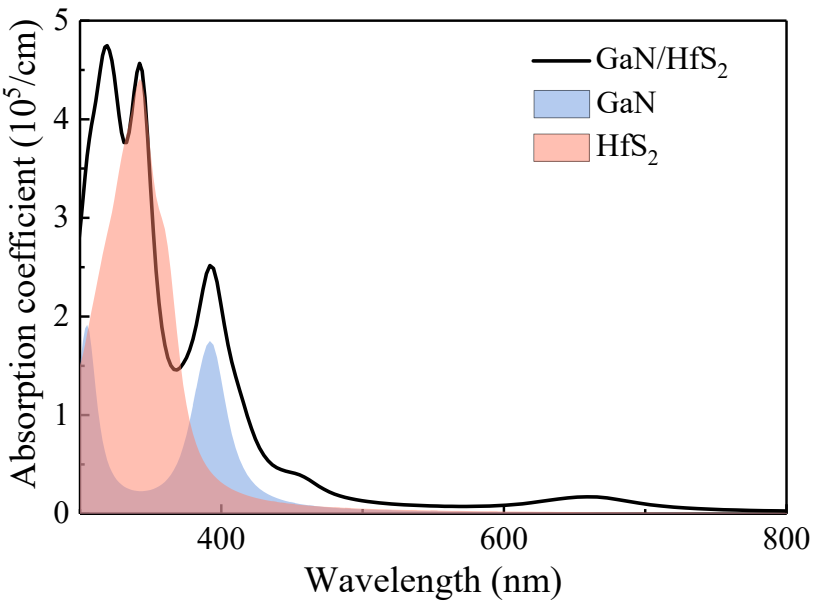

Fig. S5. Optical absorption spectra of GaN, HfS_2, and GaN/HfS_2 heterostructure.

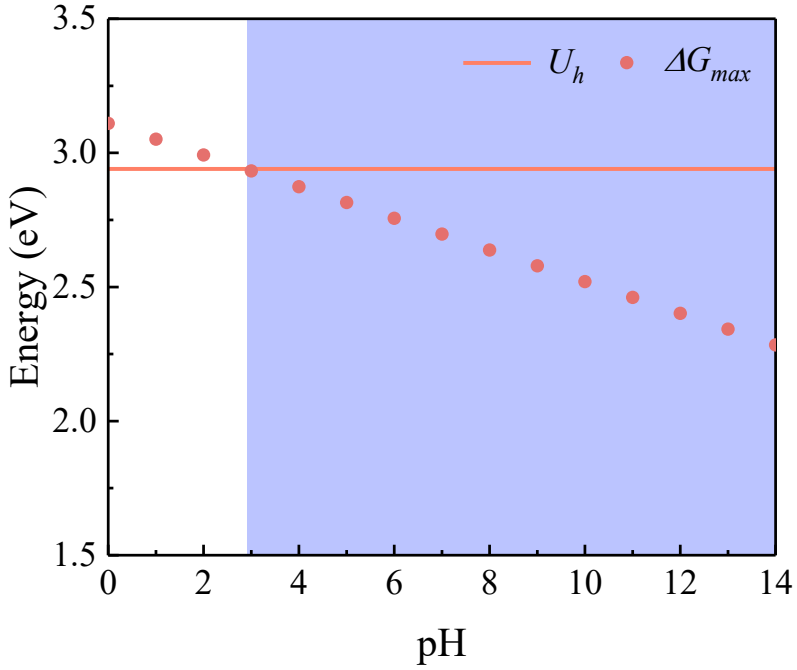

Fig. S6 The value of ΔG_{max} changed with pH. The purple area represents the pH range in which OER can proceed spontaneously.

Table. S1. The optimized lattice constant(a,b), interlayer distance between monolayers(d), binding energy(E_b) and bandgap(E_g) of all systems.

Systems	a=b(Å)	d(Å)	E_b(meV/ Å^2)	E_g(eV)
GaN	3.20	-	-	3.36
SnS_2	3.70	-	-	2.30
HfS_2	3.64	-	-	2.29
GaN/SnS_2	6.39	3.25	-16.21	1.04
GaN/HfS_2	6.36	3.35	-17.73	1.28

Structure file
1.GaN.cif

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_cell_length_c                         15.000000
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_cell_angle_beta                       90.000000
_cell_angle_gamma                      120.000000
_cell_volume                           133.212795
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   _atom_site_occupancy
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   _atom_site_fract_y
   _atom_site_fract_z
   _atom_site_adp_type
   _atom_site_U_iso_or_equiv
   _atom_site_type_symbol
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   N1         1.0     0.666667     0.333333     0.500000    Uiso  ? N
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2.SnS_2.cif

```
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   _atom_site_occupancy
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   _atom_site_fract_y
   _atom_site_fract_z
   _atom_site_adp_type
   _atom_site_U_iso_or_equiv
   _atom_site_type_symbol
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   S1      1.0     0.666649     0.333339     0.580274     Uiso  ? S
   S2      1.0     0.333312     0.666671     0.419660     Uiso  ? S
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3.HfS_2.cif

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_cell_angle_alpha                      90.000000
_cell_angle_beta                       90.000000
_cell_angle_gamma                      120.000000
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   _atom_site_fract_y
   _atom_site_fract_z
   _atom_site_adp_type
   _atom_site_U_iso_or_equiv
   _atom_site_type_symbol
   Hf1          1.0     0.000000    0.000000    0.500000    Uiso  ? Hf
   S1           1.0     0.666667    0.333333    0.580208    Uiso  ? S
   S2           1.0     0.333333    0.666667    0.419792    Uiso  ? S
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4.GaN/SnS_2.cif

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loop_
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loop_
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_atom_site_adp_type
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_atom_site_type_symbol

Ga1	1.0	0.325921	0.324658	0.378280	Uiso	?	Ga
Ga2	1.0	0.826101	0.324888	0.376456	Uiso	?	Ga
Ga3	1.0	0.325355	0.824374	0.376461	Uiso	?	Ga
Ga4	1.0	0.826034	0.824298	0.376453	Uiso	?	Ga
Sn1	1.0	0.999154	0.999611	0.565416	Uiso	?	Sn
Sn2	1.0	0.333515	0.666890	0.565429	Uiso	?	Sn
Sn3	1.0	0.666320	0.332375	0.565395	Uiso	?	Sn
S1	1.0	0.999963	0.333201	0.623853	Uiso	?	S
S2	1.0	0.332885	0.999898	0.623886	Uiso	?	S
S3	1.0	0.666166	0.665812	0.623851	Uiso	?	S
S4	1.0	0.999785	0.666437	0.507056	Uiso	?	S
S5	1.0	0.332887	0.332860	0.506749	Uiso	?	S
S6	1.0	0.666255	0.999496	0.506626	Uiso	?	S
N1	1.0	0.492707	0.157871	0.377397	Uiso	?	N
N2	1.0	0.992450	0.157739	0.377362	Uiso	?	N
N3	1.0	0.492603	0.658189	0.377354	Uiso	?	N
N4	1.0	0.992508	0.657821	0.371684	Uiso	?	N

5.GaN/HfS_2.cif

#==========
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_cell_angle_gamma	119.993591
_cell_volume	875.472136
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   _atom_site_fract_z
   _atom_site_adp_type
   _atom_site_U_iso_or_equiv
   _atom_site_type_symbol
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   N2     1.0    0.834463    0.168247    0.597951    Uiso    ? N
   N3     1.0    0.333350    0.667125    0.597192    Uiso    ? N
   N4     1.0    0.832200    0.667118    0.597950    Uiso    ? N
   S1     1.0    0.667000    0.000419    0.463148    Uiso    ? S
   S2     1.0    0.333407    0.332993    0.463149    Uiso    ? S
   S3     1.0   -0.000429    0.666576    0.463148    Uiso    ? S
   S4     1.0    0.333325   -0.000287    0.349585    Uiso    ? S
   S5     1.0    0.000309    0.333613    0.349587    Uiso    ? S
   S6     1.0    0.666417    0.666707    0.349584    Uiso    ? S
   Ga1    1.0    0.167820    0.334105    0.596988    Uiso    ? Ga
   Ga2    1.0    0.666620    0.333795    0.597339    Uiso    ? Ga
   Ga3    1.0    0.165736    0.832628    0.596988    Uiso    ? Ga
   Ga4    1.0    0.666440    0.834740    0.596984    Uiso    ? Ga
   Hf1    1.0   -0.000001    0.000008    0.406311    Uiso    ? Hf
   Hf2    1.0    0.666684    0.333340    0.406098    Uiso    ? Hf
   Hf3    1.0    0.333322    0.666659    0.406679    Uiso    ? Hf
```