Supporting Information

Boost the Large Driving Photovoltages for Overall Water Splitting in Direct Z-Scheme Heterojunctions by Interfacial Polarizations

Xu Gao[1,‡], Yanqing Shen[1,‡,*], Jiajia Liu[1], Lingling Lv[1], Min Zhou[1], Zhongxiang Zhou[1], Yuan Ping Feng[2], Lei Shen[3,*]

[1] *School of Physics, Harbin Institute of Technology, Harbin 150001, PR China*

[2] *Department of Physics, National University of Singapore, Singapore 117551*

[3] *Department of Mechanical Engineering, National University of Singapore, Singapore 117575*

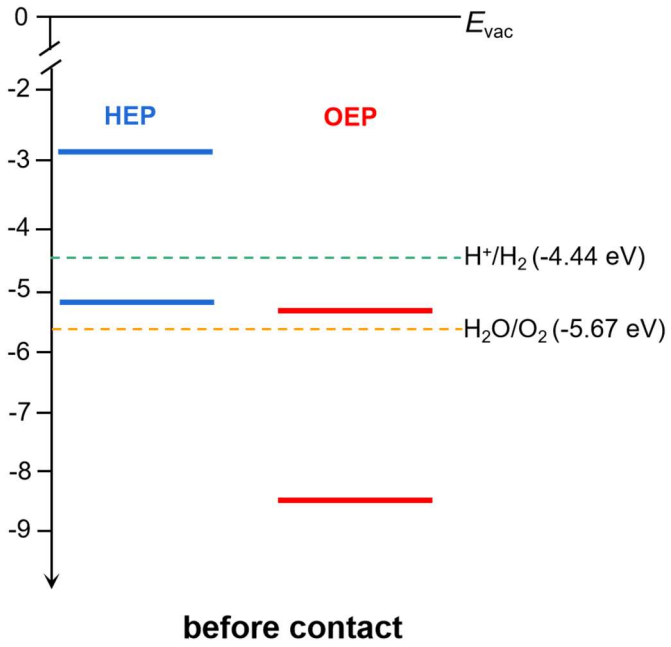

Fig. S1 Schematic of band alignments with respect to the vacuum level of the two materials (a HEP and an OEP) composing the direct Z-scheme heterojunction before contact. The green and orange dashed lines represent the reduction potential and oxidation potential of water splitting, respectively.

Table S1 Calculated lattice constants ($a = b$), equilibrium interlayer distance (d), interfacial thickness (h), interfacial binding energy (E_b), dipole moment (μ), electrostatic potential difference ($\Delta\Phi$) and the magnitude of internal electric filed (E_{int}) of the PtO_2-based heterojunction, as well as those of the isolated monolayers after full geometric optimization.

Material	$a = b$ (Å)	d (Å)	h (Å)	E_b (eV)	μ (Debye)	$\Delta\Phi$ (eV)	E_{int} (V/Å)
$PtO_2/MoSe_2$	3.24	2.77	5.35	−0.24	0.14	0.55	0.10
PtO_2/WSe_2	3.24	2.66	5.37	−0.31	0.18	0.70	0.13
PtO_2/GeC	3.22	2.87	3.56	−0.26	0.25	0.98	0.27
PtO_2	3.15	-	-	-	0	0	0
$MoSe_2$	3.32	-	-	-	0	0	0
WSe_2	3.33	-	-	-	0	0	0
GeC	3.25	-	-	-	0	0	0

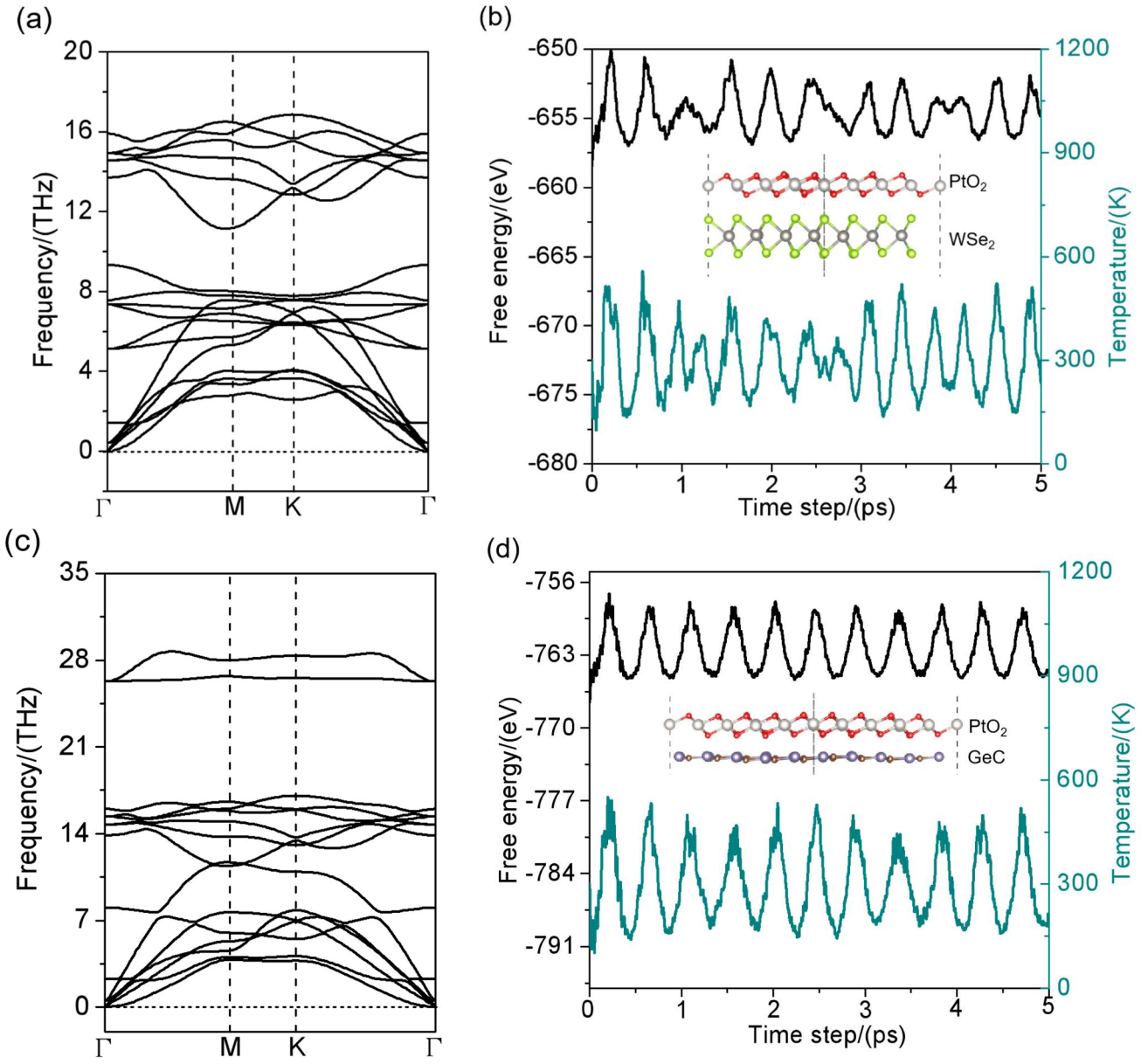

Fig. S2 Phonon dispersion and molecular dynamics simulations at 300 K of the heterojunction (a-b) PtO_2/WSe_2, and (c-d) PtO_2/GeC. The finial configurations are shown as the insets. 4 × 4 × 1 supercell (96 atoms in total) and 5 × 5 × 1 supercell (125 atoms in total) are adopted, respectively.

The phonon dispersion and molecular dynamics simulations of PtO_2/WSe_2, and PtO_2/GeC show that there are no imaginary modes in the Brillouin zone (Figs. S2(a) and S2(c)), and there are no obvious structural deformations or broken bonds after 5 ps (Figs. S2(b) and S2(d)). These together imply the robust dynamical and thermal stabilities of the heterojunction PtO_2/WSe_2 and PtO_2/GeC.

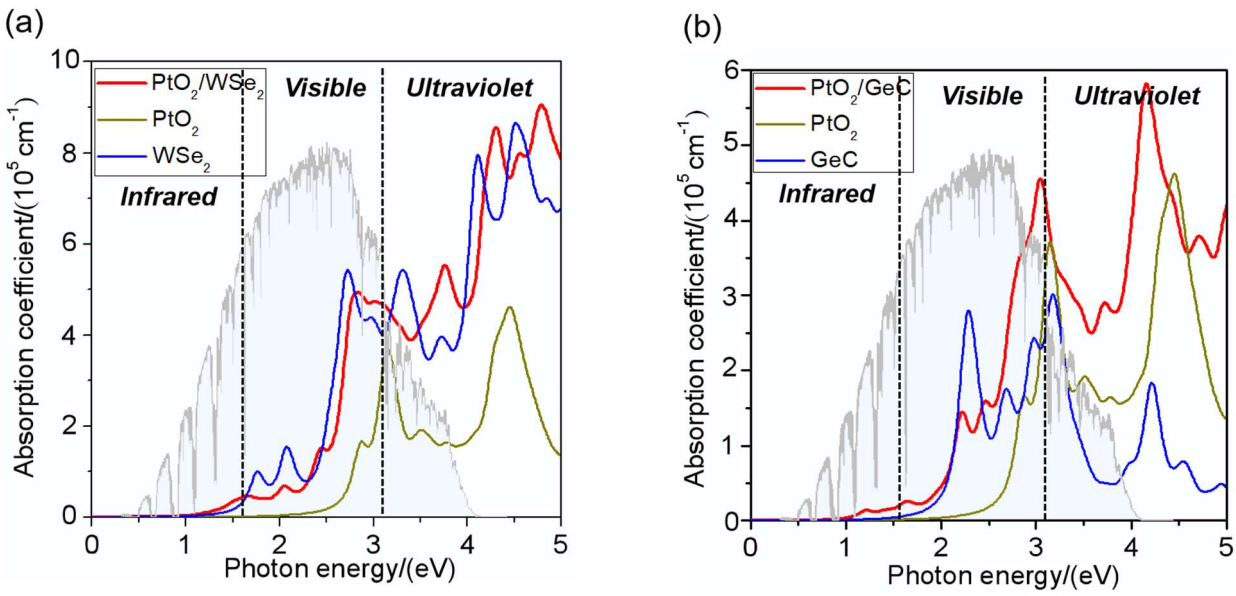

Fig. S3 Optical absorption spectrum of the heterojunction (a) PtO_2/WSe_2, and (b) PtO_2/GeC, as well as the isolated monolayers PtO_2 and $MoSe_2$ (GeC) for comparison calculated by G_0W_0 + BSE approach.

It can be observed that the heterojunction PtO_2/WSe_2 (GeC) exhibits significant absorbance of the solar spectrum inclusive of NIR light. Besides, the absorption spectrum exhibits a "red shift" as compared to its parents of monolayers with high absorption coefficient of 10^5 cm^{-1}.

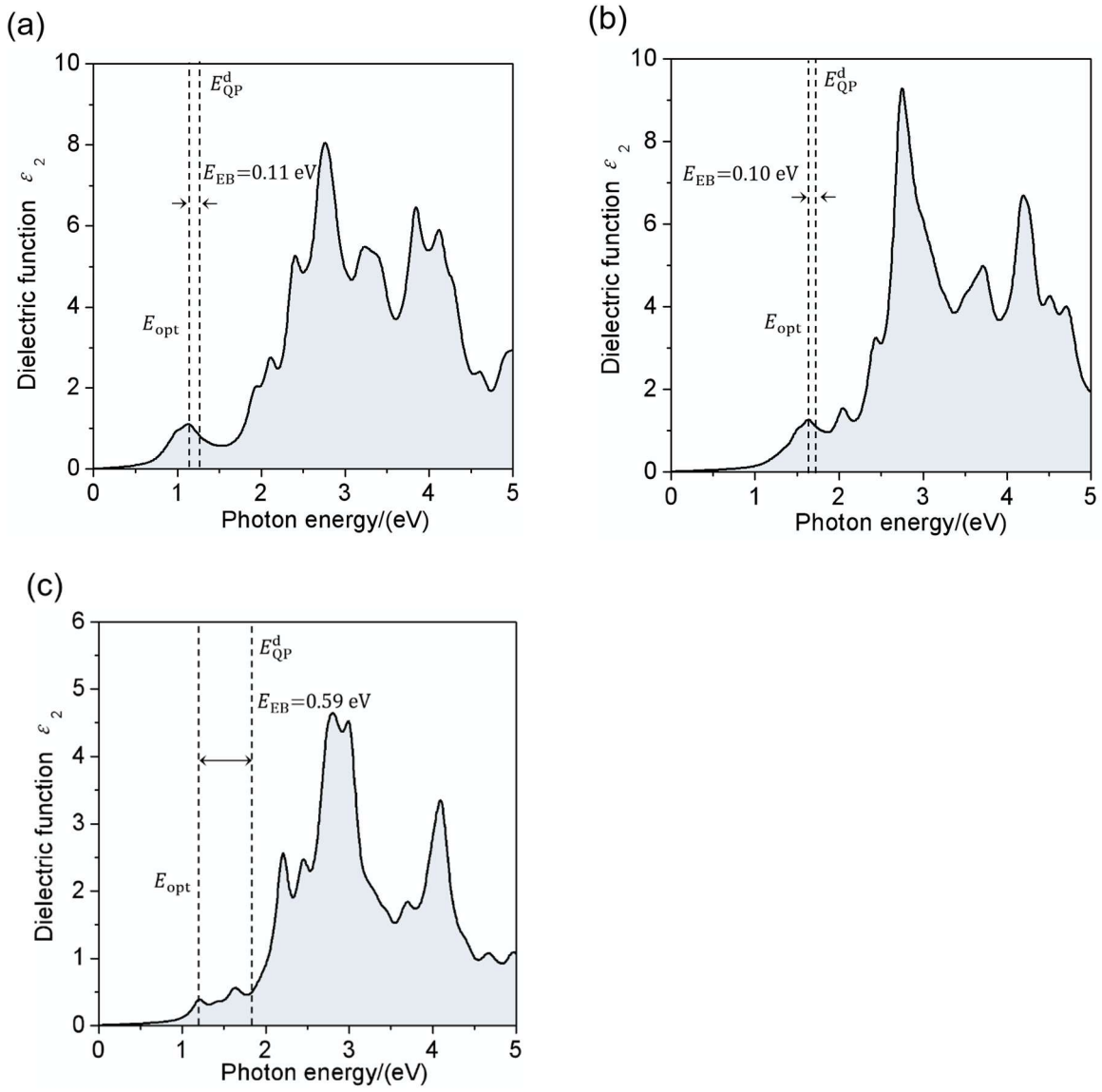

Fig. S4 Dielectric imaginary part of the heterojunction (a) $PtO_2/MoSe_2$, (b) PtO_2/WSe_2 and (c) PtO_2/GeC using G_0W_0 + BSE approach. E_{QP}^{d} and E_{opt} are the minimum direct quasiparticle band gap and optical band gap, respectively. E_{EB} is the exciton binding energy.

Table S2 Corresponding electronic properties of the studied PtO_2-based heterojunction, including the band gap at HSE06 level (E_{HSE06}), quasiparticle band gap ($E_{\mathrm{QP}}^{\mathrm{i}}$) given by G_0W_0 approach, minimum direct quasiparticle band gap ($E_{\mathrm{QP}}^{\mathrm{d}}$), optical band gap ($E_{\mathrm{opt}}$) given by G_0W_0 + BSE approach, exciton binding energy (E_{EB}), and the external potentials provided by photogenerated electrons (U_{e}) and holes (U_{h}) when under light.

Material	E_{HSE06} (eV)	E_{QP}^{i} (eV)	$E_{\mathrm{QP}}^{\mathrm{d}}$ (eV)	E_{opt} (eV)	E_{EB} (eV)	U_{e} (V)	U_{h} (V)
$PtO_2/MoSe_2$	0.29	0.82	1.24	1.13	0.11	1.48	3.94
PtO_2/WSe_2	0.46	1.21	1.70	1.60	0.10	1.44	3.91
PtO_2/GeC	0.63	1.43	1.80	1.21	0.59	2.18	3.99
PtO_2	3.25	3.52	4.20	2.86	1.34	-	3.44
$MoSe_2$	1.82	2.06	2.06	1.63	0.43	0.74	-
WSe_2	1.93	2.21	2.21	1.75	0.46	1.09	-
GeC	2.79	3.17	3.17	2.25	0.92	2.03	-

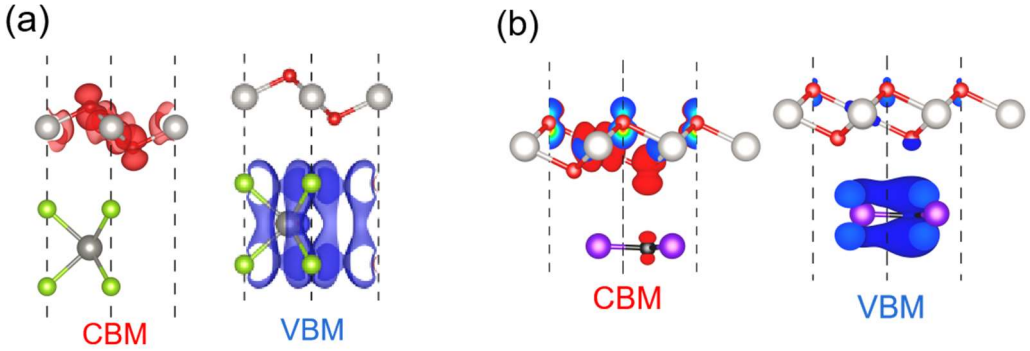

Fig. S5 Partial charge densities of CBM/VBM of the heterojunction (a) PtO_2/WSe_2 and (b) PtO_2/GeC, and the isosurface value is 0.005 e/Å^3.

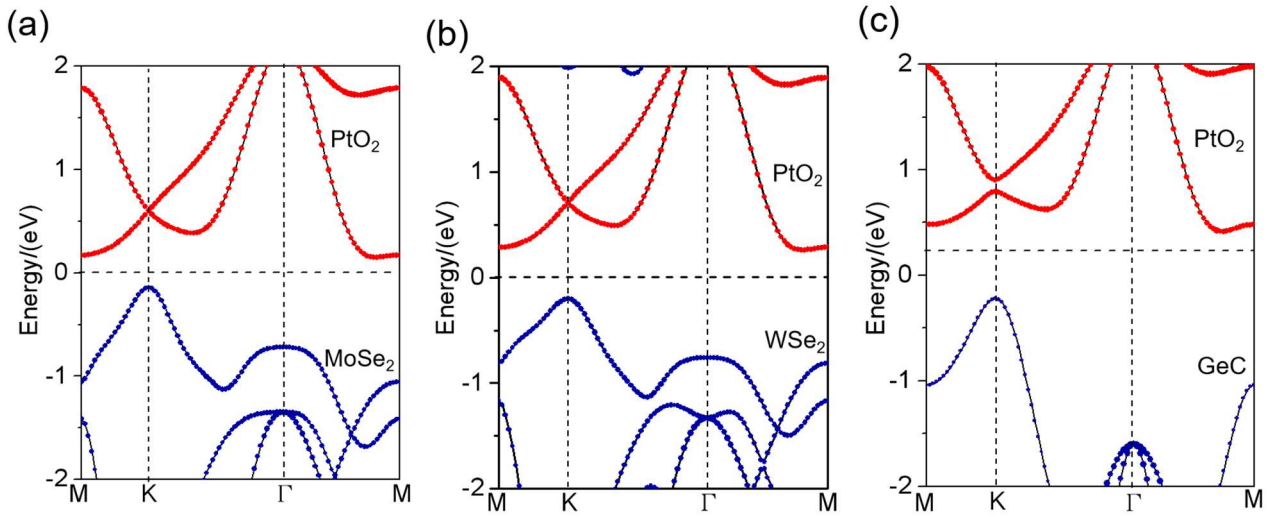

Fig. S6 Projected band structure at HSE06 level of the heterojunction (a) $PtO_2/MoSe_2$, (b) PtO_2/WSe_2 and (c) PtO_2/GeC, where Fermi level is set to zero level and indicated by the horizontal black dashed line.

Similar to the heterojunction $PtO_2/MoSe_2$, it can be seen that most of CBM is from PtO_2, while WSe_2 (GeC) contributes to the VBM in heterojunction PtO_2/WSe_2 (GeC), leading to the direct Z-scheme systems. Then, the reduction reaction occurs on WSe_2 (GeC), while oxidation reaction is on PtO_2.

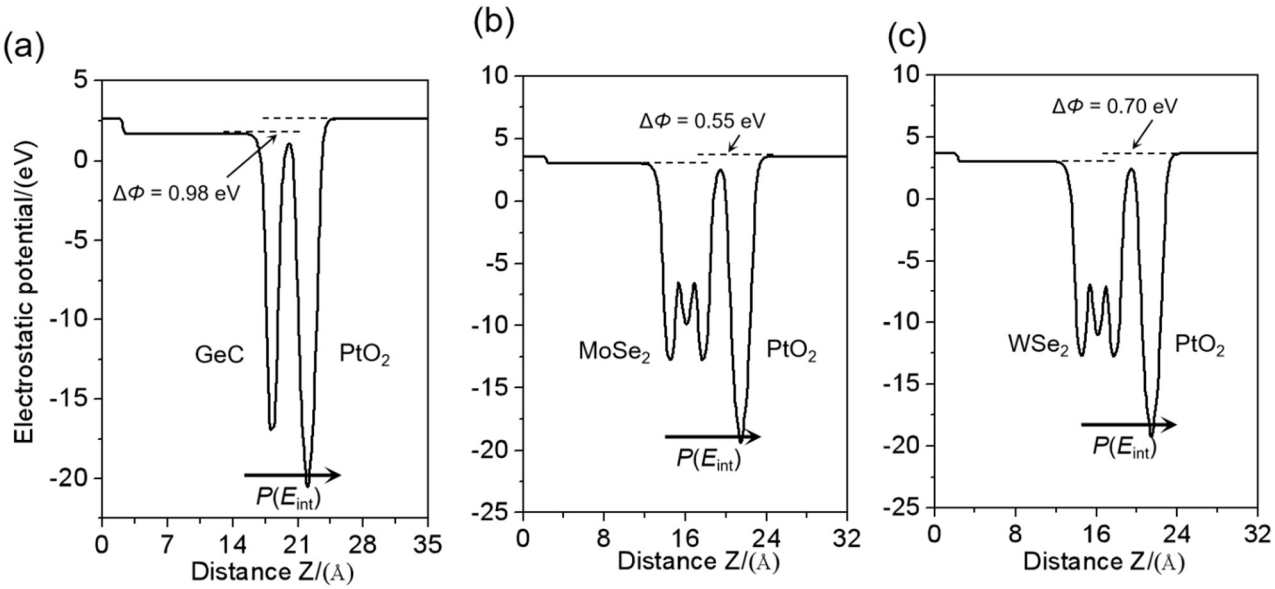

Fig. S7 Electrostatic potential of the heterojunction (a) PtO_2/GeC, (b) PtO_2/$MoSe_2$, and (c) PtO_2/WSe_2. The arrows represent the direction of polarization (P) and internal electric field (E_{int}).

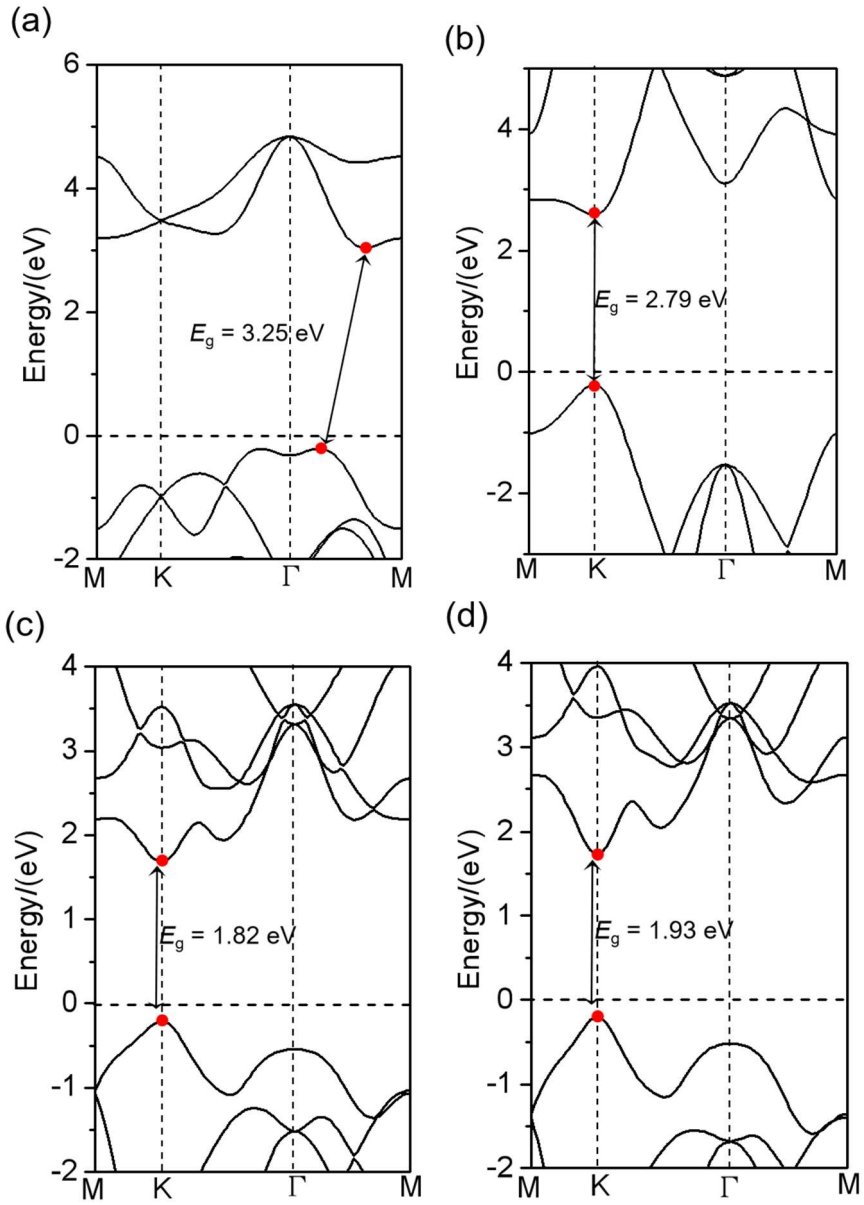

Fig. S8 Electronic band structure at HSE06 level of the isolated monolayers (a) PtO_2, (b) GeC, (c) $MoSe_2$, and (d) WSe_2, where Fermi level is set to zero level and indicated by the horizontal black dashed line. The red dots represent the CBM and VBM.

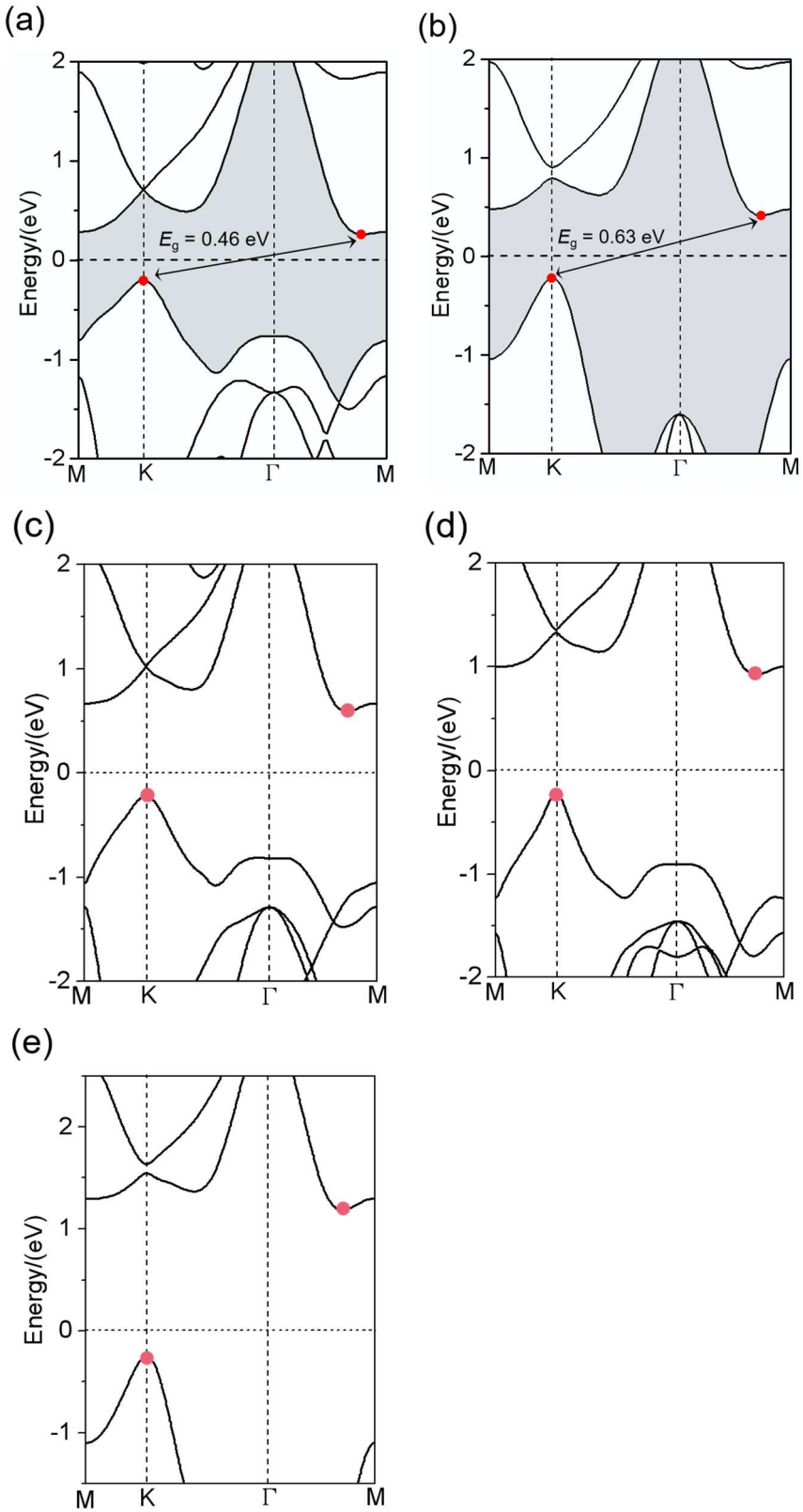

Fig. S9 HSE06 band structure of the heterojunction (a) PtO_2/WSe_2, and (b) PtO_2/GeC. G_0W_0 band structure of the heterojunction (c) $PtO_2/MoSe_2$, (d) PtO_2/WSe_2 and (e) PtO_2/GeC, where Fermi level is set to zero level and indicated by the horizontal black dashed line. The red dots represent the CBM and VBM.

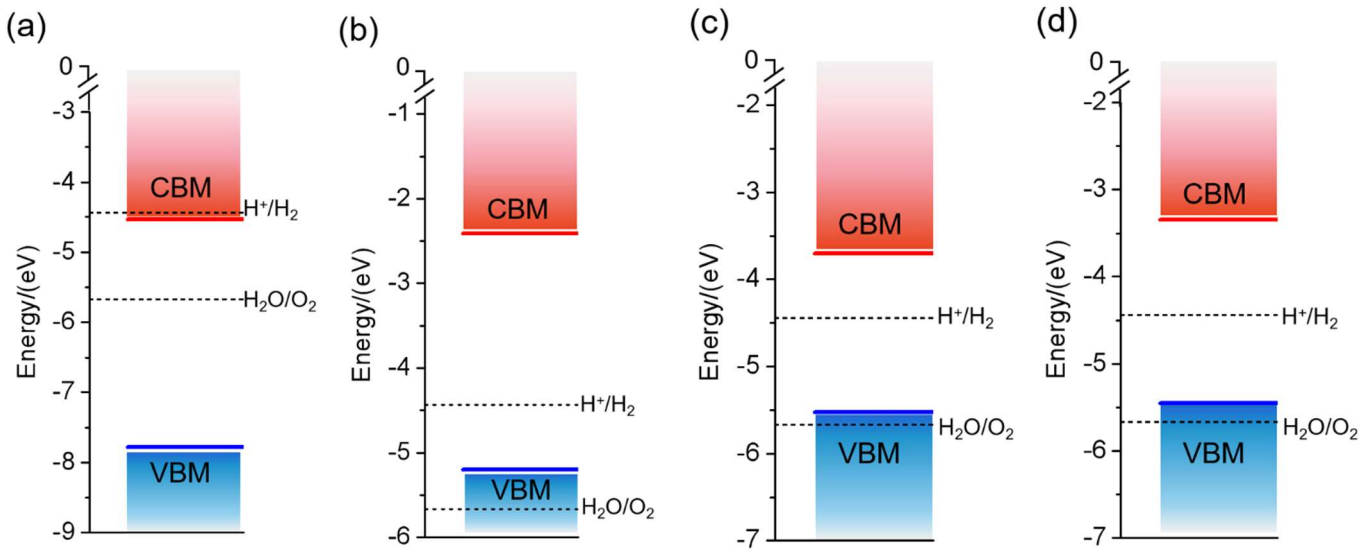

Fig. S10 Band alignments of the monolayers (a) PtO_2, (b) GeC, (c) $MoSe_2$, and (d) WSe_2, where the black dashed lines represent the reduction potential and oxidation potential of water splitting.

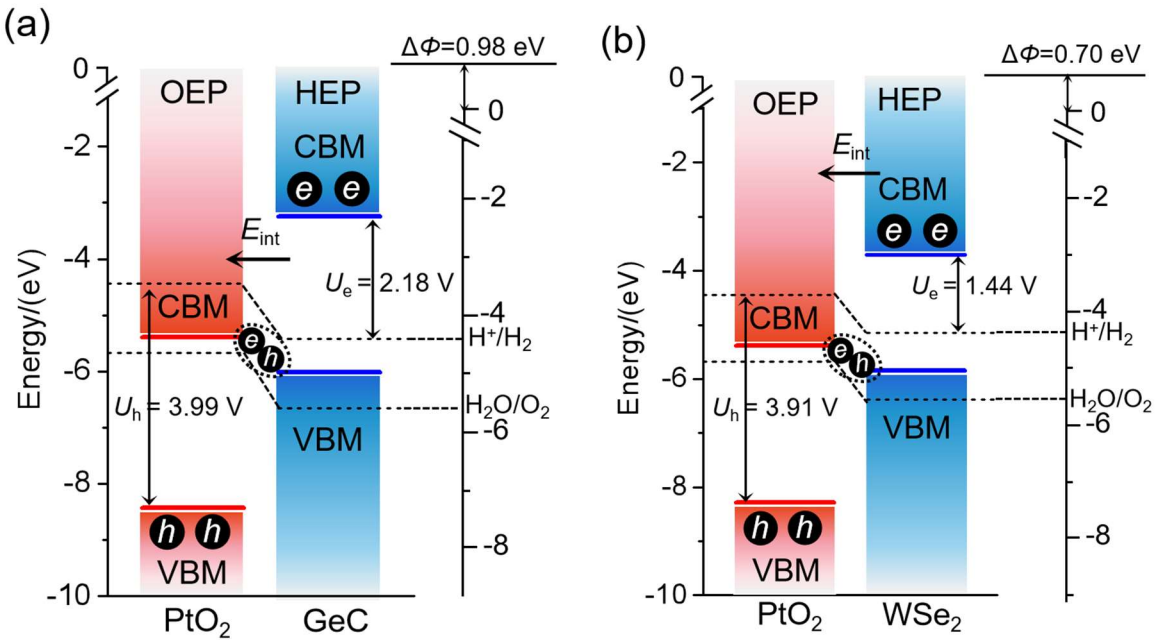

Fig. S11 Band alignments of the heterojunction (a) PtO_2/GeC, and (b) PtO_2/WSe_2. The horizontal black dashed lines represent the reduction potential and oxidation potential of water splitting, and the potentials of HEP side are bended downward by $\Delta\Phi$.

1. Gibbs free energies

The Gibbs free energy difference (ΔG) from one step to next step involved in the photocatalytic redox reactions can be evaluated using the method proposed by Norskovet et.al. [1] At pH = 0, the formula without the light irradiation can be defined as below:

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S, \quad \text{(S1)}$$

where ΔE is the adsorption energy, ΔE_{ZPE} and ΔS are the difference in zero point energy and entropy difference between the adsorbed state and the gas phase, respectively.

The half OER is considered herein, which are presented step by step as follows:

$$* + H_2O \rightarrow OH^* + H^+ + e^-, \quad \text{(S2)}$$

$$OH^* \rightarrow O^* + H^+ + e^-, \quad \text{(S3)}$$

$$O^* + H_2O \rightarrow OOH^* + H^+ + e^-, \quad \text{(S4)}$$

$$OOH^* \rightarrow * + O_2 + H^+ + e^-, \quad \text{(S5)}$$

For the half HER, it can be described in the following steps:

$$* + H^+ + e^- \rightarrow H^*, \quad \text{(S6)}$$

$$H^* + H^+ + e^- \rightarrow * + H_2, \quad \text{(S7)}$$

where * represents the substrate materials for the adsorptions, and O*, OH*, OOH* and H* represent the adsorbed intermediates during the redox reaction.

The Gibbs free energy difference of each step included in the half OER and HER is available based on the following expressions, in which the impact of extra potential and pH is taken into account:

$$\Delta G_1 = G_{OH^*} + \frac{1}{2}G_{H_2} - G_{H_2O} - G_* + \Delta G_U - \Delta G_{pH}, \quad \text{(S8)}$$

$$\Delta G_2 = G_{O^*} + \frac{1}{2}G_{H_2} - G_{OH^*} + \Delta G_U - \Delta G_{pH}, \quad \text{(S9)}$$

$$\Delta G_3 = G_{OOH^*} + \frac{1}{2}G_{H_2} - G_{O^*} - G_{H_2O} + \Delta G_U - \Delta G_{pH}, \quad \text{(S10)}$$

$$\Delta G_4 = G_* + G_{O_2} + \frac{1}{2}G_{H_2} - G_{OOH^*} + \Delta G_U - \Delta G_{pH}, \quad \text{(S11)}$$

$$\Delta G_5 = G_{H^*} - G_* - \frac{1}{2}G_{H_2} + \Delta G_U + \Delta G_{pH}, \quad \text{(S12)}$$

$$\Delta G_6 = G_* + \frac{1}{2}G_{H_2} - G_{H^*} + \Delta G_U + \Delta G_{pH}, \quad \text{(S13)}$$

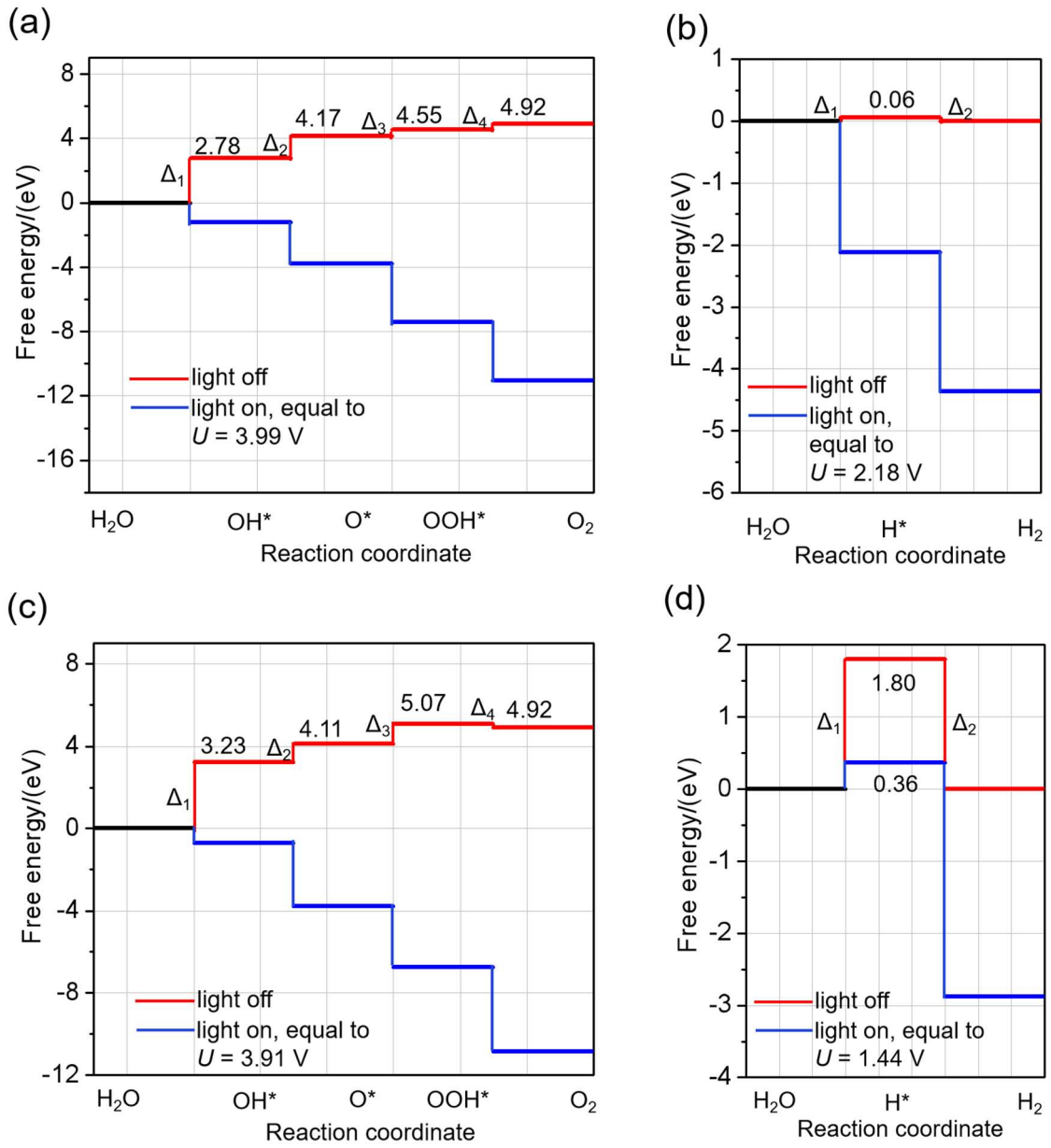

Fig. S12 Gibbs free energy profiles of OER and HER on the heterojunction (a-b) PtO_2/GeC, and (c-d) PtO_2/WSe_2 at pH = 0.

References

[1] J. K. Nørskov, J. Rossmeisl, A. Logadottir and L. Lindqvist, *J. Phys. Chem. B,* 2004, **108,** 17886−17892.