GeSe@SnS: Stacked Janus Structures for Overall Water Splitting

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Computational details

Free energy difference (ΔG) in the water redox reactions is calculated according the approach proposed by Nørskov *et al*.[1] The formula at pH = 0 without solar irradiation can be defined as below:

$$\Delta G = \Delta E + \Delta E_{zpe} - T\Delta S \quad (1)$$

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 entropies of free molecules can be found from the NIST database.[2] T represents indoor temperature in this work.

There are four steps to transform H_2O into O_2 molecule in oxidation half reaction, which can be written as:

$$* + H_2O \rightarrow *OH + H^+ + e^- \quad (2)$$

$$*OH \rightarrow *O + H^+ + e^- \quad (3)$$

$$*O + H_2O \rightarrow *OOH + H^+ + e^- \quad (4)$$

$$*OOH \rightarrow * + O_2 + H^+ + e^- \quad (5)$$

Meanwhile, hydrogen production half reaction can be decomposed into two steps, the reaction equation can be written as:

$$* + H^+ + e^- \rightarrow *H \quad (6)$$

$$*H + H^+ + e^- \rightarrow * + H_2 \quad (7)$$

where * means the adsorbed materials, $*O$, $*OH$ and $*OOH$ represent the adsorbed intermediates.

For each reaction of both oxidation and hydrogen production, the free energy difference under the effect of pH and an extra potential bias can be written as:

$$\Delta G_1 = G_{*OH} + \frac{1}{2}G_{H2} - G_* - G_{H2O} + \Delta G_U - \Delta G_{pH} \quad (8)$$

$$\Delta G_2 = G_{*O} + \frac{1}{2}G_{H2} - G_{*OH} + \Delta G_U - \Delta G_{pH} \quad (9)$$

$$\Delta G_3 = G_{*OOH} + \frac{1}{2}G_{H2} - G_{*O} - G_{H2O} + \Delta G_U - \Delta G_{pH} \quad (10)$$

$$\Delta G_4 = G_* + \frac{1}{2}G_{H2} + G_{O2} - G_{*OOH} + \Delta G_U - \Delta G_{pH} \quad (11)$$

$$\Delta G_5 = G_{*H} - \frac{1}{2}G_{H2} - G_* + \Delta G_U + \Delta G_{pH} \quad (12)$$

$$\Delta G_6 = G_* + \frac{1}{2}G_{H2} - G_{*H} + \Delta G_U + \Delta G_{pH} \quad (13)$$

where $\Delta G_{pH} = k_B T \cdot ln10 \cdot pH$ represents the free energy contributed in different H concentration. $\Delta G_U = -eU$ denotes extra potential bias provided by an electron in the electrode, where U is the electrode potential relative to the standard hydrogen electrode (SHE).

Table S1 Binding energy (eV) of different stacking patterns of the vdWHs.

	SeGe@SSn	SeGe@SnS	GeSe@SSn	GeSe@SnS
AA	-0.840	-1.039	-0.783	-0.894

AB	-0.745	-0.788	-0.735	-0.777
AC	-0.814	-1.152	-0.779	-0.864

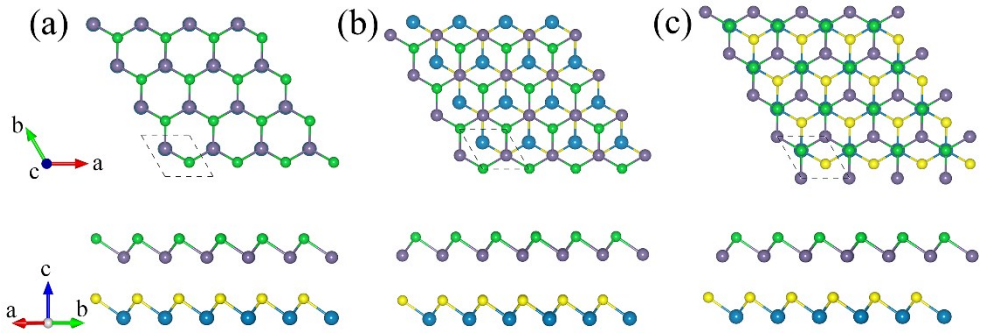

Fig. S1 Top and side views of different stacking patterns of (a) AA, (b) AB and (c) AC for SeGe@SSn. The yellow, green, purple and blue balls denote S, Se, Ge and Sn atoms, respectively.

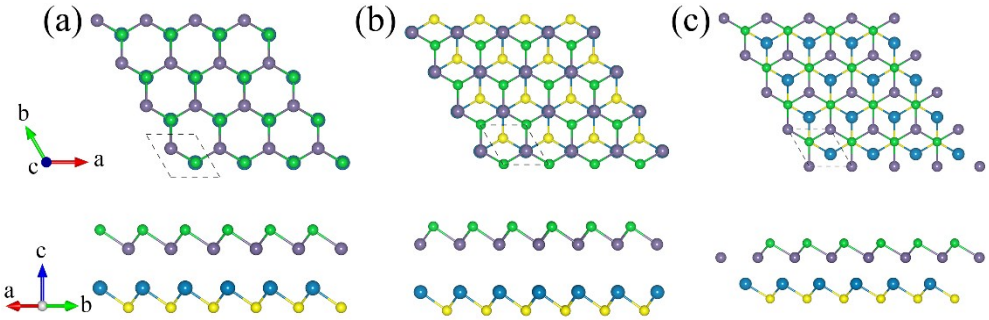

Fig. S2 Top and side views of different stacking patterns of (a) AA, (b) AB and (c) AC for SeGe@SnS.

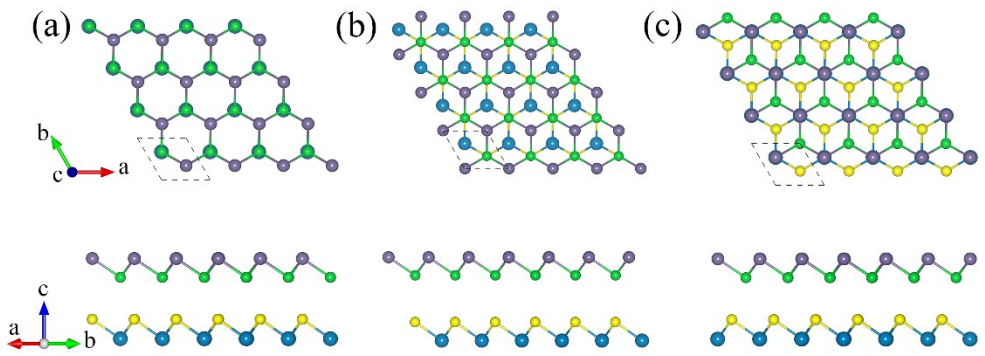

Fig. S3 Top and side views of different stacking patterns of (a) AA, (b) AB and (c) AC

for GeSe@SSn.

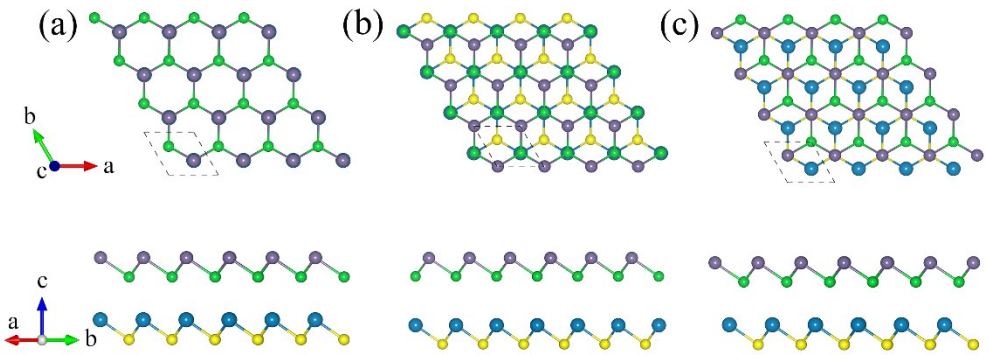

Fig. S4 Top and side views of different stacking patterns of (a) AA, (b) AB and (c) AC for GeSe@SnS.

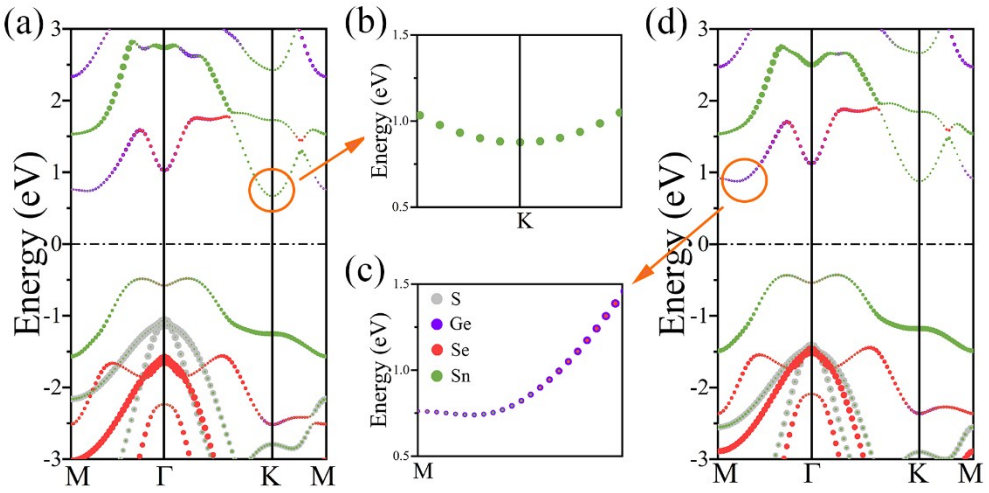

Fig. S5 Band structures with the interlayer distance of 3.1 (a) and 3.2 (d) Å of the GeSe@SnS, respectively. (b) and (c) are the enlarged plots of which are circled in orange of (a) and (d).

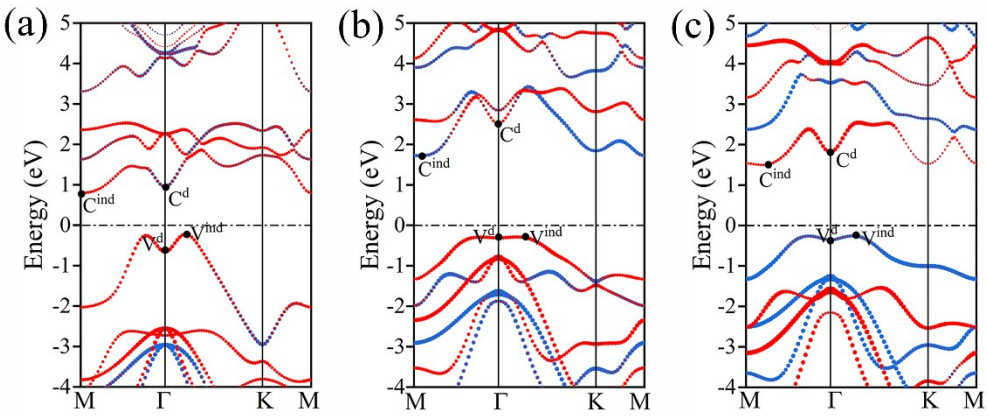

Fig. S6 Projected band structures of (a) SeGe@SnS, (b) GeSe@SSn and (c) GeSe@SnS based on HSE06 functional. Blue line represents the contribution from SnS, while red from GeSe. The horizontal dashed lines represent the Fermi level.

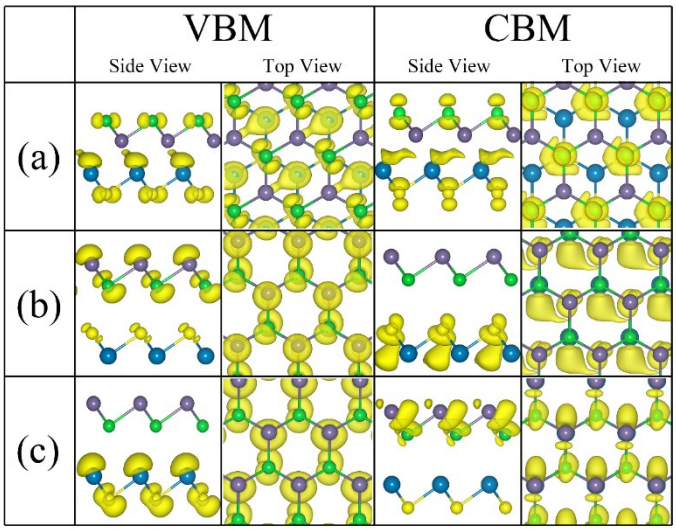

Fig. S7 Side and top views of partial charge densities of VBM and CBM corresponding to Fig. S6. The isosurface value is 0.01 eÅ^{-3}.

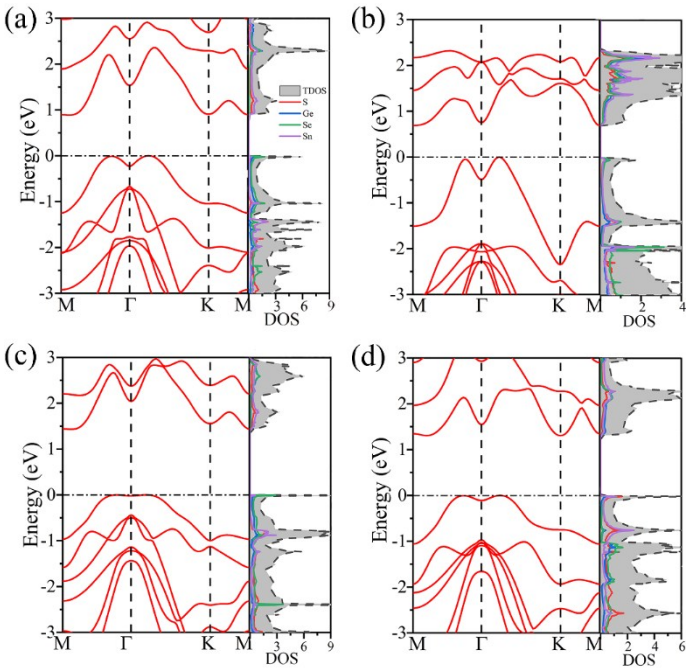

Fig. S8 Band structures and projected density of states (PDOS) of SeGe@SSn (a), SeGe@SnS (b), GeSe@SSn (c) and GeSe@SnS (d) vdWHs based on PBE level. The Fermi level is set to 0.

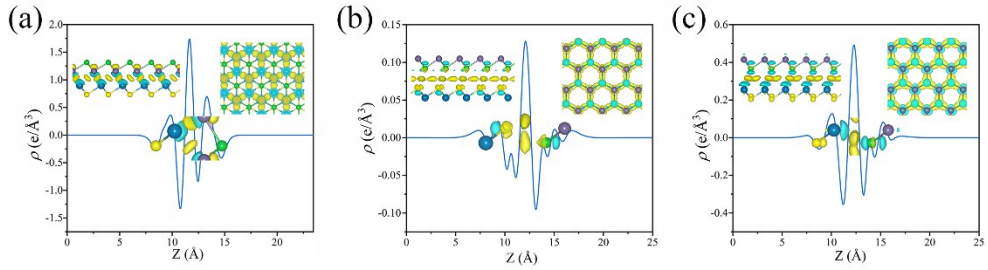

Fig. S9 Plane-integrated charge density difference for (a) SeGe@SnS, (b) GeSe@SSn and (c) GeSe@SnS. Insets are the side and top views of 3D isosurface charge density differences with yellow and cyan regions representing electron accumulation and depletion, respectively. The corresponding isosurface values are (a) 0.002 eÅ^{-3}, (b) 1 × 10^{-4} eÅ^{-3} and (c) 3 × 10^{-4} eÅ^{-3}.

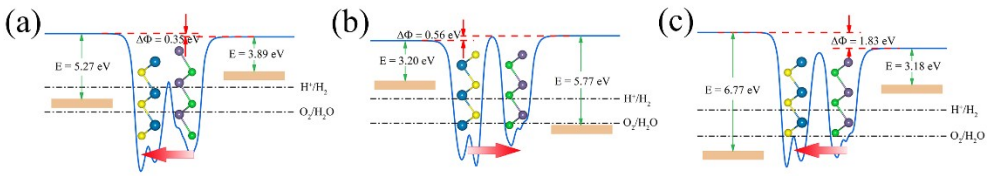

Fig. S10 Band edge positions with respect to water redox potential for (a) SeGe@SnS, (b) GeSe@SSn and (c) GeSe@SnS based on the HSE06 functional. Orange bars represent the positions of VBM and CBM. The black dashed line represents the redox potential of water splitting at pH = 0. The red arrow marks the direction of intrinsic dipole.

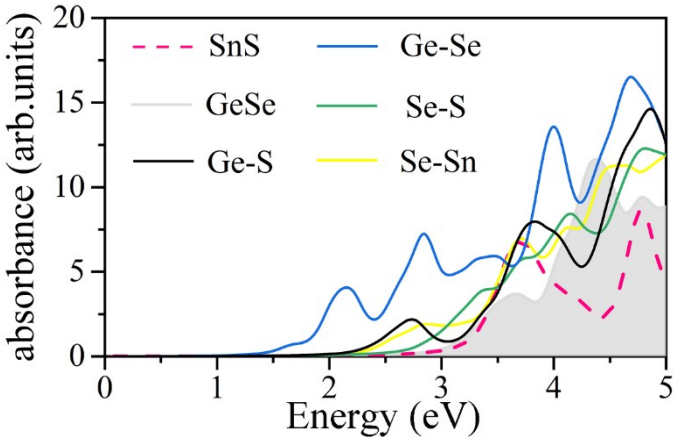

Fig. S11 The optical absorption spectra of *h*-GeSe, *h*-SnS as well as the relative vdW configurations based on HSE06 functional.

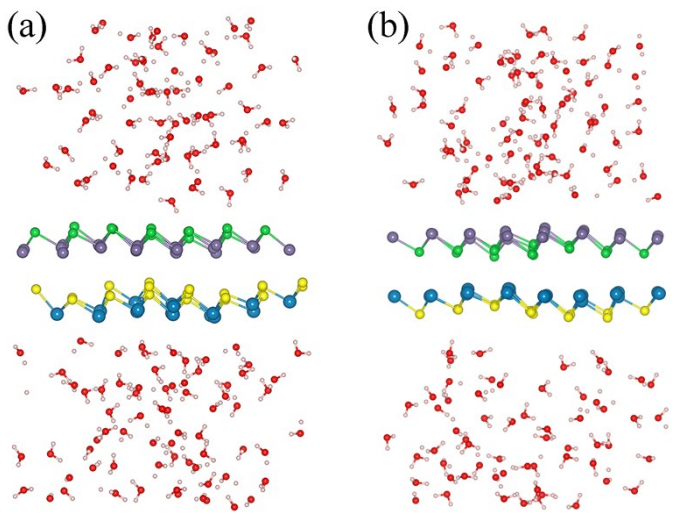

Fig. S12 Snapshots of stacked SeGe@SSn (a) and GeSe@SnS (b) structures in water solution at the end of AIMD simulations at 300 K for 5 ps. The pink, red, yellow, green, purple and blue balls denote H, O, S, Se, Ge and Sn atoms, respectively.

References

1 J. Nørskov, J. Rossmeisl, J. Logadottir and L. Lindqvist, *J. Phys. Chem. B*, 2004, **108**, 17886–17892.

2 NIST Computational Chemistry Comparison and Benchmark Database, NIST Standard Reference Database Number 101, Release 19, April 2018, edited by Russell D. Johnson, III, Available at http: //cccbdb.nist.gov/.