

## Supporting Information

### **Two-dimensional Janus monolayers SPtAZ<sub>2</sub> (A=Si, Ge; Z= N, P, As): first-principles insight into the photocatalytic properties**

Zhen Gao<sup>a</sup>, YaoHe<sup>a,\*</sup>, and Kai Xiong<sup>b,\*</sup>

<sup>a</sup>*Department of Physics, Yunnan University, Kunming 650091, People's Republic of China.*

<sup>b</sup>*Materials Genome Institute, School of Materials and Energy, Yunnan University, Kunming 650091, P. R. China.*

\*E-mail:

[yhe@ynu.edu.cn](mailto:yhe@ynu.edu.cn); [xiongekai@ynu.edu.cn](mailto:xiongekai@ynu.edu.cn)

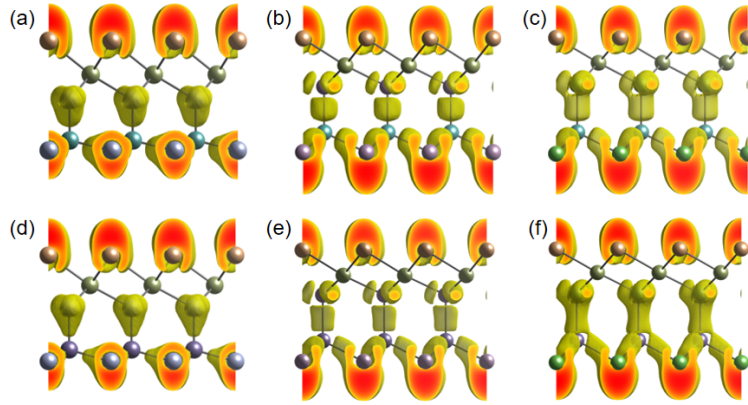


Fig S1 The electron localization function (ELF) of (a) SPtSiN<sub>2</sub>, (b) SPtSiP<sub>2</sub>, (c) SPtSiAs<sub>2</sub>, (d) SPtGeN<sub>2</sub>, (e) SPtGeP<sub>2</sub> and (f) SPtGeAs<sub>2</sub>. The isosurface for ELF is 0.75 eÅ<sup>-3</sup>.

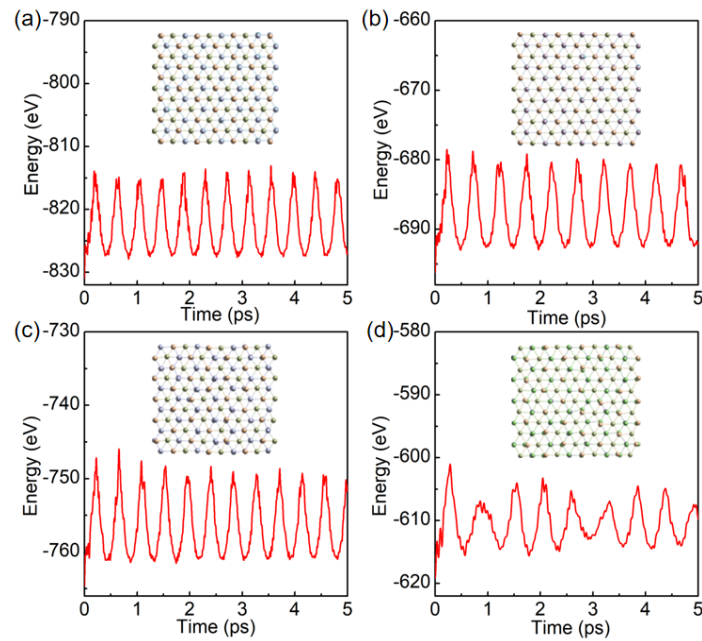


Fig S2 Variation of the energy as a function of time for the Janus (a)SPtSiP<sub>2</sub>, (b)SPtSiP<sub>2</sub>, (c)SPdGeN<sub>2</sub>, and (d)SPdGeAs<sub>2</sub> monolayers at t00K. The insets are the top view of the structure at the end of the AIMD simulation.

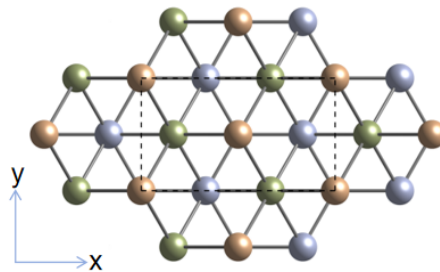


Fig S3 The calculation of carrier mobility is carried out in rectangular cell in the black dotted box, the x and y directions also been indicate.

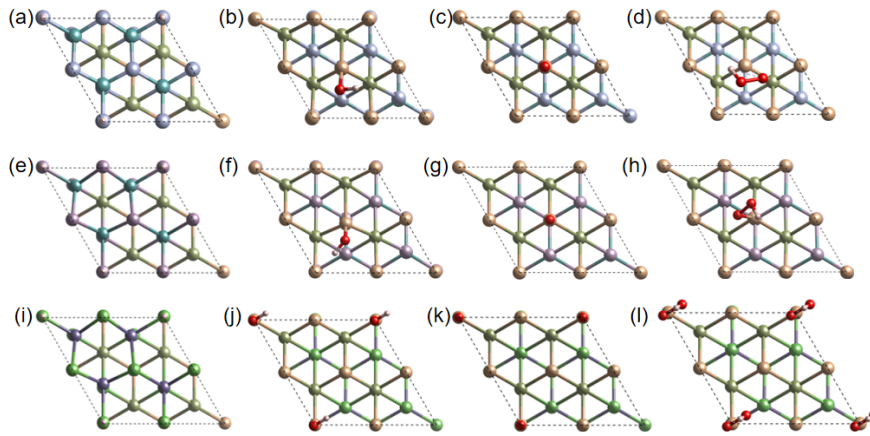


Fig S4 The most probable intermediates adsorbed on the S-side and Nout-side of (a-d) Janus SPTSiN<sub>2</sub> (e-h) SPTSiP<sub>2</sub>, and (i-l) SPTGeAs<sub>2</sub> monolayers, H\* , OH\* , O\* and OOH\* .

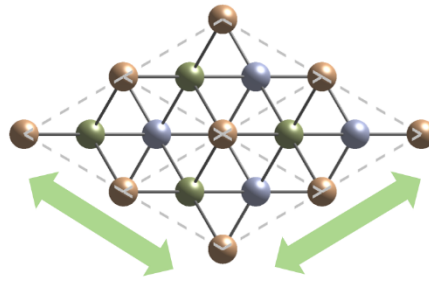


Fig S5 The top view of Janus SPTAZ<sub>2</sub> (A=Si, Ge; Z=N, P, As) under biaxial strain.

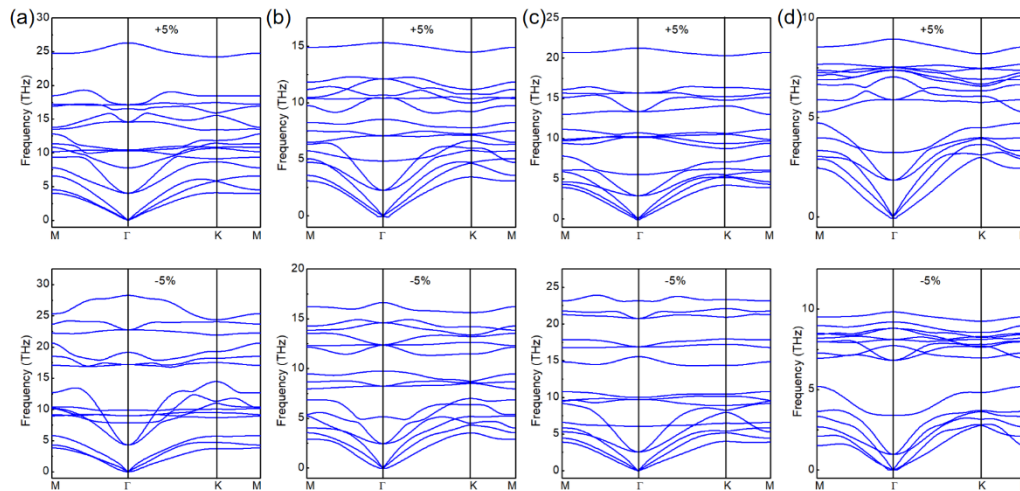


Fig S6 Phonon spectrum of (a) SPTSiN<sub>2</sub>, (b) SPTSiP<sub>2</sub>, (c) SPTGeN<sub>2</sub>, and (d) SPTGeAs<sub>2</sub> monolayers under strain of +5 % and -5%.

### The Solar-to-hydrogen (STH) Efficiency

The STH efficiency is evaluated using the methods proposed by Yang et al.<sup>1</sup> According to the

reaction process, STH efficiency is defined as the product of the efficiency of light absorption ( $\eta_{abs}$ ) and carrier utilization ( $\eta_{cu}$ ).

$$\eta_{STH} = \eta_{abs} \times \eta_{cu} \quad (S1)$$

The efficiency of light absorption is defined as:

$$\eta_{abs} = \frac{\int_{E_g}^{\infty} P(h\omega) d(h\omega)}{\int_0^{\infty} P(h\omega) d(h\omega)} \quad (S2)$$

where  $P(h\omega)$  are the AM1.5G solar energy flux at the photon energy  $h\omega$  and  $E_g$  is the band gap of the materials. The denominator represents the total power density of the reference sunlight spectrum (AM1.5G) and the numerator gives the light power density absorbed by the photocatalyst.

The efficiency of carrier utilization ( $\eta_{cu}$ ) is defined as:

$$\eta_{cu} = \frac{\Delta G_{H_2O} \int_E^{\infty} \frac{P(h\omega)}{h\omega} d(h\omega)}{\int_{E_g}^{\infty} P(h\omega) d(h\omega)} \quad (S3)$$

where  $\Delta G_{H_2O}$  is the free energy of water splitting (1.23eV) and the rest of numerator represents the effective photocurrent density. Here, E represents the photon energy that can be actually utilized in the process of water splitting.

$$E = \begin{cases} E_g, & (\chi(H_2) \geq 0.2, \chi(O_2) \geq 0.6) \\ E_g + 0.2 - \chi(H_2), & (\chi(H_2) < 0.2, \chi(O_2) \geq 0.6) \\ E_g + 0.6 - \chi(O_2), & (\chi(H_2) \geq 0.2, \chi(O_2) < 0.6) \\ E_g + 0.8 - \chi(H_2) - \chi(O_2), & (\chi(H_2) < 0.2, \chi(O_2) < 0.6) \end{cases} \quad (S4)$$

The intrinsic electric field does positive work for the electron-hole separation during the process of photocatalytic water splitting. Therefore, this part of work should be added into the total energy, and then the corrected STH efficiency of photocatalytic water splitting for 2D material with vertical intrinsic EF is calculated as:

$$\eta_{STH}' = \eta_{STH} \times \frac{\int_0^{\infty} P(h\omega) d(h\omega)}{\int_0^{\infty} P(h\omega) d(h\omega) + \Delta V \int_{E_g}^{\infty} \frac{P(h\omega)}{h\omega} d(h\omega)} \quad (S5)$$

where  $\Delta V$  is the vacuum level difference on the two respective surfaces.

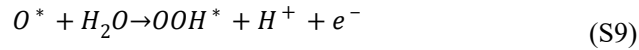
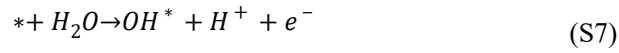
### Free Energy Difference ( $\Delta G$ )

Free energy difference ( $\Delta G$ ) in the water redox reactions is calculated according the approach proposed by Nørskov *al.*<sup>2</sup> The formula at pH=0 without solar irradiation can be defined as below:

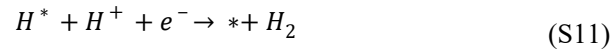
$$\Delta G = \Delta E + \Delta E_{zpe} - T\Delta S \quad (S6)$$

where  $\Delta E$  is the adsorption energy,  $\Delta E_{zpe}$  and  $\Delta S$  are the difference in zero point energy and entropy difference between the adsorbed state and the gas phase, respectively.

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



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



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

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

$$\Delta G_a = G_{OH^*} + \frac{1}{2}G_{H_2} - G_* - G_{H_2O} + \Delta G_U - \Delta G_{pH} \quad (S12)$$

$$\Delta G_b = G_{O^*} + \frac{1}{2}G_{H_2} - G_{OH^*} + \Delta G_U - \Delta G_{pH} \quad (S13)$$

$$\Delta G_c = G_{OOH^*} + \frac{1}{2}G_{H_2} - G_{O^*} - G_{H_2O} + \Delta G_U - \Delta G_{pH} \quad (S14)$$

$$\Delta G_d = G_* + \frac{1}{2}G_{H_2} + G_{O_2} - G_{OOH^*} + \Delta G_U - \Delta G_{pH} \quad (S15)$$

$$\Delta G_e = G_{H^*} - \frac{1}{2}G_{H_2} - G_* + \Delta G_U + \Delta G_{pH} \quad (S16)$$

$$\Delta G_f = G_* + \frac{1}{2}G_{H_2} - G_{H^*} + \Delta G_U + \Delta G_{pH} \quad (S17)$$

where  $\Delta G_{pH}$  ( $\Delta G_{pH} = k_B T \times \ln 10 \times pH$ ) represents the free energy contributed in different pH concentration.  $\Delta G_U$  ( $\Delta G_U = -eU$ ) 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 Zero-point energy correction ( $E_{ZPE}$ ), and entropy contribution (TS, T=298.15K) of molecules and adsorbates.

Species	ZPE	-TS
H <sub>2</sub>	0.27	-0.41
H <sub>2</sub> O	0.56	-0.67
OH*	0.34	-0.11
O*	0.05	-0.10
OOH*	0.42	-0.22

1. C.-F. Fu, J. Sun, Q. Luo, X. Li, W. Hu and J. Yang, *Nano Lett.*, 2018, 18, 6312-6317.
2. J. K. Nørskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J. R. Kitchin, T. Bligaard and H. Jónsson, *J. Phys. Chem. B*, 2004, 108, 17886-17892.