Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Two-Dimensional $SPdAZ_2$ (A=Si,Ge;Z=N,P,As) Monolayers with an Intrinsic Electric Field for High-Performance Photocatalytic

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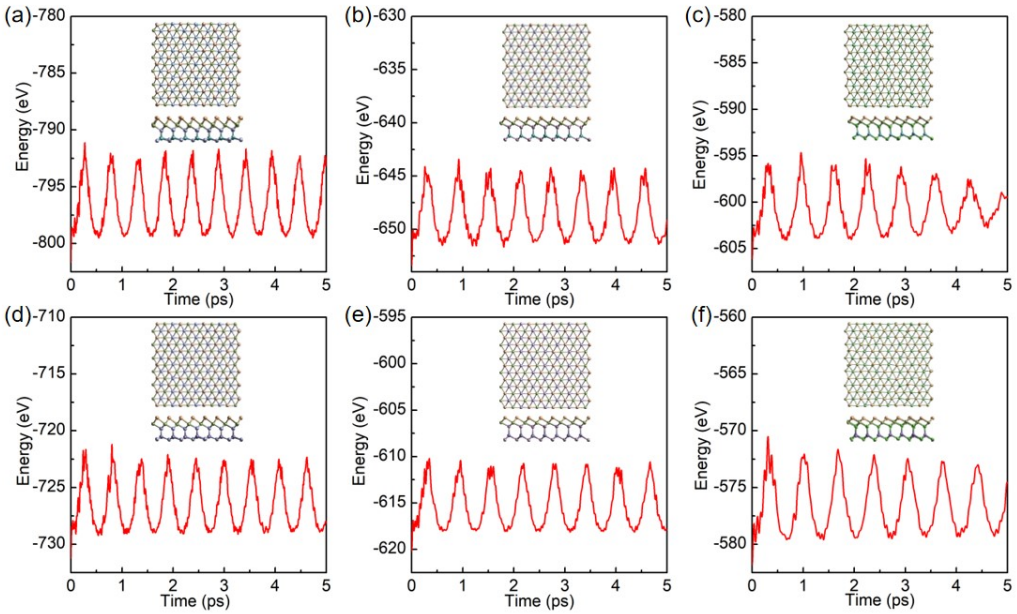

Fig S1 Variation of the energy as a function of time for the Janus (a)$SPdSiP_2$, (b)$SPdSiP_2$, (c)$SPdSiAs_2$, (d)$SPdGeN_2$, (e)$SPdGeP_2$, and (f)$SPdGeAs_2$ monolayers at 300K. The insets are the top and side views of the structure at the end of the AIMD simulation.

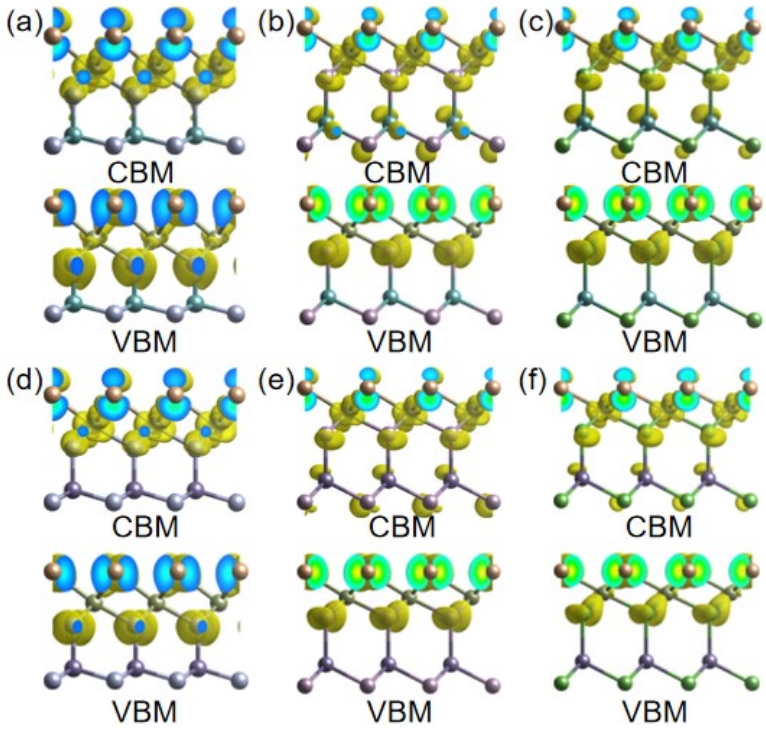

Fig S2 The charge density of the CBM and VBM of (a)$SPdSiP_2$, (b)$SPdSiP_2$, (c)$SPdSiAs_2$, (d)$SPdGeN_2$, (e)$SPdGeP_2$, and (f)$SPdGeAs_2$. The isosurface values of SPdAZ2 monolayers are taken as 0.01 $eÅ^{-3}$.

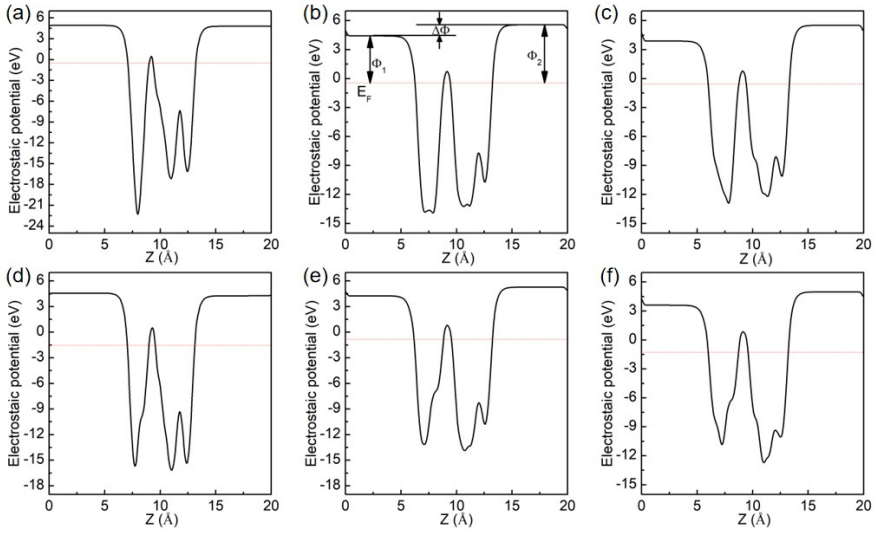

Fig S3 Electrostatic potential of 2D Janus (a)$SPdSiP_2$, (b)$SPdSiP_2$, (c)$SPdSiAs_2$, (d)$SPdGeN_2$, (e)$SPdGeP_2$, and (f)$SPdGeAs_2$.

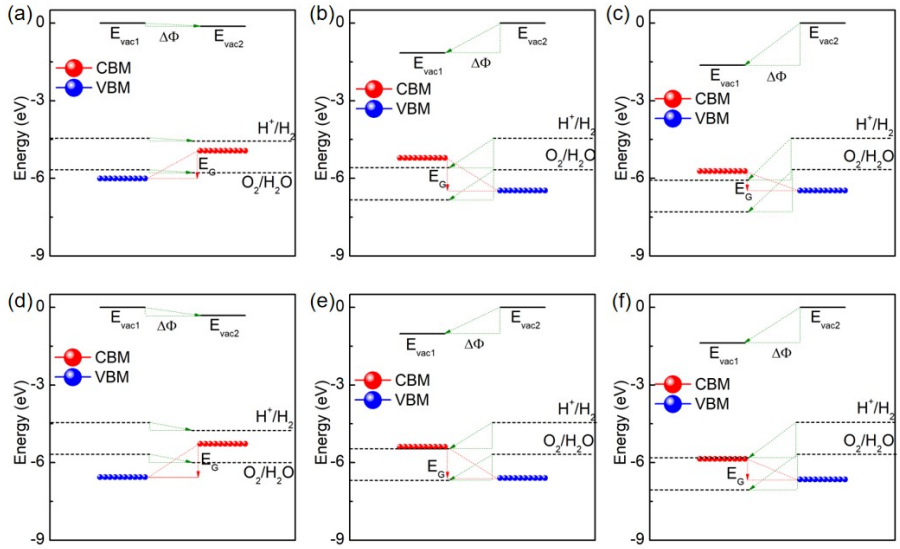

Fig S4 Band alignments with regard to the vacuum level of pristine (a)$SPdSiP_2$, (b)$SPdSiP_2$, (c)$SPdSiAs_2$, (d)$SPdGeN_2$, (e)$SPdGeP_2$, and (f)$SPdGeAs_2$ under the HSE06 functional.

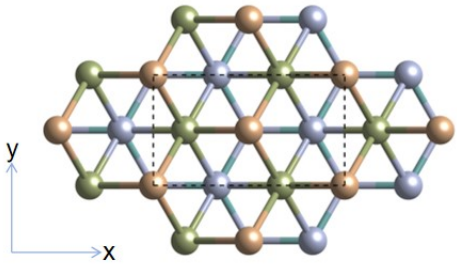

Fig S5 The calculation of carrier mobility is carried out in rectangular cell in the black dotted box, the x and y directions also been indicate.

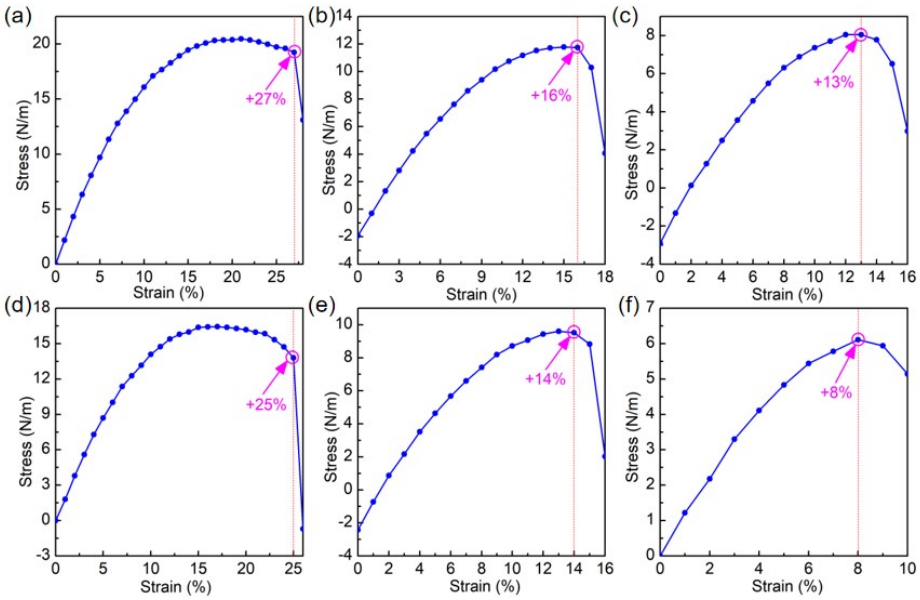

Fig S6 strain-stress curve for for 2D Janus (a)$SPdSiP_2$, (b)$SPdSiP_2$, (c)$SPdSiAs_2$, (d)$SPdGeN_2$, (e)$SPdGeP_2$, and (f)$SPdGeAs_2$ monolayers.

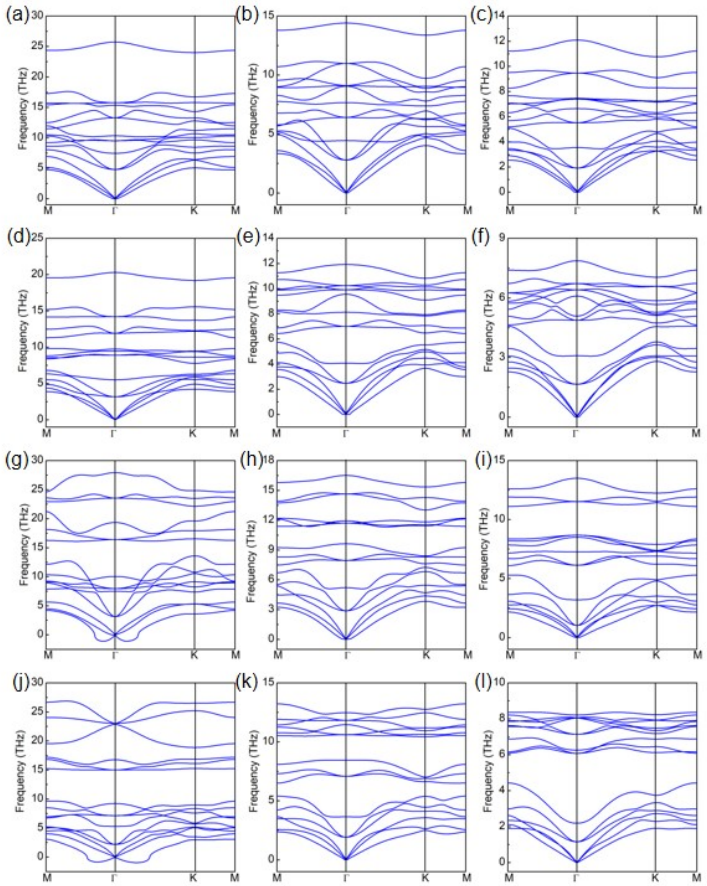

Fig S7 Phonon spectrum of $SPdSiP_2$, $SPdSiP_2$, $SPdSiAs_2$, $SPdGeN_2$, and $SPdGeP_2$ monolayers under strain of (a-e) -10% and (g-k) +10%, respectively. Phonon spectrum of $SPdGeAs_2$ monolayer under strain of (f) -8% and (l) +8%, respectively.

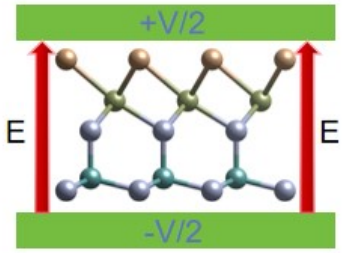

Fig S8 The schematic model of the $SPtAZ_2$ monolayers under applied-E.

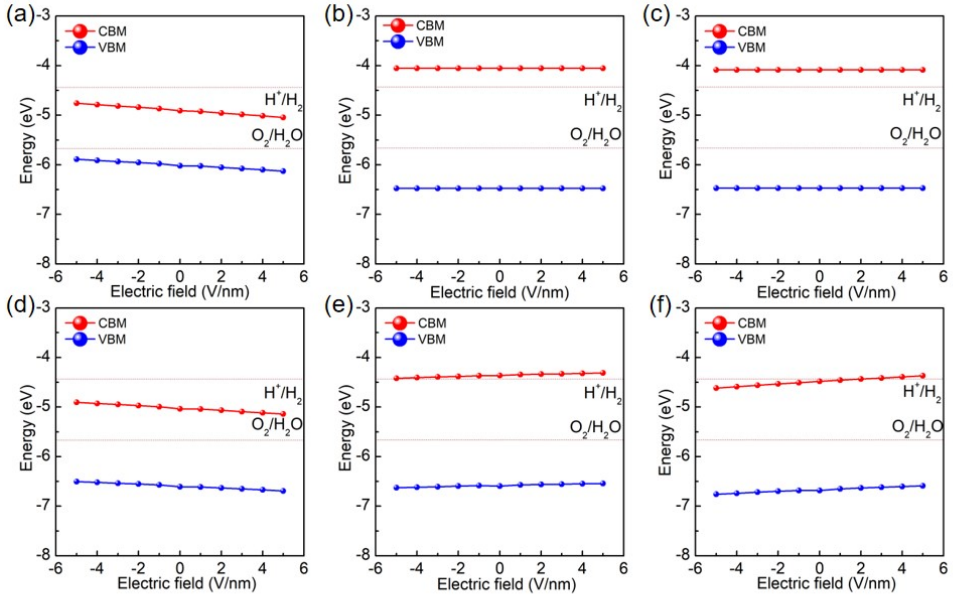

Fig S9 Band alignments of Janus (a)$SPdSiP_2$, (b)$SPdSiP_2$, (c)$SPdSiAs_2$, (d)$SPdGeN_2$, (e)$SPdGeP_2$, and (f)$SPdGeAs_2$ under external electric field.

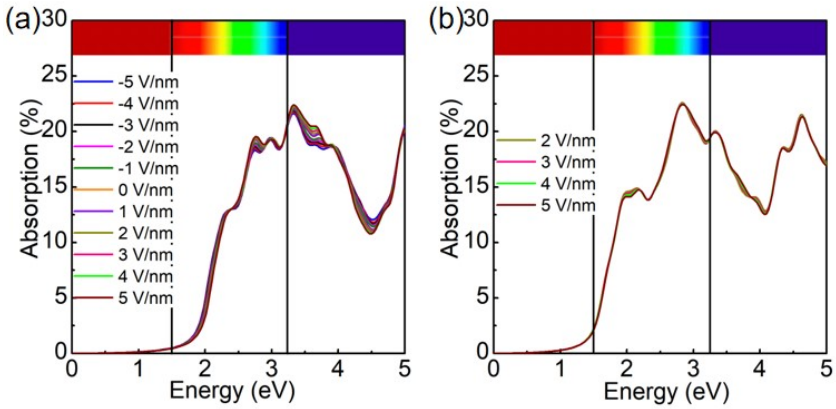

Fig S10 The light absorption of Janus (a) $SPdGeP_2$, and (b) $SPdGeAs_2$ under external electric field.

The Solar-to-hydrogen (STH) Efficiency

The STH efficiency is evaluated using the methods proposed by Yang et al.[1] According to the reaction process, STH efficiency is defined as the product of the efficiency of light absorption (η_{abs}) and carrier utilization (η_{cu}).

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

The efficiency of light absorption is defined as:

$$\eta_{abs} = \frac{\int_{E_g}^{\infty} P(h\omega)d(h\omega)}{\int_{0}^{\infty} P(h\omega)d(h\omega)} \quad \text{(S2)}$$

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 (η_{cu}) is defined as:

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

where ΔG_{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.

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

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:

$$\eta_{STH}^{'} = \eta_{STH} \times \frac{\int_{0}^{\infty} P(h\omega)d(h\omega)}{\int_{0}^{\infty} P(h\omega)d(h\omega) + \Delta\Phi \int_{E_g}^{\infty} \frac{P(h\omega)}{h\omega} d(h\omega)} \quad \text{(S5)}$$

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

1. C.-F. Fu, J. Sun, Q. Luo, X. Li, W. Hu and J. Yang, *Nano Lett.*, 2018, **18**, 6312-6317.