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

Electronic Supplementary Information

SnP_2S_6 Monolayer: a Promising 2D Semiconductor for Photocatalytic Water Splitting

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Crystallographic information of the bulk and 2D SnP_2S_6

bulk SnP_2S_6

1.0

6.0598998070	0.0000000000	0.0000000000
-3.0299499035	5.2480271772	0.0000000000
0.0000000000	0.0000000000	19.7999992371

S	Sn	P
18	3	6

Direct

0.680819988	0.673150003	0.233710006
0.326849997	0.007669985	0.233710006
0.992330015	0.319180012	0.233710006
0.347486645	0.006483336	0.567043364
0.993516684	0.341003329	0.567043364
0.658996701	0.652513325	0.567043364
0.014153321	0.339816660	0.900376678
0.660183311	0.674336672	0.900376678
0.325663358	0.985846698	0.900376678
0.681850016	0.010740042	0.065020002
0.989259958	0.671109974	0.065020002
0.328890026	0.318149984	0.065020002
0.348516673	0.344073385	0.398353338
0.655926645	0.004443308	0.398353338
0.995556712	0.651483297	0.398353338
0.015183349	0.677406728	0.731686652
0.322593302	0.337776631	0.731686652
0.662223339	0.984816670	0.731686652
0.666666687	0.333333343	0.149780005
0.333333343	0.666666687	0.483113348
0.000000000	0.000000000	0.816446662
0.666666687	0.333333343	0.425839990
0.333333343	0.666666687	0.759173334
0.000000000	0.000000000	0.092506655
0.666666687	0.333333343	0.538999975
0.333333343	0.666666687	0.872333288
0.000000000	0.000000000	0.205666646

2D SnP_2S_6 monolayer

1.0

6.0739002228	0.0000000000	0.0000000000
-3.0369501114	5.2601518930	0.0000000000
0.0000000000	0.0000000000	20.0000000000

S	P	Sn
6	2	1

Direct

0.683149993	0.672060013	0.583720028
0.327939987	0.011089981	0.583720028
0.988910019	0.316850007	0.583720028
0.327939987	0.316850007	0.416279972
0.988910019	0.672060013	0.416279972
0.683149993	0.011089981	0.416279972
0.000000000	0.000000000	0.444059998
0.000000000	0.000000000	0.555940032
0.666666687	0.333333343	0.500000000

The critical strain of fracture for SnP_2S_6 monolayer

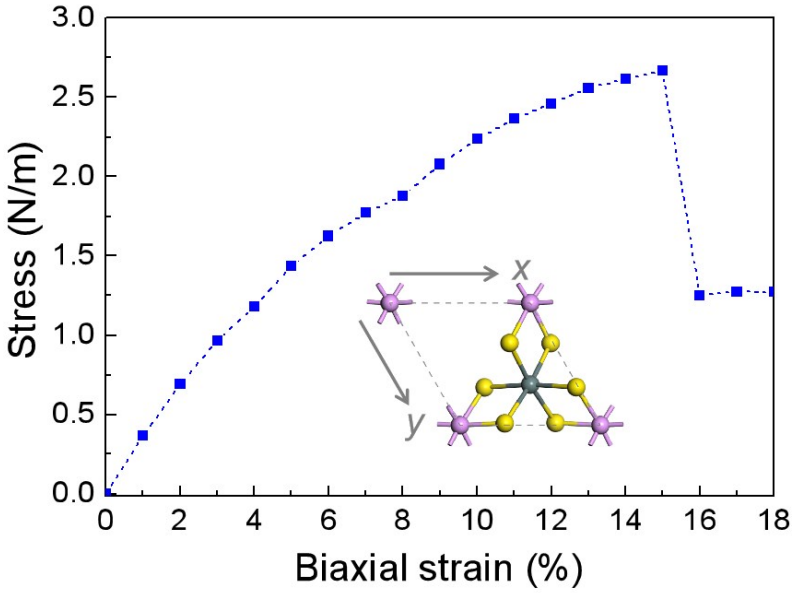

Fig. S1 The stress in the SnP_2S_6 monolayer subjected to biaxial strain. The direction of biaxial strain is marked by gray arrows.

Mechanism of Hydrogen evolution reaction on SnP_2S_6 monolayer

To compute the free energy change (ΔG) in the hydrogen reduction reaction (HER), we adopted the computational hydrogen electrode (CHE) model developed by Nørskov et al,[1,2] according to which the ΔG of an electrochemical reaction is computed as:

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

where ΔE is the DFT computed total energy difference, ΔE_{ZPE} and ΔS are the zero point energy difference and the entropy difference between the adsorbed H and the gas phase H, respectively, and T is the system temperature taken as 298.15K. ΔG_{pH} = 0.059 × pH represents the free energy contribution determined by H concentration. Here the contribution of ΔG_{pH} is zero as we only consider the situation of pH = 0. The effect of a potential bias involving one electron in the electrode is considered by shifting the energy by $\Delta G_U = -eU$, where U is the electrode potential provided by photo-generated electron for HER and is defined as the energy difference between the hydrogen reduction potential and the CBM. The free energy of one pair of proton and electron ($H^+ + e^-$) at standard conditions (pH = 0, U = 0) was taken as $1/2G_{H2}$.

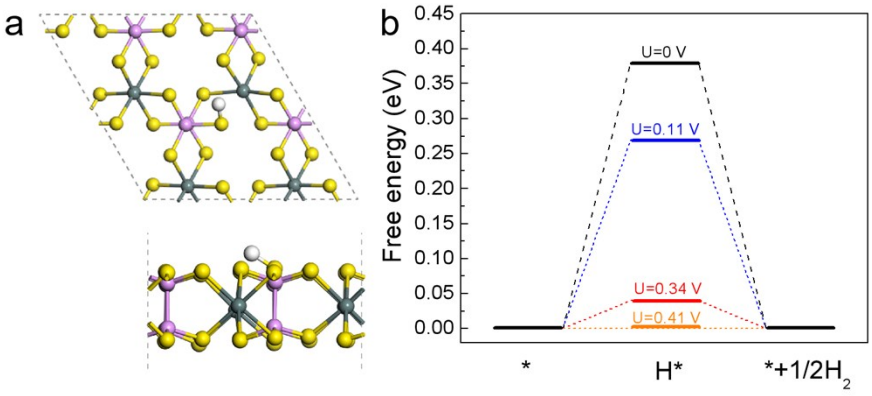

Fig. S2 (a) Adsorption of H on the surface S sites from top and side views. (b) Free energy diagrams for the pathways of hydrogen reduction reaction on SnP_2S_6 monolayer under conditions of open circuit (U=0 V), with solar irradiation (U = 0.11 V), a compressive strain of 4% with solar irradiation (U = 0.34 V) and a compressive strain of 5% with solar irradiation (U = 0.41 V).

References:

1. 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.
2. Á. Valdés, Z.-W. Qu, G.-J. Kroes, J. Rossmeisl and J. K. Nørskov, *J. Phys. Chem. C,* 2008, **112**, 9872−9879.