Electronic Supplementary Information

Copper (I) sulfide: A two-dimensional semiconductor with superior oxidation resistance and high carrier mobility

Yu Guo,[ab] Qisheng Wu,[bc] Yunhai Li,[c] Ning Lu,[d] Keke Mao,[be] Yizhen Bai,[a] Jijun Zhao,[*a] Jinlan Wang[*cf] and Xiao Cheng Zeng [*bg]

[a]*Key Laboratory of Materials Modification by Laser, Ion and Electron Beams (Dalian University of Technology), Ministry of Education, Dalian, Liaoning 116024, China*

[b]*Department of Chemistry, University of Nebraska–Lincoln, Lincoln, Nebraska 68588, United States*

[c]*School of Physics, Southeast University, Nanjing, Jiangsu 211189, China*

[d]*Anhui Province Key Laboratory of Optoelectric Materials Science and Technology, Department of Physics, Anhui Normal University, Wuhu, Anhui 241000, China*

[e]*School of Energy and Environment Science, Anhui University of Technology, Maanshan, Anhui 243032, China*

[f]*Synergetic Innovation Center for Quantum Effects and Applications (SICQEA), Hunan Normal University, Changsha, Hunan 410081, China*

[g]*Department of Chemical & Biomolecular Engineering and Department of Mechanical & Materials Engineering, University of Nebraska–Lincoln, Lincoln, Nebraska 68588, United States*

[*]Corresponding authors: zhaojj@dlut.edu.cn (J. Zhao); jlwang@seu.edu.cn (J. Wang); xzeng1@unl.edu (X. C. Zeng)

S1. Geometric structures, dynamical and thermal stability of selected Cu2S monolayers

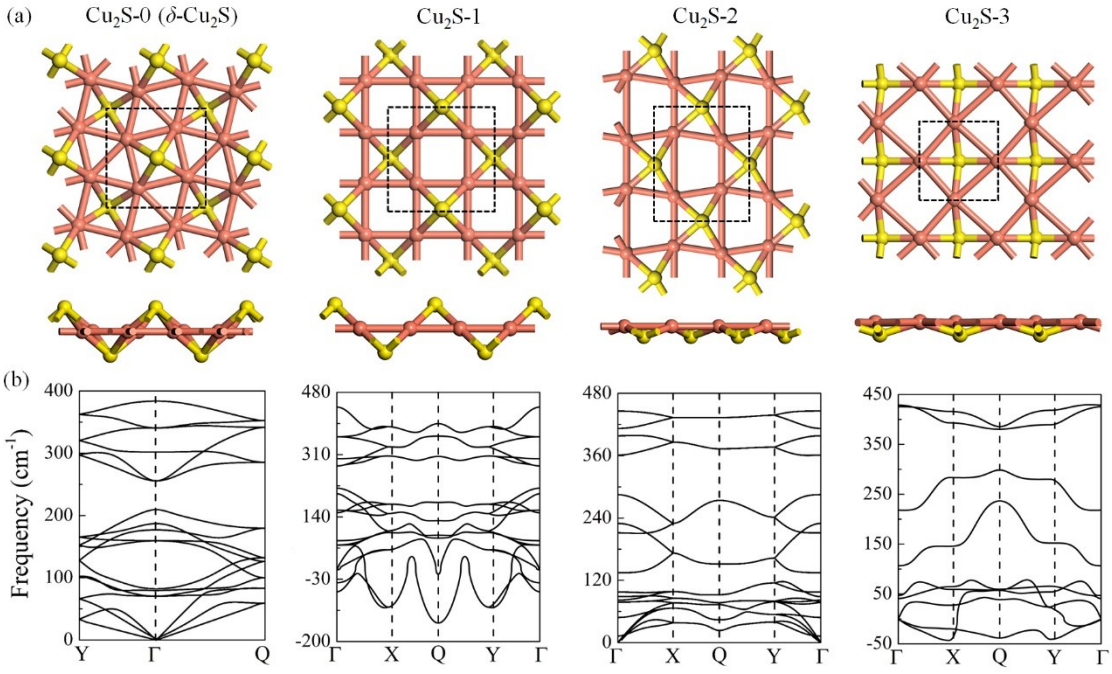

Fig. S1. (a) Four representative low-energy structures of freestanding Cu_2S monolayer predicted by using the CALYPSO code. The unit cells are denoted by dashed lines. Cu and S atoms are shown in pink and yellow, respectively. (b) Corresponding phonon dispersions of the four polymorph structures. High-symmetry points of the first Brillouin zone are: Γ (0, 0, 0), X (0.5, 0, 0), Y (0, 0.5, 0) and Q (0.5, 0.5, 0). Among four structures, only Cu_2S-0 (δ-Cu_2S) and Cu_2S-2 are dynamically stable.

Table S1. Formation energies (ΔH) of four Cu_2S monolayer structures shown in Fig. S1.

System	Cu_2S-0 (δ-Cu_2S)	Cu_2S-1	Cu_2S-2	Cu_2S-3
ΔH (eV/atom)	−0.21	−0.13	0.05	0.07

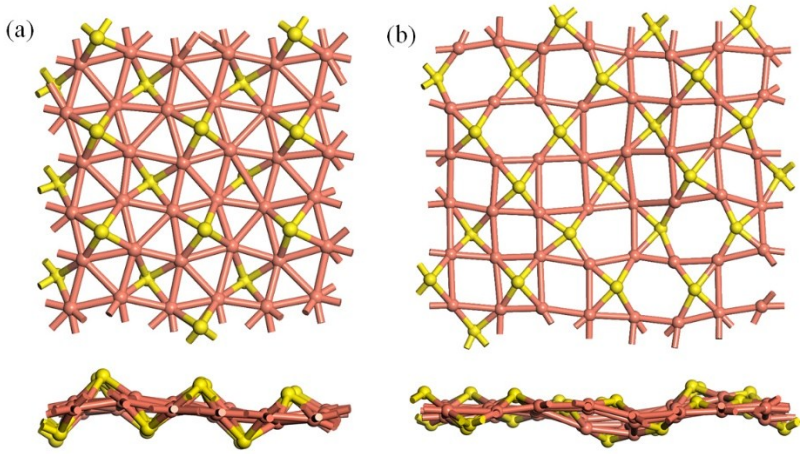

Fig. S2. Snapshots structures of the δ-Cu_2S (a) and Cu_2S-2 monolayers (b) after 10 ps Born-Oppenheimer molecular dynamic simulations, with the temperature being controlled at 300 K. Cu and S atoms are shown in pink and yellow, respectively.

S2. Geometric and electronic structures of β-Cu_2S bilayer

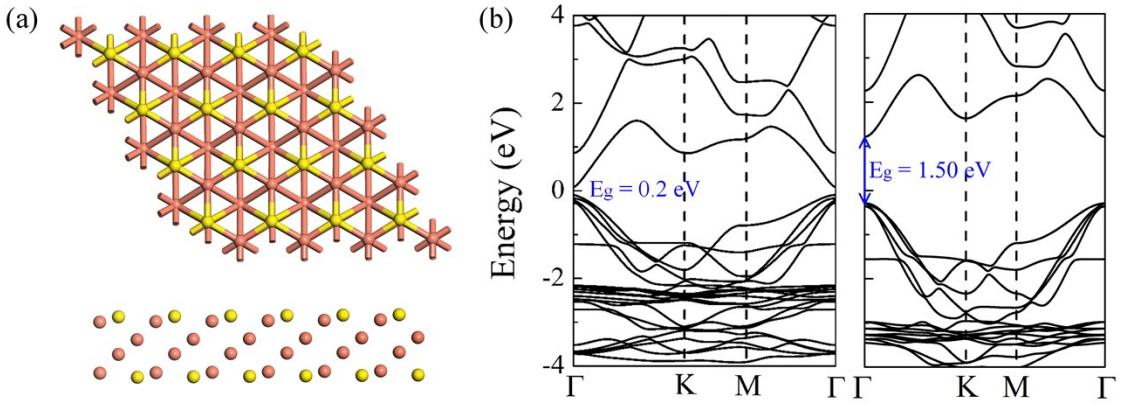

Fig. S3. (a) Top and side views of the experimentally fabricated β-Cu_2S bilayer (see *Adv. Mater.* **2016**, 28, 8271–8276). (b) Band structure of β-Cu_2S bilayer with a direct band gap (E_g) at Γ point, computed based on PBE (left panel) and HSE06 level (right panel), respectively. The Fermi level is set to zero.

S3. Snapshots of *δ*-Cu_2S monolayer taken at the end of each Born-Oppenheimer molecular dynamics (BOMD) simulation

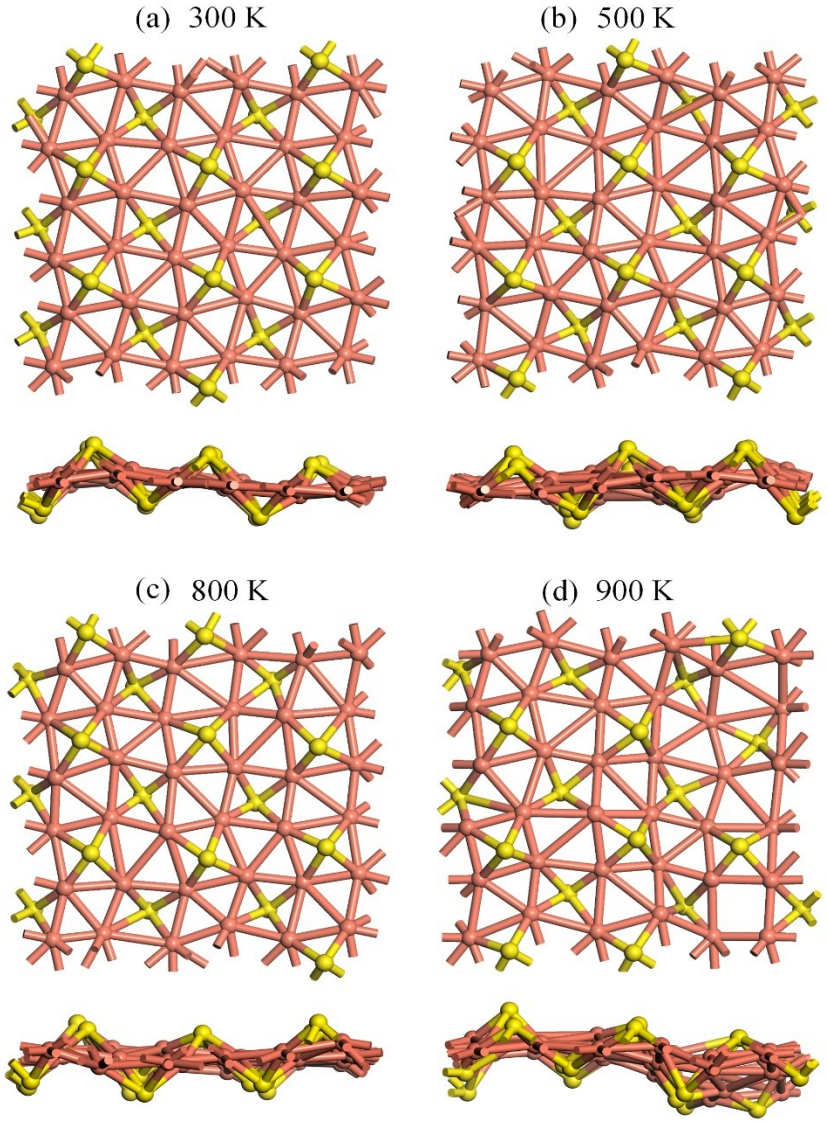

Fig. S4. Structure snapshots of δ-Cu_2S monolayer from BOMD simulations with temperature being controlled at (a) 300, (b) 500, (c) 800, and (d) 900 K, respectively. Each simulation lasts for 10 ps.

S4. Several adsorption sites for O_2 on δ-Cu_2S

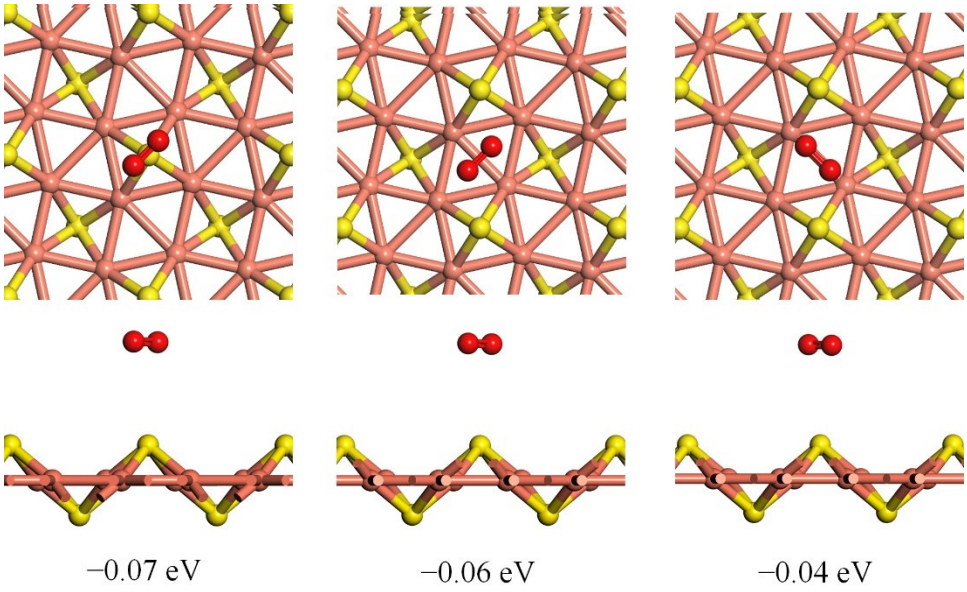

Fig. S5. Top and side views of local geometries for several other adsorption sites for O_2. The number at the bottom indicate the binding energy of O_2 adsorption on δ-Cu_2S. Since O_2 chemisorption on δ-Cu_2S exhibits only one configuration (see Fig. 3), the structures of O_2 physisorbed on δ-Cu_2S are shown here.

S5. Chemical stability of δ-Cu_2S monolayer considering experimental O_2 bonding energy

Table S2. A comparison of energies for initial (E^i), transition (E^t) and final (E^f) states, activation energy (E^a), and heat of reaction (E^H) with either the experimental or DFT calculated O_2 bonding energy as the reference. The unit of E^i, E^t, E^f, E^a and E^H is eV.

	E^i	E^t	E^f	E^a	E^H
Exp.	−1.74	0.24	−1.82	1.98	0.08
DFT	−0.09	1.89	−0.17	1.98	0.08

S6. BOMD simulations of O_2 collision with δ-Cu_2S monolayer at 300 K

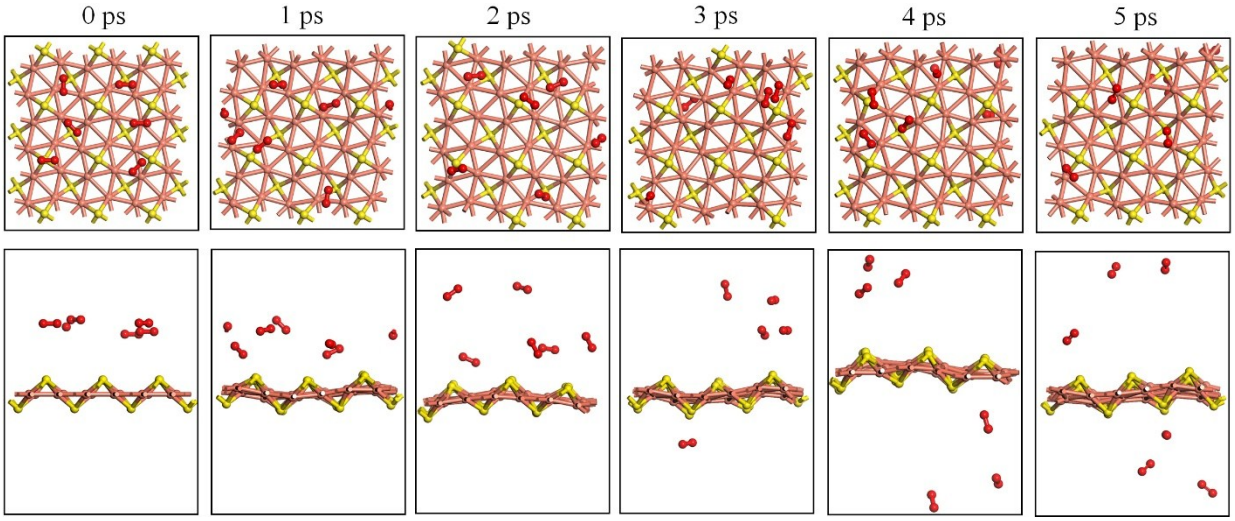

Fig. S6. Snapshots of BOMD simulations of O_2 oxidation at 300 K at 1 - 5 ps. It can be seen that O_2 molecules are typically bounced back to the vacuum after collision with the δ-Cu_2S monolayer. Hence, it seems that δ-Cu_2S monolayer exhibits superior oxidation resistance.

S7. Strain effect on the band structure of δ-Cu_2S monolayer

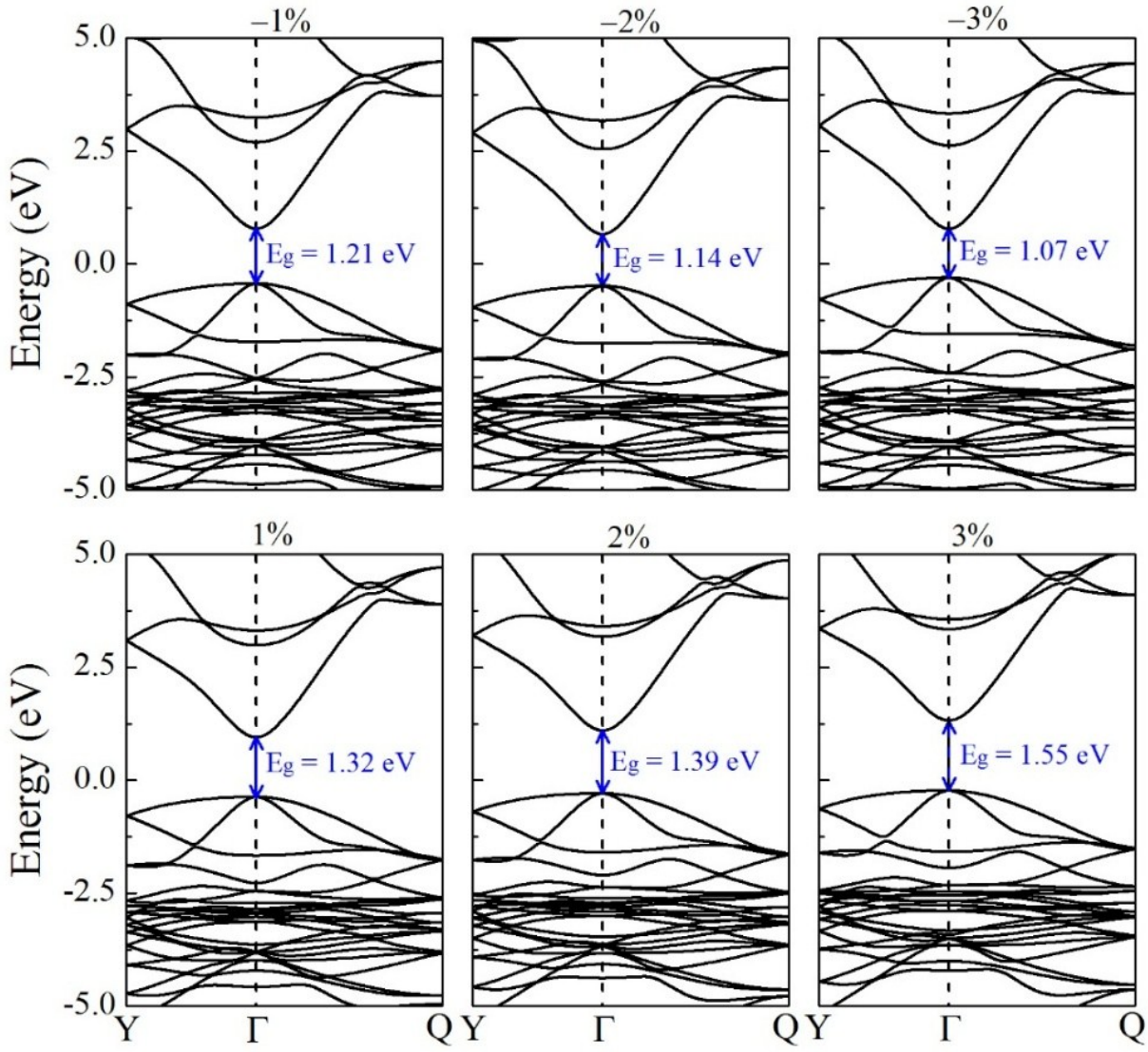

Fig. S7. Band structures of δ-Cu_2S monolayer under various lateral strain from –3% to 3%, computed based on HSE06 functional. Fermi levels are set to zero. E_g is the band gap denoted by the solid arrow.

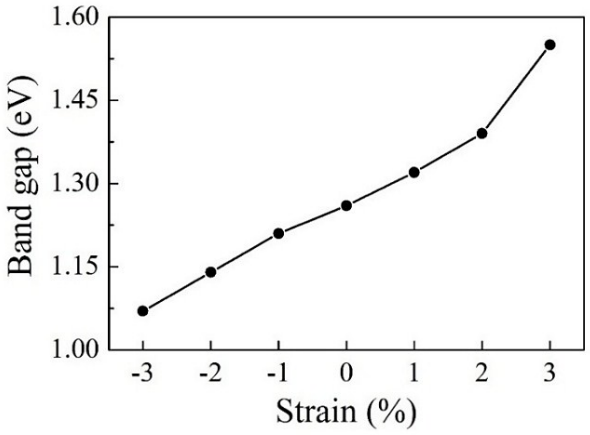

Fig. S8. Strain effect on the band gap of δ-Cu_2S monolayer calculated based on the HSE06 functional.