# Supporting Information

## $C_6N_2S$ Monolayer: An Auxetic Metal with Ultralow Diffusion Barrier and High Storage Capacity for Potassium Ion Batteries

Jiayu Gao[†,1], Wenyuan Zhang[†,1], Aitor Bergara[2,3,4], and Guochun Yang[*,1,5]

*1. State Key Laboratory of Metastable Materials Science & Technology and Key Laboratory for Microstructural Material Physics of Hebei Province, School of Science, Yanshan University, Qinhuangdao 066004, China*

*2. Physics Department and EHU Quantum Center, Universidad del País Vasco-Euskal Herriko Unibertsitatea, UPV/EHU, 48080 Bilbao, Spain*

*3. Donostia International Physics Center (DIPC), 20018 Donostia, Spain*

*4. Centro de Física de Materiales CFM, Centro Mixto CSIC-UPV/EHU, 20018 Donostia, Spain*

*5. Centre for Advanced Optoelectronic Functional Materials Research and Key Laboratory for UV Light-Emitting Materials and Technology of Ministry of Education, Northeast Normal University, Changchun 130024, China*

**Index** **Page**

**Computational Details**

The particle swarm optimization (PSO) method within the evolutionary algorithm as implemented in the Crystal structure Analysis by Particle Swarm Optimization (CALYPSO) code[1] was employed to find the lowest energy structure of the $C_6N_2S$ monolayer. Unit cells containing 1, 2, and 4 formula units (f.u.) were considered. In the first step, random structures with certain symmetries are built, in which atomic coordinates are generated by the crystallographic symmetry operations. Local optimizations using the VASP code were done with the conjugate gradients method and stopped when Gibbs free energy changes became smaller than $1\times10^{-5}$ eV per cell. After processing the first-generation structures, 60% of them with lower Gibbs free energies are selected to construct the next generation structures with PSO. 40% of the structures in the new generation are randomly generated. A structure fingerprinting technique of bond characterization matrix is applied to the generated structures, so that identical structures are strictly forbidden. These procedures significantly enhance the diversity of the structures, which is crucial for structural global search efficiency. In most cases, structural search simulations for each calculation were stopped after generating 1000 ~ 1200 structures (e.g., about 20 ~ 30 generations).

The local structural relaxations and electronic properties calculations were performed in the framework of the density functional theory (DFT) within the generalized gradient approximation (GGA) as implemented in the VASP code.[2] The $2s^22p^2$, $2s^22p^3$, and $3s^23p^4$ atomic orbitals were treated as valence states for C, N and S, respectively. The cut-off energy for the expansion of wave functions into plane waves was set to 600 eV in all the calculations.

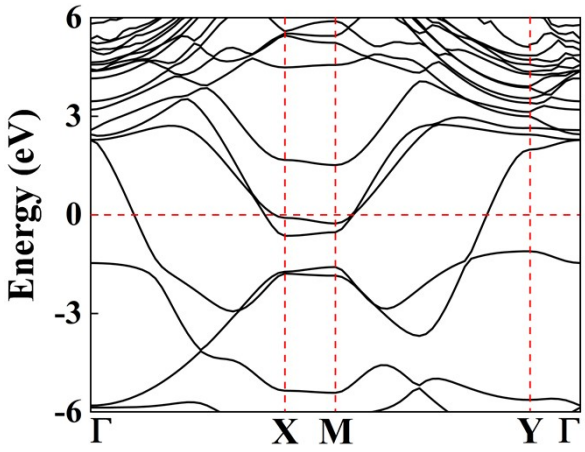


**Figure S1**. The electronic band structure of the $C_6N_2S$ monolayer calculated at the HSE06 level.

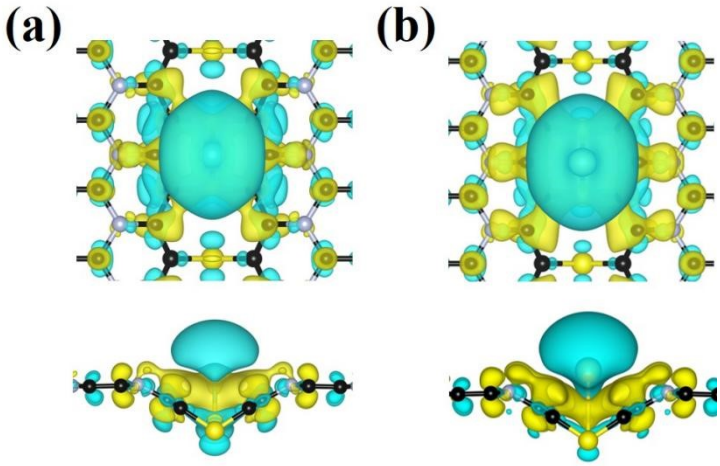


**Figure S2**. The top and side views of charge density difference (CDD) with an adsorbed Li (a) and Na (b) on the $C_6N_2S$ monolayer.

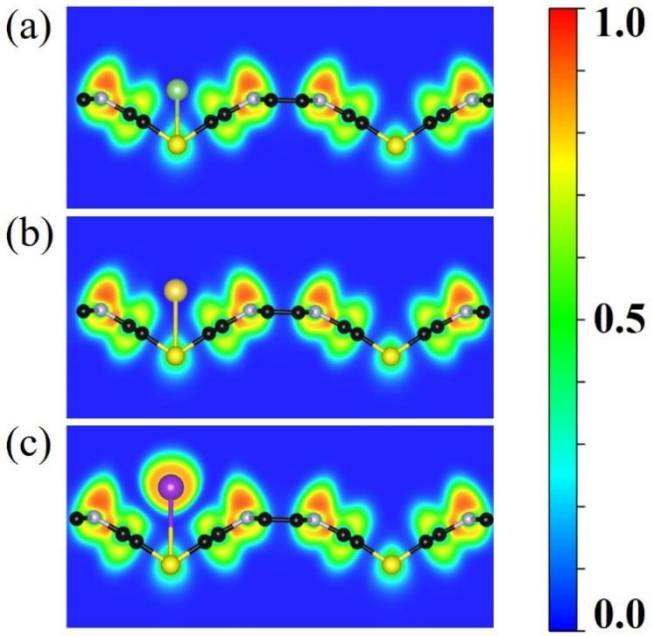


**Figure S3**. The electron localization function (ELF) maps of (a) $C_6N_2SLi$, (b) $C_6N_2SNa$, and (c) $C_6N_2SK$.

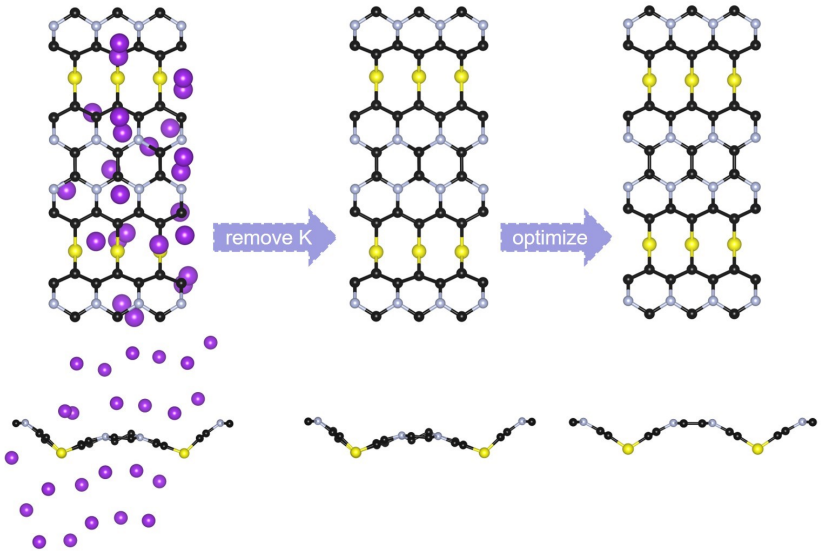


**Figure S4**. The optimized structure of $C_6N_2S$ after the removal of adsorbed K atoms.

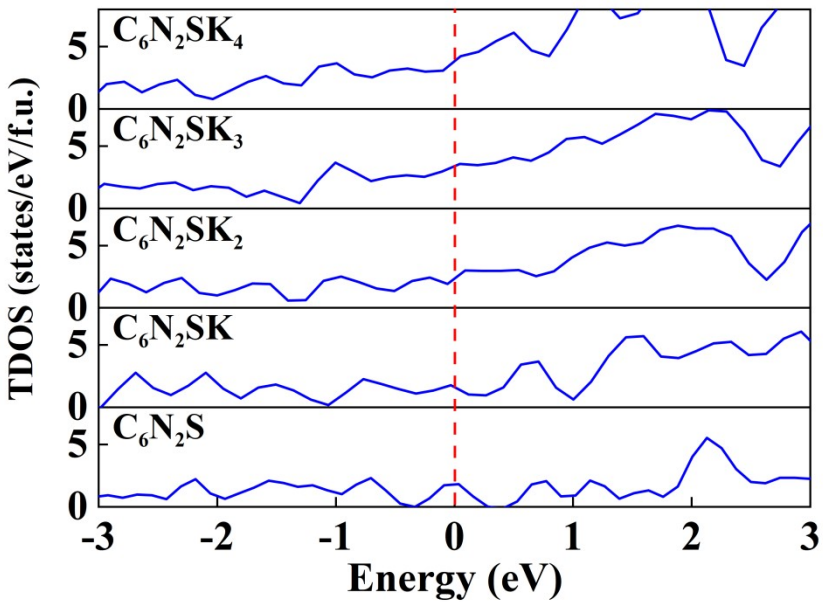


**Figure S5**. Total density of states (TDOS) of $C_6N_2S$, $C_6N_2SK$, $C_6N_2SK_2$, $C_6N_2SK_3$, and $C_6N_2SK_4$.

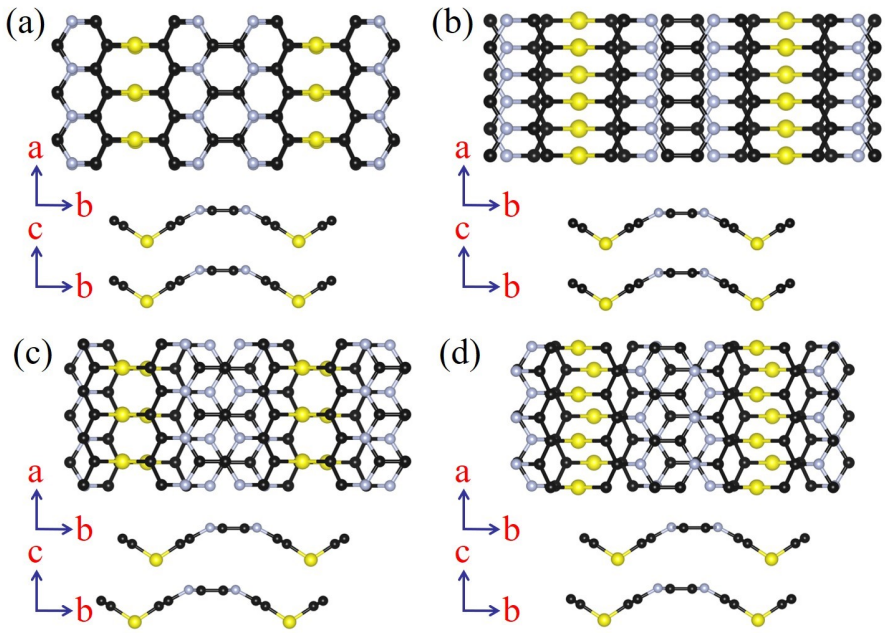


**Figure S6**. The $C_6N_2S$ bilayer structures of (a) aligned stacking, (b) *a*-direction translational stacking, (c) *b*-direction translational stacking, and (d) simultaneous translational stacking along the *a* and *b* directions.

**Table S1.** Structural information of the predicted $C_6N_2S$ monolayer.

| Phase | Space Group | Lattice Parameters (Å, °) | Wyckoff Positions (fractional) Atoms | *x* | *y* | *z* |
|---|---|---|---|---|---|---|
| $C_6N_2S$ | *Pmm*2 | $a$ = 4.85602 | C(2g) | 0.00000 | 0.07137 | 0.51945 |
| | | $b$ = 6.20827 | C(2g) | 0.00000 | 0.65564 | 0.47660 |
| | | $c$ = 19.9284 | C(2h) | 0.50000 | 0.28295 | 0.49114 |
| | | $\alpha$ = 92.2986 | N(2h) | 0.50000 | 0.15109 | 0.52118 |
| | | $\beta$ = 93.3793 | S(1b) | 0.00000 | 0.50000 | 0.43326 |
| | | $\gamma$ = 66.9783 | | | | |

**Table S2.** Elastic Constants for the $C_6N_2S$ Monolayer (in N/m).

| Structure | $C_{11}$ | $C_{12}$ | $C_{22}$ | $C_{66}$ |
|---|---|---|---|---|
| $C_6N_2S$ | 322.309 | 7.339 | 38.890 | 85.595 |

Based on the mechanical balance conditions: $C_{11}C_{22} - C_{12}C_{12} > 0$ and $C_{66} > 0$, the $C_3NS$ monolayer is mechanically stable.[3]

**Table S3.** The lattice parameters of $C_6N_2SK_n$ ($n$ = 1-4).

| lattice parameters | $n$ = 1 | $n$ = 2 | $n$ = 3 | $n$= 4 |
|---|---|---|---|---|
| $a$ (Å) | 7.398 | 7.419 | 7.412 | 7.420 |
| $b$ (Å) | 18.747 | 18.003 | 18.285 | 18.220 |

**References**


(1) Y. Wang,; J. Lv,; L. Zhu,; Y. Ma, , CALYPSO: A method for crystal structure prediction. *Computer Physics Communications* **2012,** *183*, 2063.

(2) W. A. N. Holzwarth,; A. R. Tackett,; G. E. Matthews, , A projector augmented wave (PAW) code for electronic structure calculations, part I: atompaw for generating atom-centered functions. *Comput. Phys. Commun.* **2001,** *135*, 329.

(3) M. B. Kanoun,; S. Goumri-Said; M. Jaouen, Structure and mechanical stability of molybdenum nitrides: A first-principles study. *Phys. Rev. B* **2007,** *76*, 134109.