Supporting Information of

$Ni(NCS)_2$ monolayer: a robust bipolar magnetic semiconductor

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1. Variation of magnetic moment and energy difference with *U* value

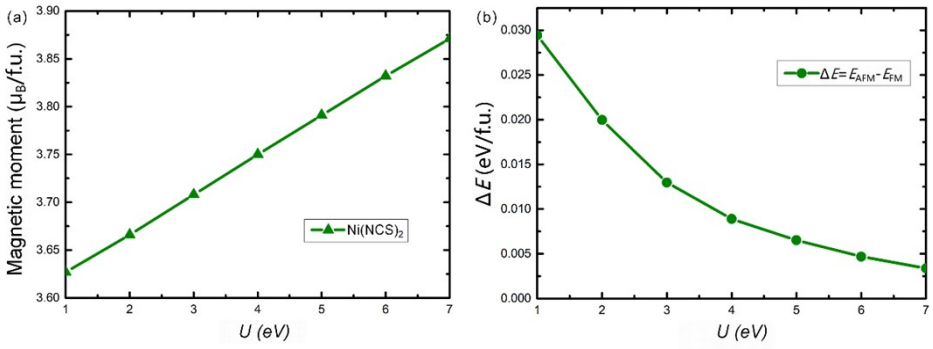

Figure S1 The changes of magnetic moment (a) and energy difference of *U* (b) in the range 1-7 respectively.

Only using the method of PBE will ignore some interrelated effects of electrons. Especially for transition metal elements, which have *3d* orbits, the method of *Hubbard Coulomb* interaction *U* should be deemed to improve the accuracy of calculation. So, the Ni atom, in the calculation process, adopts the method of PBE+*U* to deal with the strongly correlated system. In order to better find out the appropriate *U*, we also tested the *U* theoretically. The $Ni(NCS)_2$ monolayer maintains the ferromagnetic ground state regardless of how the *U* value is varied from 1 to 7. The magnetic moment on single Ni increases linearly with the increase of *U* value (as shown in Figure S1a). Not only that, but the variation of *E* with *U* is also interesting. When *U* value is between 1 and 4, the value of *E* decreases rapidly; as *U* exceeds 4 and increases, *E* value decreases gradually, and finally the curve tends to be smooth (as shown in Figure S1b). Therefore, we decide to use *U* = 4 to calculate the properties of the $Ni(NCS)_2$ monolayer. Besides, the lattice parameters of bulk after relaxation (under U_{eff} = 4 eV) is *a* = 10.6115 Å, *b* = 3.6728 Å, *c* = 6.1614 Å, respectively, which in good agreement with the experimental values (*a* = 10.5070 Å, *b* = 3.6189 Å, *c* = 6.1625 Å)[1]. Therefore U_{eff} = 4.0 eV is adopted within the GGA+*U* calculations.

2. The detailed structural information of bulk and monolayer $Ni(NCS)_2$ after relaxation.

The POSCAR of bulk $Ni_2C_4S_4N_4$

1.0

10.6115714451451488 0.0000000000000000 0.0196387409333494

0.0000000000000000 3.6728549254677425 0.0000000000000000

-1.7102150778450249 0.0000000000000000 6.3864250467001495

Ni C S N

2 4 4 4

Direct

0.0000000000000000	0.0000000000000000	0.0000000000000000
0.5000000000000000	0.5000000000000000	0.0000000000000000
0.7638007610075661	0.0000000000000000	0.1977532968400766
0.7361992389924339	0.5000000000000000	0.8022466731599280
0.2638007610075661	0.5000000000000000	0.1977532968400766
0.2361992249924398	0.0000000000000000	0.8022466731599280
0.8823548581731515	0.5000000000000000	0.7630816523888697
0.6176451418268485	0.0000000000000000	0.2369183176111349
0.3823548581731515	0.0000000000000000	0.7630816523888697
0.1176451418268485	0.5000000000000000	0.2369183176111349
0.8646660479561135	0.0000000000000000	0.1535597731076734
0.6353339520438865	0.5000000000000000	0.8464402268923266
0.3646660479561135	0.5000000000000000	0.1535597731076734
0.1353339520438865	0.0000000000000000	0.8464402268923266

The POSCAR of monolayer $Ni_2C_4S_4N_4$

1.0

10.490432881353781 0.0000000000000000 0.0000000000000000

0.0000000000000000 3.7197955245153338 0.0000000000000000

0.0000000000000000 0.0000000000000000 30.000000000000000

Ni N S C

2 4 4 4

Direct

0.0000000000000000	0.0000000000000000	0.6259499789999978
0.5000000000000000	0.5000000000000000	0.6259499789999978
0.8391252520022050	0.0000000000000000	0.6587003546736625
0.3391252520022050	0.5000000000000000	0.6587003546736625
0.1608747339978009	0.0000000000000000	0.5931896493263409
0.6608747479977950	0.5000000000000000	0.5931896493263409
0.5755375630262591	0.0000000000000000	0.6765773135955300
0.0755375850262539	0.5000000000000000	0.6765773135955300
0.4244624069737455	0.0000000000000000	0.5753126894044698
0.9244624369737409	0.5000000000000000	0.5753126894044698
0.7294223881429573	0.0000000000000000	0.6666363018586594
0.2294223881429573	0.5000000000000000	0.6666363018586594
0.2705776118570427	0.0000000000000000	0.5852537021413369
0.7705776118570427	0.5000000000000000	0.5852537021413369

3. The different magnetic configurations of ferromagnetic (FM) and antiferromagnetic (AFM) for $Ni(NCS)_2$ monolayer.

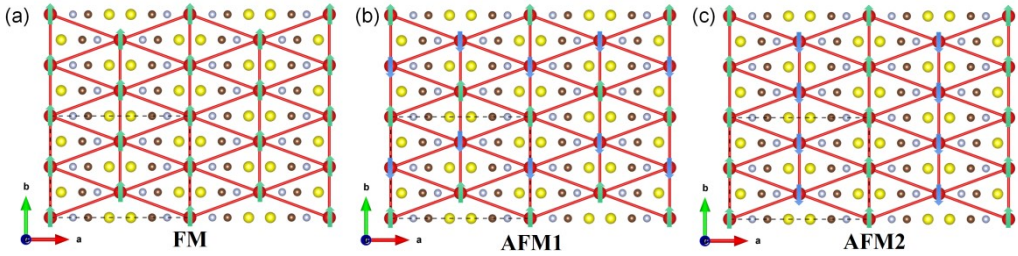

Figure S2 The different magnetic configurations of $Ni(NCS)_2$ monolayer

Based on the calculated total energies of different magnetic configurations (Figure S2) and normalized S ($|S| = 1$), the exchange parameters J_1 and J_2 can be derived by following equations:

$E_{FM} = E_0 - (J_1 + 2J_2)|S|^2 - A|S|^2$ (1)

$E_{AFM1} = E_0 - (-J_1)|S|^2 - A|S|^2$ (2)

$E_{AFM2} = E_0 - (J_1 - 2J_2)|S|^2 - A|S|^2$ (3)

E_0 is the total energy excluding the magnetic coupling (not sensitive to different magnetic states). For, anisotropy energy parameter A, spin−orbital coupling (SOC) calculations are performed on 2D $Ni(NCS)_2$ monolayer crystal to obtain the relative stability along three magnetization directions in plane, that is (100), (010), and (001) direction. A is calculated to be -415 μeV by using the magnetic anisotropy energies as below:

$$A = \frac{E(100) - E(001)}{|S|^2}$$

4. The Poisson's ratio (v) and the in-plane Young's modulus

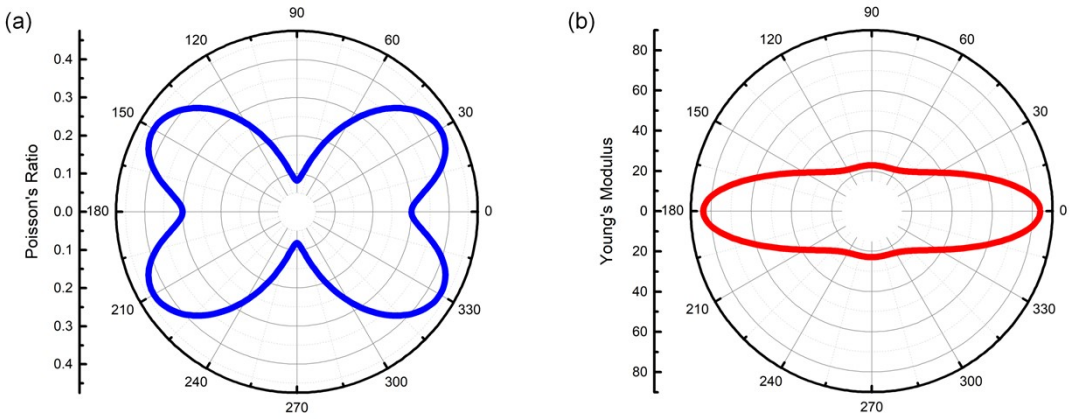

Figure S3 Calculated orientation-dependent Poisson's ratio (a), and Young's modulus (b).

The Poisson's ratio and the in-plane Young's modulus can represent the elastic properties of 2D materials, which were plotted based on the calculated elastic constants (Figure S3). The calculated the Poisson's ratios along *x*- and *y*-axis for the $Ni(NCS)_2$ monolayer are 0.30 and 0.082, respectively, suggesting its high anisotropy in space. For Young's modulus of $Ni(NCS)_2$ monolayer the maximum value is 85.9 N/m along *x*-axis, which is comparable with that of silicene

(61 N/m) and a litter lower than that of MoS_2 monolayer (123 N/m). The result also reveals strong anisotropy of $Ni(NCS)_2$ monolayer.

5. Electronic structure of $Ni(NCS)_2$ monolayer.

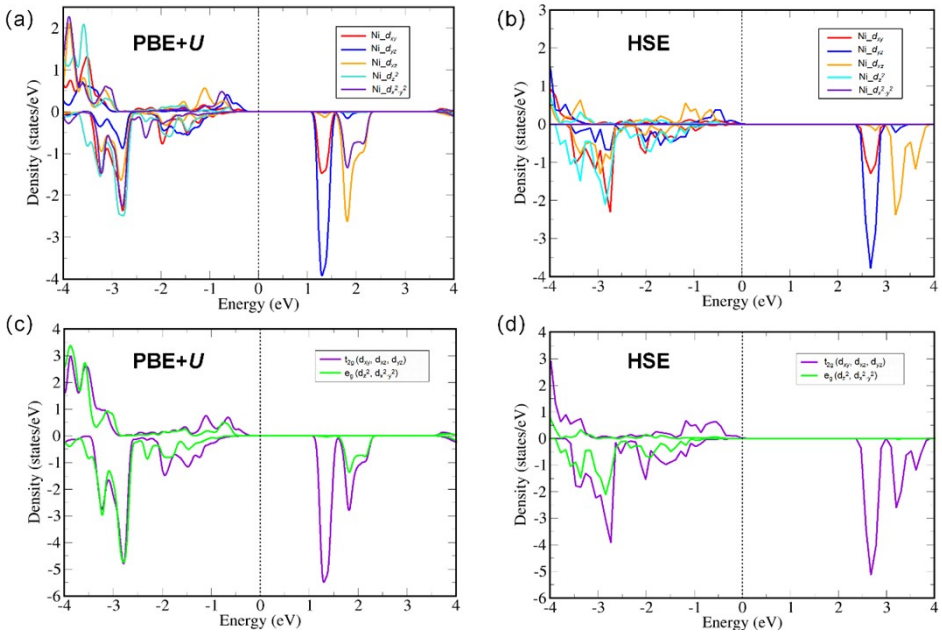

Figure S4 The orbital-projected density of states of the Ni_*d* orbit calculated under the PBE+*U* (a) and HSE06 (b) methods. The orbital-projected density of states of the t_{2g} orbit and e_g orbit calculated under the PBE+*U* (c) and HSE06 (d) methods.

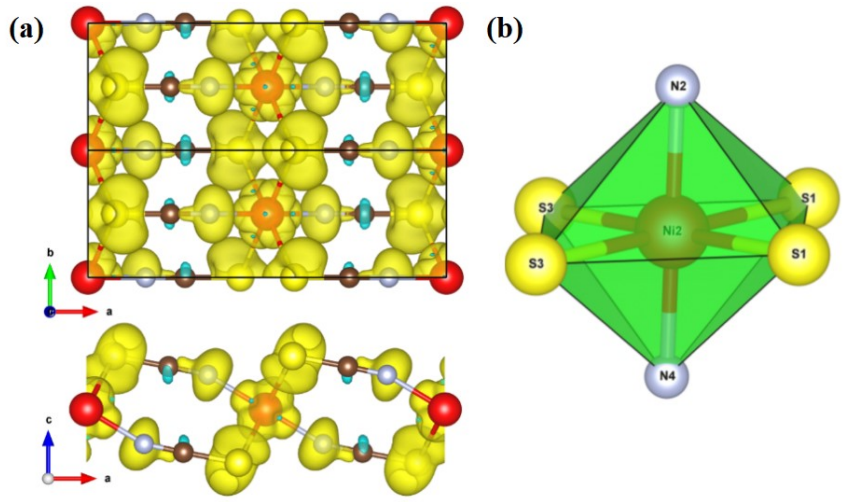

Figure S5 (a) The spin charge density distribution of $Ni(NCS)_2$ monolayer with the isosurface value of 0.002 e/bohr^3. Yellow represents spin-up and blue represents spin-down. (b) Octahedral crystal of hex-coordinated Ni atom.

6. Under the applied strain and doping, the magnetic moment change and band structures of $Ni(NCS)_2$ monolayer.

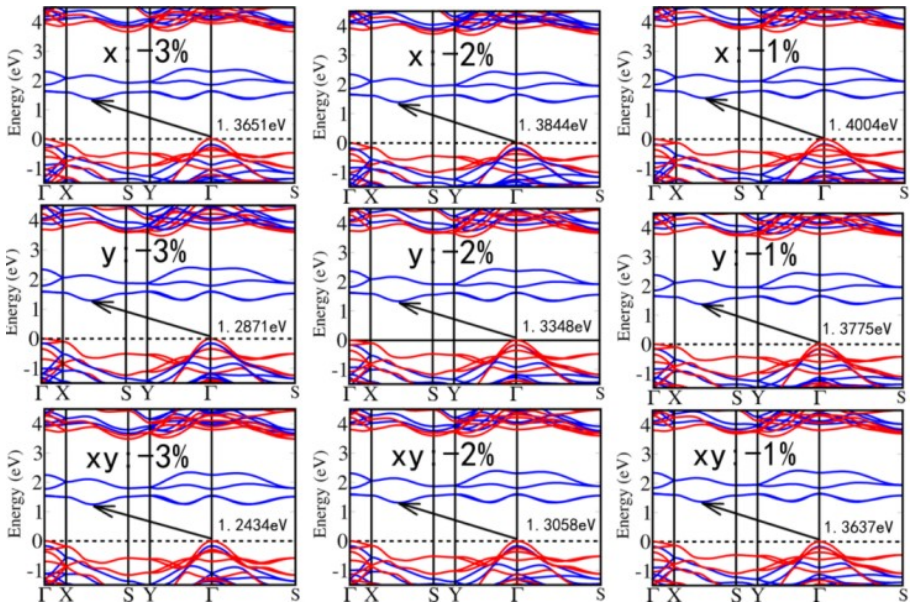

Figure S6 Band structure of $Ni(NCS)_2$ monolayer under compressive strain.

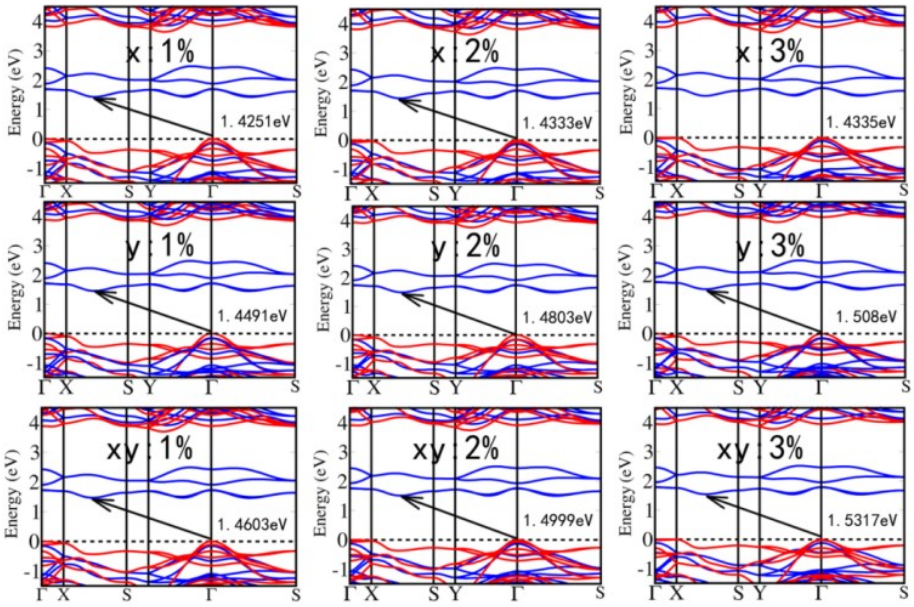

Figure S7 Band structure of $Ni(NCS)_2$ monolayer under tensile strain.

Figure S6 shows that the band gap becomes smaller with the application of a stretching -1% to -3% compressive strain whether it is uniaxial or biaxial compressive strains. Figure S7 demonstrates that a larger band gap can be obtained with tensile strain and the band gaps increases as the tensile strain increases (from 1% to 3%). This result shows tunable band gaps of $Ni(NCS)_2$ monolayer.

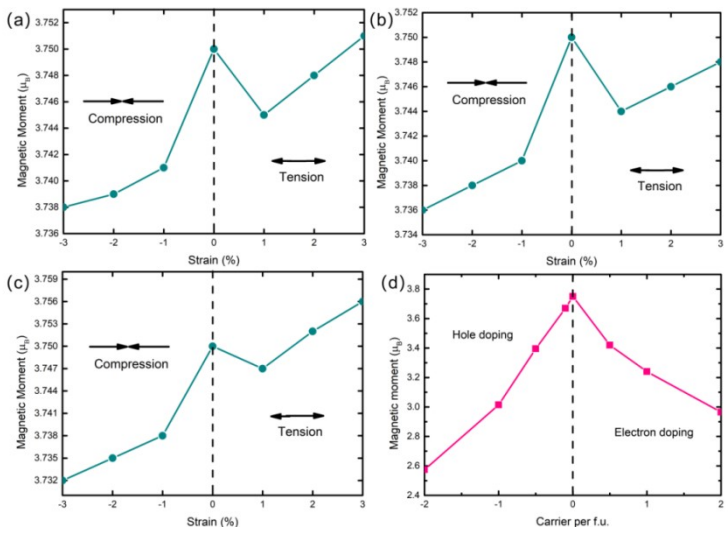

Figure S8 Changes of magnetic moment under different strain (*x*-axis (a), *y*-axis (b), and *xy*-axis (c)) and doping (d).

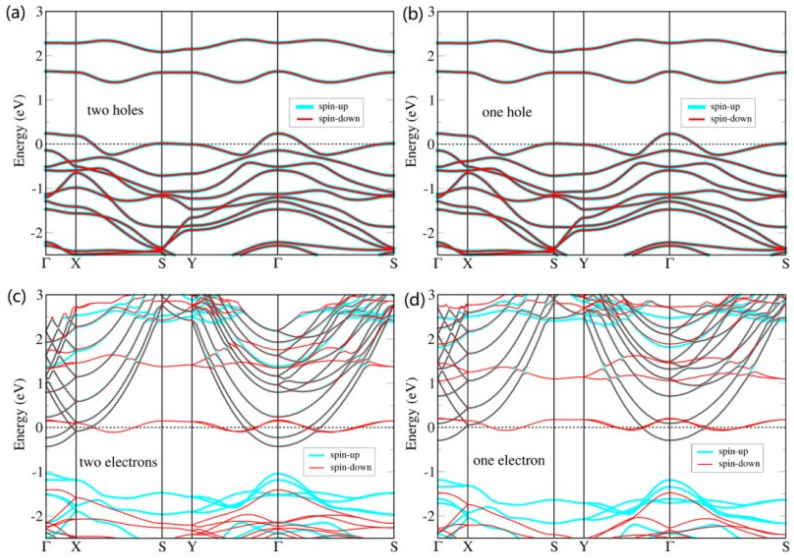

Figure S9 Band structures of doping with two holes (a), one hole (b), two electrons (c), and one electron (d), respectively.

References

1. E. N. Bassey, J. A. M. Paddison, E. N. Keyzer, J. Lee, P. Manuel, I. da Silva, S. E. Dutton, C. P. Grey and M. J. Cliffe, *Inorg Chem*, 2020, **59**, 11627-11639.