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

Supporting Information

Single-atom catalysts based on C_2N for sulfur cathode in Na-S batteries: A first-principles study

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1. Supplementary figures

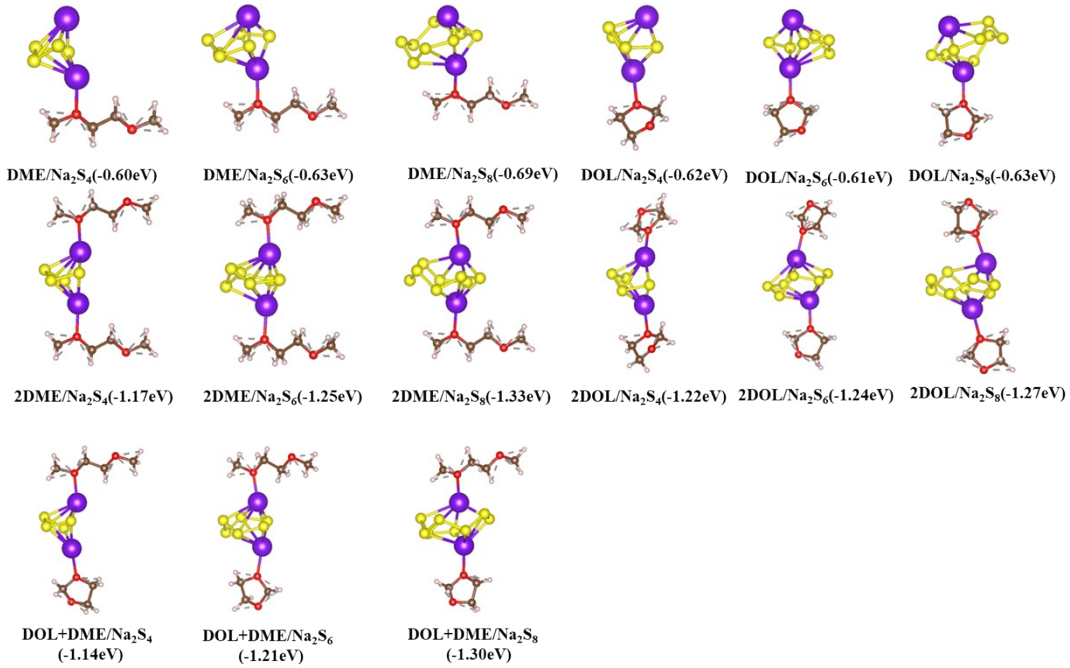

Fig. S1 The adsorption configurations and energies of one DME or one DOL molecule, as well as two DME/DOL or DOL+DME molecules with Na_2S_4/Na_2S_6/Na_2S_8.

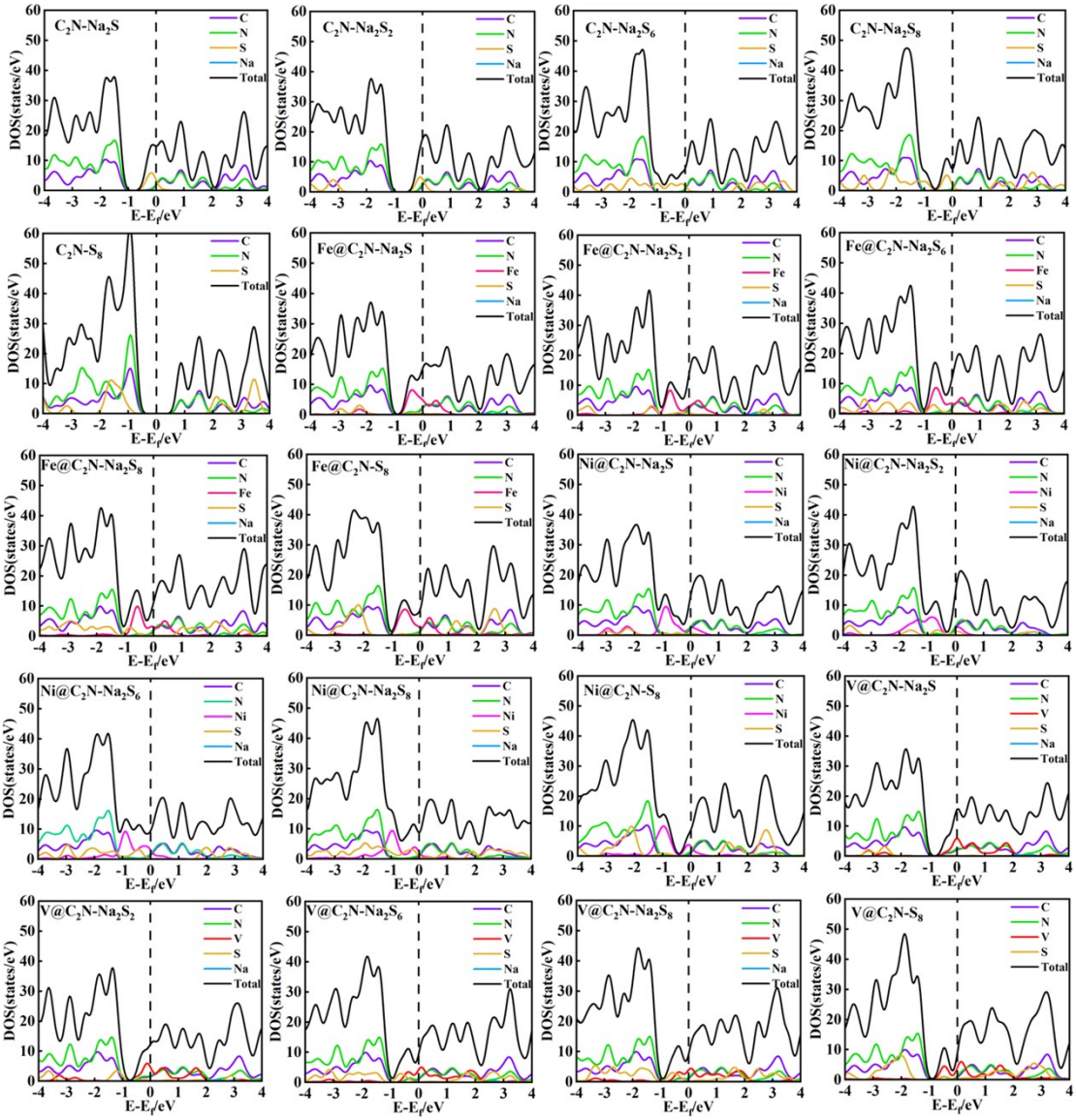

Fig. S2 The density of states of C_2N adsorbed NaPSs/S_8, Fe@C_2N adsorbed NaPSs/S_8, Ni@C_2N adsorbed NaPSs/S_8 and V@C_2N adsorbed NaPSs/S_8. The Fermi level is set to be zero (denoted as black dotted lines).

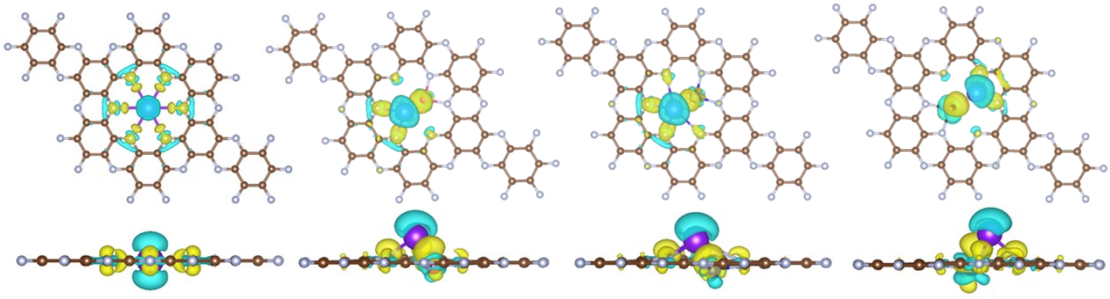

Fig. S3 The charge density difference plots of Na^+ ion anchored on the C_2N, TM@C_2N (TM = Fe, Ni and V) substrates, respectively. The iso-surface value is set as 0.002 e/Bohr3, and the yellow region represents the charge accumulation and the cyan color is the region of charge depletion.

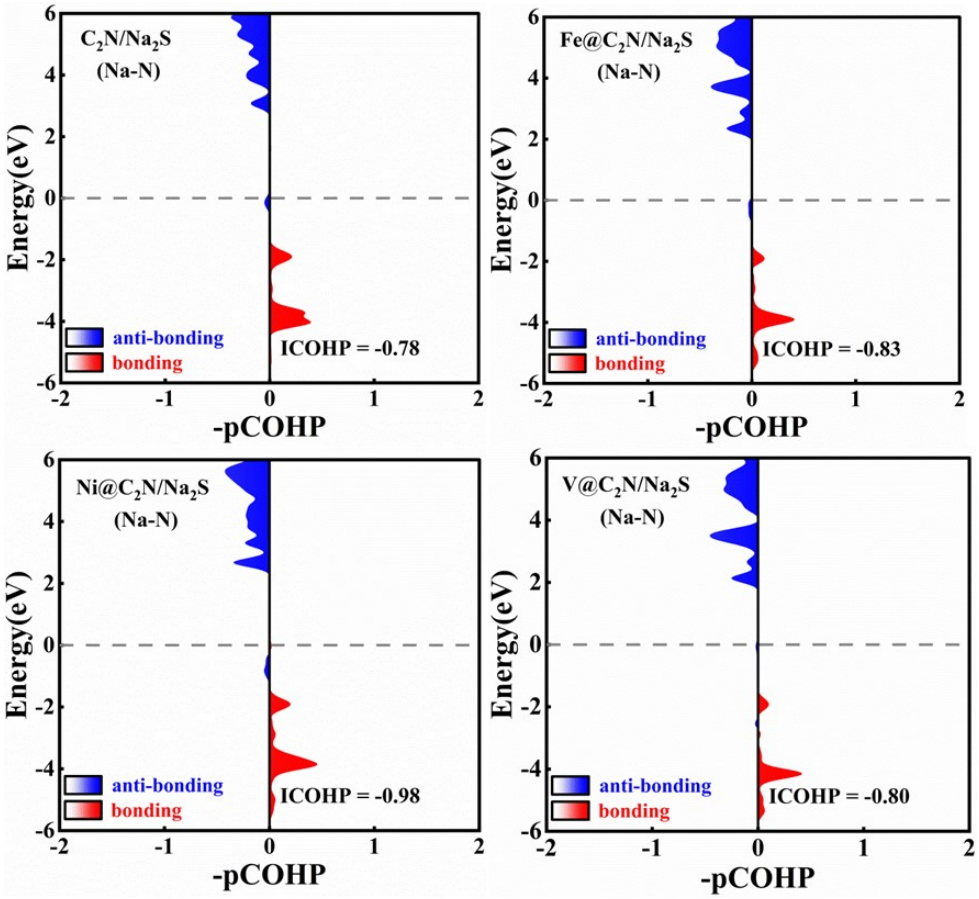

Fig. S4 The COHP results of Na-N bond in C_2N/Na_2S, $Fe@C_2N/Na_2S$, $Ni@C_2N/Na_2S$, and $V@C_2N/Na_2S$ adsorption systems.

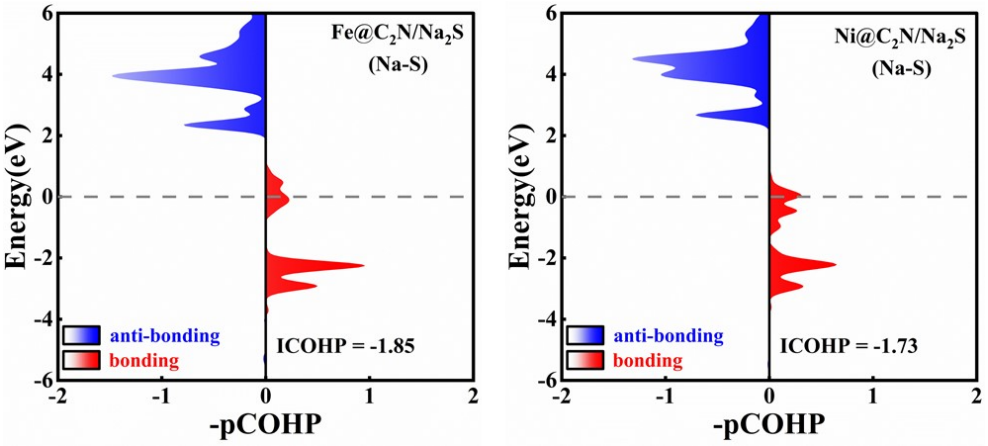

Fig. S5 The COHP results of Na-S bond in $Fe@C_2N/Na_2S$ and $Ni@C_2N/Na_2S$ adsorption systems.

2. Supplementary tables

Table S1 The data list of adsorption energies under vacuum or solvation effect of C_2N and TM@C_2N (TM = Fe, Ni and V) on S_8/NaPSs.

Structures	E_a/E_a^{sol}(C_2N (eV)	E_a/E_a^{sol}(Fe@C_2N (eV)	E_a/E_a^{sol}(Ni@C_2N (eV)	E_a/E_a^{sol}(V@C_2N (eV)
S_8	-0.66	-1.41	-1.79	-2.37
Na_2S	-3.01	-4.56	-5.23	-5.03
Na_2S_2	-3.51	-3.61	-4.80	-4.51
Na_2S_4	-2.72/-1.76	-2.94/-1.85	-3.36/-2.17	-4.89/-3.76
Na_2S_6	-2.56/-1.88	-2.59/-2.04	-2.85/-2.08	-3.46/-2.78
Na_2S_8	-2.37/-1.57	-3.69/-2.90	-3.06/-2.37	-3.80/-3.12

Table S2 The ratio of vdW contribution (R_{vdW}) of C_2N and V@C_2N adsorbing S_8/NaPSs.

Adsorption Systems	E'	$E^{no\cdot}$	$R_{vd\backslash}$
C_2N/S_8	-0.66	-0.02	97.66%
C_2N /Na_2S_8	-2.37	-1.30	45.15%
C_2N / Na_2S_6	-2.56	-1.67	34.87%
C_2N / Na_2S_4	-2.72	-1.99	26.72%
C_2N / Na_2S_2	-3.51	-3.09	12.04%
C_2N / Na_2S	-3.01	-2.64	12.17%
V@C_2N/S_8	-2.37	-1.72	27.46%
V@C_2N / Na_2S_8	-3.80	-3.59	5.42%
V@C_2N / Na_2S_6	-3.46	-3.11	10.26%
V@C_2N / Na_2S_4	-4.89	-4.68	4.34%
V@C_2N / Na_2S_2	-4.51	-4.03	10.64%
V@C_2N / Na_2S	-5.03	-4.69	6.79%

Table S3 Charge transfer amount of C_2N and TM@C_2N (TM = Fe, Ni and V) adsorbing S_8/NaPSs.

Na_2S	C_2N	Fe@C_2N	Ni@C_2N	V@C_2N
Na	-1.64	-1.64	-1.61	-1.66

S	0.71	1.02	0.90	0.95

Table S4 The adsorption energies of Na^+ ion adsorbed on the pristine C_2N, and TM@C_2N (TM = Fe, Ni and V).

	$E_a(C_2N)$ (eV)	$E_a(Fe@C_2N)$ (eV)	$E_a(Ni@C_2N)$ (eV)	$E_a(V@C_2N)$ (eV)
Na^+	-4.56	-2.77	-2.80	-2.17

Table S5 The ICOHP results of Na-S, Na-N, TM-S bond in C_2N/Na_2S, Fe@C_2N/Na_2S, Ni@C_2N/Na_2S, and V@C_2N/Na_2S adsorption systems.

Structures	Na-S	Na-N	TM-S
C_2N	-2.17	-0.78	/
Fe@C_2N	-1.85	-0.83	-5.84
Ni@C_2N	-1.73	-0.98	-6.11
V@C_2N	-1.78	-0.80	-6.55

Table S6 The data list of Gibbs free energies of C_2N and all single-atom catalysts.

	C_2N	Fe@C_2N	Ni@C_2N	V@C_2N
$*S_8$	-0.66	-1.41	-1.79	-2.37
ΔG_1	-4.27	-3.32	-3.10	-3.17
ΔG_2	0.13	0.22	0.12	-0.04
ΔG_3	0.32	0.35	0.33	0.38
ΔG_4	0.63	0.58	0.43	0.47
ΔG_5	1.11	0.05	0.26	0.13