Electronic Supplementary Information

Efficiently direct methane to methanol on CuZn hetero-diatomic catalysts with certain coordination spheres: A DFT study

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Formation energy (E_f), binding energy (E_b) and dissolution potential (U_{diss})

In order to adopt the optimal coordination configurations of the CuZn atoms embedded in nitrogen-decorative graphene, the formation energy (E_f) of CuZn-NG is calculated by using the Eq. s1 [S1,S2]:

$$E_f = E_{CuZn\text{-}NG} + 10\,\mu_C - (E_{Gra} + 6\mu_N + \mu_{Cu} + \mu_{Zn}) \quad \text{(Eq. s1)}$$

where $E_{CuZn\text{-}NG}$ is the total energy of CuZn-NG, E_{Gra} is the total energy of the pristine 6×6 graphene supercell and μ_C is the chemical potential of C atom [S3,S4], and μ_N is the chemical potential of N atom taken from a N_2 molecule in the gas phase [S5]. μ_{Cu} and μ_{Zn} are the chemical potentials of Cu and Zn atoms, respectively [S6].

In order to verify that the combination of CuZn atoms is favorable, the binding energy ( ) between the two Cu atoms or two Zn atoms or CuZn atoms and the substrate is studied and defined as Eq. S2 [S7]:

$$E_b = E_{CuZn-NG} - \quad - E_{Cu} - E_{Zn} \quad \text{(Eq. S2)}$$

where and represent the total energies of CuZn-NG and NG, respectively, / is the total energy of a Cu/Zn atom in the most stable bulk structure.

In addition, to evaluate the stability of the system in electrode working conditions, the dissolution potential ( ) is calculated as Eq. S3 [S8]:

$$U_{diss} = U^0_{diss}\text{(metal, bulk)} - E_b/N_e \quad \text{(Eq. S3)}$$

where (metal, bulk) is the standard dissolution potential of the bulk metal, is the number of transferred electrons during the dissolution.

Table S1 Binding energy ( ), standard dissolution potentials ( ) of metals, number of transferred electrons ( ) during the dissolution and dissolution potential ( ) of metals.

Species	**(eV)**	**(V)**		**(V)**
CuCu-N_PG	-1.99	0.34	2	0.84
ZnZn-N_PG	-3.15	-0.76	2	0.03
CuZn-N_PG	-2.94	0.34/-0.76	2/2	0.37/0.08
CuCu-$N_{PA}G$	-4.17	0.34	2	1.38
ZnZn-$N_{PA}G$	-5.22	-0.76	2	0.55
CuZn-$N_{PA}G$	-5.01	0.34/-0.76	2/2	1.16/0.42

Table S2 The atomic charge (|*e*|) of first CS and second CS in NG and CuZn-NG. The atomic charge changes (Δ|*e*|) of first CS and second CS when CoNi atoms embedded in NG.

		N_PG	**CuZn-N_PG**	**$N_{PA}G$**	**CuZn-$N_{PA}G$**
|*e*|	first CS	-6.90	-7.61	-5.60	-7.26
	second CS	7.12	5.79	5.73	5.31
Δ|*e*|	first CS	-0.71		-1.66	
	second CS	-1.33		-0.42	

Table S3 Adsorption energy (E_{ads}) of H_2O and H_2O_2 molecule.

Species		E_{ads} **(eV)**
CuZn-N_PG	H_2O_2	-0.33
	H_2O	-0.41
CuZn-$N_{PA}G$	H_2O_2	-0.28
	H_2O	-0.33

Table S4 The atomic charge (|*e*|) and d-band center (eV) during methane oxidation to methanol.

Species	d-band center of Cu (eV)	d-band center of Zn (eV)	Atomic charge of Cu (|*e*|)	Atomic charge of Zn (|*e*|)
CuZn-N_PG (Ⅰ)	-2.93	-7.27	0.60	1.02
Ⅱ	-2.96	-7.06	0.64	1.08
Ⅲ	-2.59	-5.70	0.90	1.19
Ⅳ	-2.48	-5.70	0.88	1.18
Ⅴ	-2.50	-5.70	0.88	1.18
Ⅵ	-2.15	-6.23	0.77	1.16
Ⅶ	-2.74	-6.95	0.61	1.09
CuZn-$N_{PA}G$ (Ⅰ)	-4.27	-6.52	0.94	1.18
Ⅱ	-4.30	-6.40	0.95	1.22
Ⅲ	-3.82	-5.43	0.99	1.24
Ⅳ	-3.73	-5.52	1.01	1.22
Ⅴ	-3.78	-5.48	1.00	1.22
Ⅵ	-3.94	-4.95	0.95	1.24
Ⅶ	-4.29	-6.15	0.95	1.24

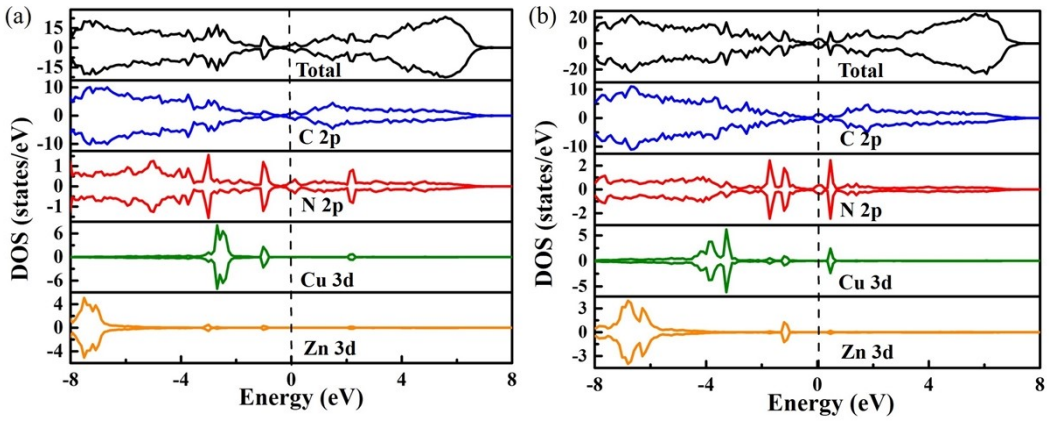

Fig. S1 Spin-polarized density of states for (a) CuZn-N_PG, (b) CuZn-$N_{PA}G$.

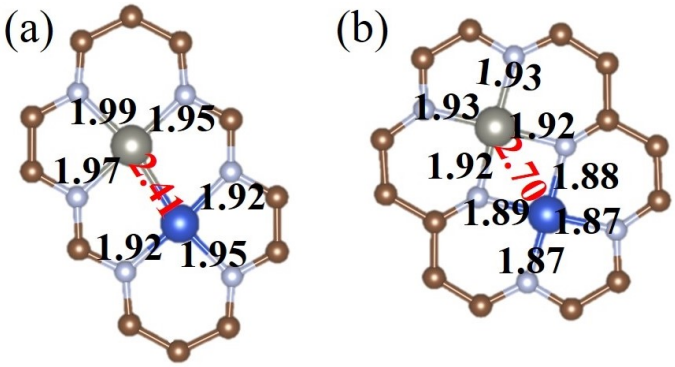

Fig. S2 The geometric structures and the mainly bonds lengths (Å) of (a) CuZn-N_PG and (b) CuZn-$N_{PA}G$.

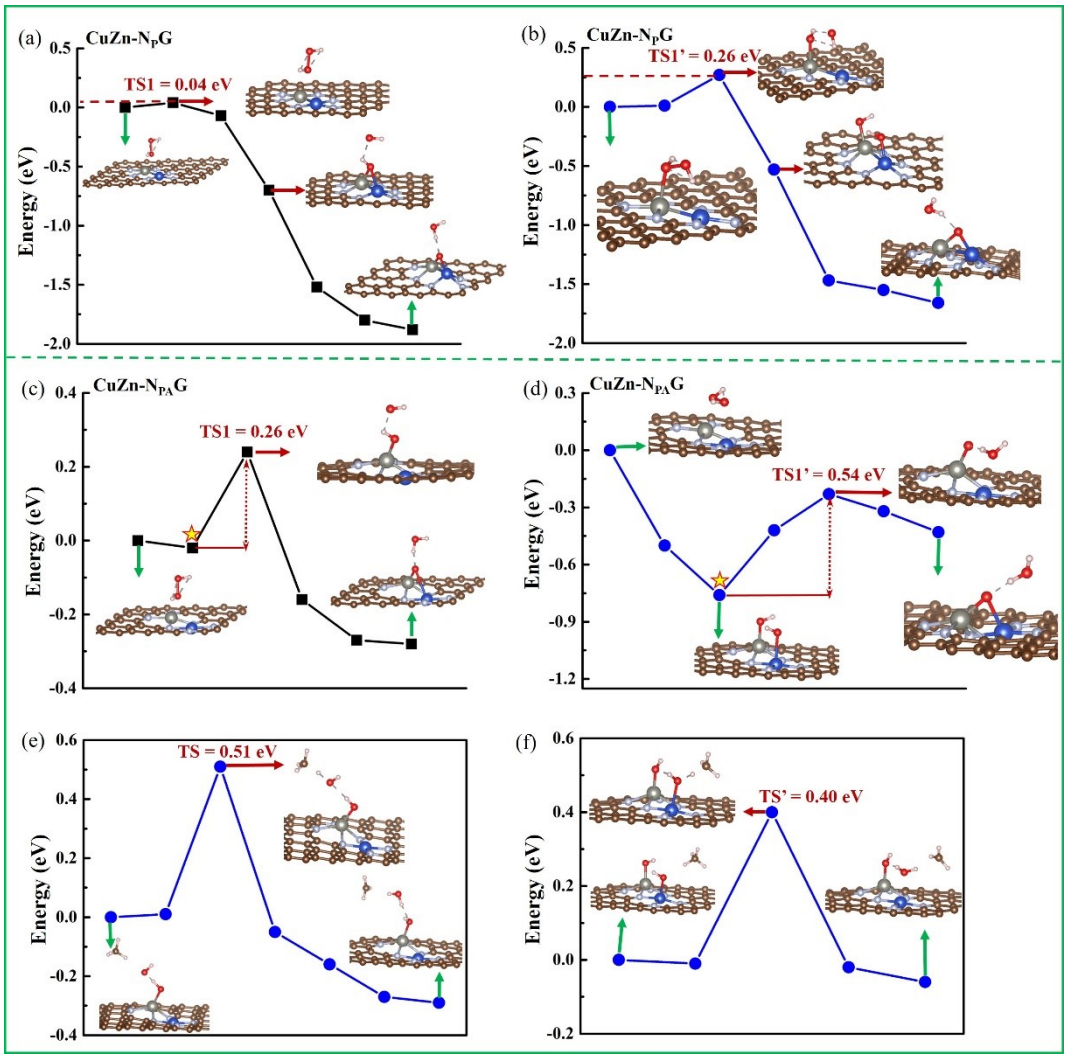

Fig. S3 Reaction pathway for H_2O_2 oxidizes CuZn atoms on (a, b) CuZn-N_PG, and (c, d) CuZn-$N_{PA}G$. The reaction pathway of (e, f) OH* activation of CH_4.

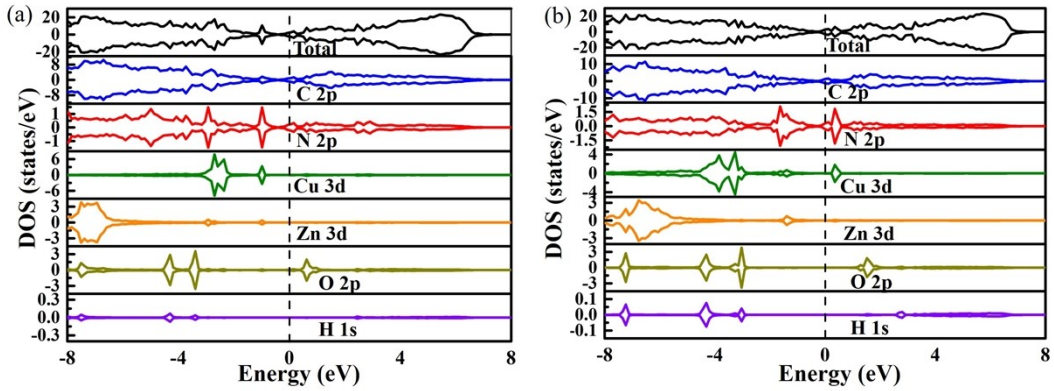

Fig. S4 Spin-polarized density of states for (a) CuZn-N_PG, (b) CuZn-$N_{PA}G$ after adsorption H_2O_2 (II-state).

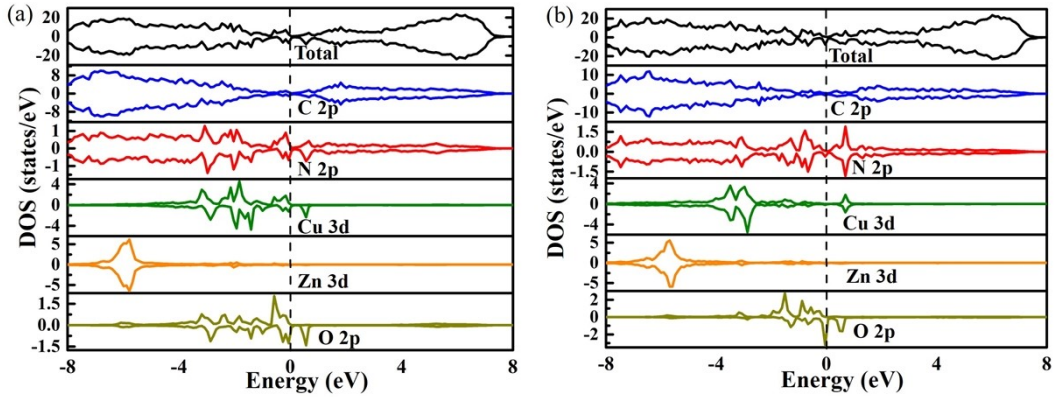

Fig. S5 Spin-polarized density of states for (a) CuZn-N_PG-O, (b) CuZn-$N_{PA}G$-O (IV-state).

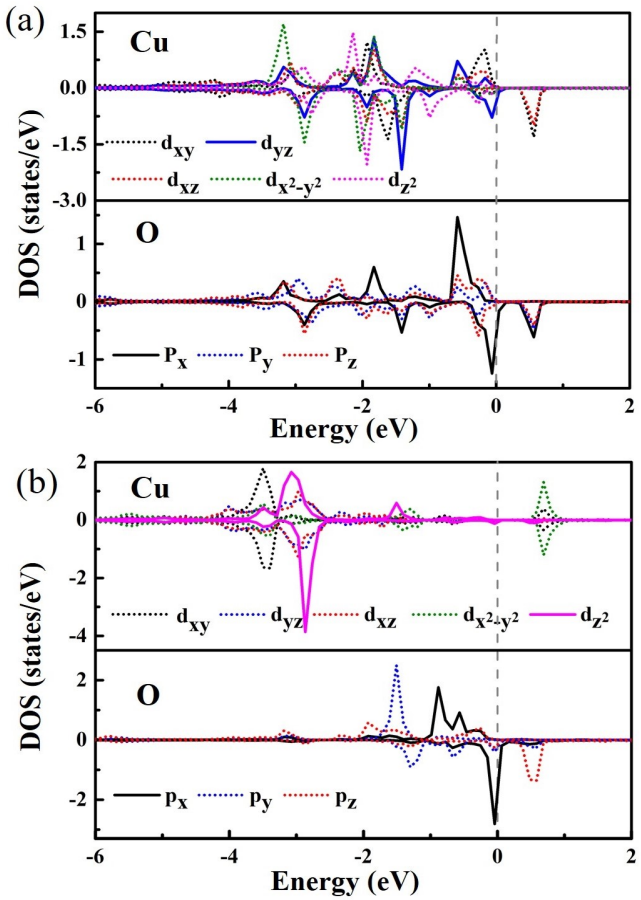

Fig. S6 Spin-polarized density of states of Cu 3d and O 2p split orbitals for (a) CuZn-N_PG-O, (b) CuZn-$N_{PA}G$-O (IV-state).

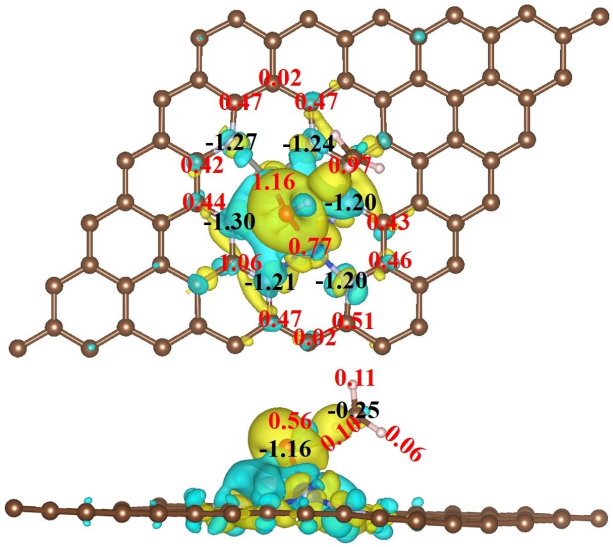

Fig. S7 The Bader charge analysis and the 3D charge density differences for CuZn-N_PG after the activation of C-H bond (VI-state), the isosurface value is 0.003 e bohr^{-3}.

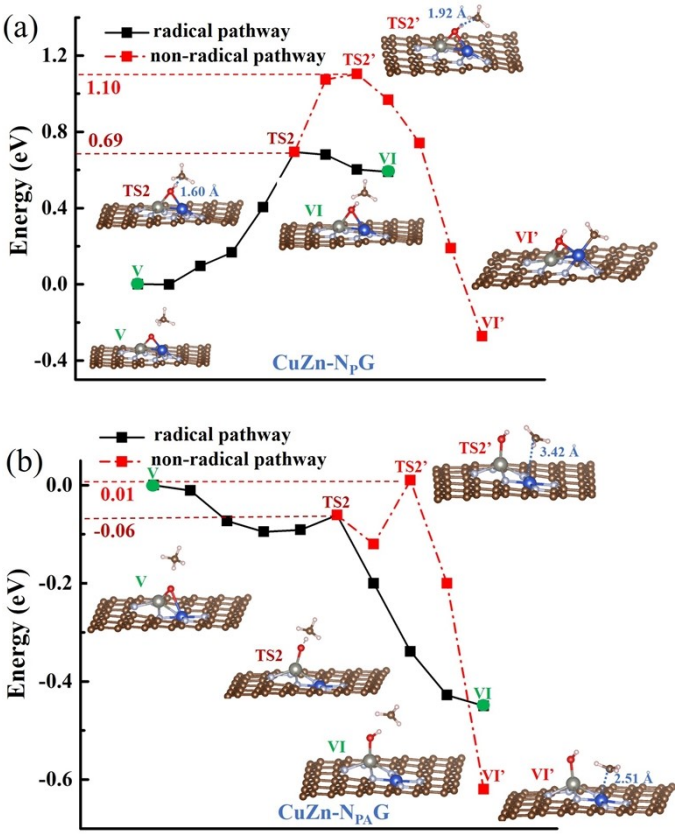

Fig. S8 The radical pathway and non-radical pathway for methane oxidation on (a) CuZn-N_PG-O and (b) CuZn-N_{PA}G-O.

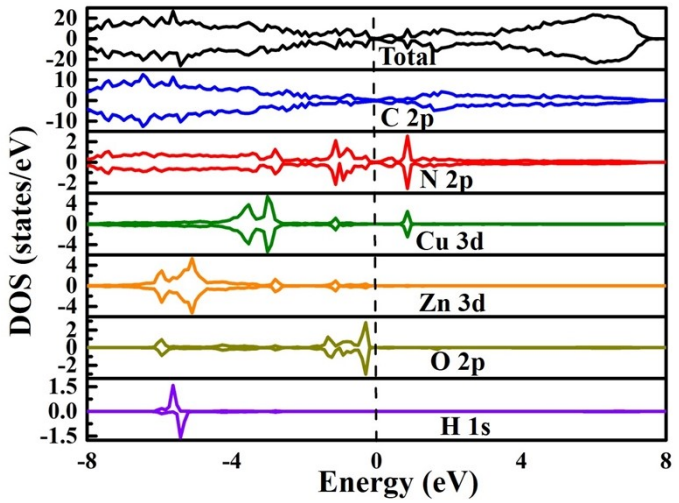

Fig. S9 Spin-polarized density of states for CuZn-N_{PA}G after the activation of C-H bond (VI-state).

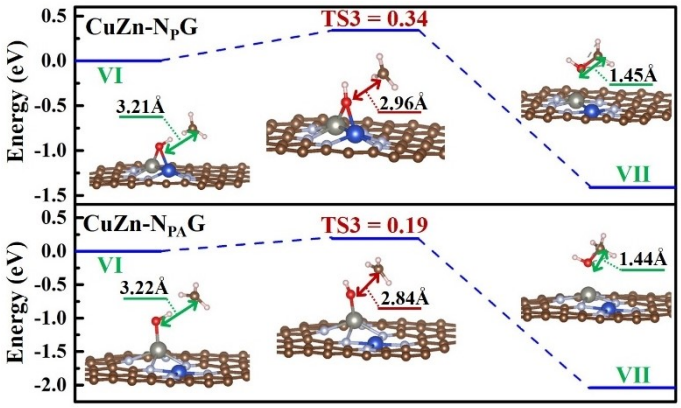

Fig. S10 Energy profile of methanol formation reaction as well as the structures of TS3, VI- and VII-state.

Table S5 △E (eV), energy difference between X-state and I-state, X= II, TS1, V, TS2,VI, TS3. Atomic charge of Cu center (|*e*|), energy barrier (eV) and change in atomic charge of Cu center (|*e*|).

Species	△E (eV)	Atomic charge of Cu (|*e*|)	Energy barrier (eV)	Change in atomic charge of Cu (|*e*|)
CuZn-N_PG(II)	-0.33	0.64		
TS1	-0.29	0.63	0.04	-0.01
V	-1.99	0.88		
TS2	-1.30	0.79	0.69	-0.09
VI	-1.40	0.77		
TS3	-1.06	0.74	0.34	-0.03
CuZn-N_{PA}G(II)	-0.28	0.95		
TS1	-0.04	0.97	0.26	0.02
V	-0.30	1.00		
TS2	-0.36	0.96	-0.06	-0.04
VI	-0.74	0.95		
TS3	-0.55	0.96	0.19	0.01

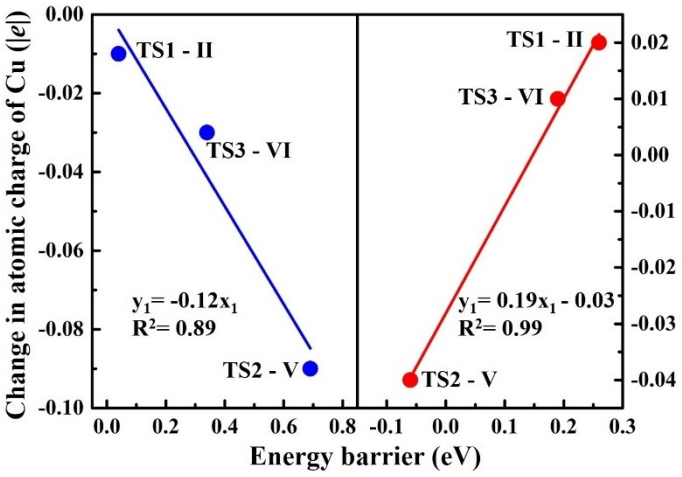

Fig. S11 The relationship between change in atomic charge of Cu center and energy barrier.

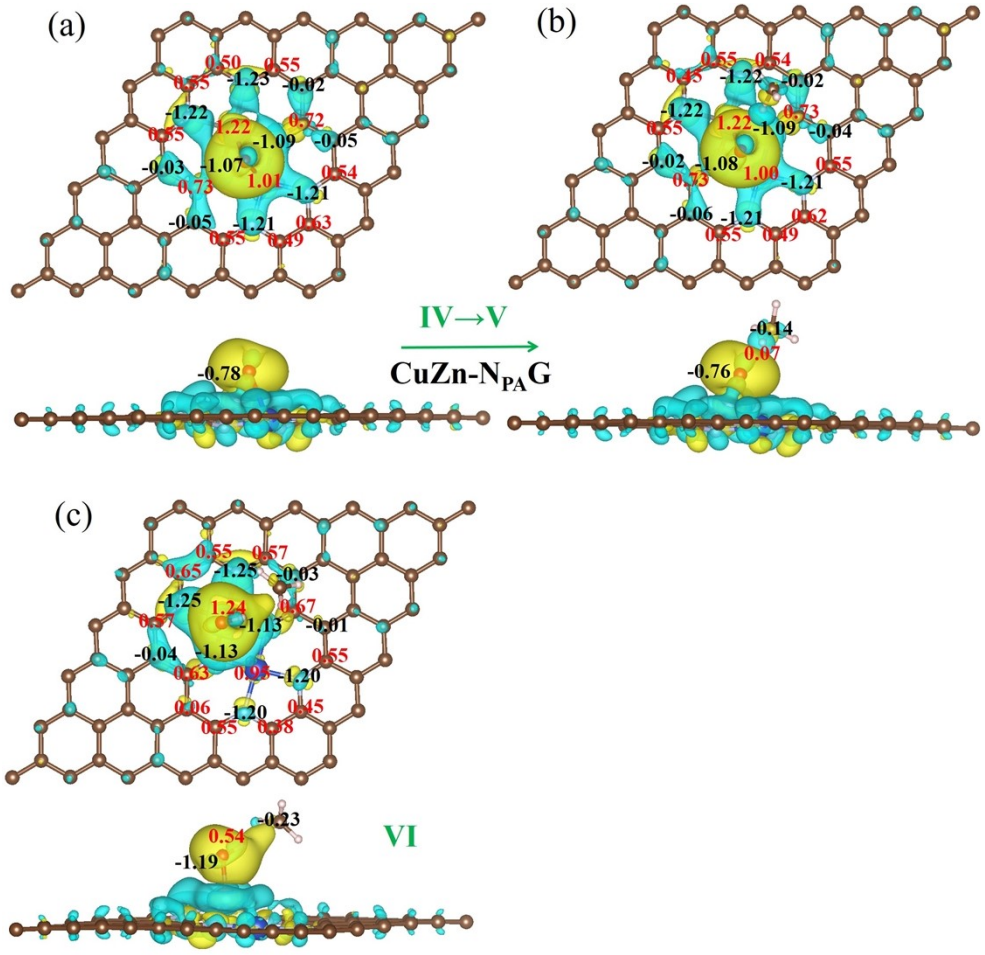

Fig. S12 Bader charge analysis and the 3D charge density differences of CuZn-N_{PA}G at (a) IV, (b) V and (c) VI-state, the isosurface value is 0.003 e $bohr^{-3}$.

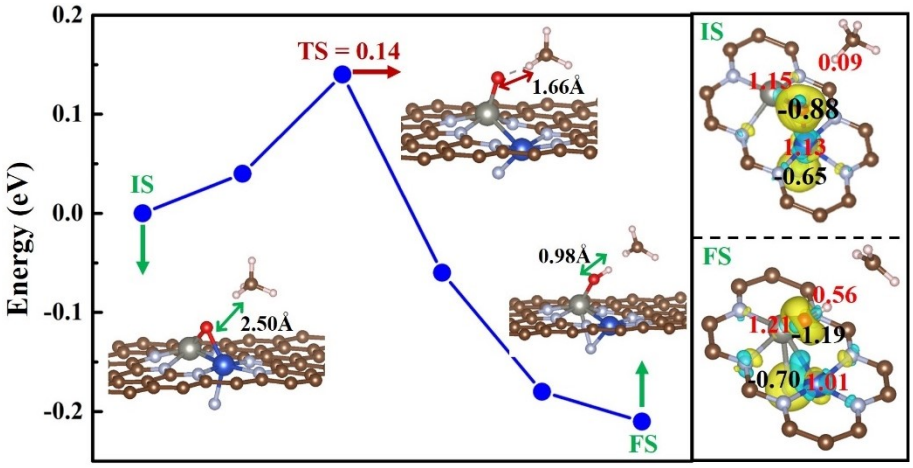

Fig. S13 Reaction pathway for methane activation on F-CuZn-N_PG-O. The Bader charge analysis and the 3D charge density differences for initial structure (IS) and final structure (FS), the isosurface value is 0.005 e $bohr^{-3}$.

References

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