Supporting Information

Efficient Urea Synthesis via One-Step N−C−N Coupling: Strong Metal-Support Interaction-Driven Planar Cu Clusters on two-dimensional Mo_2C MXene

Yue Zhang,[1] Linguo Lu,[2] Tiantian Zhao,[1] Jingxiang Zhao,[1,] Qinghai Cai,[1] Zhongfang Chen[2,*]*

[1] College of Chemistry and Chemical Engineering, and Key Laboratory of Photonic and Electronic Bandgap Materials, Ministry of Education, Harbin Normal University, Harbin, 150025, China

[2] Department of Chemistry, University of Puerto Rico, Rio Piedras Campus, San Juan, Puerto Rico 00931, USA

[*] To whom correspondence should be addressed. Email: *zhaojingxiang@hrbnu.edu.cn (J. Z).; zhongfang.chen1@upr.edu (Z.C.)*

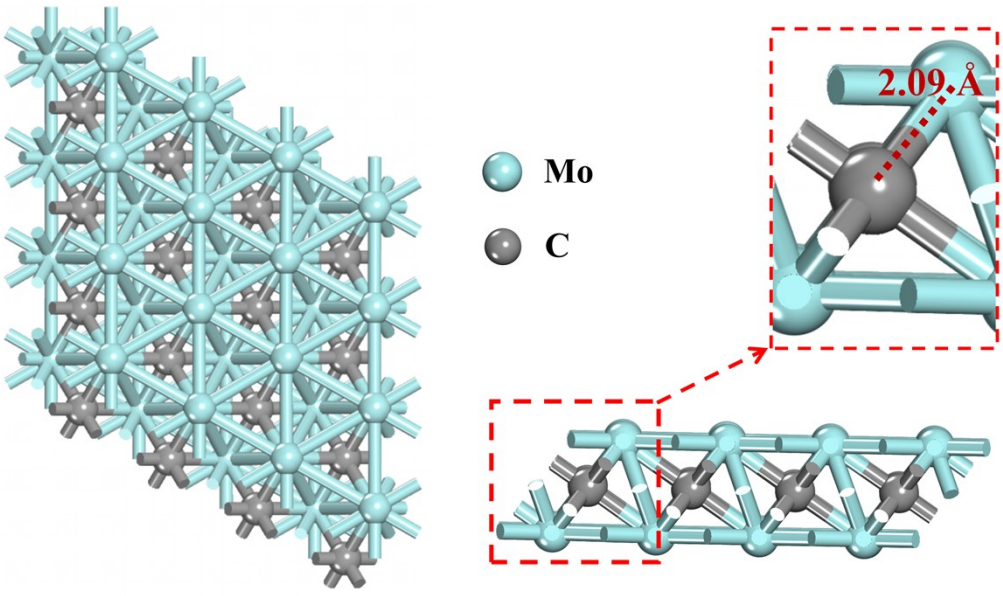
COMPUTATIONAL DETAILS

The dissolution potential (U_{diss} = U° diss(bulk) − E_f/ne) is a good parameter to evaluate the electrochemical stability of the catalyst, where U° diss(bulk), E_f and n are respectively the standard dissolution potential (U° diss(bulk)) of the bulk metal, the generation energy of the catalyst, and the number of electrons involved in the dissolution. To be specific, the standard dissolution potential for bulk metals uses the experimental standard dissolution potential of the metal atoms (U° diss(bulk)). For the generation energy, it can be calculated according to $E_f = (E_{Cu4/Mo2C} - E_{Mo2C} - 4 \times E_{Cu})/4$, where $E_{Cu4/Mo2C}$, E_{Mo2C}, and E_{Cu} are respectively the total energy per atom in the cluster system, Mo_2C, and Cu metal. Taking Cu_4/Mo_2C as an example, with U° diss(bulk) of 0.34 V, the calculated E_f is –0.50 eV. Therefore, its U_{diss} can be derived by: U_{diss} = [0.34 V – (–0.50 eV)/2e] = 0.59 V.

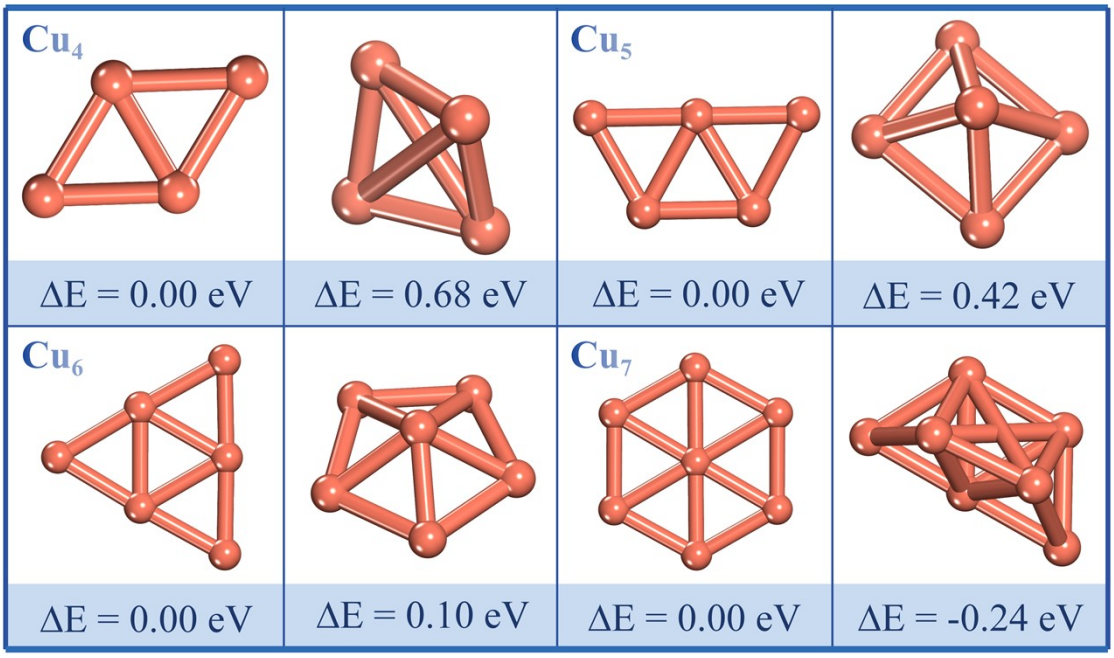
Table S1. The computed Gibbs free energy changes (ΔG, eV) of each elementary step during urea synthesis on the Cu_4/Mo_2C. The preferable elementary step was marked in red.

Elementary step	ΔG
$^* + NO \rightarrow NO^*$	–1.06
$NO^* + NO \rightarrow NO^* + NO^*$	–0.69
$NO^* + CO \rightarrow NO^* + CO^*$	0.04
$NO^* + H^+ + e^- \rightarrow NOH^*$	0.21
$NO^* + H^+ + e^- \rightarrow HNO^*$	–0.11
$NO^* + NO^* + CO \rightarrow NO^* + NO^* + CO^*$	–0.29
$NO^* + NO^* + H^+ + e^- \rightarrow NOH^* + NO^*$	0.30
$NO^* + NO^* + H^+ + e^- \rightarrow HNO^* + NO^*$	0.19
$NO^* + NO^* \rightarrow {}^*NO\text{-}NO^*$	0.21
$NO^* + NO^* + CO^* \rightarrow NO^*\text{-}NO^* + CO^*$	–0.01
$NO^* + NO^* + CO^* \rightarrow NO^*\text{-}CO^* + NO^*$	0.53
$NO^*\text{-}NO^* + CO^* + H^+ + e^- \rightarrow NOH^*\text{-}NO^* + CO^*$	–0.71
$NO^*\text{-}NO^* + CO^* + H^+ + e^- \rightarrow HNO^*\text{-}NO^* + CO^*$	–0.17
$NO^*\text{-}NO^* + CO^* + H^+ + e^- \rightarrow NO^*\text{-}NO^* + COH^*$	2.52
$NO^*\text{-}NO^* + CO^* + H^+ + e^- \rightarrow NO^*\text{-}NO^* + CHO^*$	0.95
$NOH^*\text{-}NO^* + CO^* + H^+ + e^- \rightarrow N^*\text{-}NO^* + CO^*$	–0.65
$NOH^*\text{-}NO^* + CO^* + H^+ + e^- \rightarrow HNOH^*\text{-}NO^* + CO^*$	1.14
$NOH^*\text{-}NO^* + CO^* + H^+ + e^- \rightarrow NOH^*\text{-}NOH^* + CO^*$	0.63
$NOH^*\text{-}NO^* + CO^* + H^+ + e^- \rightarrow NOH^*\text{-}NHO^* + CO^*$	0.69
$NOH^*\text{-}NO^* + CO^* + H^+ + e^- \rightarrow NOH^*\text{-}NO^* + COH^*$	2.85
$NOH^*\text{-}NO^* + CO^* + H^+ + e^- \rightarrow NOH^*\text{-}NO^* + CHO^*$	1.01
$N^*\text{-}NO^* + CO^* + H^+ + e^- \rightarrow NH^*\text{-}NO^* + CO^*$	–1.06
$N^*\text{-}NO^* + CO^* + H^+ + e^- \rightarrow N^*\text{-}NOH^* + CO^*$	–0.58
$N^*\text{-}NO^* + CO^* + H^+ + e^- \rightarrow N^*\text{-}NHO^* + CO^*$	–0.69
$N^*\text{-}NO^* + CO^* + H^+ + e^- \rightarrow N^*\text{-}NO^* + COH^*$	2.58
$N^*\text{-}NO^* + CO^* + H^+ + e^- \rightarrow N^*\text{-}NO^* + CHO^*$	1.13
$NH^*\text{-}NO^* + CO^* + H^+ + e^- \rightarrow NH_2^*\text{-}NO^* + CO^*$	0.36
$NH^*\text{-}NO^* + CO^* + H^+ + e^- \rightarrow NH^*\text{-}NOH^* + CO^*$	0.58
$NH^*\text{-}NO^* + CO^* + H^+ + e^- \rightarrow NH^*\text{-}NHO^* + CO^*$	0.67
$NH^*\text{-}NO^* + CO^* + H^+ + e^- \rightarrow NH^*\text{-}NO^* + COH^*$	2.52
$NH^*\text{-}NO^* + CO^* + H^+ + e^- \rightarrow NH^*\text{-}NO^* + CHO^*$	0.98
$NH_2^*\text{-}NO^* + CO^* + H^+ + e^- \rightarrow NH_2^*\text{-}NOH^* + CO^*$	–0.05
$NH_2^*\text{-}NO^* + CO^* + H^+ + e^- \rightarrow NH_2^*\text{-}NHO^* + CO^*$	0.26
$NH_2^*\text{-}NO^* + CO^* + H^+ + e^- \rightarrow NH_2^*\text{-}NO^* + COH^*$	1.67
$NH_2^*\text{-}NO^* + CO^* + H^+ + e^- \rightarrow NH_2^*\text{-}NO^* + CHO^*$	0.97

NH_2^*-NOH^* + CO^* + H^+ + e^- → NH_2^*-N^* + CO^*	–1.14
NH_2^*-NOH^* + CO^* + H^+ + e^- → NH_2^*-$NHOH^*$ + CO^*	0.14
NH_2^*-NOH^* + CO^* + H^+ + e^- → NH_2^*-NOH^* + COH^*	2.39
NH_2^*-NOH^* + CO^* + H^+ + e^- → NH_2^*-NOH^* + CHO^*	0.93
NH_2^*-N^* + CO^* + H^+ + e^- → NH_2^*-NH^* + CO^*	–0.85
NH_2^*-N^* + CO^* + H^+ + e^- → NH_2^*-N^* + COH^*	2.57
NH_2^*-N^* + CO^* + H^+ + e^- → NH_2^*-N^* + CHO^*	0.95
NH_2^*-NH^* + CO^* + H^+ + e^- → NH_2^*-NH_2^* + CO^*	–0.11
NH_2^*-NH^* + CO^* + H^+ + e^- → NH_2^*-NH^* + COH^*	2.38
NH_2^*-NH^* + CO^* + H^+ + e^- → NH_2^*-NH^* + CHO^*	3.79
NH_2^*-NH_2^* + CO^* + H^+ + e^- → NH_2^*-CO-NH_2^*	–1.07
NH_2^*-NH_2^* + CO^* + H^+ + e^- → $NH_3(g)$ + NH_2^* + COH^*	–0.61
NH_2^*-NH_2^* + CO^* + H^+ + e^- → NH_2^*-NH_2^* + COH^*	1.60
NH_2^*-NH_2^* + CO^* + H^+ + e^- → NH_2^*-NH_2^* + CHO^*	0.97

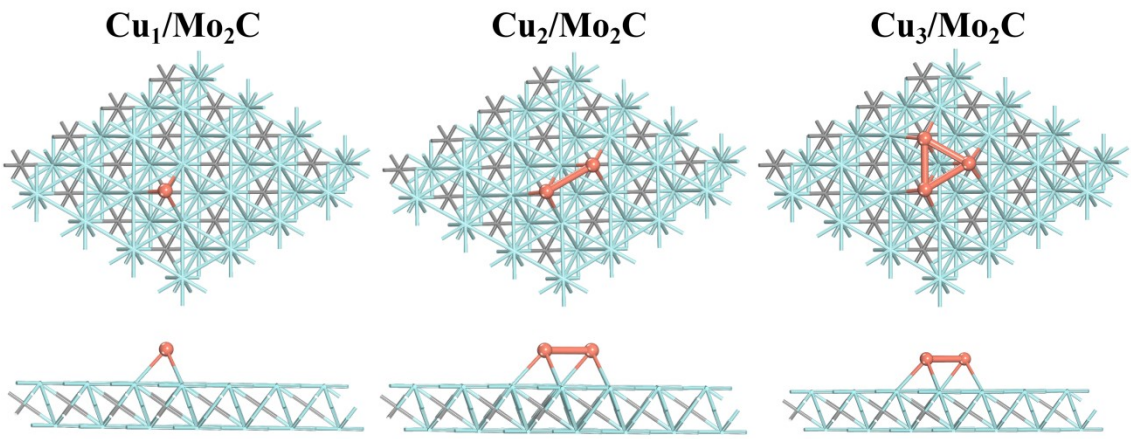


(a)

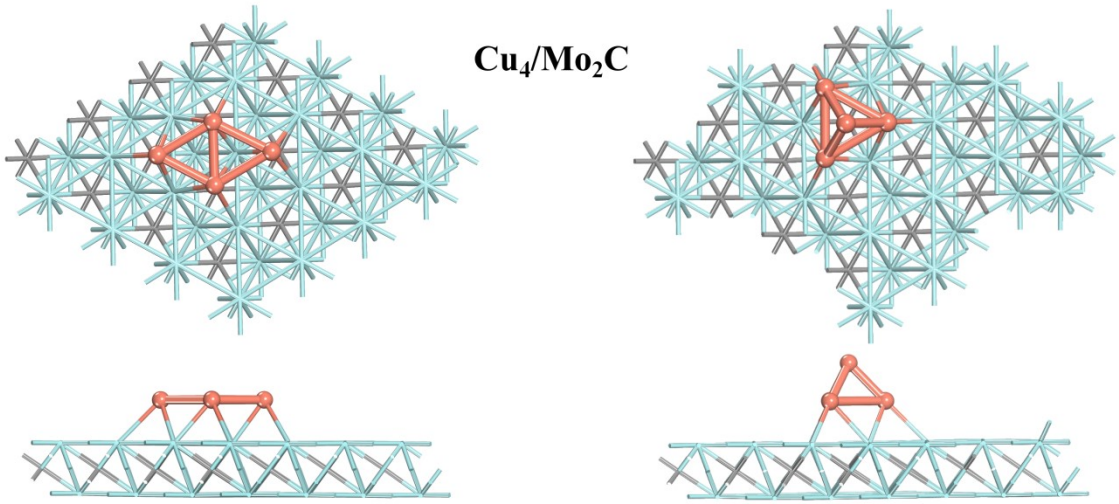


(b)

Fig. S1. (a) Top and side views of the optimized Mo_2C structure. (b) The planar and three-dimensional structures of the isolated Cu_n clusters, as well as their respective relative energies (ΔE).

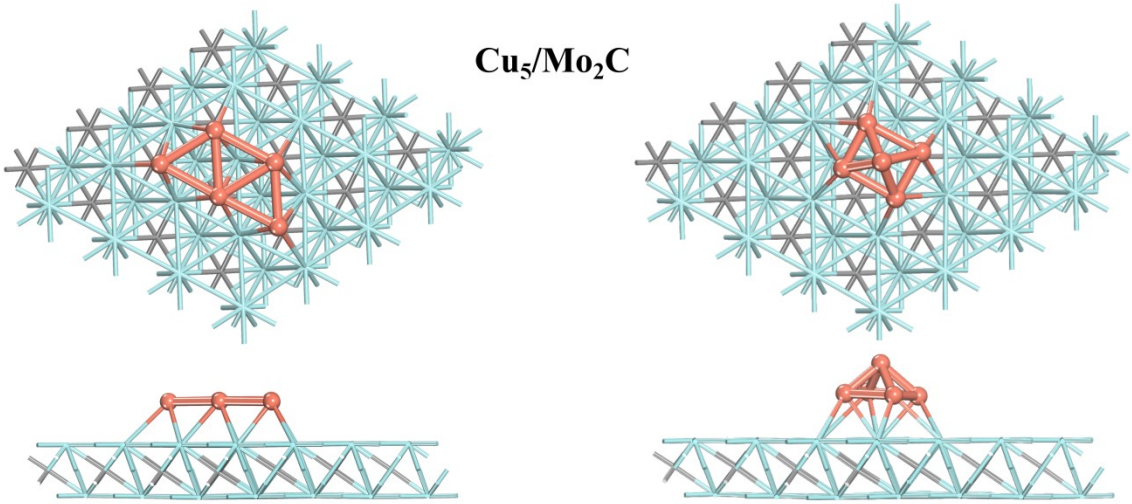


(a)



ΔE = 0.00 eV

ΔE = 1.52 eV



ΔE = 0.00 eV

ΔE = 5.67 eV

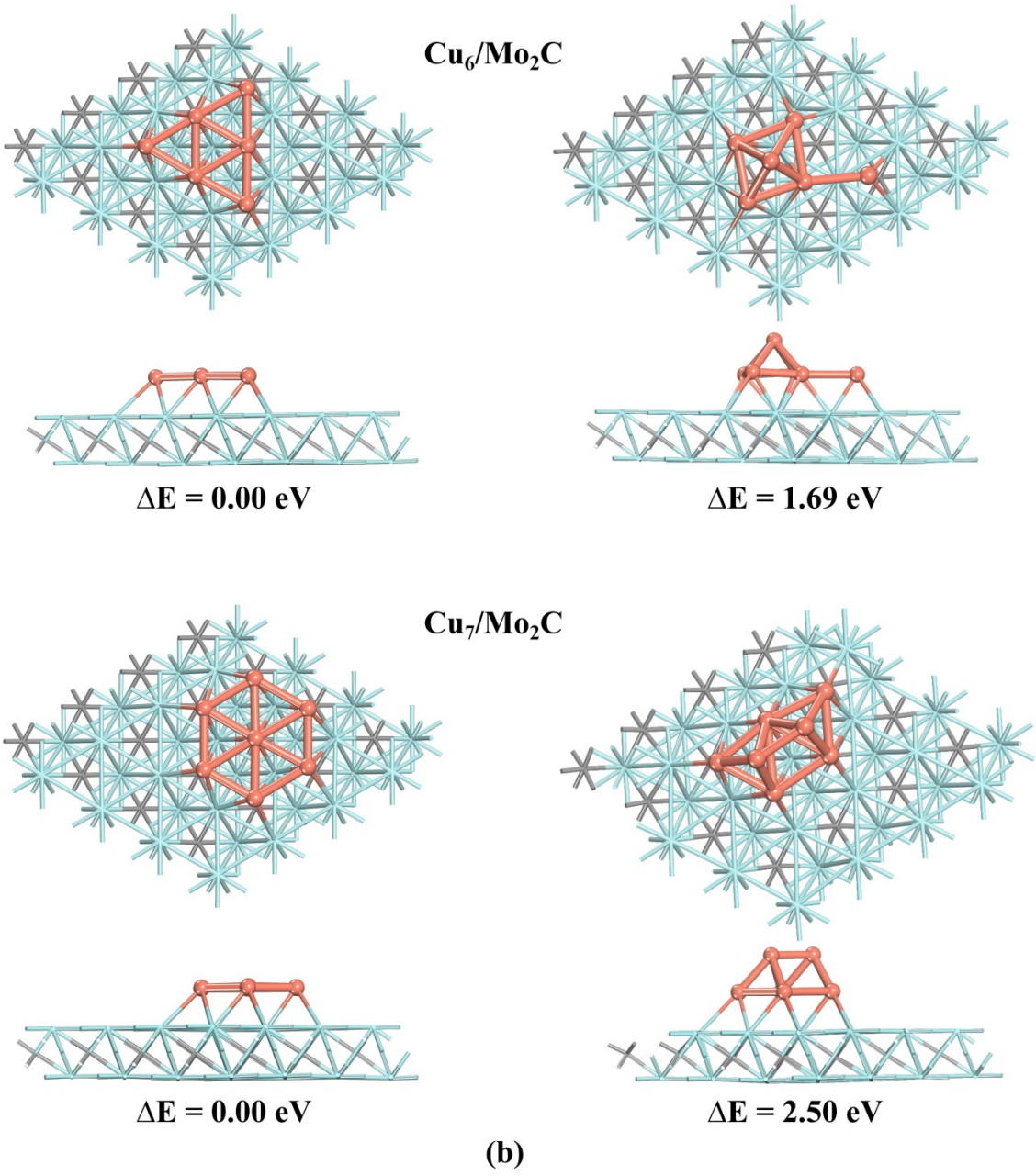


Fig. S2. The optimized configurations for (a) Cu_1, Cu_2, and Cu_3 and (b) Cu_4, Cu_5, Cu_6, and Cu_7 clusters with three-dimensional and planar structures anchored on the Mo_2C substrate and their relative energy difference (ΔE).

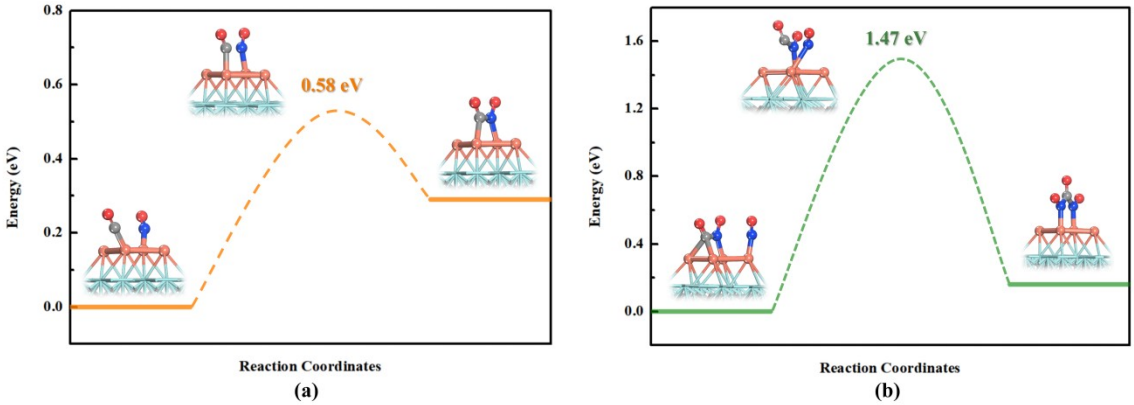
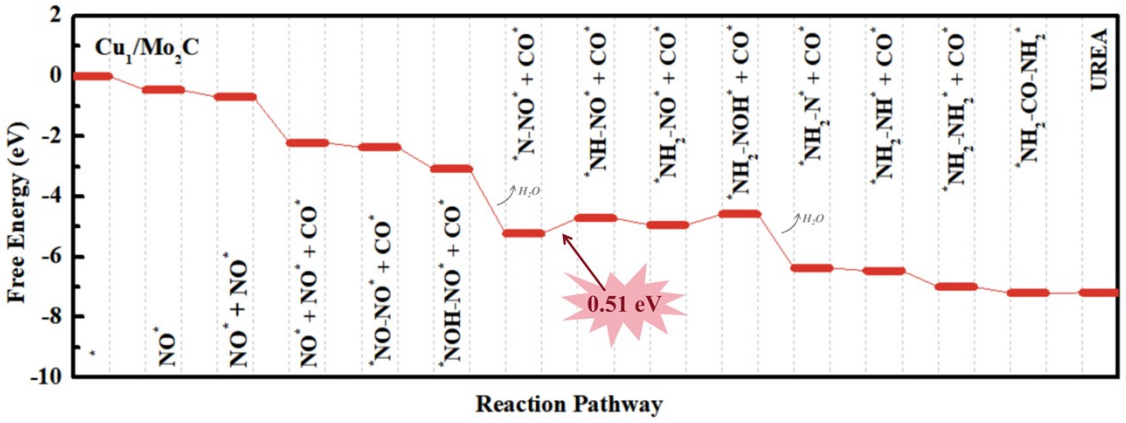
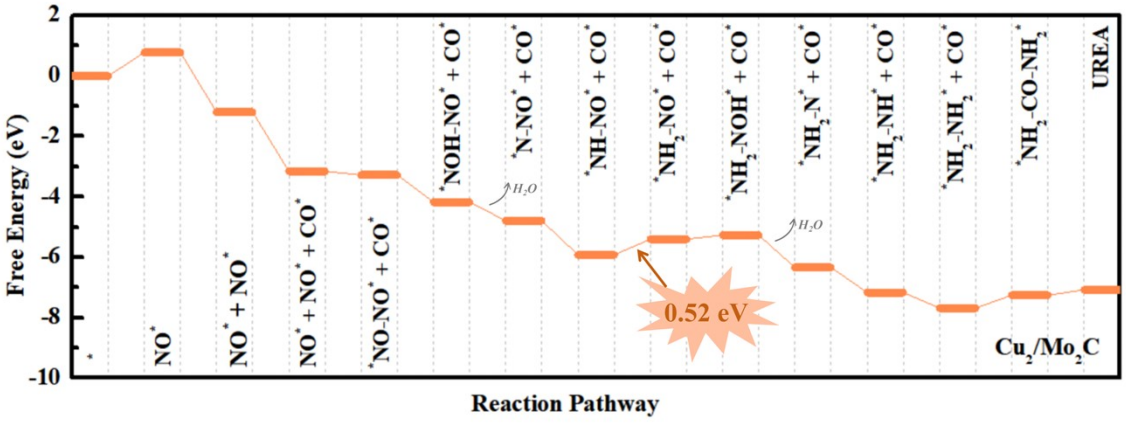
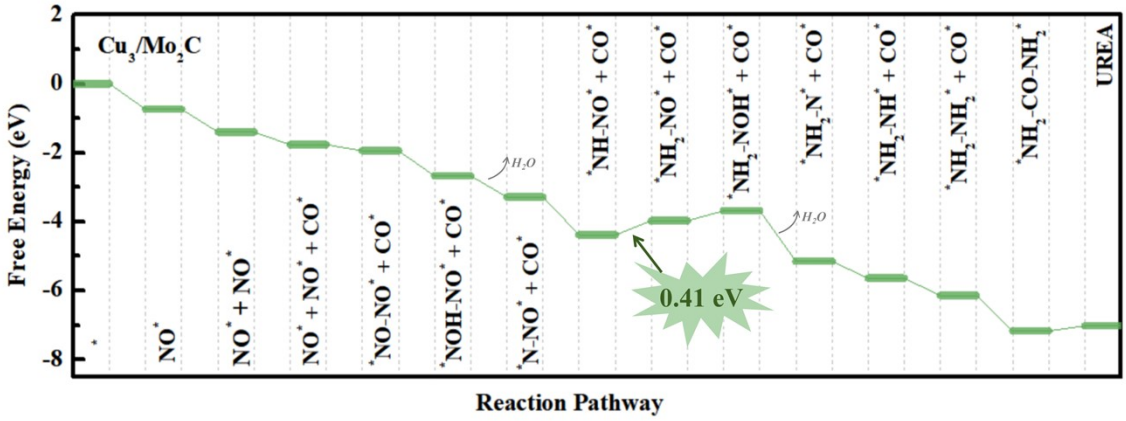
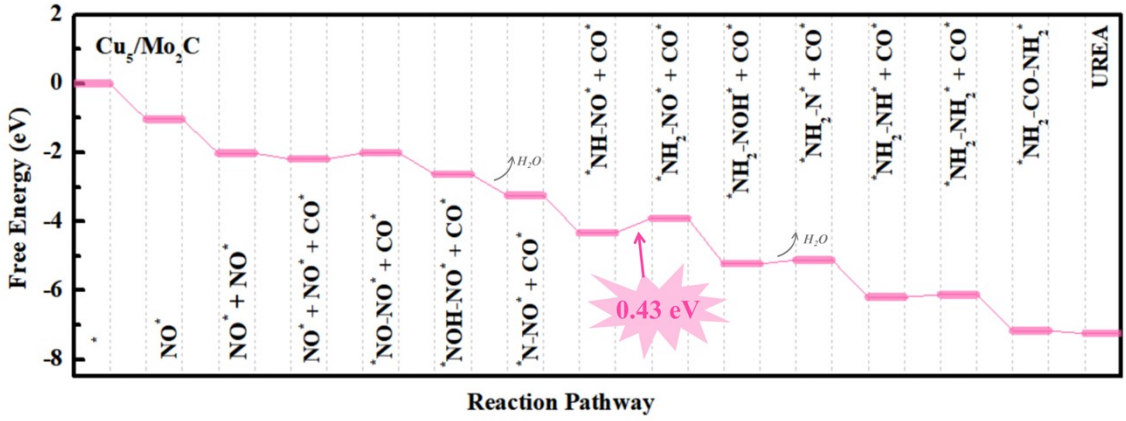


Fig. S3. The kinetic processes and the corresponding barrier for (a) the first C–N to *NOCO* and (b) the second C–N to form NOCONO* on Cu_4/Mo_2C.


Cu1/Mo2C
Free Energy (eV)
Reaction Pathway
0.51 eV
UREA


Free Energy (eV)
Reaction Pathway
0.52 eV
Cu2/Mo2C
UREA


Cu3/Mo2C
Free Energy (eV)
Reaction Pathway
0.41 eV
UREA


Cu5/Mo2C
Free Energy (eV)
Reaction Pathway
0.43 eV
UREA

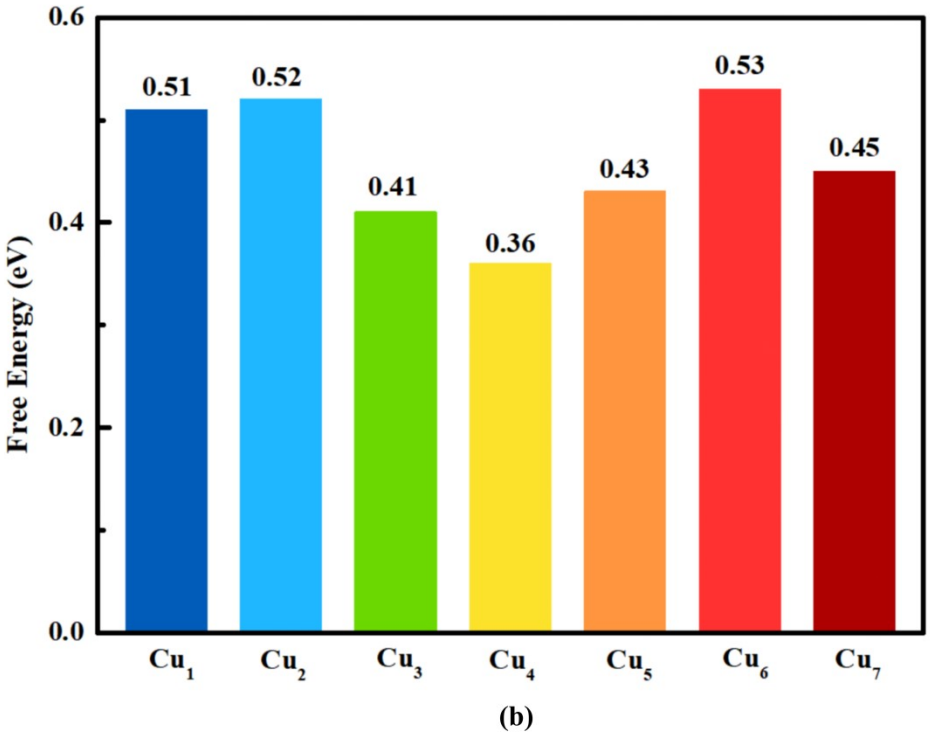


Fig. S4. (a) The Gibbs free energy profiles and (b) the maximum Gibbs free energy changes in the PDS for urea electrosynthesis on different Cu_n/Mo_2C catalysts.

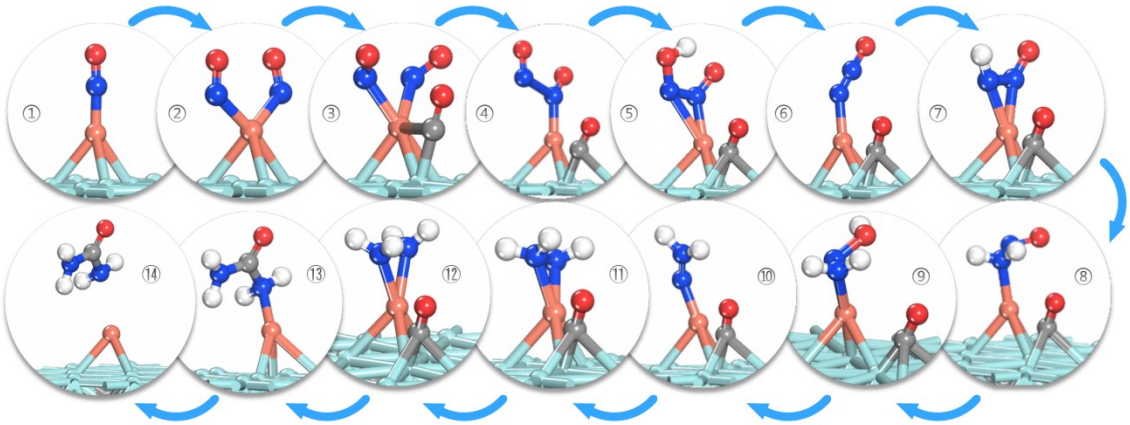
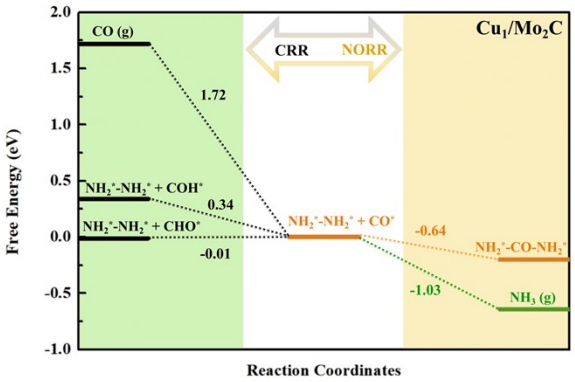
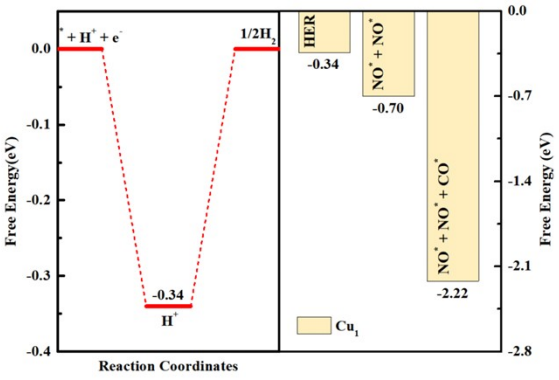
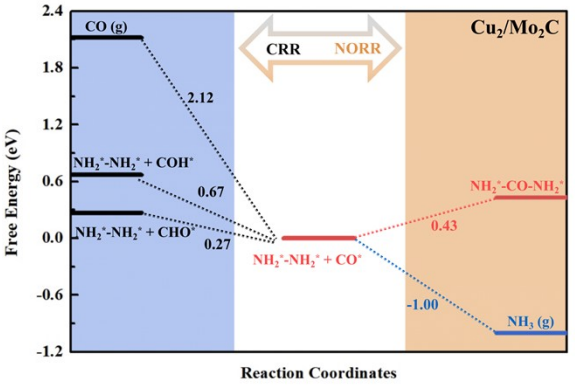
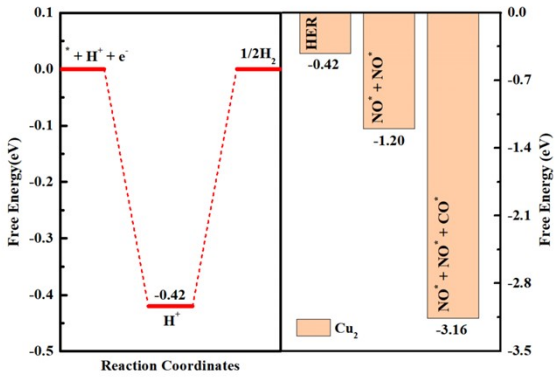


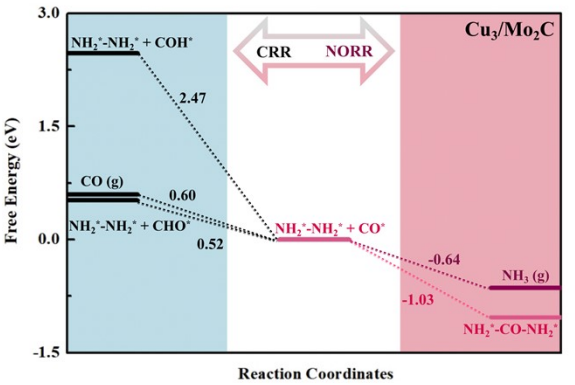
Fig. S5. All intermediates involved in the synthesis of urea on Cu_1/Mo_2C.

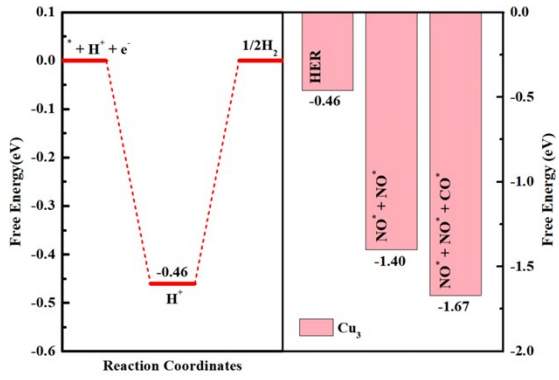

Cu1/Mo2C
CRR
NORR
CO (g)
1.72
NH2*-NH2* + COH*
0.34
NH2*-NH2* + CHO*
-0.01
NH2*-NH2* + CO*
-0.64
NH2*-CO-NH2*
-1.03
NH3 (g)
Free Energy (eV)
Reaction Coordinates

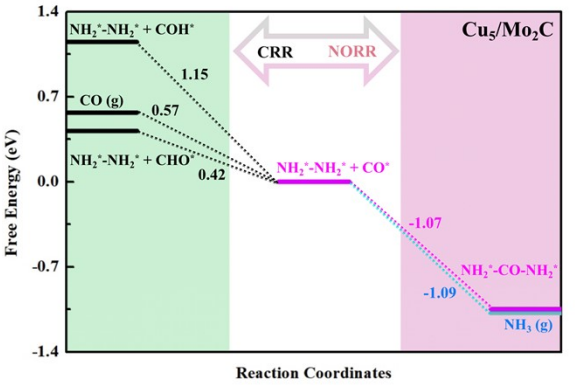

* + H+ + e-
1/2H2
-0.34
H*
HER
-0.34
NO* + NO*
-0.70
NO* + NO* + CO*
-2.22
Cu1
Free Energy(eV)
Reaction Coordinates


Cu2/Mo2C
CRR
NORR
CO (g)
2.12
NH2*-NH2* + COH*
0.67
NH2*-NH2* + CHO*
0.27
NH2*-NH2* + CO*
0.43
NH2*-CO-NH2*
-1.00
NH3 (g)
Free Energy (eV)
Reaction Coordinates


* + H+ + e-
1/2H2
-0.42
H*
HER
-0.42
NO* + NO*
-1.20
NO* + NO* + CO*
-3.16
Cu2
Free Energy(eV)
Reaction Coordinates


Cu3/Mo2C
CRR
NORR
NH2*-NH2* + COH*
2.47
CO (g)
0.60
NH2*-NH2* + CHO*
0.52
NH2*-NH2* + CO*
-0.64
NH3 (g)
-1.03
NH2*-CO-NH2*
Free Energy (eV)
Reaction Coordinates


* + H+ + e-
1/2H2
-0.46
H*
HER
-0.46
NO* + NO*
-1.40
NO* + NO* + CO*
-1.67
Cu3
Free Energy(eV)
Reaction Coordinates


Cu5/Mo2C
CRR
NORR
NH2*-NH2* + COH*
1.15
CO (g)
0.57
NH2*-NH2* + CHO*
0.42
NH2*-NH2* + CO*
-1.07
NH2*-CO-NH2*
-1.09
NH3 (g)
Free Energy (eV)
Reaction Coordinates

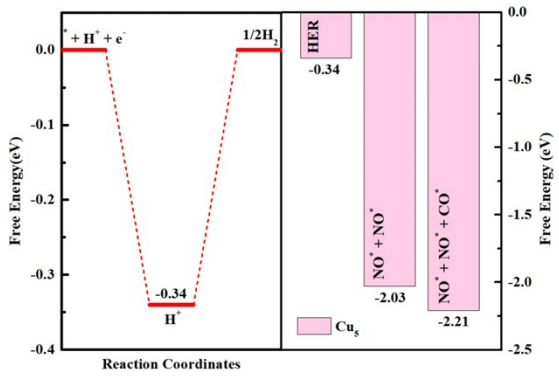

* + H+ + e-
1/2H2
-0.34
H*
HER
-0.34
NO* + NO*
-2.03
NO* + NO* + CO*
-2.21
Cu5
Free Energy(eV)
Reaction Coordinates

Fig. S6. Reaction energy landscape on the left for the subsequent reactions of co-adsorbed NH_2^*–NH_2^* and CO^* on Cu_n/Mo_2C (n = 1，2，3 , 5 , 6 , 7). On the right is the corresponding HER plot and a comparison of the hydrogen adsorption free energy (ΔG_{H^*}) with the adsorption free energy of (NO^* + NO^*) and (NO^* + NO^* + CO^*).

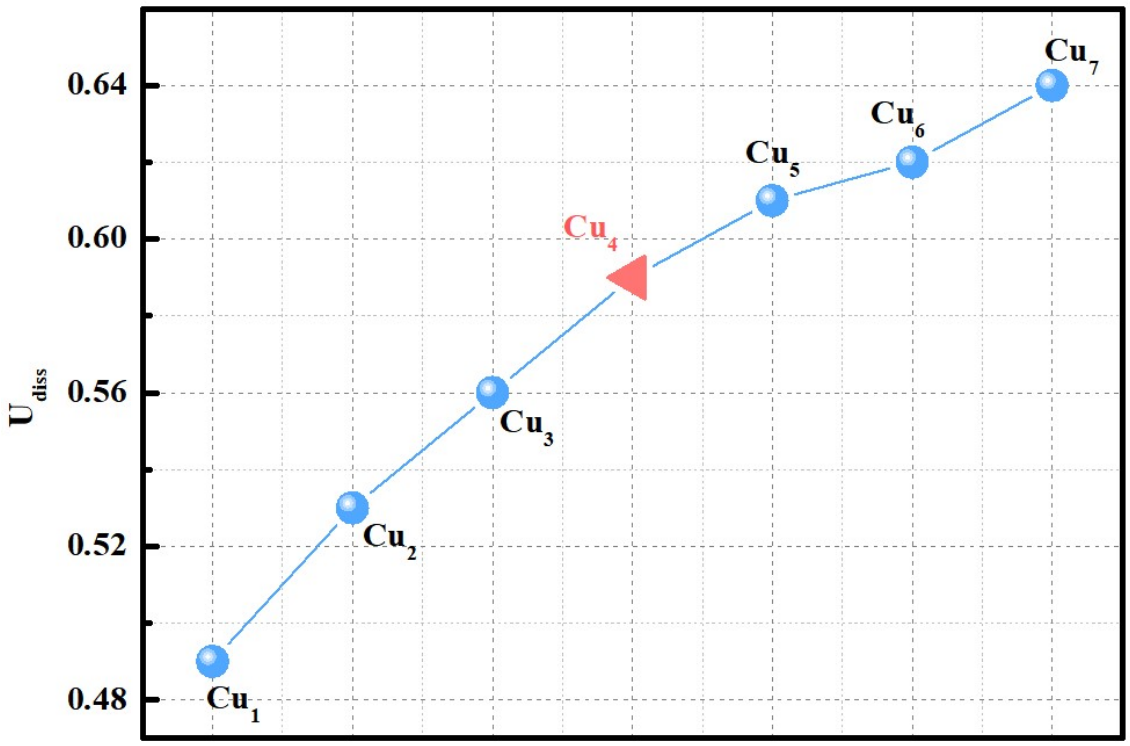


Fig. S7. The dissolution potential value of Cu_n/Mo_2C (n = 1 ~ 7).

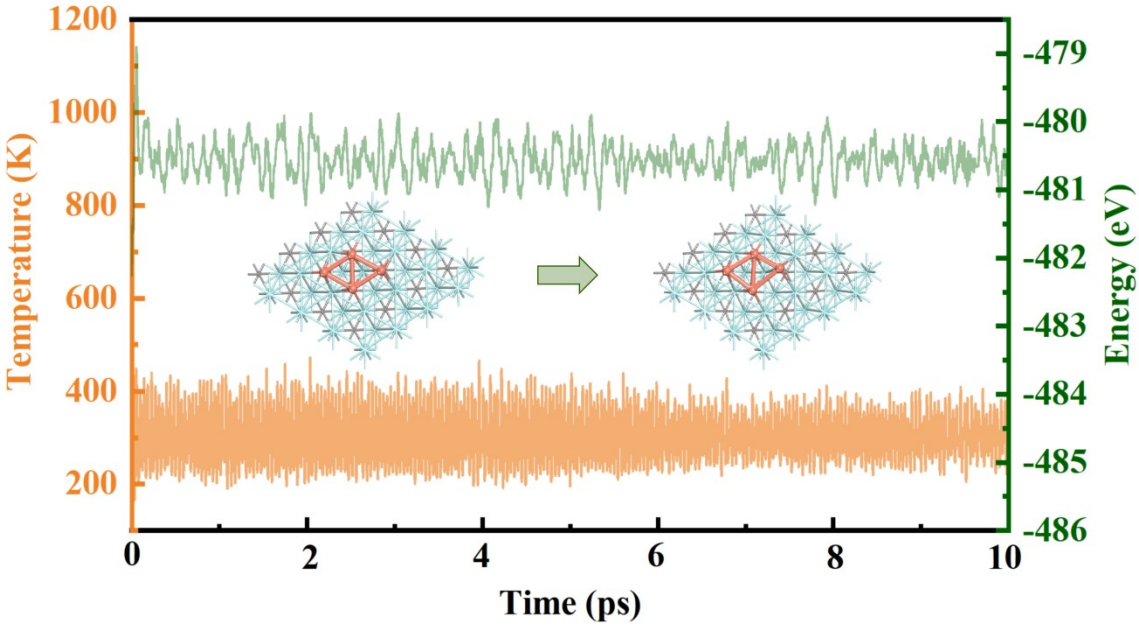


Fig. S8. Variations of temperature and energy as a function of the time for AIMD simulations of Cu_4/Mo_2C; insert are top and side views of the snapshot of atomic configuration. The simulation is run under 300 K for 10 ps with a time step of 2 fs.