Supporting Information

Cu-Doped CeO_2 Supported by MXene Nanosheets for Enhanced Electrosynthesis of Urea from Carbon Dioxide and Nitrate

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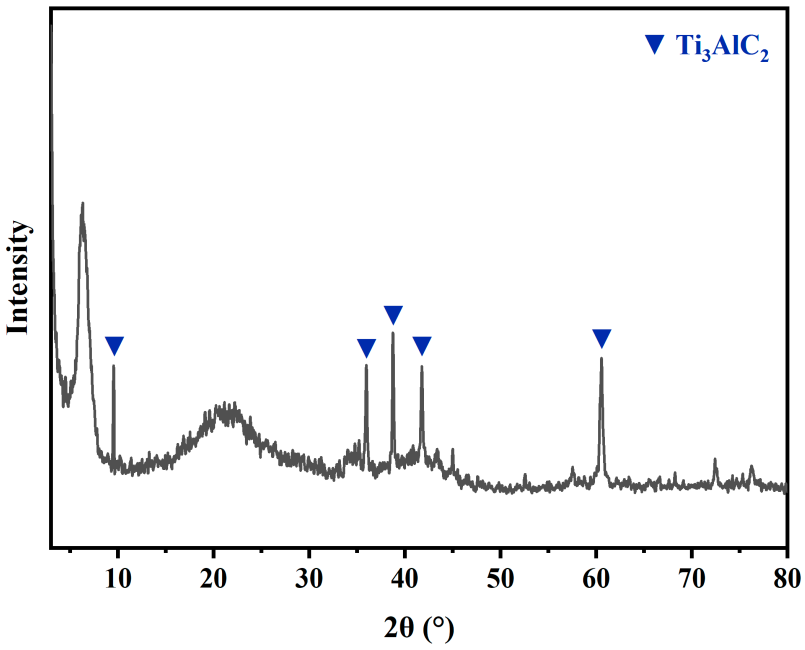


Figure S1. XRD patterns of incompletely etched Ti_3AlC_2 MAX.

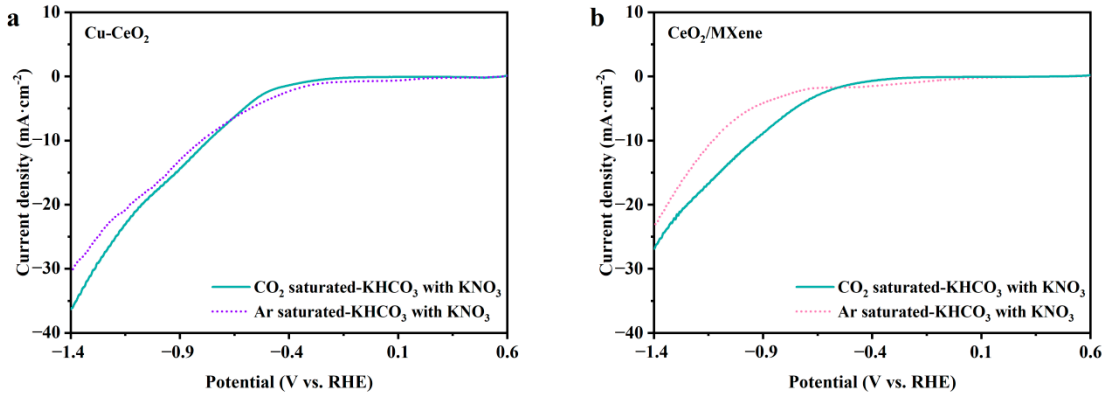


Figure S2. LSV curves for (**a**) Cu-CeO_2, and (**b**) CeO_2/MXene in the CO_2/Ar-saturated 0.1 M $KHCO_3$ containing 50 mM KNO_3, the scan rate is 10 $mV \cdot s^{-1}$.

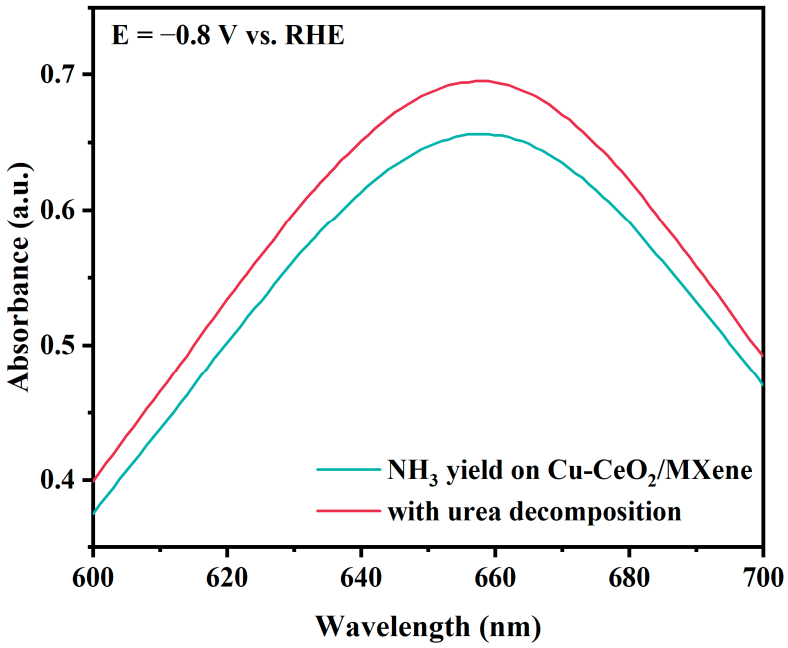


Figure S3. The UV-vis absorbance curve of Cu-CeO2/MXene under the applied potential of −0.8 V vs. RHE with and without urease decomposition.

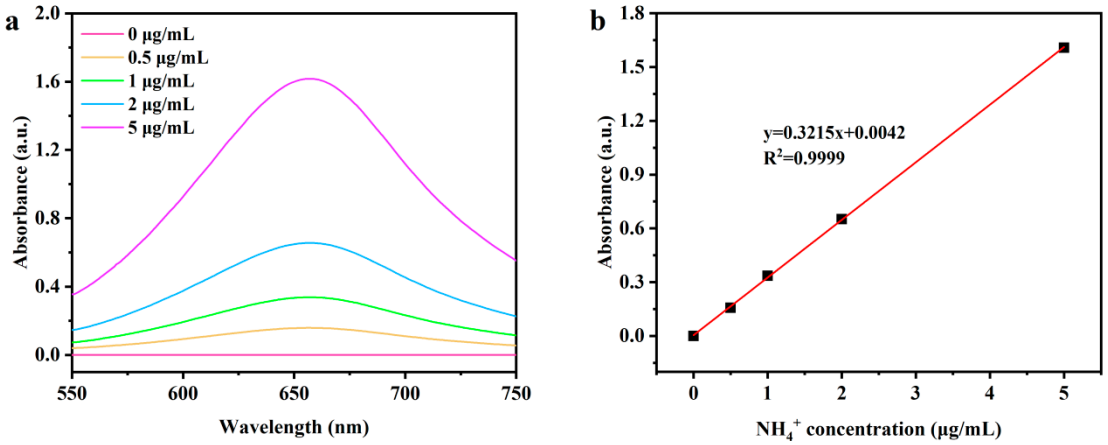


Figure S4. (**a**) UV-vis absorption spectra of different NH_4^+ concentrations. (**b**) Calibration curve used for quantifying NH_4^+ (y=0.3215x+0.0042, R^2=0.9999).

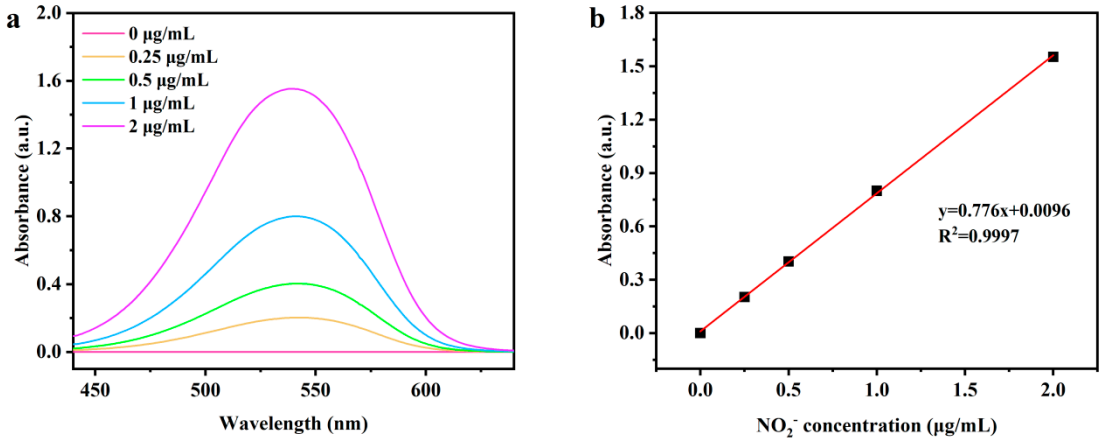


Figure S5. (**a**) UV-vis absorption spectra of different NO_2^- concentrations. (**b**) Calibration curve used for quantifying NO_2^- (y=0.776x+0.0096, R^2=0.9997).

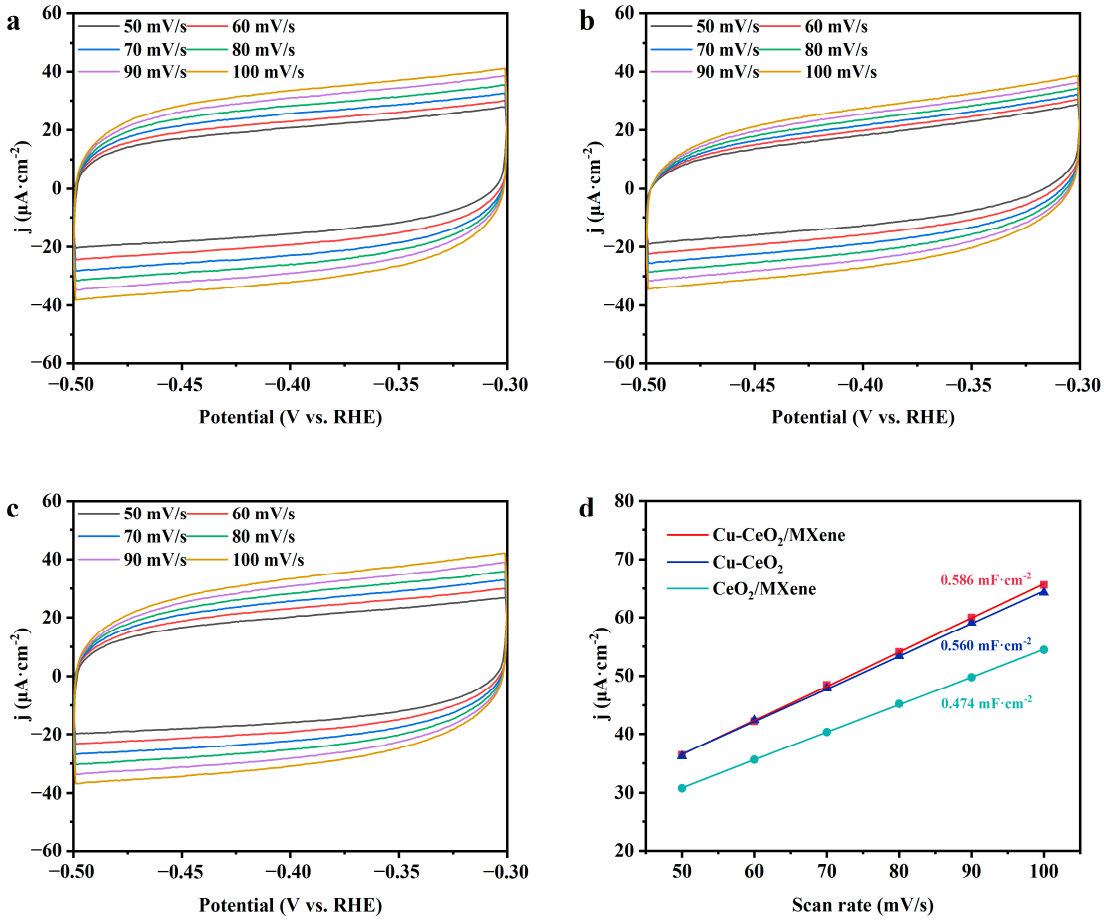


Figure S6. The cyclic voltammograms of (**a**) Cu-CeO_2/MXene, (**b**) Cu-CeO_2, and (**c**) CeO_2/MXene at different scan rates from 50 to 100 mV·s^{-1} at the potential window of −0.50 ~ −0.30 V vs. RHE. (**d**) The corresponding capacitive current at −0.40 V vs. RHE versus scan rates.

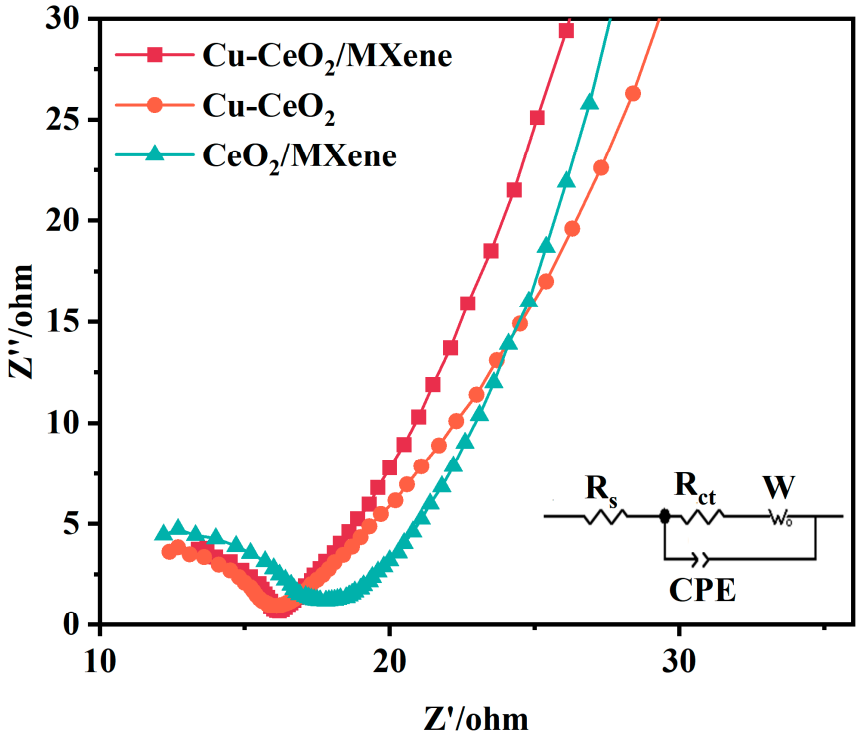


Figure S7. The electrochemical impendence spectra and equivalent electrical circuit of Cu-CeO_2/MXene, Cu-CeO_2 and CeO_2/MXene. R_s: solution resistance; R_{ct}: charge transfer resistance; W: Warburg impedance. CPE: constant phase element.

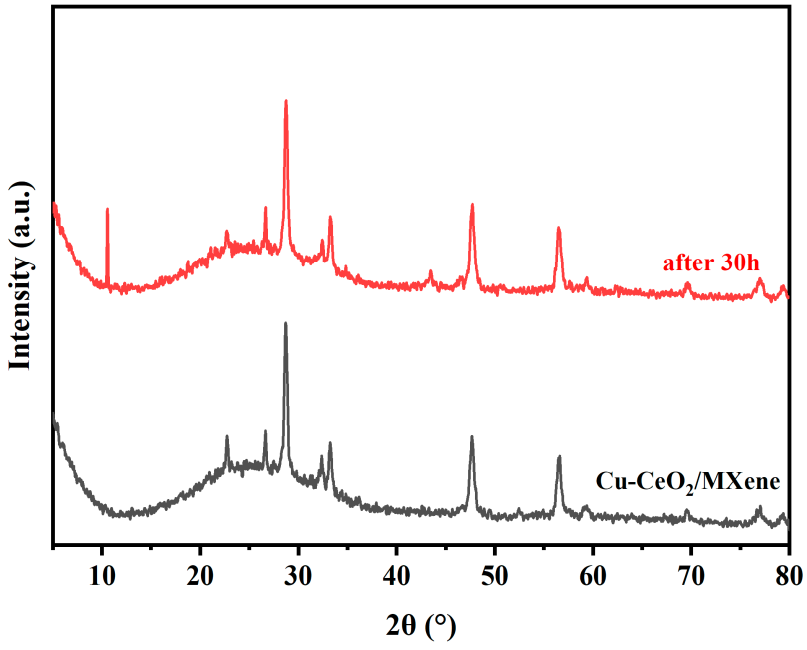


Figure S8. The XRD patterns of Cu-CeO_2/MXene loaded on the carbon paper after 30 h long-term electrolysis test.

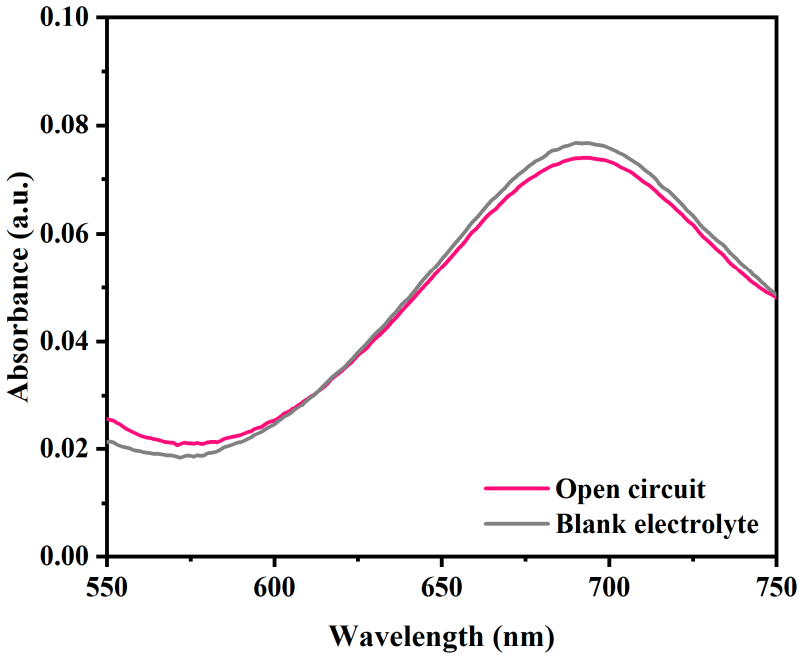


Figure S9. UV-vis absorption spectra of the open circuit opential in CO_2-saturated 0.1 M $KHCO_3$ containing 50 mM KNO_3.

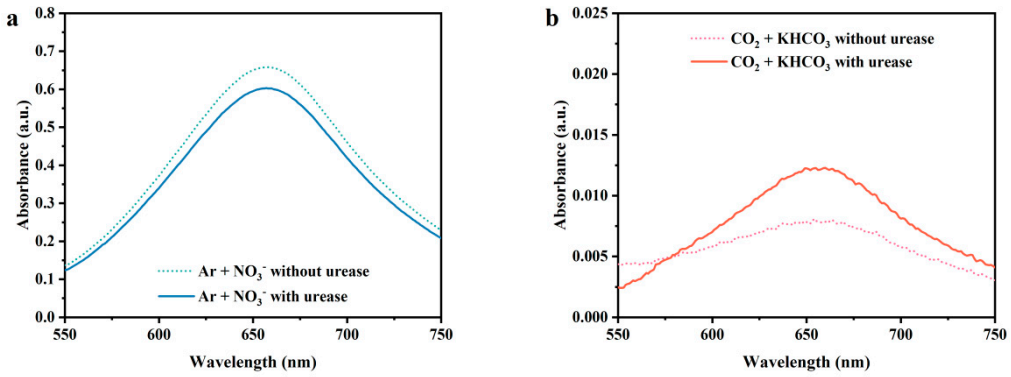


Figure S10. UV-vis absorption spectra of NH_4^+ with or without urease for a) Ar + NO_3^- and b) CO_2 + $KHCO_3$ control experiments.

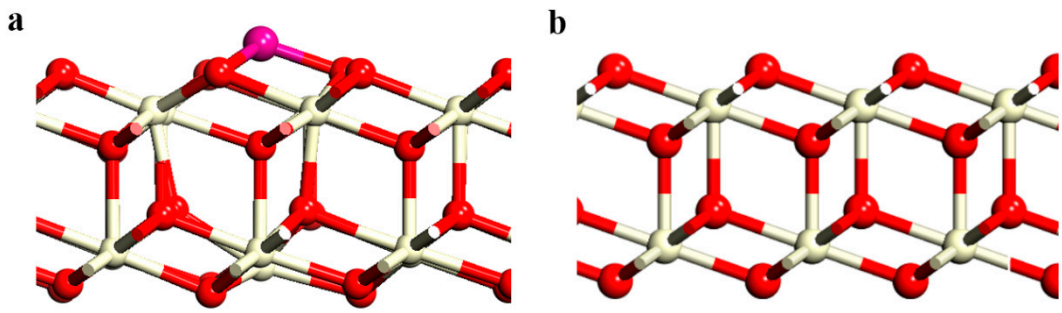


Figure S11. The structural modeling of a) Cu-CeO_2/MXene, b) CeO_2/MXene.

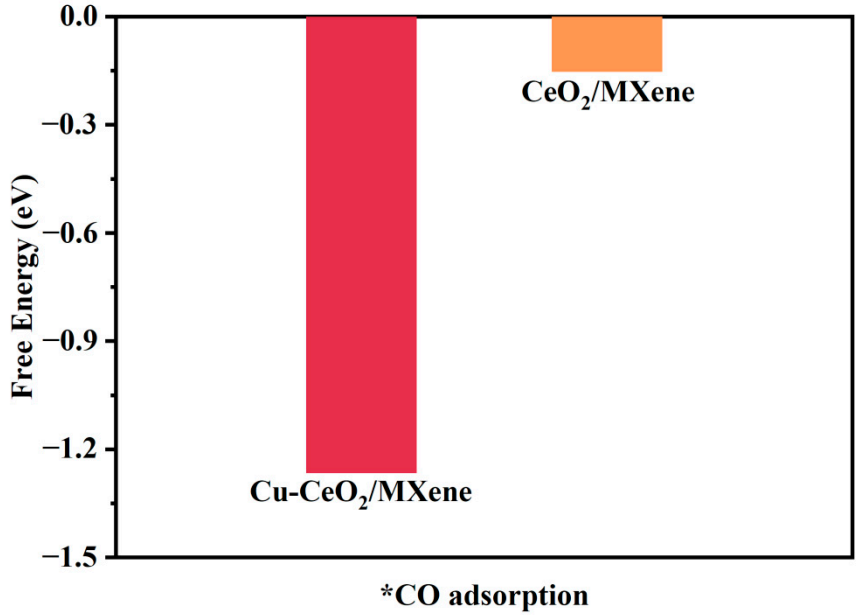


Figure S12. Adsorption energies for *CO intermediates on Cu-CeO_2/MXene and CeO_2/MXene surfaces.

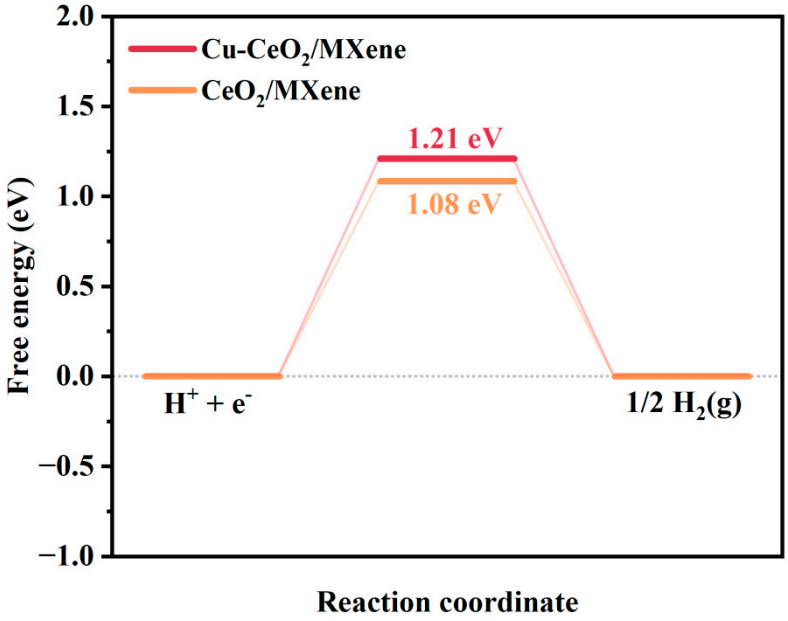


Figure S13. Free energy diagrams for the HER on Cu-CeO2/MXene and CeO2/MXene surface.

Table S1. Comparison of electrocatalytic urea synthesis performances with previous reports.

Catalysts	Electrolyte	Applied potential (V vs. RHE)	Urea yield rate ($\mu g \cdot h^{-1} \cdot mg_{cat.}^{-1}$)	FE (%)	Reference
Cu-CeO_2/MXene	0.1 M $KHCO_3$ + 50 mM KNO_3	−0.8	505.1	6.30	This work
PdCu/TiO_2	0.1 M $KHCO_3$	−0.4	201.8	8.92	[9]
Cu_1Au_8@CeO_2	0.1 M KNO_3	−0.94	813.6	45.20	[13]
Cu-CeO_2	0.1 M $KHCO_3$ + 50 mM KNO_3	−1.6	3173.6	5.29	[15]
Ru-Pd/WO_3/MXene	0.5 M $NaNO_3$ + 0.5 M $NaHCO_3$	−0.6	227.0	23.70	[19]
Ru-CeO_2	0.1 M $KHCO_3$ + 50 mM KNO_3	−0.7	1213.2	20.10	[20]
$FeNi_3$/NC	0.1 M KNO_3	−0.9	496.5	16.58	[33]

Table S2. Comparison of resistance values obtained from equivalent electrical circuit of different samples.

Sample	**R_s(Ω)**	**R_{ct}(Ω)**	**W(Ω)**
Cu-CeO_2/MXene	7.802	7.483	4.665
Cu-CeO_2	7.743	6.975	10.38
CeO_2/MXene	6.043	10.59	8.021

R_s: solution resistance; R_{ct}: charge transfer resistance; W: Warburg impedance