

Supplementary Materials for

Surface engineering on bulk Cu₂O for electrocatalytic synthesis of Urea

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Genqiang Zhang^{1*}*

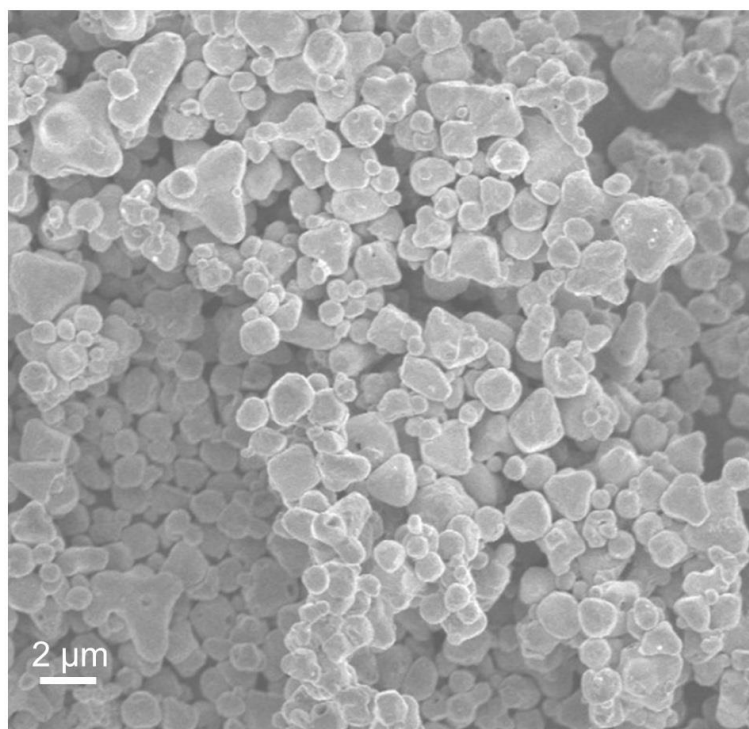
Affiliations

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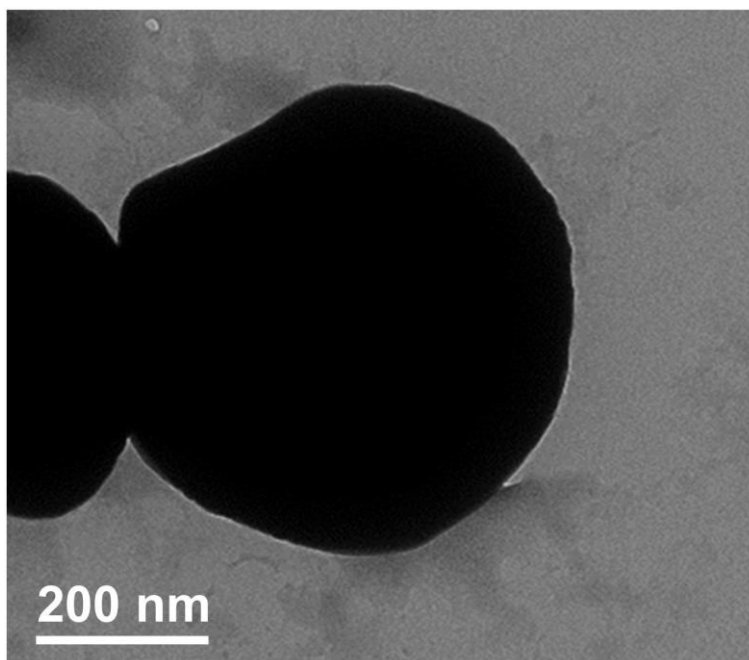
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⁺These three authors contribute equally to this work.

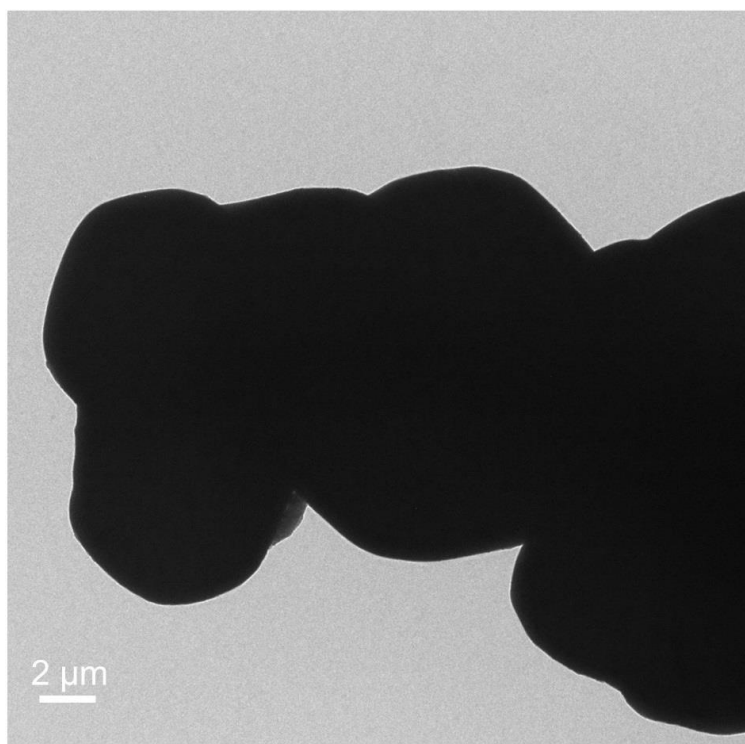
Supplementary Figures:



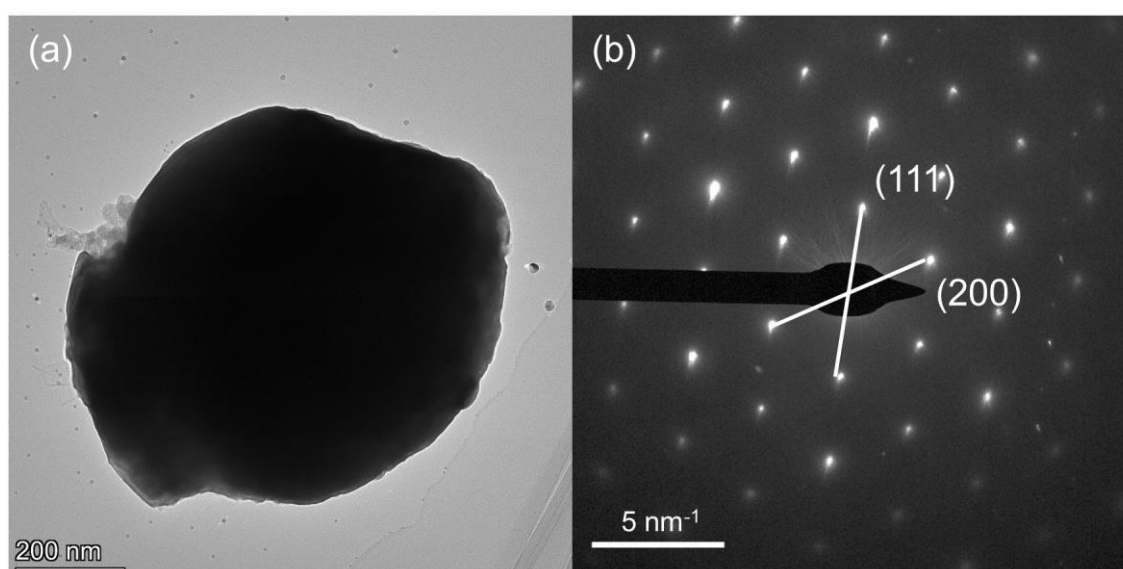
Supplementary Figure 1 | Typical SEM images of the bulk Cu_2O .



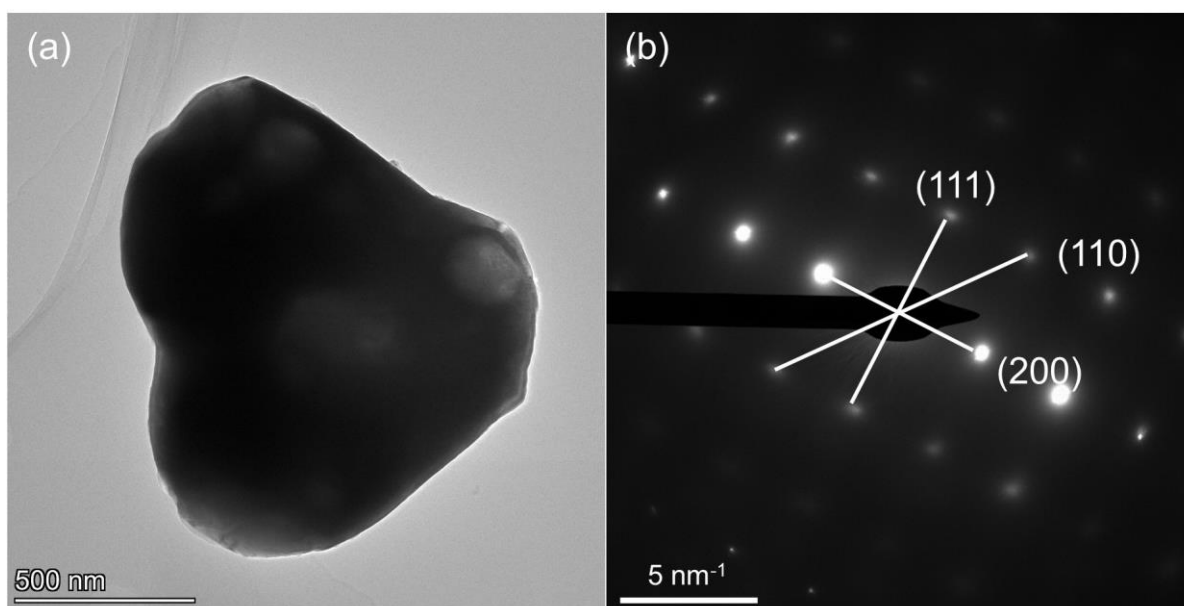
Supplementary Figure 2 | TEM images of the bulk h-Cu/ Cu_2O MPs.



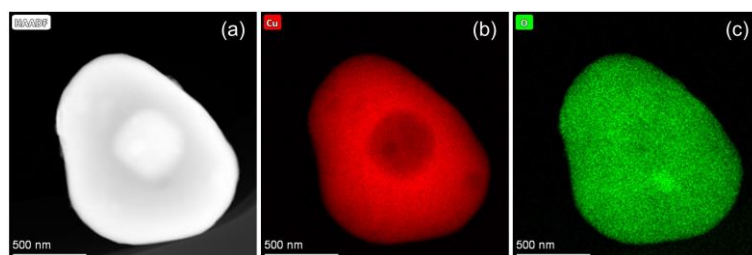
Supplementary Figure 3 | TEM images of the bulk Cu_2O .



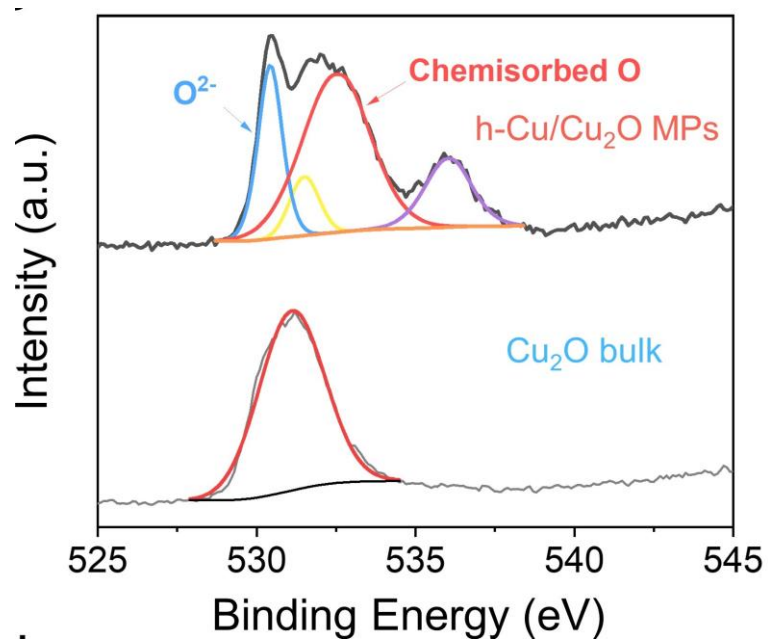
Supplementary Figure 4 | (a) TEM and (b) SAED pattern of Cu_2O , which exhibit two crystal facets: (111) and (200).



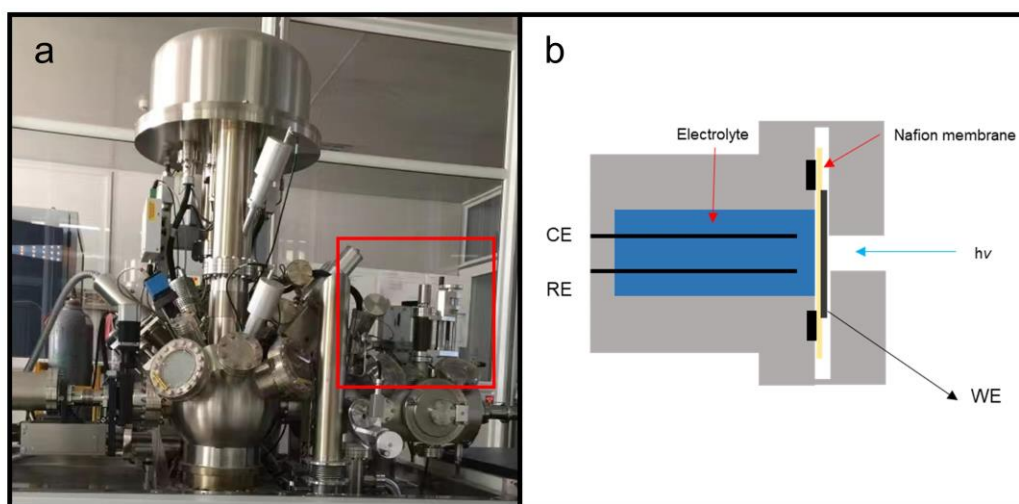
Supplementary Figure 5 | (a) TEM and (b) SAED pattern of h-Cu/Cu₂O MPs, which exhibit three crystal facets: (111), (111) and (200).



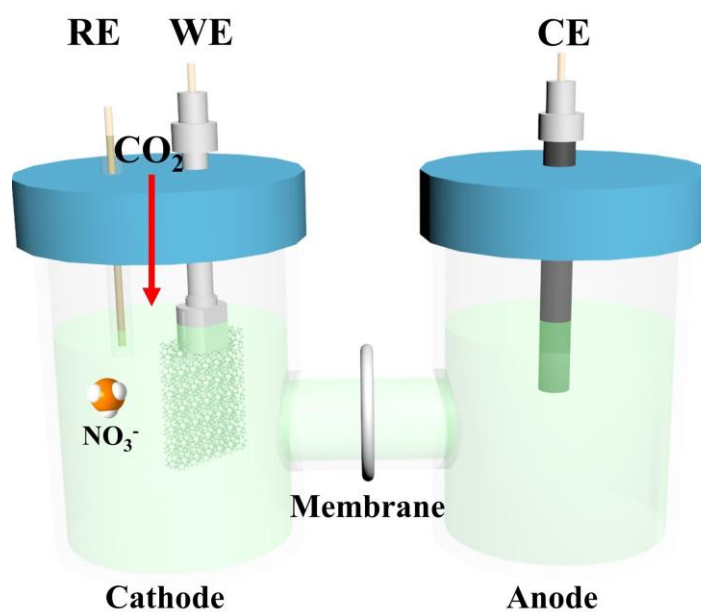
Supplementary Figure 6 | (a) High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images of h-Cu/Cu₂O MPs with corresponding elemental mapping of (b) Cu and (c) O.



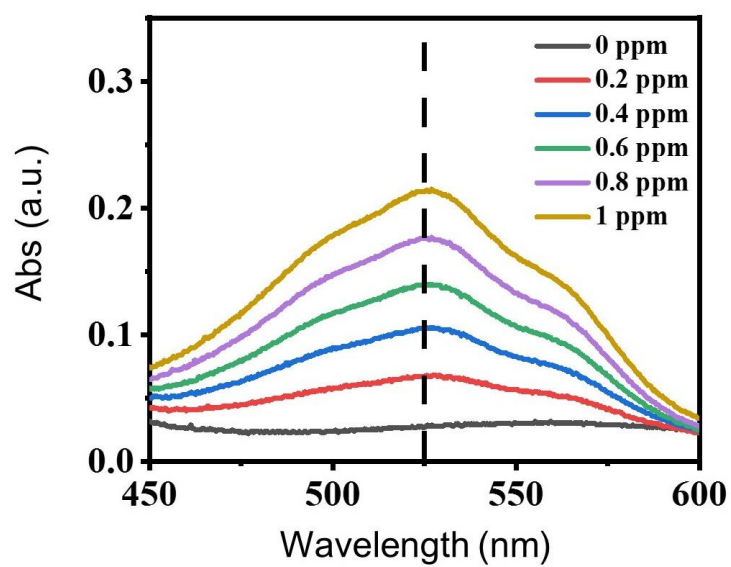
Supplementary Figure 7 | XPS spectra of O 1s of Cu₂O and h-Cu/Cu₂O MPs.



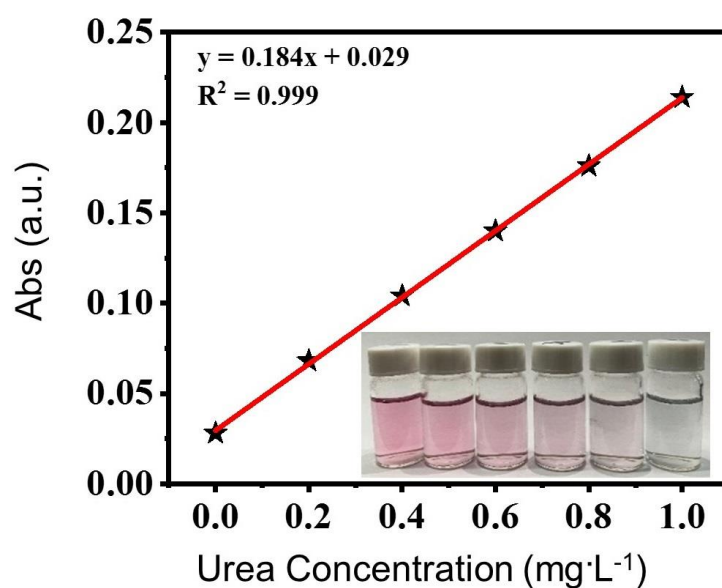
Supplementary Figure 8 | Schematic diagram of the in situ XPS test. (a) Photograph of the in situ XPS equipment. The analysis chamber pressure is ~0.3 mbar. (b) Scheme of the electrochemical cell (EC) cell.



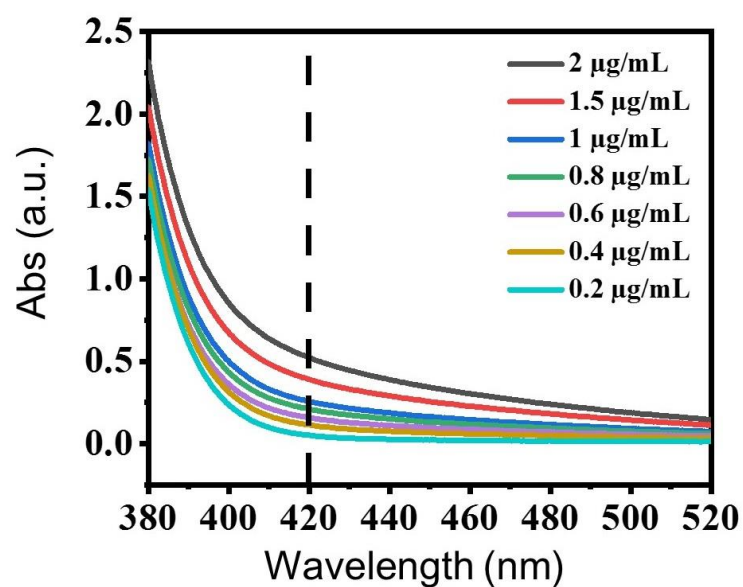
Supplementary Figure 9 | H-type electrolytic cell.



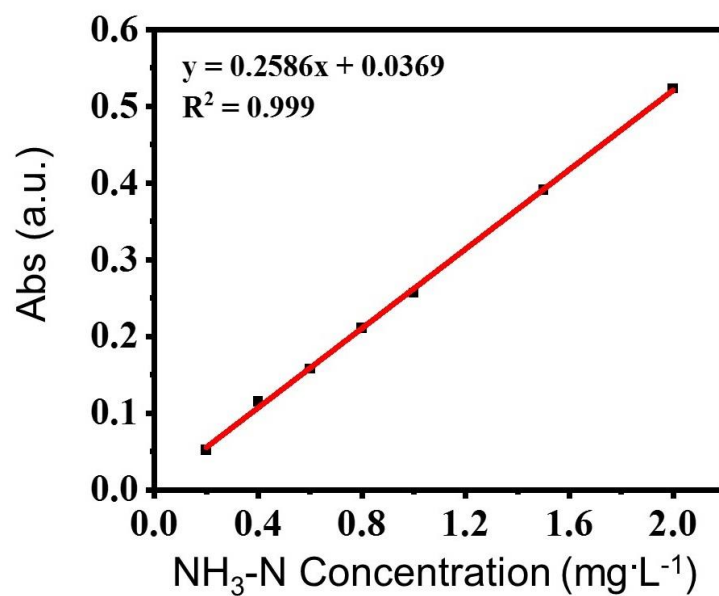
Supplementary Figure 10 | UV-vis absorption spectra of various urea concentrations. .



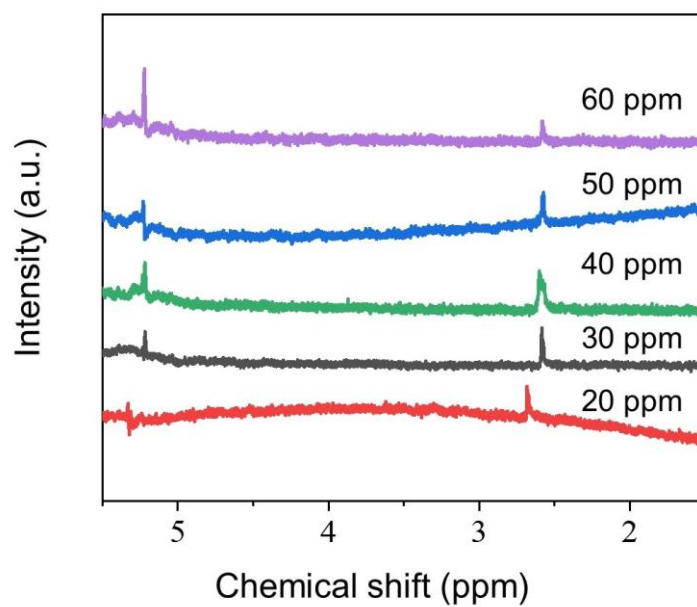
Supplementary Figure 11 | Calibration curve used for quantifying urea.



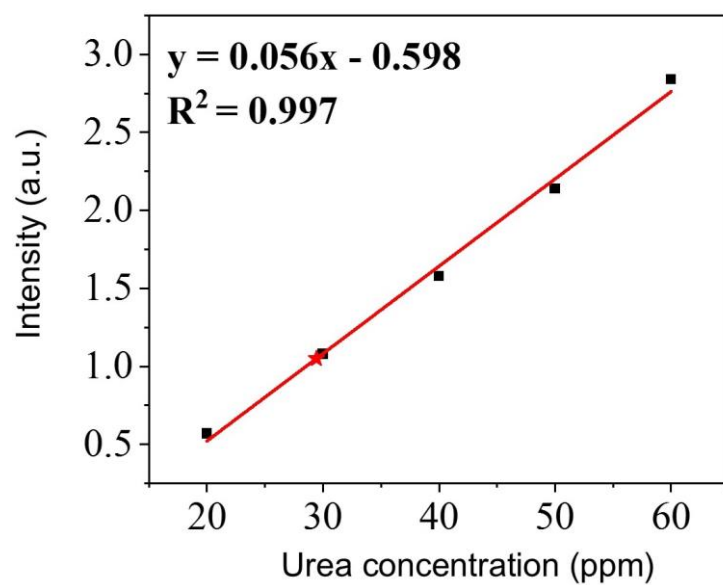
Supplementary Figure 12 | UV-vis absorption spectra of various ammonia concentrations.



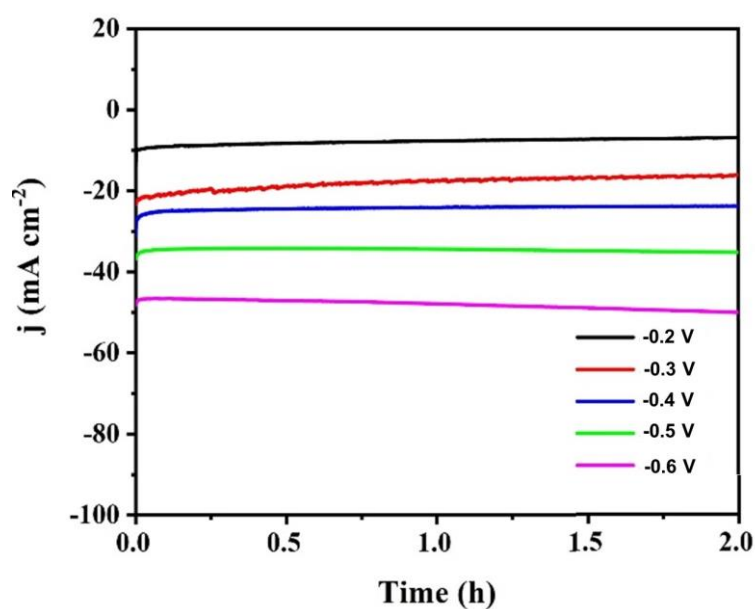
Supplementary Figure 13 | Calibration curve used for quantifying ammonia.



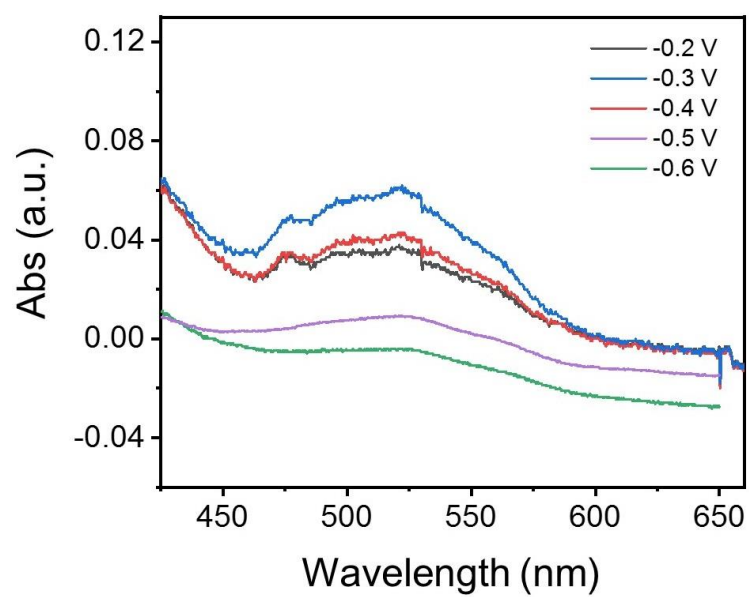
Supplementary Figure 14 | NMR signal curves corresponding to different concentrations of urea.



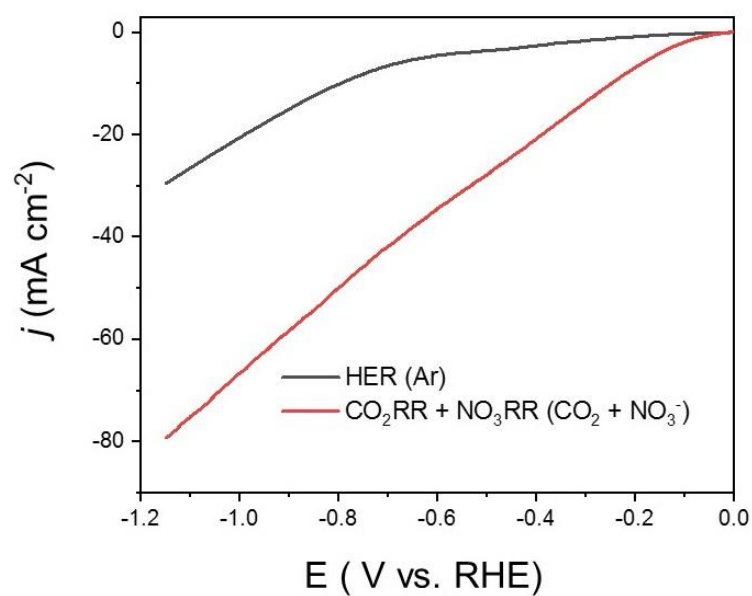
Supplementary Figure 15 | Different concentrations of urea nuclear magnetic signal corresponding to the standard curve.



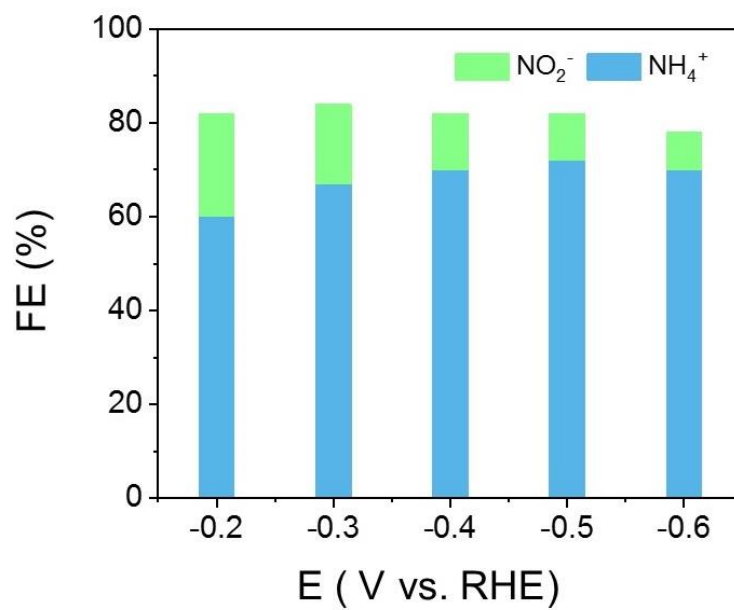
Supplementary Figure 16 | I-t curves for electrocatalytic urea synthesis at various potential at -0.2 and -0.6 V.



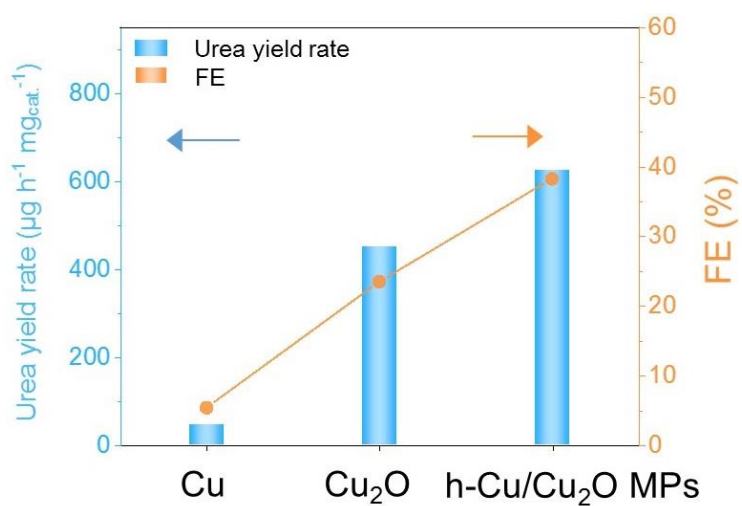
Supplementary Figure 17 | UV-vis absorption spectra of various urea concentrations at potentials of -0.2 to -0.6 V versus RHE.



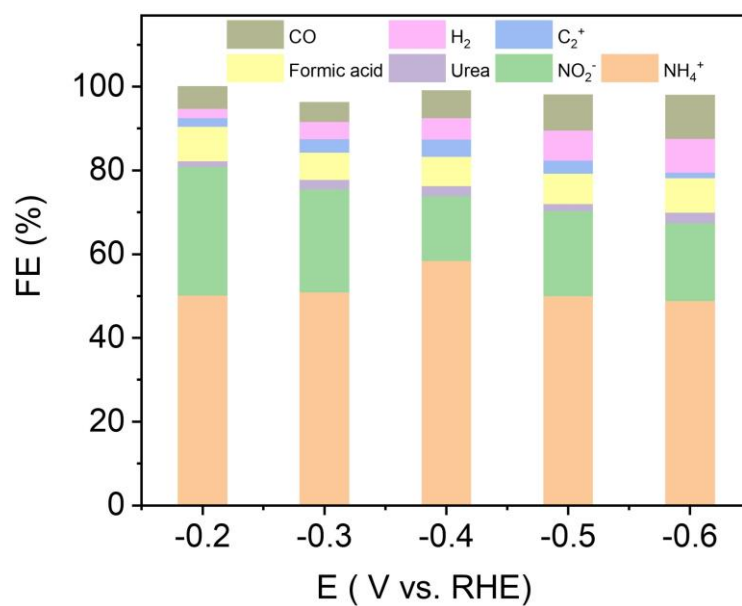
Supplementary Figure 18 | LSV curves of HER and coupling reaction of h-Cu/Cu₂O MPs.



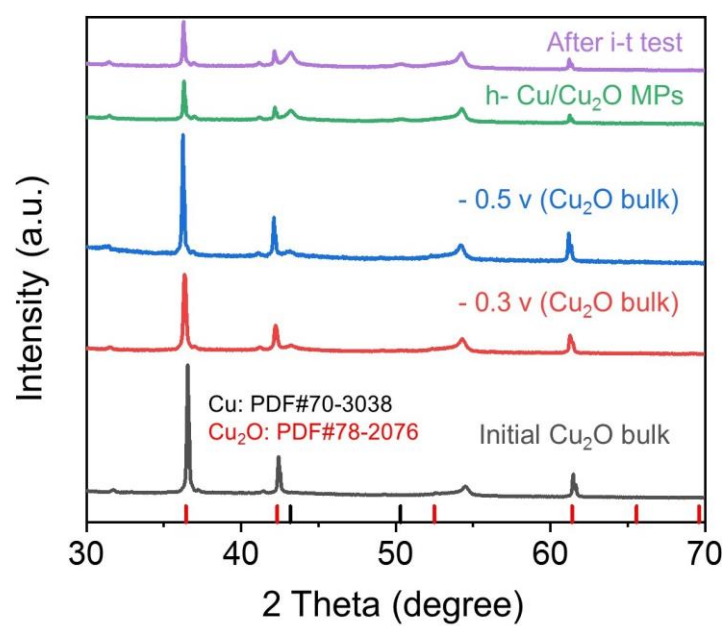
Supplementary Figure 19 | The NO₃RR Faraday efficiency of h-Cu/Cu₂O MPs at each potential.



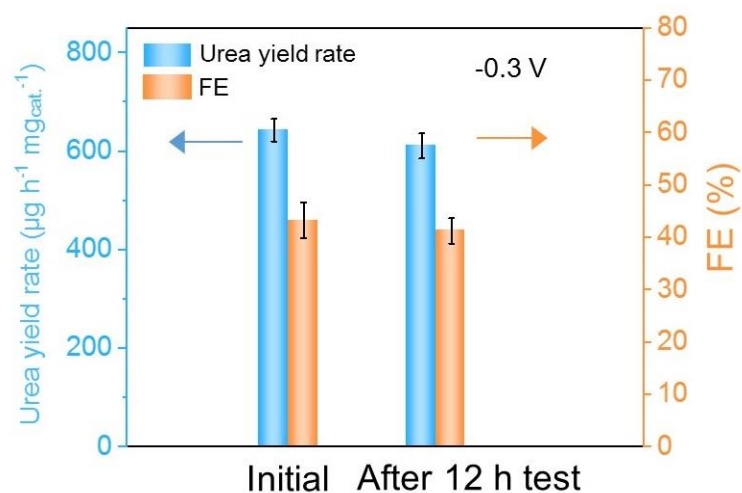
Supplementary Figure 20 | Electrochemical performance of different samples.



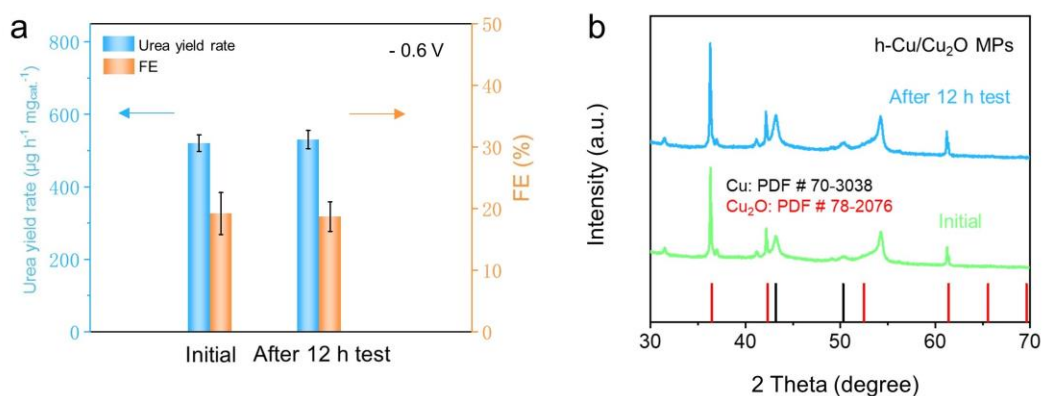
Supplementary Figure 21 | Product distribution of metallic Cu at various potentials.



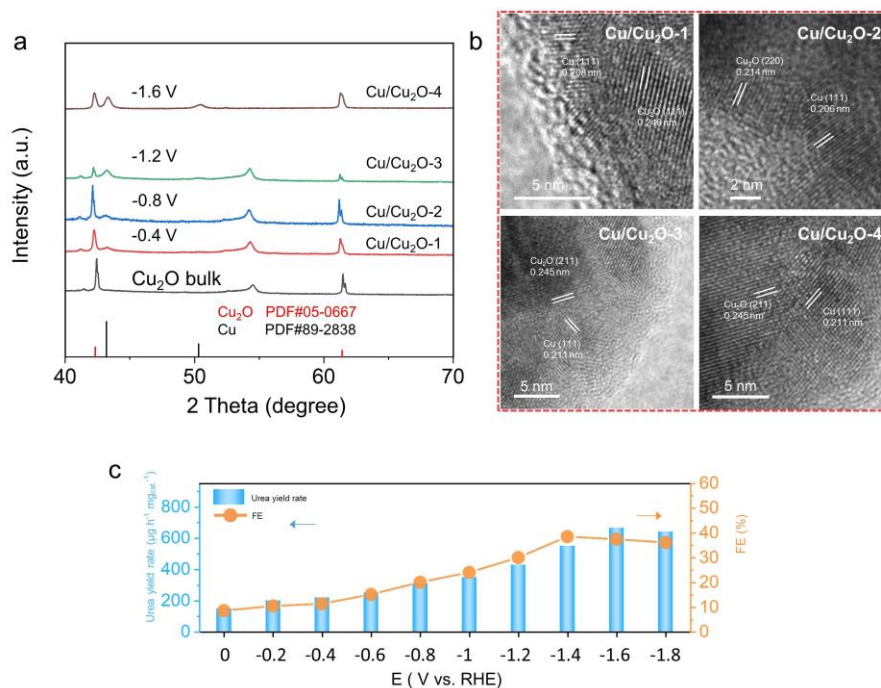
Supplementary Figure 22 | XRD patterns of h-Cu/Cu₂O MPs and contrast samples.



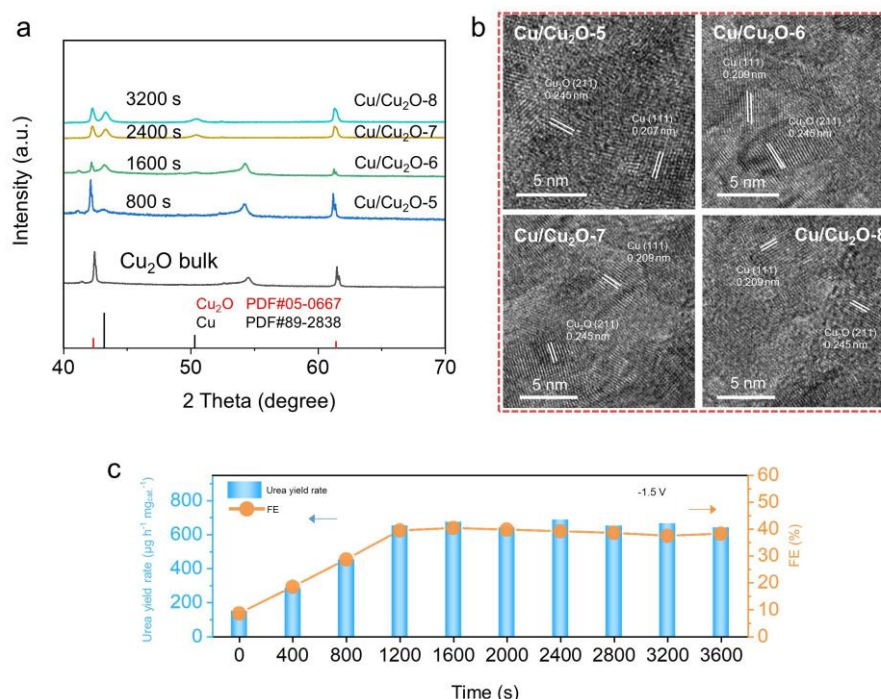
Supplementary Figure 23 | Performance of h-Cu/Cu₂O MPs before and after a 12-hour long cycle at -0.3 V versus RHE



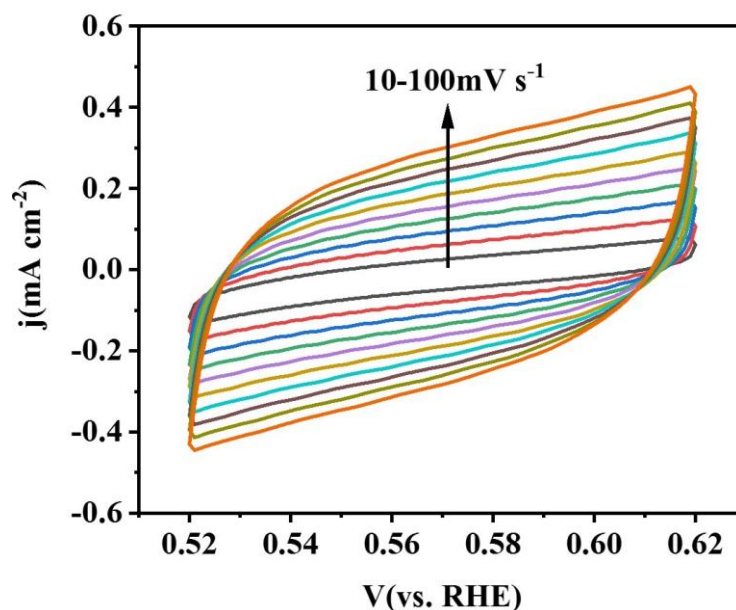
Supplementary Figure 24 | (a) Performance of h-Cu/Cu₂O MPs before and after a 12-hour long cycle at -0.6 V versus RHE, and (b) the corresponding XRD patterns.



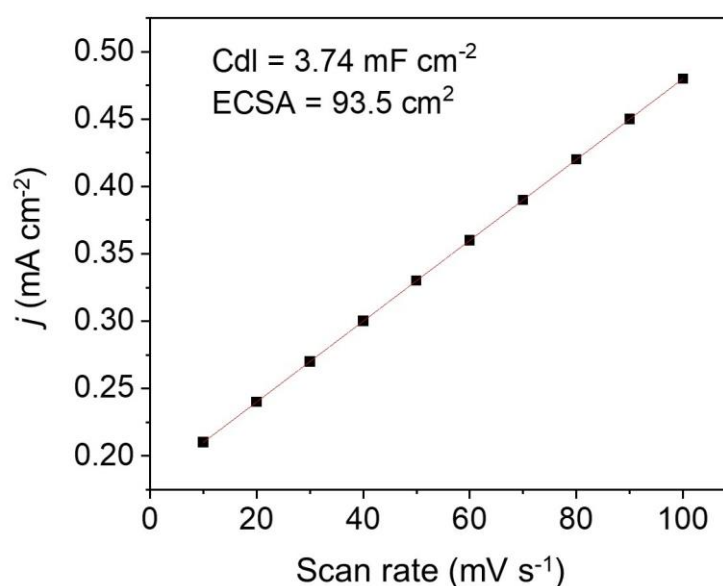
Supplementary Figure 25 | (a) XRD patterns of Cu/Cu₂O samples under different electrolysis potentials and (b) corresponding high-resolution images. (c) Performance variation of urea electro-synthesis over samples in the range of 0~ -1.8 V versus RHE.



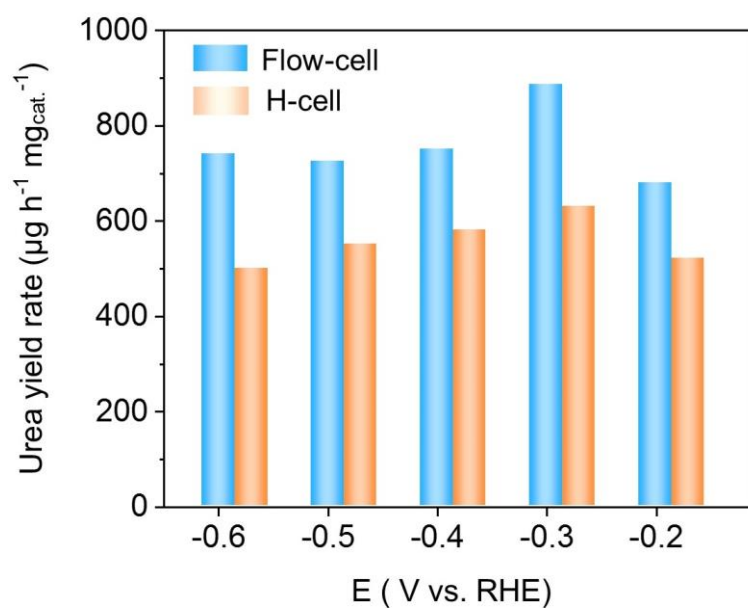
Supplementary Figure 26 | (a) XRD patterns of a series of Cu/Cu₂O samples under different electrolysis durations and (b) corresponding high-resolution images, (c) Performance variation of urea electro-synthesis over samples in the range of 0~3600 s



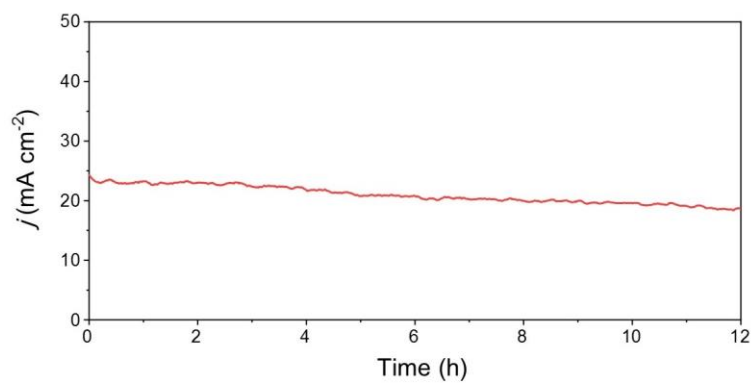
Supplementary Figure 27 | Different scan rate of CV curve.



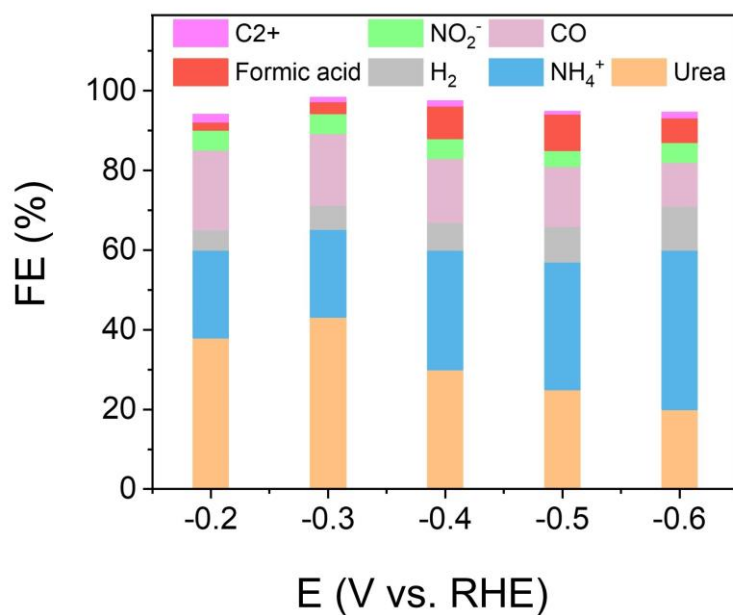
Supplementary Figure 28 | ECSA of h-Cu/Cu₂O MPs. The specific capacitance for a flat surface is generally found to be in the range of 20-60 $\mu\text{F cm}^{-2}$. In the following calculations of electrochemical active surface area, we assume 40 $\mu\text{F cm}^{-2}$. Based on the literature, the double-layer capacitance of the h-Cu/Cu₂O MPs electrode surfaces can be described by the charging current, $I_c = V \cdot C_{dl}$. (" I_c " is the charging current, " V " is the scan rate, and " C_{dl} " is the double-layer capacitance.) From the above measurements, C_{dl} is determined to be 3.74 mF cm^{-2} . Combining this with the empirically measured value of $C_{\text{Cu}_2\text{O}} = 40 \mu\text{F cm}^{-2}$, we can calculate the electrochemical active surface area as follows: $A_{\text{ECSA}} = 3.74 \text{ mF cm}^{-2} / (40 \mu\text{F cm}^{-2} \text{ cm}^{-2}_{\text{ECSA}}) = 93.5 \text{ cm}^2_{\text{ECSA}}$.



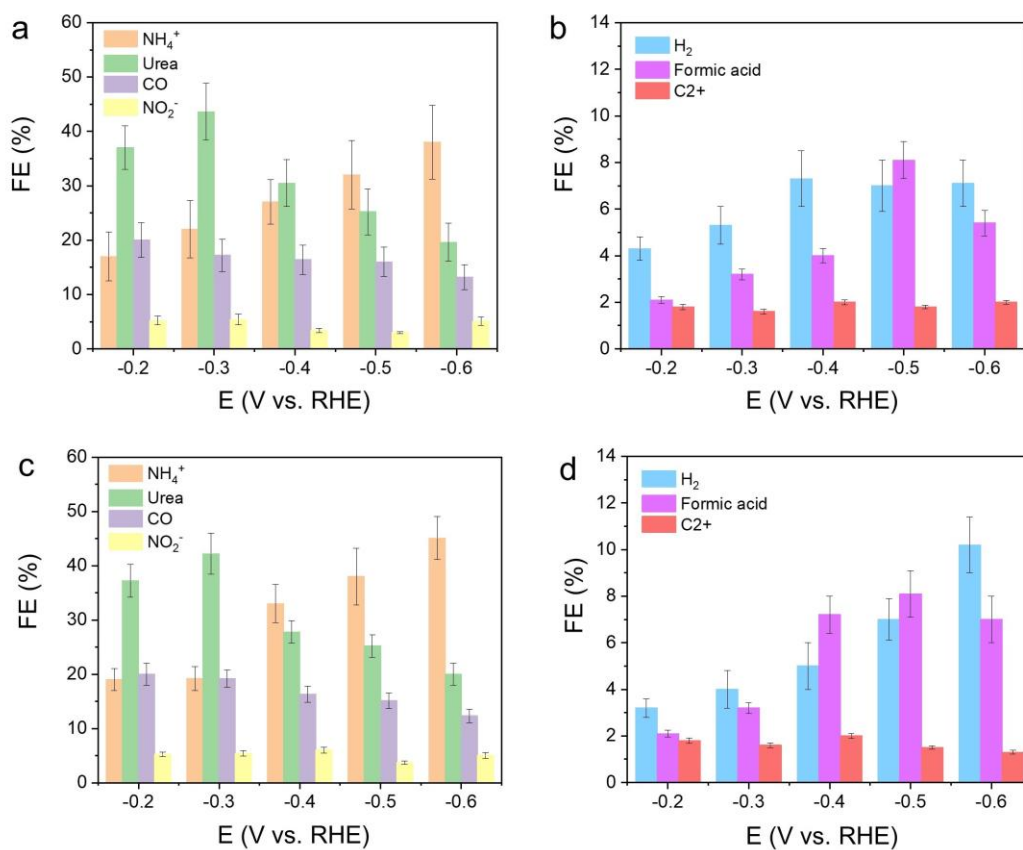
Supplementary Figure 29 | Urea yield rate of h-Cu/Cu₂O MPs using H-cell and Flow-cell at various potential at -0.2 and -0.6 V.



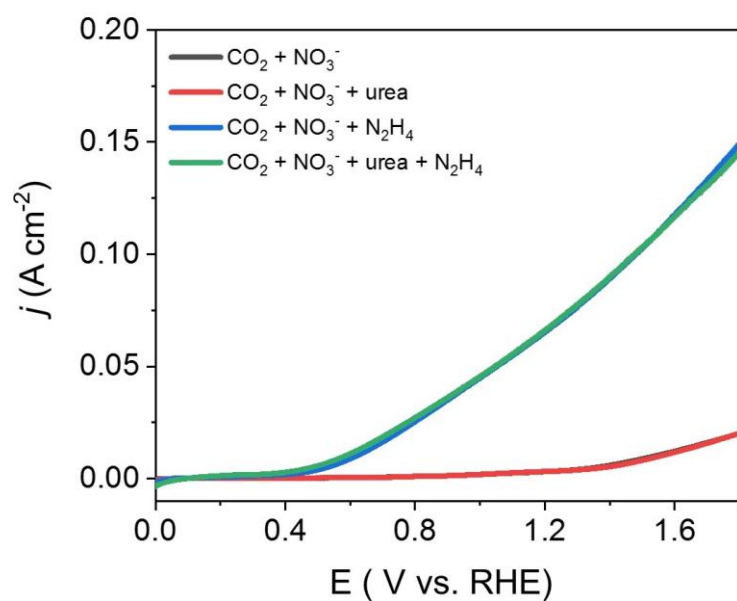
Supplementary Figure 30 | Long-term (12 hours) of CA curve.



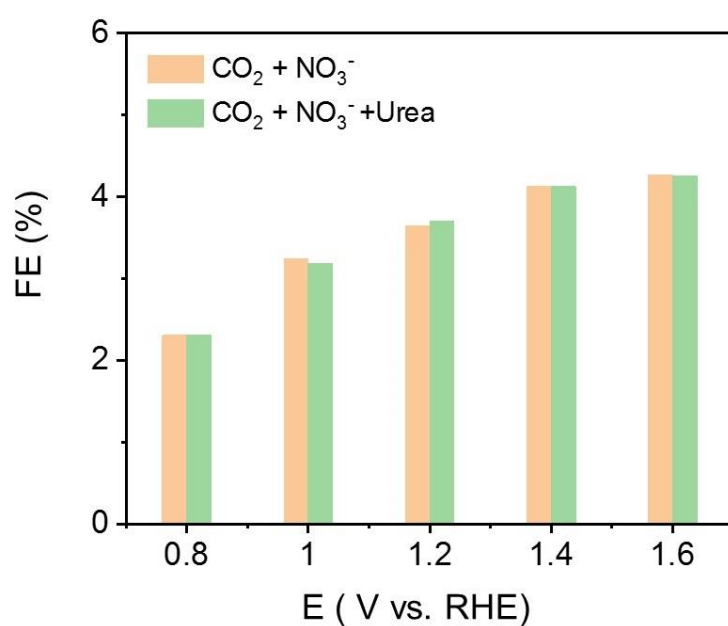
Supplementary Figure 31 | Products in the flow cell system in the range of -0.2V ~ -0.6 V versus RHE.



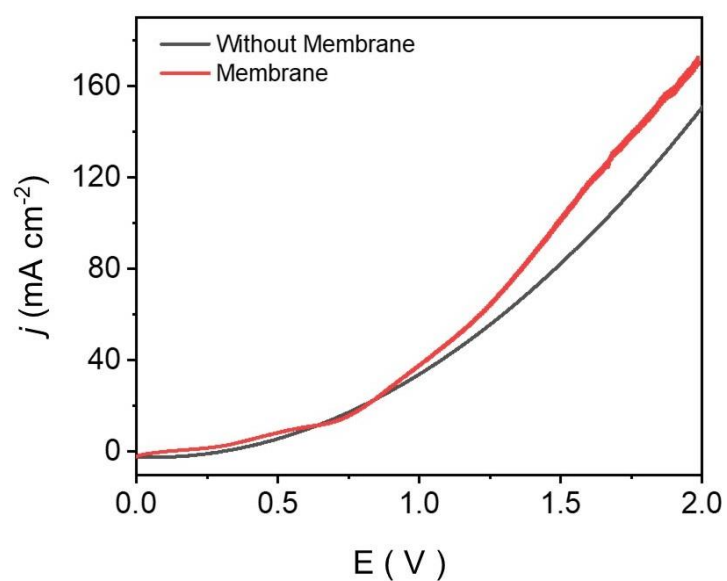
Supplementary Figure 32 | The error-bar versions of Figures 3c (a-b) and 3e (c-d). Error bars show the standard deviations calculated from three independent experiments.



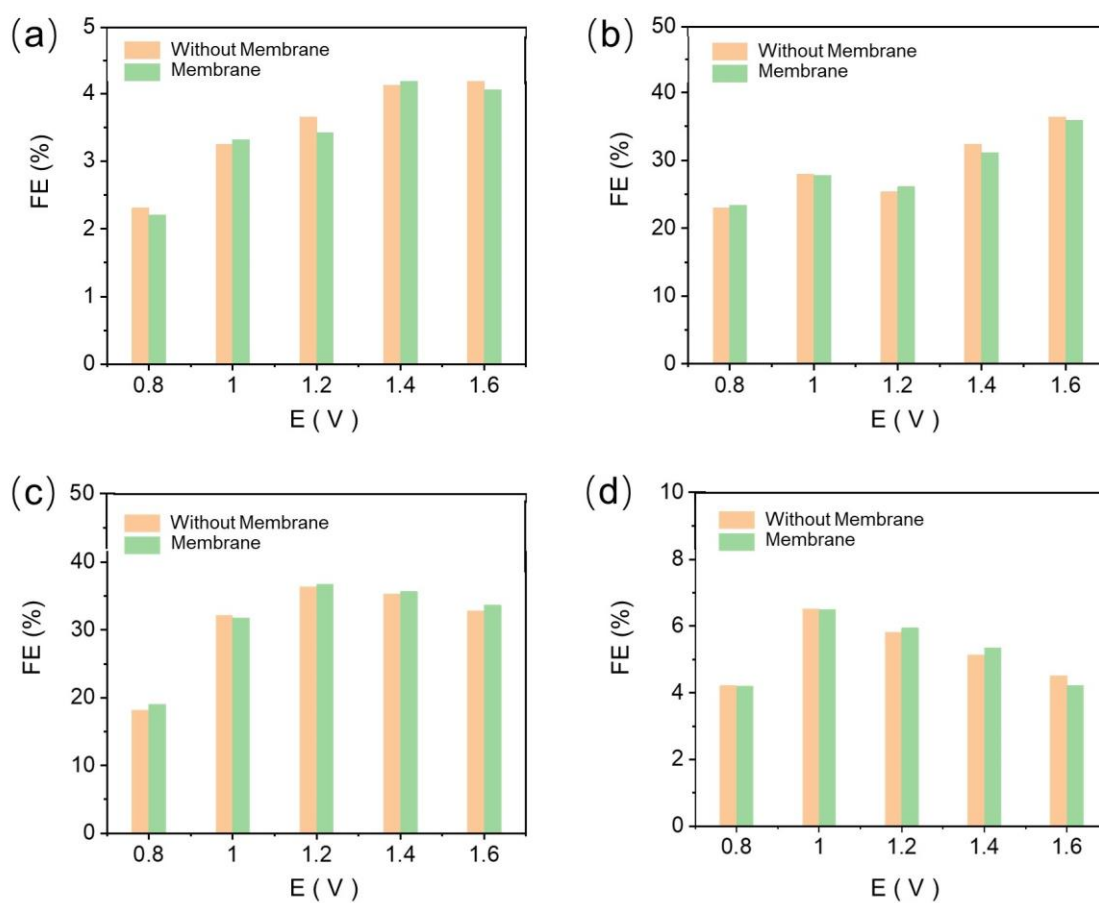
Supplementary Figure 33 | LSV curve of the comparison experiment with and without urea and hydrazine hydrate in two-electrode system.



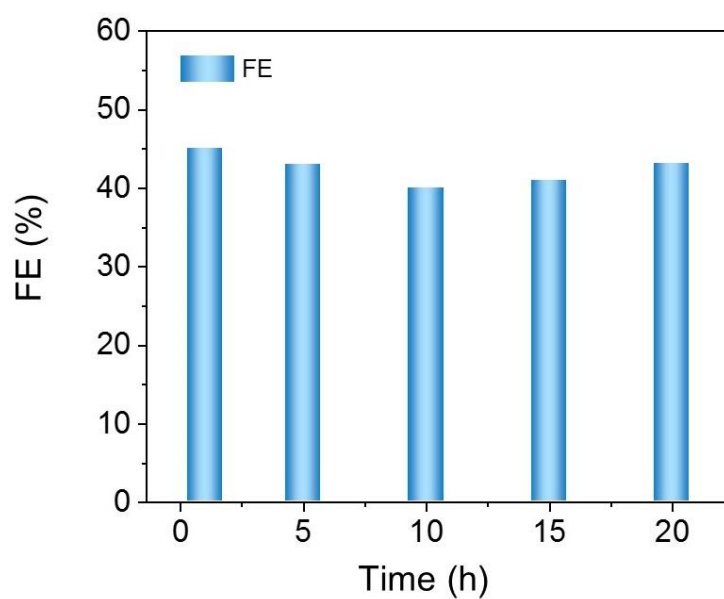
Supplementary Figure 34 | Properties of two-electrode formic acid products of h-Cu/Cu₂O MPs.



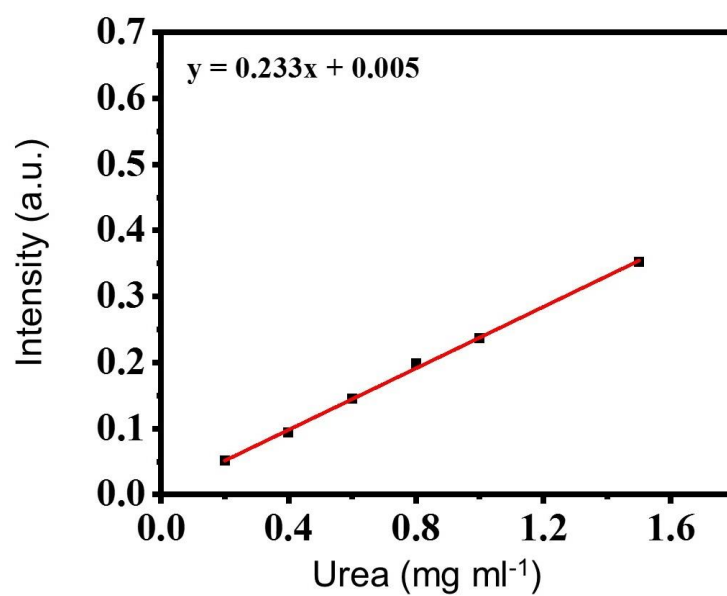
Supplementary Figure 35 | LSV curves of h-Cu/Cu₂O MPs two-electrode system with and without membrane.



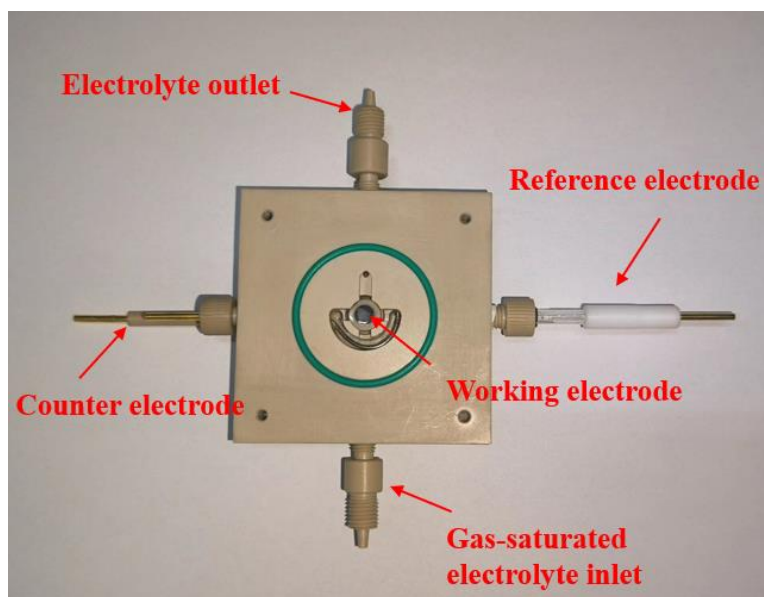
Supplementary Figure 36 | FE comparison diagram of (a) formic acid, (b) urea, (c) ammonia and (d) NO₂⁻ in two electrodes with or without membrane.



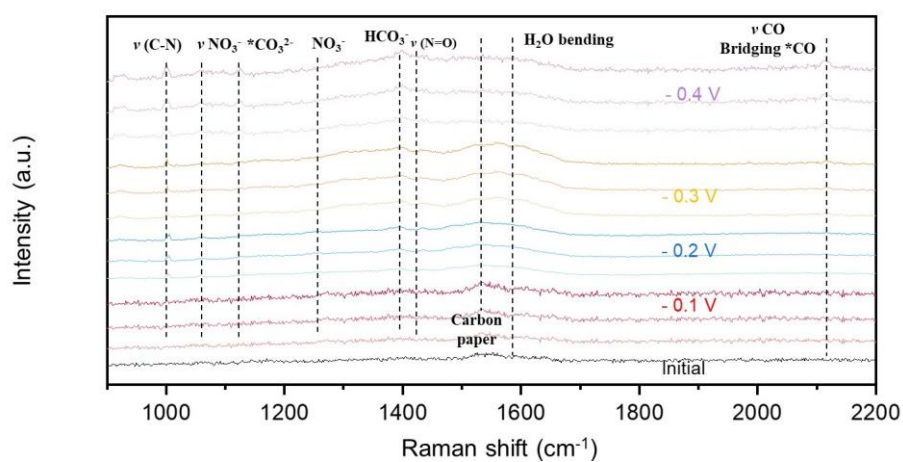
Supplementary Figure 37 | FE changes of h-Cu/Cu₂O MPs at 5h intervals during the 20-h cycle in a two-electrode system.



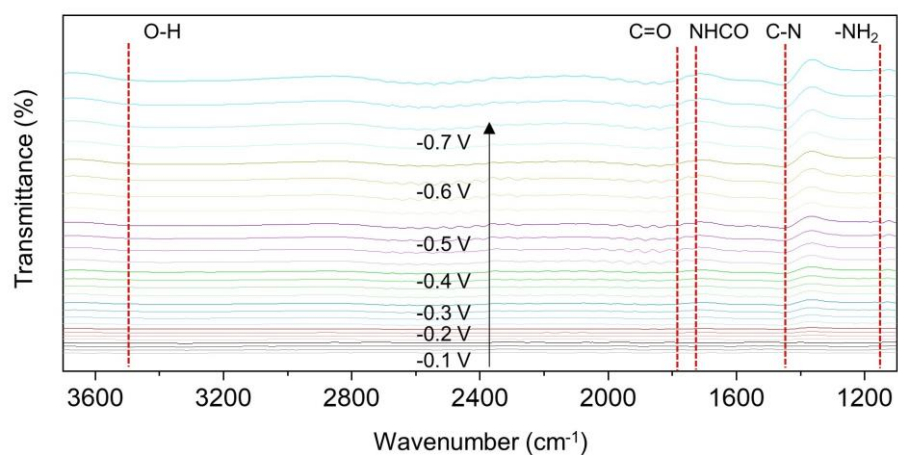
Supplementary Figure 38 | Standard curve quantification of ¹⁵N isotopic labeling.



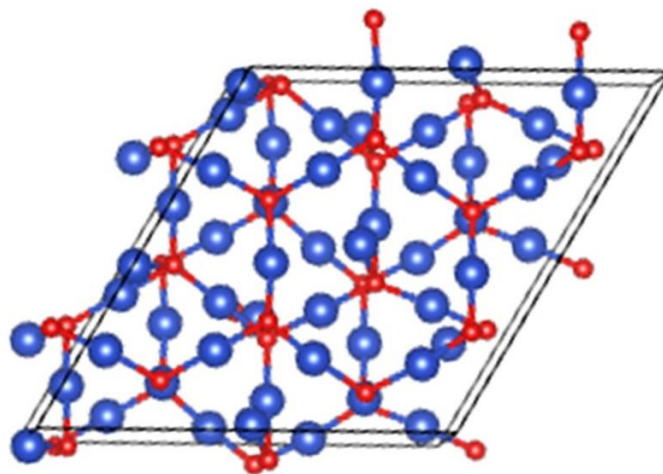
Supplementary Figure 39 | The cell for the Operando synchrotron radiation FTIR measurements.



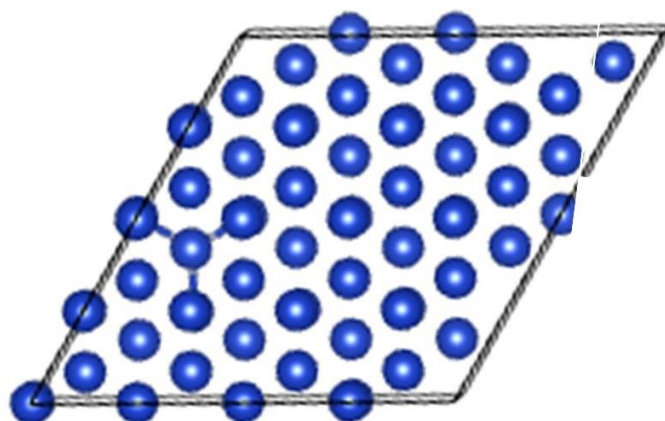
Supplementary Figure 40 | In-situ Raman spectra of h-Cu/Cu₂O MPs. For each potential, an electrochemical experiment was conducted for 5 minutes, followed by a 2-minute Raman signal scan. Three sets of Raman signals were obtained for each potential during the i-t tests.



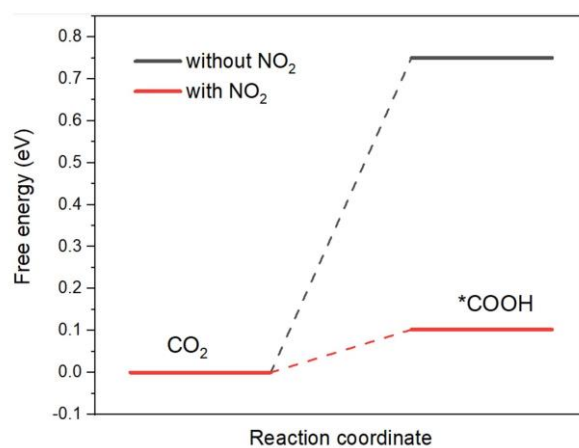
Supplementary Figure 41 | In-situ infrared spectra. Four sets of infrared signals were collected at each potential.



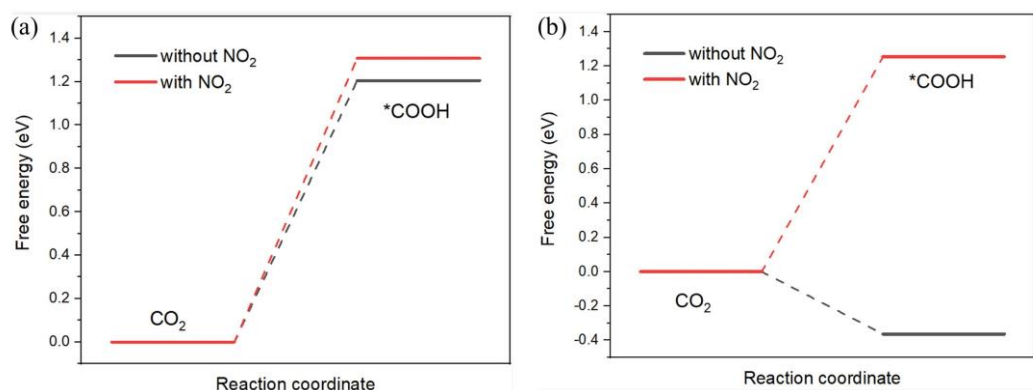
Supplementary Figure 42 | Model of Cu_2O .



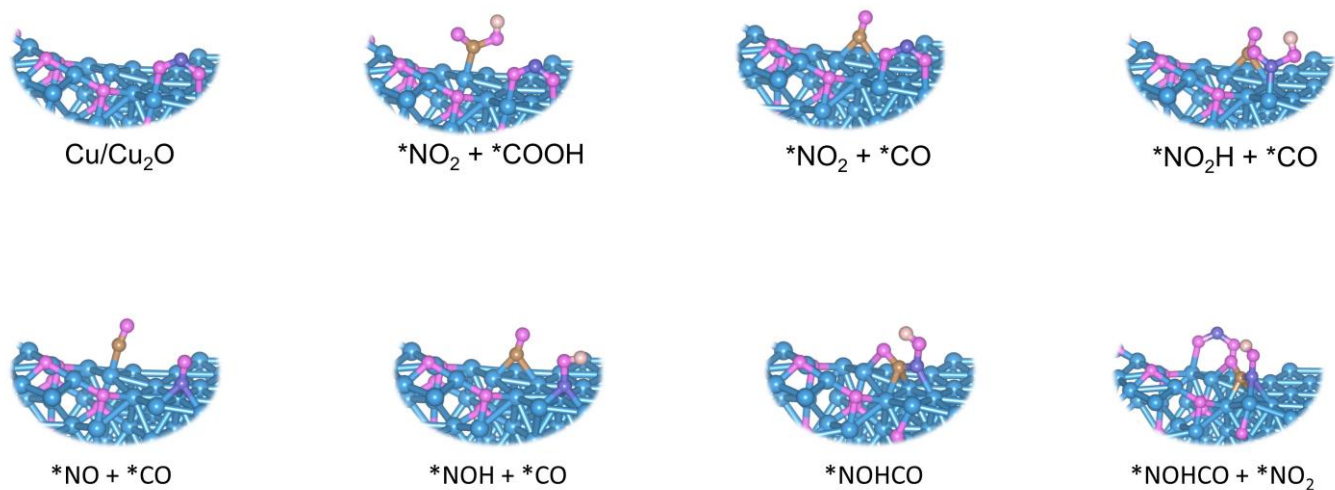
Supplementary Figure 43 | Model of Cu.



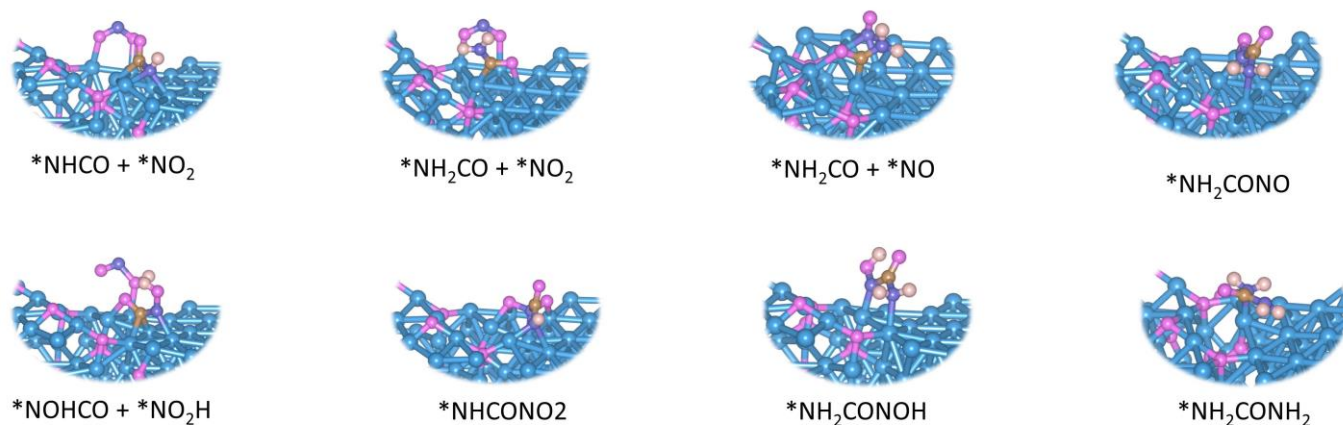
Supplementary Figure 44 | Adsorption activation energy barrier diagram of h-Cu/Cu₂O MPs for CO₂ in the presence and absence of the NO₂ intermediate.



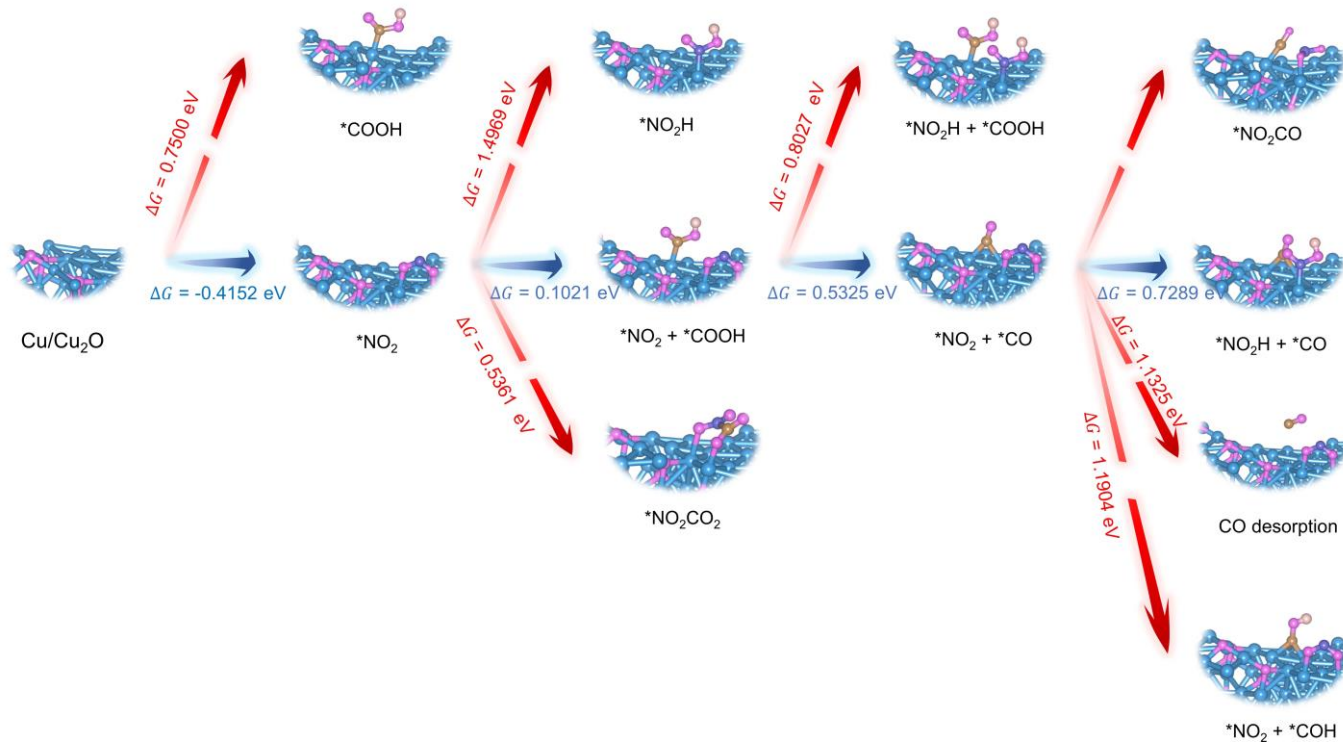
Supplementary Figure 45 | Adsorption activation energy barrier diagram of (a) Cu and (b) Cu₂O for CO₂ in the presence and absence of the NO₂ intermediate.



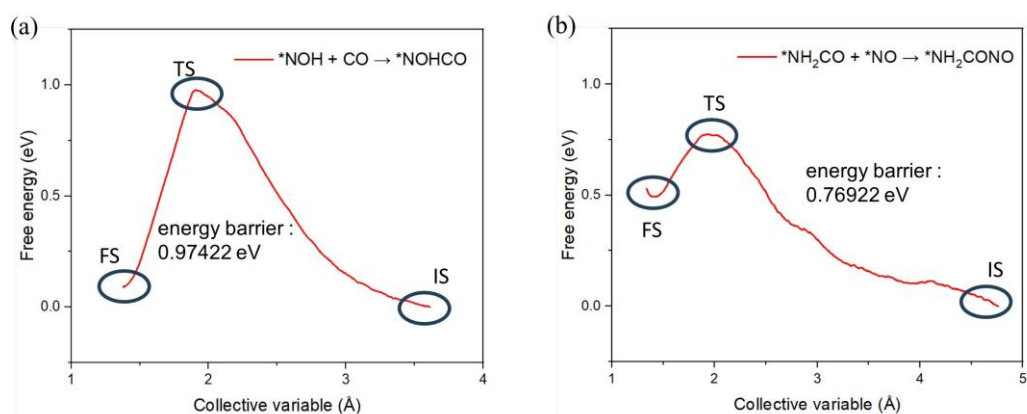
Supplementary Figure 46 | Adsorption model of reaction intermediates on h-Cu/Cu₂O MPs surface.



Supplementary Figure 47 | Adsorption model of reaction intermediates on h-Cu/Cu₂O MPs surface.



Supplementary Figure 48 | Reaction pathways, schematic diagram of intermediate adsorption configuration and corresponding energy changes of urea electrosynthesis for h-Cu/Cu₂O MPs.



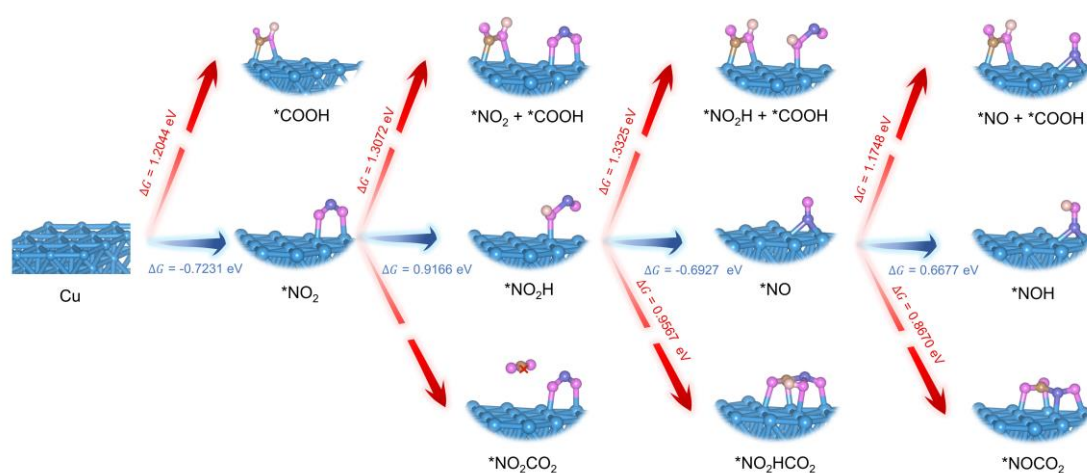
Supplementary Figure 51 | Transition state energy barrier diagrams for the two coupling steps (a) and (b) in h-Cu/Cu₂O MPs.



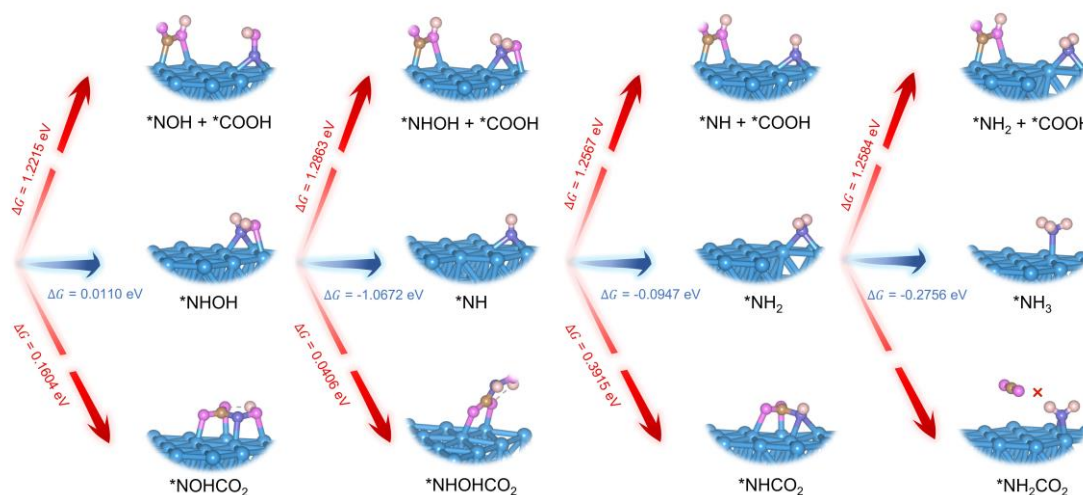
Supplementary Figure 52 | Adsorption model of reaction intermediates on Cu MPs surface.



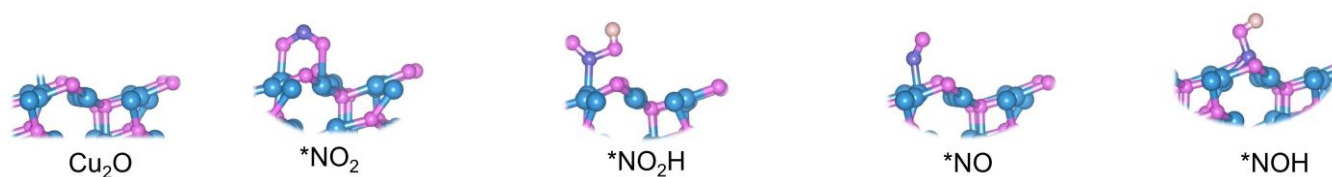
Supplementary Figure 53 | Adsorption model of reaction intermediates on Cu surface.



Supplementary Figure 54 | Reaction pathways, schematic diagram of intermediate adsorption configuration and corresponding energy changes of urea electrosynthesis for Cu.



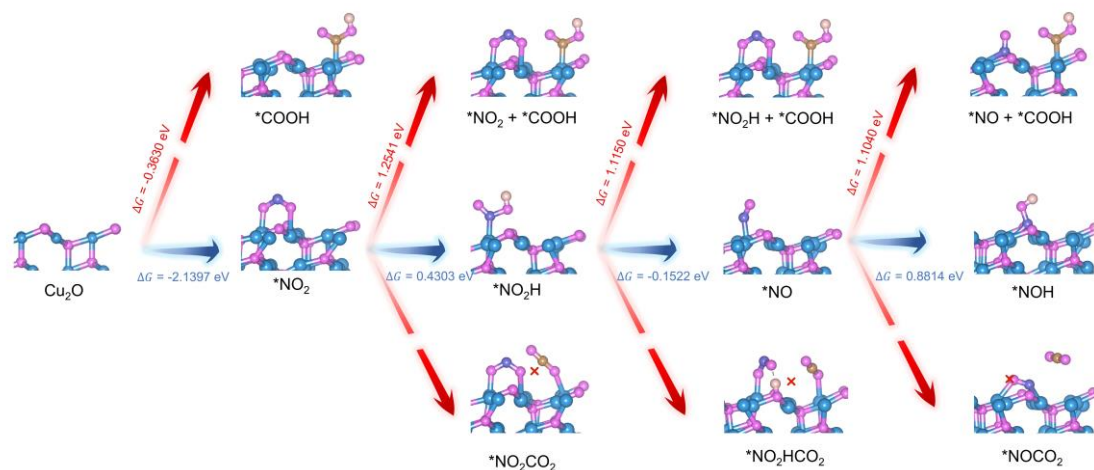
Supplementary Figure 55 | Reaction pathways, schematic diagram of intermediate adsorption configuration and corresponding energy changes of urea electrosynthesis for Cu.



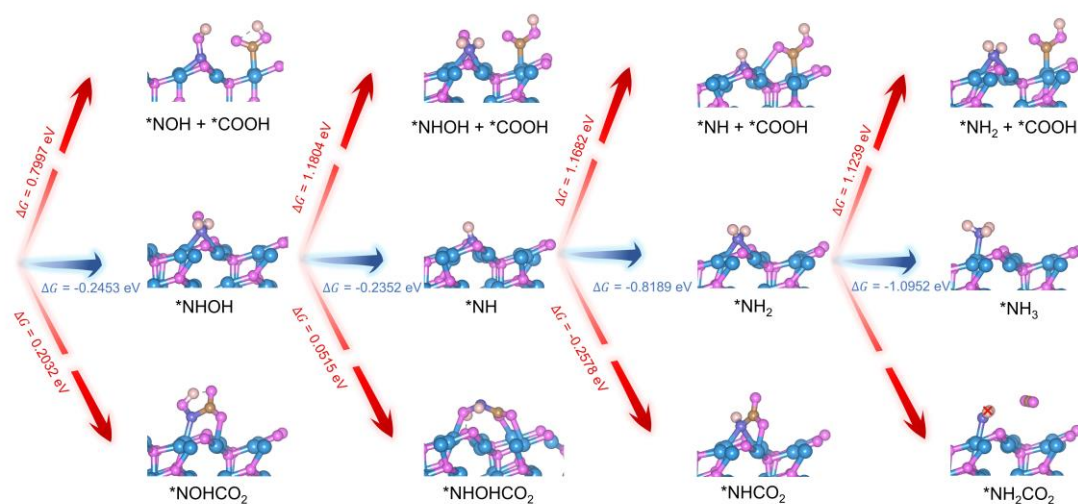
Supplementary Figure 56 | Adsorption model of reaction intermediates on Cu_2O surface.



Supplementary Figure 57 | Adsorption model of reaction intermediates on Cu₂O surface.



Supplementary Figure 58 | Reaction pathways, schematic diagram of intermediate adsorption configuration and corresponding energy changes of urea electrosynthesis for Cu₂O.



Supplementary Figure 59 | Reaction pathways, schematic diagram of intermediate adsorption configuration and corresponding energy changes of urea electrosynthesis for Cu_2O .

Supplementary Table 1. The comparison of urea electrosynthesis performance.

Catalyst	Cell configuration	Temperature	loading	Electrolyte	Membrane	Stability	Ref
PdCu/TiO ₂	Flow cell	Room temperature	0.2 mg cm ⁻²	0.1 M KHCO ₃	Nafion 117	12 hours	1
Bi-BiVO ₄	H-cell	Room temperature	0.3 mg cm ⁻²	0.1 M KHCO ₃	Nafion 211	10 hours	2
BiFeO ₃ /BiVO ₄	H-cell	Room temperature	0.3 mg cm ⁻²	0.1 M KHCO ₃	Nafion 211	10 hours	3
Te-Pd NCs	Flow cell	Room temperature	0.51 mg cm ⁻²	0.05 M KHCO ₃ + 0.01 M KNO ₂	Nafion 115	5 hours	4
Pd	Flow cell	Room temperature	--	--	--	--	5
S-In(OH) ₃	H-cell	Room temperature	0.1 mg cm ⁻²	0.5 M KHCO ₃ + 0.1 M KNO ₃	Nafion 117	--	6
B-FeNi DASC	H-cell	Room temperature	0.2 mg cm ⁻²	0.1 M KHCO ₃ + 50 Mm KNO ₃	Nafion 117	--	7
Cu@Zn	H-cell	Room temperature	--	0.2 M KHCO ₃ + 0.1 M KNO ₃	--	12 hours	8
CeO ₂ -Vo	H-cell	Room temperature	0.2 mg cm ⁻²	0.1 M KHCO ₃ + 50 Mm KNO ₃	Nafion 117	18000 seconds	9

Cu-N-C	H-cell	Room temperature	0.2 mg cm ⁻²	0.1 M KHCO ₃ + 0.1 M K ₂ SO ₄ + 0.1 M KNO ₃	Nafion	--	10
Cu-SAC	H-cell	Room temperature	0.5 mg cm ⁻²	0.1 M KHCO ₃ + 0.1 M K ₂ SO ₄ + 0.1 M KNO ₃	Nafion	8 cycle	11
Cu/Cu ₂ O	H-cell	Room temperature	1 mg cm ⁻²	0.5 M KHCO ₃ + 0.05 M KNO ₃	Nafion 117	20 hours	This work

Supplementary Table 2. Transition state energy barriers compared with the literature

Catalysts	Coupled Intermediate	Energy barrier	Journal
h-Cu/Cu₂O MPs	*NOH + *CO	0.97422 eV	This work
CuWO ₄	*NO ₂ +*CO	0.87 eV	12
C+Fe ₃ O ₄	*CO+*NH ₂	0.79 eV	13
ZnMn-N,Cl	*CO+*N ₂	0.67 eV	14
Te-Pd	*CO+*NH ₂	0.92 eV	4

Supplementary Table 3. Rate-determining step energy barriers compared with the literature

Catalysts	Rate-determining step	Energy barrier	Journal
h-Cu/Cu₂O MPs	*NH₂CO + *NO₂→*NH₂CO +*NO₂H	0.89 eV	This work
CuWO ₄	*NO ₂ +*CO ₂ →*NO ₂ +*COOH	0.93 eV	12
S-In(OH) ₃	*CO ₂ NH ₂ →*COOHNH ₂	1.58 eV	6
CuPd (111)	*NO → *HNO	0.74 eV	15
Vo-InOOH	*CO ₂ NH ₂ →*COOHNH ₂	1.04 eV	16

Supplementary Table 4. EXAFS fitting results at Cu K-edge for h-Cu/Cu₂O MPs.

	shell	CN	R(Å)	σ ²	ΔE ₀	R factor
Cu foil	Cu-Cu	12	2.54±0.01	0.0090	5.4±0.5	0.0025
h-Cu/Cu ₂ O MPs	Cu-O	0.8±0.1	1.84±0.01	0.0016		
	Cu-Cu	5.4±0.3	2.57±0.01	0.0108	8.7±1.5	0.0099
	Cu-O1	5.9±1.2	3.47±0.03	0.0101		
Cu ₂ O	Cu-O	1.8±0.1	1.86±0.01	0.0048		
	Cu-Cu	6.6±0.5	3.01±0.01	0.0192	6.3±0.8	0.0058
	Cu-O1	4.7±0.8	3.50±0.03	0.0168		

Supplementary References:

- 1 Chen, C. *et al.* Coupling N₂ and CO₂ in H₂O to synthesize urea under ambient conditions. *Nat. Chem.* **12**, 717-724 (2020).
- 2 Yuan, M. *et al.* Unveiling Electrochemical Urea Synthesis by Co - Activation of CO₂ and N₂ with Mott–Schottky Heterostructure Catalysts. *Angew. Chem. Int. Ed.* **60**, 10910-10918 (2021).
- 3 Yuan, M. *et al.* Electrochemical C–N coupling with perovskite hybrids toward efficient urea synthesis. *Chem. Sci.* **12**, 6048-6058 (2021).
- 4 Feng, Y. *et al.* Te-Doped Pd Nanocrystal for Electrochemical Urea Production by Efficiently Coupling Carbon Dioxide Reduction with Nitrite Reduction. *Nano Lett.* **20**, 8282-8289 (2020).
- 5 Zhu, X., Zhou, X., Jing, Y. & Li, Y. Electrochemical synthesis of urea on MBenes. *Nat. Commun.* **12**, 4080 (2021).
- 6 Lv, C. *et al.* Selective electrocatalytic synthesis of urea with nitrate and carbon dioxide. *Nat. Sustain.* **4**, 868-876 (2021).
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