Supplementary Information

Phosphate Tuned Copper Electrodeposition and Promoted Formic Acid Selectivity for Carbon Dioxide Reduction

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Table S1.	The analyzed	condition	for formic	acid test	using HPLC.

Analytical conditions for formic acid			
Equipment	Agilent 1260 HPLC		
Column	Alltech OA-1000 organic acid column (ID: 300 mm × 6.5 mm, particle size: 9 μm)		
Injection volume	20 μL		
Mobile phase	5 mM H ₂ SO ₄		
Flow rate	0.6 mL/min		
Temperature	55 °C		
Detector	VWD (210 nm)		
Analysis time	30 min		



Figure S1. HPLC peaks and calibration curve of formic acid in 15 % v/v electrolyte (0.1 M tetrabutylammonium tetrafluoroborate in acetonitrile) in DI water.



Figure S2. (a) XRD pattern of precipitate from Cu and phosphate with blue color (solid line), and PDF 00-001-0054 or 00-022-0548 of copper phosphate hydrate $Cu_3(PO_4)_2 \cdot 3H_2O$ (dash line). (b) ATR-FTIR of blue precipitate from Cu and phosphate, copper phosphate hydrate $Cu_3(PO_4)_2 \cdot 3H_2O$.



Figure S3. (a) SEM of Cu crystals deposited in 0.02 M CuSO₄ at -0.8 V. (b) SEM of Cu

crystals deposited in 0.01 M CuSO₄ at -0.6 V.



Figure S4. The deposited Cu micro-nano structures in the absence and presence of phosphate on FTO substrates.



Figure S5. XRD patterns of Cu crystals deposited on FTO i) substrate, at ii) -0.1 V, iii) -0.15 V, iv) -0.2 V, v) -0.25 V and vi) -0.3 V in 0.02 M CuSO₄ with 10 mM phosphate.

According to the XRD pattern, metallic Cu peak at 2θ =43.3⁰, 50.5⁰, 74.3⁰ corresponded to Cu (111), Cu (200) and Cu (220) respectively. Then the lattice mismatch calculated via equation could be obtained, 0.13, 0.31, 0.86 of Cu (111), Cu (200) and Cu (220) for FTO substrate (37.9⁰) respectively.

$$\delta = \frac{\sin \theta_1 - \sin \theta_2}{\sin \theta_2}$$

 δ : The lattice mismatch between deposited thin film and substrate

 θ_1 and θ_2 : The diffraction angle of the prominent diffraction peak for the deposited thin film and substrate respectively.

References	Cu(II) concentration (M, mol/L)	The diffusion coefficient $D_{Cu(II)}$
	0.02M	$6.9 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$
J. Electrochem. Soc. 1996, 143, 1248.	0.01 M	$7.2 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$
$D_{Cu(II)} = \left\{ (7.8 \pm 0.25) - (6.34 \pm 1.03) [Cu(II)]^{\frac{1}{2}} \right\} \times 10^{-6} \ cm$	0.0001M	$7.7 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$
	0M	7.8×10 ⁻⁶ cm ² ·s ⁻¹
	0.02M	5.18×10 ⁻⁶ cm ² ·s ⁻¹
J. Electrochem. Soc. 1989, 136, 125. $D_{Cu(II)} = \{6.33 + 2.69 log Cu(II) + 1.62 log^2 Cu(II) + 0.256 log^2 Cu(II) \}$	0.01M	$5.38 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$
	0.0001M	5.11×10 ⁻⁶ cm ² ·s ⁻¹

Table S2. The influence of Cu(II) concentration on the diffusion coefficient.



Figure S6. (a) FTO; (b) FTO electrolysis in CO₂-saturated acetonitrile at -1.25 V versus

NHE for 1 h; (c) FTO electrolysis in CO₂-saturated acetonitrile at -1.45 V versus NHE for 1 h.



Figure S7. The recorded I-t curves for CO_2 reduction during electrolysis at -1.45 V vs. NHE for 1 h.



Figure S8. (a) HPLC results for HCOOH test; (b) GC results for CO and H₂ test.

Electrocatalysts	Electrolyte	FE for major products	References
Phosphate modifed 3D Cu		81%HCOOH, 10%CO(-1.45V vs. NHE)	This work
Cu foil	MeCN	33%HCOOH, 56%CO(-1.45V vs. NHE)	
	0.1M KHCO3	CO and HCOO ⁻ as main products (> -1.2 V vs. NHE); Hydrocarbons and alcohols are favaroubly produced (< -1.3 V vs. NHE)	
Cu sheet	0.1M KHCO ₃	29%CH4, 30%C2H4, 7%EtOH, 9%HCOO ⁻ , 11%H2 (-1.41V vs. NHE)	"Formation of hydrocarbons in the electrochemical reduction of carbon dioxide at a copper electrode in aqueous solution".
	0.1M KClO ₄	10%CH4, 48%C2H4, 16%EtOH, 9%HCOO ⁻ , 7%H2 (-1.44V vs. NHE)	Chem. Soc. Fa raday Trans. I, 1989, 85, 2309.
	0.1M K ₂ HPO ₄	17%CH4, 5%HCOO ⁻ , 72%H ₂ (-1.23V vs. NHE)	
Cu, Cu ₂ O, and [Cu(cyclam)](ClO ₄) ₂ complex	DMF/H ₂ O (97:3 v/v)	90%HCOOH,10%H2 (-2.0V vs. Fc+/Fc)	"From molecular copper complexes to composite electrocatalytic materials for selective reduction of CO ₂ to formic acid". J. Mater. Chem. A, 2015, 3, 3901.
Cu foil	MeCN Propylene carbonate	CO as major product, neither CH4 nor C2H4 was produced(-2.6V vs. Ag/AgCl 0.01M LiCl in MeCN or propylene carbonate)	"Selective formation of formic acid, oxalic acid and carbon monoxide by electrochemical reduction of carbon dioxide". Bull. Chem. Soc. Jpn. 1987, 60, 2517.
Cu oxidation/reduction cylcled in the presence of halide anions		15%C ₂ H ₄ , 8%C ₂ H ₅ OH, 60%H ₂ (-1.0V vs. RHE)	"CO ₂ electroreduction with enhanced ethylene and ethanol
Cu foil	0.1M KHCO ₃	10%C ₂ H ₄ , 3%C ₂ H ₅ OH, 5%CH ₄ , 67%H ₂ (-1.0V vs. RHE)	ChemElectroChem, 2016, 3, 1012.
Cu(II)-PPh ₃	MeCN	HCOOH, (COOH)2, and CO as main products	"Cyclic voltammetric study on carbon dioxide reduction using Cu complexes as electrocatalysts". J. Electroanal. Chem. 1992, 332, 303.
Cu foil	MeCN	CO, carbonate, bicarbonate as main products	"In situ spectroscopic study of CO ₂ electroreduction at copper electrodes in acetonitrile". ACS Catal. 2016, 6, 2382.
Cu ₂ O/Cu	0.1M KCl	22%C ₂ H ₄ , 24%C ₂ H ₅ OH, 9%C ₃ H ₇ OH, H ₂ (-1.0V vs. RHE) 12%C ₂ H ₄ , 7%CH ₄ , 32%HCOO ⁻ , H ₂ (-1.6V vs. RHE)	"Electrocatalytic production of C3-C4 compounds by conversion of CO ₂ on a chloride-induced Bi-phasic Cu ₂ O-Cu catalyst". Angew. Chem. Int. Ed. 2015, 54, 14701.
Annealed Cu foil		38%HCOOH, 30%CO, H ₂ (-0.58V vs. RHE)	"CO2 reduction at low overpotential on Cu electrodes resulting
Polycrystalline Cu foil	0.1M KHCO ₃	30%HCOOH, 15%CO, H ₂ (-0.78V vs. RHE)	from the reduction of thick Cu ₂ O Films". J. Am. Chem. Soc. 2012, 134, 7231.
Amino acid modified Cu nanowire	0.1M KHCO ₃	13%C ₂ H ₄ , 21%C ₂ H ₆ , 52H ₂ %(-1.9V vs. RHE)	"Amino acid modified copper electrodes for the enhanced selective electroreduction of carbon dioxide towards

Table S3. Summary of Cu-based electrocatalysts for CO₂ reduction.

Cu nanowire	-	6%C ₂ H ₄ , 12%C ₂ H ₆ , 76H ₂ %(-1.9V vs. RHE)	hydrocarbons". Energy Environ. Sci., 2016, 9, 1687.	
Cu nanocube (44nm)		41%C2H4, 20%CH4, 20%H2(-1.1V vs. RHE)		
Cu nanocube (24nm)	0.1M KHCO ₃	9%C ₂ H ₄ , 14%CH ₄ , 15%HCOO ⁻ , 57%H ₂ (-1.1V vs. RHE)	electrochemical CO ₂ Reduction". Angew. Chem. Int. Ed. 2016, $55, 5790$	
Cu foil		20%C2H4, 20%CH4, 7%HCOO ⁻ , 44%H2(-1.1V vs. RHE)	55, 5789.	
Cu nanofoam	0.1M KHCO2	26% HCOOH, 8% HCOO ⁻ , 60% H ₂ (-1.1V vs. Ag/AgCl)	"Electrochemical reduction of CO2 at copper nanofoams". ACS	
Cu foil	0.11 KIICO3	3%HCOOH, 95%H2(-1.1V vs. Ag/AgCl)	Catal. 2014, 4, 3091.	
Cu nanowire (8.1 µm)		17%C ₂ H ₄ , 18%HCOOH, 40%H ₂ (-1.1V vs. RHE)	"Controllable hydrocarbon formation from the electrochemical	
Cu foil	0.1M KHCO3	3%C ₂ H ₄ , 12%HCOOH, 80%H ₂ (-1.1V vs. RHE)	Ed. 2016, 55, 6680.	
3D porous hollow fiber Cu	0.1M KHCO ₃	72%CO, 10%HCOOH(-0.4V vs. RHE)	"Three-dimensional porous hollow fibre copper electrodes for efficient and high-rate electrochemical carbon dioxide reduction". Nature Commun. 2016, 7, 10748.	
Cu nanoparticle Cu foil	0.1M KHCO3	CO and H ₂ as major products when size < 15nm 25%CO, 65%H ₂ ((- 1.1V vs. RHE); Larger particles favors hydrocarbon formation 60%CH ₄ , 20%C ₂ H ₄ , 20%H ₂ (-1.1V vs. RHE)	"Particle size effects in the catalytic electroreduction of CO ₂ on Cu nanoparticles". J. Am. Chem. Soc. 2014, 136, 6978.	
	0.1M KHCO ₃	15%CH4, 10%C2H4, 8%CO, 22%HCOO ⁻ , 40%H2(-0.95V vs. RHE)		
Cu foil	0.3M KBr + 0.1M KHCO ₃ 0.3M KI + 0.1M KHCO ₃	5%CH4, 7%C2H4, 27%CO, 18%HCOO ⁻ , 40%H2 (-0.95V vs. RHE)	"Tuning the catalytic activity and selectivity of Cu for CO_2 electroreduction in the presence of halides". ACS Catal. 2016, 2136.	
		41%CH4, 17%C2H4, 5%CO, 10%HCOO ⁻ , 30%H2 (-0.95V vs. RHE)		
Cu nanoparticle		76%CH4, 22%H2(-1.35V vs. RHE)	"Enhanced electrochemical methanation of carbon dioxide with a	
Cu foil	0.1M KHCO3	44%CH4, 35%H2(-1.35V vs. RHE)	136, 13319.	
Molecular copper-porphyrin complex	0.5M KHCO3	27%CH4, 17%C2H4, 10%CO, H2(-1.0V vs. RHE)	"Electrochemical CO ₂ reduction to hydrocarbons on a heterogeneous molecular Cu catalyst in aqueous solution". J. Am. Chem. Soc. 2016,	
Cu-In alloy	0.1M KHCO3	90%CO(-0.5V vs. RHE)	"Highly selective copper–indium bimetallic electrocatalyst for the electrochemical reduction of aqueous CO ₂ to CO". Angew. Chem. 2015, 127, 2174.	



Figure S9. CVs taken over a range of scan rates in a potential window where only double layer capacitance is relevant and current due to double-layer capacitance plotted against CV scan rate.

Electrode	Capatitance (mF)	Sourface Roughness Factor
Cu foil	0.05	1
Cu 5mM -0.25V	0.2	4
Cu 5mM -0.6V	1.11	22.2
Cu 10mM -0.6V	1.05	21
Cu 25mM -0.6V	0.91	18.2



Figure S10. (a) SEM and (b) EDS mapping for the Cu prepared in the presence of phosphate.



Figure S11. SEM images of Cu after CO_2 reaction (a) and after stripping off surface phosphate (b). The Cu was deposited in the presence of 10 mM phosphate at -0.6 V.



Figure S12. (a) Cyclic voltammetry cycling for the regeneration of the phosphate ligands onto the Cu surface after phosphate stripping (0.1 M KH₂PO₄/K₂HPO₄ buffer solution with pH=7, scan rate 20 mV/s) and (b) SEM image of Cu (after phosphate regeneration) after CO₂ reduction. The Cu was deposited in the presence of 10 mM phosphate at -0.6 V.



Figure S13. Possible molecular geometries of monodentate complexes (a) and bidentate complexes (b) for surface phosphate ligands.



Figure S14. The electrochemical hydrogenation of nitrobenzene to phenyl hydroxyl amine and aniline in Argon-saturated "wet" acetonitrile electrolyte.



Figure S15. Liner sweep voltammetry (LSV) of the electrode in CO₂-saturated electrolyte and corresponding Tafel plot (inset).

How to convert the potential versus reference electrode in the present system to the potential versus NHE:

Step 1: Test the redox potential of Fc+/Fc with the non-aqueous Ag/Ag^+ reference electrode (10 mM $AgNO_3$ in acetonitrile with 0.1 M tetrabutylammonium tetrafluoroborate) in the electrolyte used in CO₂ reduction:



Step 2: The $E_{1/2}$ of Fc+/Fc couple is 0.40 V vs. NHE in acetonitrile. So in the present system, the reference electrode used is 0.50 V vs. NHE. This value is similar with a report recently (J. Am. Chem. Soc. 2012, 134, 5500-5503) in acetonitrile system, where a Ag/AgNO₃ reference electrode (10 mM AgNO₃, 0.1 M nBu₄NPF₆ in acetonitrile) is 0.55 V vs. NHE. Then if apply a potential of -2.0 V versus Ag/Ag⁺ (after IR correction), then it is -1.45 V vs. NHE.