# **Electronic Supplementary Information**

# Design of Cu (I)/C-doped boron nitride electrocatalyst for efficient conversion of $\mathrm{CO}_2$ into acetic acid

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# **Experimental Section**

Materials. All chemicals were purchased from commercial sources if not mentioned otherwise. Copper (II) sulfate anhydrous, 4,4'-bromobiphenyl (98 % purity), 2,6dibromopyridine (98 % purity), boron oxide (99.98 % purity), D-(+)-glucose anhydrous (99 % purity), lithium iodide (99 % purity), lithium bromide (99 % purity), potassium iodide (99.9 % purity), tin (IV) iodide (99.998 % purity), tetraethylammonium tetrafluoroborate (TEABF<sub>4</sub>, purity > 98%), tetraethylammonium hexafluorophosphate (TEAPF<sub>6</sub>, purity > 98%), Toray Carbon Paper (CP, TGP-H-60, 19×19 cm), Nafion D-521 dispersion (5 % w/w in water and 1-propanol,  $\geq 0.92$  meg/g exchange capacity) and Nafion N-117 membrane (0.180 mm thick,  $\geq 0.90$  meg/g exchange capacity) were purchased from Alfa Aesar China Co., Ltd. 2,2'-Dipyridylamine (purity > 99%), lithium chloride (purity >98%). and tetraethylammonium perchlorate (TEAClO<sub>4</sub>, purity > 98%) were purchased from TCI. Urea (99 % purity), potassium hydroxide (85 % purity) and potassium carbonate anhydrous (99 % purity) were purchased from Sinopharm Chem. Reagent Co. Ltd. 1-Ethyl-3methylimidazolium tetrafluoroborate ([Emim]BF<sub>4</sub>, purity 99%), 1-ethyl-3->methylimidazolium trifluoromethanesulfonate ([Emim]TfO, purity > 99%), 1-ethyl-3methylimidazolium chloride ([Emim]Cl, purity > 99%), 1-ethyl-3-methylimidazolium thiocyanate ([Emim]SCN, purity > 99%), and 1-Ethyl-3-methylimidazolium nitrate ( $[Emim]NO_3$ , purity > 99%) were purchased from the Centre of Green Chemistry and Catalysis, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences. CO2 (Beijing Beiwen Gas Chemical Industry Co., Ltd., research grade) had a 99.999 % purity and used as received.

**Synthesis of C-doped BN Nanosheet (BN-C<sub>x</sub>).** The BN-C<sub>x</sub> samples were synthesized by solid-state reaction method, which was similar to that reported by other authors. <sup>S1-S2</sup> In the experiment, 1 g boron oxide, 2 g urea and a certain amount of D-(+)-glucose were ground thoroughly in an agate mortar for 2 h. The resulting mixed precursors were heated in the tube furnace at 10 °C min<sup>-1</sup> in argon (Ar) media to 1100 °C. Then they were held at 1100 °C for 10 h. After that, the products were washed with 0.1 M HCl and deionized water, and then dried at 110 °C for 12 h. A series of BN-C<sub>x</sub> were obtained, where x is the percentage weight content of glucose to boron oxide. The bulk BN sample was synthesized according to the same procedure without the addition of glucose.

Synthesis of *N*,*N*,*N'*,*N'*-tetra(2-pyridyl)-biphenyl-4,4'-diamine (Tpbpa). Tpbpa was synthesized according to the procedures reported.<sup>S3-S4</sup> In the experiment, a mixture of 2,2'-dipyridylamine (3.42 g, 0.02 mol), 4,4'-bromobiphenyl (3.74 g, 0.012 mol), potassium hydroxide (1.46g, 0.026 mol) and 0.104 g copper (II) sulfate anhydrous were added in a flask. The reaction mixture was stirred and heated to 180 °C for 8 h under N<sub>2</sub>. The reaction was monitored by TLC. Then the mixture was cooled to ambient temperature, and dissolved into dichloromethane and distilled water. The aqueous phase was discarded and the organic phase was washed with distilled water to neutral pH and then dried with MgSO<sub>4</sub>. The product was isolated by using chromatographic column with ethanol as the eluant. <sup>1</sup>H NMR ( $\delta$ , ppm; CDCl<sub>3</sub>, 298 K): 8.39 (1H, d), 7.61 (1H, dd), 7.26 (1H, d), 7.06 (1H, d), 6.97 (1H, dd).

**Synthesis of** *N*,*N*,*N*',*N*'-tetra(2-pyridyl)-2,6-pyridinediamine (Tppda). Tppda was synthesized using the method reported.<sup>S5</sup> In the experiment, a mixture of 2,2'-dipyridylamine (2.57 g, 0.015 mol), 2,6-dibromopyridine (1.19 g, 0.005 mol), potassium carbonate anhydrous

(3.45g, 0.025 mol) and 0.19 g copper (II) sulfate anhydrous were added in a flask. The reaction mixture was stirred and heated to 200 °C for 8 h under N<sub>2</sub>. The reaction was monitored by TLC. Then the mixture was cooled to ambient temperature, and dissolved into dichloromethane and distilled water. The aqueous phase was discarded and the organic phase was washed with distilled water to neutral pH and then dried with MgSO<sub>4</sub>. The product was isolated by using chromatographic column with ethanol as the eluant. <sup>1</sup>H NMR ( $\delta$ , ppm; CDCl<sub>3</sub>, 298 K): 8.31 (4H, d), 7.50 (5H, t), 7.07 (4H, d), 6.95 (4H, t), 6.69 (2H, d).

Synthesis of N-based organometallic Cu 1 and Cu 2 catalysts. In the process of synthesis of Cu-Tppda (Cu 1), 0.1 mmol Tpbpa, 0.3 mmol CuI and 8 mL distilled water were put into a Teflon-lined reactor and heated at 180 °C for 72 h. The resulting solid was washed with distilled water and ethanol and dried at 50 °C under vacuum to give yellow crystals, with a formula of  $C_{25}H_{19}Cu_2I_2N_7$ .<sup>S4</sup> IR (cm<sup>-1</sup>): 1662(vs), 1609(vs), 1541(m), 1499(m), 1452(m), 1195(w), 1028(w), 1002(w), 842(w), 762(w).

Cu-Tpbpa (Cu 2) was obtained from the mixture of 0.1 mmol Tpbpa, 0.3 mmol CuI and 8 mL distilled water according to the same procedure described above for the synthesis of Cu 1. The yellow crystals with a formula of  $C_{32}H_{24}Cu_2I_2N_6$  was obtained.<sup>S4</sup> IR (cm<sup>-1</sup>): 1582(s), 1561(m), 1472(m), 1460(vs), 1448(vs), 1426(s), 1323(m), 1302(m), 1266(m), 1162(w), 771(m), 762(m).

**Material characterizations.** Powder X-ray diffraction (XRD) patterns were collected on the X-ray diffractometer (Model D/MAX2500, Rigaka) with Cu-Kα radiation. X-ray photoelectron spectroscopy (XPS) analysis was performed on the Thermo Scientific ESCALab 250Xi using 200 W monochromatic Al Kα radiation. The 500 µm X-ray spot was

used for XPS analysis. The base pressure in the analysis chamber was about  $3 \times 10^{-10}$  mbar. Typically the hydrocarbon C1s line at 284.8 eV from adventitious carbon was used for energy referencing. Fourier transform infrared (FT-IR) spectra of BN-C<sub>x</sub> samples were obtained on a Bruker Tensor 27 FT-IR spectrometer with KBr as the diluents. Acquisition was accomplished using an accumulation rate of 32 scans at a resolution of 4 cm<sup>-1</sup> at 25 °C in the spectral range of 400 to 4600 cm<sup>-1</sup>. Solid-state <sup>13</sup>C MAS NMR experiments were conducted on a Bruker Avance III 400M spectrometer. The nitrogen adsorption/desorption isotherms of BN-Cx nanosheets were determined using a Quadrasorb SI-MP system. The microstructures of BN-Cx nanosheets were studied using the HITACHI SU8020 SEM and JEOL-2100F TEM operated at 200 kV. Photoluminescence analyses were performed on a Perkin-Elmer LS 55 luminescence spectrometer.

**Preparation of N-based Organometallic Cu (I)/BN-Cx electrodes.** 20 mg of **Cu 1** or **Cu 2** was dispersed in acetone. 5 mg of BN-Cx was added into the mixture, and the dispersion was sonicated for 30 min and was stabilized overnight. Then the sample was centrifuged, followed by washing with distilled water and freeze drying. To investigate the role of BN-Cx, we also prepared the **Cu 1** or **Cu 2**/carbon black (C, Vulcan XC 72) catalysts.

To prepare the N-based Organometallic Cu (I)/BN-Cx electrodes, 1 mg Cu 1 or Cu 2/BN-Cx was suspended in 1 mL ethanol with 20  $\mu$ L Nafion D-521 dispersion (5 wt%) to form a homogeneous ink assisted by ultrasound. Then, 200  $\mu$ L of the ink was spread onto the CP (1 cm  $\times$  1 cm) surface and then dried under room temperature. The loading of catalyst was 0.2 mg cm<sup>-2</sup>.

To recovery Cu 1 complex from a used electrode after electrolysis, the complex in the electrode was dissolved into  $CH_2Cl_2$  with the aid of ultrasound. After centrifugation, the complex solution was collected and the solvent was removed by rotary evaporation, and mass of the recovered complex was determined. The same procedures were used in the blank experiments to recover the complex from the virgin electrodes.

Electrochemical measurements and product analysis. The electrolysis experiments were conducted at 25 °C in a typical H-type cell that was similar to that used in our previous works for CO<sub>2</sub> electrochemical reduction.<sup>S6</sup> The Toray CP with the catalyst layer was cut into a piece of 1 cm  $\times$  1 cm and used as the working electrode. The Pt wire and Ag/Ag<sup>+</sup> (0.01 M AgNO<sub>3</sub> in 0.1 M TBAP-MeCN) electrode were used as the counter electrode and reference electrode, respectively. The cathode and anode compartments were separated through a Nafion 117 proton exchange membrane. A solution of IL (e.g. [Emim]BF<sub>4</sub>) with or without LiI was used as cathode electrolyte. H<sub>2</sub>SO<sub>4</sub> aqueous solution (0.5 M) was used as anodic electrolyte. Linear sweep voltammetry (LSV) measurements were first carried out. The electrolyte was bubbled with  $N_2 \mbox{ or } CO_2$  for at least 30 min to form  $N_2 \mbox{ or } CO_2$  saturated solution. The LSV measurement in gas-saturated electrolyte was conducted in the potential range of 0 to -2.5 V vs. Ag/Ag<sup>+</sup> (0.01 M AgNO<sub>3</sub> in 0.1 M TBAP-MeCN) at a sweep rate of 20 mV/s. Slight magnetic stirring was applied in the process. Electrochemical reduction of methanol was conducted over Cu (I)/BN-C<sub>30</sub> electrode at -2.2 V vs Ag/Ag<sup>+</sup> in [Emim]BF<sub>4</sub> aqueous solution with 25 mol% [Emim]BF<sub>4</sub> and 75 mol% water, in the presence of 0.01 M LiI with 1 atm CO<sub>2</sub> at ambient temperature with 5 h electrolysis.

Under the continuous stirring, CO<sub>2</sub> was bubbled into the catholyte electrolyte (2 mL/min) for 60 min before electrolysis. After that, potentiostatic electrochemical reduction of CO<sub>2</sub> was carried out with CO<sub>2</sub> bubbling (2 mL/min). The gaseous product was collected and analyzed by gas chromatography (GC, HP 4890D), which was equipped with FID and TCD detectors using helium as the internal standard. The liquid products were analyzed by <sup>1</sup>H NMR (Bruker Avance III 400 HD spectrometer) in DMSO-d<sub>6</sub> with TMS as an internal standard. The amount of acetic acid was 15.74 mg (in 30 mL electrolyte) in aqueous solution of 25 mol% [Emim]BF<sub>4</sub> and 75 mol% water in the presence of 0.01 M LiI at -2.2 V vs Ag/Ag<sup>+</sup> after an electrolysis time of five hours. <sup>1</sup>H NMR and <sup>13</sup>C NMR (decoupling) measurements of the <sup>12</sup>C and <sup>13</sup>C products were performed on a Bruker Avance 600 MHz spectrometer. The samples were measured using DMSO-d<sub>6</sub> as a lock solution and TMS as an internal standard.

**Tafel analysis.** The partial current densities for acetic acid under different potentials were measured and the equilibrium potential was obtained by extrapolation method. The activation overpotential was obtained from the difference between the equilibrium potential and the catalytic onset potential.<sup>S7</sup> Multiple electrolysis experiments were then performed at each potential to obtain the average current density versus overpotential data in the H-type electrolysis cell. Tafel plots were constructed from these data.

**IR spectroscopy study.** The species produced in the catholyte electrolyte during electrocatalytic reduction of  $CO_2$  was analyzed by IR spectroscopy with a Bruker Tensor 27 spectrometer. The IR spectrometer was equipped with a thin-layer IR cell and the IR radiation passed through a  $CaF_2$  disc window. Acquisition was accomplished using an

accumulation rate of 32 scans at a resolution of 4 cm<sup>-1</sup> at 25 °C in the spectral range of 400 to 4600 cm<sup>-1</sup>. Triplicates of each sample were measured.

#### Calculations of Faradaic efficiencies of Gasous and liquid products

## Gasous products: S8

FE = moles of products per second / theoretical moles equivalent per second

From the GC peak areas and calibration curves for the TCD detector, it can obtain the V % of  $H_2$ , and since the flow rate of the gas is controlled, the amount of moles of  $H_2$  per second can be calculated. It can also directly convert current density to theoretical moles equivalent per second since production of  $H_2$  proceeds via 2-electron paths.

# liquid products:<sup>S9</sup>

In the present work,  $[Emim]BF_4$  is stable. In NMR spectra, the C(2)-H on the cation of IL can be used as the internal standard. The relative peak area of acetic acid/C(2)-H, formic acid/C(2)-Hand methanol/C(2)-H can be calculated. Because the concentration of IL can be given, we can obtain each of product concentration (C) in the electrolyte.

The number of electrons required to produce liquid product during the entire CO<sub>2</sub> electro-reduction reaction is,

$$N = C \times V \times N_A \times ne$$

(V: the volume of catholyte; NA: Avogadro constant; n: transfer electron number)

We can obtain the Q<sub>total</sub> from the chronoamperogram and the total number of electrons measured,

$$N_{total} = \frac{Q_{total}}{e}$$

The Faradaic efficiency of each liquid product is,

$$FE = \frac{N}{N_{total}} \times 100\%$$



Scheme S1. The molecular structures for the ligands of Tppda and Tpbpa as well as the Cu complexes.



Fig. S1. XPS spectra of N 1s (A) and C 1s (B) orbits of  $BN-C_{30}$ .



Fig. S2. Characterization resultsof  $BN-C_{10}$ . A) SEM image; B) HR-TEM image; C) Elemental mappings (scale bar, 10 nm); XPS spectrum of B 1s (D), N 1s (E) and C 1s (F) orbits; G) Powder XRD pattern; H) <sup>13</sup>C solid-state NMR spectrum.



**Fig. S3.** Characterization results of  $BN-C_{50}$ . A) SEM image; B) HR-TEM image; C) Elemental mappings (scale bar, 10 nm); XPS spectrum of B 1s (D), N 1s (E) and C 1s (F) orbits; G) Powder XRD pattern; H) <sup>13</sup>C solid-state NMR spectrum.



**Fig. S4.** Characterization results of BN-C<sub>70</sub>. A) SEM image; B) HR-TEM image; C) Elemental mappings (scale bar, 10 nm); XPS spectrum of B 1s (D), N 1s (E) and C 1s (F) orbits; G) Powder XRD pattern; H) <sup>13</sup>C solid-state NMR spectrum.



Fig. S5. Characterization results of BN. A) SEM image; B) HR-TEM image; C) Powder XRD pattern.



**Fig. S6.** FT-IR spectra of BN- $C_x$  samples. Two bands observed at 1385 cm<sup>-1</sup> (a) and 782 cm<sup>-1</sup> (b) correpond to the in-plan B-N transverse stretching vibration and the out-of-plan B-N-B bending vibration, respectively.<sup>S1,S10</sup>



Fig. S7. LSV curves on Cu  $1/BN-C_{30}$  (A) and Cu  $2/BN-C_{30}$  electrodes (B) in N<sub>2</sub>or CO<sub>2</sub>saturated [Emim]BF<sub>4</sub> aqueous solution with 25 mol% [Emim]BF<sub>4</sub> and 75 mol% water in the presence of 0.01 M LiI.



Fig. S8. <sup>1</sup>HNMR spectra of a) raw electrolyte ([Emim]BF<sub>4</sub> aqueous solution with 25 mol% [Emim]BF<sub>4</sub> and 75 mol% water in the presence of 0.01 M LiI) and b) N<sub>2</sub>-saturated electrolyte after an electrolysis time of 5 h at -2.2 V vs Ag/Ag<sup>+</sup>.



**Fig. S9.** The confirmation of acetic acid (acetate) (A), methanol (B) and formic acid (formate) (C) from CO<sub>2</sub> reduction by the peak splitting observed in <sup>1</sup>H NMR (A-C) as well as <sup>13</sup>C NMR (D: a. raw electrolyte, b. using <sup>12</sup>CO<sub>2</sub>, c. using <sup>13</sup>CO<sub>2</sub>) over **Cu 1**/BN-C<sub>30</sub> electrode in CO<sub>2</sub>-saturated [Emim]BF<sub>4</sub> aqueous solution with 25 mol% [Emim]BF<sub>4</sub> and 75 mol% water in the presence of 0.01 M LiI at -2.2 V vs Ag/Ag<sup>+</sup> with an electrolysis time of 3 h.



Fig. S10. Time curves of the electrolysis processes on Cu  $1/BN-C_{30}$  and Cu  $2/BN-C_{30}$  electrodes in CO<sub>2</sub>-saturated [Emim]BF<sub>4</sub> aqueous solution with 25 mol% [Emim]BF<sub>4</sub> and 75 mol% water in the presence of 0.01 M LiI at -2.2 V vs Ag/Ag<sup>+</sup>.



Fig. S11. Emission spectra in the solid state of Tppda (black curve) as well as Cu 1 before (red curve) and after (blue curve) electrolysis at the room temperature.



Fig. S12. Current density and Faradaic efficiency of the products at different applied potentials over (A) Cu 1/C and (B) Cu 2/C electrodes in  $[\text{Emim}]BF_4$  aqueous solution with 25 mol%  $[\text{Emim}]BF_4$  and 75 mol% water in the presence of 0.01 M LiI at 1 atm CO<sub>2</sub> pressure and ambient temperature with 5 h electrolysis. Curve (a)is the current density; curves (b)-(e) are Faradaic efficiency of b) acetic acid, c) methanol, d) formic acid, and e) H<sub>2</sub> production.



Fig. S13. (A) Current density and (B) Faradaic efficiency of formic acid over  $BN-C_x$  electrodes at different applied potentials in [Emim] $BF_4$  aqueous solution with 25 mol% [Emim] $BF_4$  and 75 mol% water in the presence of 0.01 M LiI at 1 atm CO<sub>2</sub> pressure and ambient temperature with 5 h electrolysis.



**Fig. S14.** Current density and Faradaic efficiency of the products at different applied potentials over (**A**) **Cu 1**/BN-C<sub>10</sub> and (**B**) **Cu 2**/BN-C<sub>10</sub> electrodes in [Emim]BF<sub>4</sub> aqueous solution with 25 mol% [Emim]BF<sub>4</sub> and 75 mol% water in the presence of 0.01 M LiI at 1 atm  $CO_2$  pressure and ambient temperature with 5 h electrolysis. Curve (a) is the current density; curves (b)-(e) are Faradaic efficiency of b) acetic acid, c) methanol, d) formic acid, and e) H<sub>2</sub> production.



Fig. S15. Current density and Faradaic efficiency of the products at different applied potentials over (A) Cu 1/BN-C<sub>50</sub> and (B) Cu 2/BN-C<sub>50</sub> electrodes in [Emim]BF<sub>4</sub> aqueous solution with 25 mol% [Emim]BF<sub>4</sub> and 75 mol% water in the presence of 0.01 M LiI at 1 atm CO<sub>2</sub> pressure and ambient temperature with 5 h electrolysis. Curve (a) is the current density; curves (b)-(e) are Faradaic efficiency of b) acetic acid, c) methanol, d) formic acid, and e) H<sub>2</sub> production.



**Fig. S16.** Current density and Faradaic efficiency of the products at different applied potentials over (**A**) **Cu 1**/BN-C<sub>70</sub> and (**B**) **Cu 2**/BN-C<sub>70</sub> electrodes in [Emim]BF<sub>4</sub> aqueous solution with 25 mol% [Emim]BF<sub>4</sub> and 75 mol% water in the presence of 0.01 M LiI at 1 atm  $CO_2$  pressure and ambient temperature with 5 h electrolysis. Curve (a) is the current density; curves (b)-(e) are Faradaic efficiency of b) acetic acid, c) methanol, d) formic acid, and e) H<sub>2</sub> production.



Fig. S17. Current density and Faradaic efficiency of the products at different applied potentials over (A) Cu 1/BN-C<sub>30</sub> and (B) Cu 2/BN-C<sub>30</sub> electrodes in [Emim]BF<sub>4</sub> aqueous solution with 25 mol% [Emim]BF<sub>4</sub> and 75 mol% water at 1 atm CO<sub>2</sub> pressure and ambient temperature with 5 h electrolysis. Curve (a) is the current density; curves (b)-(d) are Faradaic efficiency of b) methanol, c) formic acid, and d) H<sub>2</sub> production.



**Fig. S18.** Current densities for acetic acid under different potentials and the equilibrium potential can be obtained by extrapolation method.



**Fig. S19.**A) Faradaic efficiency of the acetic acid at different applied potentials over **Cu**  $1/BN-C_{30}$  electrode (a) and CuI+Tppda ligand/BN-C<sub>30</sub> electrode (b) in [Emim]BF<sub>4</sub> aqueous solution with 25 mol% [Emim]BF<sub>4</sub> and 75 mol% water in the presence of 0.01 M LiI at 1 atm CO<sub>2</sub> pressure and ambient temperature with 5 h electrolysis. B) Faradaic efficiency of the formic acid at different applied potentials over **Cu**  $1/BN-C_{30}$  electrode (a), CuI/BN-C<sub>30</sub> electrode (b), Tppda ligand/BN-C<sub>30</sub> electrode(c), CuI+Tppda ligand/BN-C<sub>30</sub> electrode (d) and BN-C<sub>30</sub> electrode (e) in [Emim]BF<sub>4</sub> aqueous solution with 25 mol% [Emim]BF<sub>4</sub> and 75 mol% water in the presence of 0.01 M LiI at 1 atm CO<sub>2</sub> pressure and ambient temperature solution with 25 mol% electrode (b), Tppda ligand/BN-C<sub>30</sub> electrode(c), CuI+Tppda ligand/BN-C<sub>30</sub> electrode (d) and BN-C<sub>30</sub> electrode (e) in [Emim]BF<sub>4</sub> aqueous solution with 25 mol% [Emim]BF<sub>4</sub> and 75 mol% water in the presence of 0.01 M LiI at 1 atm CO<sub>2</sub> pressure and ambient temperature with 5 h electrolysis.

	Specific surface area / m <sup>2</sup> ·g <sup>-1</sup>	Pore volume / cm <sup>3</sup> ·g <sup>-1</sup>
BN	219	0.16
BN-C <sub>10</sub>	327	0.18
BN-C <sub>30</sub>	342	0.19
BN-C <sub>50</sub>	413	0.24
BN-C <sub>70</sub>	533	0.26

Table S1. The BET surface areas and pore volume of the  $\text{BN-}C_{x}.$ 

	В %	N %	С %	O %
BN-C <sub>10</sub>	46.55	35.47	8.12	9.16
BN-C <sub>30</sub>	41.39	32.51	16.53	9.57
BN-C <sub>50</sub>	32.73	26.06	30.75	10.46
BN-C <sub>70</sub>	26.38	16.18	46.83	10.61

**Table S2.** The surface element composition of the  $BN-C_x$  detected by XPS.

Electrode/	Electrode	Flectrolyte	FF / %	$CD/mA cm^{-2}$	Refs.
electrocatalysts	potential / V	Licenolyte	1 L / /0	CD / IIIA CIII	
<b>Cu 1/BN-C</b> <sub>30</sub>	-2.2 V vs. Ag/Ag <sup>+</sup>	EmimBF <sub>4</sub> (aq)+LiI	80.3	13.9	This work
N-doped nanodiamond/	1.0.1/		77 (		011
Si rod array	-1.0 V vs. RHE	0.5 M NaHCO <sub>3</sub>	//.6	< 3	511
Polyaniline	-0.4 V vs. SHE	Methanol+LiClO <sub>4</sub>	56.1	1.2	S12
Cu wire <sup>a</sup>	-2.1 V vs. Ag/Ag <sup>+</sup>	Methanol+TBABF <sub>4</sub>	23.4	< 8	S13

**Table S3.**Faradaic efficiency (FE) of acetic acid and current density (CD) in  $CO_2$  reduction using various electrodes and electrolytes.

<sup>a</sup>Electrolysis was performed at 40 atm and 20°C.

**Table S4**. Total current densities ( $j_{tot}$ ) and Faradaic efficiencies (FE) for each product over **Cu** 1/BN-C<sub>30</sub> electrode at an applied potential of -2.2 V (vs. Ag/Ag<sup>+</sup>) in CO<sub>2</sub> saturated supporting electrolyte aqueous solution containing 25 mol% supporting electrolyte and 75 mol% water in the presence of 0.01 M LiI with an electrolysis time of 5 h.

Entry	Supporting electrolyte	$j_{\text{tot}}$ / mAcm <sup>-2</sup>	$FE_{acetic \ acid}$ / %	$FE_{methanol}$ / %	FE <sub>formic acid</sub> / %	FE <sub>H2</sub> / %
1	[Emim]BF <sub>4</sub>	13.9	80.3±1.1	2.3±0.8	1.2±0.7	13.4±2.1
2	[Emim]TfO	6.8	62.4±3.2	5.4±0.5	13.8±1.8	14.5±2.5
3	[Emim]Cl	2.5	not detected	not detected	20.5±1.4	77.8±0.9
4	[Emim]SCN	10.6	not detected	12.3±0.4	37.8±0.3	45.2±0.8
5	[Emim]NO <sub>3</sub>	4.8	not detected	not detected	33.4±2.5	65.1±0.9
6	TEABF <sub>4</sub>	6.2	not detected	not detected	42.6±1.6	54.0±2.8
7	TEAPF <sub>6</sub>	7.5	not detected	not detected	38.4±2.0	60.2±3.4
8	TEAClO <sub>4</sub>	4.2	not detected	not detected	36.5±1.7	62.3±2.7

Water mole fraction	pH value <sup>a</sup>
5	5.32
15	4.93
30	4.86
45	3.85
60	3.69
75	3.35
80	3.41
90	3.89
95	4.57

**Table S5.** The pH values of [Emim]BF<sub>4</sub> aqueous solution with different water mole fractions.

a. The pH value measured by METTLER TOLEDO pH meter.

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