Supporting Information

Facet- and Structure-Dependent Catalytic Activity of Cuprous Oxide/Polypyrrole Particles Towards the Efficient Reduction of Carbon

Dioxide to Methanol

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1. Experimental Section

1.1 Materials

Catechin hydrate (98%) was purchased from Sigma Aldrich (St. Louis, MO, USA). Copper (II) nitrate trihydrate (Cu (NO₃)₂. 3H₂O, 80%) was obtained from Showa (Tokyo, Japan). Pyrrole (99.5 %) and potassium chloride (99%) were obtained from Acros Organics (Geel, Belgium). Sodium hydroxide pellets were purchased from Macron Fine Chemicals (PA, USA). Sodium sulfate, anhydrous (Na₂SO₄, 99%) was procured from Hayasi Pure Chemicals (Osaka, Japan). Potassium ferricyanide K₃[Fe(CN)₆] (99%) was obtained from Showa (Tokyo, Japan). KHCO₃ (99 %) was purchased from Merck (E. Merck, Germany). Tetrabutylammonium hexafluorophosphate (TBAPF₆) was procured from Tokyo Chemical Industry (Tokyo, Japan). Cu₂O particles (<5 μ m) and β-D-glucose (>99.8wt%) were purchased from Sigma Aldrich (St. Louis, MO, USA). LT paper (A4 size, 6 x 2.5 cm with GSM of 247.5 g m⁻²) was purchased from a stationary shop near National Taiwan University, Taiwan. Ultrapure water was obtained using a Milli-Q ultrapure (18.2 MΩ cm) system.

1.2 Instrumentation

1.2.1 Characterization of catalysts

A Raman spectroscopic system (Dongwoo Optron, KyungGiDo, Korea) with a diodepumped solid-state laser at 532 nm (100 mW) as the excitation source was used to analyze the $Cu_2O_{(OL-MH)}$ /Ppy samples coated on silica wafers at an accumulation time of 300 s. Aliquots of the aqueous growth solutions were taken at different reaction intervals of preparation of $Cu_2O_{(OL-MH)}$ /Ppy particles. The UV-vis absorption spectra of aqueous solutions were then recorded using a Cintra 10e double-beam UV-vis spectrophotometer (GBC Scientific Equipment, Victoria, Australia). Zahner EIM6ex impedance analyzer (Kroanch, Germany) was used to record electrochemical impedance spectroscopy (EIS) and the Nyquist plots were obtained in the frequency range 0.1 Hz to 100 kHz. Mott-Schottky plots of Cu₂O_(OL)/Ppy and $Cu_2O_{(OL-MH)}/Ppy$ were obtained by recording the impedance vs. potential plots at a frequency of 10 Hz in 0.1 M Na₂SO₄ solution (pH 7.0) under dark. The morphology of Cu₂O_{(OL-MH}/Ppy particles was investigated using a JSM-1200EX II transmission electron microscope (JEOL, Tokyo, Japan) and a Hitachi S-2400 scanning electron microscope (Hitachi High-Technologies, Tokyo, Japan) equipped with an energy-dispersive X-ray spectrometer (EDS). HAADF-STEM images with in-situ EDS and elemental mapping were taken using Philips Tecnai F20 G2 FEI-TEM (Roanoke, VA, USA). Prior to transmission electron microscopy (TEM) and STEM measurements, the Cu₂O_(OL-MH)/Ppy LT paper was soaked in 2 mL of ultrapure water prior to sonication for 5 min to remove the Cu₂O_(OL-MH)/Ppy particles. The aqueous solution of Cu₂O_(OL-MH)/Ppy particles. _{MH}/Ppy particles (2 µL) was placed onto formvar/carbon film Cu grids (200 mesh; Agar Scientific) and/or 200-mesh C-coated Ni grid and dried overnight at ambient conditions (27 °C). A VG ESCA210 electron spectroscope from VG Scientific (West Sussex, UK) was employed for XPS measurements of fresh Cu₂O_(OL-MH)/Ppy particles and that used for CO₂ reduction. Prior to XPS measurements, aliquots (10 µL) of the aqueous dispersions of asprepared samples dropped onto Si substrates and dried overnight at ambient conditions. Before performing inductively coupled plasma-mass spectrometry (ICP-MS) analysis using an Elan 6000 inductively coupled plasma mass spectrometer system from Perkin-Elmer (Wellesley, MA, USA), fresh Cu₂O_(OL-MH)/Ppy coated LT paper (control) and one that had been used in electrolysis of CO₂ for 15 h were digested separately in concentrated HNO₃ solution (69%) overnight. Each of the digested solutions (1 mL) was diluted with 14 mL of ultrapure water. Standard copper solutions (1, 2.5, 5, 7.5 and 10 ppm) and digested sample solutions were analyzed sequentially. From the calibration curves, amounts of Cu present in the paper electrodes before and after electrolysis were determined.

1.2.2 Product analysis

The gaseous products of CO₂ reduction catalyzed by Cu₂O_(OL-MH)/Ppy particles were determined using a GCMS-QP2010 GC-MS system from Shimadzu (Tokyo, Japan). Triplicate or duplicate GC runs were recorded. Before recording chromatograms, the column, ion source, interface, and injector temperatures were set at 100, 200, 250 and 230 °C, respectively. Detection of CO in the gaseous products was conducted using a Perkin Elmer Gas Chromatograph Clarus 480 system (Waltham, MA, USA) equipped with a thermal conductivity detector (TCD) and DB 5 column. The column, injector and detector temperatures were set at 80, 250 and 110 °C, respectively. The methanol formed in the liquid phase was analyzed using a HP 6890 Series GC system fitted with a HP 5973 mass selective detector. Prior to recording the chromatograms, the oven and column temperatures were set at 50 and 175 °C, respectively.

1.2.3 Preparation of Cu₂O_(OL-MH)/Ppy particles

According to our previous report, $Cu_2O_{(OL-MH)}/Ppy$ particles were prepared on a LT paper through a simple hydrothermal approach.¹ NaOH solution (30 mL, 7.5 M) was mixed with $Cu(NO_3)_2$ solution (3 mL, 0.1 M) and the mixture was stirred for 30 min. An LT paper (7 x 2.5 cm) soaked in pyrrole solution (5 mL) for 5 min was rolled and introduced immediately into $Cu(NO_3)_2/NaOH$ solution, which was stirred for 30 min. Catechin (60 mg) was subsequently added into the solution and the resulting solution was stirred and heated in an oil bath at 80 °C for 1 h to complete oxidative polymerization of pyrrole and reduction of Cu^{2+} ions to form Ppy and Cu_2O particles, respectively. After 1 h, the LT paper turned dark brown, indicating the formation of octahedra and icosahedra-like (microflowers) $Cu_2O_{(OL-MH)}/Ppy$ on its surface. The as-prepared LT paper is represented as $Cu_2O_{(OL-MH)}/Ppy$ particles LT paper hereafter. The $Cu_2O_{(OL-MH)}/Ppy$ LT paper was then removed and soaked in 100 mL ultrapure water for 10 min to remove excess NaOH. The $Cu_2O_{(OL-MH)}/Ppy$ LT paper allowed to dry overnight prior to use. Bare LT paper, pyrrole coated LT paper without $Cu_2O_{(OL-MH)}/Ppy$ and $Cu_2O_{(OL)}/Ppy$ were used as controls to compare with the electrocatalytic activity of $Cu_2O_{(OL-MH)}/Ppy$ LT paper toward CO_2 reduction.

1.2.4 Electrochemical reduction of carbon dioxide

The electrochemical reduction of CO_2 was carried out in a 50 mL three-necked glass cell. Bare LT paper, pyrrole coated LT paper, $Cu_2O_{(OL)}$ /Ppy LT paper and $Cu_2O_{(OL-MH)}$ /Ppy LT paper electrodes were used separately as a working electrode. To provide a better electrical contact, one end of the paper electrode was fixed with a Cu tape (0.5 cm). The working area of all the paper electrodes used was ~5 cm². An Ag/AgCl electrode containing 3 M KCl was used as a reference electrode. All potentials measured against the Ag/AgCl reference electrode were converted to a reversible hydrogen electrode (RHE) by using equation (1).²

$$E_{RHE} = E_{Ag/AgCl} + E_{Ag/AgCl}^{o} + 0.059 \, pH \tag{1}$$

 $E_{Ag/AgCl} = 0.197 V$. The pH value of the CO₂ saturated 0.5 M KHCO₃ solution was determined to be 7.6. A Pt wire with 0.5 mm diameter was used as a counter electrode. The electrodes were separately introduced through necks of the glass cell. The CO₂ gas tube was fitted into the neck adjacent to the working electrode. 25 mL of CO₂ saturated 0.5 M KHCO₃ solution was used as the electrolyte. CO₂ gas was purged into the electrolyte solution for 30 min prior to electrolysis. During electrolysis, CO₂ atmosphere in the solution remained constant. Prior to electrolysis, the glass cell was sealed completely with at least four or five layers of Teflon and/or Parafilm to prevent the release of gaseous products. Because of high hydrophobicity, we applied parafilm oil on top of the parafilm prior to and during CO₂ electrolysis and ensured that no gases were released from the electrochemical cell. CO₂ reduction in 25 mL of CO₂ saturated 0.5 M KHCO₃ solution was monitored by cyclic voltammetry using CHI 760D electrochemical work station, which was operated in the potential range between 0.64 to -1.15 V vs. RHE at a scan rate of 20 mV s⁻¹. Controlled potential electrolysis was carried out at the $Cu_2O_{(OL-MH)}/Ppy$ LT papers by applying -0.45, -0.65 or -0.85 V vs. RHE for various times up to 60 min for the production of methanol. The methanol formed in the liquid phase was analyzed using GC. Triplicate or duplicate GC runs were recorded. While CO and H₂ formed in the head space of the electrochemical cell were analyzed using GC-TCD and GC-MS. By applying a standard addition method, the peak areas were used to calculate the amount of methanol and CO formed in the liquid and gaseous phases, respectively. The Faradaic efficiencies of methanol and CO were calculated using equation (2).

Faradaic efficiency =
$$\frac{n_l \times n \times F}{\int_0^t I dt} \times 100\%$$
 (2)

where n_1 represents the number of moles of CO/or methanol; n is the number of electrons required to convert CO₂ into CO (n = 2) or methanol (n = 6), and F is the Faraday's constant (96485.33 C mol⁻¹), and I is the total current.



Fig. S1. HAADF-STEM image of one single $Cu_2O_{(OL-MH)}/Ppy$ particle and mapping of elements (B) Cu-K (C) Cu-L (D) N-K, and (E) O-K present in the marked area (1). Insets to (B-E): mappings of elements Cu, N and O present in the marked area (2), respectively.



Fig. S2. SEM image of $Cu_2O_{(OL)}$ /Ppy coated LT paper. Catechin (6.26 mM), $Cu(NO_3)_2$ (9.09 mM), and 13.64 M NaOH were used. The marked circles and the arrows indicate the corresponding Cu microstructures. Insets: magnified views of $Cu_2O_{(OL)}$ /Ppy particles.



Fig. S3. Representative SEM images taken during different growth stages of single $Cu_2O_{(OL-MH)}$ /Ppy particle (A-E). The corresponding models with geometrical shapes: (F) octahedron, (G-H) great dodecahedron, (I) small stellated dodecahedron and (J), icosahedron.



Fig. S4. I-V curves recorded at the (A) $Cu_2O_{(OL-MH)}/Ppy$ LT paper and (B) Cu_2O particles coated LT paper electrodes before and after 25 and 50 cycles of bending at an maximum bending angle of 96.8°.



Fig. S5. Batch-to-Batch reproducibility of $Cu_2O_{(OL-MH)}$ /Ppy electrodes toward the reduction of CO₂. (A) CVs of $Cu_2O_{(OL-MH)}$ /Ppy electrodes in CO₂ saturated 0.5 M KHCO₃ solution (pH 7.6). Scan rate: 20 mV s⁻¹. (B) Current densities determined at -0.85 V vs. RHE from the CV curves shown in (A).

Determination of mass specific active site density of catalysts

We used an electrochemical approach to determine the mass specific active site density (SD_M) of the catalysts.³ Prior to recording the voltammograms, electrolyte (0.5 M NaOH) was purged with N₂ gas for 45 min. N₂ purging was continued during the measurements to ensure efficient mass transport. 20 CV cycles of the Cu₂O_(OL-MH)/Ppy electrode was then separately recorded over the potential range from -0.75 to 0.6 V vs. Ag/AgCl reference electrode at a scan rate of 50 mV s⁻¹ in N₂-saturated 0.5 M NaOH solution. After achieving stable currents (at least five voltammograms), one voltammogram was recorded over the same potential range in N2saturated 0.5 M NaOH solution, which was considered as the background voltammogram (black curve in Fig. S6A). To adsorb glucose on the electrode surface, 20 CV cycles were scanned over the same potential range in 10 mM glucose containing N₂-saturated 0.5 M NaOH solution. The characteristic peaks of Cu transitions (I), (II), and (III) as well as increased oxidation and reduction peak currents confirmed the glucose adsorption on the electrode (red curve).¹ The glucose adsorbed electrode was then transferred to fresh electrolyte and 20 CV cycles were scanned over the same potential range to remove loosely adsorbed glucose molecules. This electrode was then placed in a fresh electrolyte and one voltammogram (blue curve) was recorded as shown in Fig. S6A. The CV curve shown in Fig. S6C was subtracted from the background to obtain the background subtracted voltammogram. The anodic peak current at 0 V in the background subtracted voltammogram was then integrated to obtain the CV area (AV) (or) the charge. The SD_M value was calculated from equation (3):

$$SD_{M} (active site g^{-1}) = \frac{Integrated CV area (A \times V) \times N (sites mol^{-1})}{n \times scan rate (V s^{-1}) \times F (C mol^{-1}) \times m(g)}$$
(3)

Where, N is the Avogadro number (6.023 x 10^{23} sites mol⁻¹), and F is the Faraday constant (96485.33 C mol⁻¹). The voltammograms were recorded at a scan rate of 0.05 V s⁻¹. From the

ICP-MS analysis, the mass of Cu loaded onto the electrode was determined to be 1.12 mg (0.00112 g). From equation (4), number of electrons (n) transferred during the glucose adsorption process was found to be 2.

$$Cu_2 0 + 2 0 H^- \to 2 Cu 0 + H_2 0 + 2e^-$$
(4)

The SD_M (active site g^{-1}) value of 3.96 x 10¹⁸ sites g^{-1} for Cu₂O_(OL-MH)/Ppy electrode was determined by substituting these values in equation (5).

$$SD_{M} \text{ (active site g^{-1})} = \frac{7.104 \times 10^{-5} (A \times V) \times 6.023 \times 10^{23} \text{ (sites mol^{-1})}}{2 \times 0.05 (V \, s^{-1}) \times 96485.33 (C \, mol^{-1}) \times 0.00112 (g)}$$
(5)
= 3.96 x 10¹⁸ sites g⁻¹

CV curves of $Cu_2O_{(OL)}/Ppy$ electrode were also recorded under similar conditions as shown in Fig. S6B. The SD_M (active site g⁻¹) value of 2.29 x 10¹⁸ sites g⁻¹ for $Cu_2O_{(OL)}/Ppy$ electrode was determined by substituting these values in equation (6).

$$SD_{M} \text{ (active site } g^{-1}\text{)} = \frac{4.101 \times 10^{-5} (A \times V) \times 6.023 \times 10^{23} \text{ (sites mol}^{-1}\text{)}}{2 \times 0.05 (V s^{-1}) \times 96485.33 (C mol^{-1}) \times 0.00112 (g)}$$
(6)
= 2.29 x 10¹⁸ sites g⁻¹



Fig. S6. CV curves of $Cu_2O_{(OL-MH)}/Ppy$ modifed LT paper (A) and CV curves of $Cu_2O_{(OL)}/Ppy$ electrodes modifed LT paper (B) recorded at a scan rate of 50 mV s⁻¹ in N₂ saturated 0.5 M NaOH solutions. The experimental conditions are shown in the legends. (C) CV curves of $Cu_2O_{(OL-MH)}/Ppy$ modifed LT paper and $Cu_2O_{(OL)}/Ppy$ modifed LT paper after glucose adsorption and cleaning steps.



Fig. S7. (A) CVs of Cu₂O_(OL-MH)/Ppy modified LT paper electrode recorded at different scan rates in the non-Faradaic region. (B) Plot of double layer capacitance vs. scan rate.



Fig. S8. Mott-Schottky plots of $Cu_2O_{(OL)}/Ppy$ (A) and $Cu_2O_{(OL-MH)}/Ppy$ (B) modified LT paper electrodes. The interfacial capacitance (C) values were derived from the impedance vs. potential curves recorded in 0.1 M Na₂SO₄ under dark.



Fig. S9. CVs of bare (A), $Cu_2O_{(OL)}/Ppy$ (B) and $Cu_2O_{(OL-MH)}/Ppy$ (C) electrodes recorded in 0.01 M Ferrocene and 0.1 M TBAPF₆ containing acetonitrile at a scan rate of 50 mV s⁻¹.



Fig. S10. Energy level diagrams of $Cu_2O_{(OL-MH)}/Ppy$ and $Cu_2O_{(OL)}/Ppy$ modified LT papers.



Fig. S11. Gas chromatograms of H_2 obtained for electrolysis of CO_2 using $Cu_2O_{(OL-MH)}/Ppy$ modified LT papers at (A) -0.45 V and (B) -0.65 V for 15 h.

Fig. S12. Gas chromatogram of standard CO (99%) after electrolysis at the $Cu_2O_{(OL-MH)}/Ppy$ LT paper electrode at -0.85 V vs. RHE in CO₂ saturated 0.5 M KHCO₃ solution (A). The calibration plot of CO (B). Two gas chromatograms of gaseous products collected at -0.85 V vs. RHE for 30 min (C).

Fig. S13. Deconvoluted C_{1s} , O_{1s} , N_{1s} , $Cu_{2p1/2}$ and $Cu_{2p3/2}$ core level XPS spectra of $Cu_2O_{(OL-MH)}/Ppy$ (A) before and (B) after electrolysis at -0.85 V for 1 h.

Fig. S14. UV-Vis absorption spectra of aqueous solutions taken at different reaction intervals. Cu(NO₃)₂/NaOH aqueous solution (A), Cu(NO₃)₂/NaOH aqueous solution containing pyrrole modified LT paper (B), after adding catechin into the aqueous solution in (B) and heated at 80 °C (C). The photographs of aqueous solutions are shown in the insets. UV-Vis absorption spectra of different aqueous solutions and electrolytes before and after electrolysis (D). Water (a), KHCO₃ (b), NaOH (c), KHCO₃ and NaOH mixture (d), KHCO₃ solution after electrolyzed at -0.85 V for 30 min (e), KHCO₃ solution after electrolyzed at -0.85 V for 1 h (f), KHCO₃ solution after electrolyzed at -0.85 V for 1 h and spiked with NaOH solution (g). All aqueous solutions in (D) were diluted two-fold to obtain a final volume of 1 mL. After dilution, the final concentrations of KHCO₃ and NaOH are 0.25 and 0.05 M, respectively.

Fig. S15. (A) Electrolysis of $Cu_2O_{(OL-MH)}$ /Ppy coated LT paper in CO₂ saturated 0.5 M KHCO₃ solution (pH 7.6) at -0.85 V for 15 h. The active working area of the electrode: 5 cm⁻². (B) ICP-MS results obtained before and after electrolysis at -0.85 V for 15 h.

Fig. S16. High resolution SEM images of $Cu_2O_{(OL-MH)}$ /Ppy taken before (A) and after (D) 60 min of electrolysis at -0.85 V in CO₂ saturated 0.5 M KHCO₃ solution (pH: 7.6). Magnified SEM images (B and E) taken from the squared areas in (A) and (D), respectively. Scale bars in (A and D) are 1 µm and those in (B) and (E) are 100 nm. Magnified views of squared areas in (B) and (E) are shown in (C) and (F), which were used to measure the Ppy shell thickness using the image J software. The dotted circles and the arrows indicate the Ppy layers used for the thickness measurements.

Fig. S17. High resolution STEM images of $Cu_2O_{(OL-MH)}/Ppy$ taken before electrolysis (A) and after 60 min of electrolysis at -0.85 V in CO₂ saturated 0.5 M KHCO₃ solution (B). The SAED patterns taken before electrolysis (C) and after electrolysis (D).

Table S1 Comparison of shape-, size- and facet-dependent CO_2 reduction activity and selectivity of

Cu/Cu_2O and noble metal electrodes/or nanomaterials

Electrodes/ Nanomaterials	Shape, size, (crystal Facets)	Electrolyte (M)/(*pH)	Time (min)	Applied potential (V)	Liquid products (FE%)	Gaseous products (FE%)	Ref.
Cu nanofoam	3D pores, (211)	KHCO ₃ (0.1)/(6.8)	^a NA	^b -1.1	HCOOH (26%) CH ₃ OH & C ₂ H ₅ OH (<1%)	$\begin{array}{c} (\mathbf{T}\mathbf{L},76) \\ \mathbf{C}_{2}\mathbf{H}_{4}, \mathbf{C}_{2}\mathbf{H}_{6}, \\ \mathbf{C}_{4}\mathbf{H}_{6} \\ (<2\%), \\ \mathbf{H}_{2} (\sim 58\%) \end{array}$	4
Cu ₈₅ -Pt ₁₅ alloy	Nanocubes, 8-10 nm, (100)	KHCO ₃ (0.5)/(7.3)	30	^b -1.75	NA	H ₂ (~70%) CO (~20%) CH ₂ (10%)	5
Cu nanocrystals	Spheres, 27 nm, (111) (200)	KHCO ₃ (0.1)	60	°-1.1	HCOO ⁻ (7.6%) CH ₃ CHO (0.4%) CH ₃ OH (8.1%) Glyoxal (0.1%)	$H_{4}(10.0)$ $H_{2}(54.7\%)$ CO(3.3%) $CH_{4}(16.0\%)$ $C_{2}H_{4}(9.3\%)$	6
	Nanocubes, 44 nm, (111) (200)	KHCO3 (0.1)	60	°-1.1	HCOO ⁻ (3.6%) HCHO (0.19%) Glyoxal (0.1%) Glycol aldehyde (0.2%) CH ₃ COO ⁻ (0.2%) CH ₃ CHO (1.1%) CH ₃ OH (2.6%) C ₂ H ₅ OH (3.7%) 1-propanol (2.7%) Allyl alcohol (0.4%) Propionaldehyde (0.6%)	H ₂ (20.5%) CO (2.1%) CH ₄ (20.2%) C ₂ H ₄ (41.1%)	
Cu Nanostructures	Electrochemically reduced Cu nanowires, diameter: 50-100 nm, length: 10-50 µm, (111), (220)	KHCO ₃ (0.1)/(6.8)	60	°-0.4	HCOOH (~8%)	H ₂ (61.8%) CO (23.5%)	7
Cu ₂ O/Cu	Cu ₂ O-derived Cu electrode	KHCO ₃ (0.1)/(6.8)	40	°-1.03	HCOO ⁻ (1.72%) CH ₃ COO ⁻ (0.33%) C ₂ H ₅ OH (8.55%) 1-propanol (3.36%)	H ₂ (54.2%) CO (0.23%) CH ₄ (0.72%) C ₂ H ₄ (23.19%)	8
Cu single crystal electrodes	Cu electrode, (100)	KHCO ₃ (0.1)/(6.8)	40	°1.05	HCOO ⁻ (4.23%) CH ₃ COO ⁻ (0.68%) C ₂ H ₅ OH (2.72%)	$\begin{array}{c} (1.137.4) \\ H_2 (37.33\%) \\ CO (1.24\%) \\ CH_4 \\ (27.67\%) \\ C_2H_4 \\ (21.86\%) \end{array}$	
	Cu electrode, (111)	KHCO ₃ (0.1)/(6.8)	40	°1.05	HCOO ⁻ (6.8%) CH ₃ COO ⁻ (0.81%) C ₂ H ₅ OH (2.6%)	H ₂ (36.23%) CO (4.98%) CH ₄ (28.05%) C ₂ H ₄ (16.76%)	
	Cu electrode, (110)	KHCO ₃ (0.1)/(6.8)	40	°1.05	HCOO ⁻ (4.98%) CH ₃ COO ⁻ (1.15%) C ₂ H ₅ OH (7.41%)	H ₂ (33.7%) CO (2.63%)	

						CH ₄ (21.56%) C ₂ H ₄ (25.17%)	
Cu ₂ O films	Cu ₂ O pyramids, (110) orientation, film thickness: 3 C cm ⁻²	KHCO ₃ (0.1)/(6.8)	60	°-1.1	НСООН (20%)	CO (~3%) C ₂ H ₄ (~40%) Methane (~7%)	9
	Cu ₂ O pyramids, (100) orientation	KHCO ₃ (0.1)/(6.8)	60	°-1.1	NA	CO (~2.5%) C ₂ H ₂ (~26%) C ₃ H ₆ (~28%) Methane (~6-7%)	
	Cu ₂ O pyramids, (111) orientation	KHCO ₃ (0.1)/(6.8)	60	°-1.1	NA	CO (~3- 3.5%) C ₂ H ₄ (~24%) C ₃ H ₆ (~26%) Methane (~3-4%)	
Cu-In electrode	Large irregularly shaped Cu-In grains, 50-100 nm, (211), (100), (111)	KHCO ₃ (0.1)	60	°-0.3	NA	CO (23%) H ₂ (3%) CO (~80%)	10
				°-0.5	NA	H ₂ (~15- 16%)	
Ag	Triangular Ag nanoplates, 1-12 nm, (111), (100)	KHCO ₃ (0.1)	NA	°-0.856	NA	CO (96.8%)	11
Pd	Pd nanoparticles, 2.4 nm, (111), (211)	KHCO ₃ (0.1)/(6.8)	NA	°-0.89	HCOOH (1.3%)	CO (91.2%)	12
	(211) Pd nanoparticles, 3.7 nm, (111),				HCOOH (0.37%)	CO (91.2%)	
Au	Concave rhombic dodecahedron Au nanoparticles, 120 nm, (331), (221), and (553)	KHCO ₃ (0.1)	NA	°-0.57	HCOOH (0.2%)	CO (93.1%) H ₂ (7.3%)	13
$Cu_2O_{(OL-MH)}/Ppy$	$Cu_2O_{(OL-MH)}/Ppy$ particles, 4.3 \pm 0.9 $\mu m,$ (111), (311) and (211)	KHCO ₃ (0.5)	60	°-0.85	CH ₃ OH (93 ± 1.2%)	CO (7%)	This work

^aNA not available ^b Potentials were measured against Ag/AgCl ^cPotentials were converted to RHE

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