

## **Uniform Wrapping of Copper(I) Oxide Nanocubes by Self-Controlled Copper-Catalyzed Azide–Alkyne Cycloaddition toward Selective Carbon Dioxide Electrocatalysis**

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#### **References**

## 1-1 Chemicals

Cu<sub>2</sub>O nanocubes<sup>1</sup>, 1,3,5-triethynylbenzene(**Ph**)<sup>2</sup>, 1,3,5-tris(azidomethyl)benzene(**3Az**)<sup>3</sup> and 4,4'-diazidebiphenyl(**2Az**)<sup>4</sup> were synthesized according to the literature. Nafion<sup>TM</sup>(Aldrich, 5w% in alcohol/water), Dimethylsulfoxide(nacalai tesque), ethanol(Kanto Chemical) KHCO<sub>3</sub>(Katayama Chemicals) were used as purchased. Ultrapurified water (> 18MΩ, Millipore Direct-Q UV3) was used in preparation and electrolysis. CO<sub>2</sub> gas(99.995 %) was purchased from NIPPON EKITAN Co.

## 1-2 Apparatus

TEM images were collected with JEOL JEM-2010. SEM images were collected with Hitachi FE-SEM S-5200. FT-IR spectra was collected using JASCO FT/IR-4600 with ATR attachment.

## 1-3 Nanocube modification

56 mg of Cu<sub>2</sub>O nanocube was dispersed in 9 mL DMSO/H<sub>2</sub>O 8:1 (v/v) and sonicated for 1h. **Ph** (16 μmol) and azide monomer (17 μmol of **3Az** or 24 μmol of **2Az**) were added to the solution. Reaction was continued under various condition of temperature and time. Each sample was collected by centrifugation and designated in accordance with the reaction temperature, time, and modified azide monomer.

For contact angle measurement, Cu<sub>2</sub>O was electrodeposited on Cu electrode (3mmφ, 99.9%, the Nilaco Corp.) from Cu<sup>2+</sup> according to the literature method<sup>5</sup> and modified by immersion in a solution containing the same amounts of **Ph** and azide monomer as the solution used in the nanocube modification for 20 h at room temperature.

For IR measurements, polymers from the same monomers were prepared by conventional CuAAC method as follows and used for comparison with modified nanocubes.

**Ph** (9.9 mg, 66 μmol), azide monomer (15.4 mg (66 μmol) of **3Az** or 23.3 mg(99 μmol) of **2Az**), CuSO<sub>4</sub> · 5H<sub>2</sub>O (16 mg, 66 μmol), sodium ascorbate (12 mg, 66 μmol) was reacted in 10 mL dimethylsulfoxide at room temperature for 20 h. The formed precipitation was separated by filtration and washed with dimethylsulfoxide and acetone then dried in vacuo.

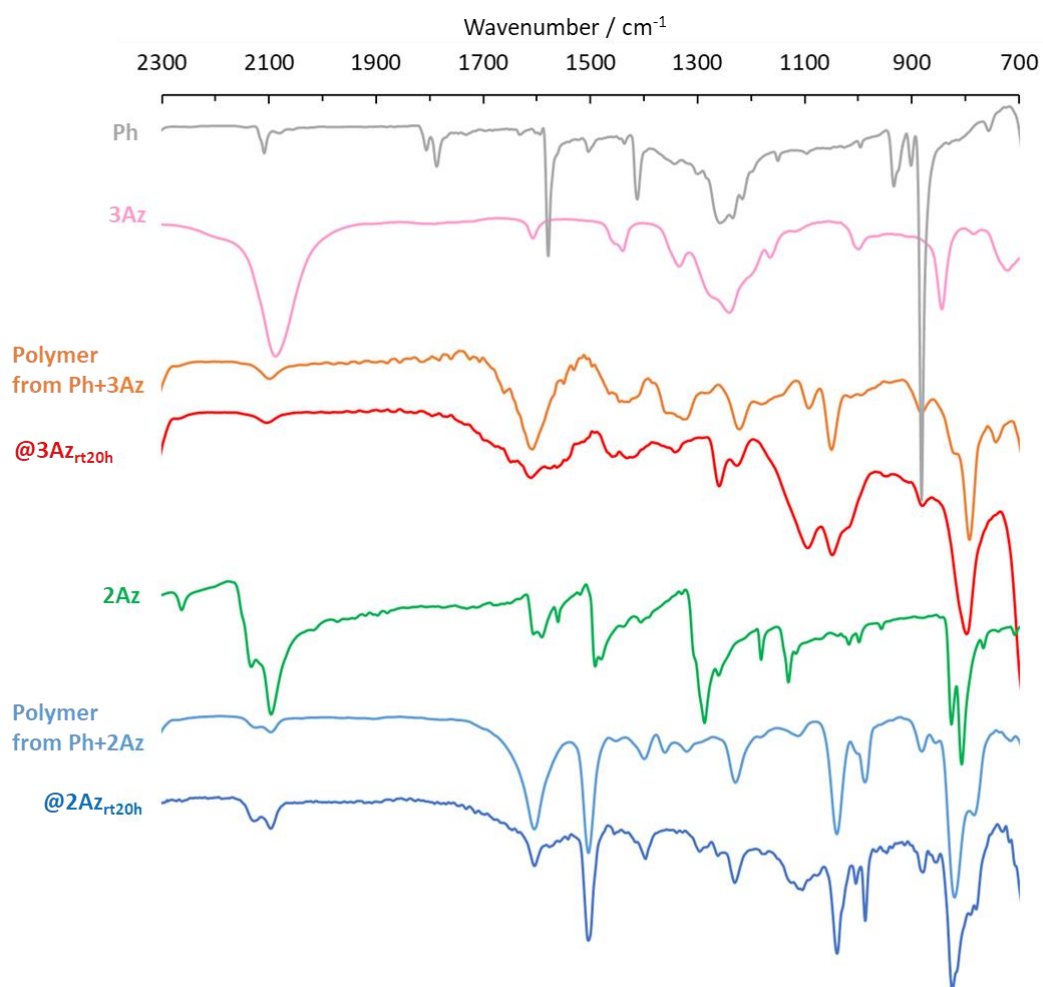
## 1-4 Electrode preparation

A glassy carbon electrode(3mmφ) was made of the cross section of glassy carbon rod (Tokai Carbon Co. Ltd.) embedded in grass tube, and polished with Bicalox0.05CR (0.05μm alumina abrasive). 1 mg of Cu<sub>2</sub>O nanocubes, 10uL of Nafion solution(5 w%) were dispersed in 1mL of ethanol and the solution was ultrasonicated until it gave a uniform dispersion. 5 uL of the liquid was drop-casted on glassy carbon and used for CO<sub>2</sub> electrolysis. For SEM observations of nanocubes after CO<sub>2</sub> reduction, carbon plates (the Nilaco Corp.) were used as a substrate instead of a glassy carbon disc.

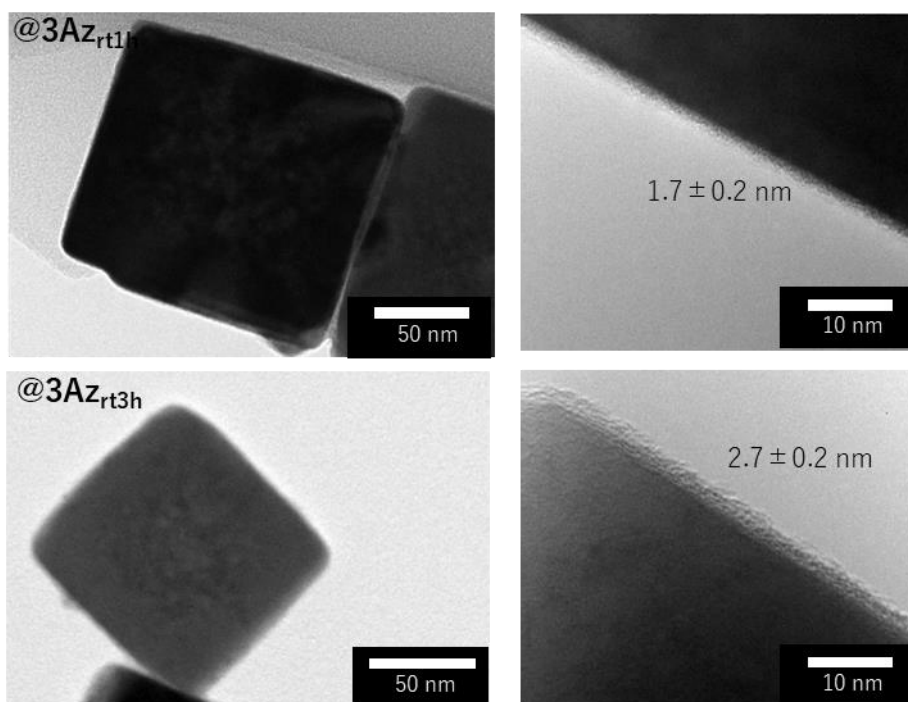
## 1-5 CO<sub>2</sub> reduction procedure and product analysis

The CO<sub>2</sub> reduction activity of modified electrodes was investigated in CO<sub>2</sub> saturated 0.1M KHCO<sub>3</sub>aq (pH 6.8). The three-electrode setup was connected to a potentiostat (ALS 650D). Ag/AgCl was used

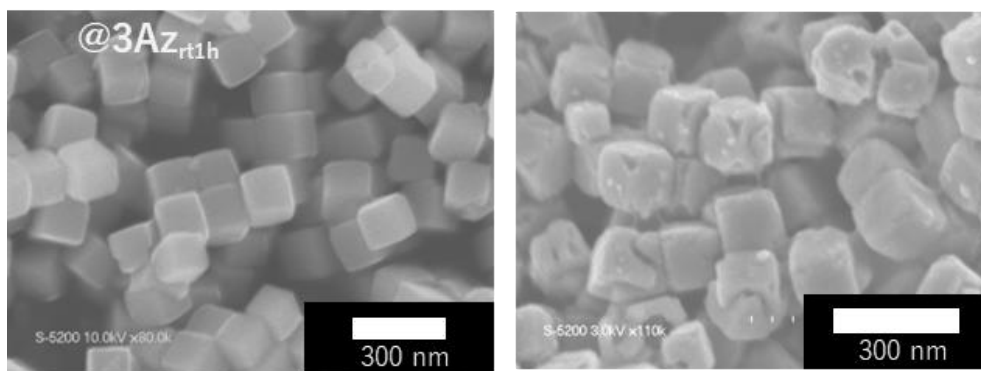
as a reference electrode. carbon rod was used as counter electrode. The applied potential was converted to RHE according to the equation,  $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 \text{ V} + 0.0591 \times \text{pH}$ . The  $\text{CO}_2$  electrolysis experiments were performed two-compartment cell. In gas-tight cathodic compartment a copper working electrode and Ag/AgCl electrode were placed. It was separated to open anodic compartment equipped with carbon rod counter electrode by 10mm $\phi$  ion-exchange membrane (Selemion<sup>TM</sup> AMV). Electrolysis was performed for 10 min with stirring (ca. 600 rpm), without additional supply of  $\text{CO}_2$ . Copper electrodes were first cathodized at -2.0V vs. Ag/AgCl for at least 10 min until they steadily formed products, to remove the weakly physisorbed materials and reduce oxidized copper species prior to collection of  $\text{CO}_2$ RR products.  $\text{CO}_2$  was bubbled through the electrolyte prior to each data collection, and depletion of  $\text{CO}_2$  by electrolysis is estimated at up to a few %, from passed charge (typically 1 C) to the amount of  $\text{CO}_2$  in solution (34 mM, 6.2 mL). For the quantification of gaseous product, 0.1 mL of gas product was collected from the head space (9.9 mL) of the gas-tight compartment and introduced in gas chromatograph (Shimazu-2010) equipped with a 2.0m  $\times$  1.0mm ID column packed with SHINCARBON ST, and BID-2010 detector. The electrolysis data were collected for at least three separately prepared electrodes, and averaged.



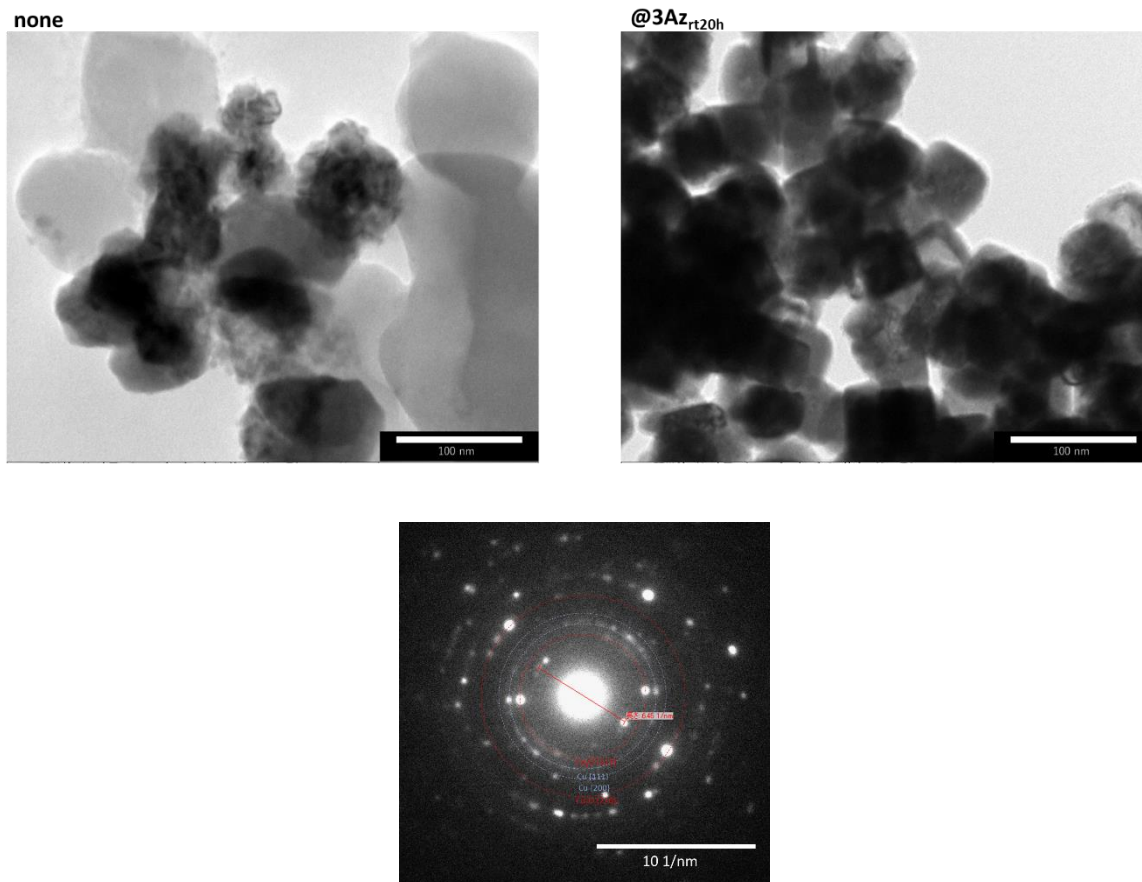
**Figure S1** IR Spectra of monomers, separately prepared polymers, and modified Cu<sub>2</sub>O nanocubes.



**Figure S2** Transmission electron microscopy images of modified Cu<sub>2</sub>O nanocubes: @3Az<sub>rt1h</sub> (upper), and @3Az<sub>rt3h</sub> (below). Values within the magnified images (left) show the average thickness of the observed layers collected from multiple cubes.

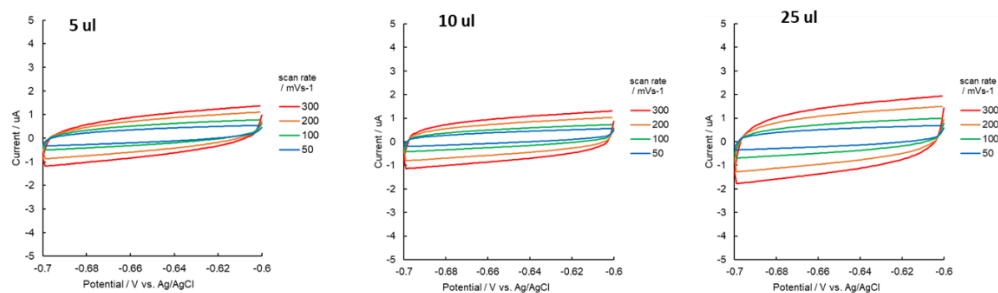


**Figure S3** Scanning electron microscopy images of @3Az<sub>rt1h</sub> before(left) and after(right) CO<sub>2</sub> electrolysis for 40 min at  $-1.4$  V vs. RHE, CO<sub>2</sub> saturated with 0.1 M KHCO<sub>3</sub> (aq).

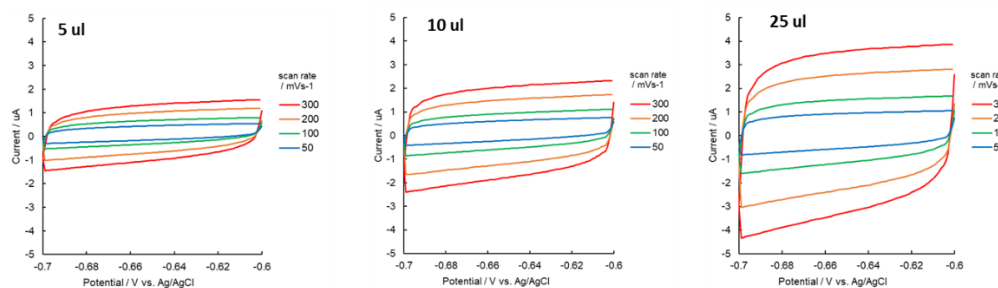


**Figure S4** Transmission electron microscopic images (TEM) of **none** (upper left) and **@3AZ<sub>rt</sub>20h** (upper right), after CO<sub>2</sub> electrolysis directly on TEM grid at -1.4 V vs. RHE for 40 min. Electron diffraction image of **@3AZ<sub>rt</sub>20h** (below) is also shown.

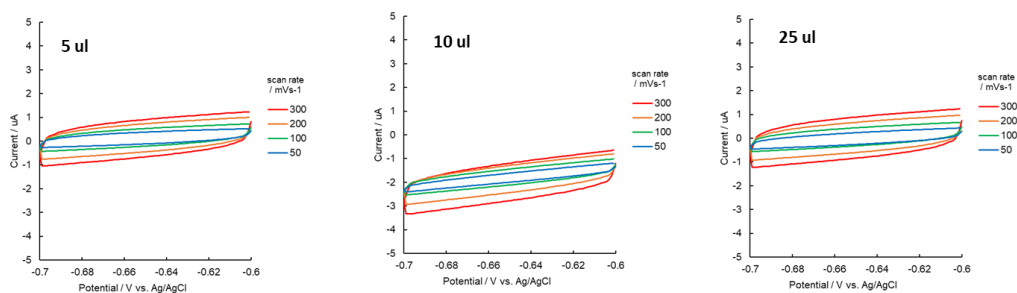
(a) none, before electrolysis



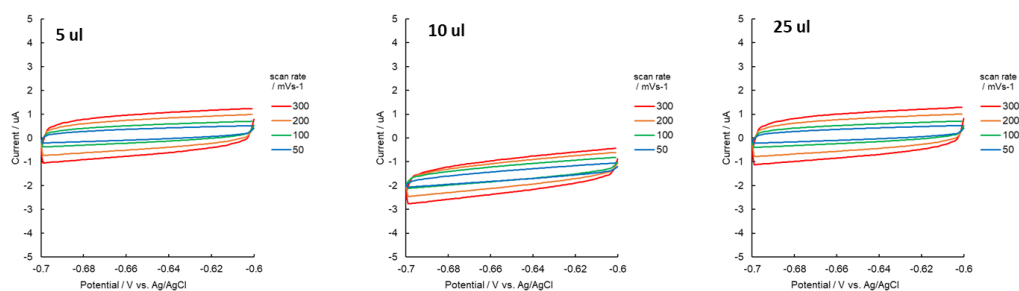
(b) none, after electrolysis



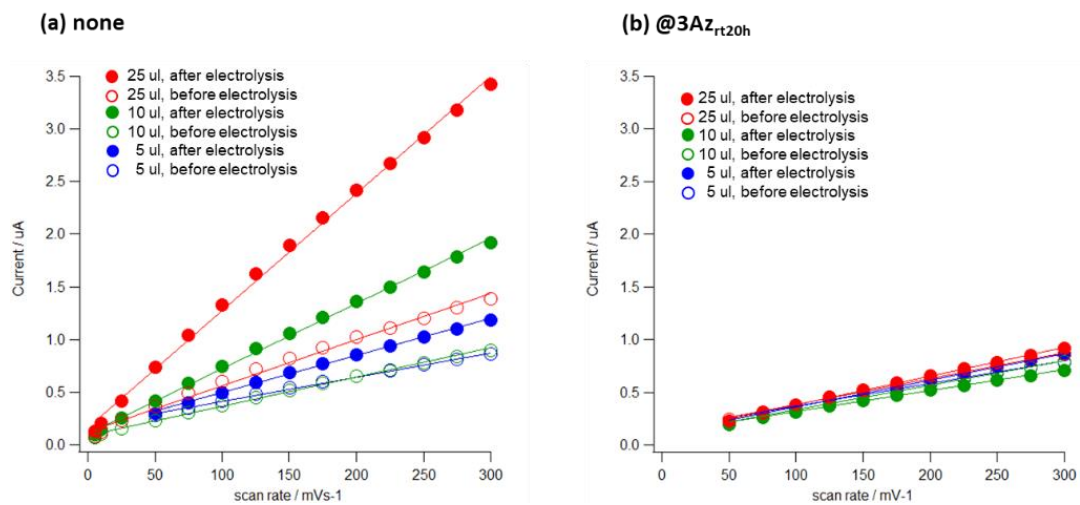
(c) @3Az<sub>rt20h</sub> before electrolysis



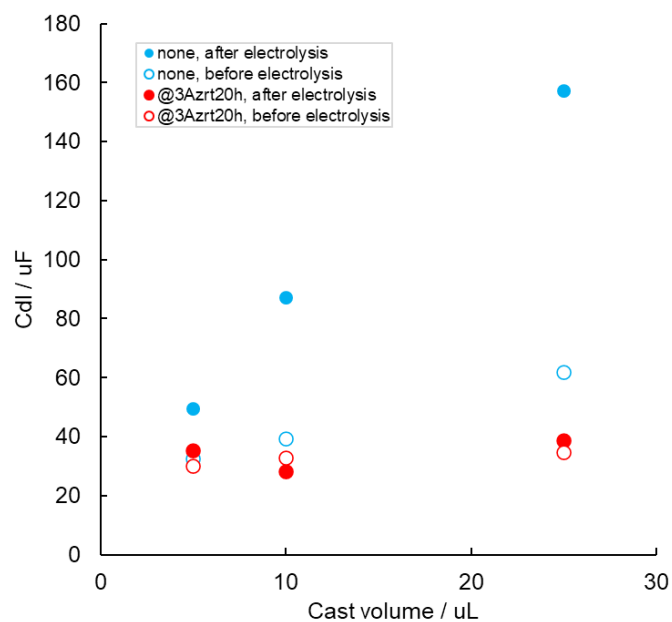
(d) @3Az<sub>rt20h</sub>, after electrolysis



**Figure S5** Cyclic voltammograms of electrodes with catalyst loading on glassy carbon, before and after CO<sub>2</sub> electrolysis at -1.4 V vs. RHE for 40 min. Only a part of all the scans are shown for clarity. The volume denotes the amount of catalyst ink containing 1mg catalyst and 10 uL Nafion(5 w%) in 1mL EtOH, loaded on 3 mm $\phi$  glassy carbon.

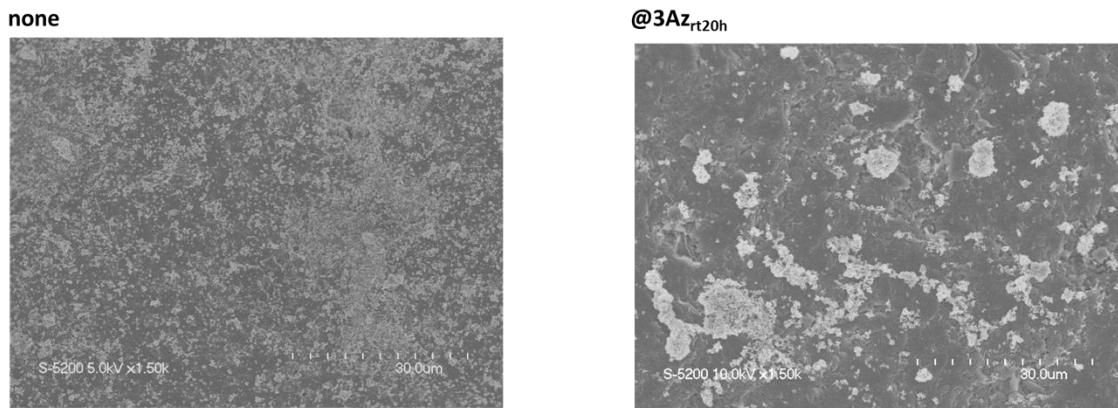


**Figure S6** Scan rate dependence of halved current density difference between anodic and cathodic scan at -0.65 V vs. Ag/AgCl. Regression lines used for capacitance calculation are also shown.

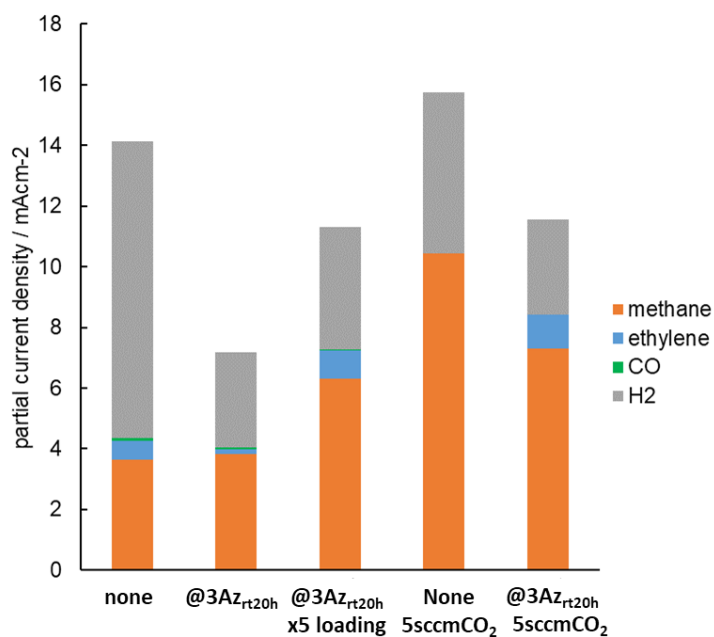


**Figure S7** Double layer capacitance ( $C_{dl}$ ) of electrodes with catalyst loading.

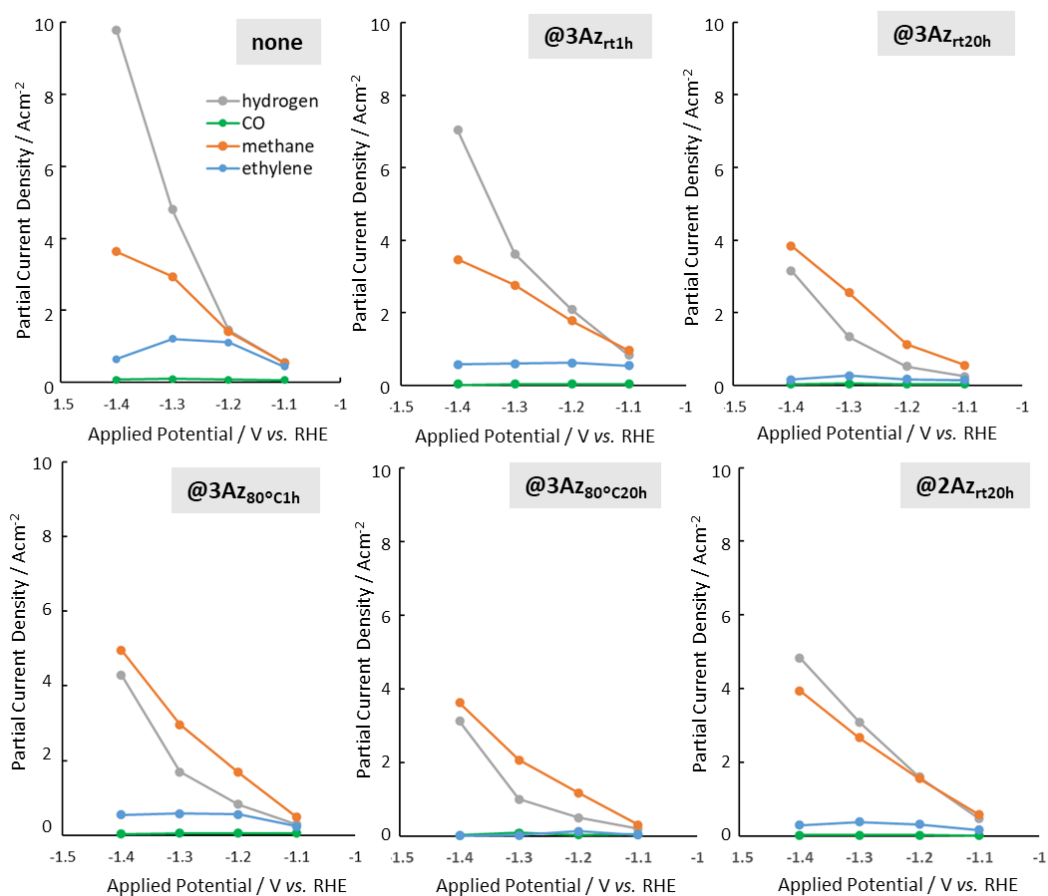




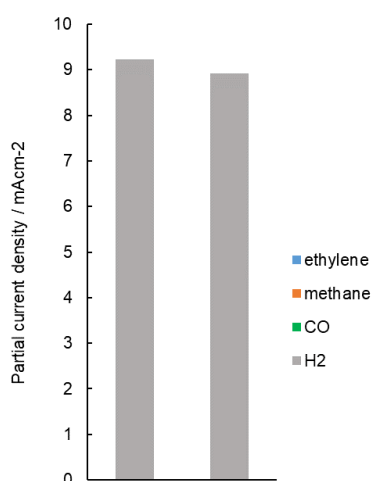
**Figure S8** Low magnification scanning electron microscopy (SEM) images of **none** (left) and **@3Az<sub>rt20h</sub>** (right) on carbon plates.



**Figure S9** Partial current density of reduction products of CO<sub>2</sub> electrolysis at  $-1.4$  V vs. RHE in  $0.1$  M KHCO<sub>3</sub> (aq). “x5 loading” denotes the catalyst loading was increased by five times. “5sccmCO<sub>2</sub>” denotes CO<sub>2</sub> gas was continuously passed through the electrolyte, instead of the closed system applied to all other CO<sub>2</sub> electrolysis under CO<sub>2</sub> saturation prior to electrolysis.



**Figure S10** CO<sub>2</sub> reduction product dependence on applied potential in CO<sub>2</sub> saturated 0.1 M KHCO<sub>3</sub> (aq). All data are the average of three separately prepared electrodes.



**Figure S11** Partial current density of reduction products of CO<sub>2</sub> electrolysis with @3AZ<sub>rt20h</sub> at -1.4 V vs. RHE, Ar saturated 0.1 M KHCO<sub>3</sub> (aq).

(a) **Ph+3Az**



(b) **Ph+2Az**



**Figure S12** Contact angle images of electrodeposited Cu<sub>2</sub>O on Cu electrode modified with **Ph+3Az**(a) and **Ph+2Az**(b).

## References

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