Stable and Selective Electrochemical Reduction of Carbon Dioxide to Ethylene on Copper Mesocrystals

*Chung Shou Chen, Albertus D. Handoko, Jane Hui Wan, Liang Ma, Dan Ren and Boon Siang Yeo**

SUPPORTING INFORMATION

S1. Determination of Faradaic Efficiencies of Gaseous and Liquid Products Using Gas Chromatography (GC) and Nuclear Magnetic resonance (NMR) Spectroscopy Data

A representative set of GC data obtained during CO_2 electroreduction on Cu mesocrystals is presented in Supporting Table 1.

Supporting Table 1: Data obtained from the GC analysis of CO_2 reduction products using Cu mesocrystal (Catalyst A). The volume of the sampling loops are 1 cm^3 (for CH_4, C_2H_4, C_2H_6 and CO), and 0.5 cm^3 (for H_2).

			Amount of gaseous products (mol)				
Sampling No.	Time of sample injection (s)	Current (mA)	CH_4	C_2H_4	C_2H_6	CO	H_2
1	230	10.850	3.04×10^{-10}	3.29×10^{-9}	2.82×10^{-11}	4.97×10^{-10}	5.14×10^{-8}
2	900	9.100	3.54×10^{-10}	4.46×10^{-9}	2.29×10^{-11}	5.35×10^{-10}	4.28×10^{-8}
3	1570	8.228	4.33×10^{-10}	5.02×10^{-9}	3.68×10^{-11}	6.72×10^{-10}	3.97×10^{-8}
4	2240	8.331	5.98×10^{-10}	6.28×10^{-9}	5.23×10^{-11}	9.49×10^{-10}	4.97×10^{-8}
5	2910	7.665	5.41×10^{-10}	5.72×10^{-9}	5.19×10^{-11}	7.59×10^{-10}	3.59×10^{-8}
6	3580	7.342	5.23×10^{-10}	4.98×10^{-9}	4.33×10^{-11}	7.77×10^{-10}	3.67×10^{-8}
Average (3~6)		7.8915	5.24×10^{-10}	5.50×10^{-9}	4.61×10^{-11}	7.89×10^{-10}	4.05×10^{-8}

Calculation of Faradaic Efficiencies (%) of Gaseous Products

To ensure that the reported data is from a system under equilibrium condition, only the 3rd - 6th GC measurements were used for calculating the Faradaic efficiencies.

Let:

Recorded amount of product = y (mol)

Recorded current = I (A)

Recorded flow rate = r (sccm) = $\frac{r}{60}$ cm^3 s^{-1}

Volume of sampling loop = V cm^3

No. of moles of electrons required for reducing CO_2 to a particular product

$$e_{output} = y \times \text{No. of electrons required to obtain 1 molecule of product} \quad (1)$$

The number of electrons required to form a molecule of C_2H_6, C_2H_4, CH_4, CO (from CO_2) and H_2 (from H^+) are 14, 12, 8, 2 and 2 electrons respectively.[1]

Total number of moles of electrons measured during the sampling period (this data is obtained from the chronoamperomogram):

$$e_{input} = \frac{Q}{F} \quad (2)$$

where F = Faraday constant, 96485 C mol^{-1}; and Q = measured charge

The measured charged can be determined using Faraday's laws of electrolysis:

$$Q = I \times t \quad (3)$$

The time required to fill the sampling loop (t):

$$t = \frac{\frac{V}{r}}{60} \text{ seconds} \quad (4)$$

$$\text{Faradaic efficiency of the product} = \frac{e_{output}}{e_{input}} \times 100\% \quad (5)$$

Example: Calculation of the FE of C_2H_4 using data No. 3 in Supporting Table 1.

Recorded current = 8.228 mA

Amount of C_2H_4 detected = 5.02×10^{-9} mol

Flow rate of CO_2 = 20 sccm

V = 1 cm^3

No. of moles of electrons required for reducing CO_2 to C_2H_4:

$e_{output} = (5.02 \times 10^{-9}) \times 12 = 6.024 \times 10^{-8}$ moles

Time required to fill the 1 cm^3 sampling loop:

$$t = \frac{\frac{1}{20}}{60} = 3 \text{ seconds}$$

The total number of moles of electrons measured during the sampling period:

$$e_{input} = \frac{0.008228 \times 3}{96485} = 2.558 \times 10^{-7} \text{ moles}$$

$$\text{Faradaic efficiency of } C_2H_4 = \frac{6.024 \times 10^{-8}}{2.558 \times 10^{-7}} \times 100\ \% = 23.55\ \%$$

Calculation of Faradaic Efficiencies (%) of Formate

Formate was quantified using NMR. The NMR signals of known concentrations of formate and phenol (internal standard) in six standard solutions were first determined. The ratio of their NMR peak area (R) was then calculated:

$$R = \frac{Peak\ area\ of\ formate\ at\ 8.3ppm}{Peak\ area\ of\ phenol\ at\ 7.2ppm} \quad (6)$$

R was plotted as a function of formate concentration. The slope of our calibration curve was 340.7 M^{-1}.

Using the calibration curve, we can determine the concentration of formate in the catholyte:

$$\text{Formate concentration} = \frac{R}{340.7}\ M \quad (7)$$

The total volume of catholyte in cathodic compartment is 0.032 L. Hence, the number of moles of formate in the cathodic compartment is:

$$n_{formate} = 0.032\ L \times \text{Formate concentration (M)} \quad (8)$$

The number of moles of electrons required to reduce CO_2 to formate is:

$$e_{output} = n_{formate} \times 2e^- \quad (9)$$

The total number of moles of electrons measured during the sampling period:

$$e_{input} = \frac{Q}{F} \quad (10)$$

$$\text{The Faradaic efficiency of formate} = \frac{e_{output}}{e_{input}} \times 100\%$$

Example: Quantification of formate formed during CO_2 electroreduction on Cu mesocrystal catayst

The ratio of the NMR peak areas of formate and phenol:

$$R = \frac{0.3187}{3.0881} = 0.103$$

Number of moles of electrons required to reduce CO_2 to formate

$$e_{output} = \left(0.032 \times \frac{0.103}{340.7}\right) \times 2 = 1.93 \times 10^{-5}\ \text{moles.}$$

Most of the charges during the first 200s of the CO_2 reduction process are used for reducing CuCl to Cu mesocrystals (see, for example, Figure 1a). Hence, we only take into account the charges that passed through the electrode from 200-4200 seconds. From the chronoamperomogram,

$$Q = 34.44\ C$$

Hence, the total number of moles of electrons measured

$$e_{input} = \frac{34.44}{96485} = 3.57 \times 10^{-4}\ \text{moles.}$$

$$\text{Faradaic efficiency of formate} = \frac{1.93 \times 10^{-5}}{3.57 \times 10^{-4}} \times 100\ \% = 5.41\ \%$$

These calculations were repeated for the rest of the values in Supporting Table 1, and the Faradaic efficiencies are presented in Supporting Table 2.

Supporting Table 2: Faradaic efficiencies of products obtained from CO_2 reduction on Cu mesocrystals.

Faradaic Efficiencies (%)							
Sampling No.	CH_4	C_2H_4	C_2H_6	CO	H_2	Formate (accumulative)	Total
1	0.72	11.70	0.12	0.29	60.94	5.41	
2	1.00	18.92	0.11	0.38	60.51		
3	1.35	23.55	0.20	0.53	62.07		
4	1.85	29.09	0.28	0.73	76.75		
5	1.82	28.80	0.30	0.64	60.25		
6	1.83	26.18	0.27	0.68	64.31		
Average (3~6)	**1.71**	**26.90**	**0.26**	**0.64**	**65.84**	**5.41**	**100.76**

S2. pH values for electrolytes used in this work

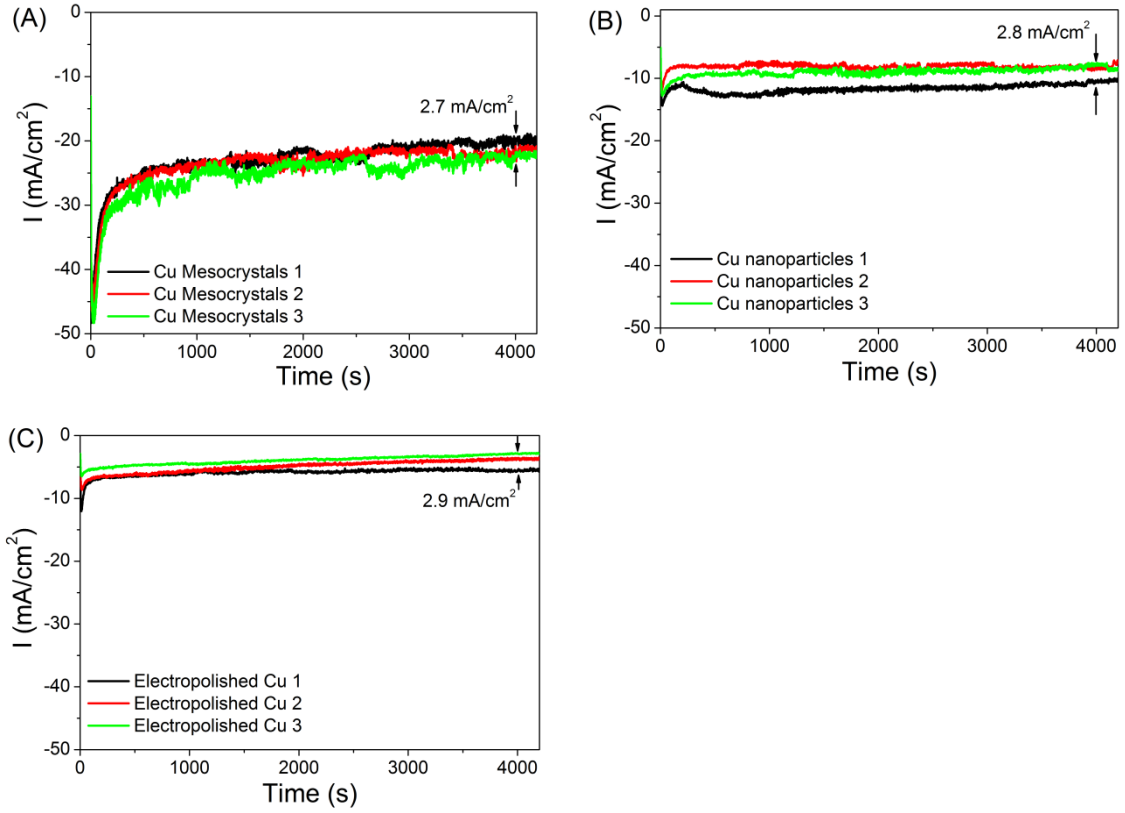
The pHs of the electrolytes used in this work were determined using a pH meter (MP220, Mettler Toledo), and are listed in Supporting Table 3. These values were checked against previous measurements when available.[1-4]

Supporting Table 3: pH values for electrolytes used in this work

Electrolytes	pH
0.1 M $KHCO_3$ saturated with CO_2	6.8
0.1 M $KHCO_3$ saturated with Ar	8.8
0.1 M $KHCO_3$ saturated with CO	8.8
0.1 M KCl	6.2

S3: Reproducibility of Experiments

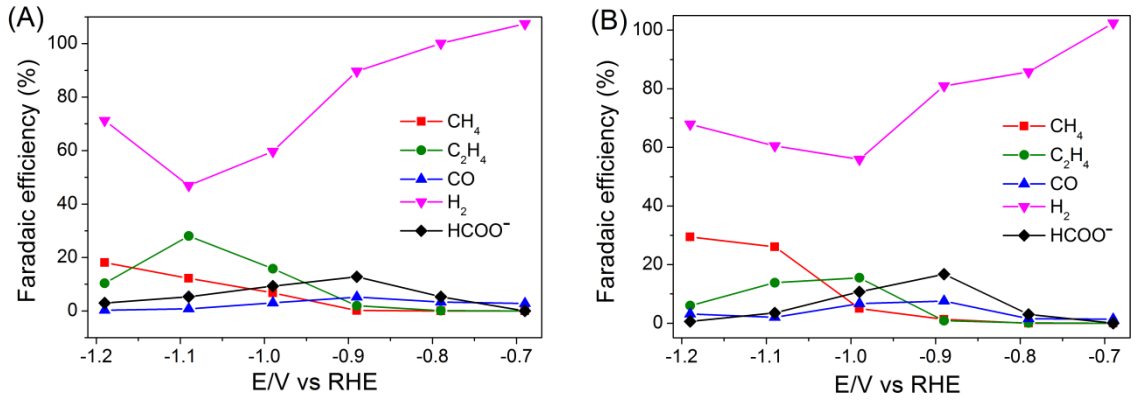
All measurements were repeated for at least three times to check for reproducibility of data. Representative chronoamperomograms of this study for Catalysts A, B and C are presented in Supporting Figure 1. The current densities (compared at 4000 seconds) of each set of catalysts varies within 3 mA cm^{-2}.



Supporting Figure 1: Chronoamperomograms of (A) Cu mesocrystals, (B) Cu nanoparticles and (C) electropolished Cu surfaces. The data was collected at -0.99 V. Electrolyte: 0.1 M $KHCO_3$ saturated with CO_2.

S4: Faradaic Efficiencies of Catalysts B and C

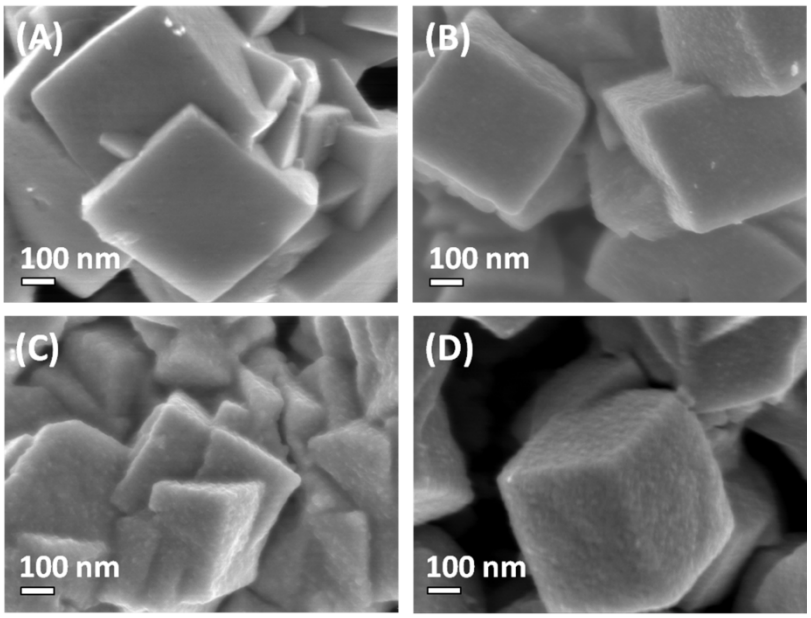
The Faradaic efficiencies for the CO_2 electroreduction products of Catalysts B (Cu nanoparticles) and C (electropolished Cu) as a function of potential are presented in Supporting Figure 2. The values for Catalyst C are consistent with previous reports.[5]



Supporting Figure 2: Faradaic efficiencies for the CO_2 electroreduction products of (A) Catalyst B and (B) Catalyst C as a function of potential.

S5: Growth Sequence of Cu Mesocrystals

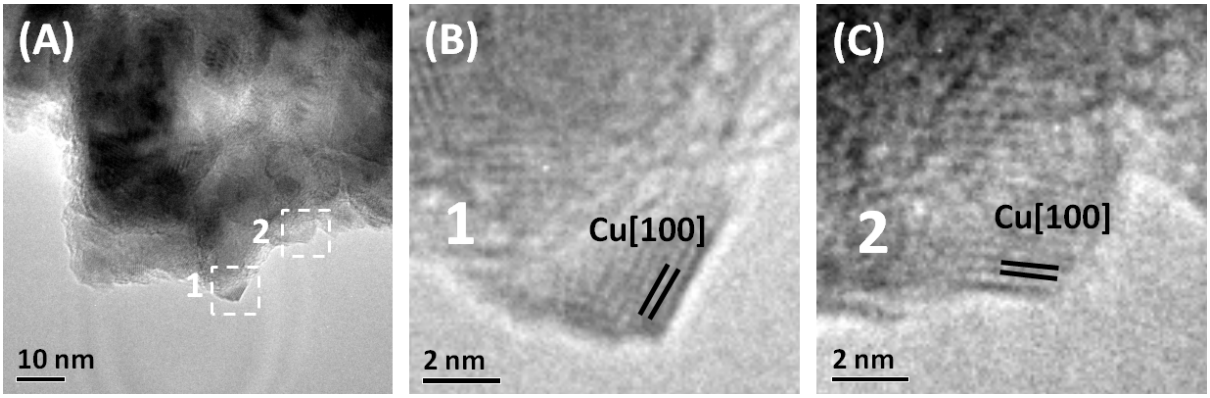
The growth sequence of the Cu mesocrystals were elucidated by SEM imaging of KCl-electrochemically roughened Cu electrodes between 10 to 100 seconds from the start of the CO_2 electroreduction process (Supporting Figure 3). Well-defined cuboid shaped Cu particles were observed as early as 10 sec into the CO_2 electroreduction (Supporting Figure 3A). Cu mesocrystals started to appear on the cuboids' surface after 20 seconds (Supporting Figure 3B and C), and the full arrangement coverage was obtained after 100 seconds (Supporting Figure 3D). This mesostructural arrangement was retained throughout the CO_2 electroreduction.



Supporting Figure 3: SEM micrographs of the Cu mesocrystals electrodes analyzed at different times from the start of the CO_2 reduction at -0.99 V: (A) 10, (B) 20, (C) 40, and (D) 100 seconds.

S6: TEM Micrographs of Cu Mesocrystals

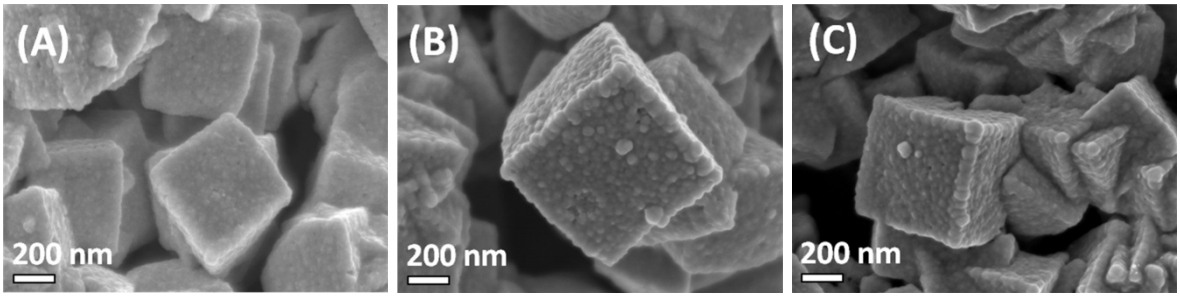
Additional TEM micrographs of Cu mesocrystals (Catalyst A) are shown in Supporting Figure 4. Numerous $(200)_{Cu}$ terminated face and rough steps/edges were found on the Cu mesocrystals.



Supporting Figure 4: TEM micrographs of the Cu mesocrystals at different magnifications. (B and C) Increased magnification of marked regions 1 and 2 shown in (A) respectively.

S7: SEM Micrographs of Cu Mesocrystals after CO_2 Reduction at Different Electrode Potentials

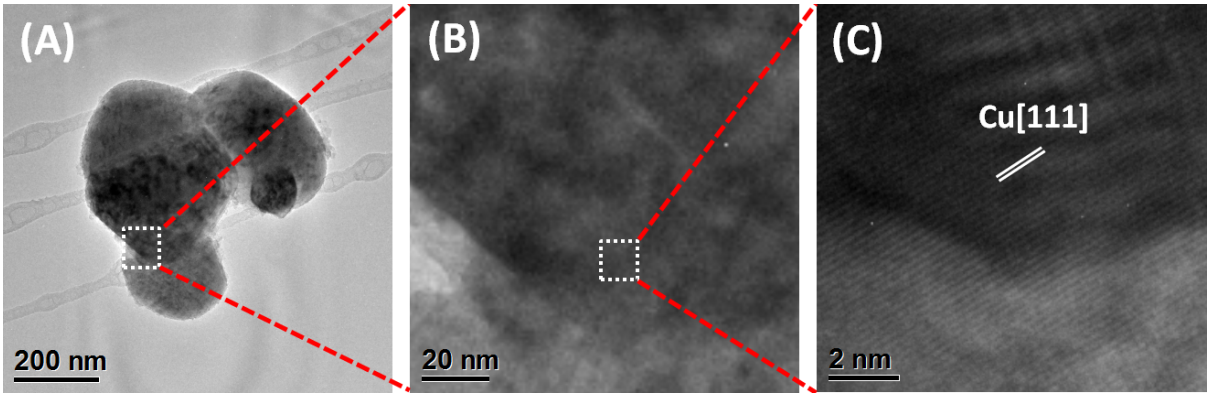
Supporting Figure 5 demonstrates that similar Cu mesocrystals were observed at different reduction potentials.



Supporting Figure 5: SEM micrographs of Cu mesocrystals after CO_2 reduction at different electrode potentials (A) -0.69 V, (B) -0.79 V, and (C) -0.89 V.

S8: TEM Micrographs of the Cu Nanoparticles (Catalyst B)

The TEM micrographs of electrodeposited Cu nanoparticles (Catalyst B) are shown in Supporting Figure 6. These electrodeposited Cu nanoparticles are crystalline and rounded, and showed no clear termination facet.



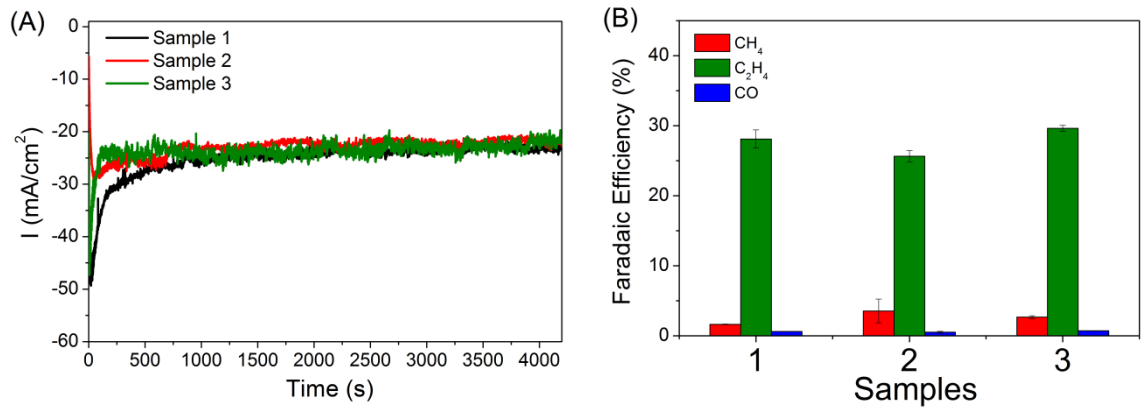
Supporting Figure 6: TEM micrographs of electrodeposited Cu nanoparticles taken at increasing magnifications. (B and C) Increasing magnifications of the section marked in (A).

S9: Stability and Robustness of Cu Mesocrystal Catalysts

Two experiments were performed to demonstrate the stability and robustness of the Cu mesocrystal catalysts against environmental contaminants and Cl^-.

Experiment 1: The Cu mesocrystals were removed from the electrochemical cell mid-reaction, and exposed to the environment for several minutes. They were then rinsed with deionized water and re-introduced to the electrochemical cell for another 4200 sec of CO_2 reduction. It can be seen that their activity (current density) and selectivity (product Faradaic efficiency) remained similar despite exposure to the atmosphere (Supporting Figure 7, Sample 2).

Experiment 2: Chloride anions (0.01 M KCl) was added to the 0.1 M $KHCO_3$ electrolyte prior to the start of the CO_2 electroreduction. The current density and selectivity of the CO_2 reduction process did not change significantly as result of the added Cl^- (Supporting Figure 7, Sample 3). This test also demonstrates that small quantities of Cl^- liberated during the reduction of CuCl to Cu mesocrystals do not play a role in the selective reduction of CO_2 to C_2H_4.



Supporting Figure 7: (A) Chronoamperomograms recorded during CO_2 reduction at -0.99 V, and (B) product faradaic efficiency of Samples 1, 2 and 3. Sample 1: Cu mesocrystals, Sample 2: Cu mesocrystals that have been removed mid-reaction, and exposed to the atmosphere, Sample 3: Cu mesocrystals with 0.01 M KCl added to the 0.1 M $KHCO_3$ electrolyte.

Further References

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2. A. A. Panova, P. Pantano and D. R. Walt, *Anal. Chem.*, 1997, **69**, 1635-1641.
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