Supplementary Materials: Electroreduction of CO_2 into Ethanol over an Active Catalyst: Copper Supported on Titania

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2. Results and Discussion

2.1. Performance Comparison of Different Cu-Supported TiO_2 Catalysts

EDX analysis of Cu/TiO_2 catalysts

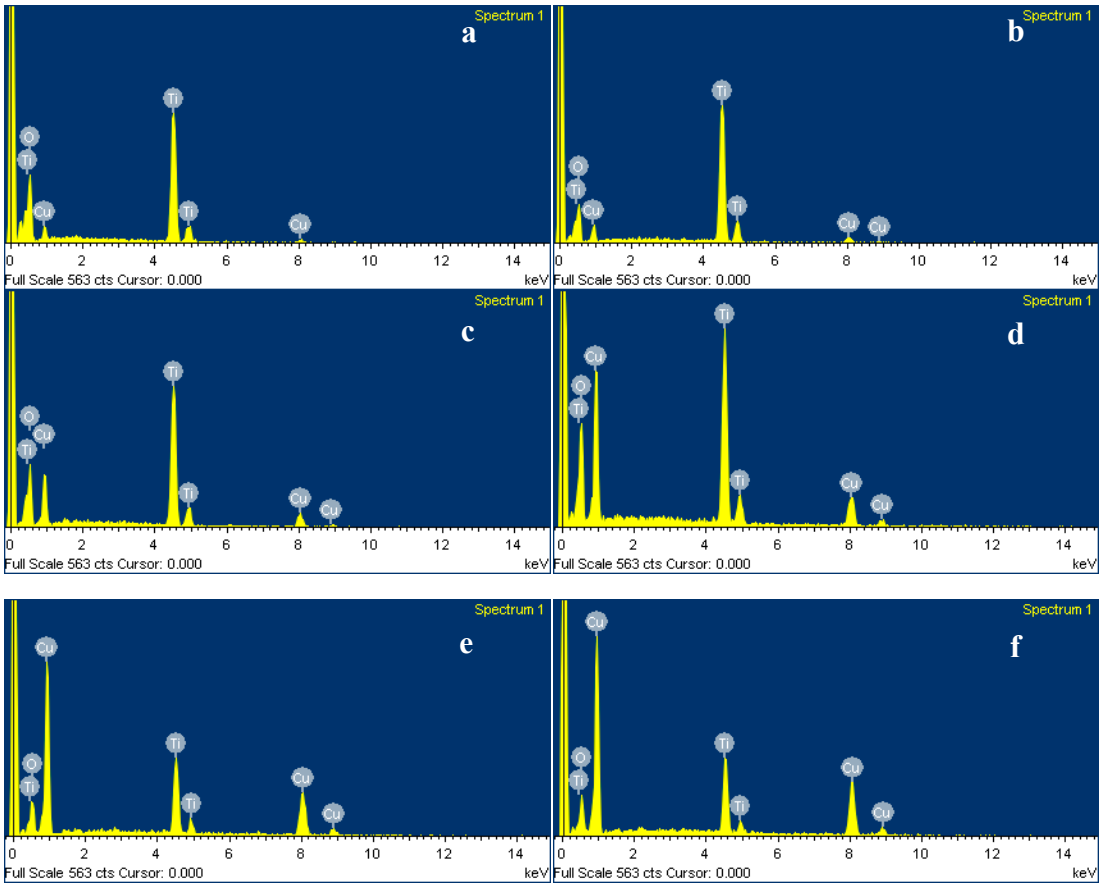


Figure S1. The EDX spectrums of Cu/TiO_2: (**a**) 5 wt % Cu/TiO_2, (**b**) 10 wt % Cu/TiO_2, (**c**) 20 wt % Cu/TiO_2, (**d**) 40 wt % Cu/TiO_2, (**e**) 60 wt % Cu/TiO_2, and (**f**) 80 wt % Cu/TiO_2.

SEM Analysis of Cu/TiO_2 Catalysts

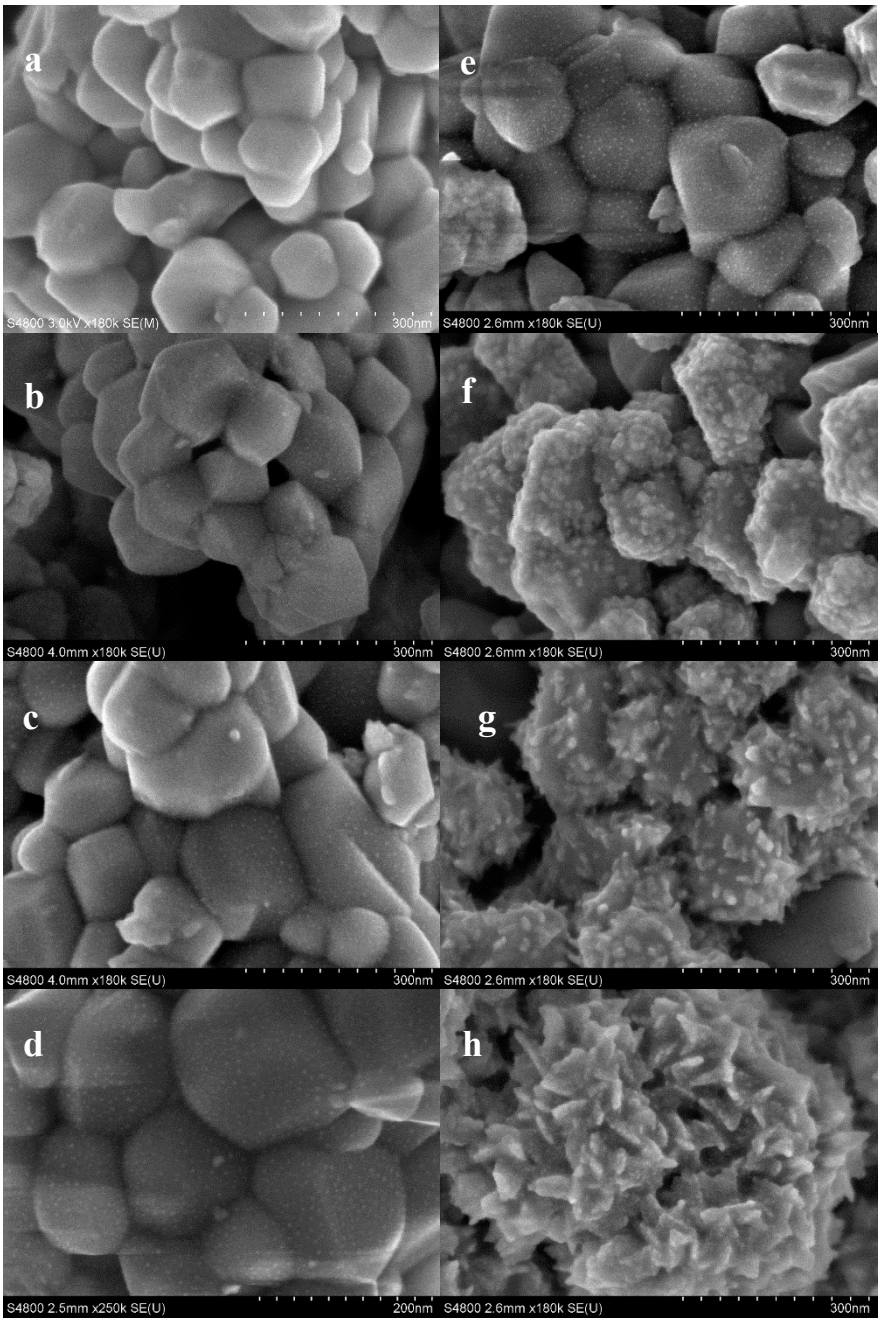


Figure S2. SEM images of (**a**) pure TiO_2, (**b**) 5 wt % Cu/TiO_2, (**c**) 10 wt % Cu/TiO_2, (**d**) 20 wt % Cu/TiO_2, (**e**) 40 wt % Cu/TiO_2, (**f**) 60 wt % Cu/TiO_2, (**g**) 80 wt % Cu/TiO_2, and (**h**) pure Cu NPs.

2.2. Catalyst Activity in a Standard Three-Electrode Cell

the Material Characterization of 40 wt % Cu/C

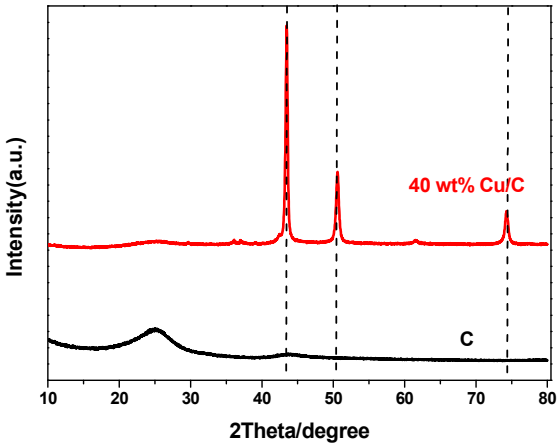


Figure S3. XRD pattern of pure C (black line) and 40 wt % Cu/C (red line)

40 wt % Cu/C was synthesized by the similar method. From Figure S3, it demonstrates that desired 40 wt % Cu/C materials were successfully fabricated, and all the diffraction peaks of the one were well indexed to the hybrid of Cu and C phase, of which the significant characteristic diffraction peaks for Cu NPs were represented by the dash lines.

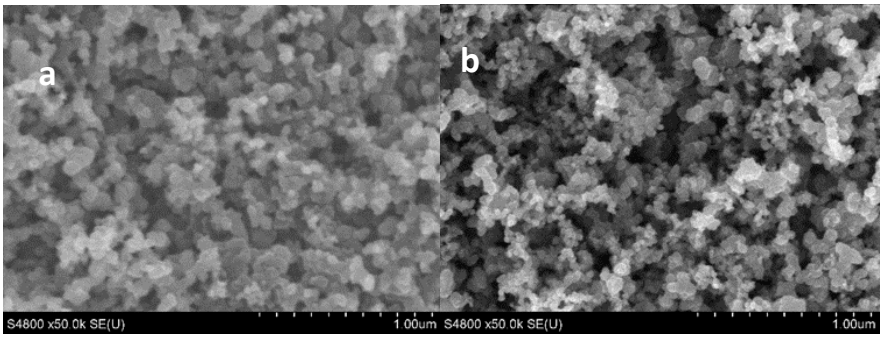


Figure S4. SEM images of pure C (**a**) and 40 wt % Cu/C (**b**).

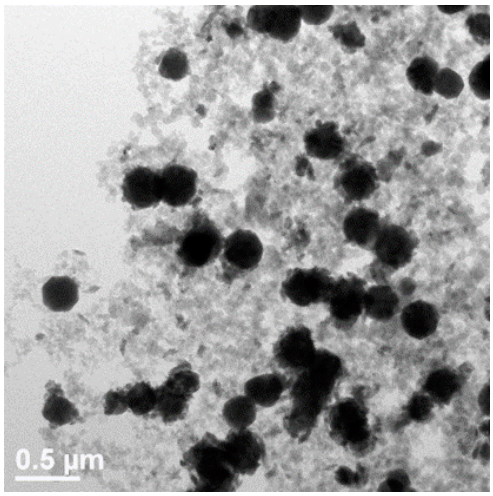


Figure S5. TEM images of 40 wt % Cu/C.

Figure S4 presents the SEM image of 40 wt % Cu/C and pure C. It can be found that there is no ability to distinguish the Cu and C, but from TEM image of 40 wt % Cu/C in Figure S5, obvious Cu NPs with an average size of about 200 nm were loaded on the surface of C. It reconfirmed that TiO_2 assists to create and stabilize small and well-dispersed Cu NPs

2.3. The Electrocatalytic Activity of Various Cu/TiO₂

Gas Chromatograms of Product Solution

The GC dates were obtained with gas chromatography-flame ionization detector (GC-FID) (SHIMADZU, GC-2014C) and manual injection of 1 μL of reaction solution. The peak at about 6.7 min was verified as ethanol by comparison to standard solutions. The produce of n-propanol and the internal standard substance isopropanol have very different retention times, at around 10.2 min and 9.8 min, respectively. Sometimes, trace methanol, which is not discussed in the paper for its little amount, could be detected at ca 4.2 min.

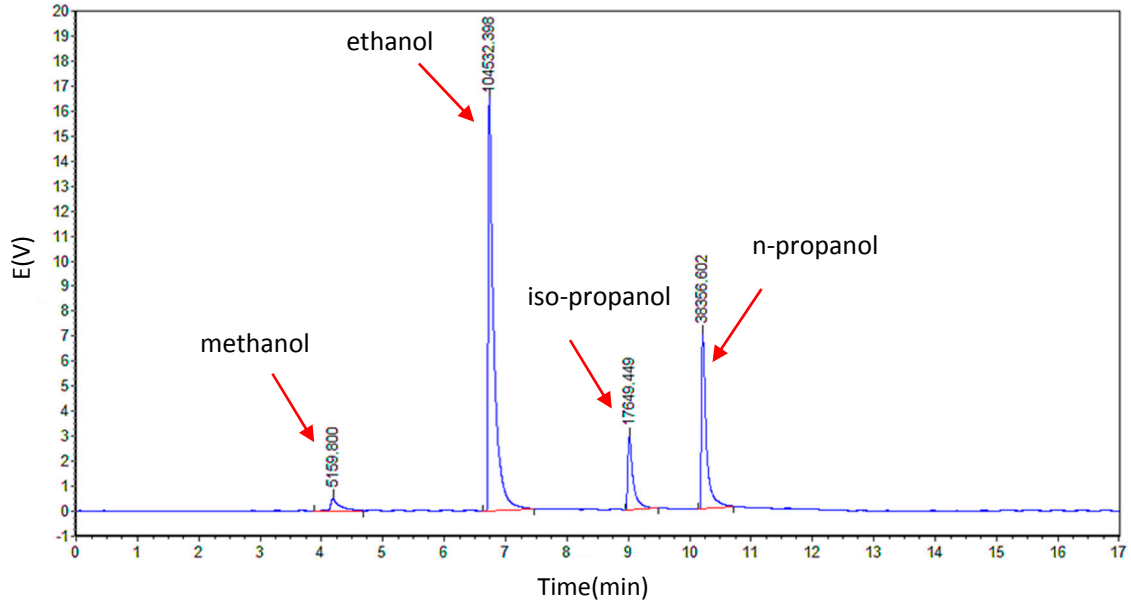


Figure S6. Gas chromatogram of product solution after a certain time bulk electrolysis of 0.2 M KI solution saturated with CO_2 at a constant cathodic potential.

The Faradaic efficiency for a specific product is calculated according to the following equation:

$$FE = \frac{z \cdot n \cdot F}{Q} \quad (1)$$

where z is the theoretical number of e^- exchanged to form the desired product, n is the number of moles produced, F is the Faraday constant (F = 96485 C/mol), and Q is the total charge applied in the process.

TEM Histograms of Cu/TiO_2 Catalysts

The average Cu particle size of the Cu/TiO_2 catalysts is below 20 nm. TEM histograms of Cu particle size distribution from the Cu/TiO_2 catalysts are shown in Figure S4. As the express of the electrolysis experiment, the 60 wt % Cu/TiO_2 catalyst exhibits more serious agglomeration than 40 wt % Cu/TiO_2 catalyst.

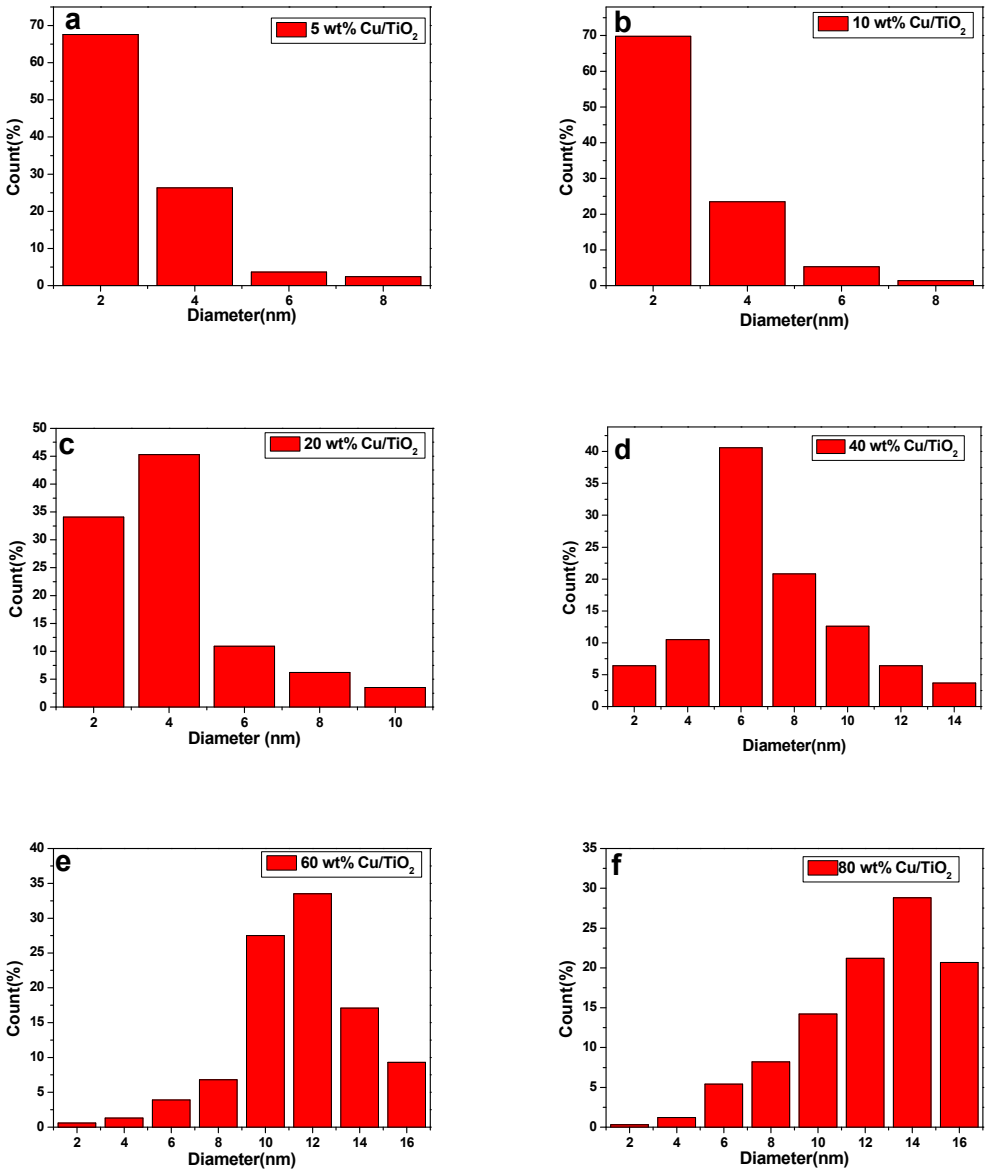


Figure S7. TEM histograms of the Cu particle size distribution from: (**a**) 5 wt % Cu/TiO_2, (**b**) 10 wt % Cu/TiO_2, (**c**) 20 wt % Cu/TiO_2, (**d**) 40 wt % Cu/TiO_2, (**e**) 60 wt % Cu/TiO_2, and (**f**) 80 wt % Cu/ TiO_2.

Electrochemistry Surface Area (ECSA) Test

In order to test the active surface of various Cu/TiO_2 samples, the double layer capacitance in N_2-saturated 0.5 M H_2SO_4 was measured by CV in a potential range from 0.35 V to 0.10 V vs. SCE without faradaic process occurred. The scan rates (ν) were 20 mV/s, 40 mV/s, 60 mV/s, 80 mV/s, and 100 mV/s, respectively. The double layer capacitance (C_{dl}) was calculated by measuring the capacitive current associated with double-layer charging from the scan-rate dependence of CV stripping. ECSA was estimated from the ratio of C_{dl} for the working electrode and the corresponding smooth metal electrode, if Cs the average C of smooth metal Cu surface (C_s) is 20 μF/cm² [1], that is, ECSA=C_{dl}/C_s. Additionally, the C_{dl} was estimated by plotting the cathodic current (I_c) at −0.25 V vs. SCE against the scan rate ($C_{dl}=I_c/\nu$). As shown in Figure S8, CV curves are recorded for various Cu/TiO_2 and 40 wt% Cu/C samples, different samples exhibit different C_{dl} and ECSA (summarized in Table S1).

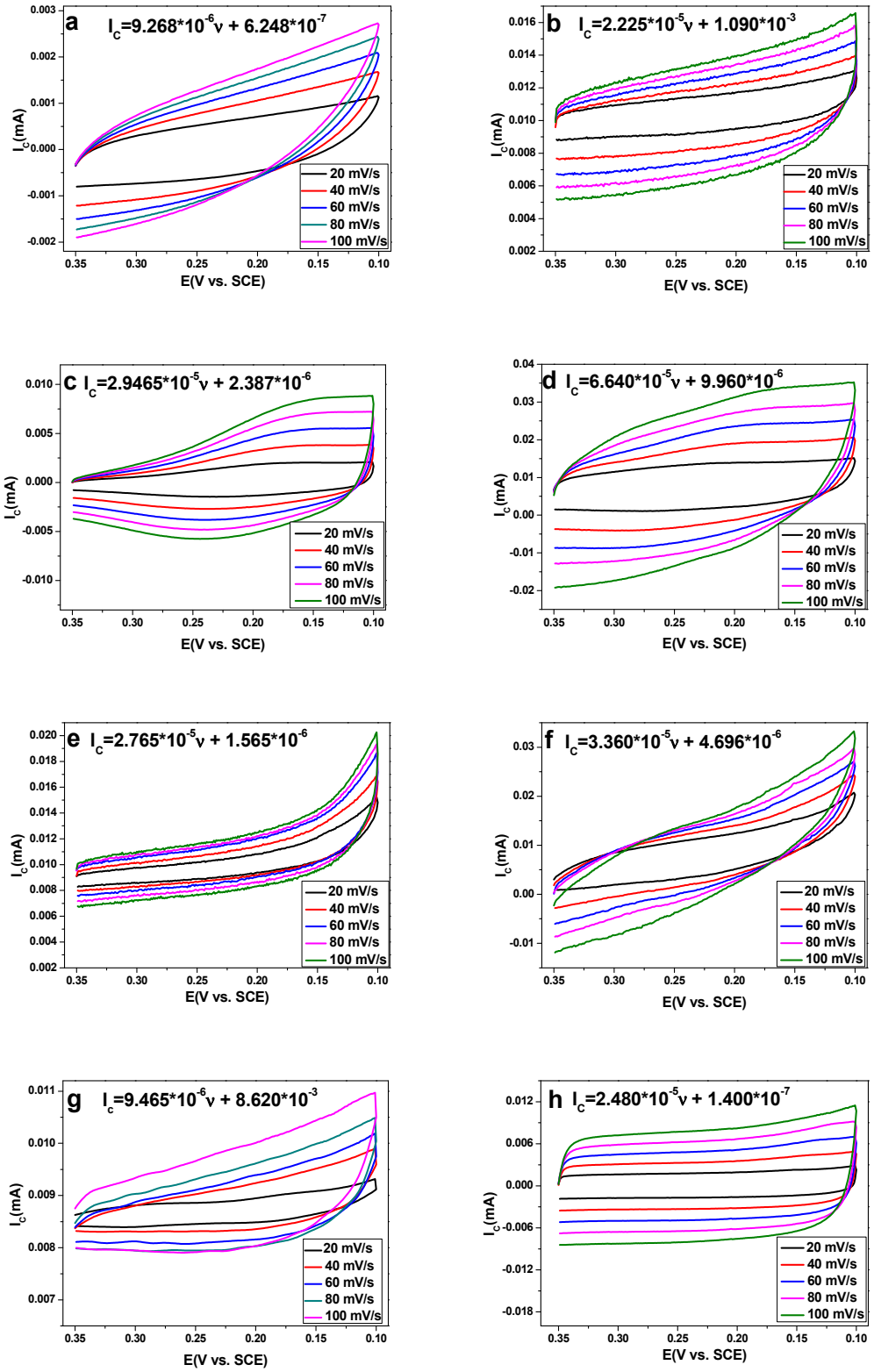


Figure S8. CVs in the capacitance current range (from 0.35 to 0.10 V vs. SCE) with (**a**) 5 wt % Cu/TiO_2; (**b**) 10 wt % Cu/TiO_2; (**c**) 20 wt % Cu/TiO_2; (**d**) 40 wt % Cu/TiO_2; (**g**) 60 wt % Cu/TiO_2; (**f**) 80 wt % Cu/TiO_2; (**g**) pure Cu NPs, and (**h**) 40 wt % Cu/C in N_2-saturated 0.5 M H_2SO_4 solution.

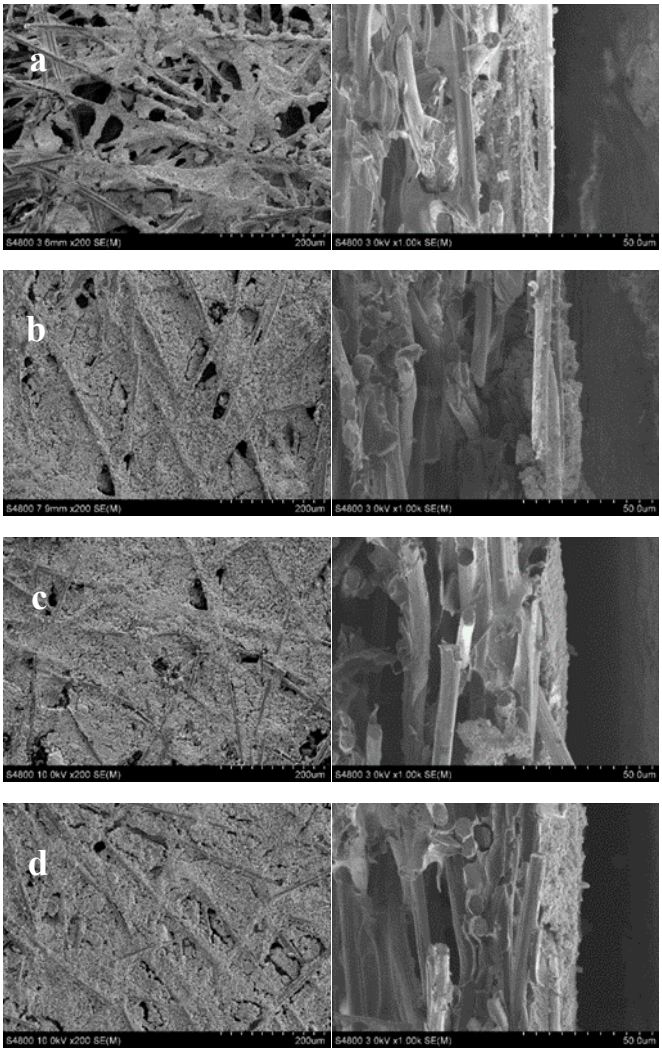
Table S1. The analysis of ECSA and J_{ECSA} for ethanol and n-propanol on various Cu/TiO_2 and 40 wt % Cu/C catalysts

Catalyst	C_{dl} (μF)	ECSA[a] (cm^2)	J_{ECSA} (mA/cm^2)	
			ethanol	n-propanol
5 wt % Cu/TiO_2	9.268	0.46	0.25	0.16
10 wt % Cu/TiO_2	22.25	1.11	0.54	0.24
20 wt % Cu/TiO_2	29.46	1.47	0.64	0.25
40 wt % Cu/TiO_2	66.40	3.32	2.37	0.54
60 wt % Cu/TiO_2	27.65	1.38	0.57	0.33
80 wt % Cu/TiO_2	33.60	1.68	0.85	0.39
pure Cu NPs	9.465	0.47	0.21	0.13
40 wt % Cu/C	24.80	1.24	0.57	0

[a] Geometic area is 1 cm^2.

2.4. Electrocatalytic Characterization

SEM Analysis of 40 wt % Cu/TiO_2 Electrodes



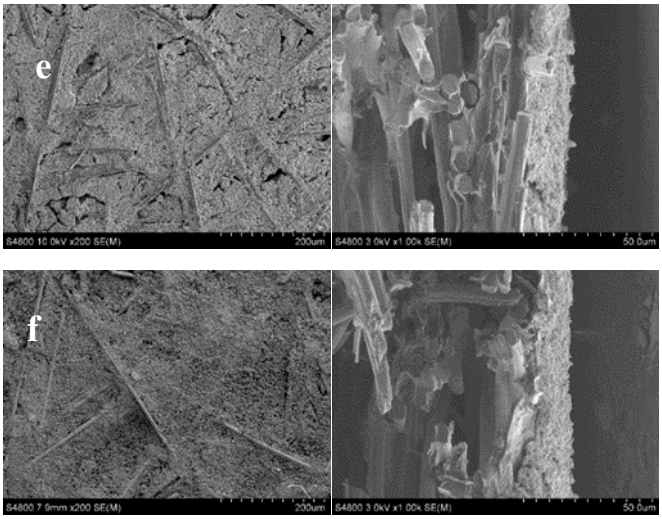


Figure S9. SEM images of the 40 wt % Cu/TiO_2 electrodes containing: (**a**) 0.5, (**b**) 1, (**c**) 2, (**d**) 3, (**e**) 4, and (**f**) 5 mg/cm^2.

Comparison the SEM Images before and after 25 h Reaction

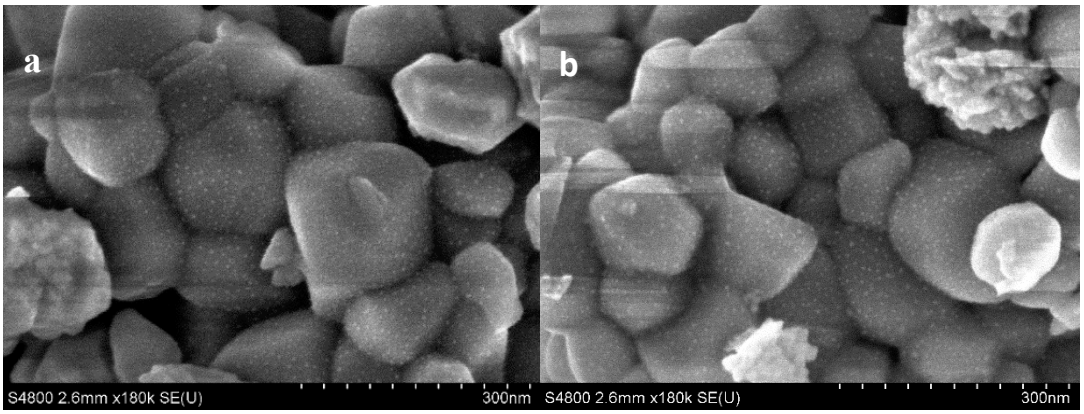


Figure S10. SEM images of 40 wt % Cu/TiO_2 (**a**) before and (**b**) after 25 h CO_2 electrochemical reduction.

Reference

Gao, S.; Lin, Y.; Jiao, X.C.; Sun, Y.F.; Luo, Q.Q; Zhang, W.H.; Li, D.Q.; Yang, J.L.; Xie, Y. Partially oxidized atomic cobalt layers for carbon dioxide electroreduction to liquid fuel. *Nature* **2016**, *529*, 68–71.