

Supply information of
Coupling electrochemical CO₂ reduction to syngas
with chloride-mediated dye degradation to CO₂ in
one-compartment cell

Honglei Chen^a, Jiahong Zeng^a, Yanming Li^a, Caitao Kang^a, Chenglong Ding^a, Yao Li^a,

Changli Li^{a*}, Jingfu He^{a*}

a. School of Materials, Shenzhen Campus of Sun Yat-sen University, Shenzhen, Guangdong
518107, P. R. China

Changli Li* – School of Materials, Shenzhen Campus of Sun Yat-sen University, Shenzhen,
Guangdong 518107, P. R. China; Email: lichli5@mail.sysu.edu.cn

Jingfu He* – School of Materials, Shenzhen Campus of Sun Yat-sen University, Shenzhen,
Guangdong 518107, P. R. China; Email: hejf27@mail.sysu.edu.cn

Experimental section

1.1. Materials

KHCO_3 (AR, 99.5%), KCl (99.5%), K_2SO_4 (99.5%), Methyl orange (MO, 96%), KH_2PO_4 (99.5%), K_2HPO_4 (99.5%) were purchased from Macklin (Shanghai). The anion exchange membrane (AEM, FFA-3-50) was ordered from Fumasep (Germany). The Ag/AgCl (3.5 M KCl) reference electrodes and Pt wire counter electrode were purchased from Gooss union (Tianjin). Carbon dioxide (CO_2 , $\geq 99.99\%$) and nitrogen was purchased from Gerui Special Gas Plant (Shenzhen).

1.2 Synthesis of Catalyst.

1.2.1 Pretreatment of carbon cloth (CC).

The CC was ultrasonicated for 15 min with acetone, deionized water and ethanol, respectively. After that, the cleaned CC was dried under infrared light for 5 min.

1.2.2 Magnetically sputtered Cu, Ag, Bi, Ni-Fe.

We prepared Cu, Ag, Bi and Ni-Fe films on CC by magnetron sputtering at room temperature with pure Cu, Ag, Bi, Ni-Fe target, deposited at Ar (99.99%) 25 sccm, working pressure of 1 Pa and sputtering power of 30 W (Cu), 40 W (Ag), 20 W (Bi) for 5 min and 200 W Ni-Fe (9 min).

1.3 Characterization

The crystalline structures were characterized by X-ray diffraction (XRD; Bruker D8 Advance) at a scanning rate of 5° min^{-1} in the 2θ range of $10\text{--}90^\circ$. X-ray photoelectron spectroscopy (XPS) was carried out on an Thermo Scientific K-Alpha Nexsa using $\text{Al-K}\alpha$ radiation. Calibrate the binding energy according to the carbon signal (binding energy = 284.8 eV). Scanning electron microscope (SEM) images were operated using a +Regulus 8100 (Hitachi Corporation of Japan)

instrument. The ^1H NMR is tested by mixing the sample and DMSO containing the TMS (internal standard) with a volume ratio of 4-1 (AVANCE NEO 400MHZ). The anode pollutant MO, whose characteristic peak at 466 nm (azo Group) was measured by ultraviolet-visible spectrophotometer (UV-vis). The % removal was calculated using initial and final concentrations of dye in the reaction as follows,

$$\text{RE}_{\text{MO}} = (C_0 - C_t)/C_0 \times 100\%$$

where C_0 is the initial MO concentration (mg/L), and C_t is the MO concentration at different electrolysis time (mg/L).

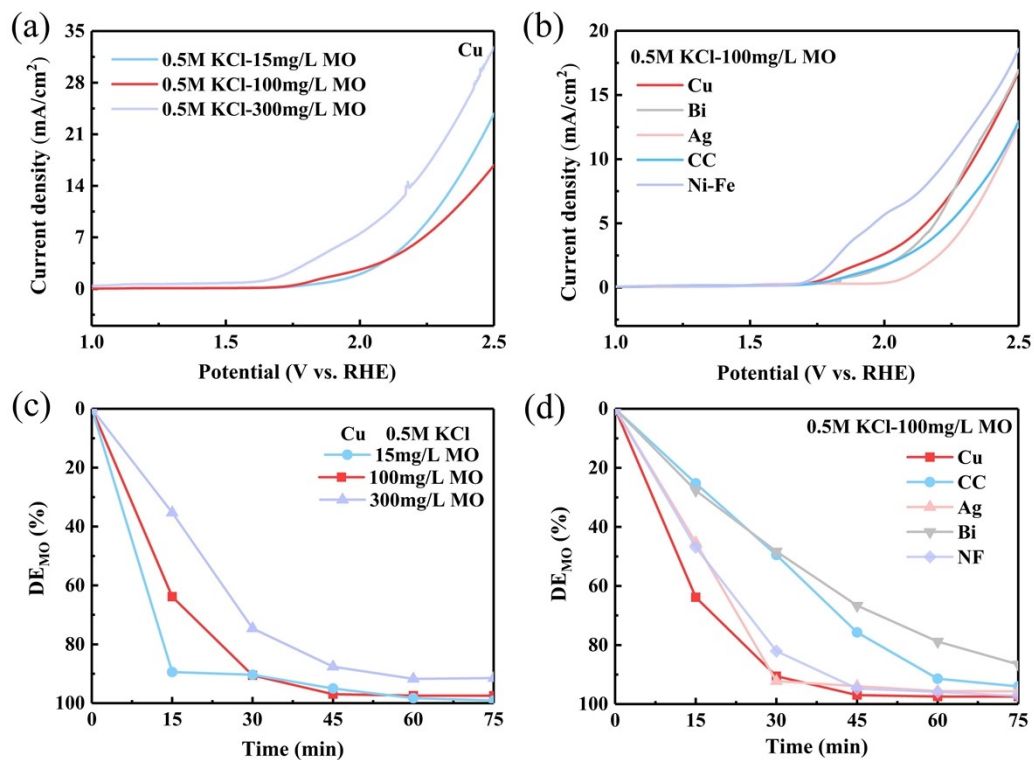
The gas products produced by cathode CO_2RR including H_2 , CO and CH_4 , which were detected and quantified using gas chromatography (GC, Shimadzu 2014) with two detectors (TCD and FID).

Electrochemical measurements were conducted using an electrochemical workstation (CHI760E, China) with a typical three-electrode system or two-electrode system. Except the cathodic CO_2RR uses an H-type cell, the rest of the tests were conducted using single-chamber electrolyzer. For three-electrode system, prepared materials were cut into a $1 \text{ cm} \times 1.5 \text{ cm}$ (guarantee the effective test area for 1 cm^2) rectangle as working electrode, Pt wire as the counter electrode, and Ag/AgCl as the reference electrode. Various electrolytes were employed for the measurements and all the electrolyte was purged with 50 sccm (the gas flow rate was set via a mass flow controller) CO_2 for 30 min to saturate CO_2 in solution before the electrochemical measurement. For parallel comparison with literature values, potentials were measured vs. Ag/AgCl and converted to the reversible hydrogen electrode (RHE) according to the Nernst equation:

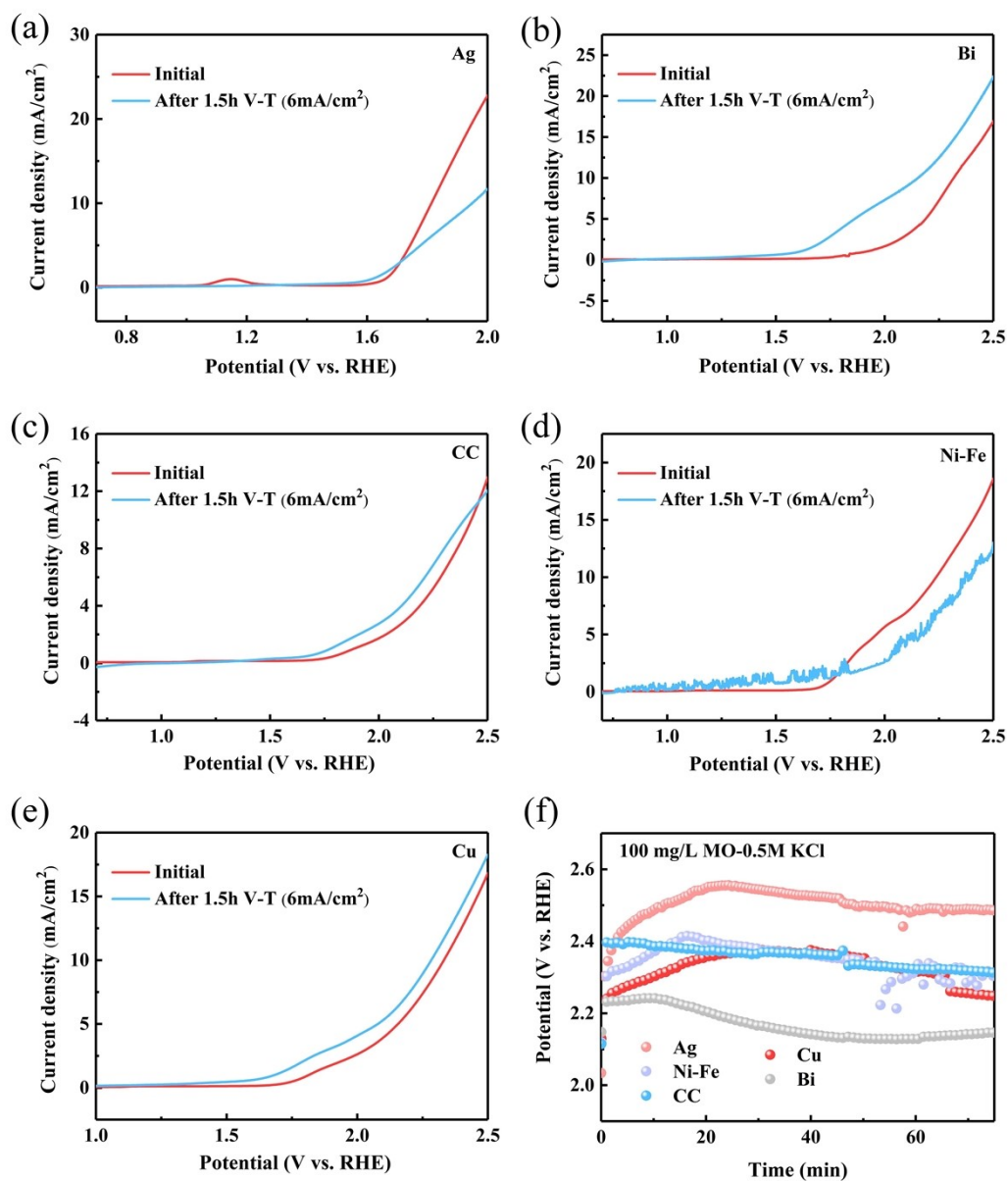
$$E(\text{RHE}) = E(\text{vs. Ag/AgCl}) + 0.059 \text{ pH} + 0.197 \text{ V}$$

The linear sweep voltammetry (LSV) was recorded at a scan rate of 10 mV s^{-1} . The anode durability was tested at the current density of 6 mA cm^{-2} for 1.25 h, which is the test condition for anodic MO degradation. For cathodic CO_2RR test, the V-T measurement was selected at the current density of -6 mA cm^{-2} for 1.25 h. And the Faraday efficiency of the cathode products could be calculated as below:

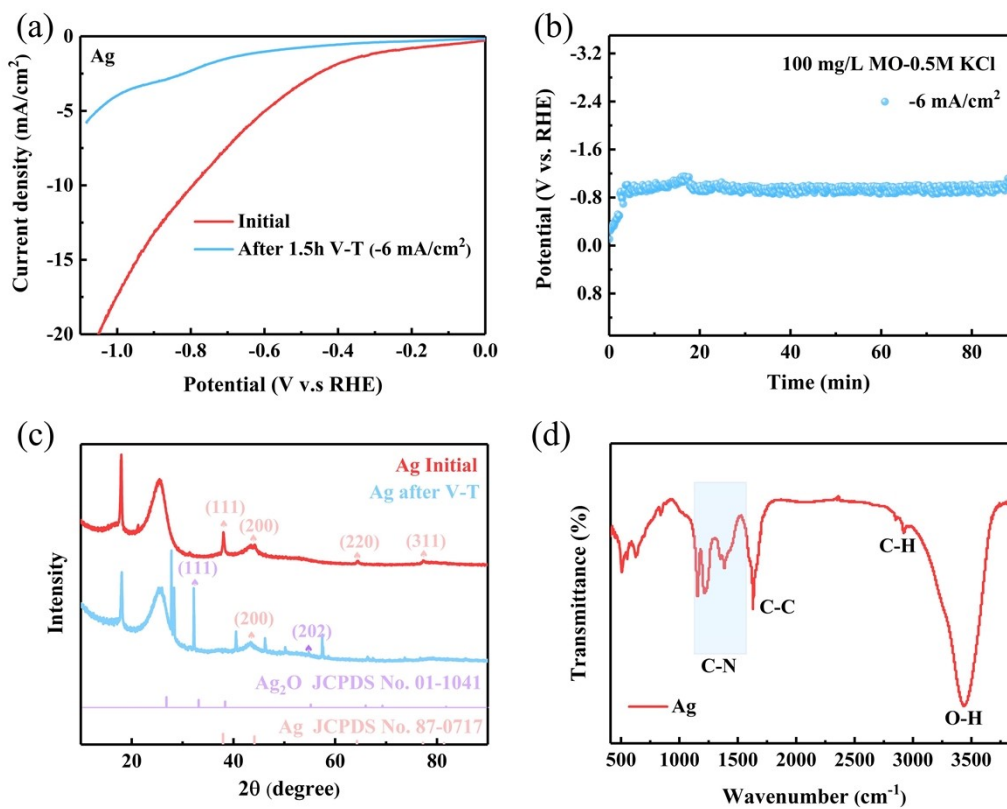
$$FE_{\text{gas product}} = \frac{n \times F \times N}{Q} \times 100\% = \frac{\left(V_{\text{gas}} \times \frac{C_{\text{gas product}}}{V_m} \times 10^{-5} \right) \times F \times e^{-\text{transfer number}}}{i \times t} \times 100\%$$



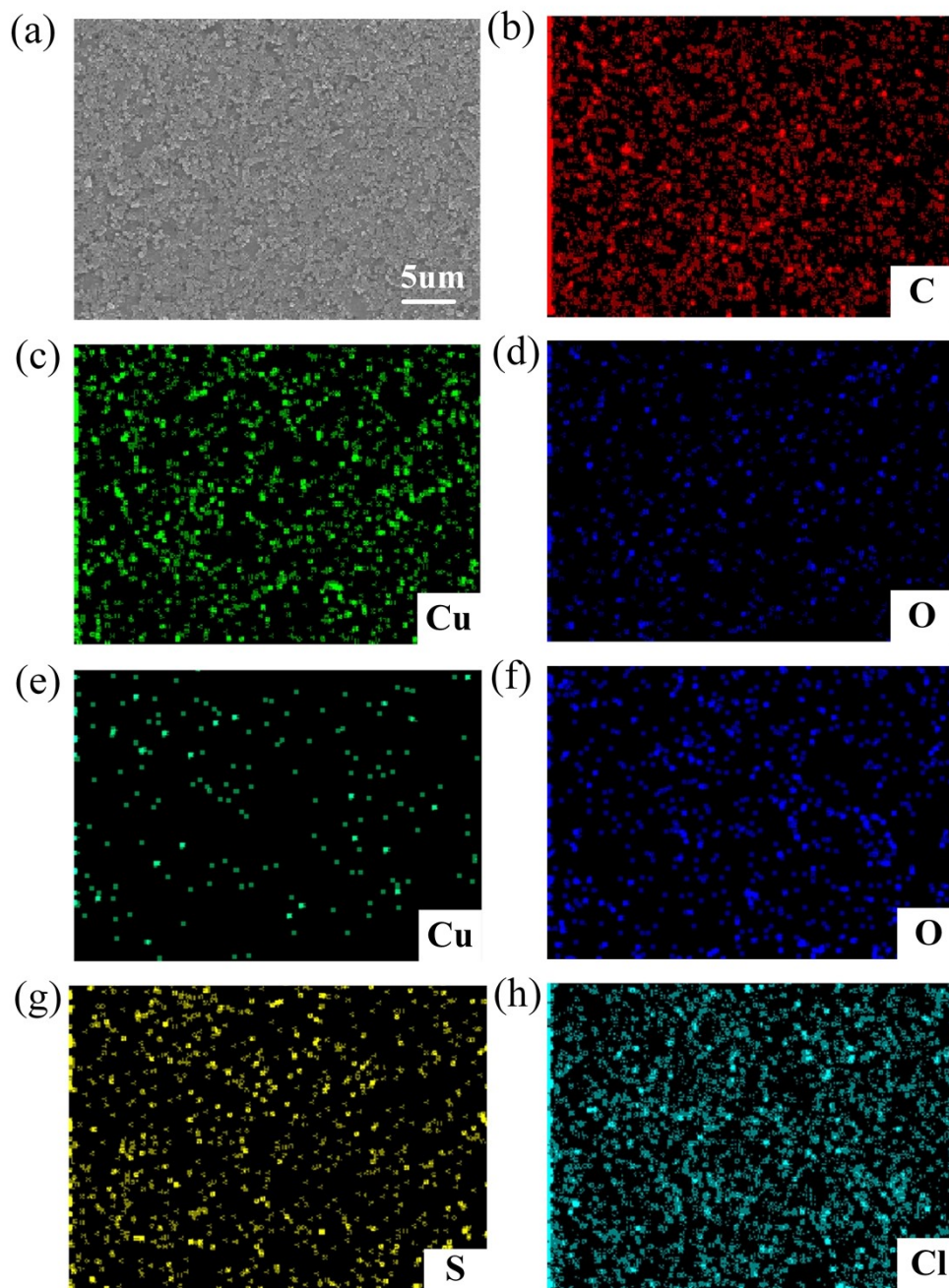
Supply Figure 1. (a) Anodic LSV of Cu catalyst in different electrolytes. (b) Anodic LSV of different catalysts in 100 mg/L MO-0.5M KCl electrolyte. (c) Degradation efficiencies of different MO concentrations by Cu catalyst. (d) Degradation efficiencies of different catalysts in 100 mg/L MO-0.5M KCl electrolyte.



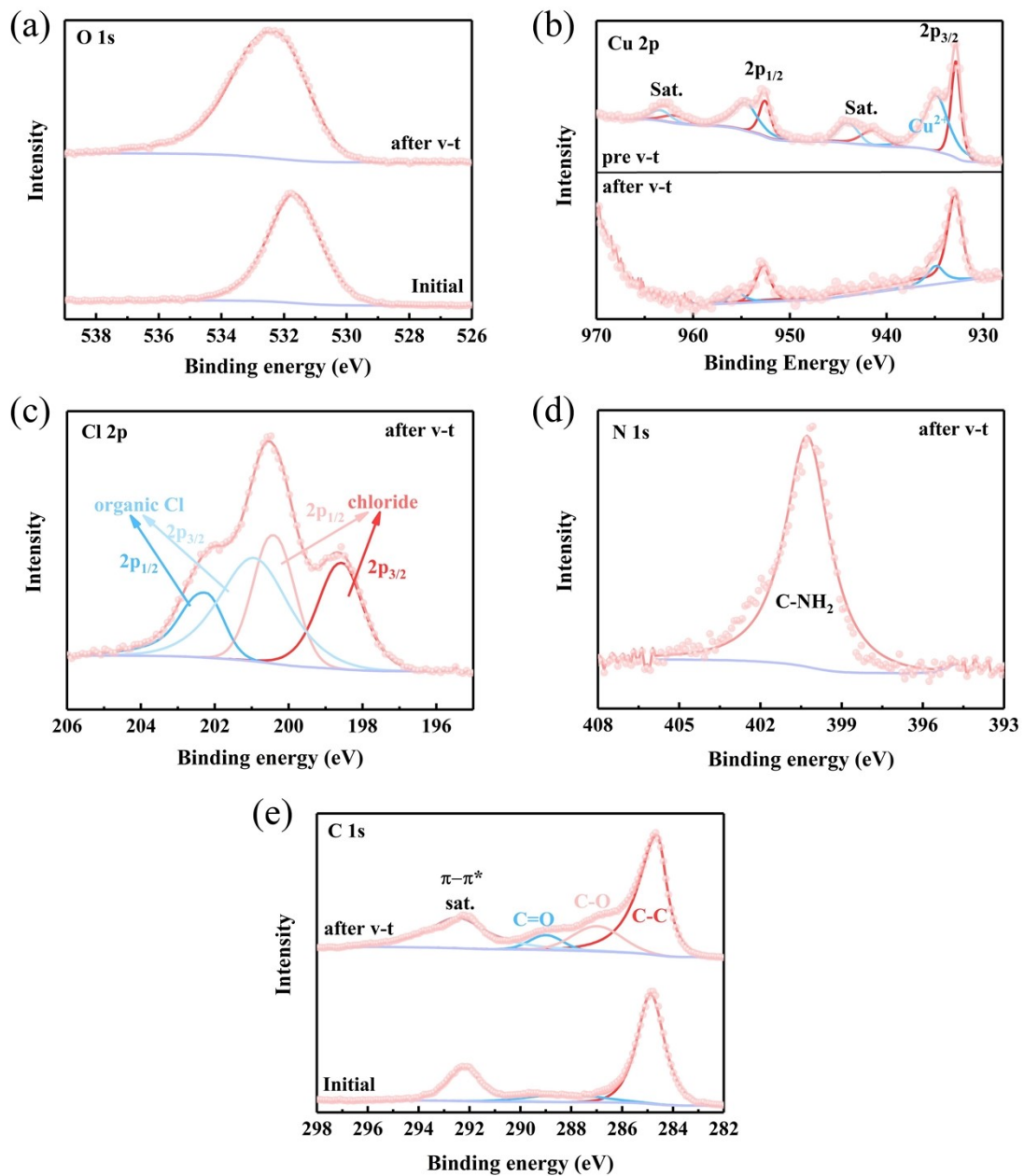
Supply Figure 2. LSV curves in 100 mg/L MO-0.5M KCl by different catalysts before and after 90 min V-T test (6 mA/cm²). (a) Ag; (b) Bi; (c) CC; (d) Ni-Fe; (e) Cu. (f) V-T test (6 mA/cm²) for various catalysts.



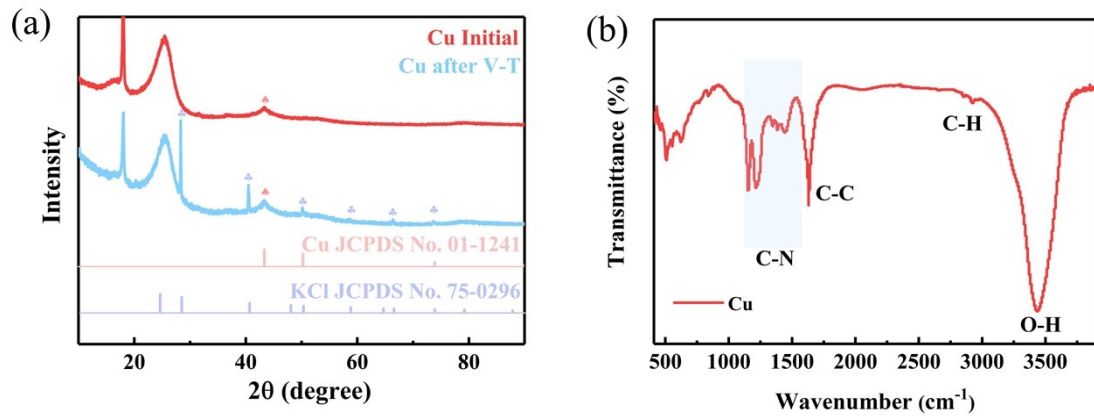
Supply Figure 3. (a) LSV curves of Ag catalyst before and after 90 min V-T test (-6 mA/cm²); (b) V-T test; (c) XRD patterns of Ag before and after V-T test; (d) FT-IR of Ag after V-T test.



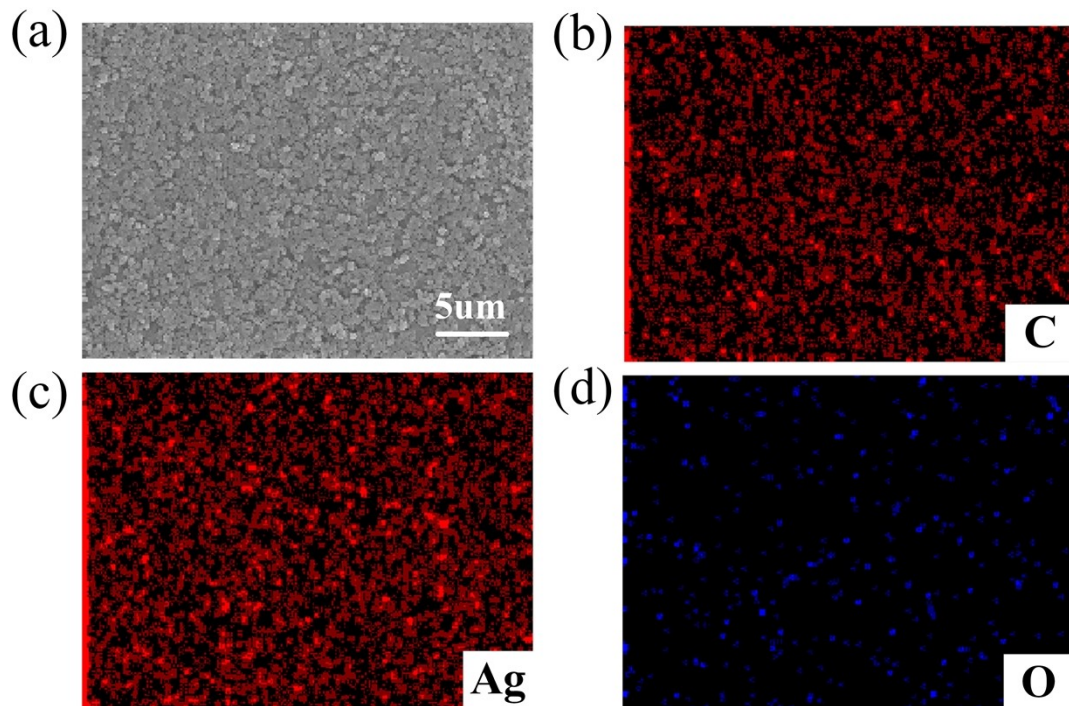
Supply Figure 4. EDS mappings of Cu catalyst (a-d) before 90 min V-T test (6 mA/cm²) and (e-h) after V-T test.



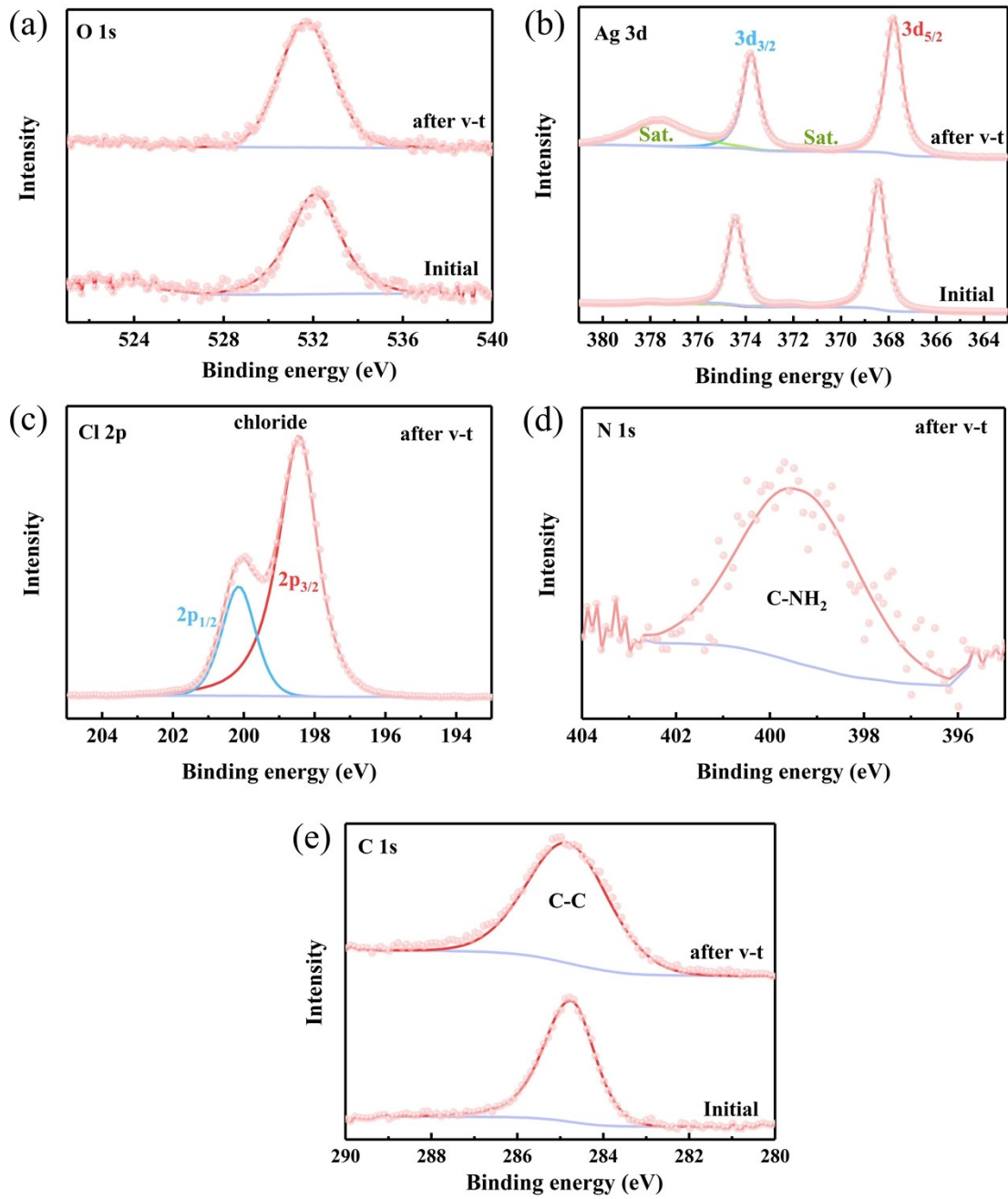
Supply Figure 5. XPS of Cu before and after 10 min V-T test (6 mA/cm²).



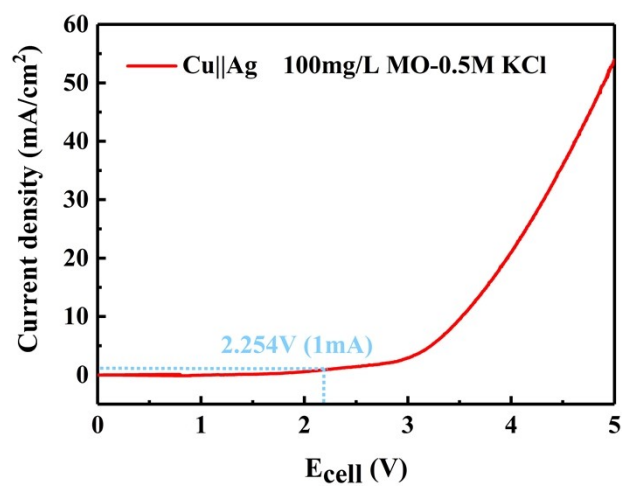
Supply Figure 6. (a) XRD pattern of Cu before and after 90 min V-T test (6 mA/cm²); (b) FTIR of Cu after V-T test.



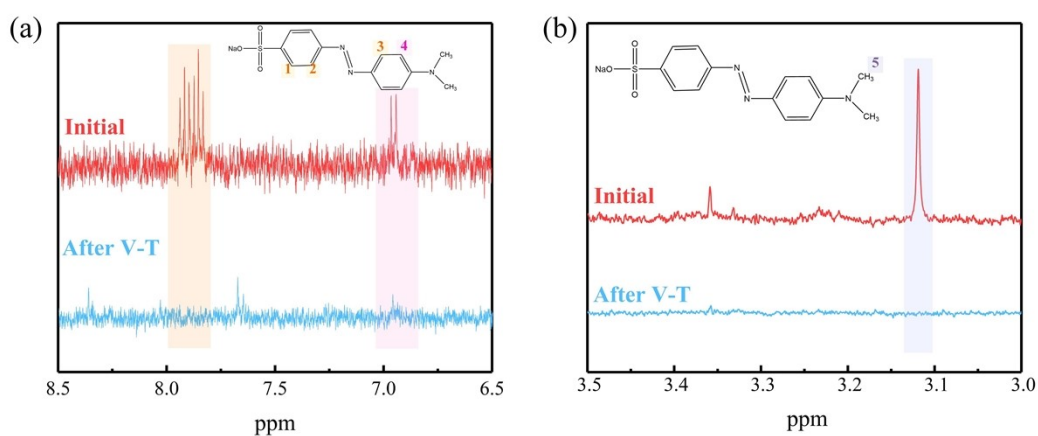
Supply Figure 7. EDS mappings of Ag before V-T test (-6 mA/cm²).



Supply Figure 8. XPS of Ag before and after V-T test (-6 mA/cm²).



Supply Figure 9. LSV of coupled integrated system with Cu anode for MO degradation and Ag cathode for CO₂RR in 100 mg/L MO-0.5M KCl electrolyte.



Supply Figure 10. ¹H NMR spectra of Methyl Orange before (red line) and after degradation (blue line). (a) Signals between 6.6 ppm and 8.0 ppm corresponding to the protons of the aromatic rings. (b) Singlet peak at 3.12 ppm is attributed to the two methyl groups attached to the nitrogen atom.