

## Support information

**Chemicals and Materials.** The pieces of customized 6 cm × 6 cm Cu mesh (200 mesh, 0.05 mm wire diameter, 99.99% purity) were purchased from Anping County Chulin Metal Mesh Co., Ltd. Cerium (III) nitrate, hexahydrate ( $\text{CeN}_3\text{O}_9 \cdot 6\text{H}_2\text{O}$ , 99.99%) were purchased from Shanghai Boer Reagent Co., Ltd. 5-hydroxymethyl-2-furaldehyde ( $\text{C}_6\text{H}_6\text{O}_3$ , 99%), ethanol ( $\text{C}_2\text{H}_5\text{OH}$ , AR) and Potassium hydroxide (KOH, 99.99%) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Copper (II) nitrate trihydrate ( $\text{CuN}_2\text{O}_6 \cdot 3\text{H}_2\text{O}$ , 98%) were purchased from Sinopharm Inc. All chemicals were used as received without further purification and ultrapure water (Millipore, 18.2 MΩ cm) used for all processes.

**Synthesis of Cu mesh catalysts.** Based on our previous work<sup>1</sup>, we carried out the following preparative scheme for this reaction. First, the pieces of customized Cu mesh were cleaned by sonication in ethanol and ultrapure water for 5 min, respectively. Then, two precleaned Cu mesh pieces were chrono-potentiometrically cycled in 0.15M  $\text{Ce}(\text{NO}_3)_3$  solution by applying an alternating current of ±200mA (each segment for 40 s) for 400 segments on an electrochemical station (CORRTEST CS310X). Note that the area of the Cu mesh immersed into the electrolyte is around 24 cm<sup>2</sup> (6 cm × 4 cm), therefore the current density is fixed at 8.3 mA cm<sup>-2</sup>. After finishing electrochemical treatment, the obtained

samples were immersed into ultrapure water with 10 min sonication to remove blockage. Finally, the samples were dried at 60 °C for 8 h and denoted as Ec CM-Ce. To better illustrate the role of electrochemical treatment in the preparation process, we set up another set of  $\text{Cu}(\text{NO}_3)_2$  as a control for the solution system, which we denoted as Ec CM.

**Products analysis.** The reactants and products were analyzed qualitatively and quantitatively by high performance liquid chromatography (HPLC, Agilent). After the constant potential reaction, samples from the anode chamber were taken to analyze the sample solution by HPLC using a ZORBAXEclipseXDB-C18(5 $\mu$ m.4.6x-250mm) column and an ultraviolet detector at  $\lambda=265$  nm. The experimental conditions were as follows: the column temperature was maintained at 35 °C; mobile phase A was methanol and B was 5 mM aqueous ammonium formate solution, the ratio of A to B was 1:9, and the flow rate was 0.45 mL/min. The retention times of FDCA, HMF and DFF were 19.8, 43.1 and 53.6 min, respectively, during the 60 min run time. The amounts of reactants and oxidation products were calculated by the external standard method, which was used to calculate the conversion of HMF, the yield of oxidation products, and the Faraday efficiency for the production of FDCA, respectively, where F stands for the Faraday constant of 96,485 C/mol as shown in Eqs. (1-4).

$$\text{Conversion}(\%) = \left( 1 - n_{\text{HMF-instant}}/n_{\text{HMF-initial}} \right) \times 100\% \quad (1)$$

$$Selectivity(\%) = (n_{product}/n_{HMF-consumed}) \times 100\% \quad (2)$$

$$Yield(\%) = (n_{product}/n_{HMF-initial}) \times 100\% \quad (3)$$

$$FE(\%) = (n_{product}/n \times F \times Q) \times 100\% \quad (4)$$

where  $n_{HMF-initial}$ ,  $n_{HMF-instant}$ , and  $n_{HMF-consumed}$  represent the initial, instant, and consumed moles of HMF, respectively, and  $n_{product}$  represents the moles of products. In formula (4),  $n$ ,  $F$ , and  $Q$ , respectively, represent the number of transferred electrons, Faraday constant (96485C mol<sup>-1</sup>), and total transferred charges for the generation of specific product.

**Characterization.** X-ray powder diffraction patterns (XRD) was recorded using a Bruker X-ray diffractometer using Cu K $\alpha$  radiation ( $\lambda = 1.540589 \text{ \AA}$ ). The results were acquired in the range of 10-80° with a step size of 0.12° and a scan speed of 10°/min.

Scanning electron microscope (SEM) was performed on a Nova NanoSEM 450 field emission SEM, which was operated at the accelerating voltage of 15 kV and the detector current of 10 mA. Energy dispersive spectrometer (EDS, TEAMEDS, China) was applied to study the dispersion of element.

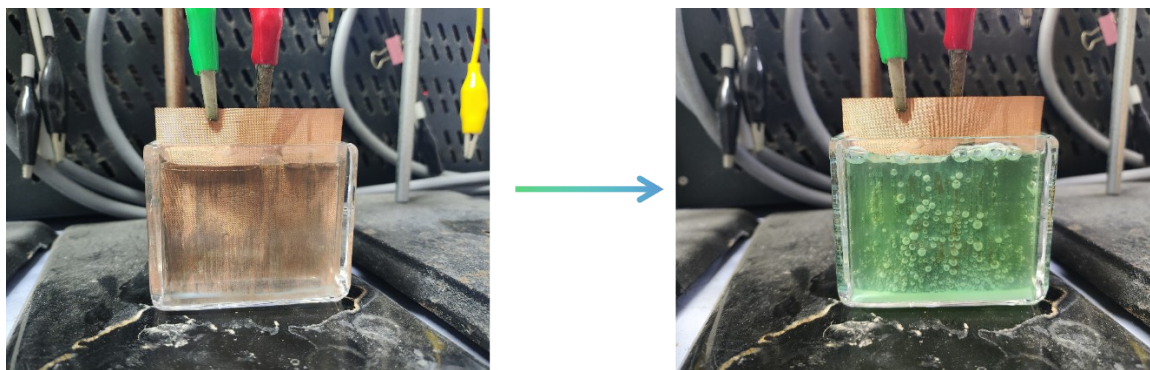
XPS was performed on a Thermo Scientific K-Alpha spectrometer, using a monochromatic Al-K radiation source (1486.6 eV, pass energy 20.0 eV). The binding energies (BEs) were calibrated using the C1s peak at 284.8 eV as a reference. Sputter etching was performed using the Ar<sup>+</sup>ion gun over a 2 × 2 mm raster size and ion energy was set as 2000

eV. There are 5 etching levels and each level maintains 2000 s. Spectra were obtained after each etching level.

Surface-enhanced In situ ATR-IR (SEIRAS) was measured at PerkinElmer spectrum 100 spectrometer equipped with a mercury cadmium telluride (MCT) detector, a variable angle specular reflectance accessory (Jiaxing Puxiang Tech. Ltd.) and cell (Jiaxing Puxiang Tech. Ltd.) including a Pt counter electrode (CE), an Ag/AgCl reference electrode (RE), a gas inlet port and a gas outlet port. As the working electrode (WE), CP supported catalyst was tightly contacting the surface of the silica prism. Before electrochemical measurements, the electrolyte (7mM HMF, 0.1M KOH) was injected into the cell. A CHI1242C potentiostat was employed to record the electrochemical response. The spectrum was collected step-wisely from OCV to 0.7V vs. RHE with a dwell time of 2 min at each potential. The exact preparation process can be found in our previous work<sup>2</sup>.

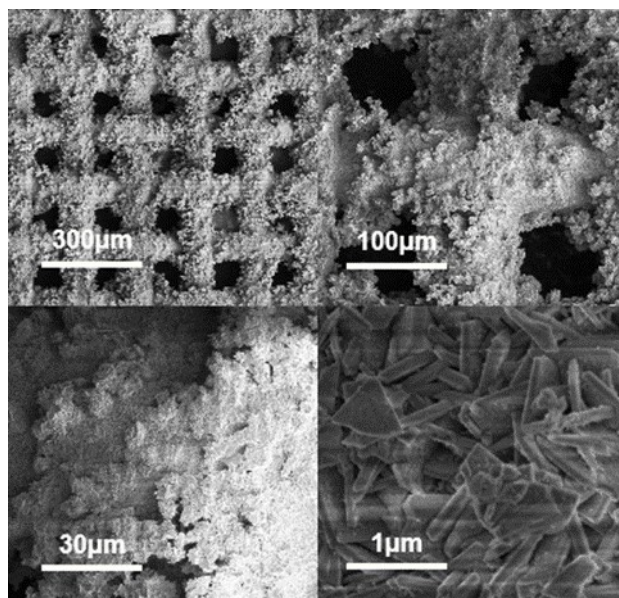
Surface Enhanced In situ Raman (SERS) is an innovation on single crystal silicon(Shandong YuanJing Electronic Technology Co., Ltd) wafers that combines our previous work experience with the work of Li<sup>3</sup>. Raman spectra were measured by microscopic confocal Raman Spectrometer (LabRAM HR, Horiba J.Y.) under ambient conditions with 532 nm laser source. The cell (Jiaxing Puxiang Tech. Ltd ) including a Pt counter electrode (CE), an Ag/AgCl reference electrode (RE), a gas inlet

port and a gas outlet port. Before electrochemical measurements, the electrolyte (7mM HMF, 0.1M KOH) was injected into the cell. A CHI1242C potentiostat was employed to record the electrochemical response. The spectrum was collected step-wisely from OCV to 0.7V vs. RHE with a dwell time of 5 min at each potential.



**Figure S1.** Electrochemical treatment of CM in  $\text{Ce}(\text{NO}_3)_3$  solution yields

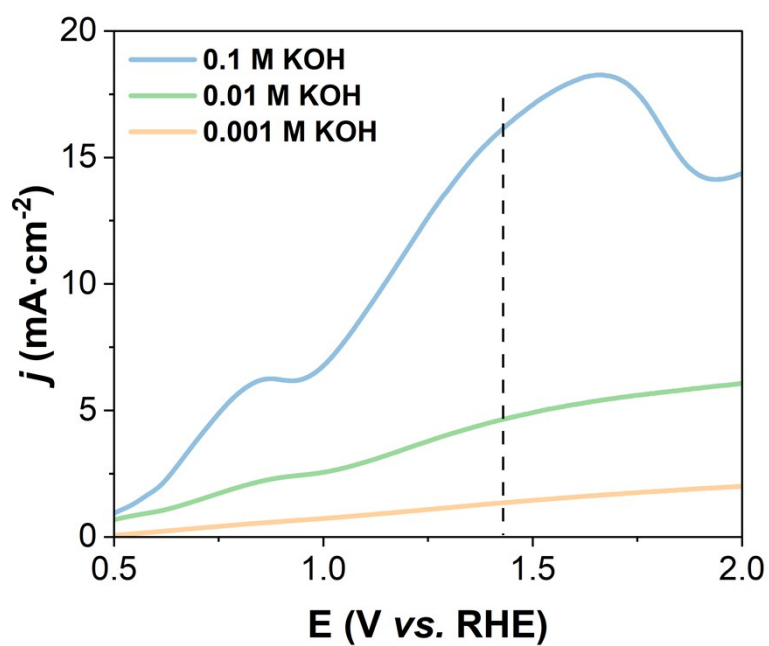
Ec CM-Ce



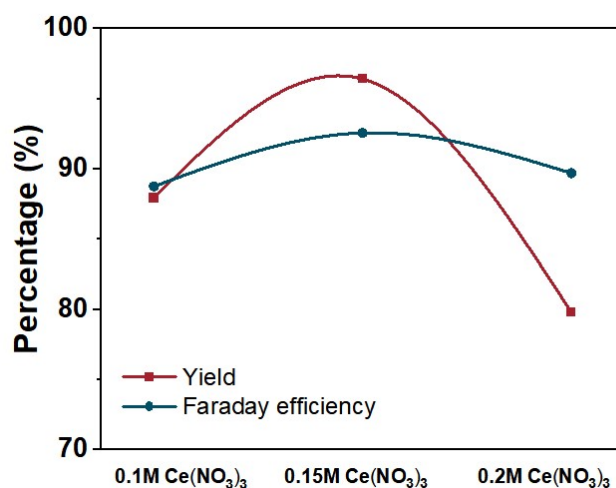
**Figure S2.** SEM images of Ec CM-Ce at different scales.



**Figure S3.** Digital photograph of H-type divided cell reactors.

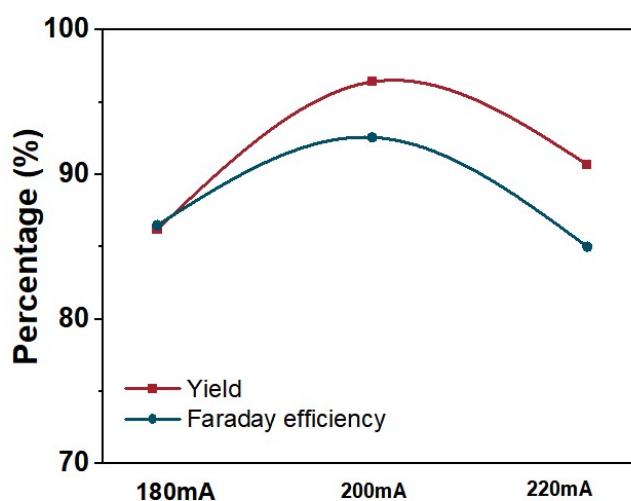


**Figure S4.** LSV curves of HMFOR Ec CM-Ce at different KOH concentrations



**Figure S5.** The optimization of electrochemical parameters. HMF oxidation performance of corresponding samples.

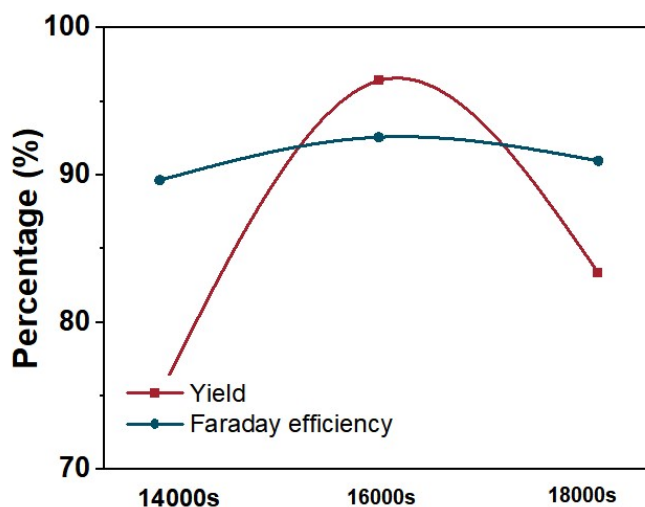
Setting of other parameters:  $\pm 200$  mA for the applied alternating current; 40 s for the processing time of single segment; 400 for the number of segments. Therefore, the concentration of  $\text{Ce}(\text{NO}_3)_3$  electrolyte still remains at 0.15 mol/L.



**Figure S6.** The optimization of electrochemical parameters. HMF oxidation performance of corresponding samples.

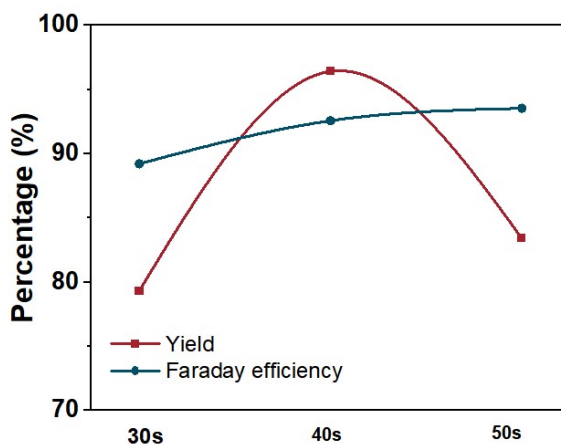
Setting of other parameters:  $\text{Ce}(\text{NO}_3)_3$  electrolyte still remains at 0.15 mol/L ;  $\pm 200$  mA for the applied alternating current; 40 s for the

processing time of single segment. Therefore, this parameter is changed to 400 (16000s).



**Figure S7.** The optimization of electrochemical parameters. HMF oxidation performance of corresponding samples.

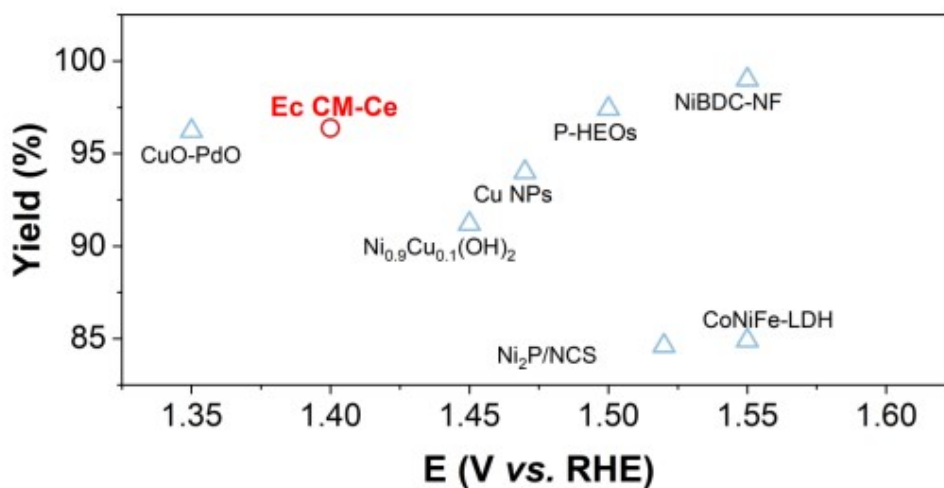
Setting of other parameters:  $\text{Ce}(\text{NO}_3)_3$  electrolyte still remains at 0.15 mol/L ; 40 s for the processing time of single segment; 400 for the number of segments. Therefore, the optimal applied current value is  $\pm 200$  mA.



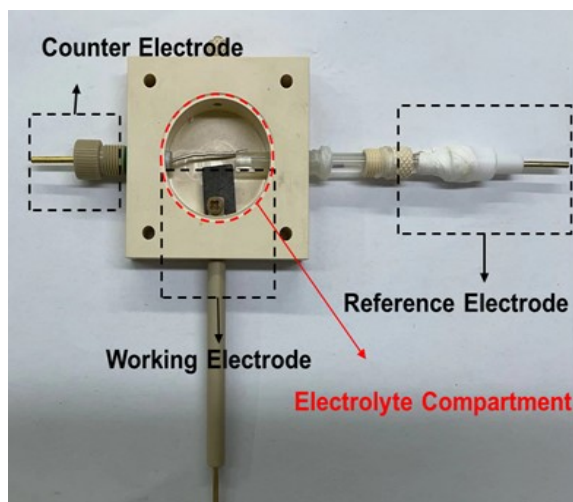
**Figure S8.** The optimization of electrochemical parameters. HMF oxidation performance of corresponding samples.



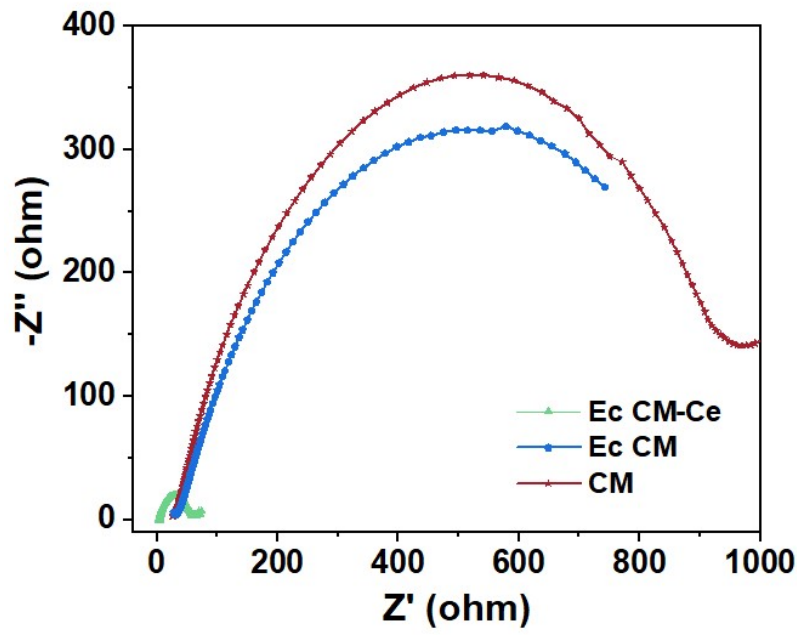
Setting of other parameters:  $\text{Ce}(\text{NO}_3)_3$  electrolyte still remains at 0.15 mol/L ;  $\pm 200$  mA for the applied alternating current ;400 for the number of segments. Therefore, the optimal applied current value is 40s.



**Figure S9.** Comparison of reaction voltage and yield of Ec CM-Ce with other catalysts in HMFOR.



**Figure S10.** Digital photograph of in situ Raman cell.



**Figure S11.** Repeated EIS test: Nyquist plots of the CM, Ec CM and Ec CM-Ce samples in HMFOR.

## References

1. Liu, Q.; Wu, H.; Gu, H.; Jiang, Z.; Zhang, W.; Li, H.; Wang, Z.; Liu, P.; Li, D.; Zhu, M., Electrochemical Synthesis of Copper Mesh-Supported Thermo-Catalysts. *Small* **2023**.
2. Li, J.; Li, J.; Liu, X.; Chen, J.; Tian, P.; Dai, S.; Zhu, M.; Han, Y.-F., Probing the role of surface hydroxyls for Bi, Sn and In catalysts during CO<sub>2</sub> Reduction. *Applied Catalysis B: Environmental* **2021**, 298.
3. Wei, D.-Y.; Yue, M.-F.; Qin, S.-N.; Zhang, S.; Wu, Y.-F.; Xu, G.-Y.; Zhang, H.; Tian, Z.-Q.; Li, J.-F., In Situ Raman Observation of Oxygen Activation and Reaction at Platinum–Ceria Interfaces during CO Oxidation. *Journal of the American Chemical Society* **2021**, 143 (38), 15635-15643.