Supporting information for

Electrocatalytic conversion of nitrophenol pollutant to value-added product coupled with in-situ separation via cation shuttling

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Experimental Section

Chemical and materials

We used the following materials in our experiments: Nafion^{tm} 117 membrane, Ir black (HICAIr100, Cotrun New Energy), carbon felt (Avcarb G300A, SCI Materials Hub). We purchased the following chemicals from Sigma-Aldrich: acetic oxide, sodium hydroxide (NaOH, 99%), 4-Nitrophenol (4-NP, 99%), sodium 4-nitrophenol (4-NP-Na, 99%), 4-Aminophenol (4-AP, 99%), sulfuric acid, sodium sulfate (Na_2SO_4, 99%), sulfuric acid (H_2SO_4, 99%).

Catalyst synthesis

The graphite fiber was severally washed by acetone, ethanol and ultrapure water under ultrasonic method for 40 min, dried at 343 K for 10 h. These pretreated materials were marked as graphite felt (GF). The pretreated GF was anodized consisted of several successive cycles in an undivided three-electrode cell system, and 0.05 M Na_2SO_4 aqueous solution was used as supporting electrolyte. In each cycle, the potential of the working electrode was scanned a back and forth between 0 V and 2 V at a scan rate of 30 mV s^{-1}. After the electrochemical treatment of 15 successive cycles, the samples were dried at 80 °C for 24 h, and the modified electrodes were marked as oxidized graphite fibers (OGF).

Two pieces of Nafion^{tm} 117 membrane (3×3 cm) were sequentially treated as follows:

1. Pre-treatment in H_2O_2 solution: Immersed in 5% hydrogen peroxide (H_2O_2) at 60°C for 1 hour to remove organic contaminants and enhance surface hydrophilicity.

2. Activation in H_2SO_4 solution: Subsequently transferred to 10% sulfuric acid (H_2SO_4) and heated at 100°C for 1 hour to fully protonate sulfonic acid groups ($-SO_3H$), optimizing proton conductivity.

3. Cation exchange membranes (CEM) (Anode side): Stored in 10% H_2SO_4 at room temperature, ensuring efficient H^+ transport near the anode compartment

4. CEM (Cathode side): Soaked in 1 mol/L NaOH for 24 hours, enabling selective Na^+ conduction adjacent to the cathode compartment.

Electrochemical performance and product analysis

The initial investigation 4-NP reduction reaction (4-NPRR) was carried out using a membrane electrode assembly (MEA) system with a Nafion^{tm} 117 proton exchange membrane to screen optimize reaction conditions. All working electrodes had a geometric surface area of 1 cm^2. An Ir black-coated titanium fiber was used as the anode for the oxygen evolution reaction. Full cell potentials were measured against the anode, and cathodic potentials were measured against an Ag/AgCl reference electrode (saturated KCl, BASi). The measured cathodic potentials were then converted to the RHE reference scale using the following equation:

$$E\ (vs\ RHE) = E\ (vs\ Ag/AgCl) + 0.197\ V + 0.0591 \times pH \quad (1)$$

We conducted the 4-NPRR using a three-chamber flow cell separated by a Nafion^{tm} 117 membrane. OGF catalysts were used as work electrodes, limited to a geometric size of 1 cm × 1 cm and a thickness of 3 mm for the cathode. The catholyte consisted of 40 mL of 0.08 M 4-NP-Na and 0.02 M 4-NP. An IrO_2-coated titanium felt and 0.5 M H_2SO_4 solution were employed as the anode and anolyte, respectively. 1 M NaOH was passed into the middle cell. Cathodic potentials were measured against a saturated KCl Ag/AgCl reference electrode. Full-cell voltages were measured against the anode. The electrolyte was circulated through the flow cell at a rate of 50 ml/min using peristaltic pumps (Lead Fluid BT100S-1). Under alkaline conditions, 4-AP exhibits poor stability. Therefore, unless otherwise specified, all experiments in this study were conducted using oxygen-free distilled water under argon atmosphere and keep away from light.

Products were qualitatively and quantitatively analyzed by high performance liquid chromatography (HPLC, Agilent 1260 Infinity Series) equipped with a variable wavelength detector (VWD) at 230 nm. The column (InfinityLab Poroshell 120 SB-Aq, 4.6 × 250 mm) was operated at 25℃ with a binary gradient pumping method containing CH_3CN and H_2O with 10 mM ammonium formate at a flow rate of 1 mL/min. The CH_3CN fraction was kept at 10% (v/v) until 6.50 minute and then increased from the initial 10% (v/v) to 28% over 6.5-9 minute, then was increased from 28% to 60% over 15-18 minute. 4-AP were eluted around 4.5 minutes. The standard samples of 4-AP were purchased for quantitative analysis. Qualitative analysis of 4-NPRR products was conducted by Gas Chromatography-Mass Spectrometer (GC-MS). Guaiacol was selected as an appropriate internal standard for the quantitative analysis. The Na^+ ions concentration was determined by ion chromatography (ICS-900, Thermo). The Faradaic efficiency (FE) to 4-AP was calculated using the following equation:

$$FE_{4-AP} = \frac{6 \times n_{4-AP} \times F}{I \times t} \quad (2)$$

Where $n_{4\text{-AP}}$ is the total amount of 4-AP (in moles), F is the faradaic constant, I (in amperes) is the current, and t (in seconds) is the time for the constant current. The yield (Y%) were calculated using the following equation:

$$Y\% = \frac{moles\ of\ 4-AP\ consumed}{0.01} \times 100\% \quad (3)$$

the cation cross-over ratio is calculated by

$$Cation\ cross\ over\ ratio = \frac{\Delta n\ cation\ \ in\ cathode(mol)}{n\ cation\ (initial) in\ middle\ layer(mol)} \times 100\% \quad (4)$$

Production rate were calculated using the following equation:

$$Productivity = \frac{n_{4-AP}}{area\ of\ WE * t} \quad (5)$$

Here, area of WE in the productivity formula represents the geometrical area of working electrode as 1 cm^2

The calculation formula for "Ee-factor" is as follows (6)

$$Ee\text{-}factor = \frac{Mass\ of\ electrolyte\ consumed}{Mass\ of\ 4\text{-}AP\ production}$$

The calculation formula for "E-factor" is as follows (7)

$$E\text{-}factor = \frac{Mass\ of\ (Electrolyte\ consumed + Consumed\ solution + Unconverted\ 4\text{-}N}{Mass\ of\ 4\text{-}AP\ production}$$

Materials characterization

The morphological analysis and elemental distribution were studied by a scanning electron microscope (SEM, Thermo Scientific Apreo 2C) equipped with an energy dispersive spectroscopy detector. X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha$^+$) were employed to characterize the crystal structure and elemental state of OGF catalyst. Fourier transform infrared spectrometer was conducted using a Nicolet IS50 spectrometer detector for spectroscopic insights.

In-situ infrared reflection absorption spectroscopy (IRRAS, Thermal Scientific Nicolet is50 FT-IR), equipped with an A-type mercuric cadmium telluride (MCT) detector, was employed to investigate the mechanism of the electrocatalysis reaction.

Synthesis of paracetamol

Dry a 250 mL round-bottom flask and sequentially add: 50 mL of solution purified through middle chamber, 10 mL acetic anhydride, 15 mL glacial acetic acid 3-4 boiling chips. Heat under reflux using an electric mantle (maintain 110-115°C) for 4 hours. After reaction completion Perform the following: 1. Remove acetic acid using rotary evaporator (85-90°C water bath). 2. Pour residue into equal volume ice-water mixture. 3. Stir to crystallize. 4. Perform suction filtration. 5. Wash crystals with ice-water until near-neutral pH. 6. Dry under suction to obtain crude product. 7. The crude product is dissolved in hot water and add 0.1g activated carbon to decolorize. 8. Cooling and crystallization after filtration. 9. Pure paracetamol was obtained after filtration. This method was used for industrial synthesis of paracetamol with a yield of 95%.

The overall production yield is calculated by

$$\% = \frac{moles\ of\ paracetamol}{0.01} \times 100\% \quad (8)$$

Techno-economic analysis (TEA)

We conducted a TEA to assess the plant-gate levelized cost of paracetamol product (US$ per kg of paracetamol) from 4-AP synthesized in three chamber flow cell based on a modified model from some previous work[1-4]. The underlying assumptions for the model presented in Table S1 are as follows:

1. The plant's capacity is set at 1000kg of paracetamol per day.
2. The total catalyst cost is computed based on factors such as the geometric surface area of the electrolyzer, and electrode preparation costs (e.g., chemicals, electrolyzer, furnace, and heating 5% all catalyst costs).
3. The membrane cost accounts for 5% of the total electrolyzer cost.
4. The overall electrolyzer cost is established at $920/m^2, drawn from a documented case of CO_2 reduction electrolyzer[5].
5. The steel bomb used to synthesize paracetamol cost 100,000$

6. The electricity prices at 8 ¢/kWh

7. The separation cost is assumed to be 20% of total cost. The separated solvent is assumed to be recyclable[5].

8. The capacity factor, indicating the fraction of time the plant is operational during a day, is assumed as 0.8, corresponding to 19.2 operational hours daily.

9. The prices of 4-NP, 4-NP-Na are \$2.43/kg and \$0.79/kg, respectively, the prices of 4-AP, paracetamol, acetic oxide are \$2.69/kg \$4.87/kg and \$0.63/kg, respectively (from Alibaba).

TEA cost components

We calculate the cost components using the following equations:

Catalyst Cost per Unit Area (\$/m^2): The cost per unit area of the catalyst was calculated by multiplying the G300A price per unit area by the total surface area required (in square meters.)

$$Catalyst\left(\frac{\$}{m^2}\right) = G300A\ price\left(\frac{g}{m^2}\right) \times tatal\ Surface\ area\ needed\ (m^2) \tag{9}$$

Steel bomb cost (\$/kg): The steel bomb used to synthesize paracetamol cost per kilogram by dividing 100,000\$ by the product of 365 days, steel bomb lifetime (years), and daily production quantity (kg/day).

$$Steel\ bomb\ cost\left(\frac{\$}{kg}\right) = \frac{100{,}000\$}{Steel\ bomb\ lifetime\ (year) \times 365\ day \times production\ (\frac{kg}{day})} \tag{10}$$

Membrane Cost per Kilogram (\$/kg): The membrane cost per kilogram is calculated by dividing 5% of the total electrolyzer cost by the product of 365 days, electrolyzer lifetime (years), and daily production quantity (kg/day).

$$Membrane\ cost\left(\frac{\$}{kg}\right) = \frac{Total\ cost\ of\ electrolyzer\ (\$) \times 5\%}{Electrolyzer\ lifetime\ (year) \times 365\ day \times production\ (\frac{kg}{day})} \tag{11}$$

Electrolyzer Cost per Kilogram (\$/kg): The electrolyzer cost per kilogram is calculated by dividing the product of total electrolyzer cost and capital recovery factor by the product of capacity factor, daily production quantity, and electrolyzer lifetime.

$$Electrolyzer\ cost\left(\frac{\$}{kg}\right)=\frac{Total\ electrolyzer\ cost\ (\$)\times Capital\ recovery\ factor}{Capitcity\ factor\times Production\ (\frac{kg}{day})} \quad (12)$$

Total Surface Area Needed (m^2): The total surface is calculated by dividing the total current required (in amperes) by the current density (in milliamperes per square meter).

$$Tatal\ Surface\ \ (m^2)=\frac{Total\ current\ needed\ (A)}{Current\ density\ (\frac{mA}{m^2})} \quad (13)$$

Total Electrolyzer Cost: The total electrolyzer cost is calculated by multiplying the total surface area required (in square meter) by the cost square meter ($/$m^2$).

$$Total\ electrolyzer\ cost=Total\ surface\ (m^2)\times price\ per\ m^2\ (\frac{\$}{m^2}) \quad (14)$$

Total Current Needed (A): The total current required (in amperes) is calculated using the faraday constant, the plant capacity (in kilograms per day), the number of electron transfers, the molecular weight of the product, and the Faraday efficiency.

$$Total\ Current\ (A)=\frac{Plant\ capacity\left(\frac{kg}{day}\right)\times No.\ of\ electron\ ransfered\times 96485\ (\frac{C}{mol})}{Product\ molecular\ weight\left(\frac{kg}{mol}\right)\times 86400\left(\frac{second}{day}\right)\times FE\ (\%)}$$

(15)

Capital Recovery Factor: The capital recovery factor is calculated the discount rate and the electrolyzer's lifetime, accounting for the time value of money.

$$Captical\ recovery\ factor=\frac{Discount\ rate\times(1+Discount\ rate)^{lifetime}}{(1+Discount\ rate)^{lifetime}-1} \quad (16)$$

Electricity Cost per Kilogram ($/kg): The cost of electricity per kilogram is obtained by dividing the product of the power consumed (in kilowatts), 24 hours, and the electricity cost per kilowatt-hour by the plant capacity (in kilograms per day).

$$Electricity\ cost\left(\frac{\$}{kg}\right)=\frac{Power\ consumed\ (KW)\times 24\left(\frac{hour}{day}\right)\times Electricity\ cost\ (\frac{\$}{kwh})}{Plant\ capacity\ (\frac{kg}{day})} \quad (17)$$

Power Consumed (kW): The power consumed (in kilowatts) is determined by dividing the product of the power consumed (in kilowatts), 24 hours, and the electricity cost per kilowatt-hour by the plant capacity (in kilograms per day).

$$Power\ consumed\ (kW) = \frac{Power\ consumed\ (kW) \times 24\left(\frac{hour}{day}\right) \times Electricity\ cost\ \left(\frac{\$}{kwh}\right)}{Plant\ capacity\ \left(\frac{kg}{day}\right)} \quad (18)$$

Maintenance Cost per Day ($/day): The maintenance cost per day is calculated by multiplying the maintenance frequency, maintenance factor (as a percentage of capital cost), and the total capital cost (in dollars per kilogram).

$$Maintenance\ cost\left(\frac{\$}{day}\right) = Maintenance\ frequency \times Maintenance\ factor\ (\%\ of\ Capital\ cost) \times Total\ capital\ cost\ \left(\frac{\$}{kg}\right) \quad (19)$$

Balance of Plant Cost per Kilogram ($/kg): The balance of plant cost per kilogram is determined by multiplying the balance of plant factor (as a percentage) with the capital cost (in dollars per kilogram).

$$Balance\ of\ plant\left(\frac{\$}{kg}\right) = Balance\ of\ plant\ factor\ (\%) \times Captital\ cost\left(\frac{\$}{kg}\right) \quad (20)$$

Installation Cost per Kilogram ($/kg): The installation cost per kilogram is obtained by multiplying the Lang factor (as a percentage) with the capital cost (in dollars per kilogram).

$$Installation\left(\frac{\$}{kg}\right) = Lang\ factor\ (\%) \times Captital\ cost\left(\frac{\$}{kg}\right) \quad (21)$$

Supporting tables and figures

Breakdown of TEA	Details
Capital cost	Electrolyzer ($920/m^2), anode, cathode, and membrane, preparation cost, steel bomb
Installation cost	Lang factor (50%) × Capital cost

Maintenance cost	Maintenance frequency (1/day) × Maintenance factor (5% of Capital cost) × Total capital cost ($/kg)
Balance of plant	Balance of plant factor (%) × Capital cost
Separation cost	20% of total cost[5, 6].
Electricity cost	Full-cell potential, FE, and electricity price
Input chemical cost	4-NP, 4- NP-Na, acetic oxide cost, electrolyte

Table S1. A modified model of TEA for paracetamol production from 4-NP.

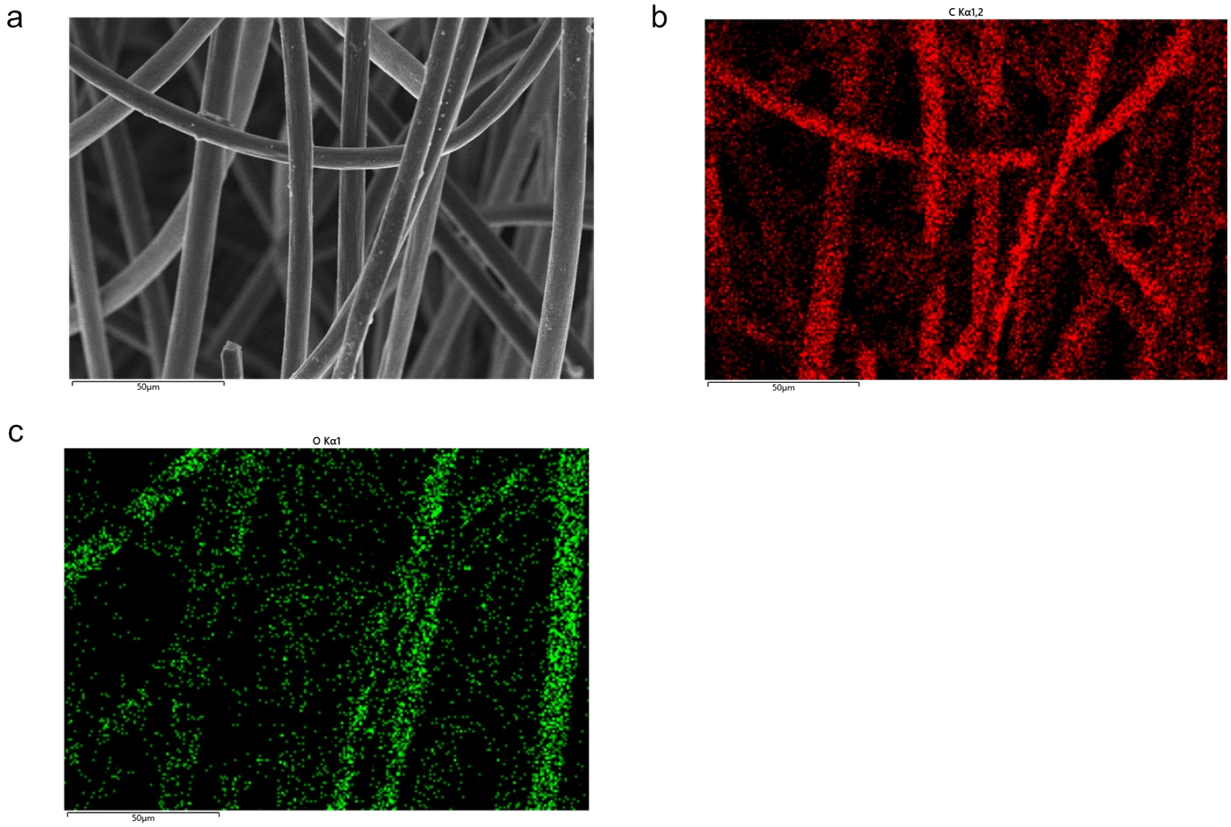

Figure S1. The structure of the OGF by SEM (a) SEM image, (b-c) SEM-EDS mapping images.

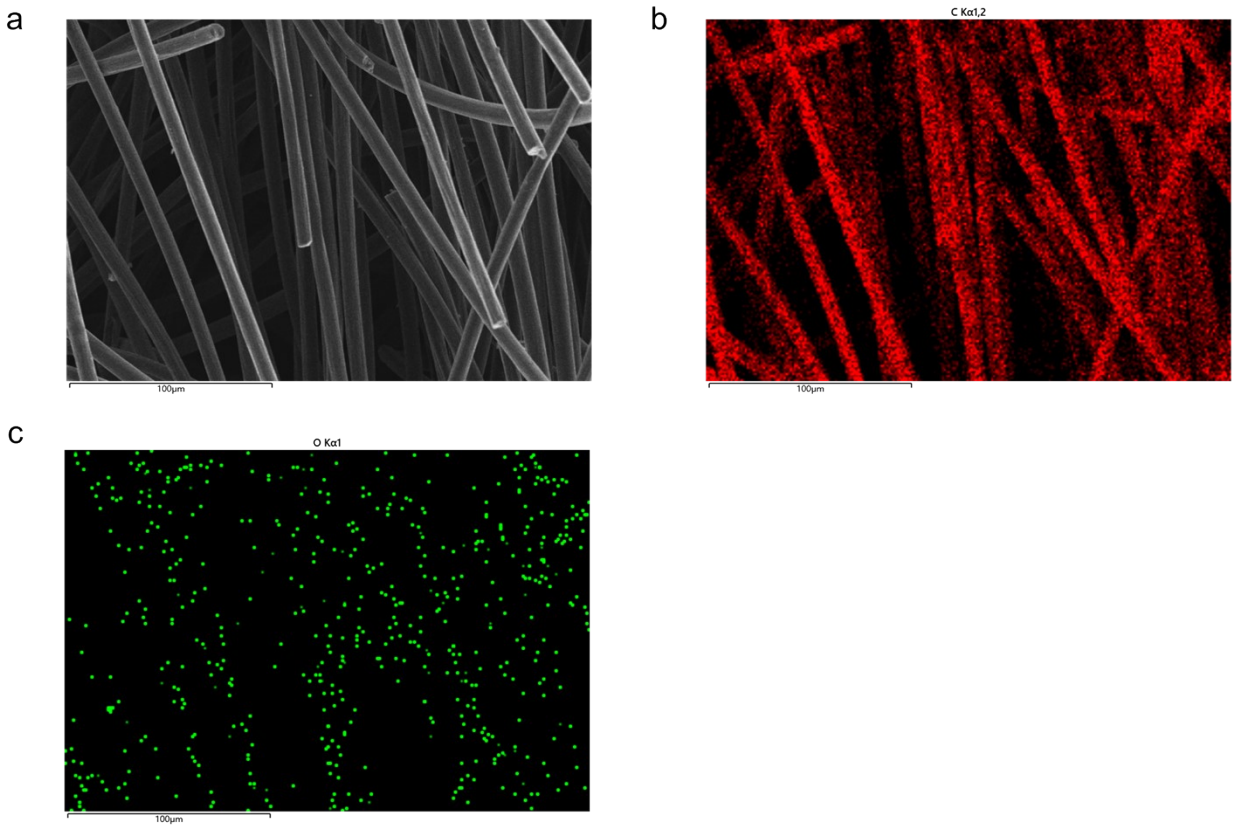

Figure S2. The structure of the GF by SEM (a) SEM image, (b-c) SEM-EDS mapping images.

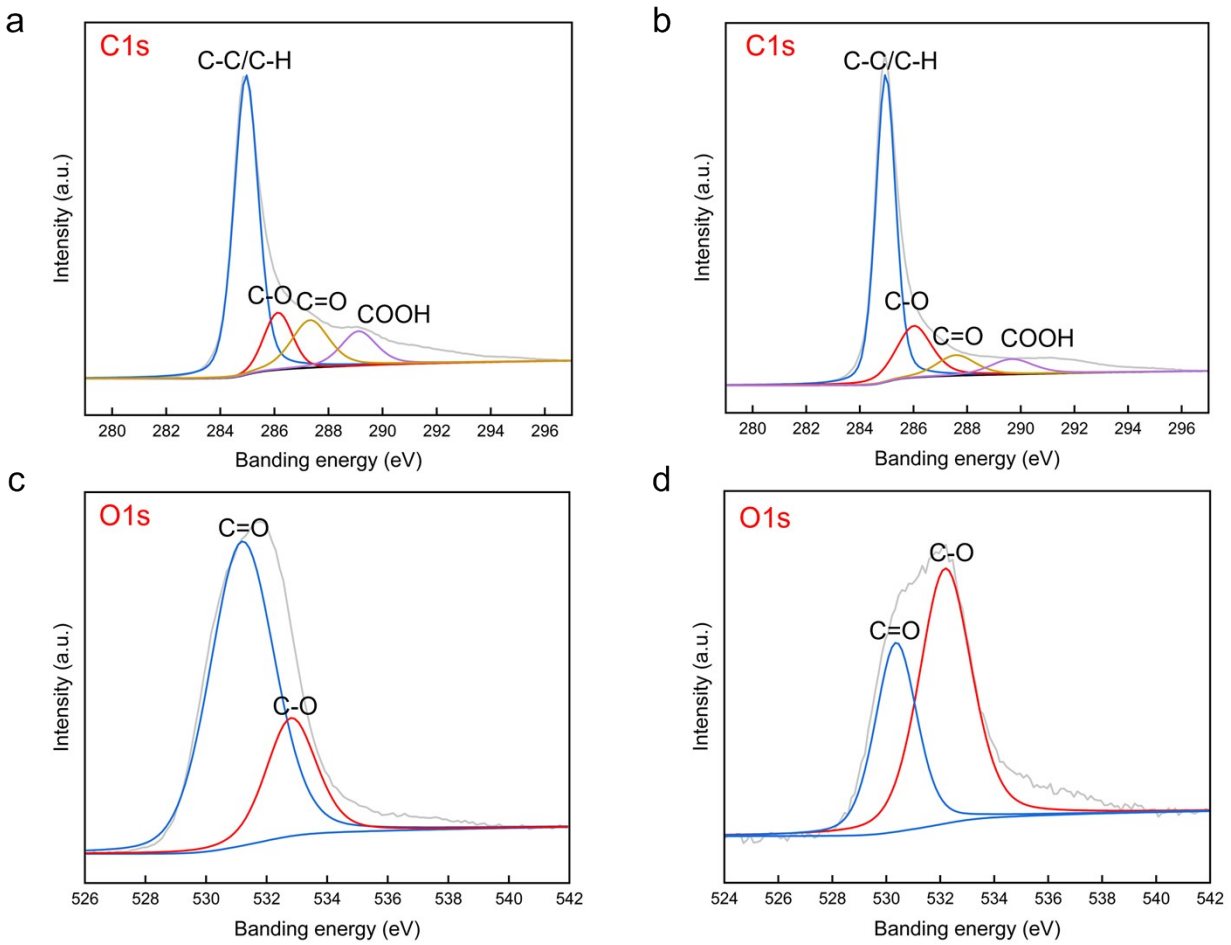

Figure S3. The XPS spectrum analysis of the OGF and GF. (a) C1s XPS high resolution spectrum of OGF. (b) C1s XPS high resolution spectrum of GF. (c) O1s XPS high resolution spectrum of OGF. (d) O1s XPS high resolution spectrum of GF.

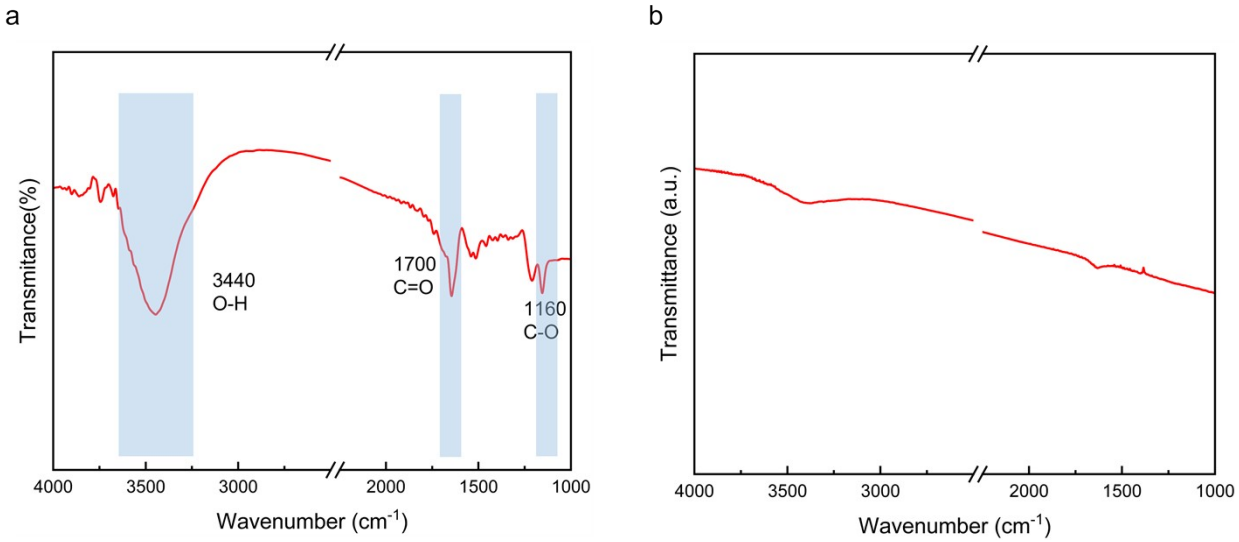

Figure S4. (a) The FTIR spectrum analysis of the OGF. We attribute the bands centered at 3440 cm^{-1} (O-H stretch) 1700 cm^{-1} (C=O) and 1160 cm^{-1} (C-O stretch)[7]. (b) The FTIR spectrum analysis of the GF.

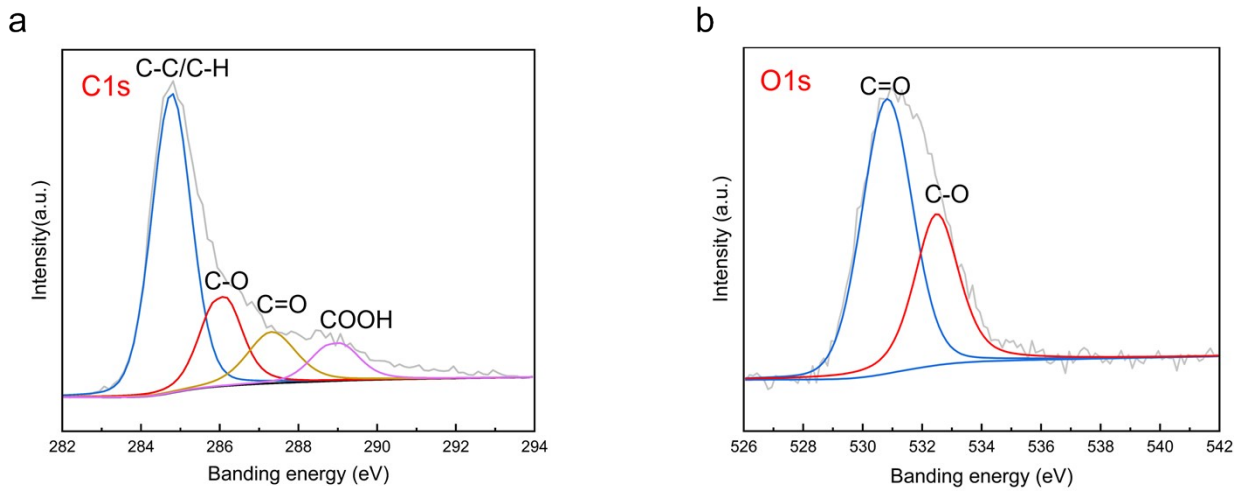

Figure S5. The XPS spectrum analysis of the OGF after reaction. (a) C1s XPS high resolution spectrum. (b) O1s XPS high resolution spectrum of OGF.

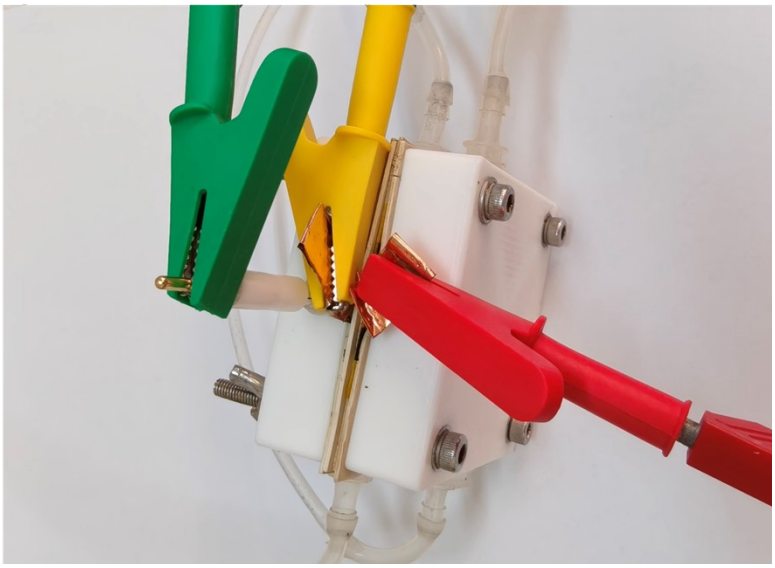

Figure S6. Photograph of the two-chamber MEA system.

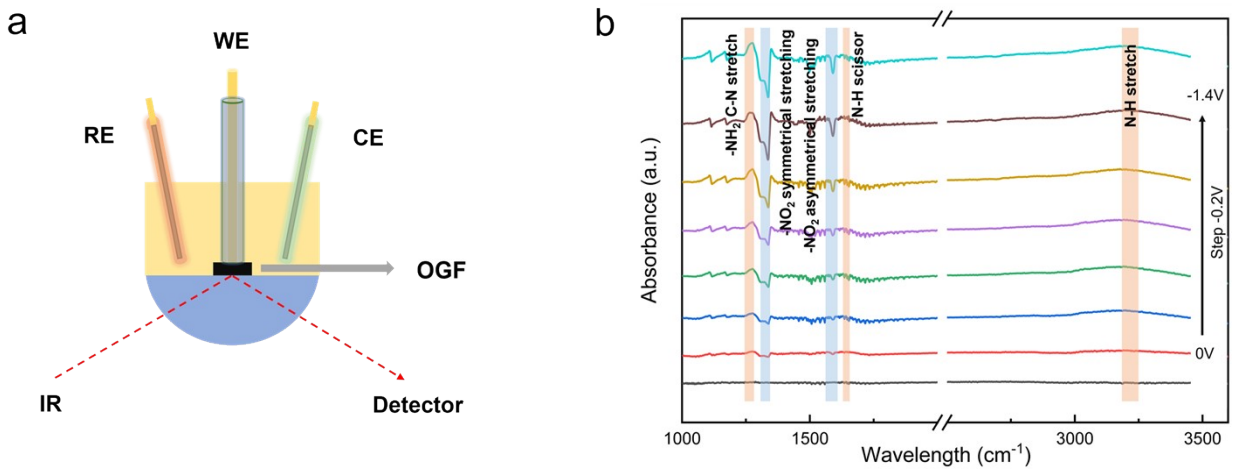

Figure S7. (a) In situ IRRAS configuration for the 4-NPRR. OGF, Ag/AgCl, and Pt mesh as the work, reference, and counter electrode, respectively. (b) *In-situ* IRRAS configuration for the 4-NPRR in a potential range of 0V and -1.4V vs. Ag/AgCl (with saturated KCl).

Figure S8. Photograph of the three-chamber flow cell system.

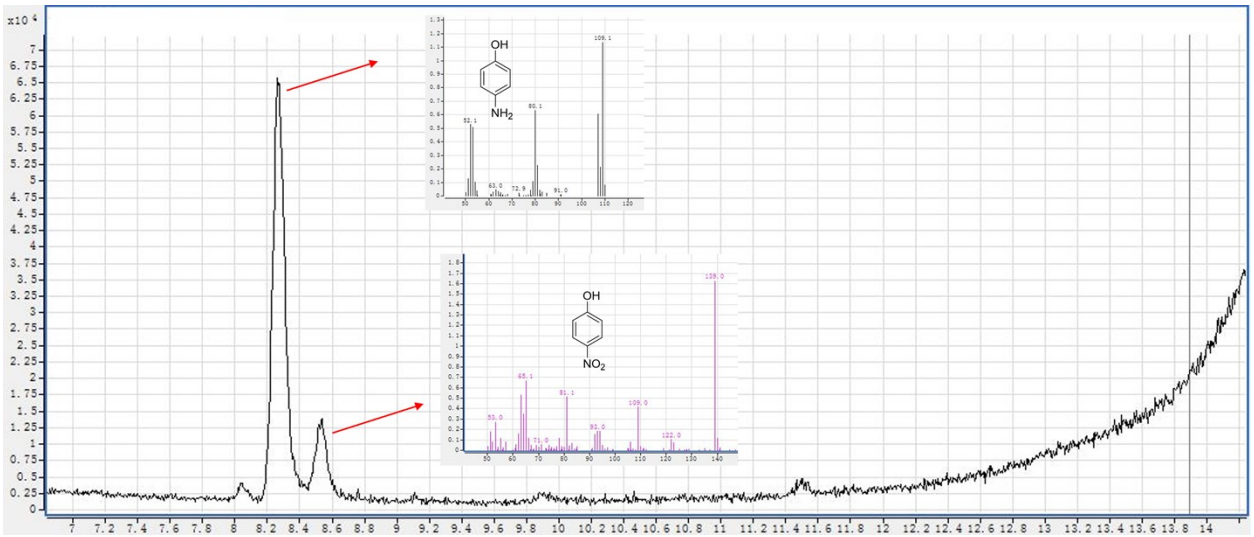

Figure S9. GC-MS results of 4-AP from 4-NPRR on OGF catalyst at 200 mA cm^{-2} after a course of 8-h reaction.

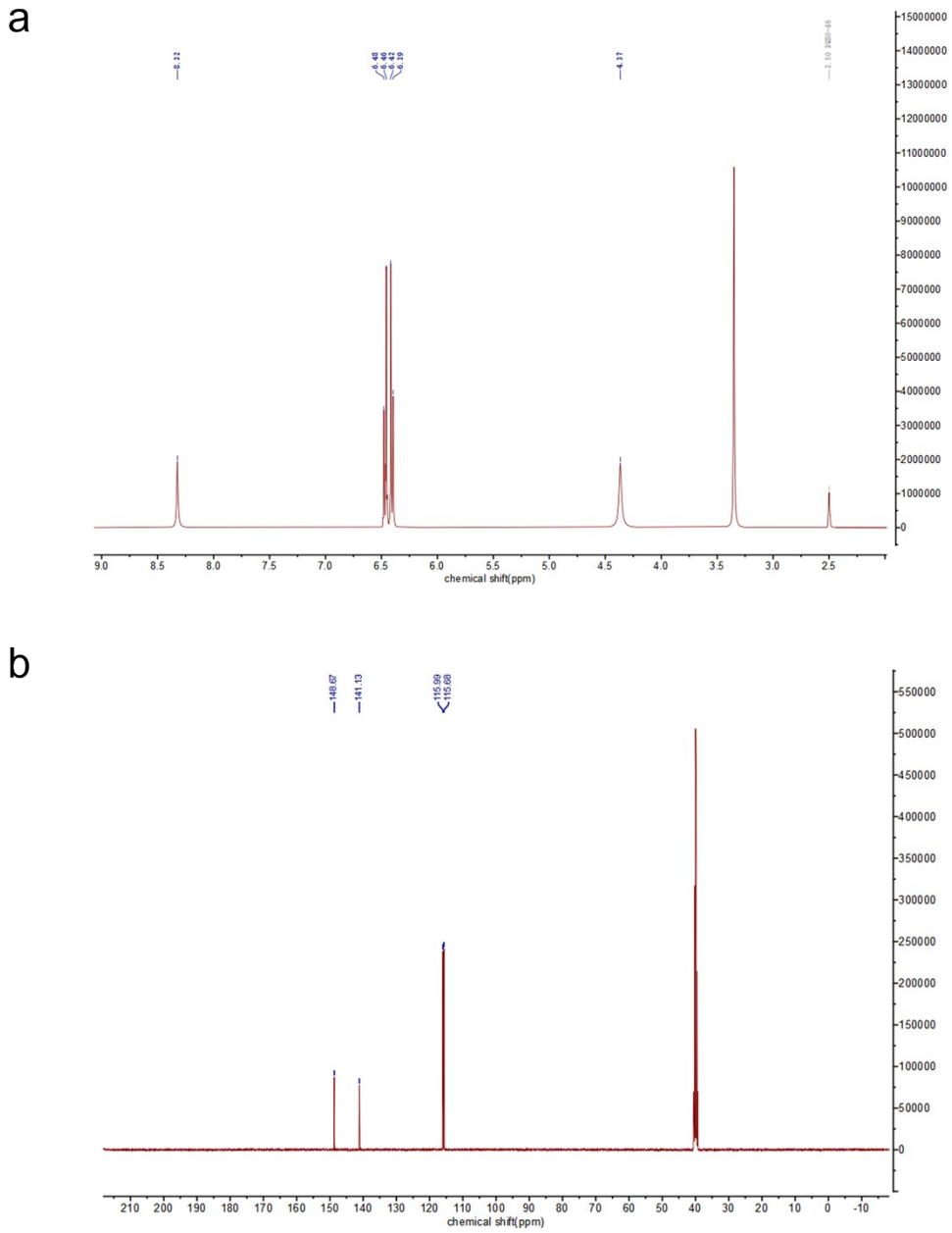

Figure S10. The 1H NMR (a) and 13C NMR (b) of 4-aminophenol. HNMR (400 MHz,DMSO) δ 8.32 (s, 1H),6.50-6.37 (m, 3H),4.37 (s, 1H) 13CNMR (101 MHz, DMSO) δ 148.67, 141.13, 115.99, 115.68.

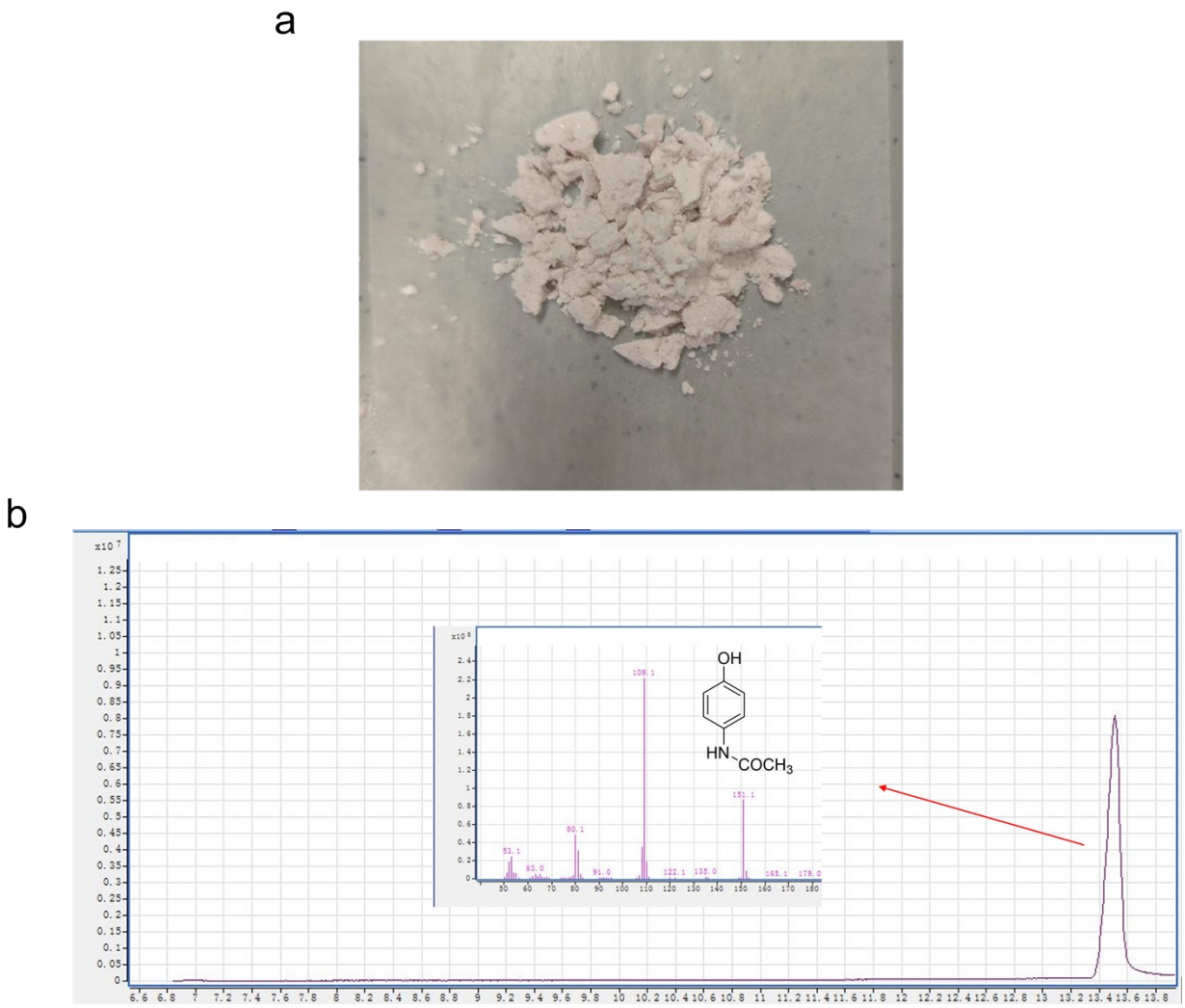

Figure S11. (a). Photograph of the paracetamol synthesized directly using the 4-AP solution purified from the middle chamber. (b). Mass spectra of paracetamol synthesized directly using the 4-AP solution purified from the middle chamber.

References

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