Grave-to-cradle Dry Reforming of Plastics via Joule Heating

Qing Ma, [a] Yongjun Gao,*[a] Bo Sun[b] Jianlong Du,[a] Hong Zhang[a] and Ding Ma*[b]

[a] Hebei Research Center of the Basic Discipline of Synthetic Chemistry, College of Chemistry and Materials Science, Hebei University, Baoding, 071002, China

[b] Beijing National Laboratory for Molecular Sciences, New Cornerstone Science Laboratory, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

*Corresponding author: Yongjun Gao (yjgao@hbu.edu.cn), Ding Ma (dma@pku.edu.cn)

Contents

Supplementary Methods

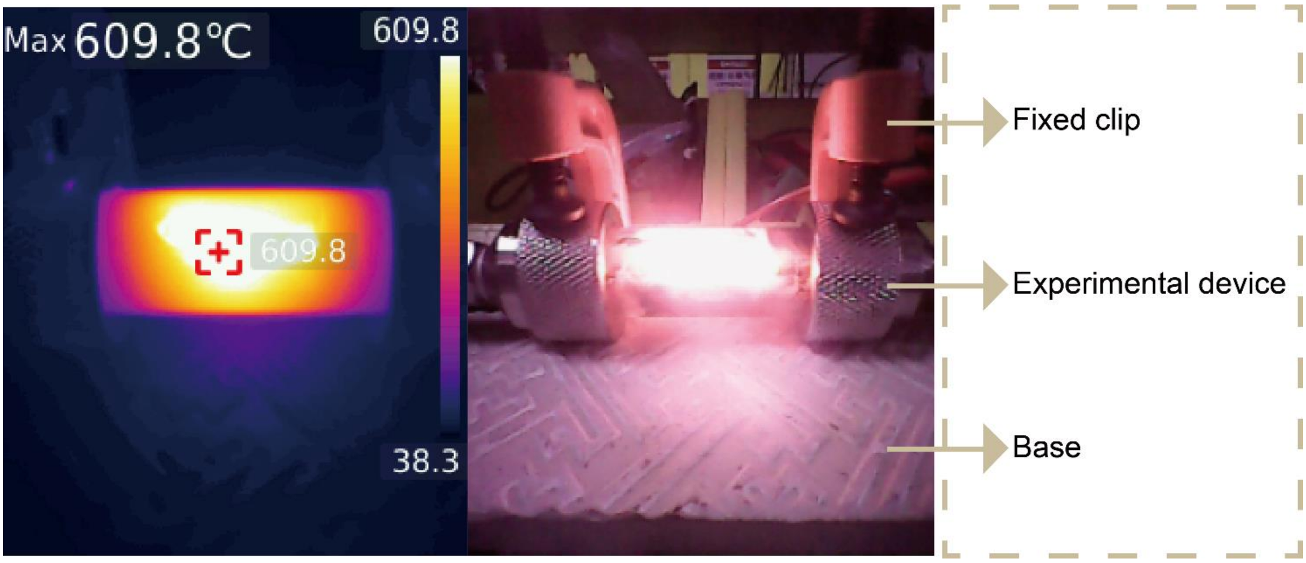
Transmission Electron Microscope (TEM) characterization

For TEM characterizations, the samples were dispersed in ethanol and dropped onto 300-mesh carbon-coated copper grids. TEM characterizations were carried out on a FEI Tecnai G2 F20 S-TWIN transmission electron microscope.

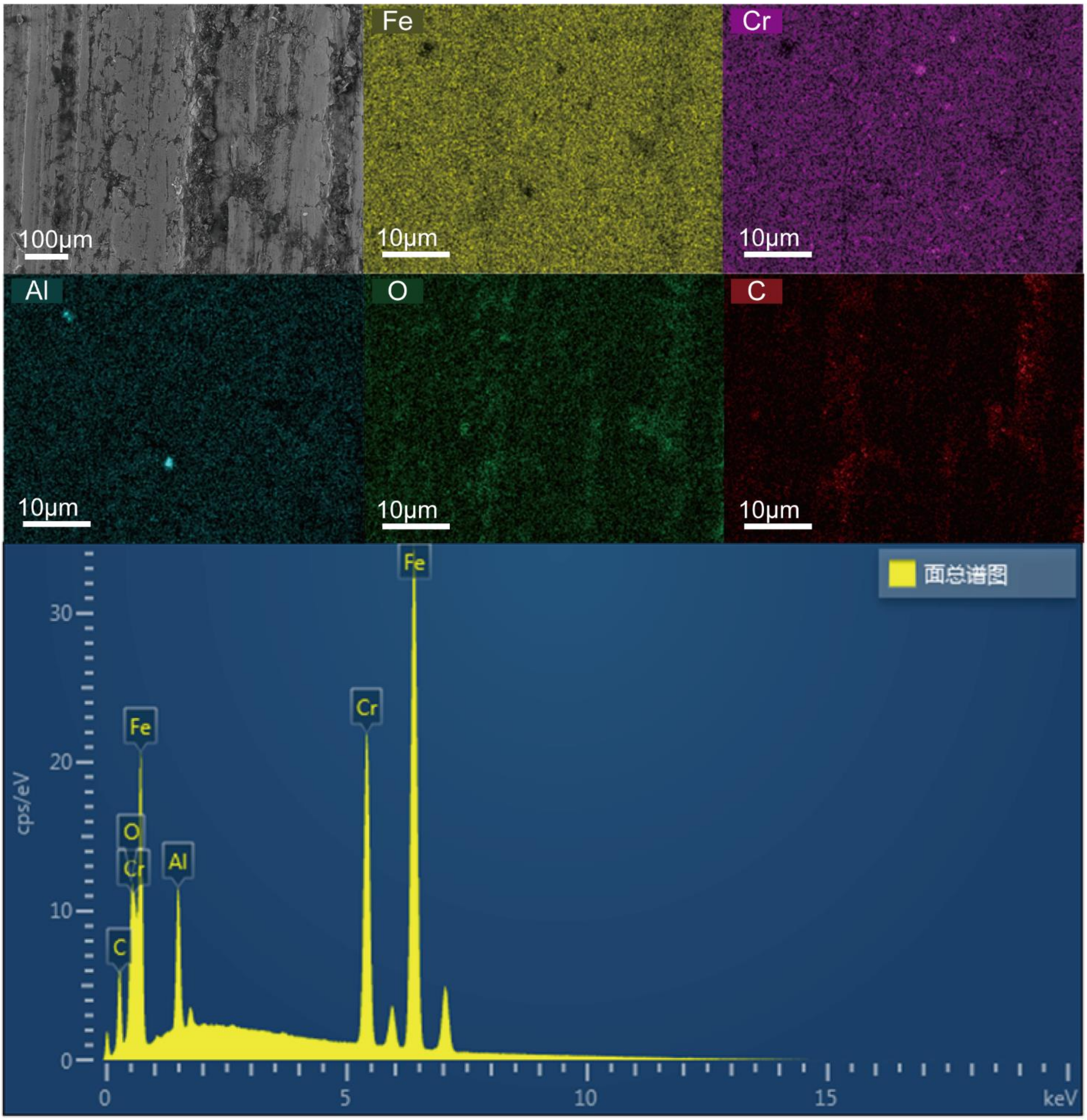
Scanning Electron Microscope (SEM) characterization and Energy-dispersive X-ray spectroscopy (EDS)

A Zeiss Merlin high-resolution scanning electron microscope was used to characterize the surface morphology of the samples after PE dehydrogenation and FeCrAl heating wire. The surface elemental mapping analyses were carried out by EDS detector equipped on the SEM.

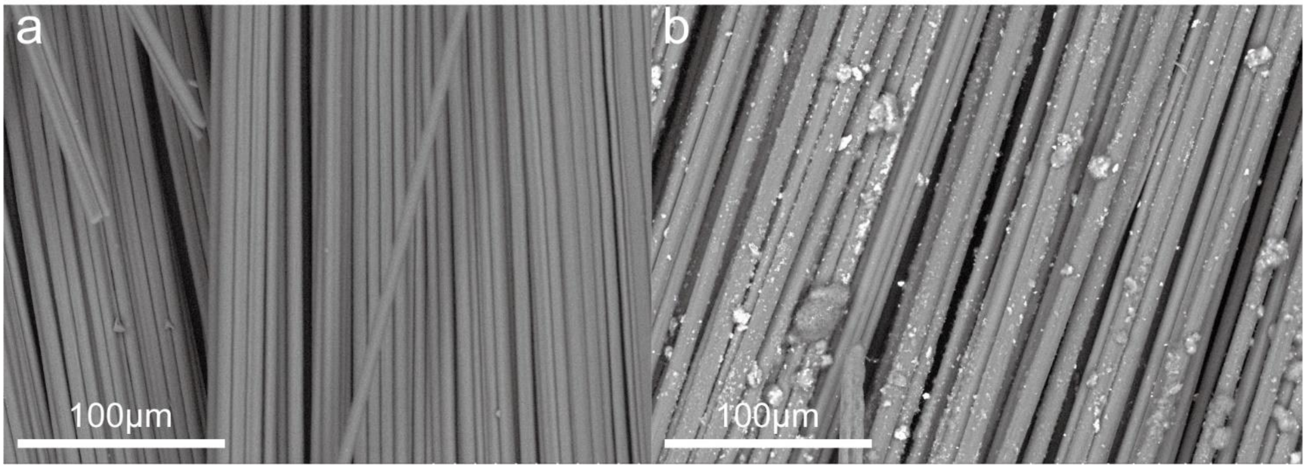
Supplementary Figures



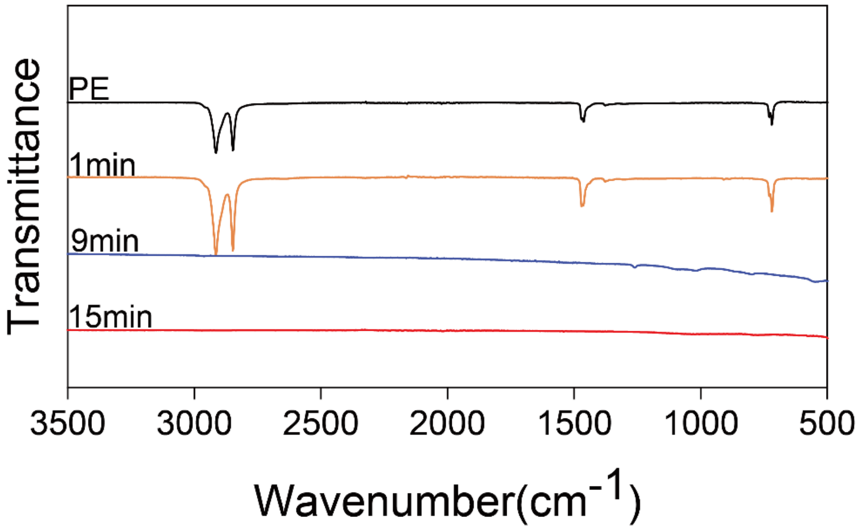
Supplementary Fig. 1 Infrared thermal image and optical image of experimental device. Reaction conditions:14 mg PE, 44 mg CO_2, 4 A(6 Ω).



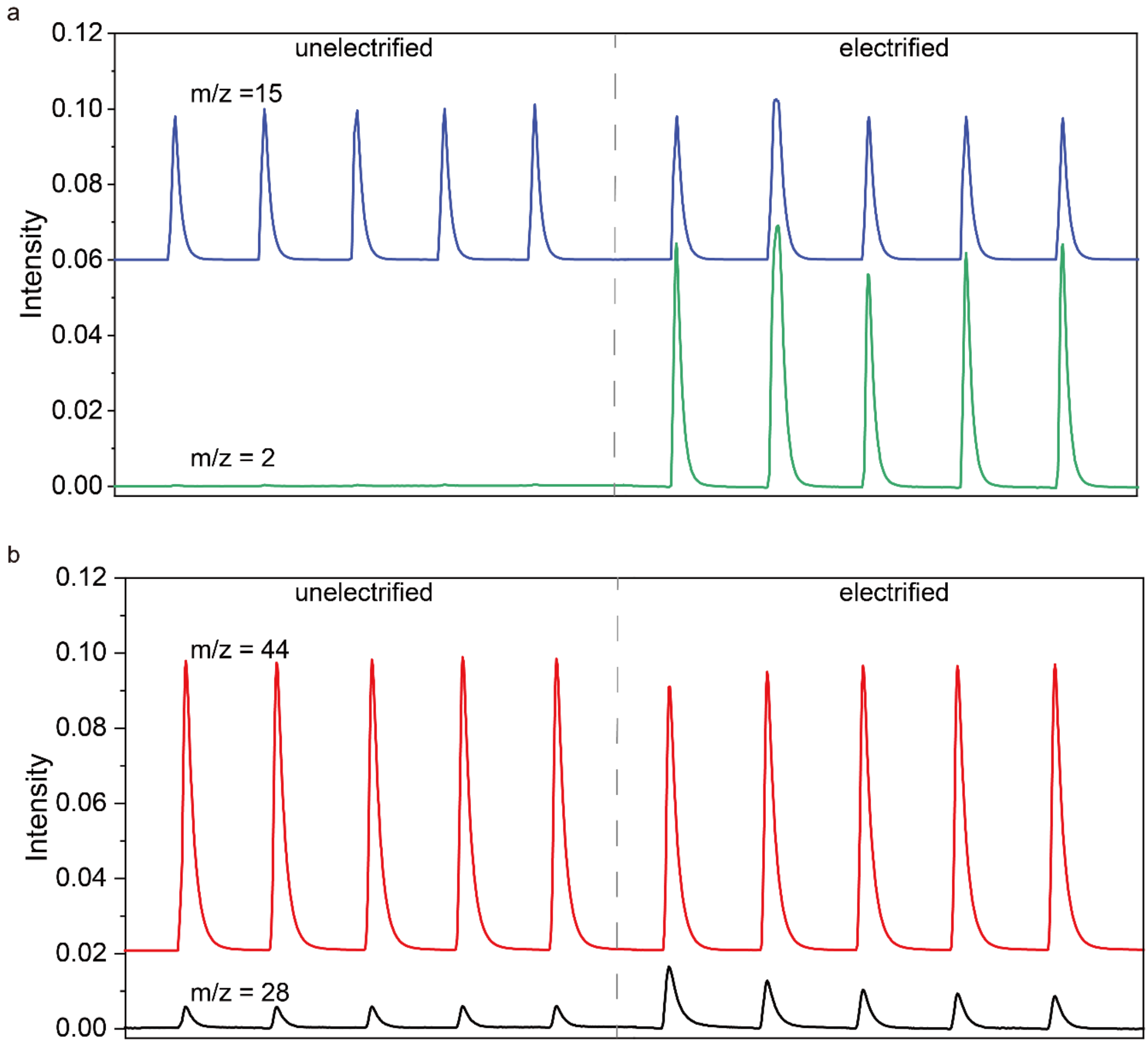
Supplementary Fig. 2 SEM and Energy-dispersive X-ray spectroscopy (EDS) mapping images of fresh FeCrAl heating wire.



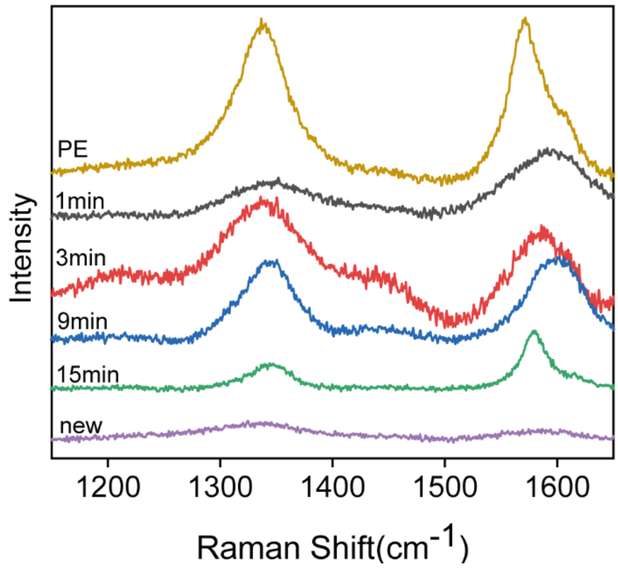
Supplementary Fig. 3 SEM images of carbon fibers a) before and b) after reaction. Experimental conditions: 14 mg PE, 44 mg CO_2, 15 min.



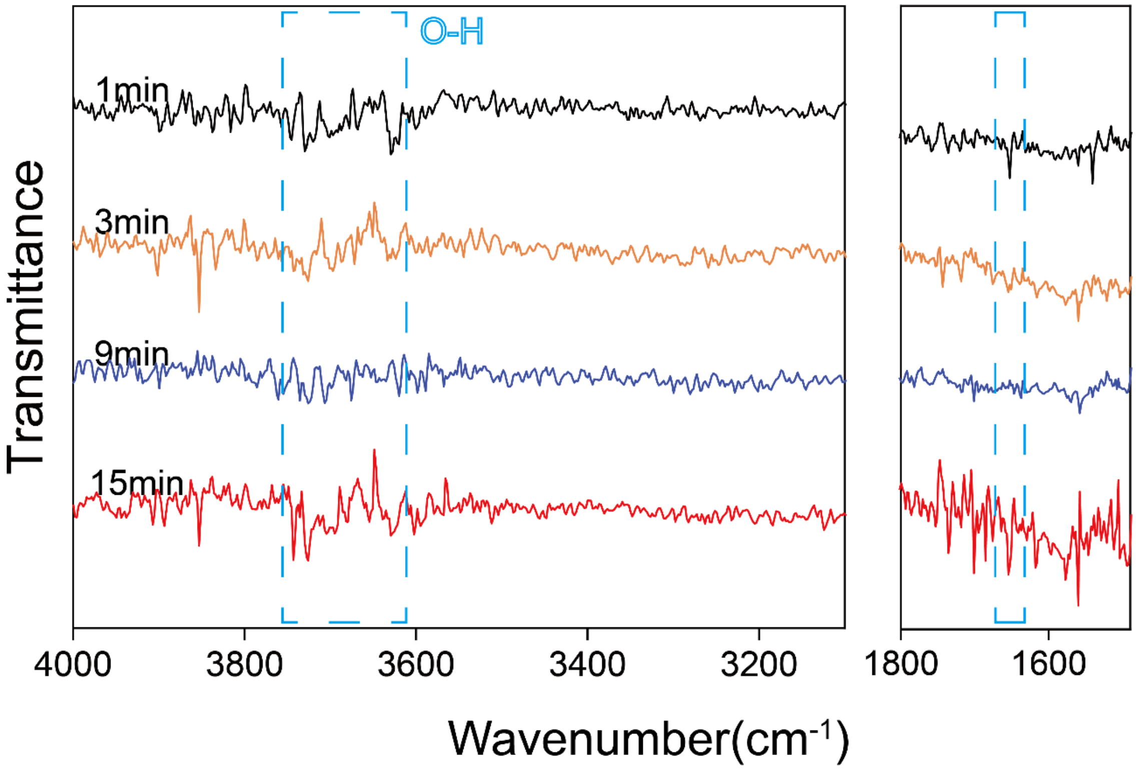
Supplementary Fig. 4 Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) spectra of solid samples (PE reforming with CO_2 after different reaction time) at different reaction time. Reaction conditions:14 mg PE, 44 mg CO_2, 4 A(6 Ω).



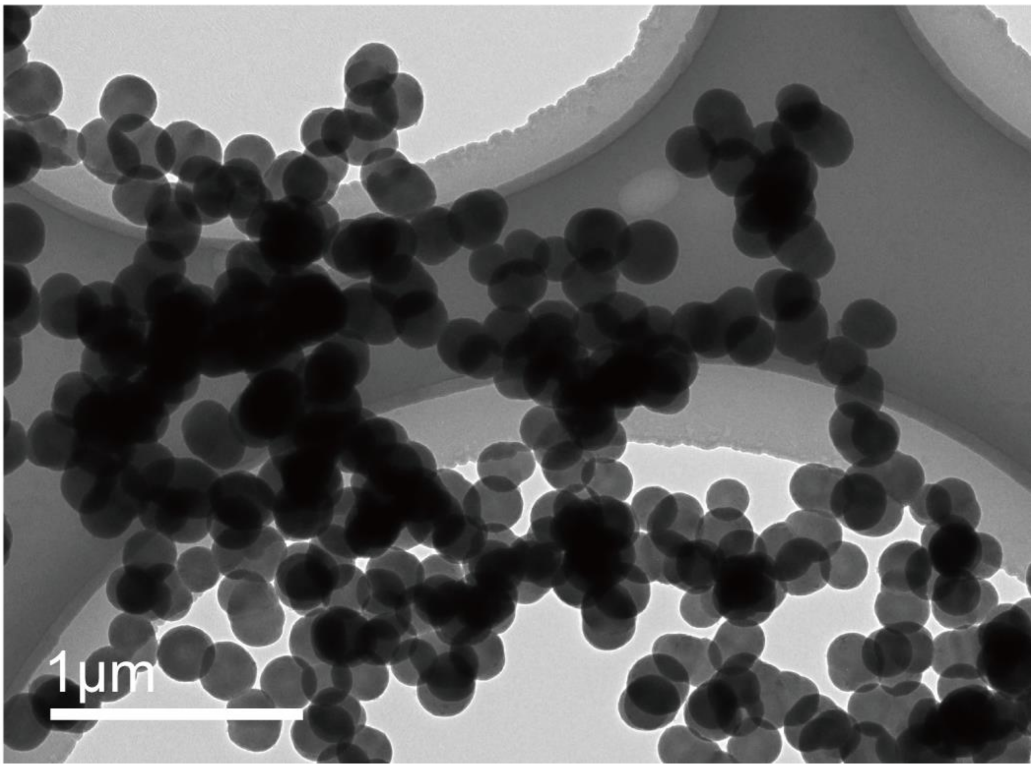
Supplementary Fig. 5 Mass spectrometric signals of pulse experiments. a The dehydrogenation of methane. **b** the CO_2 reduction over unelectrified / electrified FeCrAl resistance wire. Experimental conditions: Ar =10 mL/min, CH_4 =10 mL/min, CO_2 =10 mL/min.



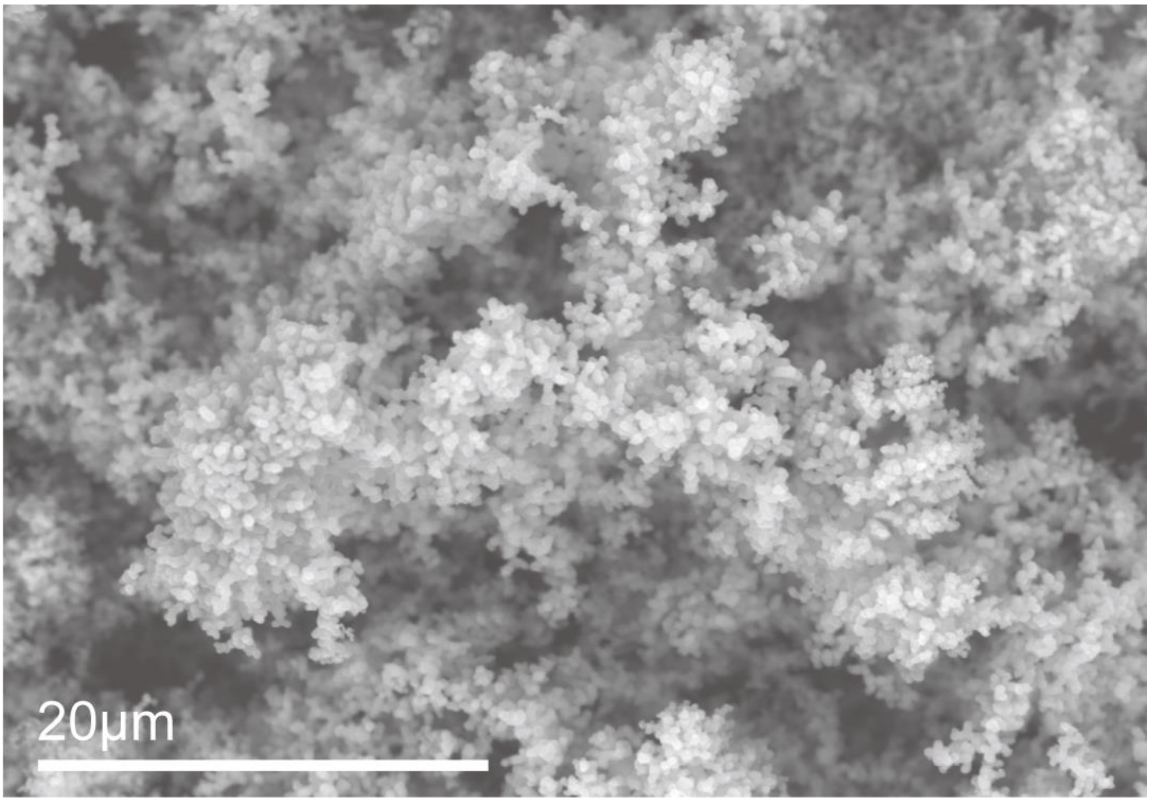
Supplementary Fig. 6 Raman spectra of electrified FeCrAl wire at different reforming time.



Supplementary Fig. 7 Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) spectra of FeCrAl wire at different reaction time. Reaction conditions:14 mg PE, 44 mg CO_2, 4 A (6 Ω).



Supplementary Fig. 8 TEM image of residual carbon achieved in PE dehydrogenation. Reaction conditions: 14 mg PE, Ar, 4 A (6 Ω), 15 min.



Supplementary Fig. 9 SEM image of residual carbon achieved in PE dehydrogenation. Reaction conditions:14 mg PE, Ar, 4 A (6 Ω), 15 min.

Supplementary Tables

Supplementary Table 1. The detailed weight analysis from one practical experiment.[1]

Conditions	Part	Weight (g)[2]
Before reaction	PE	0.0140
	A (Porcelain boat + wire)	9.3547
	B (Quartz tube)	44.9872
After reaction	**C** (Porcelain boat + wire + quartz tube)	54.3544

1 Reaction conditions:14 mg PE, Ar, 4 A (6 Ω), 15 min.
2 All involved mass was weighted by a balance, and the mass of carbon was calculated by the following formula:

$$n_C(\text{mmol}) = \left(\frac{C-A-B}{12}\right)*10^3 \quad (1)$$

Supplementary Table 2. The detailed products distribution, carbon balance and mass balance in the PE dehydrogenation.

Reaction time(min)	n_{H2} (mmol)	n_{CO} (mmol)	n_{CO2} (mmol)	n_{CH4} (mmol)	n_{C2+} (mmol)	n solid (mmol)	Carbon balance (%)	Mass balance (%)
15	1.003	0.000468	0.000430	0.0137	0.000759	1.05	106.5	106.2

$$carbon\ balance = \frac{n_{CO} + n_{CO_2}(on\ GC) + n_{CH_4} + 2n_{C_2H_x} + 3C_3H_x + \frac{m_{solid}}{12}}{\frac{m_{PE}}{14} + n_{CO_2}(original)} \times 100\% \quad (2)$$

$$mass\ balance = \frac{2n_{H_2} + 28n_{CO} + 44n_{CO_2}(on\ GC) + 16n_{CH_4} + 30n_{C_2H_6} + 28n_{C_2H_4} + 44C_3H_8 + m_{solid}}{m_{PE} + m_{CO_2}(original)} \times 100\% \quad (3)$$

Supplementary Table 3. The detailed products distribution with carbon fiber as heating element in dry reforming of PE.

Reaction time(min)	n_{H2} (mmol)	n_{CO} (mmol)	n_{CO2} (mmol)	n_{CH4} (mmol)	N_{C2+} (mmol)	n solid (mmol)	Carbon balance of reaction (%)
15	0.57	1.18	0.26	0.018	0.003	0.29	87

Supplementary Table 4. The quantitative analysis of various products from the large-scale reaction [1]

Reaction time(min)	n_{H2} (mmol)	n_{CO} (mmol)	n_{CO2} (mmol)	n_{CH4} (mmol)	n_{C2+} (mmol)	m solid (mg)	Carbon balance (%)
30	45.3	101.4	110	2.5	1.7	480	99

1 Reaction conditions: 1g PE, 3.3g CO_2, 18Ω, 30min.

Supplementary Table 5. Oxygen balance during the CO_2 reduction

Reaction time(min)	n_{CO2} (mmol)	n_{CO} (mmol)	Increased Mass of heating wire (mg)	Increased moles of O in heating wire (mmol)
1	0.93	0.06	0.6	0.0375
3	0.91	0.08	0.8	0.0500
6	0.62	0.26	2.2	0.1354
9	0.30	0.62	2.6	0.1625
15	0.26	0.67	10.3	0.6417

Supplementary Table 6. Life cycle inventory (LCI) for LCA calculation model

Item	Category	Quantity
Raw materials consumption	Polyethylene (PE)	0.014 g
	Waste CO_2[1]	0.044 g
Energy consumption	Electricity[2]	0.024 kwh
Total product: Syngas (0.0493 g)		

Supplementary Table 7. LCI of PV system (collected from Greet software 2022)

Item	Category	Quantity
PV electric system	Copper Wire	3867.6386 kg
	Brass	7.5034 g
	Zinc	15.0068 kg
	Steel	290.3213 kg
	Nylon 6	86.2892 kg
	High-Density Polyethylene	3727.5248 kg
	Polyvinyl Chloride	235.5171 kg
	Polycarbonate	0.7503 kg
	Liquid Epoxy	0.7503 kg
PV mounting	Aluminum	6.2511 lb
	High-Density Polyethylene	1.4033 g
	High-Impact Polystyrene Resin	7.0167 g
	Steel	1.4999 kg
	Copper wire	0.1000 kg
	Polyurethane Rigid Foam	60 g
	Electricity[2]	14.9500 Wh
Inverter	Aluminum	894 kg
	Steel	9792 kg
	Polypropylene	150 kg
	Electricity[2]	15196 MJ

	Diesel For Non-Road Applications	90MJ
	Natural Gas	5112 MJ
	Tin	3.8371 kg
	Magnet	13.9720 kg
	Copper wire	2277 kg
	Nylon 6	485 kg
	Polyethylene Terephthalate (PET)	300 kg
	Acrylic Acid	150 kg
PV module treatment	Electricity[2]	189.8491 Btu
	Diesel For Non-Road Applications	30.7151 Btu
	Electricity[2]	0.1113 kwh
	Diesel For Non-Road Applications	64.8315 kJ
	Total product: Solar PV system (1 item)	

[1]In the actual experimental status, CO_2 compressed gas is used.

[2]The electricity power consumption in all models is China mix which can be selected in the GREET 2022 (Greenhouse gases, Regulated Emissions, and Energy use in Technologies).

Supplementary Table 8. The higher heating values (HHV) of gaseous products and chemical energy of PE.

Chemicals	HHV[1] (KJ/mol)	Chemical Energy (MJ/kg)
H_2	286	
CO	283	
CH_4	889	
C_2H_4	1418	
C_2H_6	1560	
C_3H_6	2220	
PE	--	45.9[2]

Supplementary Table 9. The energy recovery efficiency of the reforming system powered by a photovoltaic power system (PV) utilizing solar irradiation or Chinese electricity grids.

<table>
<tr><th rowspan="2">Chemicals/electricity</th><th rowspan="2">n (mmol)</th><th rowspan="2">Chemical energy (KJ)</th><th rowspan="2">Output energy (KJ)</th><th rowspan="2">Input energy (KJ)</th><th colspan="2">Energy recovery efficiency[3] (%)</th></tr>
<tr><th>Electricity grids</th><th>Solar PV system</th></tr>
<tr><td>H_2</td><td>0.71</td><td>0.2031</td><td rowspan="6">0.6912</td><td>-</td><td rowspan="8">0.60</td><td rowspan="8">107.5</td></tr>
<tr><td>CO</td><td>1.70</td><td>0.4811</td><td>-</td></tr>
<tr><td>CH_4</td><td>0.00672</td><td>0.0060</td><td>-</td></tr>
<tr><td>C_2H_4</td><td>0.0004487</td><td>0.00064</td><td>-</td></tr>
<tr><td>C_2H_6</td><td>9.868E-05</td><td>0.00015</td><td>-</td></tr>
<tr><td>C_3H_6</td><td>7.74884E-05</td><td>0.00017</td><td>-</td></tr>
<tr><td>PE</td><td>1 (14 mg)</td><td></td><td></td><td>0.6426</td></tr>
<tr><td>Electricity</td><td>-</td><td>-</td><td></td><td>115.2</td></tr>
</table>

The chemical energy of gaseous products was calculated according to the moles and the HHV or chemical energy listed in Supplementary Table 7. For example, the chemical energy of H_2 achieved in the optimal reaction can be achieved as follow:

$$0.71\times10^{-3} mol \times 286 KJ / mol = 0.2031 KJ \quad (4)$$

The output energy is the sum of the chemical energy of all products.

The input energy in the optimal reaction powered by electricity grids includes the chemical energy of PE and the electricity consumption that was measured by a coulombmeter. According to the coulombmeter, 0.032 KWh of electricity was consumed in an optimal reaction, which corresponds to the energy of 115.2 kJ.

The energy recovery efficiency in an optimal reaction powered by electricity grids was calculated according to the following formula:

Energy recovery efficiency = output energy / (PE chemical energy + electricity energy) × 100 % (5)

However, the energy recovery efficiency of a reaction powered PV system under solar irradiation was calculated according to the following formula:

Energy recovery efficiency= output energy / (PE chemical energy) × 100 % (6)

Supplementary References

1. https://www.liquisearch.com/heat_of_combustion/heat_of_combustion_tables.

2. Splitstone PL, Johnson WH. The enthalpies of combustion and formation of linear polyethylene. *Journal of Research of the National Bureau of Standards Section A, Physics and Chemistry* **78**, 611 (1974).

3. Luo J*, et al.* Leveraging CO_2 to directionally control the H_2/CO ratio in continuous microwave pyrolysis/gasification of waste plastics: Quantitative analysis of CO_2 and density functional theory calculations of regulation mechanism. *Chem. Eng. J.* **435**, 134794 (2022).