Supplementary information for

Platinum/nitrogen-doped carbon/carbon cloth: a bifunctional catalyst for electrochemical reduction and carboxylation of CO_2 with excellent efficiency

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1. Materials and Instruments

All reagents were used as received.

Potentiostatic, galvanostatic electrolysis and linear sweep voltammograms were performed using a CHI 660C electrochemical Station (Shanghai Chenhua Instruments Company).

Liquid phase products were analyzed by ^1H-NMR spectra recorded on an Ascend 400 (500 MHz, Bruker, Germany) spectrometer. Products from CO_2 electroreduction were also analyzed by Gas Chromatography (Agilent 7890A). The product yield of phenylpropionic acids was determined by a high performance liquid chromatography (HPLC) instrument (DIONEX Ultimate 3000 pump) equipped with a UV detector.

Microstructure, SAED and EDX spectra were analyzed using FEI JEOL-7800F field emission scanning electron microscope (FE-SEM). Transmission electron microscopy (TEM), high-resolution TEM (HRTEM) images and element mapping analysis were observed with JEM-2100F field emission electron microscope with an accelerating voltage of 120 kV.

X-ray diffraction (XRD) patterns were recorded by a Rigaku MiniFlex 600 powder diffractometer using Cu Kα radiation (k= 1.5406 Å) with a scan step of 0.05° between

10° and 80°.

N_2 adsorption was carried out at 77 K on a Micromeritics ASAP 2460 instrument after outgassing the samples for 10 h under vacuum at 573 K. Specifc surface area (BET) and pore-size distribution were calculated from corresponding N_2 adsorption-desorption isotherm, applying the BET equation.

X-ray photoelectron spectroscopy (XPS) measurements were performed on a Perkin-Elmer PHI 5000C ESCA system.

2. General methods

Synthesis of Pt-NPs@NCNFs@CC: Pt-NPs@NCNFs@CC were synthesized using an electrospinning process. Firstly, 1.6 g of polyacrylonitrile (PAN, Mw = 130000) powder was dissolved in 20 mL of DMF in a three-necked bottle by vigorously stirring of the mixture for 2 hour over a water bath kettle at 60 °C to get a homogenous solution. Then, 0.6 g of $ZnCl_2$ and 20 mg of $K_2PtCl_2 \cdot 6H_2O$ were dropped into the PAN/DMF solution and the mixture was stirred at 60 °C for 2 hour. The above mixture was stirred for another 10 hours, then the precursor solution was obtained.

The precursor solution was electrospun directly onto the coated carbon cloth substrate using a parallel-plate apparatus. The precursor solution was transferred into a syringe with a stainless copper needle at the tip. The needle was connected to a high voltage power supply. The applied potential, solution flow rate and spin distance were 21 kV, 0.7 mL/h and 12 cm, respectively. All the experiments were performed at room temperature.

The nanofibrous materials were preoxidated in air at 220 °C for 1 hour and then carbonized under Ar gas flow at an optimal temperature of 800 °C for 1 hours to generate a high graphitization. Then, the products were cooled to room temperature under Ar atmosphere. The heating rate was 5 °C/min from room temperature to 800 °C. Then, Pt-NPs@NCNFs@CC was obtained.

0, 10 and 40 mg of $K_2PtCl_2 \cdot 6H_2O$ were also added to generate different precursor solution for comparison. The corresponding materials were named as NCNFs@CC, Pt-NPs@NCNFs@CC-10 and Pt-NPs@NCNFs@CC-40, respectively.

The precursor solution with 20 mg of $K_2PtCl_2 \cdot 6H_2O$ was also electrospun and carbonized under 700 and 900 °C for comparison. The corresponding materials were named as Pt-NPs@NCNFs@CC-700 and Pt-NPs@NCNFs@CC-900, respectively.

CO_2 reduction procedure: Linear sweep voltammograms were recorded in an undivided cell. An Ag/AgCl was the reference electrode, and a Pt foil (10 mm × 10 mm) was the counter electrode. An aqueous electrolyte of 20 mL 0.1 M $KHCO_3$ solution was used as the electrolyte, which was bubbled with 1.0 atm N_2 or CO_2 (99.995%). The Scan rate was 0.1 V s^{-1}.

Pt-NPs@NCNFs@CC was cut into a square with 2×2 cm size (or specific size we need), which could be used directly as cathode to test the catalytic activity for CO_2 electroreduction. The reduction process was performed with a conventional three-electrode electrochemical H-type cell, with a piece of Nafion®117 membrane as a separator. An Ag/AgCl was the reference electrode, and a Pt foil (10 mm × 10 mm) was the counter electrode. An aqueous electrolyte of 20 mL 0.1 M $KHCO_3$was used as electrolyte, which was bubbled with 1.0 atm CO_2 (99.995%) to be saturated with CO_2.

All potentials initially measured in this work were converted to the reversible hydrogen electrode (RHE) by following the Nernst equation:

$E(RHE) = E(Ag/AgCl) + 0.199 + 0.059 \times pH$

Carboxylation procedure: Pt-NPs@NCNFs@CC was cut into a square with 2×2 cm size, which could be used directly as cathode for the carboxylation of different substrates with CO_2. A typical carboxylation was carried out in a mixture of 0.1 M substrate and 0.1 M tetraethylammonium iodide (TEAI) in 20 mL of CO_2-saturated MeCN in an undivided glass cell, with a Pt-NPs@NCNFs@CC cathode and a sacrificial magnesium (Mg) anode. No additive catalyst was needed in the reaction solution. The CO_2 pressure was 1 atm and the reaction took place at room temperature.

3. Characterization of Pt-NPs@NCNFs@CC and other catalysts.

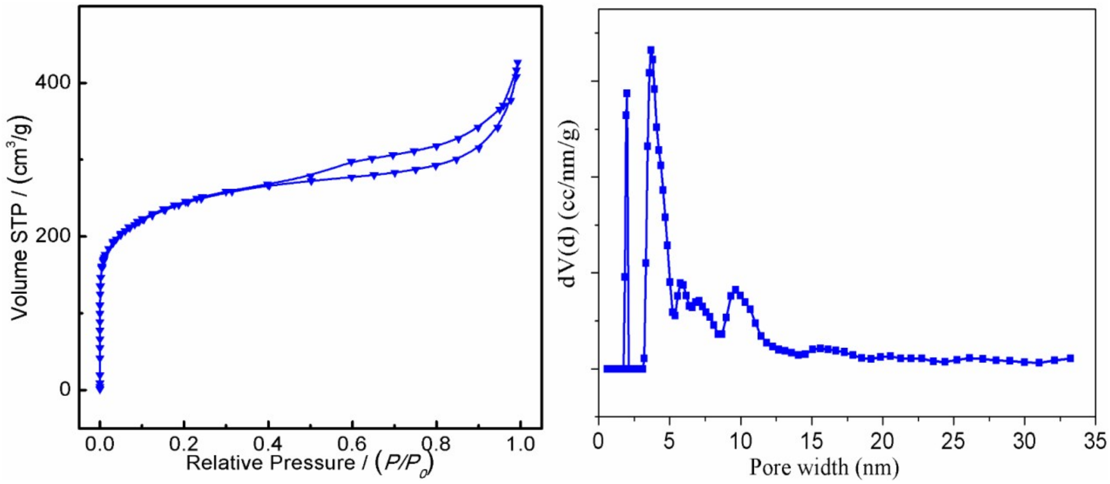


Fig. S1 N_2 adsorption-desorption isotherms (left) and pore width distribution (right) of Pt-NPs@NCNFs@CC.

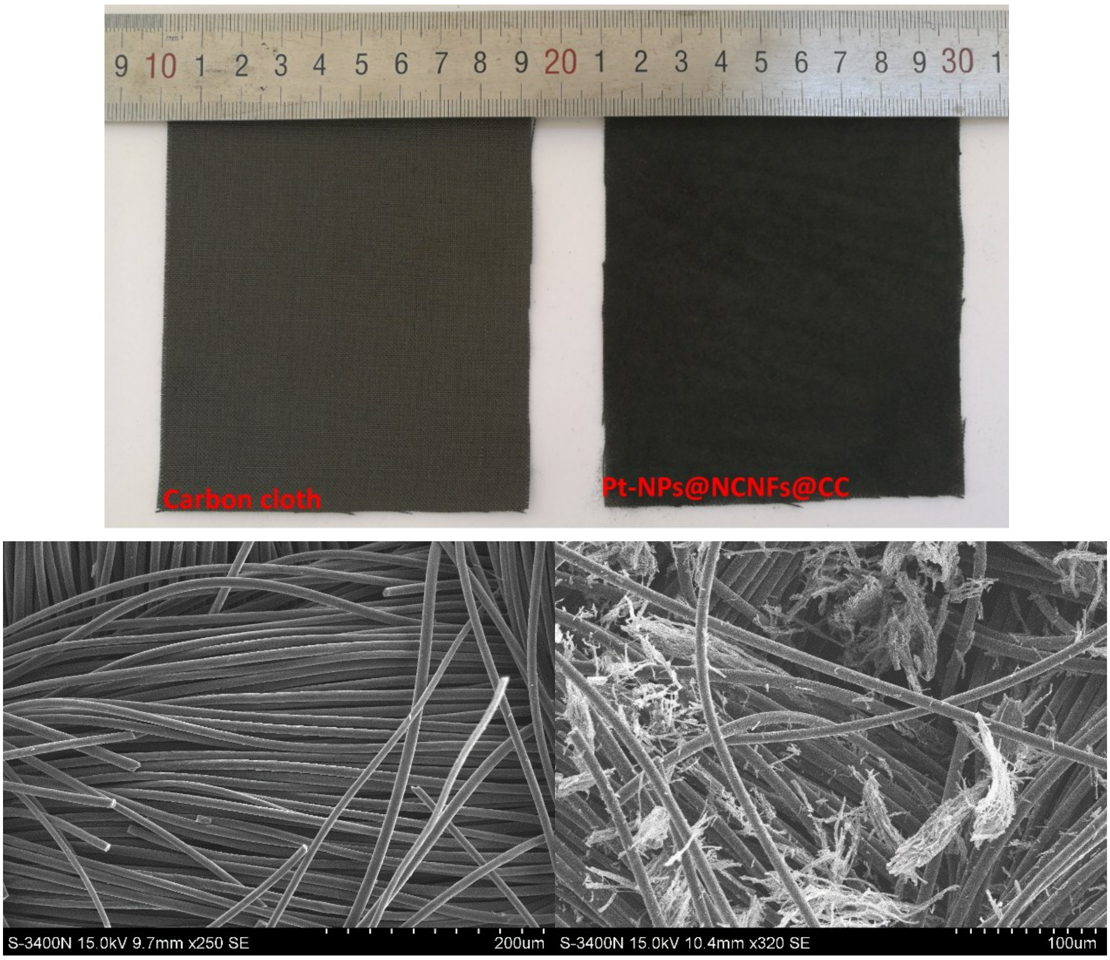


Fig. S2 Images of pure carbon cloth and Pt-NPs@NCNFs@CC (up); FE-SEM patterns of pure carbon cloth (left) and Pt-NPs@NCNFs@CC after scraping away the nanofiber layer (right).

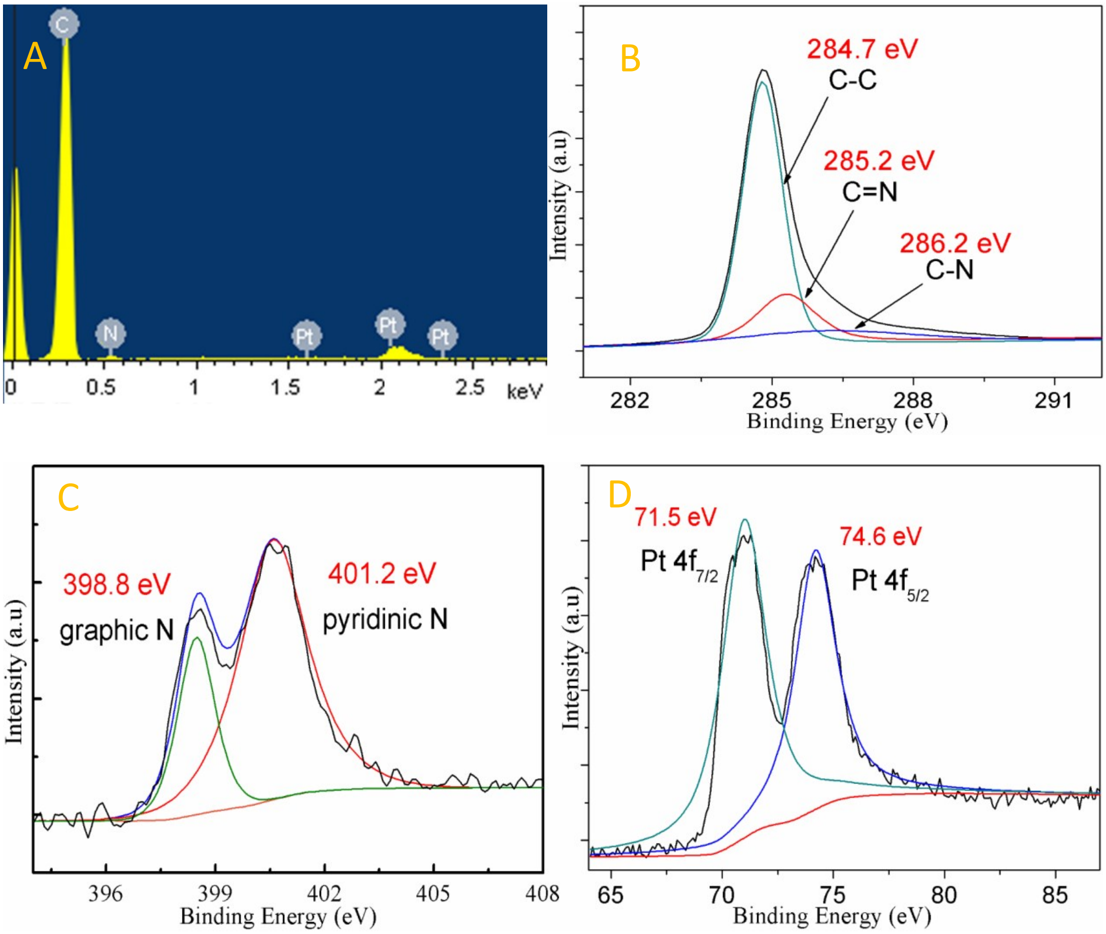


Fig. S3 EDX spectra of Pt-NPs@NCNFs@CC, showing the signals corresponding to C, N and Pt (A). XPS spectra of Pt-NPs@NCNFs@CC, C 1s (B), N 1s (C) and Pt 4f (D).

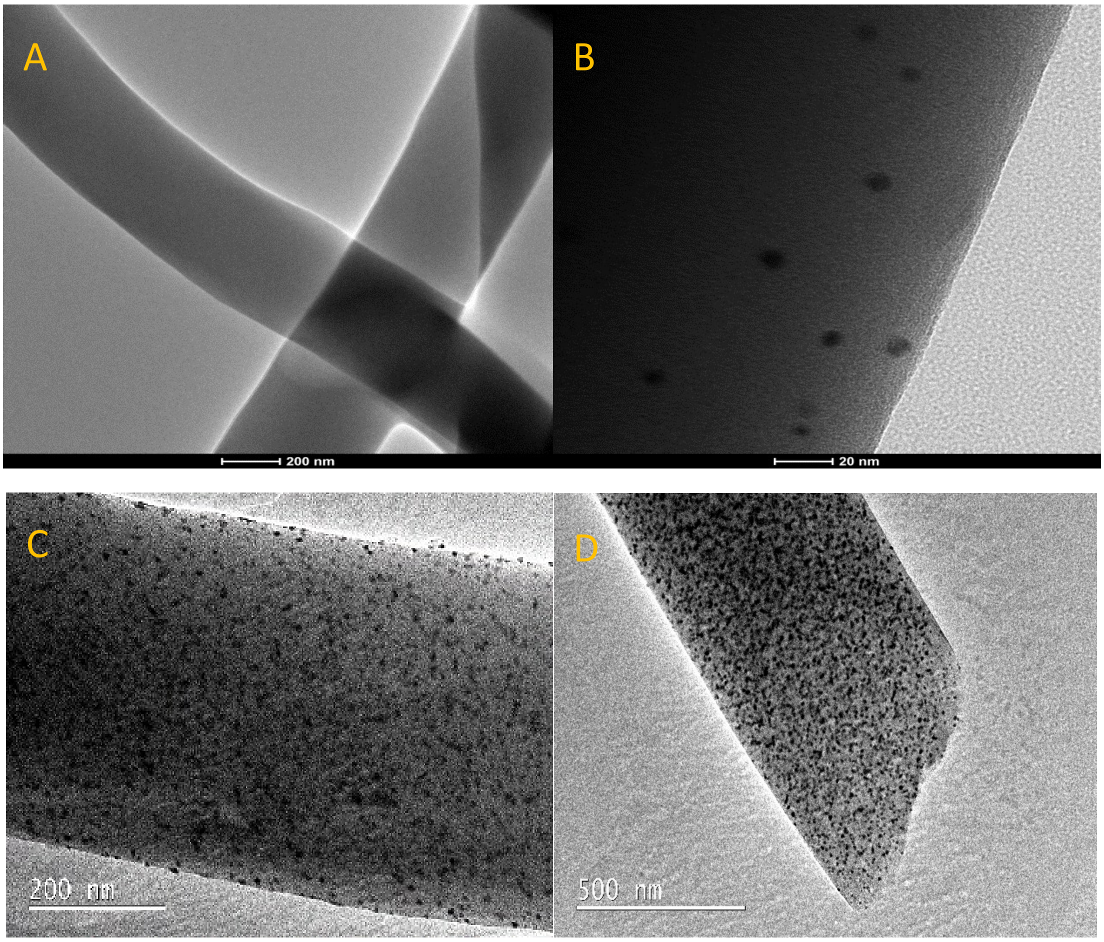


Fig. S4 TEM patterns of NCNFs@CC (A), Pt-NPs@NCNFs@CC-10 (B), Pt-NPs@NCNFs@CC (C) and Pt-NPs@NCNFs@CC-40 (D).

As shown in Fig. S4, the amount of Pt NPs in nanofibers increase from NCNFs@CC, Pt-NPs@NCNFs@CC-10, Pt-NPs@NCNFs@CC to Pt-NPs@NCNFs@CC-40.

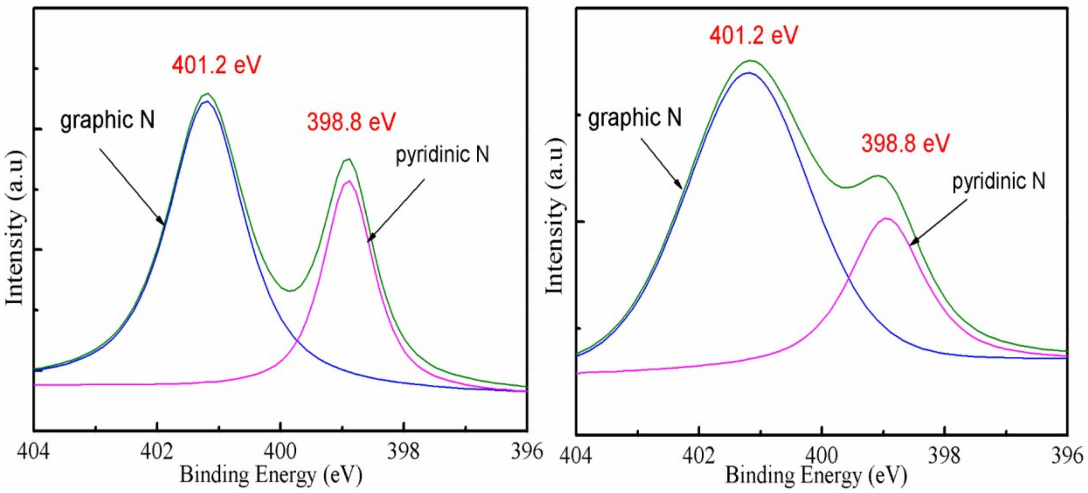


Fig. S5 XPS spectrum of Pt-NPs@NCNFs@CC-700 (left) and Pt-NPs@NCNFs@CC-900 (right).

As shown in Fig. S5, Pt-NPs@NCNFs@CC-700 contains 34 at% pyridinic nitrogen and Pt-NPs@NCNFs@CC-900 contains 27 at% pyridinic nitrogen.

4. Electrochemical reduction of CO_2 using Pt-NPs@NCNFs@CC and other catalysts.

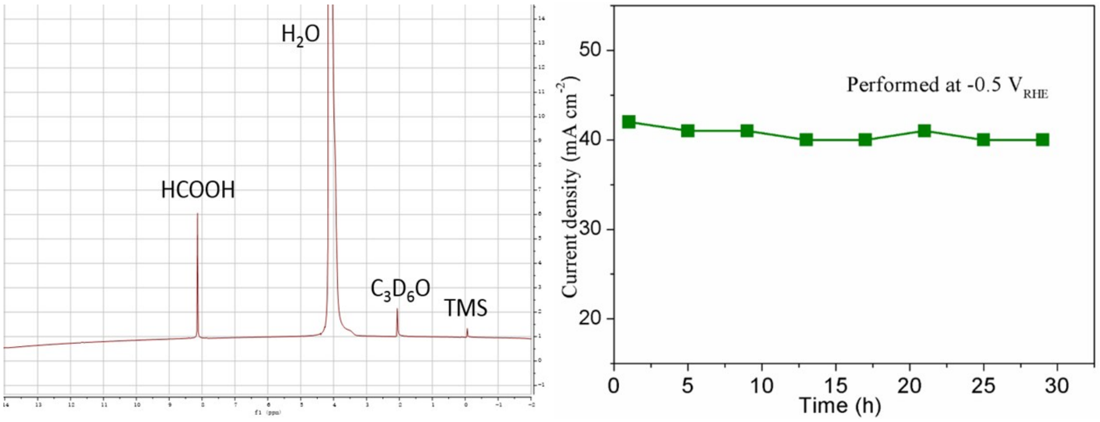


Fig. S6 ^1H NMR spectrum of products from CO_2 electroreduction (left); Long-time test performed at -0.5 V_{RHE} potential using Pt-NPs@NCNFs@CC (2×2 cm) as working electrode, anode: Pt foil, 20 mL CO_2-saturated 0.1 M $KHCO_3$ solution, temperature: 25 °C, 1 atm (right).

Table S1 Electrochemical reduction of CO_2 at various cathodes [a]

Entry	Cathode	Faradaic efficiency / %
1	Pt-NPs@NCNFs@CC	91
2	NCNFs@CC	8
3	Pt-NPs@NCNFs@CC-10	73
4	Pt-NPs@NCNFs@CC-40	91
5	Pt-NPs@NCNFs@CC-700	80
6	Pt-NPs@NCNFs@CC-900	76
7	CC	0
8	Pt NPs	0

[a] Electrochemical reduction of CO_2 was carried out in an divided cell at -0.5 V_{RHE} cathode potential. Electric charge: 100 C; anode: Pt foil; solution: 20 mL CO_2-saturated 0.1 M $KHCO_3$ solution; temperature: 25 °C; pressure: 1 atm.

$$CO_2 + * \longrightarrow *CO_2 \qquad (1)$$

$$*CO_2 + H^+ (aq.) + e^- \longrightarrow *COOH \qquad (2)$$

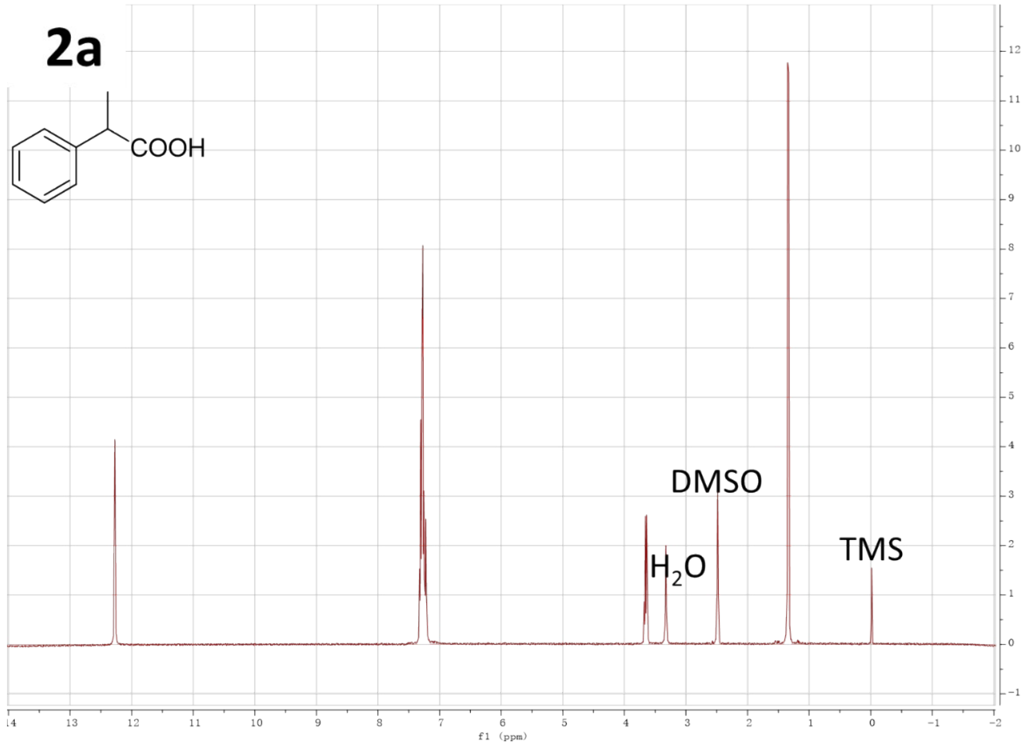
$$Pt + H^+ (aq.) + e^- \longrightarrow Pt\text{-}H \qquad (3)$$

$$Pt\text{-}H + *CO_2 \longrightarrow *COOH + Pt \qquad (4)$$

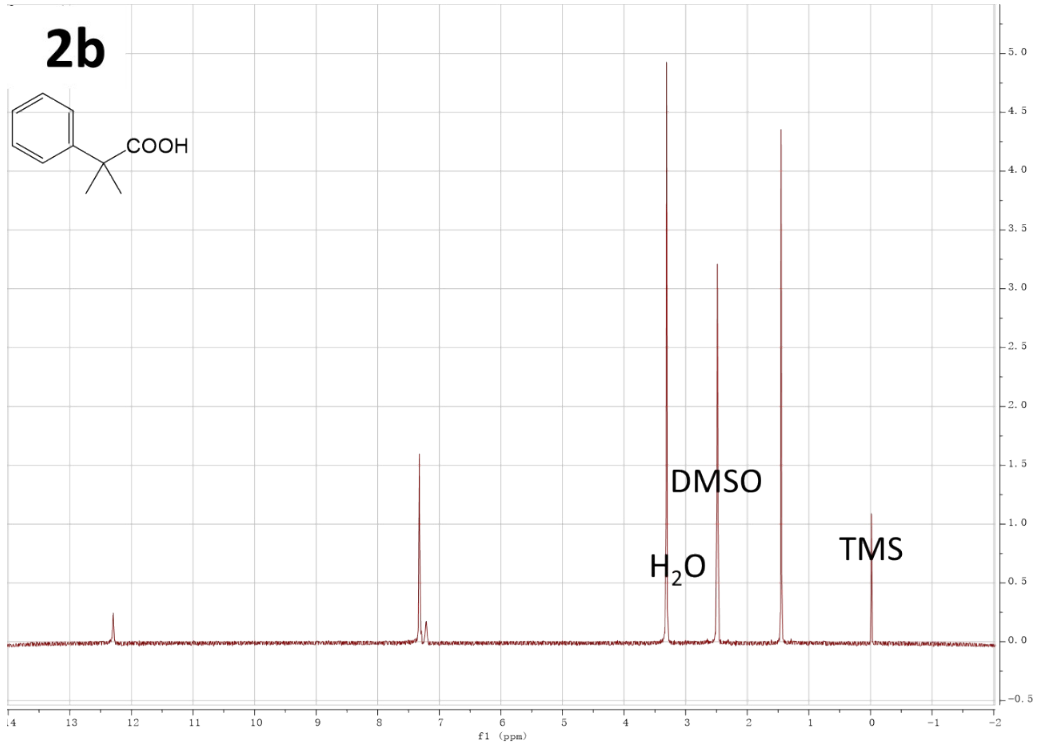
Scheme S1

5. Electrochemical carboxylation of CO_2 at Pt-NPs@NCNFs@CC cathode.

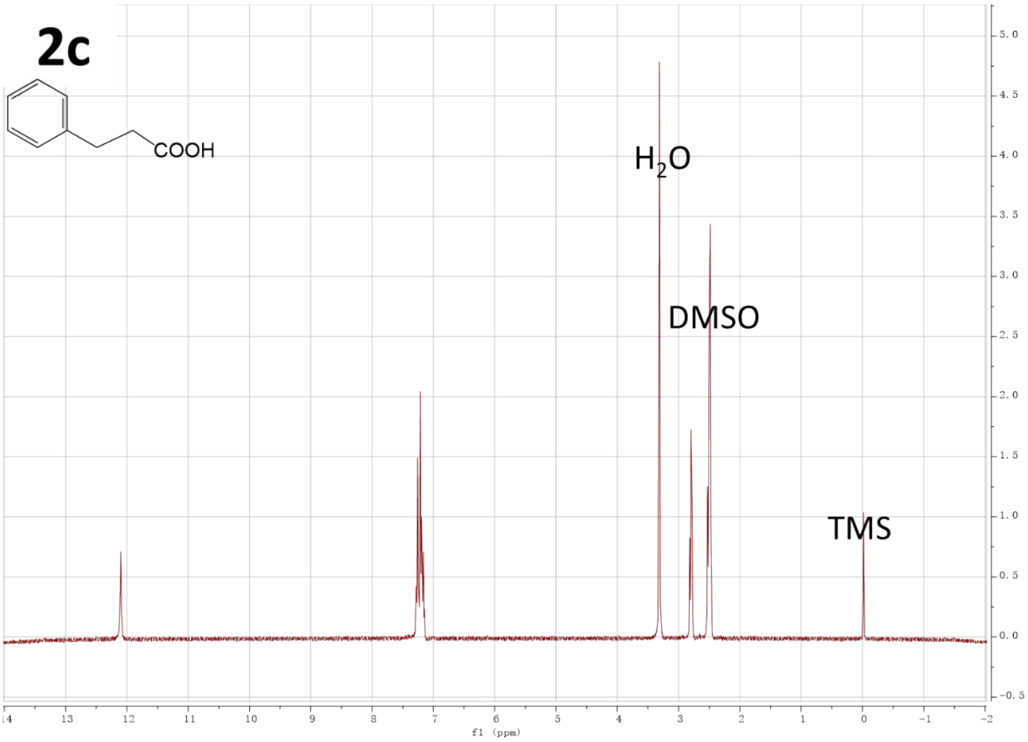
2a



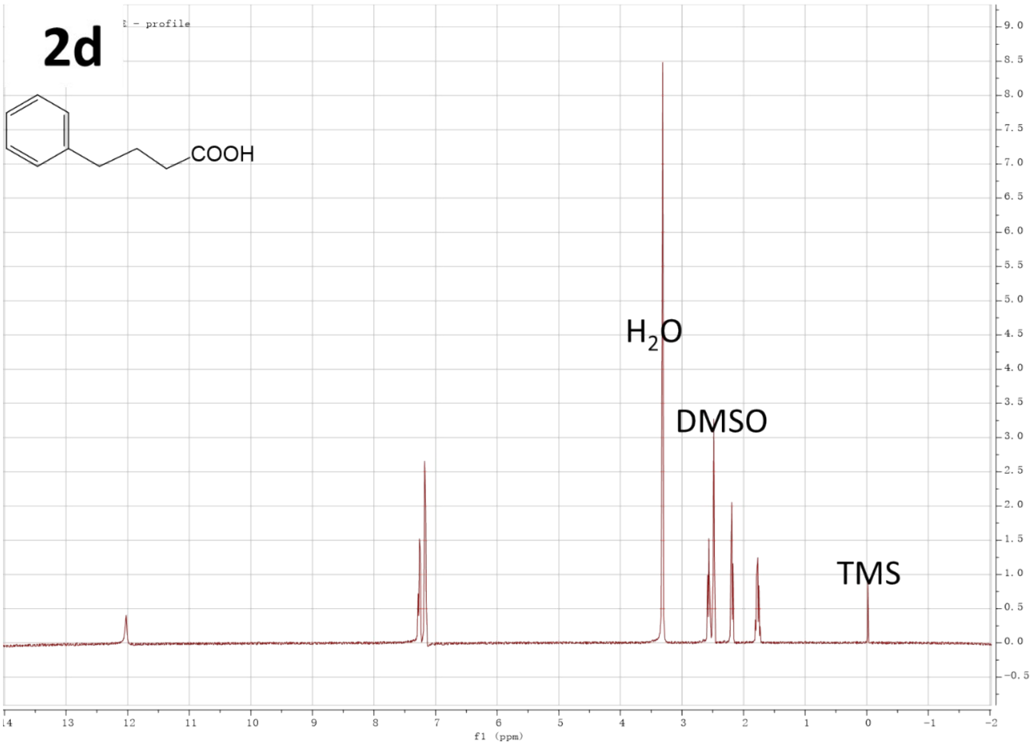
2b



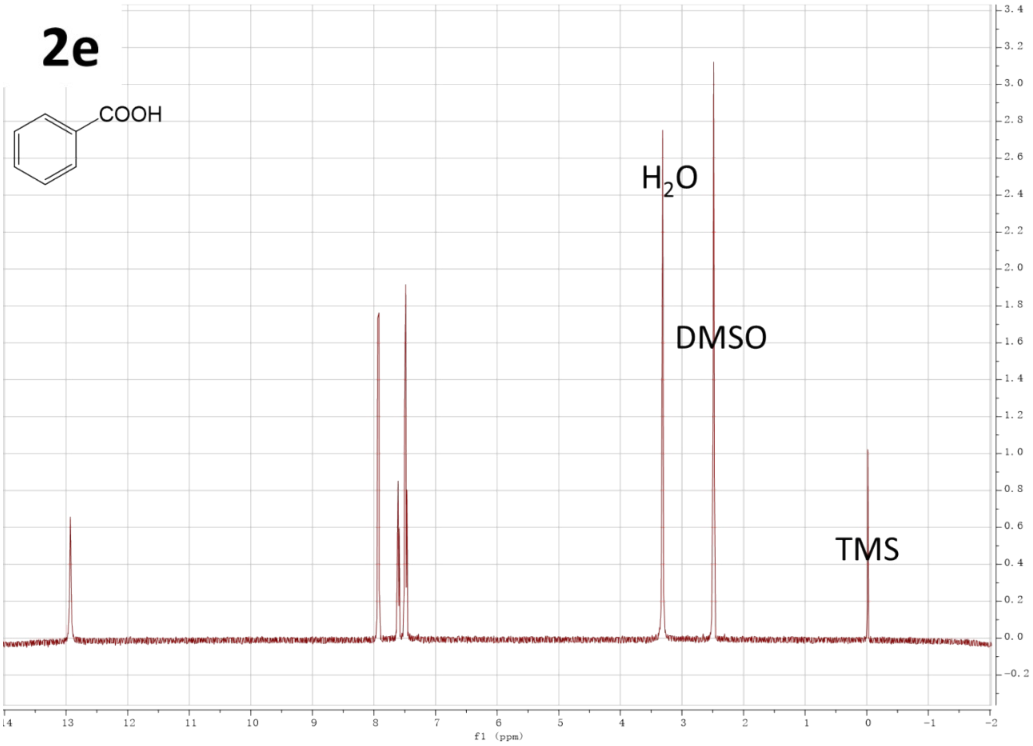
2c


COOH
H$_2$O
DMSO
TMS
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
f1 (ppm)

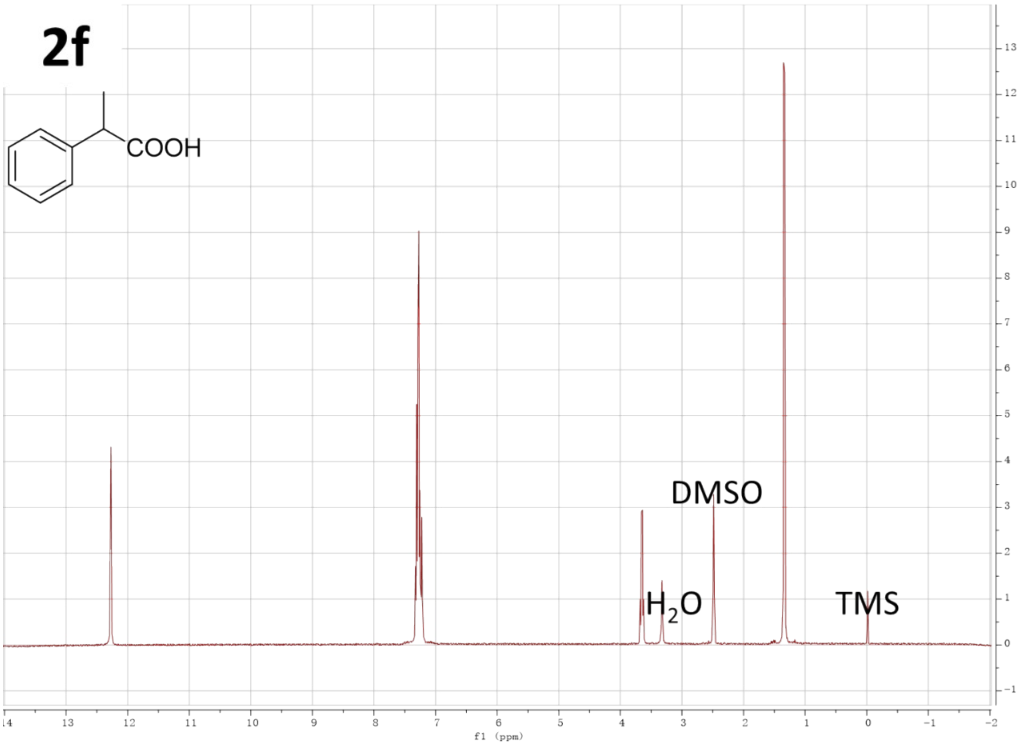
2d


1 − profile
COOH
H$_2$O
DMSO
TMS
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
f1 (ppm)

2e


COOH
H$_2$O
DMSO
TMS
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

2f


COOH
DMSO
H$_2$O
TMS
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

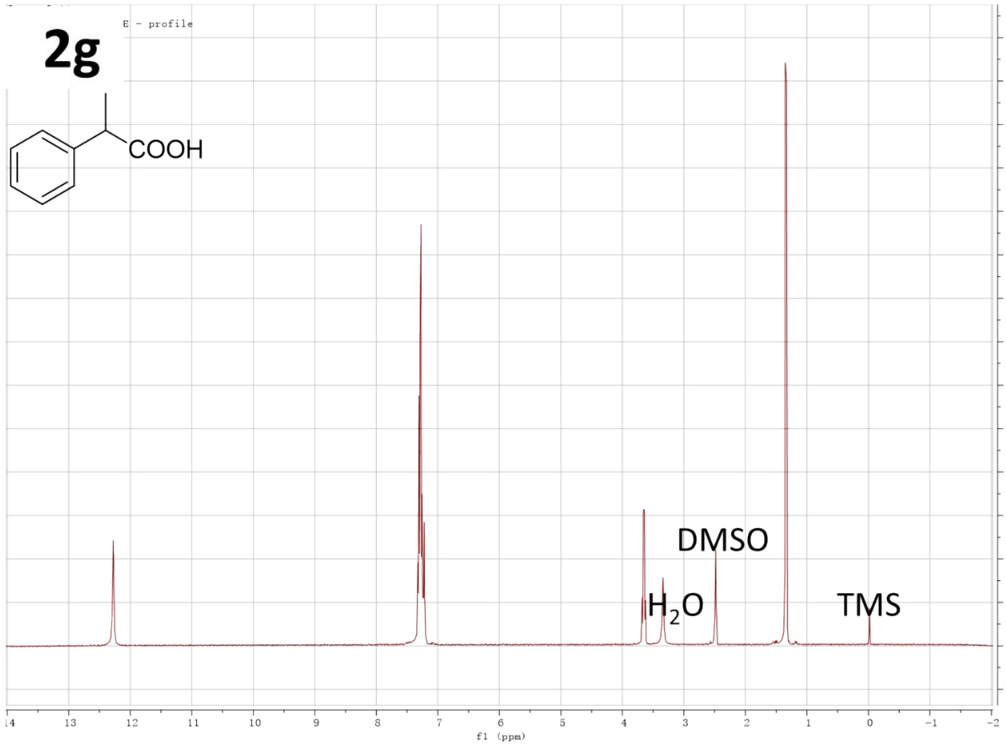


Fig. S7 ^{1}H NMR spectrum of products from CO_2 carboxylation with halides.

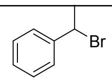
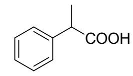
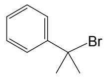
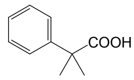
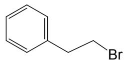
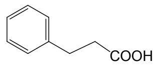
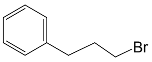
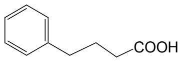
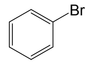
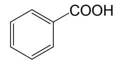
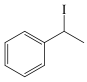
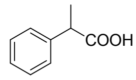
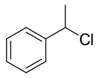
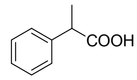
Table S2 Electrocatalytic carboxylation of **1a** under various conditions [a]

Entry	Q / F mol^{-1}	Current density / mA cm^{-2}	Solvent	*Yield* / %[b]
1	1.5	3	MeCN	61
2	2.0	3	MeCN	79
3	2.5	3	MeCN	99
4	3.0	3	MeCN	97
5	2.5	1	MeCN	72
6	2.5	2	MeCN	88
7	2.5	4	MeCN	86
8	2.5	5	MeCN	81
10	2.5	3	DMF	86
11	2.5	3	Methanol	72
12	2.5	3	Ethanol	89

[a] Electrolysis was carried out in an undivided cell. Cathode: Pt-NPs@NCNFs@CC; anode: Mg; volume of solvent: 20 mL; supporting electrolyte: 0.1 mol L^{-1} TEAI; substrate concentration: 0.1 mol L^{-1}. [b] Determined by HPLC.

The influence of current density, electric quantity and solvent was investigated to increase the yield of target product. Under optimized conditions, **2a** with 99% yield was obtained (Table S2, entry 3).

Table S3 Electrochemical carboxylation of different substrates at Pt-NPs@NCNFs@CC cathode [a].

Entry	Substrate	Product	Yield[b] (%)
1	 **1a**	 **2a**	99
2	 **1b**	 **2b**	92
3	 **1c**	 **2c**	78
4	 **1d**	 **2d**	57
5	 **1e**	 **2e**	67
6	 **1f**	 **2f**	95
7	 **1g**	 **2g**	82

[a] Anode: Mg, 20 mL CO_2-saturated MeCN, 0.1 M substrate, supporting electrolyte: 0.1 M TEAI, current density: 3 mA cm^{-2}, charge: 2.5 F mol^{-1}, CO_2 pressure: 1 atm, room temperature. [b] Determined by HPLC.

Under same reaction conditions as Table 1, entry 1, certain yield of target products could also be achieved with these substrates. As is obvious from the results summarized in Table S3, Pt-NPs@NCNFs@CC cathode could be applicable to the electrochemical carboxylation of CO_2 with wide range of substrates.

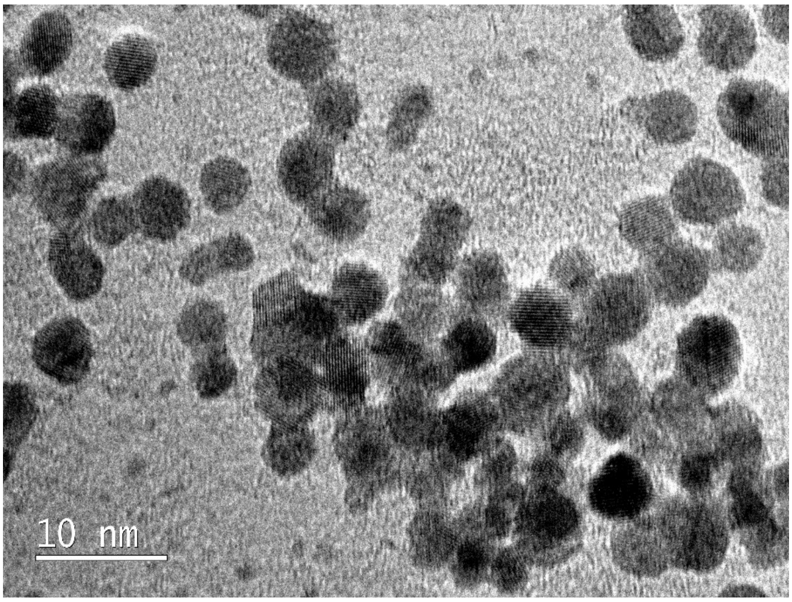


Fig. S8 TEM pattern of pure Pt NPs.

Pure Pt NPs were synthesized based on the method reported in (*Nanoscale, 2017, 9, 2963-2968).* According to TEM patterns, this pure Pt NPs have an average particle size of 5 nm. Pure Pt NPs were loaded onto carbon cloth (Pt-NPs/CC) for carboxylation reactions.

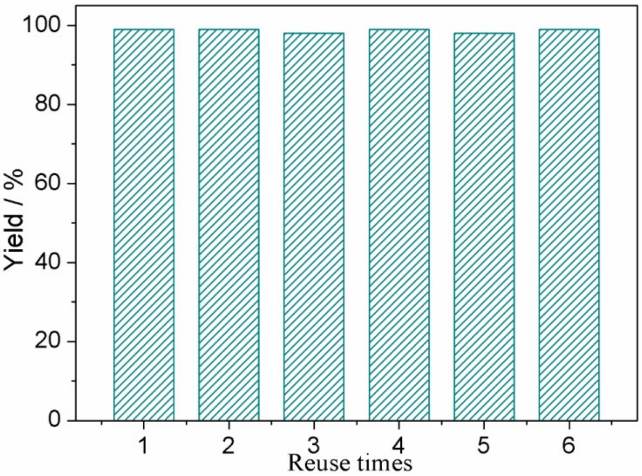


Fig. S9 Reuse test of Pt-NPs@NCNFs@CC for CO_2 carboxylation under the same conditions as Table 1 entry 1.

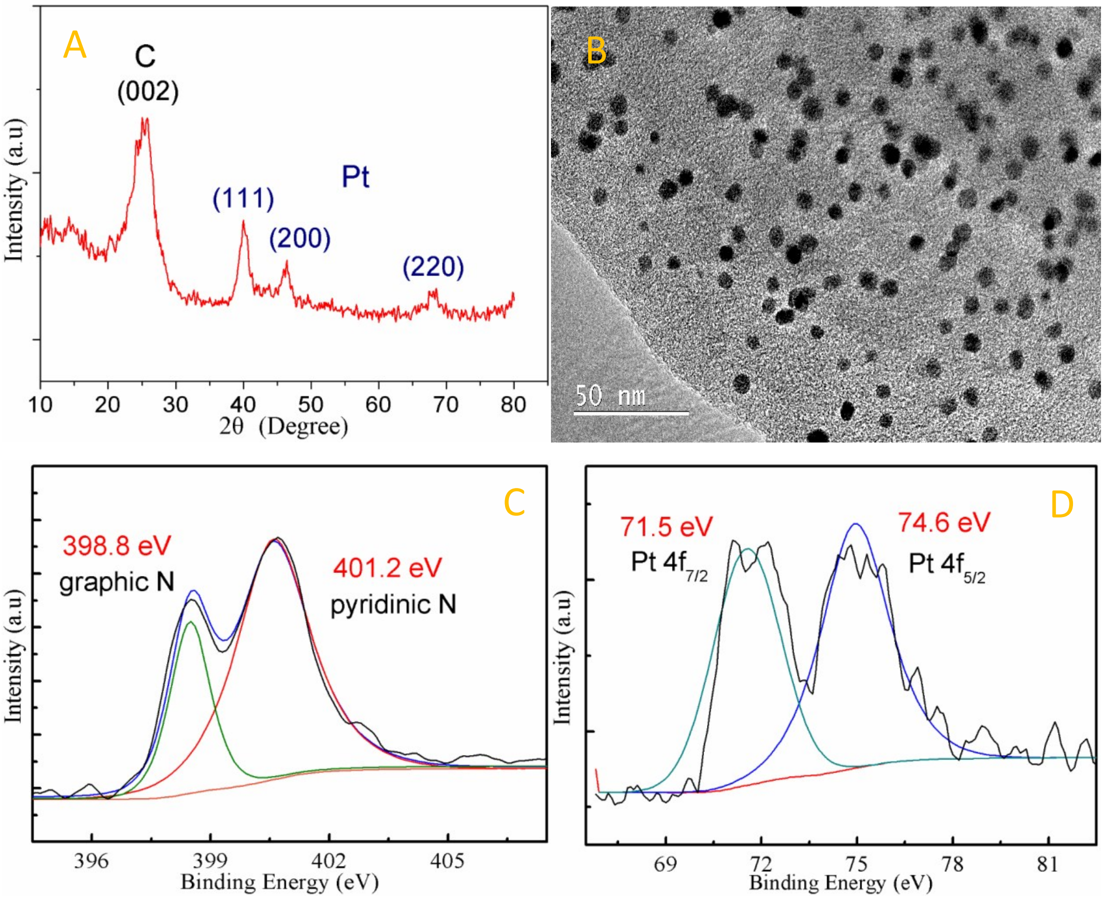


Fig. S10 XRD patterns (A), TEM images (B), XPS patterns (C, D) of Pt-NPs@NCNFs@CC after all the reactions.

After CO_2 reduction and carboxylation reactions, the Pt-NPs@NCNFs@CC cathode was characterized by multiple methods. According to the XRD patterns of Pt-NPs@NCNFs@CC after reuse, the signal intensity corresponding to C and metallic Pt NPs didn't change. In addition, the TEM images showed these Pt NPs were still well distributed within the nanofibers and had no tendency to aggregate. The XPS patterns indicated that pyridinic N didn't get obvious loss and Pt composition still remained Pt^0 state. In a word, Pt-NPs@NCNFs@CC composite owns remarkable stability and reusability, which shows great potential for practical applications.