

Supporting Information

Conjugated polyimides modified self-supported carbon electrodes for electrochemical conversion of CO<sub>2</sub> to CO

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## Reagents and materials

Pyromellitic dianhydride (PMDA), Melamine (MA), N-Methyl-2-pyrrolidinone (NMP) were all purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Potassium bicarbonate, hydrochloric acid (HCl, 36-38%), and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30%) were purchased from Tianjin Yongda Chemical Reagent Co., Ltd. The carbon cloths (CC), carbon papers (CP), and Cabot Vulcan XC72R conductive black carbon were all purchased from Shanghai Hesen Electronics Co., Ltd. Nafion-117 proton exchange membranes and Nafion solution (5 wt%) were purchased from Dupont® company (USA). The carbon dioxide (CO<sub>2</sub>, 99.999%), argon (Ar, 99.999%), and nitrogen (N<sub>2</sub>, 99.999%) were purchased from Shenyang Zhaote Special Gas Co., Ltd. All the chemicals were used without further purification unless otherwise noted.

## Instrumentation condition

FT-IR spectra were recorded as powders using the Shimadzu AIM-9000 spectrometer. UV-vis spectra were obtained on a Shimadzu UV-2600 spectrophotometer. The X-ray diffraction (XRD) patterns were obtained on a Bruker (Germany) D8 Advance diffractometer with Cu K $\alpha$  radiation in the range of 10°–80° (2 $\theta$ ). The scanning electron microscope (SEM) images and elemental mapping images were performed in a Hitachi SU8000. Transmission electron microscope (TEM) images were obtained from a JEOL JEM-2100 at an acceleration voltage of 200 kV. BET was carried out with Quantachrome Nova 4000e. X-ray photoelectron spectroscopy (XPS) measurement was carried out on an ESCALAB Mk II (Vacuum generators) spectrometer with an Al K X-ray source (240 W). CP MAS NMR was obtained on a Bruker (Germany) 400M spectrometer, operating at a spinning rate of 10 kHz, a 4-second recycle delay, a 6.5  $\mu$ s pre-scan delay, and equipped with a 4 mm spinner.

## Fabrication of CPI-A and CPI-S on carbon cloth

Typically, 5 mg of CPI powder and 30  $\mu$ L of Nafion solution (5 wt%) were dispersed in 470  $\mu$ L ethanol by means of sonication for 1 h to form a homogeneous black ink. The working electrodes was then fabricated by loading the ink onto a carbon paper (1 cm x 1 cm).

## Electrochemical experiments

The electrochemical measurements were conducted by a CHI 760 electrochemical analyzer (Shanghai, Chenhua Co., China) in a three-electrode H-cell arrangement separated by a Nafion 117 membrane containing 0.5 M KHCO<sub>3</sub> electrolyte at a constant temperature using a circulating water bath during the reaction. Before the tests, the Nafion 117 membrane was protonated by boiling in ultrapure water for 1 h and treating in H<sub>2</sub>O<sub>2</sub> (3%) aqueous solution at 80 °C for another 1 h in sequence. The membrane was then treated in 0.5 M H<sub>2</sub>SO<sub>4</sub> for 1 h at 80 °C and finally stored in ultrapure water overnight. Typically, an Ag/AgCl (in saturated KCl electrolyte) electrode was used as the reference electrode and a platinum foil electrode (1 cm  $\times$  2 cm) as the counter electrode. The electrolyte was pre-saturated with high-purity CO<sub>2</sub> (99.999%) for 30 min with a flow rate of 30 standard cubic centimeter per minute (sccm). Before data collection, all working electrodes were

cleaned and activated by steady-state potential sweeping cycles in the range of 0.5 V to -1.5 V vs. RHE at  $1000 \text{ mV} \cdot \text{s}^{-1}$  in an Ar-saturated 0.5 M  $\text{KHCO}_3$  solution for 20 cycles. For  $\text{CO}_2\text{RR}$  tests, a potentiostatic test was conducted for 2 h in a  $\text{CO}_2$ -saturated 0.5 M  $\text{KHCO}_3$  solution (70 mL) under atmospheric pressure and constant temperature. Unless otherwise specified, the 0.5 M  $\text{KHCO}_3$  solution (pH = 8.3) was adopted as the electrolyte in the linear sweep voltammetry (LSV) and cyclic voltammetry (CV). The measured potentials vs. Ag/AgCl were converted to a reversible hydrogen electrode (RHE) scale according to the Nernst equation ( $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059\text{pH} + 0.205 = E_{\text{Ag/AgCl}} + 0.695$ ).

## Computation detail

DFT approaches have been employed herein. The Perdew–Burke–Ernzerhof (PBE)[1] exchange-correlation functions have been used both for gas and solid phases (i.e., under periodical conditions) and, for the sake of consistency, all of the calculations were accomplished by Dmol3 software[2]. The combination of a numerical double- $\zeta$  quality basis set [including polarization functions on all atoms, i.e., double- $\zeta$  numerical with polarization (DNP)] and an effective core potential for the metal atoms was adopted. The inclusion of explicit van der Waals terms for Grimme DFT-D3 correction in the calculations has been chosen because of their importance when describing interparticle interaction[3-5].

According to the computational hydrogen electrode model, the Gibbs free energy change ( $\Delta G$ ) was calculated using[6]:

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S$$

Where E is the total energy resulting from DFT calculations; ZPE is the zero-point energy calculated from vibrational frequencies; T is the temperature at 298 K; and S is the entropy, which can be obtained from standard thermodynamics tables for gaseous species[7] or from vibrational frequencies for adsorbed species.

## Supplementary Figures

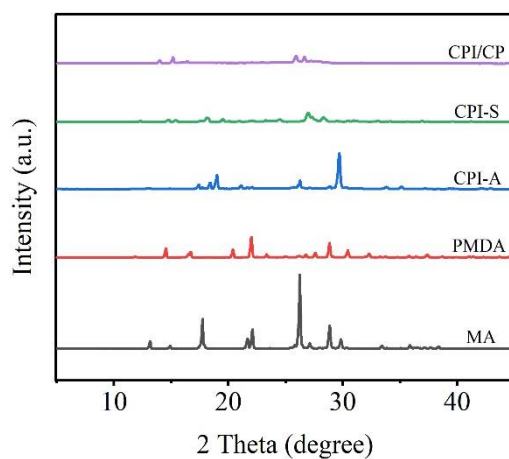


Figure 1. XRD of CPI/CP, CPI-A, CPI-S and raw materials.

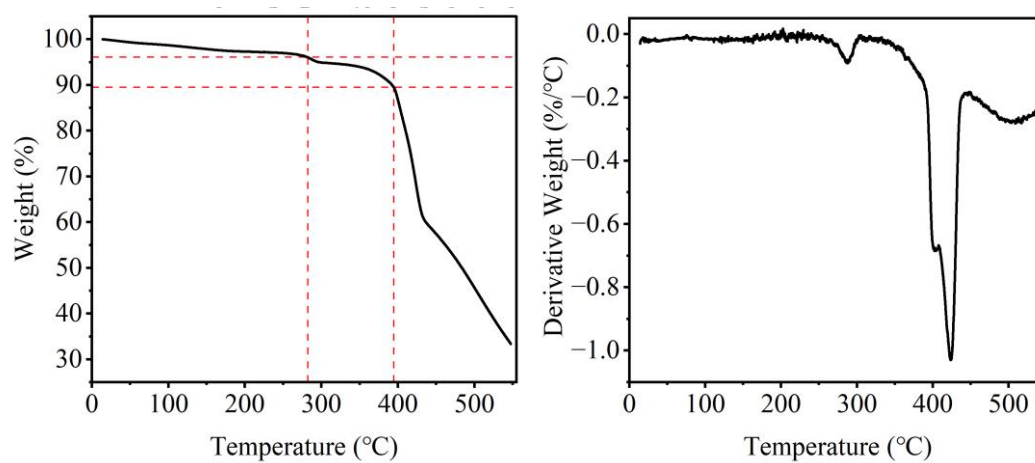


Figure 2. TGA and DTA of CPI/CP

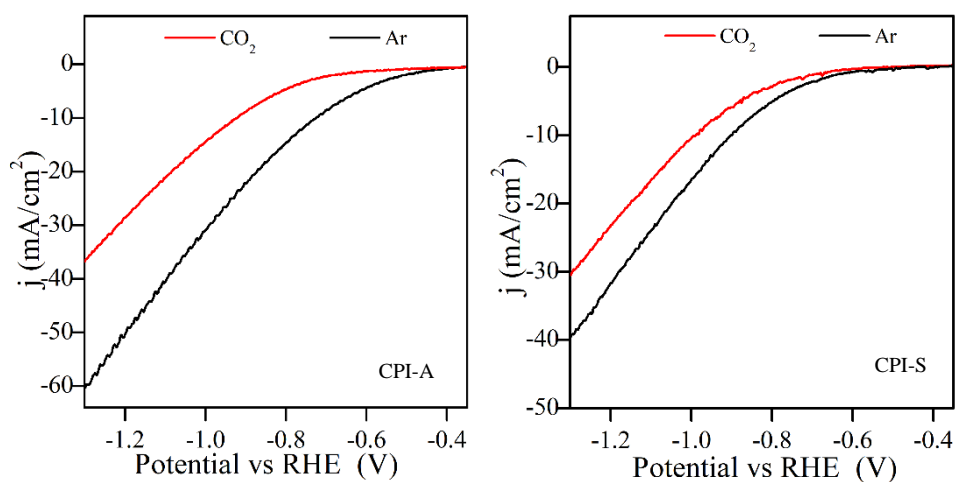


Figure 3. The LSV of CPI-A & CPI-S

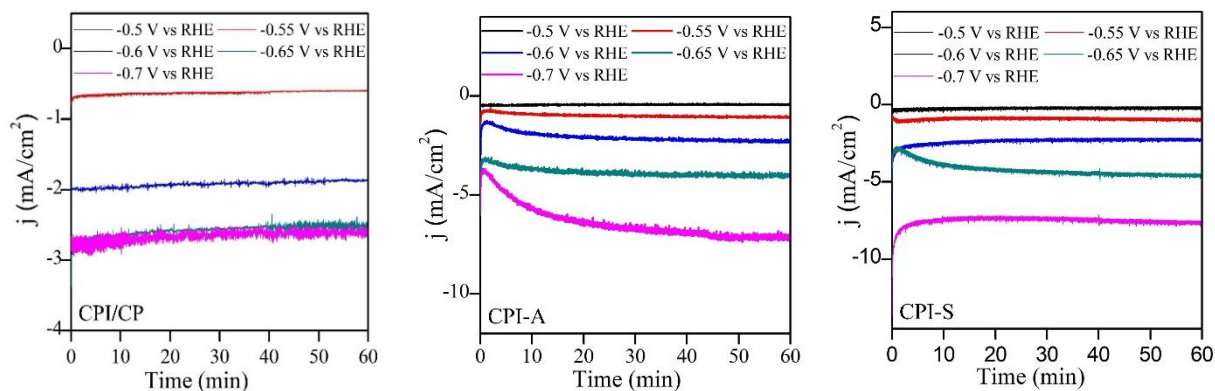


Figure 4. Potentialstatic tests at various potentials

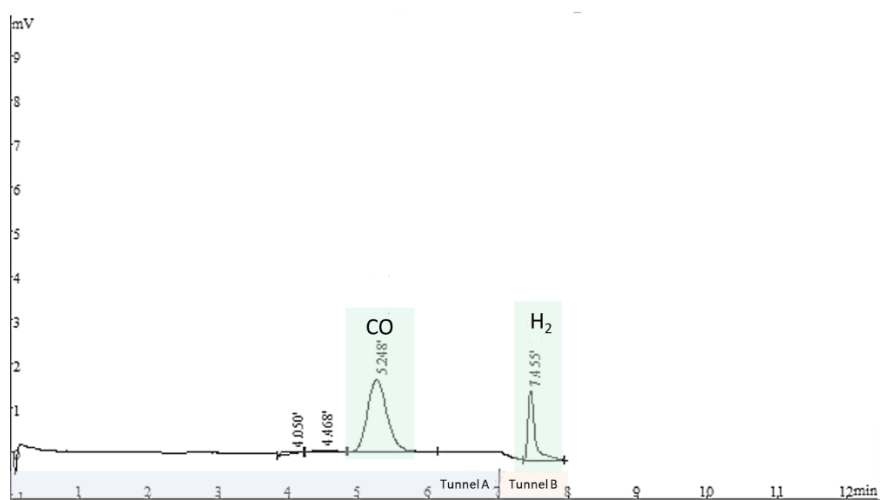


Figure 5. Example of GC detection results

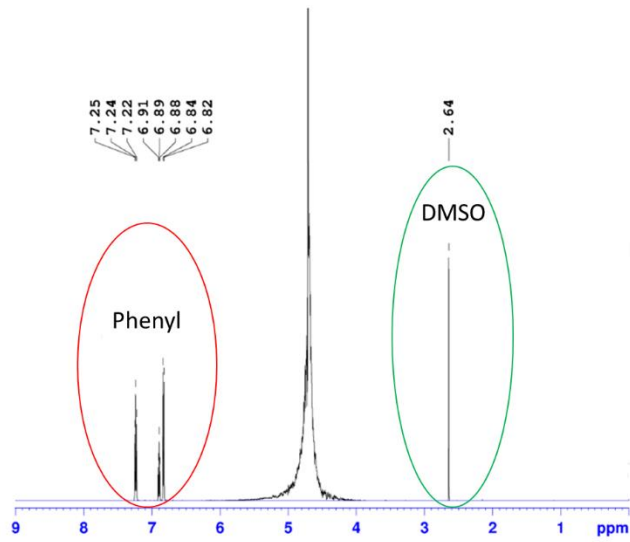


Figure 6.  $^1\text{H}$  NMR using WEFT technique

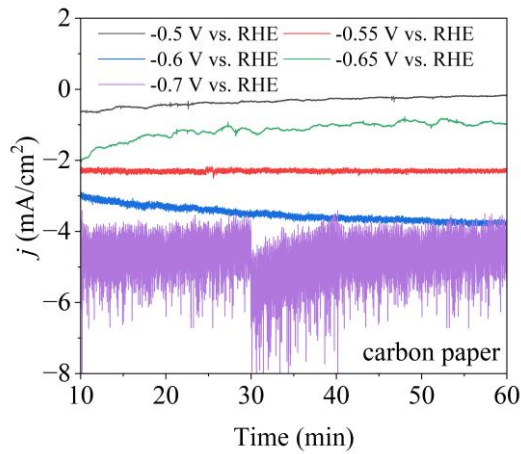


Figure 7. Electrolysis at various potentials with carbon paper as the counter electrode

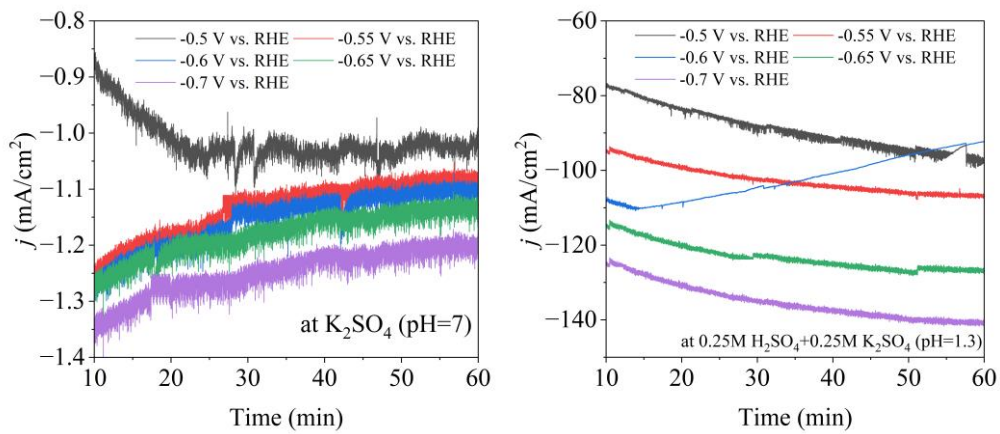


Figure 8. Electrolysis at various potentials under neutral and acidic media

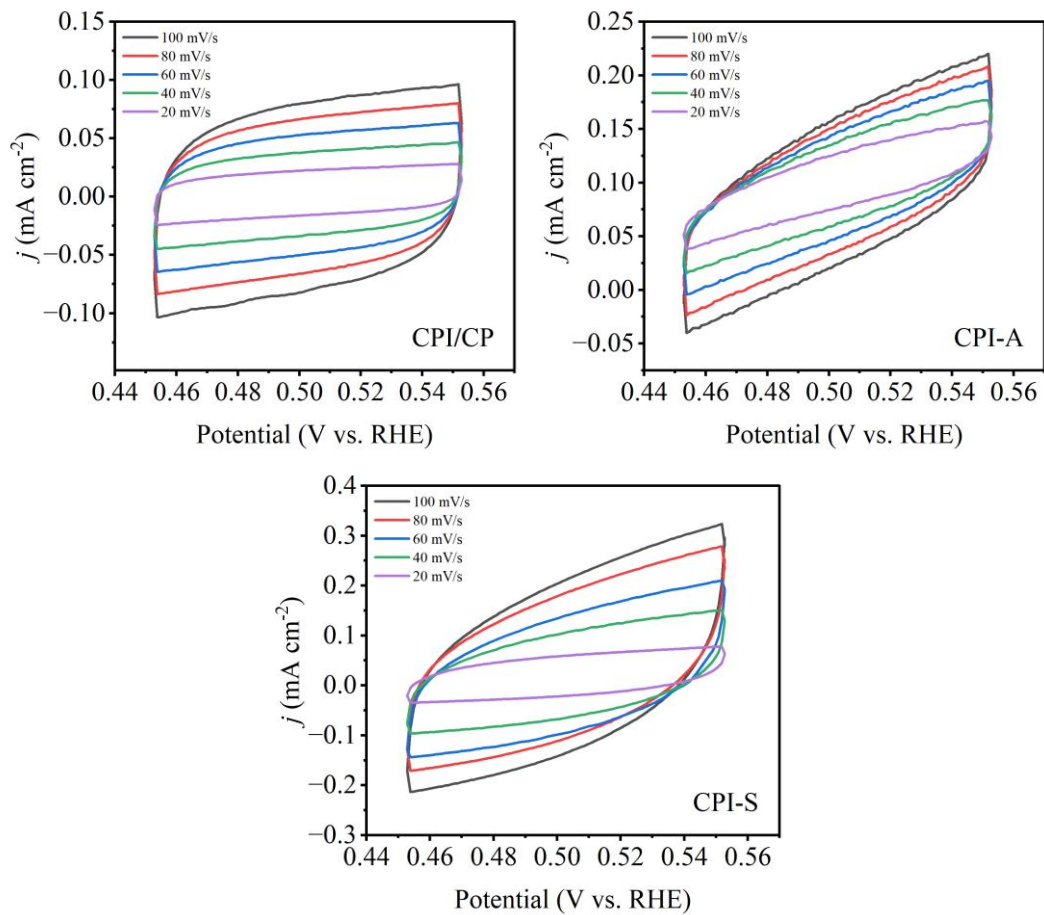


Figure 9. CV spectra of CPI/CP, CPI-A, and CPI-S in non-Faradaic region with different scan rates.

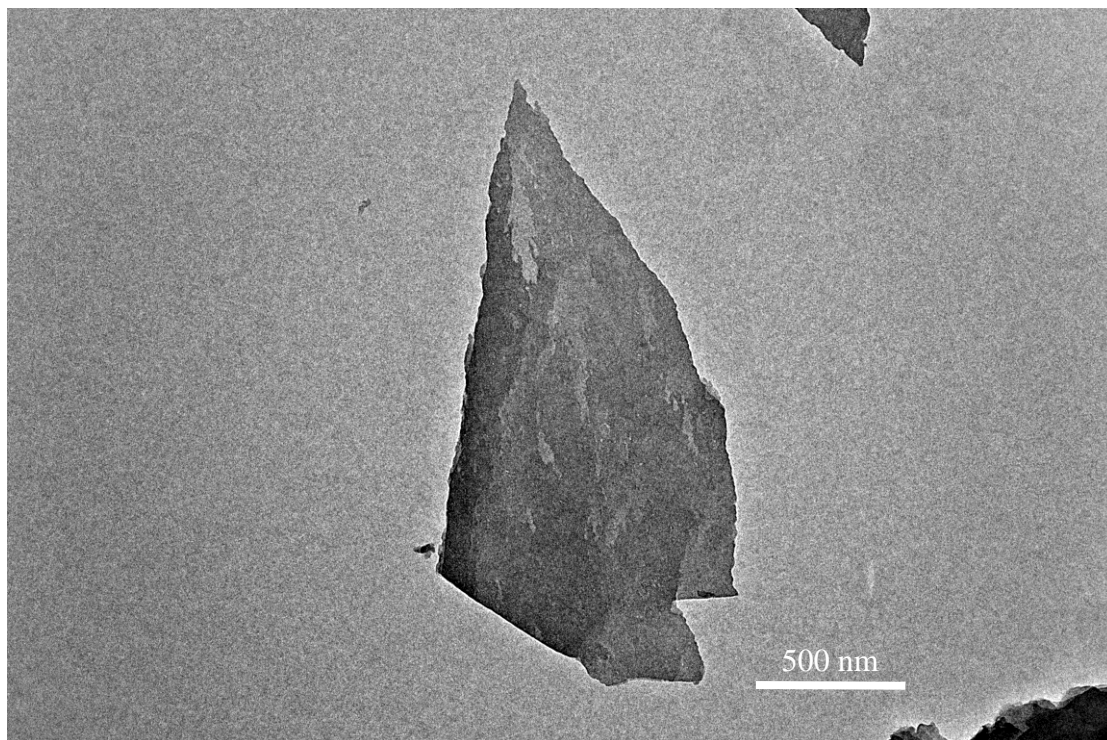


Figure 10. TEM image of CPI nanosheets exfoliated from CPI/CP after long-term electrocatalysis.

## Supplementary Tables

Table 1. The comparison of catalytic performance among reported electrocatalysts for the conversion of CO<sub>2</sub> to CO.

Catalyst	Electrolyte	E (V vs. RHE)	FE <sub>CO</sub> (%)	CO current density (mA cm <sup>-2</sup> )	Reference
NCNTs-1	KHCO <sub>3</sub>	-0.78	80	0.7	<i>Angew. Chem. Int. Ed.</i> <b>2015</b> , 54 (46), 13701-5
NG	KHCO <sub>3</sub>	-0.5	85	0.8	<i>ACS Nano</i> <b>2015</b> , 9 (5), 5364-5371
C <sub>3</sub> N <sub>4</sub> /MWCNT	KHCO <sub>3</sub>	-0.75	60	0.5	<i>Chemistry</i> <b>2016</b> , 22 (34), 11991-6
CPSN	NaHCO <sub>3</sub>	-1.0	11	1.2	<i>ChemSusChem</i> <b>2016</b> , 9 (10), 1085-9
NCNTS	KHCO <sub>3</sub>	-1.1	78	3.9	<i>ChemSusChem</i> <b>2016</b> , 9 (6), 606-16
NCNTs-2	NaHCO <sub>3</sub>	-0.9	85	5.3	<i>Electrochim. Acta</i> <b>2017</b> , 245, 561-568
MPC-1000	KHCO <sub>3</sub>	-0.71	62	3.1	<i>J. Mater. Chem. A</i> <b>2017</b> , 5 (25), 13104-13111
NRMC-900-3	KHCO <sub>3</sub>	-0.6	82	2.9	<i>ACS Energy Lett.</i> <b>2018</b> , 3 (9), 2292
FC	NaClO <sub>4</sub>	-0.6	89.6	0.249	<i>Angew. Chem. Int. Ed.</i> <b>2018</b> , 57 (31), 9640-9644
N,F-C	KHCO <sub>3</sub>	-0.6	90	1.9	<i>ACS Catal.</i> <b>2019</b> , 9 (3), 2124-2133
N,S-CN	KHCO <sub>3</sub>	-0.55	93.4	5.91	<i>ChemSusChem</i> <b>2020</b> , 13 (3), 539-547
PNC	KHCO <sub>3</sub>	-0.6	74	0.71	<i>Ind. Eng. Chem. Res.</i> <b>2021</b> , 60, 7739
BPNC	KHCO <sub>3</sub>	-0.5	81.8	0.37	<i>Renewable Energy</i> <b>2021</b> , 177, 636-642
NBMC-1000	KHCO <sub>3</sub>	-0.55	95	2.7	<i>Appl. Catal. B Environ.</i> <b>2021</b> , 298, 120543
NPC-1000	KHCO <sub>3</sub>	-1.2 (vs. Ag/AgCl)	70.1	0.55	<i>J. CO<sub>2</sub> Util.</i> <b>2022</b> , 58, 101908
N-CNTs/N-rGO	KHCO <sub>3</sub>	-0.60	100	3	<i>ACS Appl. Mater. Inter.</i> <b>2023</b> , 15, 31, 37593
CPI/CP	KHCO <sub>3</sub>	-0.65	90.7	1.9	<b>This work</b>



## Reference

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