Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Informations

Assembly of Highly Overall CO_2+H_2O Cell with the Matchup of CO_2 Reduction and Water Oxidation Catalyst

Zhang Li, Hong-Lin Zhu, Zhong-Yi Li, Yue-Qing Zheng*

Research Center of Applied Solid State Chemisty, Chemistry Institute for Synthesis and Green Application, Ningbo University, Ningbo, 315211, P. R. China

*Corresponding author: Yue-Qing Zheng

E-mail address: zhengyueqing@nbu.edu.cn

Tel/fax: +86 574 87600747

1.1 Characterization

The Powder X-ray diffraction was carried out with a Bruker D_8 Focus X-ray diffractometer with Cu-Kα radiation (λ = 1.54178 Å). The C, H and N microanalyses were performed with a Perkin Elmer 2400II elemental analyzer. Thermogravimetric measurements were carried out from room temperature to 800°C on preweighed samples using a Seiko Exstar 6000 TG/DTA 6300 apparatus with a heating rate of 10°C/min. The X-ray photoelectron spectroscopy (XPS) was obtained on Escalab 250Xi instrument with a monochromatic Al Kα X-ray radiation source. The content of metal ions was determined by inductively coupled plasma optical emission spectrometer (ICAP 7200 ICP-OES). Scanning Electron Microscope (SEM) analysis was performed by using a Hitachi"s new SU-70 type of thermal field emission instruments. The low and high resolution transmission electron microscopy (TEM) and the corresponding energy dispersive spectroscope mapping analyses were performed on JME-2100. The liquid products were performed by Bruker 400 HZ NMR spectroscopy with TMS as an internal standard. The content of CO was analyzed by gas chromatograph (GC-2060) with flame ionization detector (FID).

1.2 Evaluation of electrochemical activity of OER

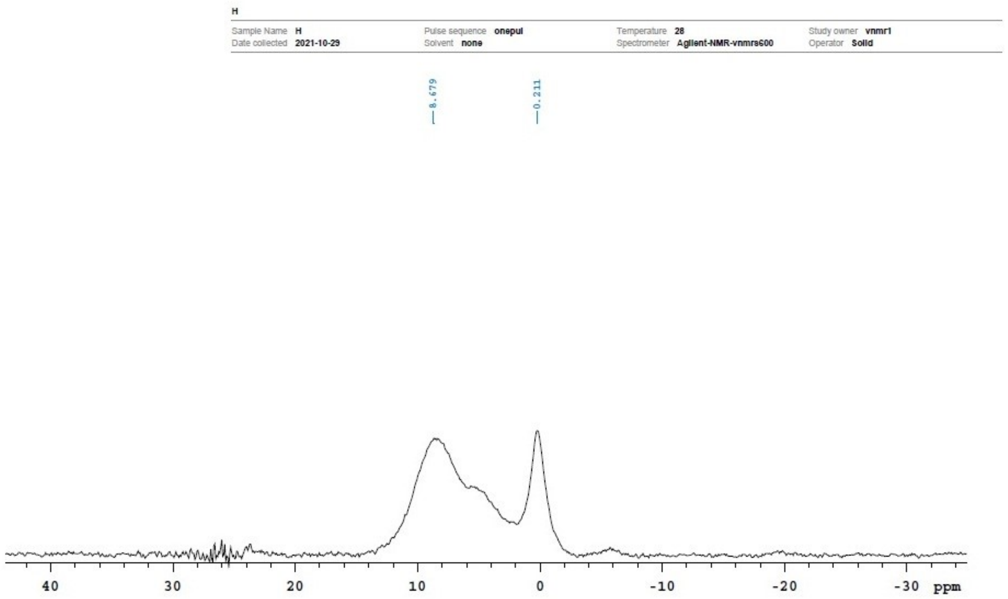
The working electrode was prepared by dispersing 2.5 mg of γ-$NiOOH/NiCO_3/Ni(HCOO)_2$ catalyst into a mixture of 60 μL Nafion solution, 300 μL isopropyl alcohol and 200 μL deionized water with 30 min of sonication. 58 μL well dispersed catalyst ink was drop casted onto the carbon cloth of 1.0 cm^2 in geometric area. All electrochemical measurements were performed in an electrochemical workstation (CHI 760E, Shanghai) with a three-electrode system. The as-synthesized γ-$NiOOH/NiCO_3/Ni(HCOO)_2$ electrode as working electrode (1 cm×1 cm), the Pt wire electrode as counter electrode and an Ag/AgCl electrode (saturated KCl) was used as reference electrode. All electrochemical tests were performed in 1 M KOH electrolyte and carried out at 298K temperature. All electrode potential were transformed to the reversible hydrogen electrode (RHE), the equation: E (RHE) = E (Ag/AgCl) + 0.197 V+0.0591*pH, and the overpotential (η) was derived from the formula: $\eta = E_{RHE}-1.23$ V.

1.3 Evaluation of electrochemical reduction CO_2

The working electrode was prepared by dispersing 5.0 mg CoPc/Fe-N-C in a mixture of 100 μL Nafion solution, 600 μL isopropyl alcohol and 400 μL deionized water with 30 min of sonication. 35 μL well dispersed catalyst ink was drop casted onto the carbon cloth. The electrochemical measurements were carried out with three-electrode system in 0.5 M KHCO3 solution on CHI 760E electrochemical workstation (ChenHua, Shanghai). The as-synthesized CoPc/Fe-N-C electrode was used as the working electrode, Pt foil and Ag/AgCl electrode was denoted as counter electrode and reference electrode, respectively. All the measured potentials vs. Ag/AgCl were converted to reversible hydrogen electrode (RHE): E_{RHE} = EAg/AgCl+ 0.059 × pH + 0.197 V. The value of Faradaic efficiency (FE) was calculated according to the formula: FE = 2F × n_{CO} / Q = 2F ×n_{CO} / (I × t), where F is 96485 C/mol and n_{CO} is the molar mass of CO. The TOF value of the electrocatalyst via mass loading was calculated as follows: TOF(S-1) = $\frac{I \cdot FE/2F}{m \cdot \omega/M_r}$, where I is the current, m is the catalyst mass in the electrode, ω is the Co loading in the catalyst, Mr is the atomic mass of Co with 58.9 g mol-1. The value of TOF was also carried out by electrochemical surface area (ECSA) normalization with EDLC value of graphene. The ECSA was calculated by the electrochemical double-layer capacitance (Cdl) with the cyclic voltammetry (CV) curves in non-Faradaic potential region.

1.4 Evaluation of overall CO_2+H_2O coupling electrocatalysis

The overall CO_2+H_2O electrocatalysis was performed on a H-cell electrolyzer with a Nafion117 membrane to separate the cathode and anode. The anode was heterostructured γ-$NiOOH/NiCO_3/Ni(HCOO)_2$ nanosheet in the media of 1 M KOH electrolyte, and CoPc/Fe-N-C was used as cathode in 0.5 M $KHCO_3$ electrolyte.



H

Sample Name H
Date collected 2021-10-29
Pulse sequence onepul
Solvent none
Temperature 28
Spectrometer Agilent-NMR-vnmrs600
Study owner vnmr1
Operator Solid

Figure S1 The solid state ^{1}H NMR of γ-NiOOH/NiCO$_3$/Ni(HCOO)$_2$.

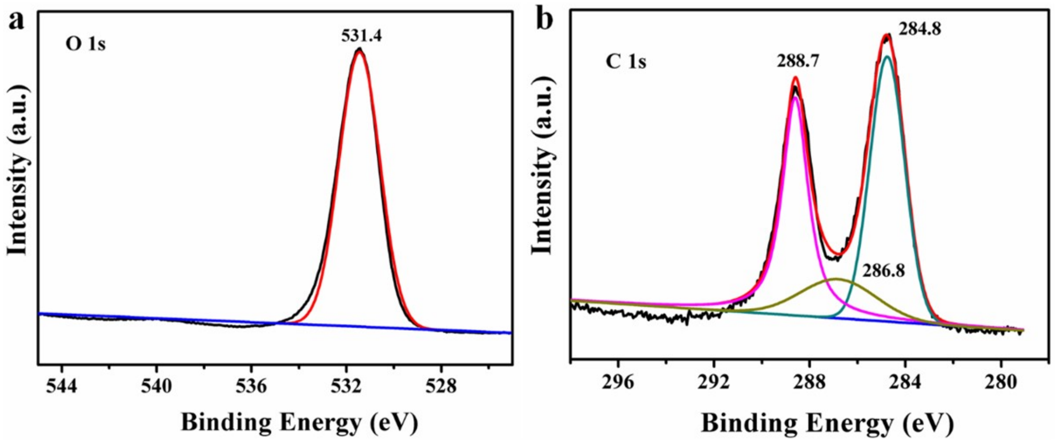


Figure S2 XPS spectra of the O 1s and C 1s for γ-NiOOH/NiCO$_3$/Ni(HCOO)$_2$.

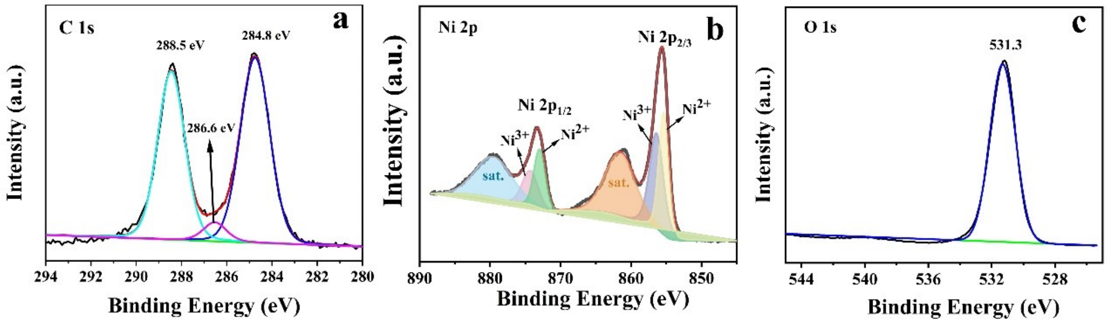


Figure S3 XPS spectra of the C 1s (a), O 1s(b), and Ni 2p (c) for γ-

NiOOH/$NiCO_3$/$Ni(HCOO)_2$ at the end of the electrochemical tests.

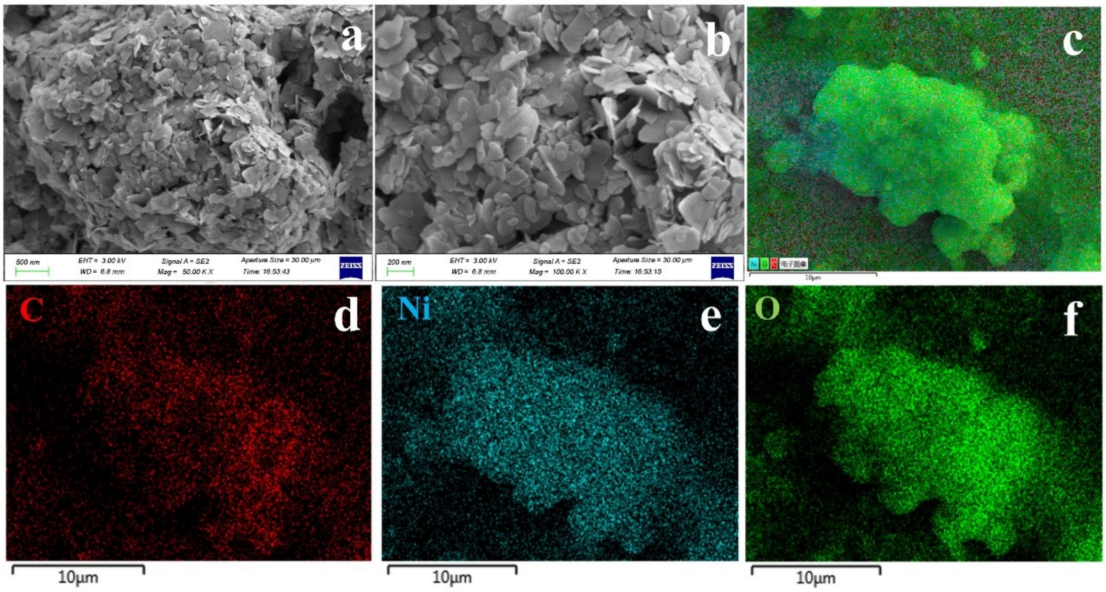


Figure S4 (a, b) SEM spectra and Corresponding C (d), Ni (e), and O (f) elemental mapping of γ-NiOOH/$NiCO_3$/$Ni(HCOO)_2$ at the end of the electrochemical tests.

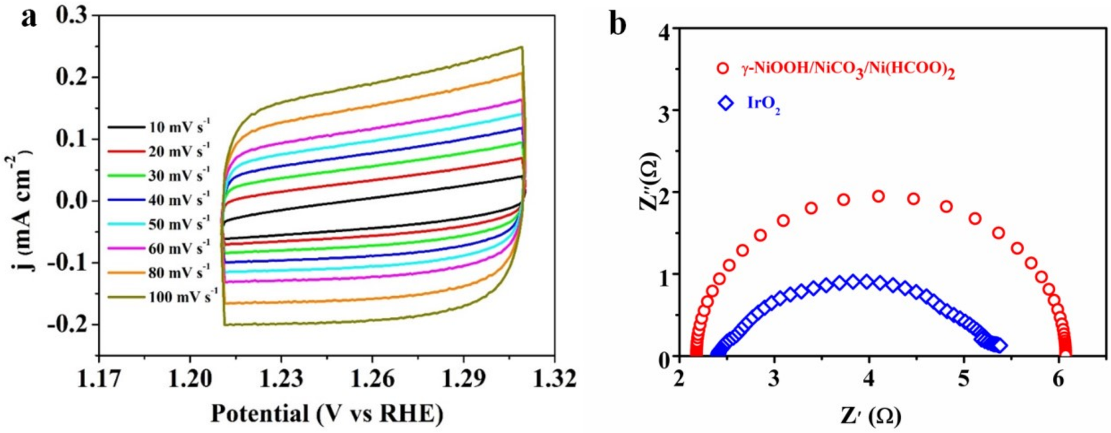


Figure S5 (a) CV curves of γ-NiOOH/$NiCO_3$/$Ni(HCOO)_2$ with different scan rate. (b) Nyquist plots of γ-NiOOH/$NiCO_3$/$Ni(HCOO)_2$ and IrO_2.

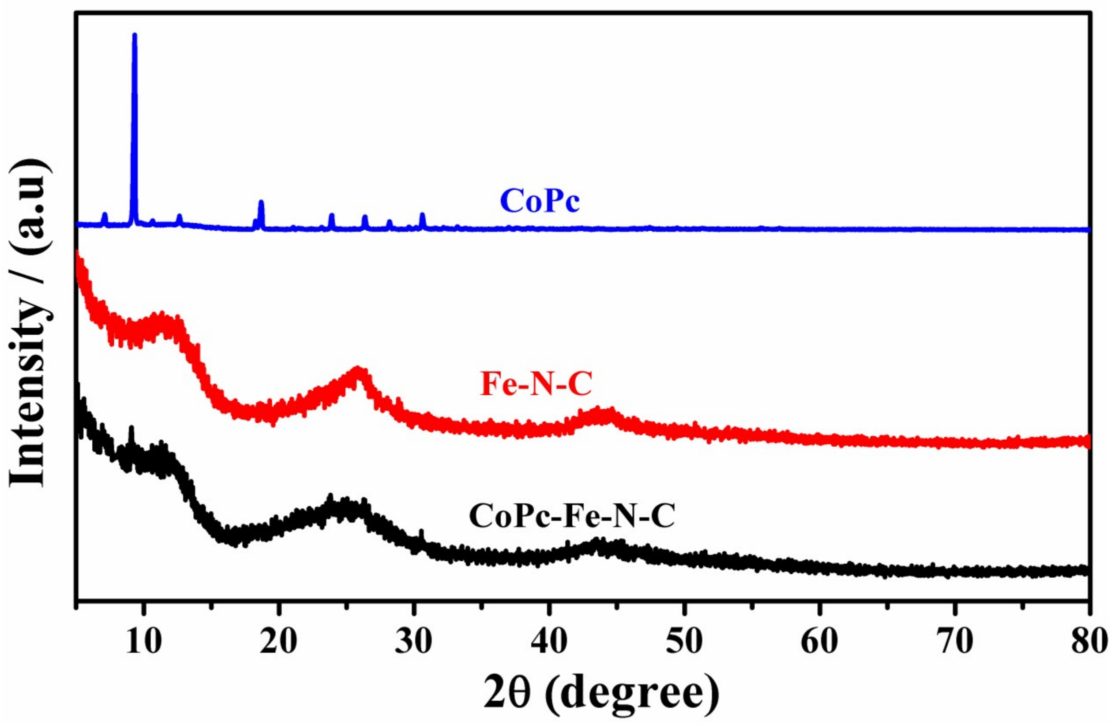


Figure S6 XRD patterns of CoPc/Fe-N-C.

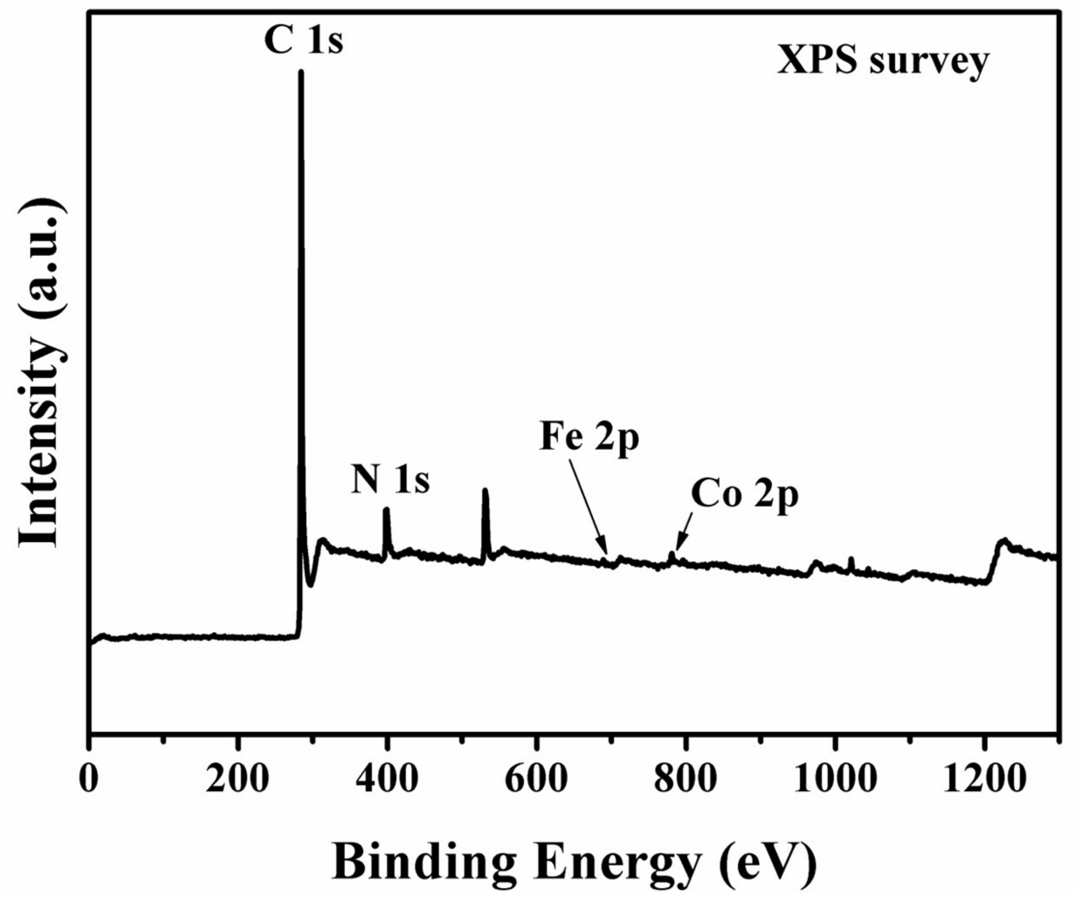


Figure S7 XPS spectra of CoPc/Fe-N-C.

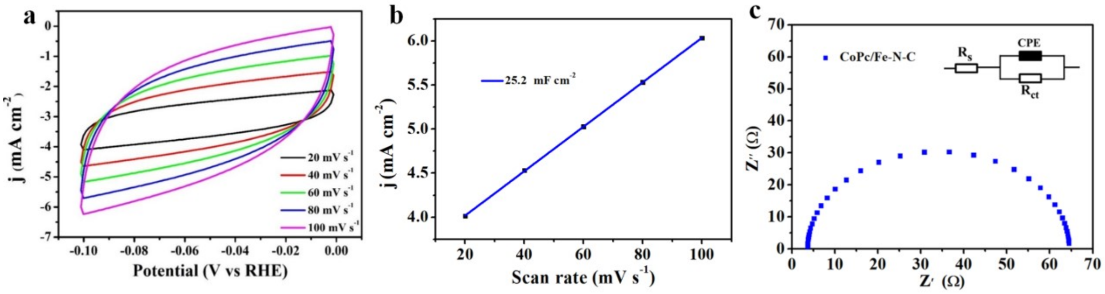


Figure S8 (a) CVs plots in the non-faradaic potential of CoPc/Fe-N-C. (b) Current densities against the scan rates of CoPc/Fe-N-C. (c) Nyquist plot of CoPc/Fe-N-C.

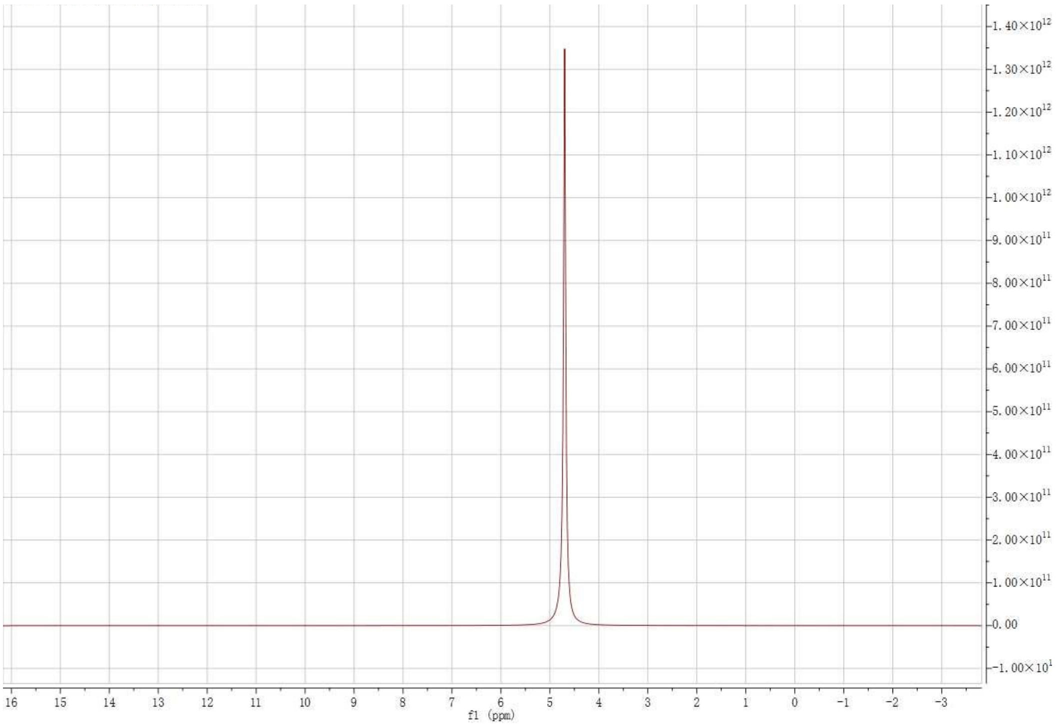


Figure S9 ^{1}H NMR spectrum of electrolysis liquid product for CoPc/Fe-N-C.

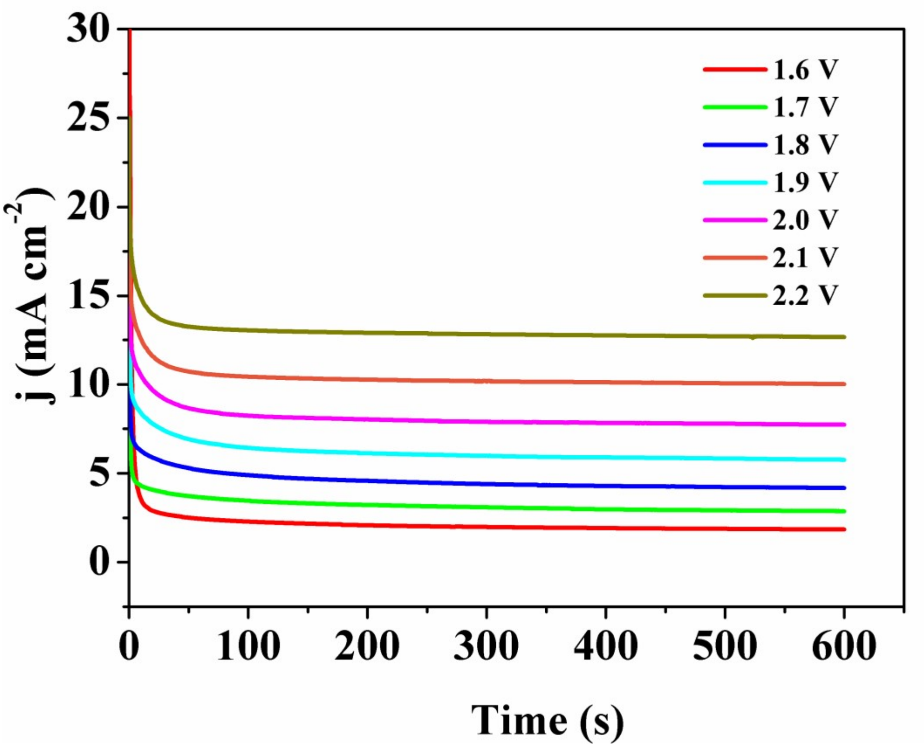


Figure S10 Current densities of overall cell at various potentials.

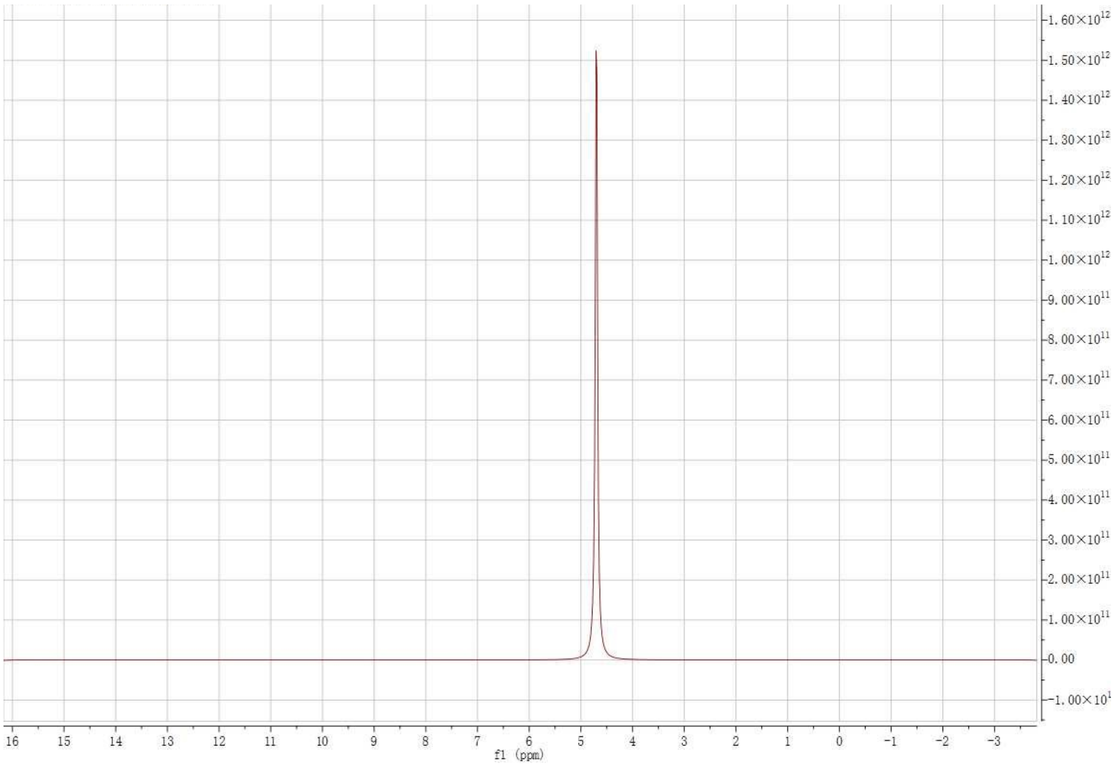


Figure S11 ^{1}H NMR spectrum of electrolysis liquid product for overall CO_2+H_2O reaction.