

Supporting Information

Efficient electrocatalytic reduction of CO₂ to CO enhanced by synergistic effect of N, P on carbon aerogel

Yifan Yan,^a Hongzhi Wang,^{*b} Xinze Bi,^a Yuezhu Zhao^a and Mingbo Wu^{*a}

^aCollege of New Energy, State Key Laboratory of Heavy Oil Processing, China University of Petroleum (East China), Qingdao 266580, China.

^bCollege of Chemistry and Chemical Engineering, Ocean University of China, Qingdao, 266100, China

E-mail: Hongzhi Wang(wanghz@ouc.edu.cn), Mingbo Wu(wumb@upc.edu.cn)

Experimental section

Synthesis.

Synthesis of carbon aerogel (CA): In a typical preparation for CA, 2 g starch was dispersed in 10 mL deionized water under vigorous stirring at room temperature. Then, 40 mL deionized water was heated to 100 °C. The starch solution was poured into heated deionized water under vigorous stirring for 5 min. Finally, the above solution was transferred into a petri dish and cooled at room temperature to obtain hydrogel. The hydrogel was freeze-dried in a vacuum to obtain xerogel. The obtained xerogel was carbonized under N₂ atmosphere at 900 °C for 2 h (at a carbonization heating rate of 20 °C min⁻¹), CA was yield.

Synthesis of N-doped carbon aerogel (NCA), P-doped carbon aerogel (PCA) and N, P-co-doped carbon aerogel (NPCA): The method of preparing NCA was the same as the above method of preparing CA, except that 0.5 g urea was added to the initial 40 mL deionized water. The PCA was prepared by the same method except that 1 g phytic acid solution was added to the initial 40 mL deionized water. The NPCA was prepared by adding 0.5 g urea and 1 g phytic acid solution to 40 mL deionized water.

Synthesis of N³P¹CA, N⁵P¹CA, N¹P³CA, and N¹P⁵CA: The methods of preparing N³P¹CA and N⁵P¹CA were the same as the above method of preparing NPCA, except that change the amount of urea to 1.8 g and 3 g, respectively. The preparation methods of N¹P³CA and N¹P⁵CA were the same as above, but the amount of phytic acid added was different, which was 2.55 g and 4.26 g respectively.

Characterizations.

The surface morphologies of the catalysts were observed by scanning electron microscopy (SEM, Hitachi S-4800, Japan). X-ray diffraction (X 'Pert PRO MPD, Holland) was used to characterize the crystal structures of the samples. Raman spectra of all catalysts were determined by LabRAM HR Evolution Raman spectrometer (Renishaw RM2000, Britain) with 532 nm laser. The elemental composition of different catalysts was analyzed by X-ray photoelectron spectrometer (XPS, Escalab 250Xi, UK). All spectra were collected under ambient conditions.

Electrochemical Measurements.

All electrochemical measurements were performed on an electrochemical workstation (CHI 760E, CH Instrument, China) using a three-electrode system. The only difference is that the detection of hydrogen evolution reaction (HER) was performed with 1 M Na₂SO₄ electrolyte in a single cell, while the rest of the measurements, including linear sweep voltammetry (LSV), performance test, Tafel

plots, electrochemical impedance spectroscopy (EIS), cyclic voltammograms (CV) were all performed with 0.5 M KHCO₃ (PH=7.4) as the electrolyte in the H cell. The cathode and anode chambers were separated by a proton exchange membrane (Nafion 117) with 30 mL of electrolyte on each side. The Ag/AgCl saturated with KCl solution and Pt net were used as reference electrode and counter electrode respectively, and the prepared aerogels could be directly used as working electrode by cutting them to the desired shape and size and clamping them with electrode clamp. Before the electrocatalytic CO₂ reduction began, CO₂ was first passed into the electrolyte at least 30 min to saturate the solution. Then the potential was changed to measure and the gas and liquid products were analyzed. The gas phase products were analyzed by on-line gas chromatography (BFR-3420A, China), and the liquid phase products were analyzed by liquid chromatography (LC-2030 Plus, SHIMADZU, Japan).

The following formula was used to convert the potential used in the experiment into a reversible hydrogen electrode (RHE).

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.0591 \times \text{pH} + E^0_{\text{Ag/AgCl}}$$

Where E_{RHE} is the conversion potential; $E_{\text{Ag/AgCl}}$ is the actual measured potential; $E^0_{\text{Ag/AgCl}}$ is 0.197 V, which is the standard electrode potential of Ag/AgCl electrode; the pH is 7.4 in this experiment.

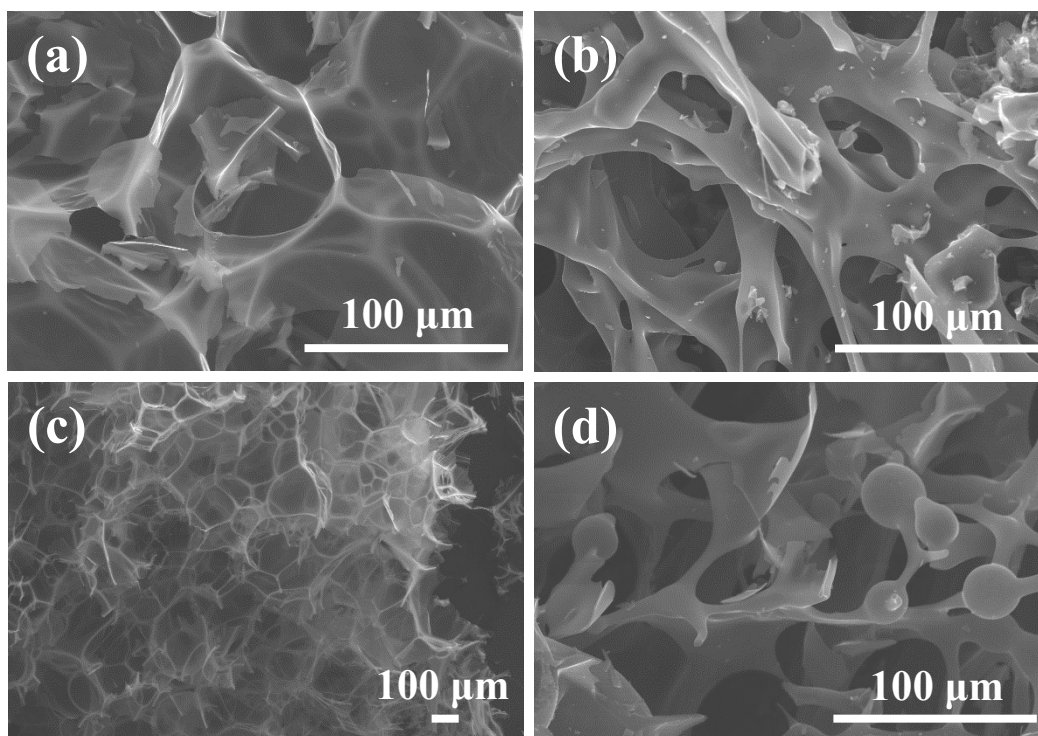


Fig. S1 The SEM images of CA (a), NCA (b), PCA (c), and NPCA (d).

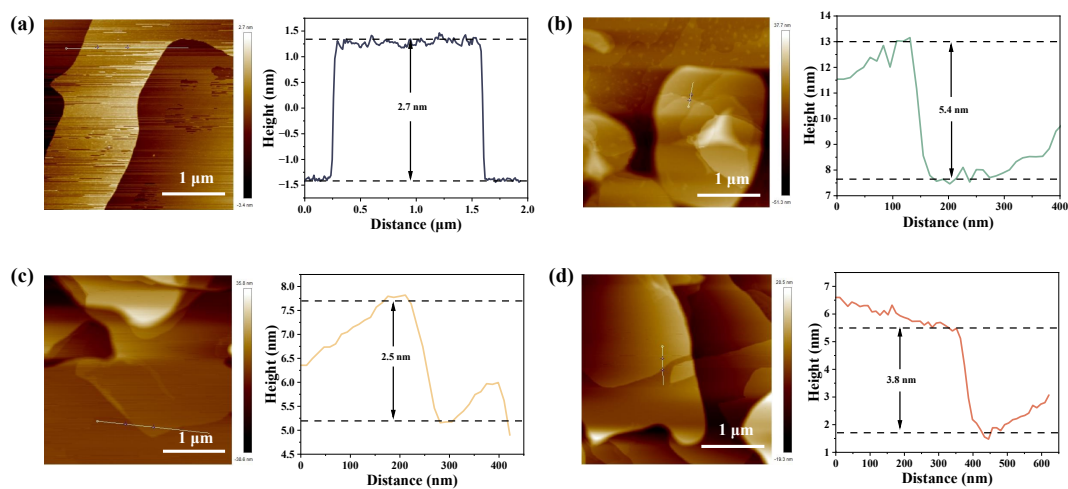


Fig. S2 The AFM images of (a) CA, (b) NCA, (c) PCA and (d) NPCA.

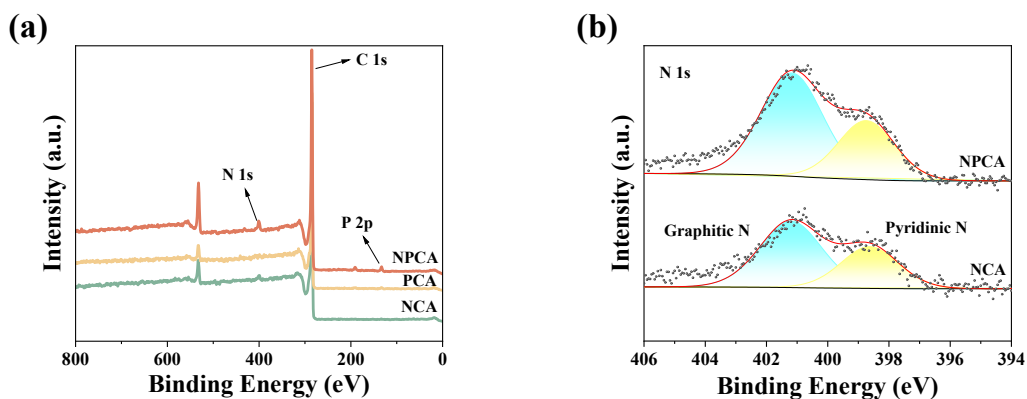


Fig. S3 (a) The total XPS curves for NCA, PCA, and NPCA. (b) N 1s XPS spectra of NCA and NPCA samples.

The total XPS curves of NCA, PCA, and NPCA exhibit that there are N and P elements in NPCA, while there is no P element in NCA and no N element in PCA (**Fig. S3a**). The N 1s spectra of both NCA and NPCA display two components of N, including pyridinic N (398.7 eV) and graphitic N (401.2 eV) (**Fig. S3b**).

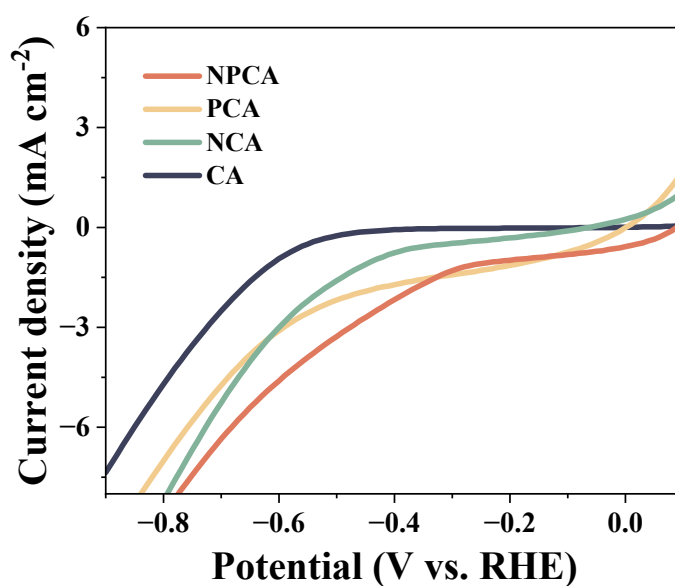


Fig. S4 LSV curves of different catalysts in an H-cell with the CO₂-saturated 0.5 M KHCO₃ solution.

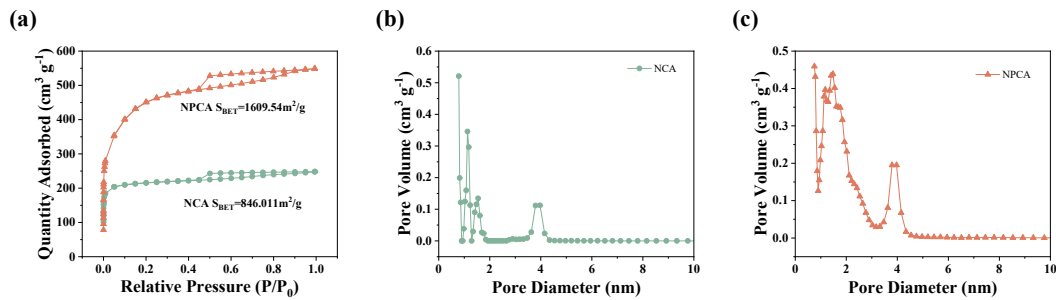


Fig. S5 (a) Nitrogen adsorption-desorption isotherms of NCA and NPCA. Porous size distribution of NCA (b) and NPCA (c).

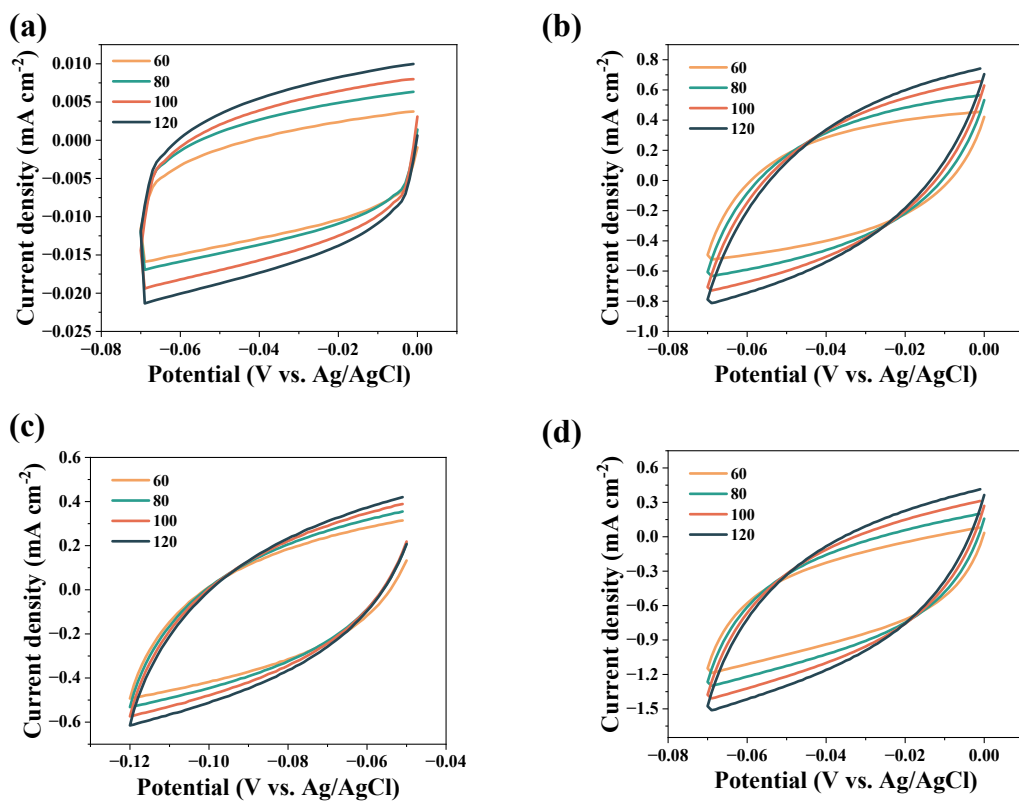


Fig. S6 Cyclic voltammograms of (a) CA, (b) NCA, (c) PCA, and (d) NPCA catalysts at different sweep rates.

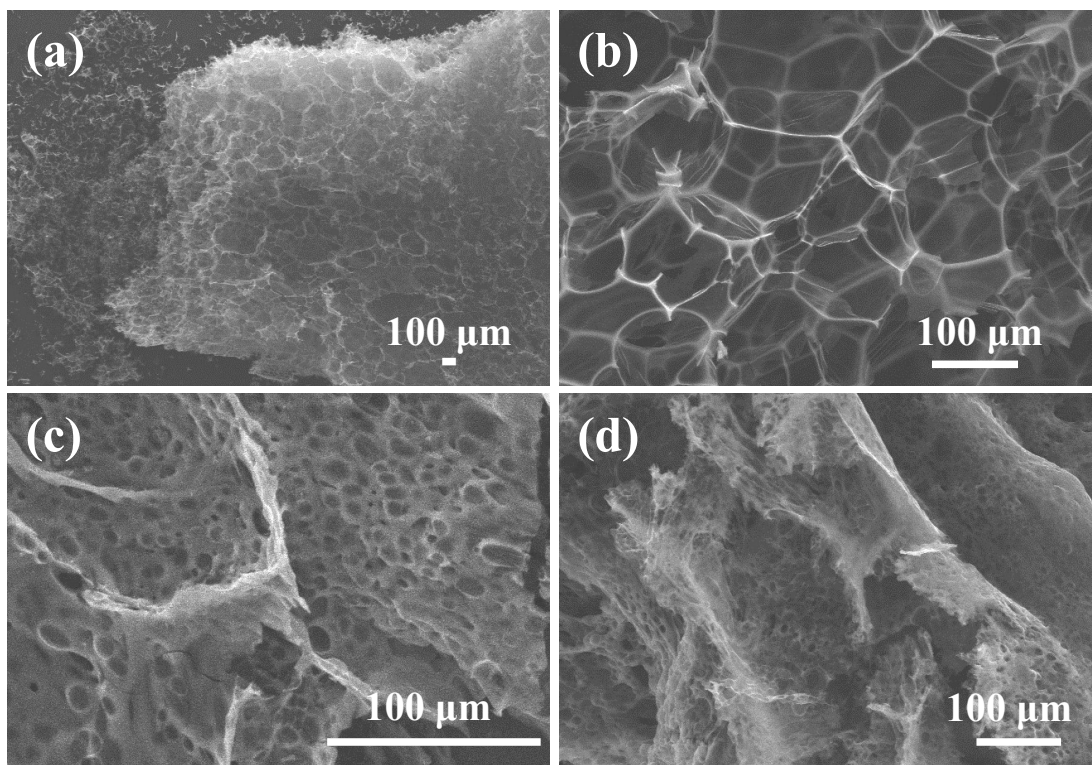


Fig. S7 The SEM images of N¹P⁵CA (a), N¹P³CA (b), N³P¹CA (c), and N⁵P¹CA (d).

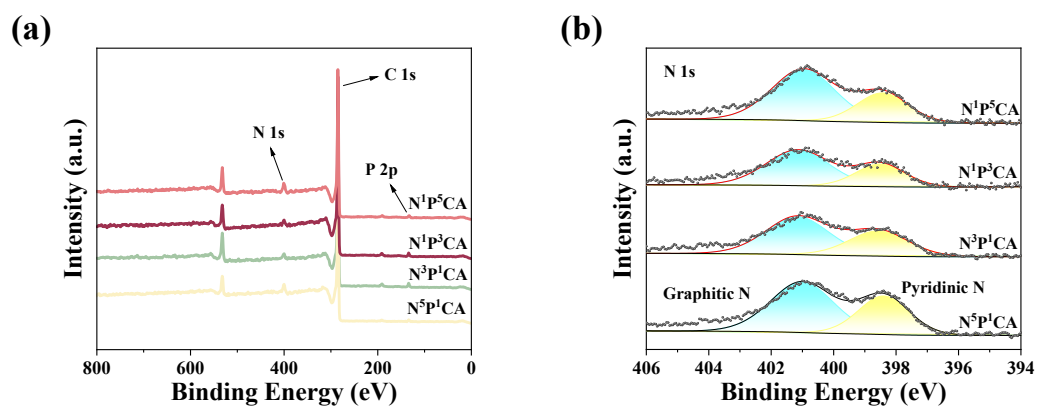


Fig. S8 (a) The total XPS curves for N¹P⁵CA, N¹P³CA, N³P¹CA, and N⁵P¹CA. N 1s

(b) XPS spectra of samples with different N, P doping amounts.

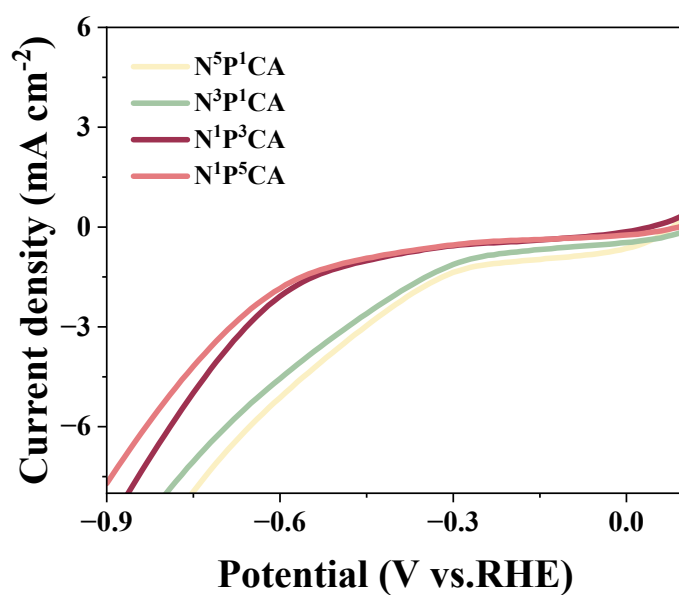


Fig. S9 LSV curves of N¹P⁵CA, N¹P³CA, N³P¹CA, and N⁵P¹CA in 0.5 M KHCO₃ solution.

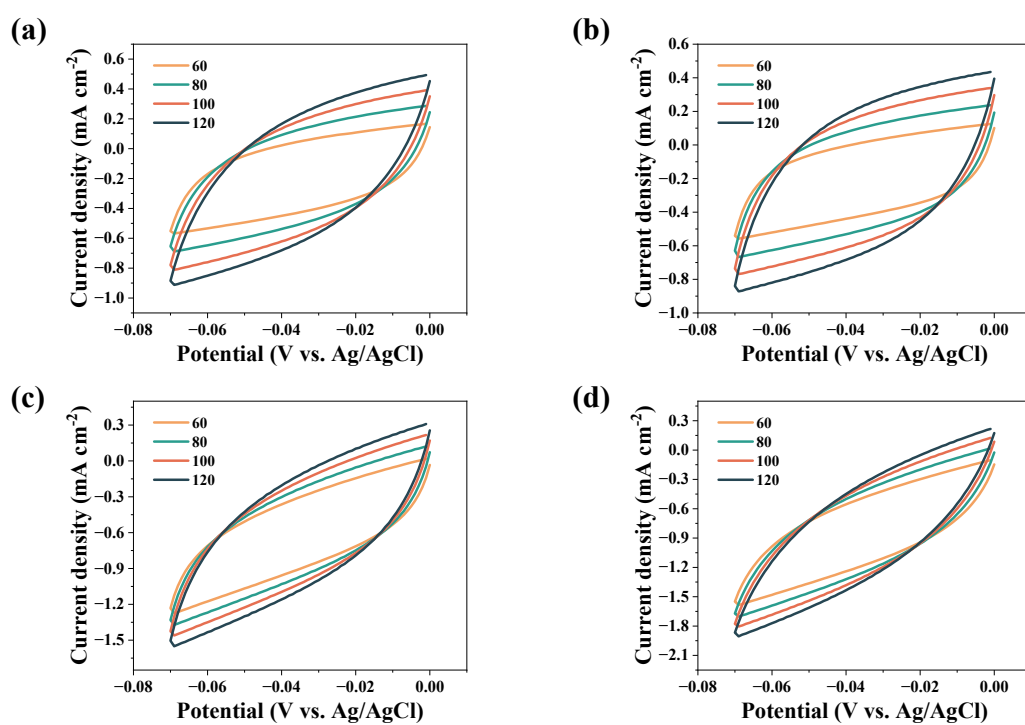


Fig. S10 Cyclic voltammograms of N¹P⁵CA (a), N¹P³CA (b), N³P¹CA (c), and N⁵P¹CA (d) catalysts at different sweep rates.

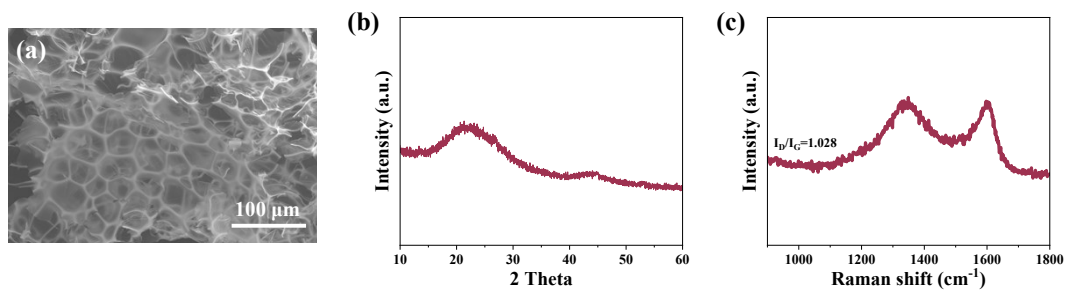


Fig. S11 (a)SEM image, (b) XRD pattern and (c) Raman spectrum of $\text{N}^1\text{P}^3\text{CA}$ after 35h CO_2ER at -1.2 V.