Supporting Information


Selective Etching of Nitrogen-Doped Carbon by Steam for Enhanced Electrochemical CO₂ Reduction

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Methods

Synthesis of N-doped carbon nanotube (CN-CNT): Synthesis of CN-CNT referred to our previous work \cite{1}. CNT films were tailored and transferred to a silicon wafer-made substrate with two ends fixed. Then samples were transferred into tube furnace to go through a chemical vapor deposition (CVD) process. The temperature was raised to 1060°C with Ar (110 sccm) and H₂ (10 sccm) were used as carrying and protecting gas, respectively. When the temperature stablized, the growing of N-doped graphene layers got started by introducing another Ar (40 sccm) through acetonitrile solution. After 5 minutes of re-growth, Ar (40 sccm) through acetonitrile solution was stopped and CN-CNT was prepared when the tube furnace cooled down.

Synthesis of steam-treated N-doped carbon nanotube (CN-H-CNT): After growing N-doped graphene layers for CN-CNT mentioned in the last step, Ar (40 sccm) through acetonitrile solution was stopped, while Ar (40 sccm) through deionized water was introduced, and steam treating would last for 2 minutes.

Synthesis of steam-treated carbon nanotube (H-CNT): CNT films were tailored and transferred to a silicon wafer-made substrate with two ends fixed. Then samples were transferred into tube furnace to go through a CVD process. The temperature was raised to
1060°C with Ar (110 sccm) and H₂ (10 sccm) were used as carrying and protecting gas, respectively. When the temperature stabilized, Ar (40 sccm) through deionized water was introduced. After 2 minutes of steam treating, Ar (40 sccm) through deionized water was stopped and HCNT was prepared when the furnace cooled down.

**XPS analysis:** The binding energies of the XPS spectra were calibrated based on the peak energy positions of standard samples, including Au 4f\(7/2\) (83.95 eV), Ag 3d\(5/2\) (368.26 eV) and Cu 2p\(3/2\) (932.65 eV), measured using Al-K\(\alpha\) X-rays. For C 1s, N 1s and O 1s narrow scans, the pass energy was set to 40 eV. The N 1s spectrum was fitted by combination of the peak components represented by the Gaussian-Lorentzian function after Shirley-type background subtraction. For CN-CNTs, the binding energies of pyridinic, pyrrolic, graphitic and oxidized N were fitted to 398.2, 400.5, 401.3, and 403.4 eV. For CN-H-CNTs, the binding energies of pyridinic, pyrrolic, graphitic and oxidized N were fitted to 398.1, 400.5, 401.6 and 404.6 eV, respectively. The full-width-at-half-maxima (FWHA) for pyridinic, pyrrolic and graphitic N used for fitting were fixed at 1.5 eV to achieve the best fitting results.

**Electrochemical measurements:** Electrochemical tests were carried out in a custom-made three electrode cell. The samples were cut into appropriate size and employed as cathode directly. A leak free Ag/AgCl electrode was used as a reference electrode and Pt wire as counter electrode. For CO₂ reduction experiments, cyclic voltammetry (CV) with a scan rate of 20 mV s\(^{-1}\) was carried out in CO₂-saturated 0.1 M KHCO₃ solution (pH of 6.8). All the electrochemical measurements were controlled by CHI660D electrochemical workstation (CH Instrument Inc., USA) at room temperature (25 ± 1 °C). The gas products were analyzed using Shanghai Ramiin GC 2060 gas chromatograph equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). \(^1\)H nuclear magnetic resonance (NMR) spectroscopy (Bruker AVANCEAV III HD 500) was used to quantify liquid products. 1 ml D₂O (deuterated water) was added into 5 ml electrolyte, then 0.5µl dimethyl sulfoxide (DMSO, Alfa Aesar, 99.99%) was added as an internal standard. Pre-saturation method was
used to suppress water peak. Tafel slopes were calculated from the corresponding linear sweep voltammetry plots derived from the total current density and faradaic efficiency of CO production. The electrochemically active surface area (ECSA) of the electrode was determined by measuring the double layer capacitance ($C_{dl}$), which is derived from the CVs (Scan rates were 5, 10, 20 40 and 80 mV·s$^{-1}$) measured at the range of 0.1 to 0.2 V vs. RHE (Figure S3). The $C_{dl}$ was estimated by plotting the $\Delta J (J_a - J_c)$ at 0.15V vs. RHE against the scan rates and the slop was twice $C_{dl}$ \cite{2}.  


Supporting Figures

Figure S1. Optical photo of CNT, H-CNT, CN-CNT and CN-H-CNT.

Figure S2. XPS spectra of (a) O 1s and (b) C 1s for CN-H-CNT and CN-CNT, respectively. After the steam treatment, a shoulder peak appeared at the high binding energy side (533.1 ± 0.3 eV) in the O 1s spectra, corresponding to C–O groups. For C 1s spectra, there were no obvious difference between CN-H-CNT and CN-CNT.
Figure S3. Cyclic voltammetry curves at different scan rates of (a) H-CNTs, (b) CN-CNTs and (c) CN-H-CNTs. (d) Charging current density differences ($\Delta J = J_a - J_c$) plot against scan rates to calculate $C_{dl}$, which was used to represent the ECSAs.

Figure S4. CV test of CN-H-CNT and CN-CNT in Ar-saturated 0.1M KHCO$_3$ electrolyte, 20 mV s$^{-1}$. 
**Figure S5.** Stability performance of CN-H-CNT for CO$_2$ reduction operated at potentiostatic mode of -0.5 vs. RHE.

**Figure S6.** (a) Stability performance of CN-CNTs for CO$_2$ reduction operated at potentiostatic mode of -0.5 vs. RHE for 28,000 s. (b) Stability of faradaic efficiency of CN - CNTs for CO$_2$ reduction at potentiostatic mode of -0.5 V vs. RHE for 28,000 s.
Figure S7. (a) XPS spectra and atomic distribution of CN-H-CNTs after 24,000 s of electrochemical test. (b) Summary of N atomic content. (c) Total atomic concentration in CN-H-CNTs after electrochemical test.
References

