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# 含氮金属有机框架衍生的铜基催化剂电催化还原二氧化碳

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# Cu-based Catalyst Derived from Nitrogen-containing Metal Organic Frameworks for Electroreduction of $CO_2$

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## NMR 产物标定

核磁共振氢谱($^1H$ NMR)在 600 MHz 下由 Agilent Technologies 的 DD2-600 液体超导核磁共振谱仪得到。取含有一定浓度的内标物(DMSO) 50 μL，100 μL $D_2O$ 加入到 400 μL 电解液溶液中制得核磁样。在 $^1H$ NMR 波谱测试中采用水峰压制。对峰面积进行积分，通过产物的 NMR 标线：产物与内标物的峰面积之比 $S_1 : S_2$ 与产物的浓度曲线可以计算出溶质产物的浓度。产物的 NMR 标线及其线性方程如下图 S1 和表 S1 所示。样品在电解质中的 $^1H$ NMR 波谱如图 S1 所示。

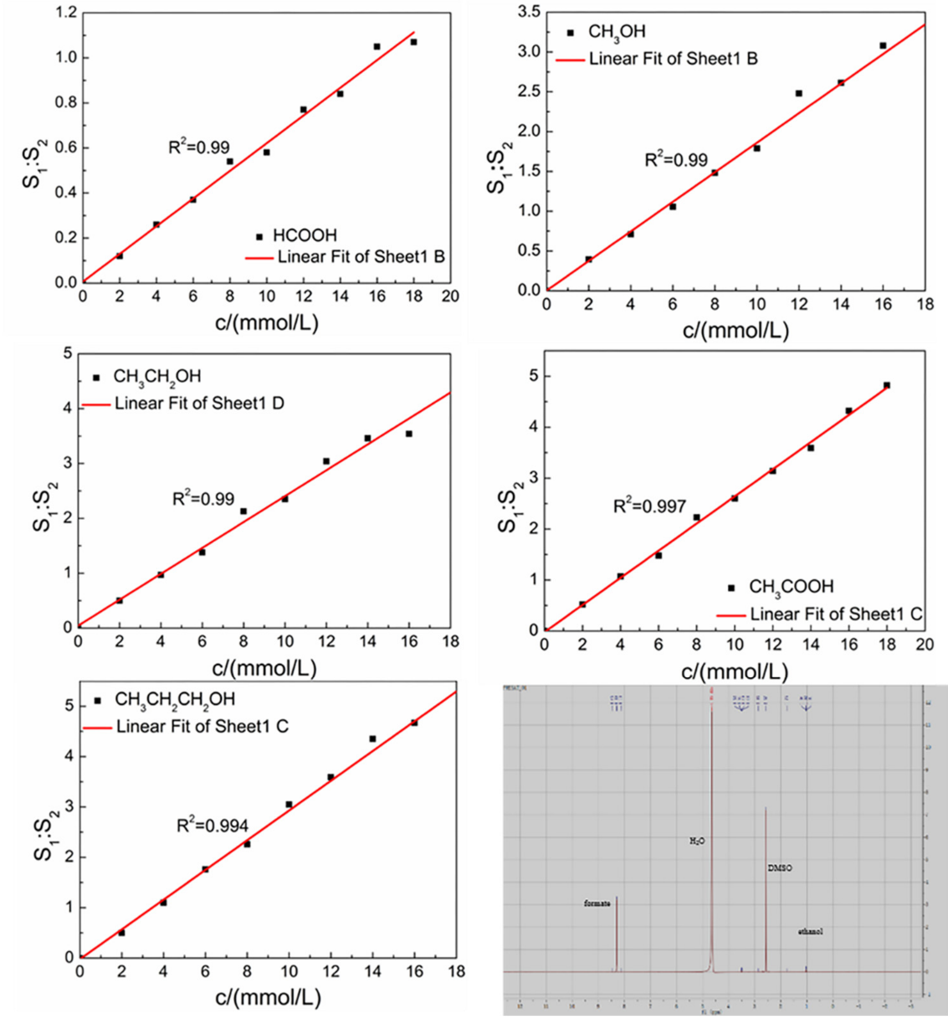


图 S1　各种产物的核磁标线及样品在电解液中的核磁共振氢谱

**Fig. S1　The NMR standard lines of each products and $^1H$ NMR spectrum of samples in electrolyte.**

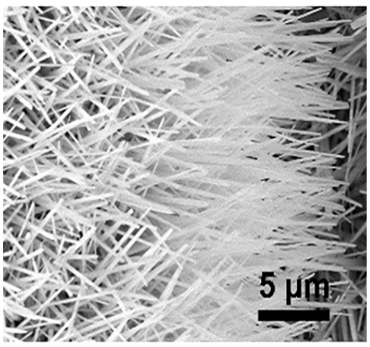


图 S2　$Cu(OH)_2$ NA/CF 的 SEM 图

**Fig. S2　SEM image of $Cu(OH)_2$ NA/CF.**

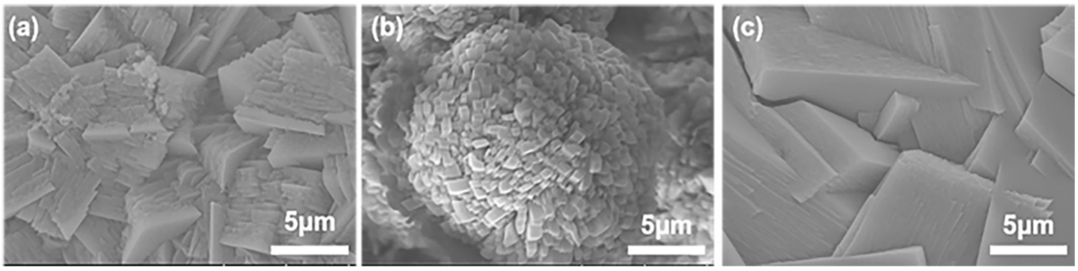


图 S3　三种溶剂反应 72 h 所得的 Cu-NBDC 的 SEM 图

**Fig. S3　SEM images of Cu-NBDC reacted for 72 h with three kinds of solvent.**

(a) 20 mL DMF; (b) 10 mL DMF, 10 mL $H_2O$ and (c) 10 mL DMF, 10 mL EtOH.

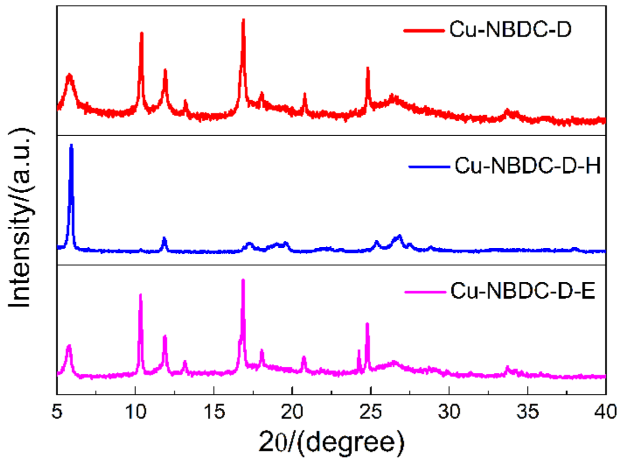


图 S4　三种 Cu-NBDC 粉末的 XRD 谱图

**Fig. S4　XRD patterns of three kinds of Cu-NBDC powders.**

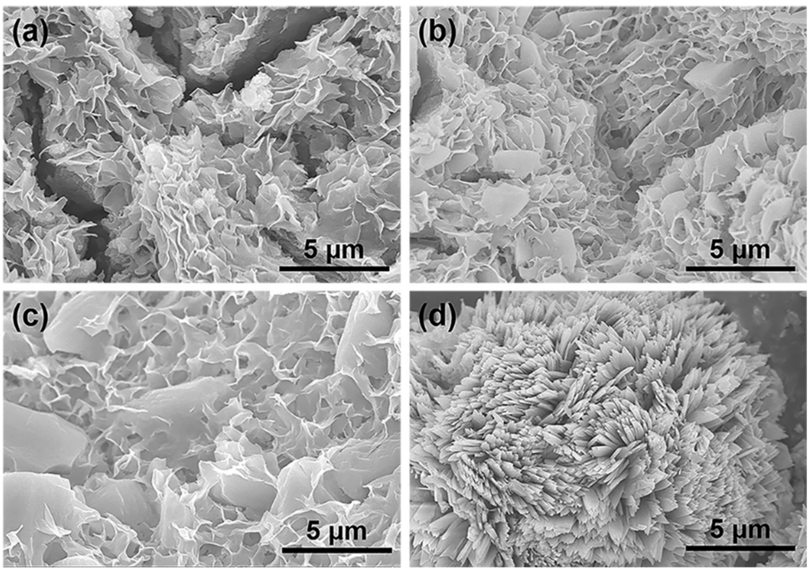


图 S5　不同溶剂比制备的 Cu-NBDC 的 SEM 图

**Fig. S5　SEM images of Cu-NBDC prepared by varying the solvent ratio.**

(a) $V$(DMF) : $V$($H_2O$ )= 100 : 1; (b) $V$(DMF) : $V$($H_2O$) = 20 : 1; (c) $V$(DMF) : $H_2O$) = 10 : 1; (d) $V$(DMF) : $V$($H_2O$) = 5 : 1.

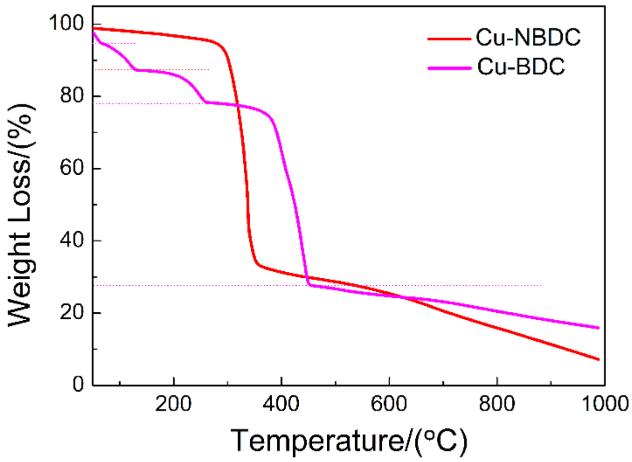


图 S6　Cu-NBDC 与 Cu-BDC 的热重分析图

**Fig. S6　TGA for Cu-NBDC and Cu-BDC.**

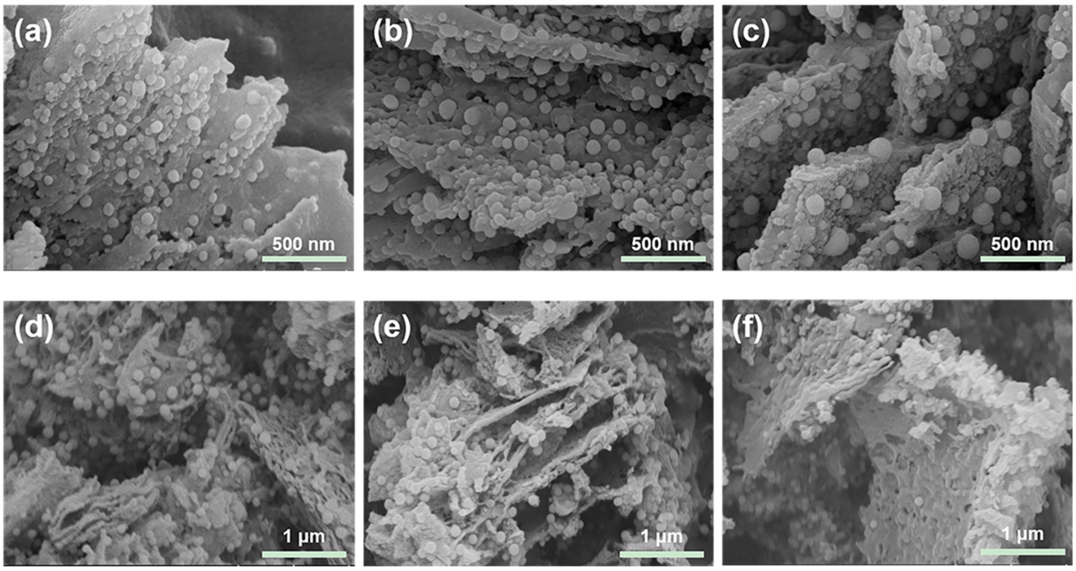


图 S7　不同温度下退火的 $Cu_2O$/Cu@NC 与 $Cu_2O$/Cu@C 的 SEM 图

**Fig. S7　SEM images of $Cu_2O$/Cu@NC and $Cu_2O$/Cu@C annealed at different temperatures.**

(a) $Cu_2O$/Cu@NC-400; (b) $Cu_2O$/Cu@NC-600; (c) $Cu_2O$/Cu@NC-800; (d) $Cu_2O$/Cu@C-400; (e) $Cu_2O$/Cu@C-600 and (f) $Cu_2O$/Cu@C-800.

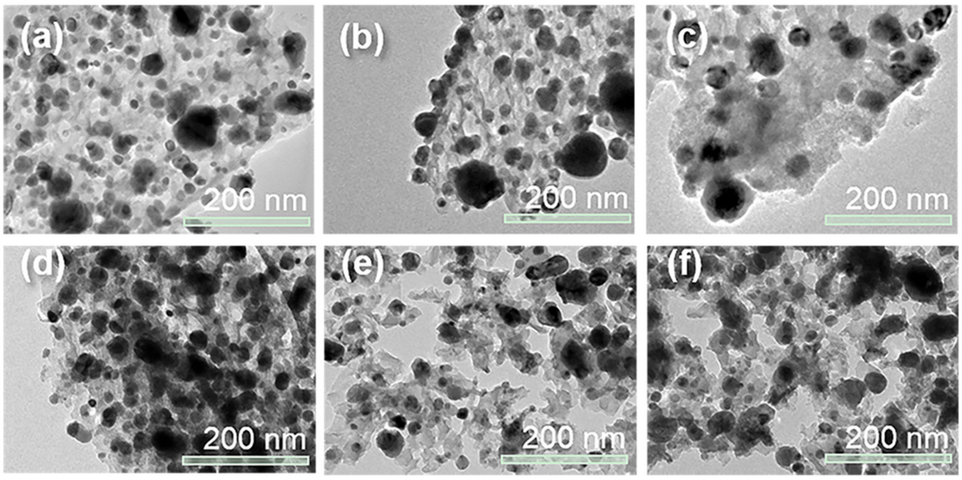


图 S8　不同温度下退火的 $Cu_2O$/Cu@NC 与 $Cu_2O$/Cu@C 的 TEM 图

**Fig. S8　TEM images of $Cu_2O$/Cu@NC and $Cu_2O$/Cu@C annealed at different temperatures.**

(a) $Cu_2O$/Cu@NC-400; (b) $Cu_2O$/Cu@NC-600; (c) $Cu_2O$/Cu@NC-800; (d) $Cu_2O$/Cu@C-400; (e) $Cu_2O$/Cu@C-600 and (f) $Cu_2O$/Cu@C-800.

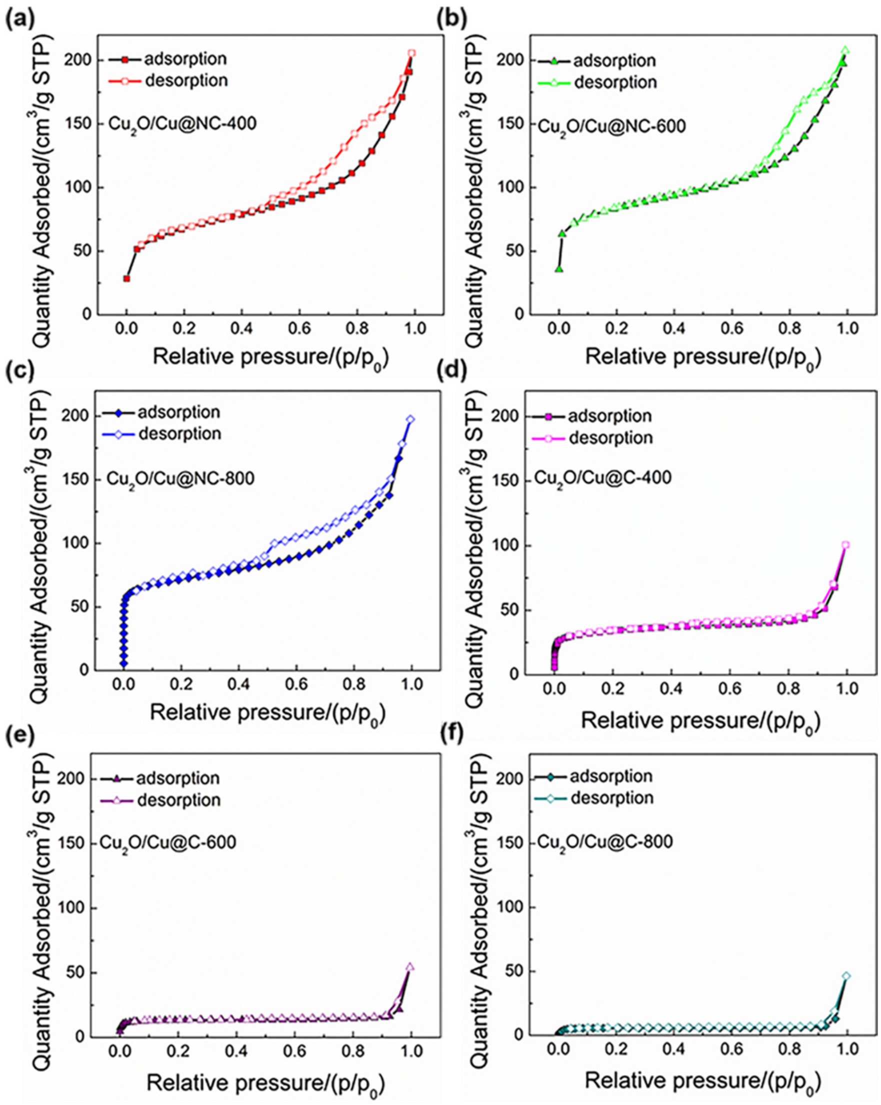


图 S9　不同温度退火的 $Cu_2O$/Cu@NC 与 $Cu_2O$/Cu@C 的氮气吸-脱附曲线

**Fig. S9　$N_2$ adsorption-desorption isotherms of $Cu_2O$/Cu@NC and $Cu_2O$/Cu@C annealed at different temperature.**

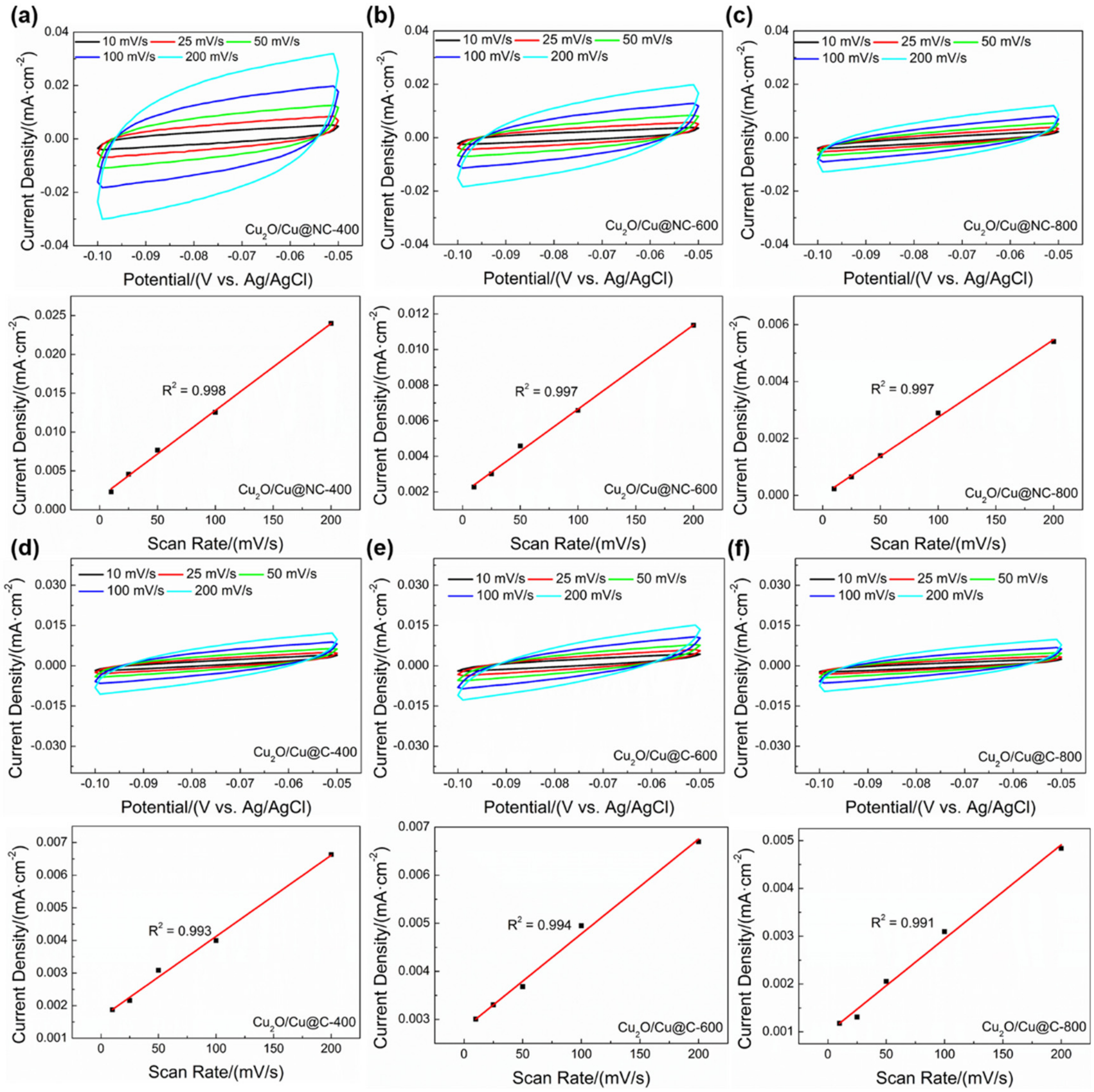


图 S10　测定不同样品的电化学比表面积

**Fig. S10　Determining Electrochemical specific surface area of different samples.**

(a) $Cu_2O/Cu@NC-400$; (b) $Cu_2O/Cu@NC-600$; (c) $Cu_2O/Cu@NC-800$; (d) $Cu_2O/Cu@C-400$; (e) $Cu_2O/Cu@C-600$ and (f) $Cu_2O/Cu@C-800$.

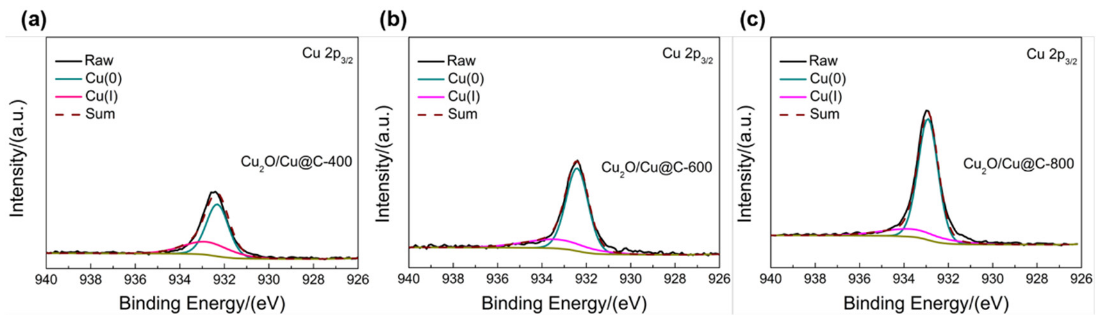


图 S11　Cu 2$p_{3/2}$ 的高分辨 XPS 光谱图

**Fig. S11　High-resolution XPS spectra of Cu 2$p_{3/2}$.**

(a) $Cu_2O/Cu@C-400$; (b) $Cu_2O/Cu@C-600$ and $Cu_2O/Cu@C-800$.

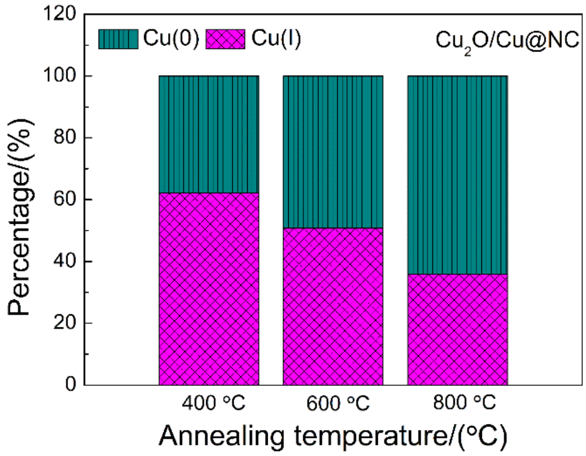


图 S12　不同退火温度下样品中的 $Cu/Cu_2O$ 含量百分比

**Fig. S12　$Cu/Cu_2O$ content for $Cu_2O/Cu@NC$ annealed at different temperatures.**

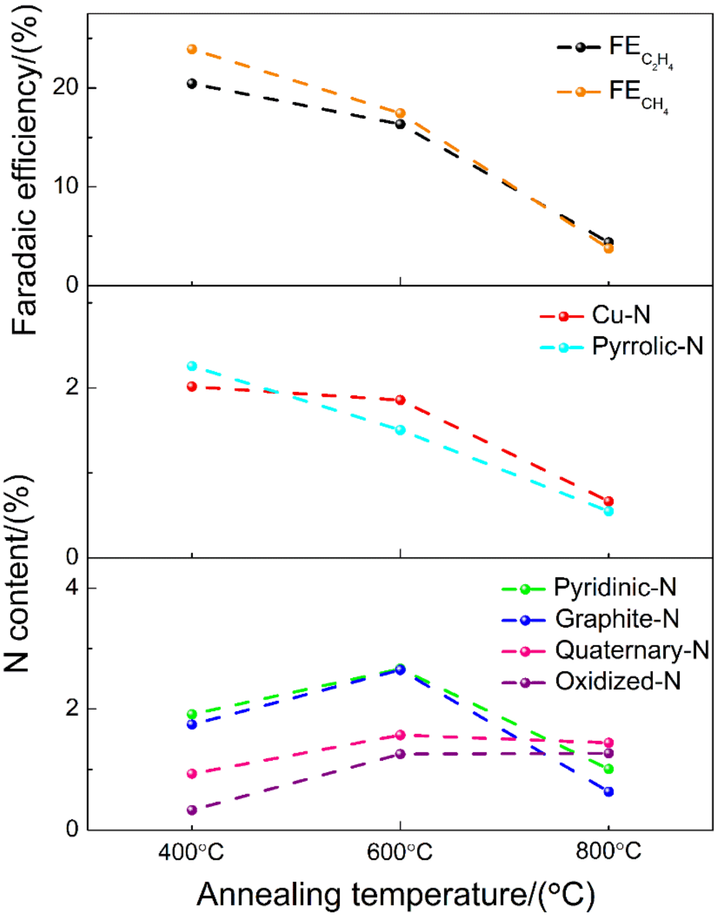


图 S13　$Cu_2O/Cu@NC$ 中 N 含量函数性与乙烯和甲烷的最大法拉第效率图

**Fig. S13　The maximum faradaic efficiency for $C_2H_4$ and $CH_4$ as a function of N functionality content in $Cu_2O/Cu@NC$.**

**表 S1 产物浓度($x$)与产物与内标物峰面积之比 $S_1 : S_2$ ($y$)的线性关系**

**Table S1 The linear fitting between the concentration of the product ($x$) and the ratio of product to internal standard area $S_1 : S_2$ ($y$).**

| Product | Equation |
|---|---|
| HCOOH | $y = 0.0614x + 0.0069$ |
| $CH_3OH$ | $y = 0.18x + 0.004$ |
| $CH_3CH_2OH$ | $y = 0.236x + 0.045$ |
| $CH_3COOH$ | $y = 0.266x - 0.02109$ |
| $CH_3CH_2CH_2OH$ | $y = 0.29x - 0.02$ |

**表 S2 不同退火温度样品的比表面积**

**Table S2 Specific surface area of samples annealed at different temperature.**

| Sample | Specific surface area ($m^2·g^{-1}$) | | |
|---|---|---|---|
| | 400 °C | 600 °C | 800 °C |
| $Cu_2O$/Cu@NC | 230.24 | 278.49 | 225.23 |
| $Cu_2O$/Cu@C | 109.56 | 41.48 | 16.41 |

**表 S3 不同样品的电化学比表面积**

**Table S3 Electrochemical specific surface area (ECSA) of different samples.**

| Sample | Specific surface area ($m^2·g^{-1}$) | | |
|---|---|---|---|
| | 400 °C | 600 °C | 800 °C |
| $Cu_2O$/Cu@NC | 1.23 | 0.52 | 0.30 |
| $Cu_2O$/Cu@C | 0.27 | 0.22 | 0.22 |

**表 S4 不同温度下制备的 $Cu_2O$/Cu@NC 的原子浓度(%)**

**Table S4 Atomic concentration (%) of $Cu_2O$/Cu@NC prepared at different temperatures.**

| sample | Cu | N | C | O |
|---|---|---|---|---|
| $Cu_2O$/Cu@NC-400 | 2.99 | 9.09 | 70.39 | 17.54 |
| $Cu_2O$/Cu@NC-600 | 3.58 | 11.42 | 72.24 | 12.76 |
| $Cu_2O$/Cu@NC-800 | 6.22 | 5.57 | 71.42 | 16.80 |

**表 S5 不同温度下制备的 $Cu_2O$/Cu@C 的原子浓度(%)**

**Table S5 Atomic concentration (%) of $Cu_2O$/Cu@C prepared at different temperatures.**

| sample | Cu | C | O |
|---|---|---|---|
| $Cu_2O$/Cu@C-400 | 2.83 | 80.34 | 16.83 |
| $Cu_2O$/Cu@C-600 | 3.46 | 84.05 | 12.49 |
| $Cu_2O$/Cu@C-800 | 6.09 | 83.95 | 9.96 |

表 S6　不同温度下制备的 $Cu_2O$/Cu@NC 中 Cu(0)与 Cu(I)浓度(%)

**Table S6　Cu(0) and Cu(I) concentration (%) in $Cu_2O$/Cu@NC prepared at different temperature.**

| sample | Cu(I) | Cu(0) |
|---|---|---|
| $Cu_2O$/Cu@NC-400 | 62.11 | 37.89 |
| $Cu_2O$/Cu@NC-600 | 50.76 | 49.24 |
| $Cu_2O$/Cu@NC-800 | 35.90 | 64.10 |

表 S7　不同温度下制备的 $Cu_2O$/Cu@NC 的 N 物种浓度(%)

**Table S7　Atomic concentration (%) of N species in $Cu_2O$/Cu@NC prepared at different temperatures.**

| sample | Pyridinic-N | Cu-N | Pyrrolic-N | Graphitic-N | Quaternary-N | Oxidized-N |
|---|---|---|---|---|---|---|
| $Cu_2O$/Cu@NC-400 | 1.915 | 2.015 | 2.255 | 1.645 | 0.930 | 0.330 |
| $Cu_2O$/Cu@NC-600 | 2.666 | 1.856 | 1.523 | 2.548 | 1.570 | 1.257 |
| $Cu_2O$/Cu@NC-800 | 1.010 | 0.664 | 0.548 | 0.635 | 1.443 | 1.270 |