

Electronic Supplementary Information

One-Step Synthesis of Macroporous Cu-g/C₃N₄ Nanofiber Electrocatalyst for Efficient Oxygen Reduction Reaction

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Supplementary Methods

Materials synthesis. The detail synthesis procedures for the macroporous Cu-g/C₃N₄ nanofibers was summarized as follows. First, 0.5 g of PEO was added into 5.5 g of deionized water and then stirred for 1 h to form a uniform solution. Then, 0.5 g of melamine and 1 mmol of Copper (II) acetate monohydrate (Cu(COO)₂•H₂O) were added into the PEO aqueous solution separately. Here, to verify the effect of Cu-content on the final microstructures of the MCNFs, we also prepared another sample by adding 0.5 g of melamine and 2 mmol of Cu(COO)₂•H₂O into the PEO aqueous solution. After stirring for 2 h, 6 g of PTFE water emulsion (containing 60 wt.% of PTFE NPs) was added into the above transparent solution, and then stirred for overnight to obtain stable and viscous sol for electrospinning. Finally, the as-spun nanofiber membranes were calcined at 900 °C in N₂-atmosphere for 2 h with a heating rate of 5 °C/min to obtain the macroporous Cu-g/C₃N₄ nanofibers. Here, to verify the effect of pyrolysis temperature on the final microstructures of the MCNFs, we also calcined the as-spun nanofibers at 1000 °C in N₂-atmosphere for 2 h with the same heating rate. For comparison, we also synthesized C-g/C₃N₄ nanofibers with the same procedures except for not adding the Cu(COO)₂•H₂O when preparing the spinning sol.

Preparation of ORR catalysts. Firstly, the catalyst inks were prepared by mixing 2 mg of Cu-g/C₃N₄ nanofiber material with 45 μL (5 wt.%) of Nafion solution and 1 mL of ethanol and then undergoing an ultrasonic dispersion for 20 min. Then, 30 μL of the catalyst suspension was dropped onto the polished platinum carbon electrode and dried at room temperature naturally. The catalyst loading was calculated roughly as 0.29 mg/cm². For comparison, a commercial Pt/C (20 wt.%) catalyst was also prepared in the same way, and the catalyst loading was 0.098 mg/cm².

The ORR measurements. The ORR electrochemical tests were conducted in a three-electrode system, where the counter electrode was a Pt mesh, the reference electrode was a saturated calomel electrode, and the working electrode was an RDE electrode with catalysts. The CV curves were obtained by testing in 0.1 M KOH with saturated oxygen atmosphere from -1.0 V to 0.2 V at a scanning speed of 50 mV/S. Subsequently, the LSV curves were obtained by adjusting the scanning speed to 5 mV/S, and the polarization curves were tested at different rotation rates of 400, 625, 900, 1225, 1600, 2025 rpm to explore the ORR reaction kinetics. The stability of the material was judged by comparing the half-wave potential changes of the LSV curves before and after the 1000th CV cycles. The cycling stability test was conducted by running 1000 cycles in a stable voltage range of 0.4~ 0.6V.

Supplementary Figures

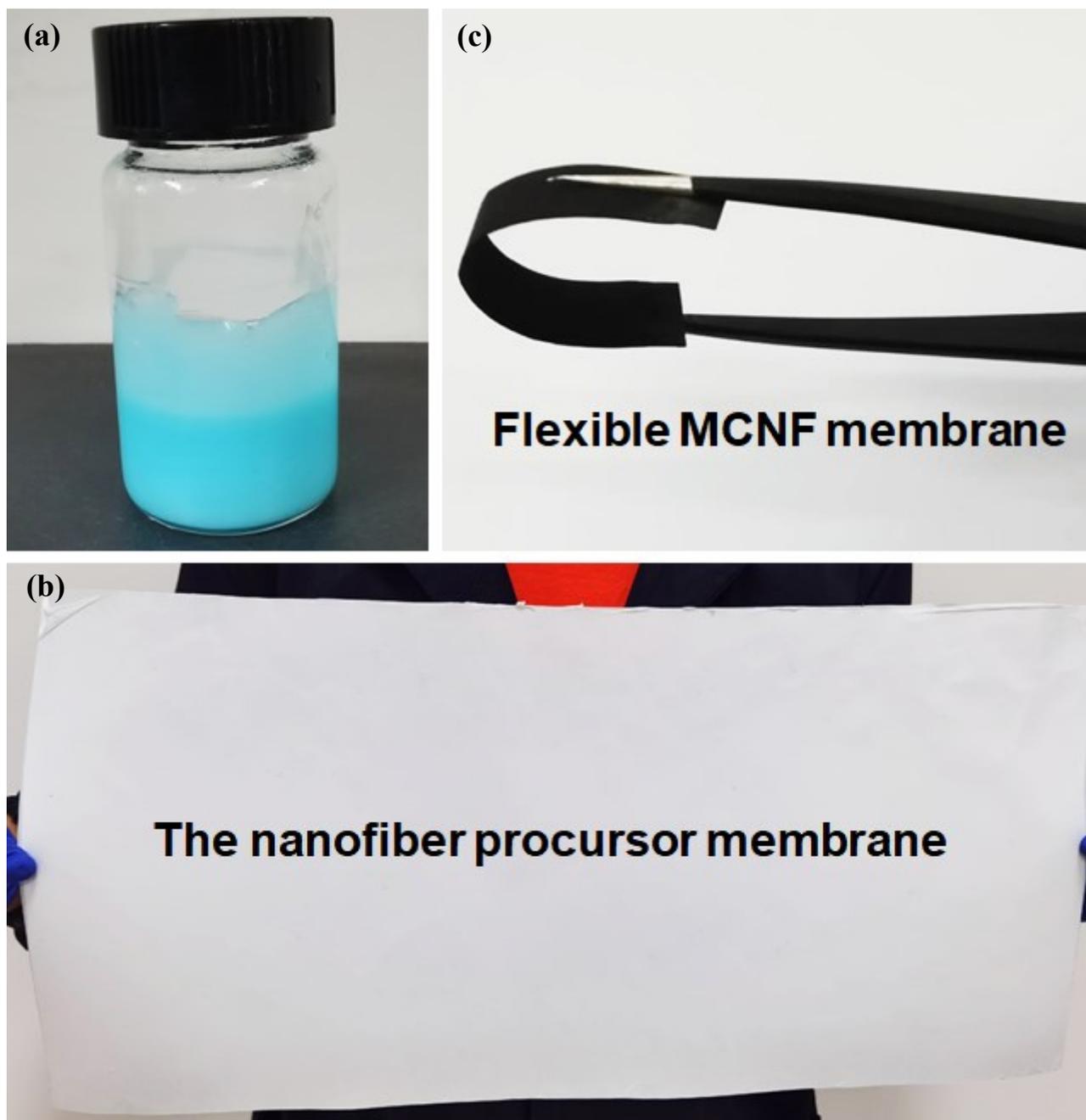


Fig. S1. Digital photos of materials during the material synthesis processes. (a) The precursor sol showed a blue color and a high viscosity. (b) The white nanofiber precursor membrane were soft and extensible. (c) Demonstration of the flexible MCNF membrane.

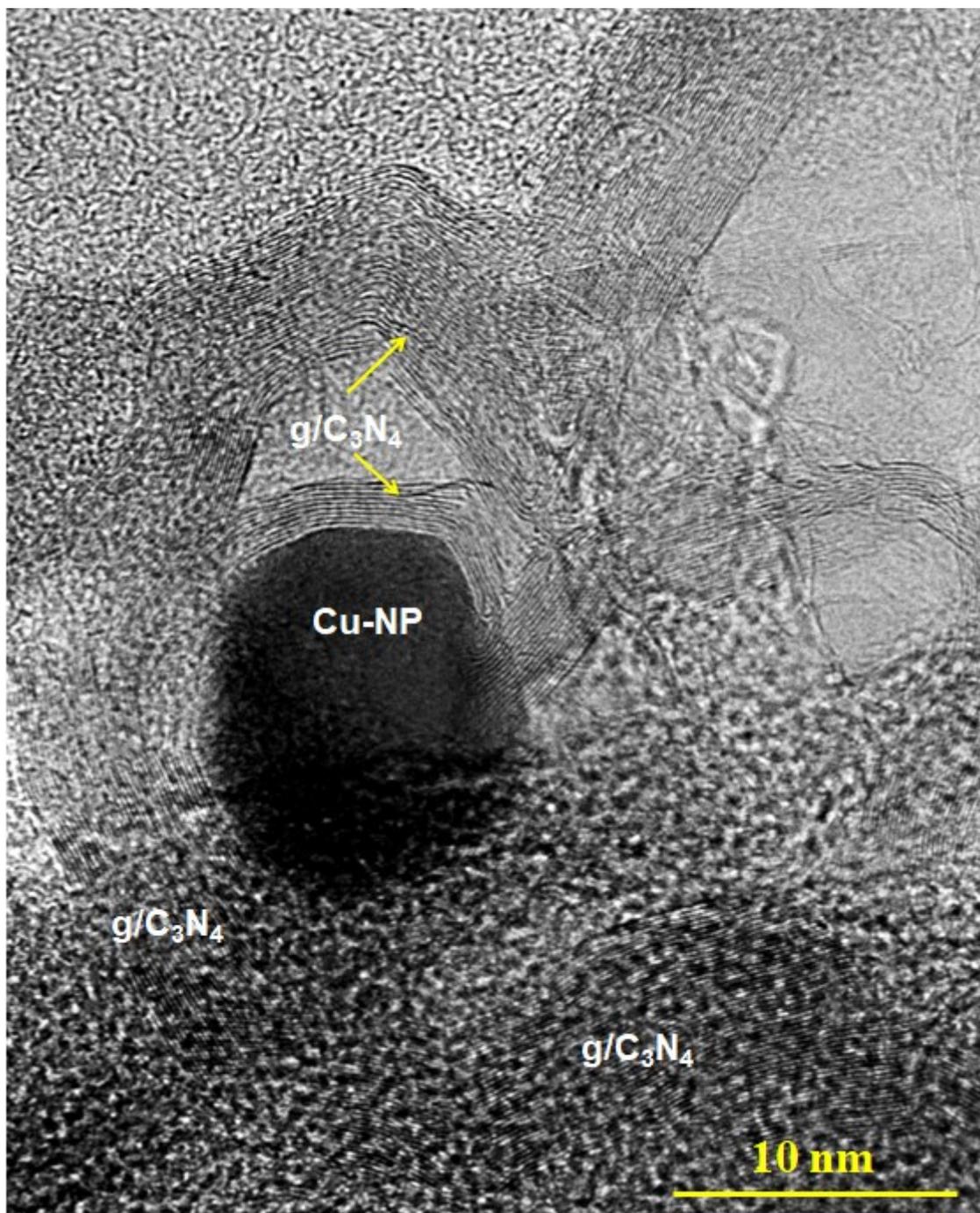


Fig. S2. A high resolution TEM image of the Cu-g/C₃N₄ nanofibers. It is clearly that Cu-NPs were well surrounded by g/C₃N₄ nanosheets.

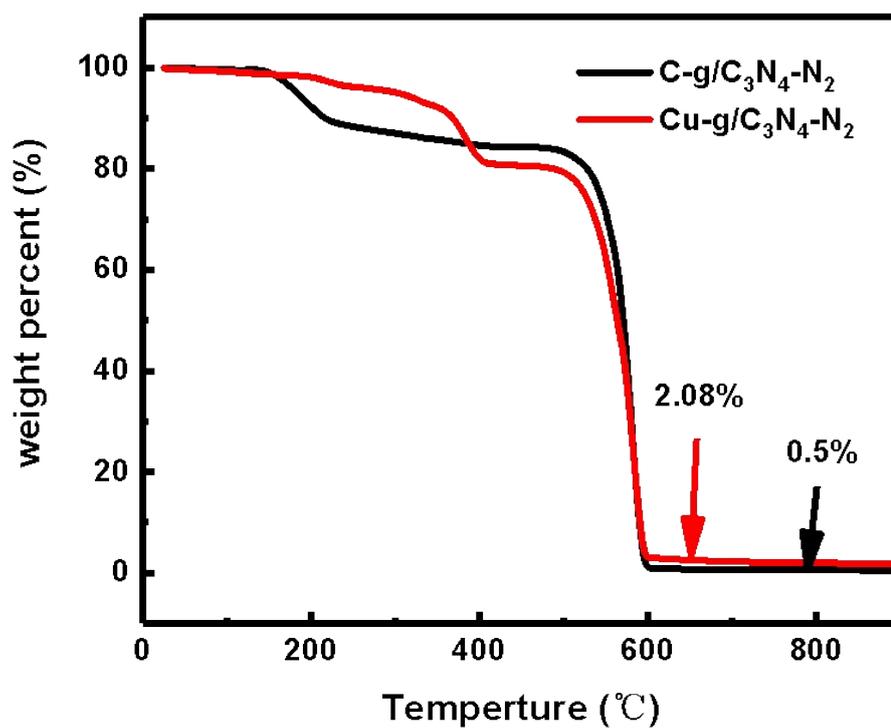


Fig. S3. TG analysis of two different nanofiber precursor membranes. Without doping Cu, the carbon yield of C-g/C₃N₄ was only ~ 0.5 wt.%. In comparison, after doping Cu, the carbon yield was improved to 2.08 wt.%.

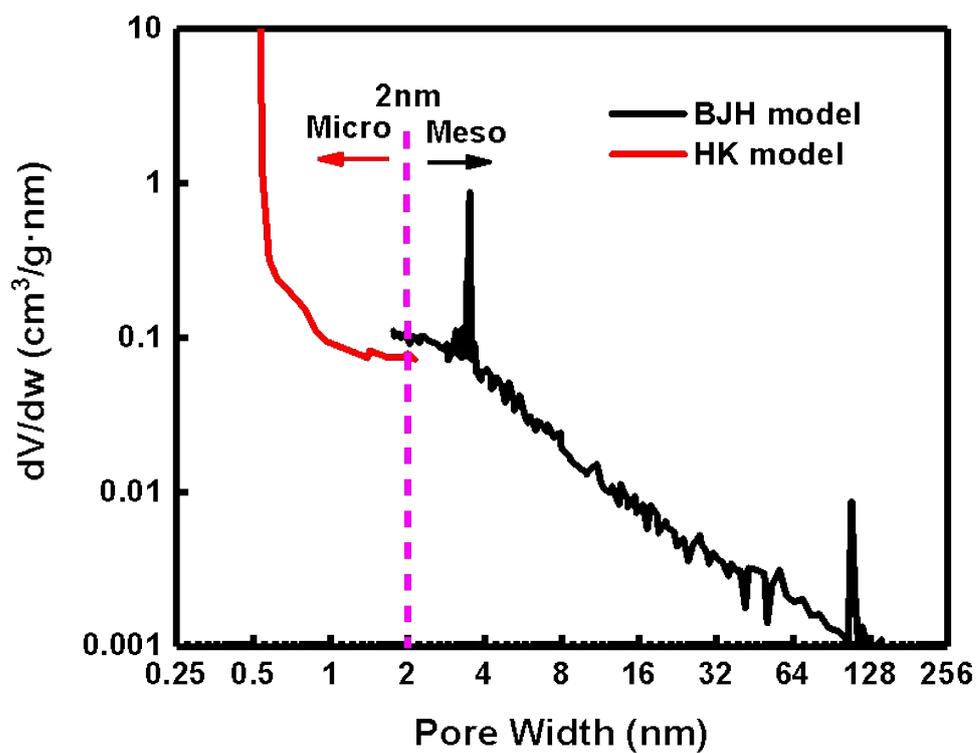


Fig. S4. Aperture distribution analysis of the Cu-g /C₃N₄ nanofibers with the BJH-HK model. The BJH-HK model curve proved the existence of micropores (< 2 nm) and mesopores (2~50 nm) in the Cu-g/C₃N₄ nanofibers.

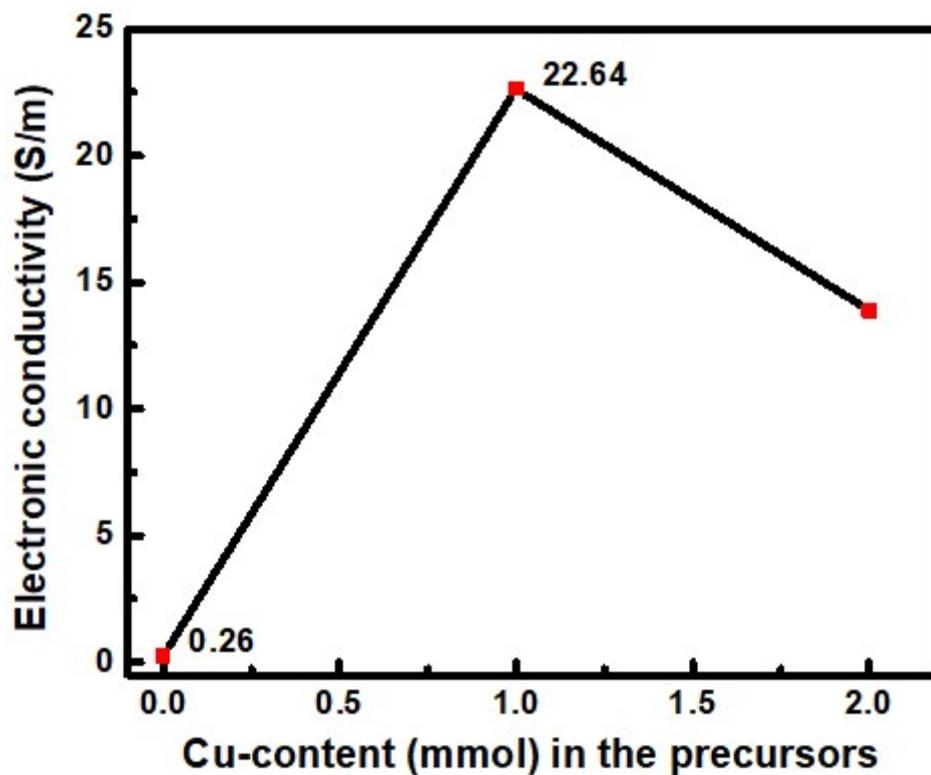


Fig. S5. The conductivity measurements of the macroporous nanofiber materials with different Cu-contents. At first, the electrical conductivity of the final nanofibers was increased significantly by increasing the Cu-contents from 0 to 1 mmol (in the spinning sol), but the conductivity decreased when further increasing the Cu-contents to 2 mmol.

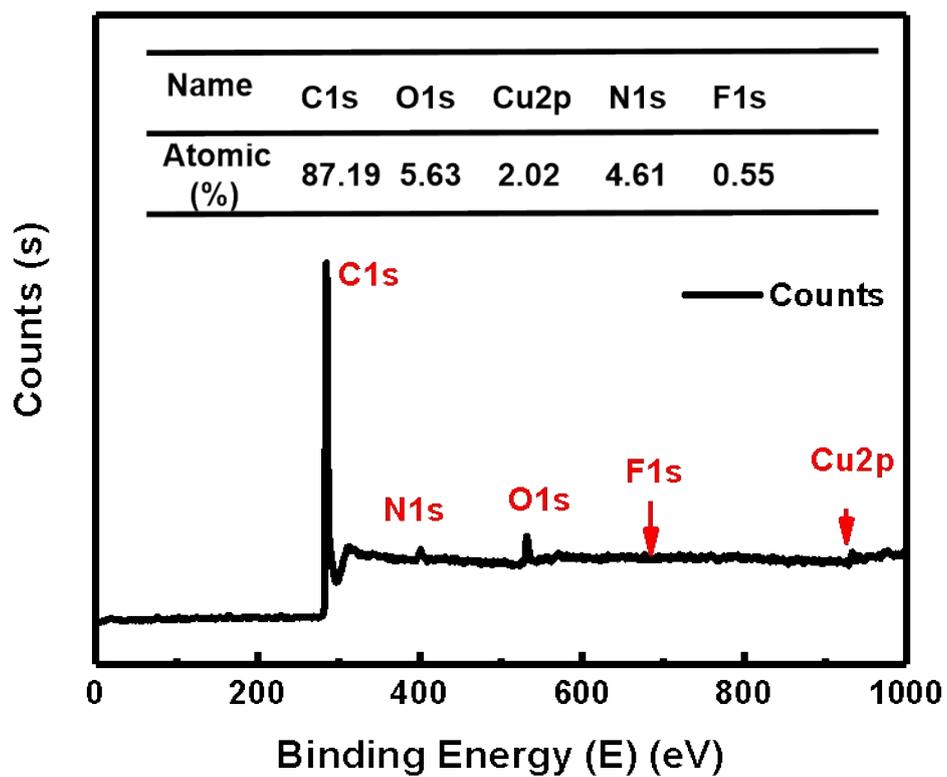


Fig. S6. XPS spectrogram of the macroporous Cu-g/C₃N₄ nanofibers. The XPS spectrum shows obvious C1s, N1s, O1s, F1s and Cu 2p peaks and their weight percents are 87.19%, 4.61%, 5.63%, 0.55% and 2.02%, respectively.

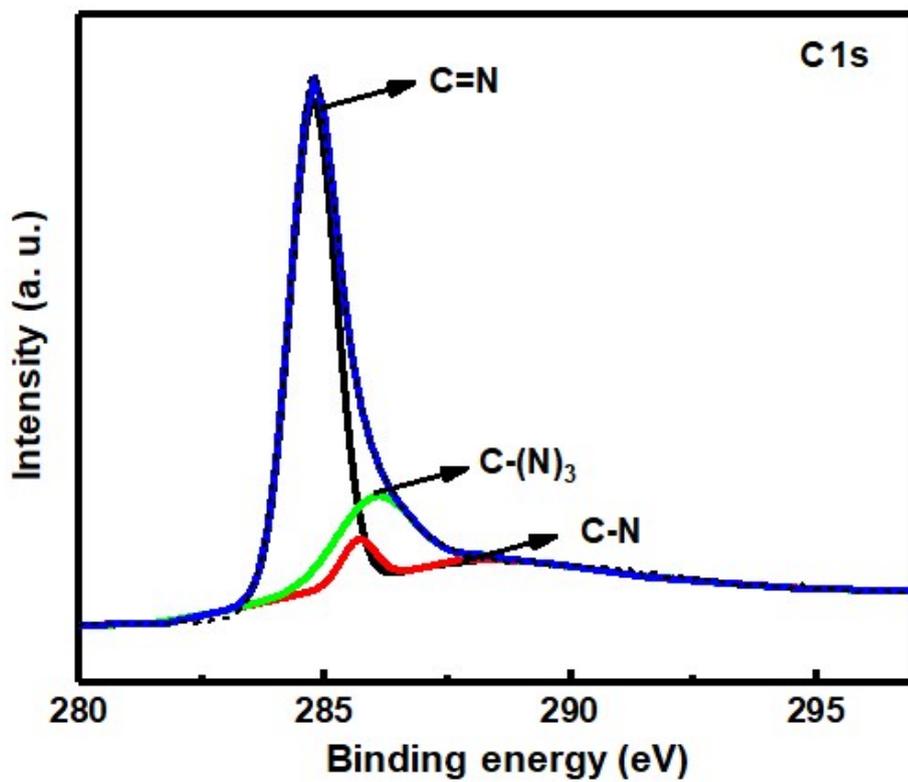


Fig. S7. High resolution XPS spectra of C1s. There were three peaks at 284.7 eV, 285.9 eV and 288.3 eV, corresponding to C=N, C-(N)₃ and C-N, respectively.

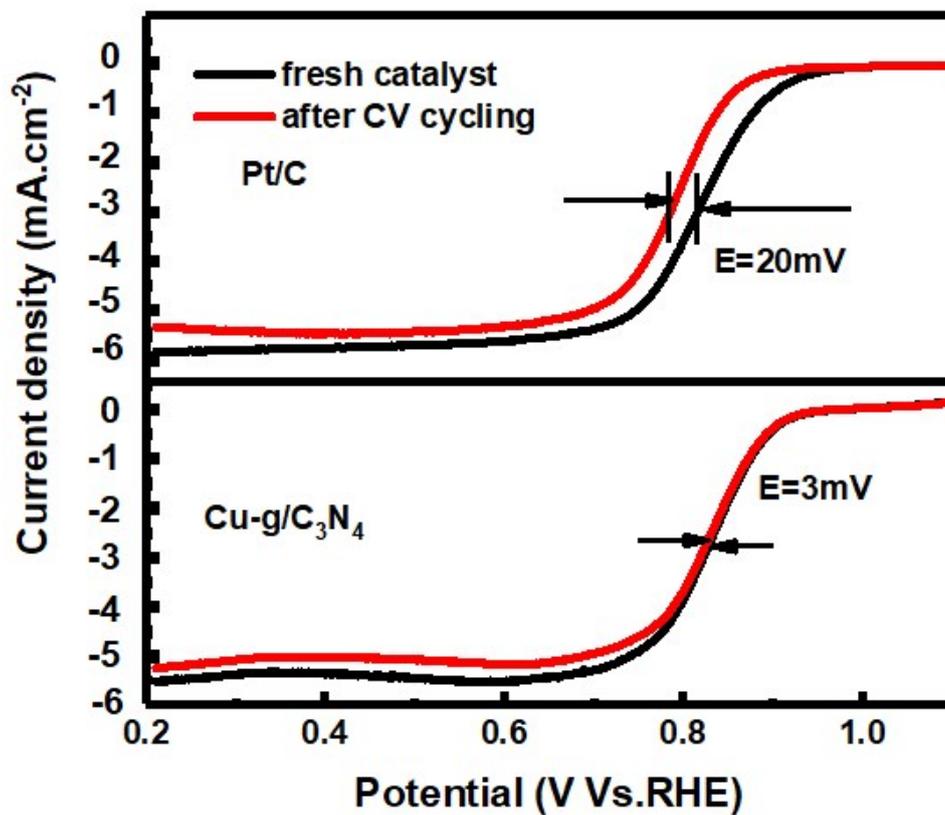


Fig. S8. Comparison of LSV curve of the Cu-g/C₃N₄ and Pt/C materials before and after 1000 CV cycles. The curves before and after the cycle of Cu-g /C₃N₄ catalyst were in good agreement with almost no potential loss, but the potential loss of Pt /C catalyst was about 20 mV, which can prove the stability of Cu-g /C₃N₄ catalyst.

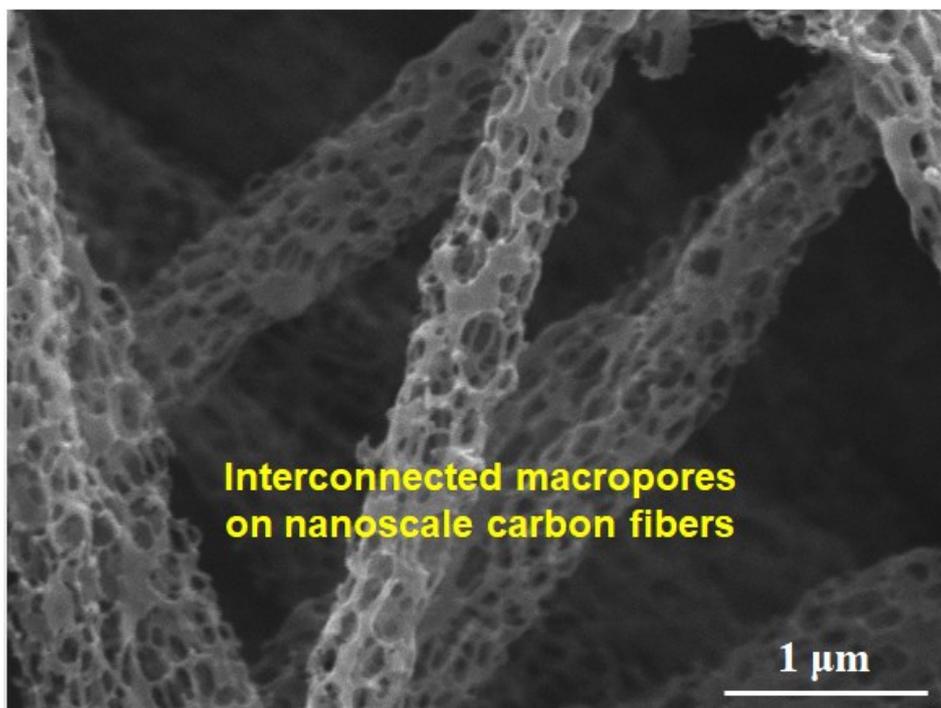


Fig. S9. The morphology of electrospun MCNFs that fabricated with PEO as the carbon precursor and the PTFE as pore inducer. There were clearly interconnected macropores on the nanoscale CNFs.

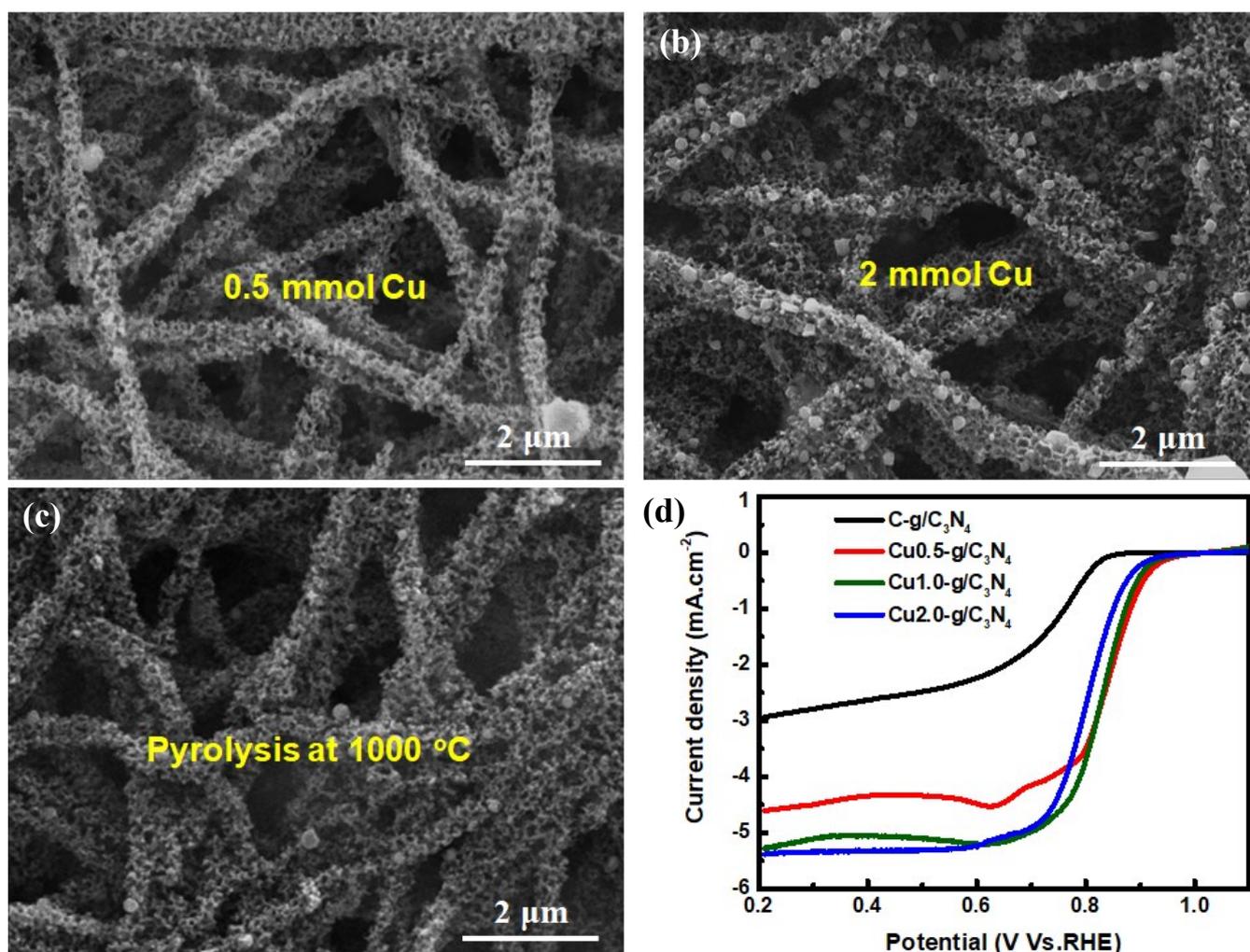


Fig. S10. The morphology and ORR activities of the Cu-g/C₃N₄ nanofiber catalyst that synthesized under different conditions. (a) and (b) Surface morphology of the Cu-g/C₃N₄ nanofibers that contained different Cu-contents. (c) Surface morphology of the Cu-g/C₃N₄ nanofibers that synthesized at 1000 °C. (d) The ORR activities of the nanofibrous catalysts that contained different contents of Cu.