

Electronic Supplementary Information

Graphene nanoribbons hybridized carbon nanofibers: remarkably enhanced graphitization and conductivity, and excellent performance as support material for fuel cell catalysts

*Chaonan Wang^a, Hongrong Gao^a, Hong Li^a, Yiren Zhang^a, Bowen Huang^a, Junhong Zhao^b, Yan Zhu^a, Wang Zhang Yuan^{*a} and Yongming Zhang^{*a}*

^a *School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, China*

^b *School of Chemistry and Chemical Engineering, Anyang Normal University, Anyang 455000, China*

** Corresponding author: wzhyuan@sjtu.edu.cn (W.Z.Y.), ymzsztu@gmail.com (Y.Z.).*

Experimental Section

Materials. MWCNTs (Purity, gt. 95%; length: 10 μm ; diameter: gt. 50 nm) were purchased from Chengdu Organic Chemicals (Chengdu, China). Before use, they were pretreated in 6 M HNO_3 for 3 h, then washed with deionized water (DIW) and dried in vacuum at room temperature for 24 h. polyacrylonitrile (PAN), $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (Pt, 38%), and commercial Pt/XC72R catalyst were obtained from J&K Technology Ltd., Kunming Boren Precious Metals Co. Ltd. and Johnson Matthey (JM)

Catalysts Corporation, respectively. Electrodes were supplied by Shanghai Chenhua Instrument Co., Ltd. Concentrated sulfur acid (95-98%), dimethyl formamide (DMF), potassium permanganate (KMnO₄), hydrogen peroxide (H₂O₂, 30%), sodium borohydride (NaBH₄), methanol and concentrated hydrochloric acid were provided by Sinopharm Chemical Reagent Co., Ltd. (SCRC, China) and used as received.

Apparatus. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) morphologies were observed by a JEOL2100F and a JSM-6701F (both from Japan Electron Optics Laboratory Co., Ltd.), respectively. IR spectra were recorded on a Perkin-Elmer Paragon 1000PC spectrometer. Raman spectra were taken from a Jobin Yvon Micro-Raman Spectroscopy (RamLab-010), equipped with a holographic grating of 1800 lines/mm and a He-Ne laser (532 nm) as the excitation source. Powder X-ray diffraction (XRD) experiments were conducted on a D/max-2200/PC (Japan Rigaku Corp.) using CuK α radiation (1.5418 Å). The size of Pt nanoparticles (NPs) was roughly calculated according to the Scherrer's equation ($D = \frac{0.89\lambda}{B \cos \theta}$) using the typical Pt (2 2 0) peak.

Preparation of graphene oxidation nanoribbons (GONRs). GONRs was prepared according to Tour's method.^[1] Firstly, 0.1 g of MWCNTs was suspended in 10 ml of H₂SO₄ under vigorous stirring for 2 h. Then, 0.4 g of KMnO₄ was slowly added into the suspension. After stirring at room temperature for 1 h and at 80 °C for another hour, the mixture was poured into 400 ml of DIW. Afterwards, 2 ml of H₂O₂ (30%) was added to the mixture, which was subsequently centrifuged and washed with HCl (3.3%) aqueous solution and DIW successively for several times. Finally, the obtained GONRs were dried in vacuum at 50 °C for 8 h.

Fabrication of graphene nanoribbons-carbon nanofibers (G-CNFs). The GONR-PAN precursor was first prepared by electrospinning. Certain amount of GONRs were dissolved in 10 ml of DMF and sonicated at room temperature for 0.5 h. Then 1 g of PAN was added and the mixture was stirred to achieve a viscous homogeneous solution. The electrospinning conditions were set as below: a DC voltage of 18 kv, a tip-collector distance of 12 cm, a relative humidity of 35% and a feed rate of 0.2 ml/h. The nanofibers were collected and dried at 60 °C for 12 h in vacuum. The obtained GONR-PAN nanofibers were preoxidized at 280 °C in air for 5 h, and further carbonized at 900 °C for 3 h in argon atmosphere to yield the resulting G-CNF composite. By changing the weight ratios of GONRs to PAN, the composite films denoted as CNF, G_{0.5}-CNF, G₁-CNF, G₂-CNF, G₃-CNF and G₅-CNF with GNRs of 0, 0.5, 1, 2, 3 and 5 wt% were produced, respectively. During the carbonation process, GONRs were reduced into GNRs via a carbothermic process. MWCNTs-embedded carbon nanofibers (M₂-CNFs, with 2 wt% MWCNTs) were also prepared according the above procedure.

Synthesis of Pt/G₂-CNF and Pt/M₂-CNF hybrid catalysts. Pt NPs were deposited on composite CNFs via a chemical reduction process. Taking the preparation of Pt/G₂-CNF for example, 100 ml of G₂-CNF (1 mg/ml) aqueous dispersion was prepared by ultrasonification, into which H₂PtCl₆ aqueous solution (4 mg/ml) was dropped under nitrogen. Then 100 ml of NaBH₄ (1 mg/ml) was added dropwise. After stirring for 3 h and standing for 5 h, the resulting Pt/G₂-CNF (28 wt% Pt) hybrids were filtrated and washed with DIW for several times. The resulting product was dried in vacuum at 50 °C for 10 h. For comparison, Pt/M₂-CNF, Pt/CNF (28 wt% Pt) and Pt/G₂-CNF (40) (40 wt% Pt) were prepared with the similar procedure.

Electronic conductivity measurement. Electronic conductivity of the carbon nanofiber membranes in tangent direction was measured with a two-electrode AC impedance method by using an Autolab

PGSTA302 electrochemical test system (Eco Chemie, Netherland) at room temperature. Electronic conductivity (σ) was calculated from impedance data as follows:

$$\sigma = \frac{L}{R \cdot A}$$

where L is the distance between two electrodes, A is the cross-sectional area of the sample, and R is the resistance of hybrid nanofiber membrane.

Electrochemical test. The electrochemical measurement was carried out by a standard three-probe cell using an Autolab PGSTAT302 (Metrohm) electrochemical test system at room temperature. A glassy carbon electrode (3 mm o.d.), a platinum foil and an Ag/AgCl electrode were used as working, counter and reference electrodes, respectively. 10 μ l of the catalyst paste, which was prepared by mixing the electrocatalyst (5 mg), Nafion (5 wt%, 50 μ l) and ethanol (1 ml), was utilized. Electrochemically active surface area (ECSA) of the hybrid catalyst was calculated from cyclic voltammetry (CV) curves via the equation of $ECSA = \frac{Q}{mC}$.^[2] The CV curves were recorded ranging from -0.25 to 1 V in 0.5 M H₂SO₄ solution at a scan rate of 50 mV/s. The methanol electrooxidation reaction activity was detected via CV tests in 1 M CH₃OH + 0.5 M H₂SO₄ mixture solution, ranging from -0.25 to +1 V, at a scan rate of 50 mV/s. The linear sweep voltammetry (LSV) experiments were accomplished in a mixture of 0.5 M H₂SO₄ + 1 M CH₃OH at a scan rate of 5 mV/s. The chronoamperometry (CA) test was carried out in a mixture of 0.5 M H₂SO₄ + 1 M CH₃OH, the potential stepped from the open circuit potential (0.45 V). After 2 s, the potential was stepped to 0.35 V for 2 s, and then to 0.4 V for 1800 s. High-purity nitrogen was bubbled during all the tests.

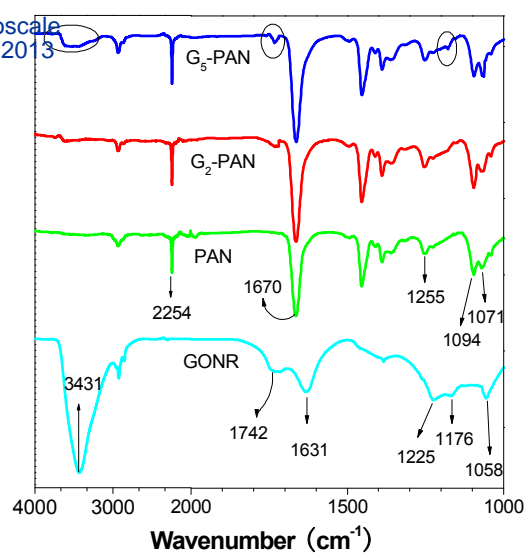


Fig. S1 ATIR spectra of GONRs and the electrospun nanofibers of PAN, G₂-PAN and G₅-PAN.

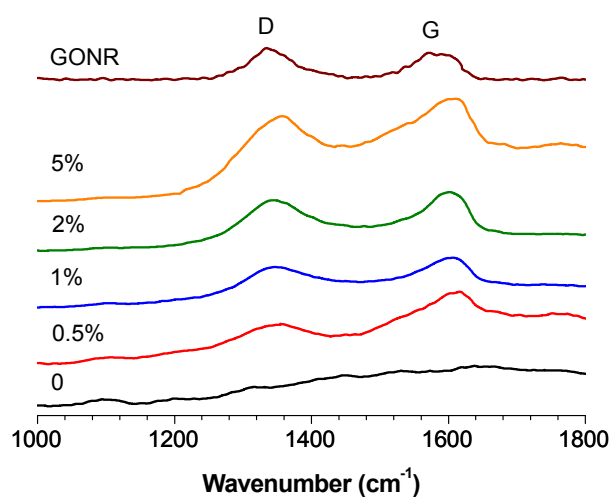


Fig. S2 Raman spectra of the electrospun nanofibers of pure PAN, G_{0.5}-PAN, G₁-PAN, G₂-PAN, G₅-PAN and pure GNR membrane.

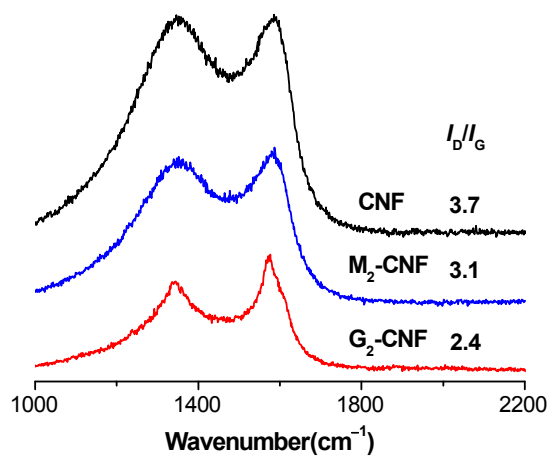


Fig. S3 Raman spectra of the carbonization nanofibers of CNFs, M₂-CNFs and G₂-CNF.

References

1. D. V. Kosynkin, L. Amanda, S. Alexander, J. R. Lomeda, D. Ayrat, P. B. Katherine and J. M. Tour, *Nature*, 2009, **458**, 872-876.
2. A. Halder, S. Sharma, M. S. Hegde and N. Ravishankar, *J. Phys. Chem. C*, 2009, **113**, 1466–1473.