**Supporting Information** 

Solution-Processed PEDOT:PSS-Graphene Composites as Electrocatalyst for Oxygen

**Reduction Reaction** 

Miao Zhang, Wenjing Yuan, Bowen Yao, Chun Li\* and Gaoquan Shi

Department of Chemistry and Key Laboratory of Bioorganic Phosphorus Chemistry and

Chemical Biology (Ministry of Education), Tsinghua University, Beijing 100084, China

E-mail: chunli@mail.tsinghua.edu.cn

Calculation of the Kinetic Parameters for ORR

The electron transfer numbers (n) for ORR based on the RDE measurements were estimated with the Koutecky-Levich equation as the follows:

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K}$$

$$B = 0.2nFC_0(D_0)^{2/3}v^{-1/6}$$

in which J,  $J_L$ ,  $J_K$  are current density, the diffusion-limiting current density, and the kinetic current density, respectively;  $\omega$  is the rotating rate in rpm, B can be determined by the slope of K-L plots based on Levich equation, n represents the transferred electron number per oxygen molecule, F is the Faraday constant (96 485 C mol<sup>-1</sup>),  $C_0$  is the concentration of  $O_2$ ,  $D_0$  is the diffusion coefficient of oxygen in 0.1 M KOH (1.9  $\times$  10<sup>-5</sup> cm<sup>2</sup> s<sup>-1</sup>) and  $\nu$  is the kinematic viscosity  $(0.01 \text{ cm}^2 \text{ s}^{-1})$ .

The electron transfer numbers (n) and  $HO_2^-$  yields based on the RRDE measurements at 1600 rpm were calculated by the following equations: [S1]

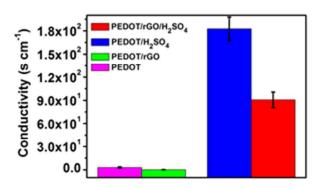
$$n = 4I_D/(I_D + I_R/N)$$

1

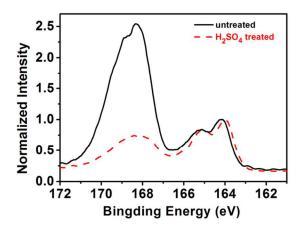
$$HO_2^-\% = 200 \times \frac{I_R/N}{I_D + I_R/N}$$

where  $I_D$  is the faradic disk current,  $I_R$  is the faradic ring current, and N = 0.37 is collection efficiency.

[S1] U. A. Paulus, T. J. Schmidt, H. A. Gasteiger, R. J. Behm, *J. Electroanal. Chem.* **2001**, 495,134.



**Figure S1.** Conductivities of PEDOT:PSS and PEDOT:PSS/rGO composite before and after treatment with concentrated H<sub>2</sub>SO<sub>4</sub>.



**Figure S2.** S 2p XPS spectra of PEDOT:PSS films before and after the treatment with concentrated H<sub>2</sub>SO<sub>4</sub>.

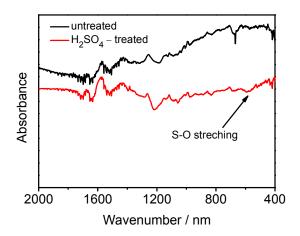


Figure S3. FTIR spectra of PEDOT:PSS films before and after the H<sub>2</sub>SO<sub>4</sub> treatment.

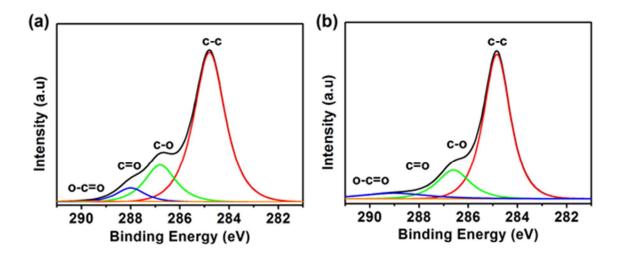
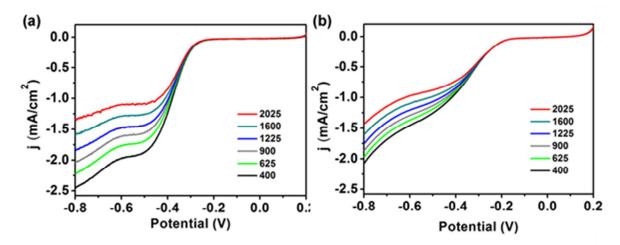
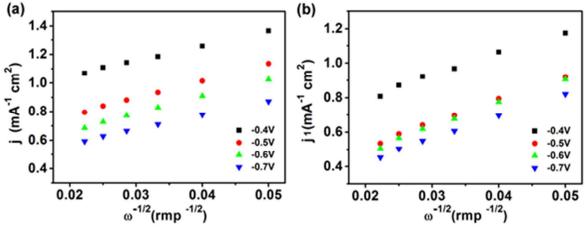


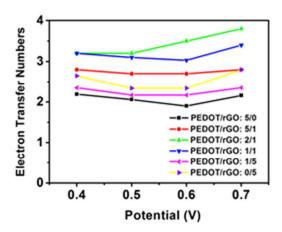
Figure S4. C 1s XPS spectra of rGO films before (a) and after (b) the H<sub>2</sub>SO<sub>4</sub> treatment.



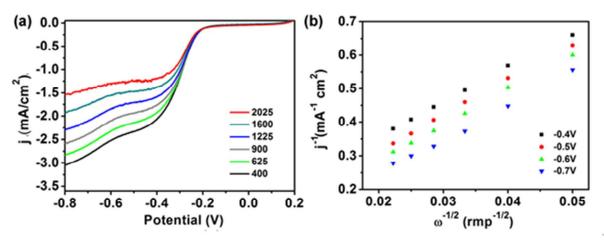
**Figure S5.** (a) RDE voltammograms for the ORR of the H<sub>2</sub>SO<sub>4</sub>-treated PEDOT:PSS (a) and rGO (b) on GC electrode in O<sub>2</sub>-saturated 0.1M KOH solutions at a scan rate 10 mV/s with different rotation speeds.



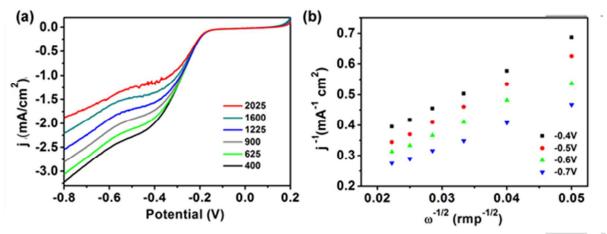
**Figure S6.** Koutecky–Levich plots of ORR on the H<sub>2</sub>SO<sub>4</sub>-treated PEDOT:PSS (a) and rGO (b) electrodes.



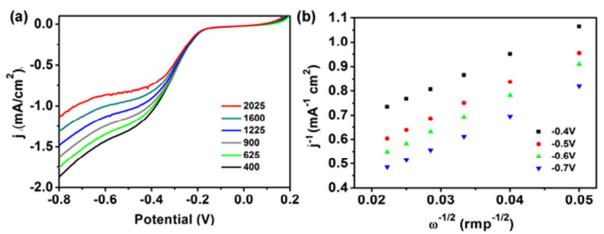
**Figure S7.** Electron transfer numbers as a function of the overpotential of the composites with different mass ratios of PEDOT:PSS to rGO (w/w).



**Figure S8.** (a) RDE voltammograms for the ORR of H<sub>2</sub>SO<sub>4</sub>-treated PEDOT:PSS/rGO (5:1, w/w) on GC electrode in O<sub>2</sub>-saturated 0.1M KOH solutions at a scan rate 10 mV/s with different rotation speeds. (b) Koutecky–Levich plots at different electrode potentials.



**Figure S9.** (a) RDE voltammograms for the ORR of H<sub>2</sub>SO<sub>4</sub>-treated PEDOT:PSS/rGO (1:1, w/w) on GC electrode in O<sub>2</sub>-saturated 0.1M KOH solutions at a scan rate 10 mV/s with different rotation speeds. (b) Koutecky–Levich plots at different electrode potentials.



**Figure S10.** (a) RDE voltammograms for the ORR of H<sub>2</sub>SO<sub>4</sub>-treated PEDOT:PSS/rGO (1:2, w/w) on GC electrode in O<sub>2</sub>-saturated 0.1M KOH solutions at a scan rate 10 mV/s with different rotation speeds. (b) Koutecky–Levich plots at different electrode potentials.