

Electronic Supplementary Information (ESI)

# **Facile Synthesis of Hybrid Graphene and Carbon Nanotube as Metal-Free Electrocatalyst with Active Dual Interfaces for Efficient Oxygen Reduction Reaction**

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### 1. Experimental

**Preparation of PDAC functionalized multi-walled carbon nanotubes (pMWNT) and graphene oxide (GO) to synthesize the hybrid rGO/pMWNT electrode.** pMWNT were prepared by following method. 50 mg of MWNT (10 - 15 nm diameter, Hanwha Nanotech Corp.) were mixed with 2 wt. % of poly(diallyldimethylammonium chloride) (PDAC) in 100 mL of water in the presence of 3 wt. % of NaCl. Then, stable pMWNT suspension was prepared by ultrasonication for 1 h.<sup>S3</sup> Graphene oxide (GO) was prepared from a commercial graphite (Aldrich) by modified Hummers method and exfoliated using ultrasonication. The resulting brown solution was mixed with pMWNT suspension at a specific ratio (GO:pMWNT = 0.5:1 - 10:1). GO in a mixed solution was reduced into reduced graphene oxide (rGO) by adding hydrazine (35 wt. % in water, Aldrich) followed by heating at 100 °C for 2 hours. Finally, the suspension of rGO/pMWNT was filtered by Nylon membrane filter (pore size of 0.2 μm, Corning) and redispersed at a concentration of 0.50 mg/mL of rGO. rGO sheets were stabilized by PDAC functionalization to prevent restacking. PDAC Functionalized rGO was written as rGO for simple notation.

**Preparation of rGO, pMWNT and rGO/pMWNT<sub>(0.5:1)</sub> thin films for contact angle measurement.** rGO, pMWNT and rGO/pMWNT<sub>(0.5:1)</sub> solutions were filtered with anodic aluminum oxide (AAO) membrane. After several times washing with deionized water, uniform films were formed on the membrane. To measure contact angle, a water droplet was dropped on each film and the contact angle image was captured immediately after forming the contact interface.

**Preparation of catalysts ink and working electrode.** Actual concentrations of each solution were 2.3 mg/ml for rGO, 2.8 mg/ml for pMWNT and 1.5 mg/ml for rGO/pMWNT<sub>(0.5:1)</sub>, respectively. For comparison, 20% Pt on Vulcan XC-72 catalysts (Premetek Co.) ink was prepared by ultrasonically mixing 2 mg of the catalyst powder with 2 mL in distilled water at least 1 h. Then, 6 μL of each solution including Pt/C catalyst was loaded on the polished glassy carbon (GC) electrode of 4 mm diameter (RRDE Pt Ring/GC Disk Electrode, cat. NO. 011162, ALS Co., Ltd.). Corresponding loading densities were 109 μg<sub>Cat</sub>/cm<sup>2</sup> for rGO, 133 μg<sub>Cat</sub>/cm<sup>2</sup> for pMWNT, 71.2 μg<sub>Cat</sub>/cm<sup>2</sup> for rGO/pMWNT<sub>(0.5:1)</sub>, and 20 μg<sub>Pt</sub>/cm<sup>2</sup> for Pt,

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respectively. Before applying each catalyst, glassy carbon electrodes were polished with 0.05  $\mu\text{m}$  polishing alumina to maintain a good condition of working electrode (PK-3 Electrode Polishing kit, ALS Co., Ltd.). Catalyst-coated GC electrodes were then dried under vacuum at room temperature for at least 20 min.

**Rotating Ring Disk Electrode (RRDE) experiment.** Rotating ring disk electrode (RRDE) (ALS Co., Ltd) experiments were carried out using the as-prepared catalysts film (deposited on GC electrode) as the working electrode in 0.1 M KOH alkaline electrolyte. Pt wire and SCE are used as a counter and a reference electrode, respectively. Before RRDE test, 0.1 M KOH electrolyte was bubbled with pure oxygen gas (99.9%) for 30 min. Electrochemical characterization was conducted using bi-potentiostat (IviumStat). 10 mV of scan rate was swept from 0.15 to -0.8 V and sufficient ring potential of 0.4 V was biased to oxidize intermediate during ORR. The collection efficiency ( $N$ ) was determined under Ar atmosphere using 10 mM  $\text{K}_3[\text{Fe}(\text{CN})_6]$ , which is around 0.41. This value is very close to its theoretical value of 0.42. Hydrogen peroxide yields and the number of electrons transferred ( $n$ ) were calculated using the equations below. Furthermore, rotating disk electrode (RDE) (ALS Co., Ltd) experiments were carried out under aforementioned condition to construct the Koutecky–Levich plot.

$$H_2O_2(\%) = 100 \frac{2I_r / N}{I_d + I_r / N} \quad (1)$$

$$n = 4 \frac{I_d}{I_d + I_r / N} \quad (2)$$

**Calculating the number of transferred electrons ( $n$ ) of the as-prepared catalysts from the slope of the Koutecky–Levich plot.** Koutecky-Levich plot relates the current density ( $i$ ) to the rotation rate of electrode ( $\omega$ ) and allows one to determine both kinetic current ( $i_k$ ) and number of transferred electrons ( $n$ ) involved in ORR.

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_{dl}} = \frac{1}{i_k} + \frac{1}{B\omega^{0.5}} \quad (3)$$

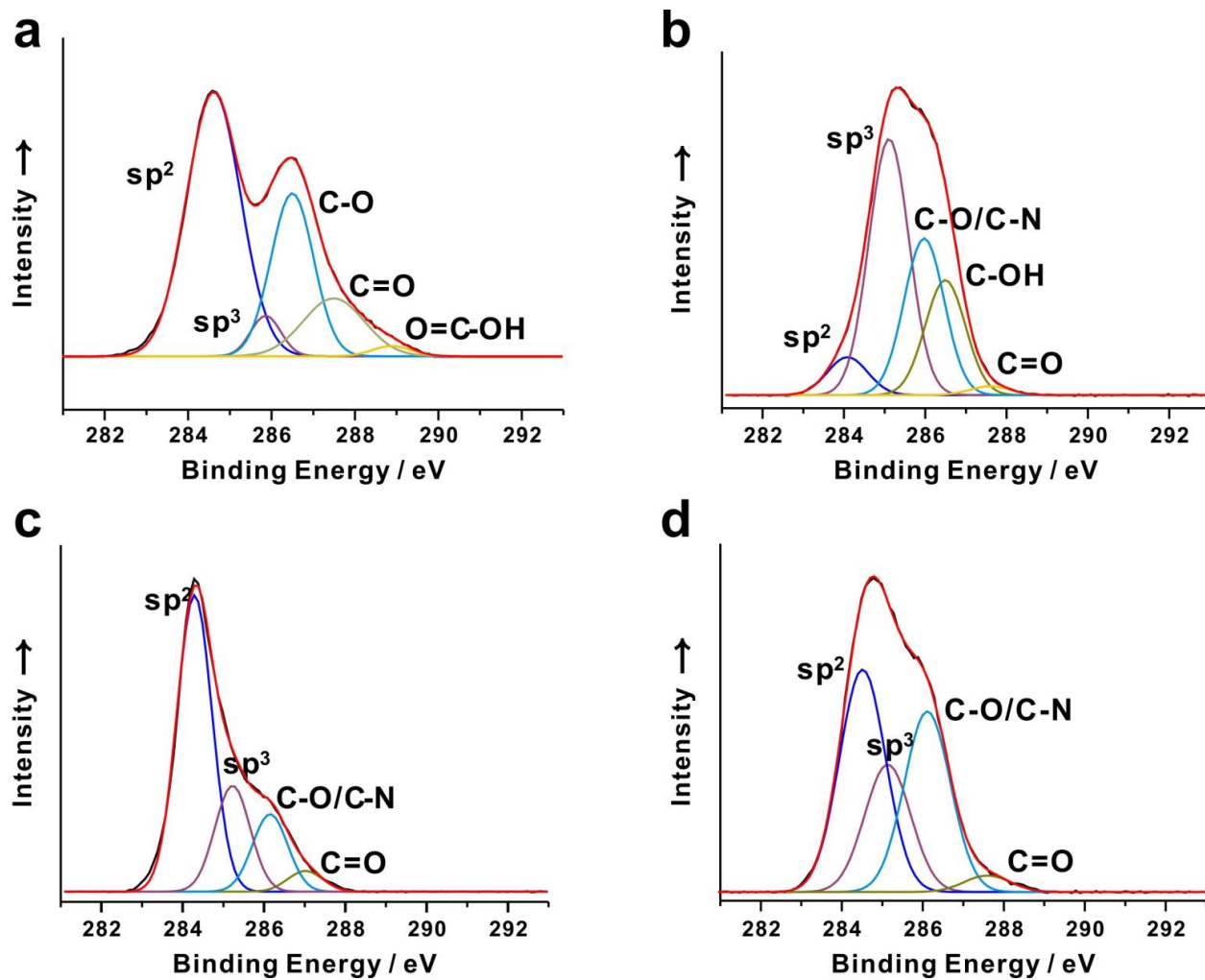
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$$i_k = nFAkC_{O_2} \text{ (Kinetic current)} \quad (4)$$

$$\begin{aligned} i_{dl} &= 0.62nFAC_{O_2}D_{O_2}^{2/3}\nu^{-1/6}\omega^{1/2} \text{ (Diffusion current)} \quad (5) \\ &= 0.620\left(\frac{2\pi}{60}\right)^{1/2}nFAC_{O_2}(\omega' = \text{rpm number})^{1/2}D_{O_2}^{2/3}\nu^{-1/6} \\ &= 0.2nFAC_{O_2}(\omega' = \text{rpm number})^{1/2}D_{O_2}^{2/3}\nu^{-1/6} \end{aligned}$$

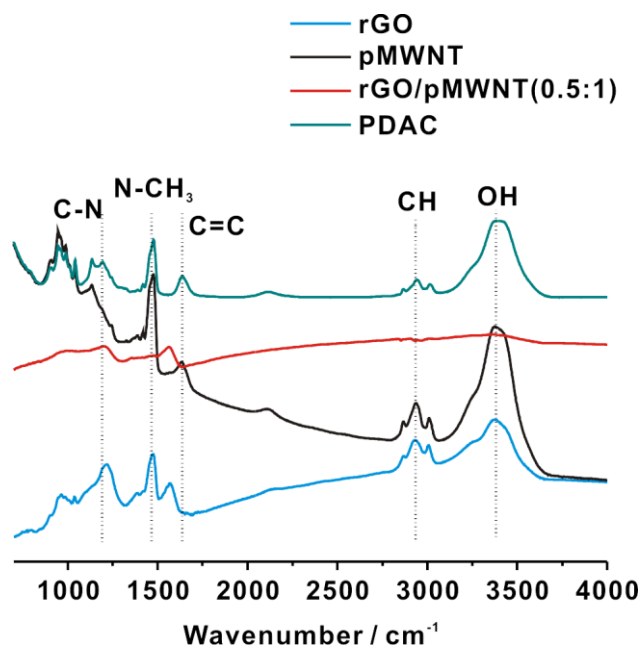
where  $i_k$  represents the kinetic current;  $i_{dl}$  is diffusion limiting current;  $n$  is the number of electrons transferred per  $O_2$  molecule;  $F$  is the Faraday constant (96485 C/mol);  $A$  is the geometric area of the disk electrode ( $7.06 \times 10^{-6} \text{ m}^2$ );  $k$  (m/s) is the rate constant for the ORR;  $C_{O_2}$  is the saturated concentration of  $O_2$  in solution (1.21 mol/m<sup>3</sup> in 0.10 M KOH);  $\nu$  is the kinematic viscosity ( $1 \times 10^{-6} \text{ m}^2/\text{s}$  in 0.10 M KOH);  $D_{O_2}$  is the diffusion coefficient of  $O_2$  in solution ( $1.87 \times 10^{-9} \text{ m}^2/\text{s}$  in 0.10 M KOH).  $\omega$  and  $\omega'$  are the angular frequency of the rotation (rad/s) and electrode rotation rate in rpm, respectively. 0.2 is a constant when the rotation speed is expressed in rpm. From the linear relationship between  $i^{-1}$  vs  $\omega^{1/2}$  based on the Koutecky-Levich equation, we can obtain the electrons transferred ( $n$ ) from the slope.

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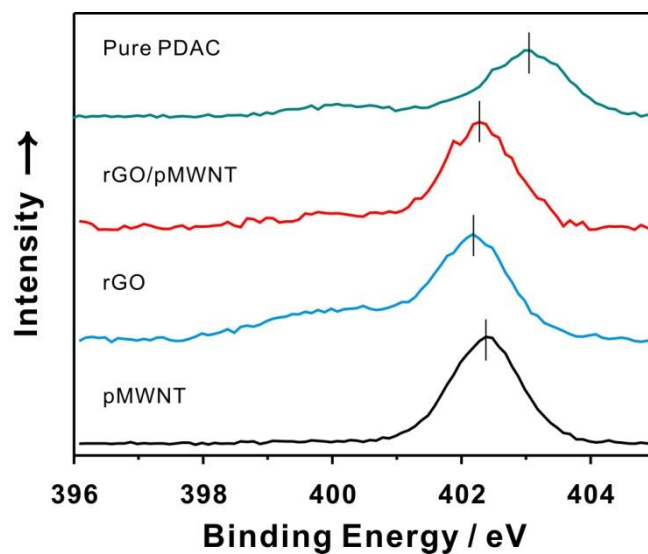
**Fig. S1** High-resolution C 1s XPS spectra of all samples used in the study. (a) GO, (b) pMWNT, (c) rGO/pMWNT<sub>(0.5:1)</sub>, and (d) rGO.

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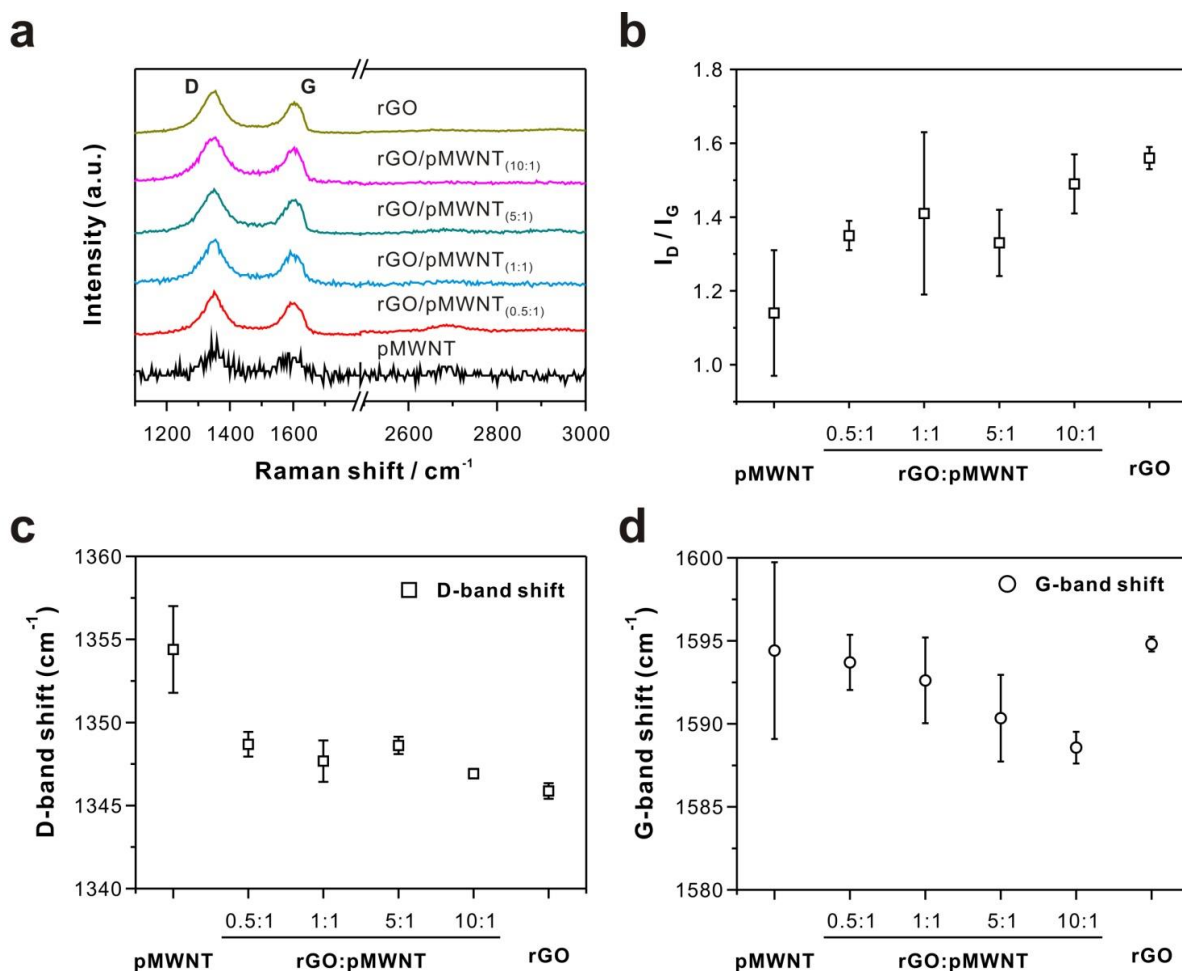
**Fig. S2** FT-IR spectra of rGO, pMWNT, rGO/pMWNT<sub>(0.5:1)</sub>, and pure PDAC. All peaks are assigned with the data of previous literature.<sup>S3</sup>

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**Fig. S3** High-resolution N 1s XPS spectra of all samples used in the study. Negative shift of N 1s peak from 402 eV (pure PDAC) to 401.5 eV (pMWNT) can be attributed to intermolecular charge-transfer of quaternary ammonium nitrogen.

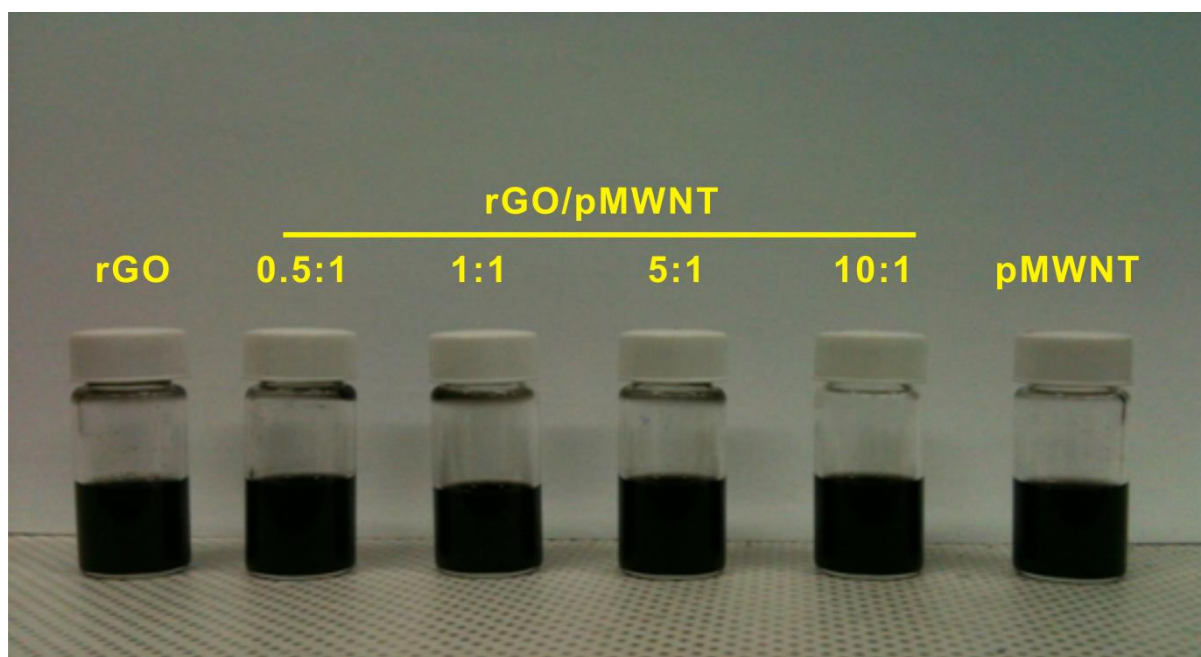
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**Fig. S4** (a) Raman spectra of all samples used in the study, (b) ratio of  $I_D/I_G$ , (c) D-band shift, and (d) G-band shift of all samples. The  $I_D/I_G$  ratio increased from 1.14 in pMWNT to 1.35 in rGO/pMWNT<sub>(0.5:1)</sub> and even to 1.49 in rGO/pMWNT<sub>(10:1)</sub>, indicating the disordered graphitic structures of hybrid electrocatalysts upon introduction of rGO into pMWNT. The  $I_D/I_G$  ratio was measured at least 5 different points of each sample. Up-shift of G bands from 1594.2  $\text{cm}^{-1}$  in pMWNT to 1588.6  $\text{cm}^{-1}$  in rGO/pMWNT<sub>(10:1)</sub> illustrated the charge transfer between rGO and pMWNT.

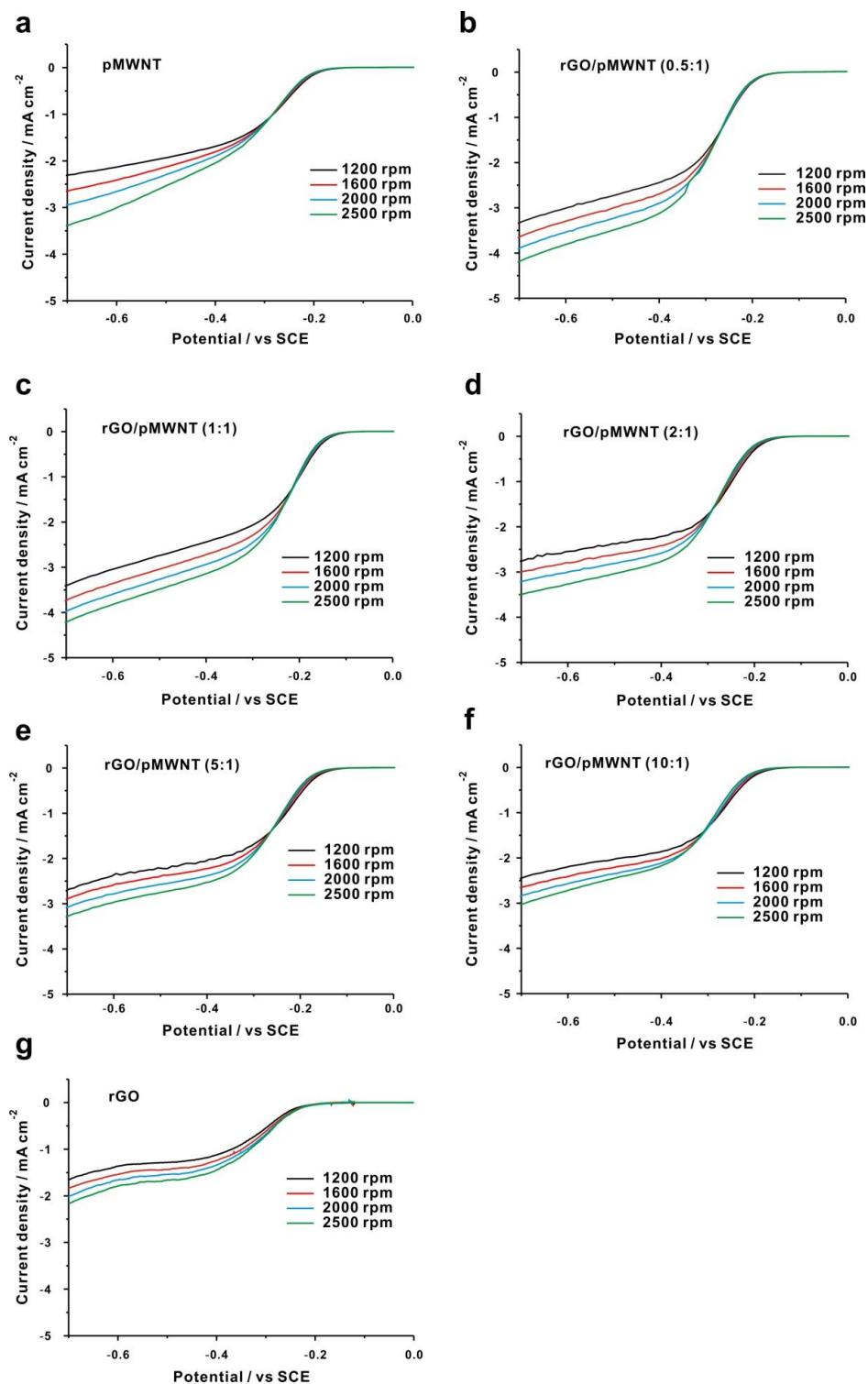


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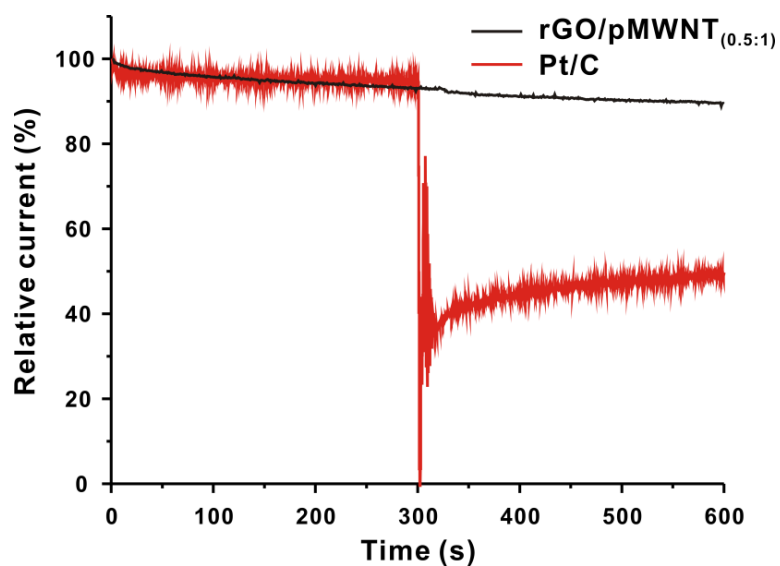
**Fig. S5** Photograph of each suspension prepared in this study at a concentration of 0.50 mg/mL. The stability of the suspension remained over 8 months.

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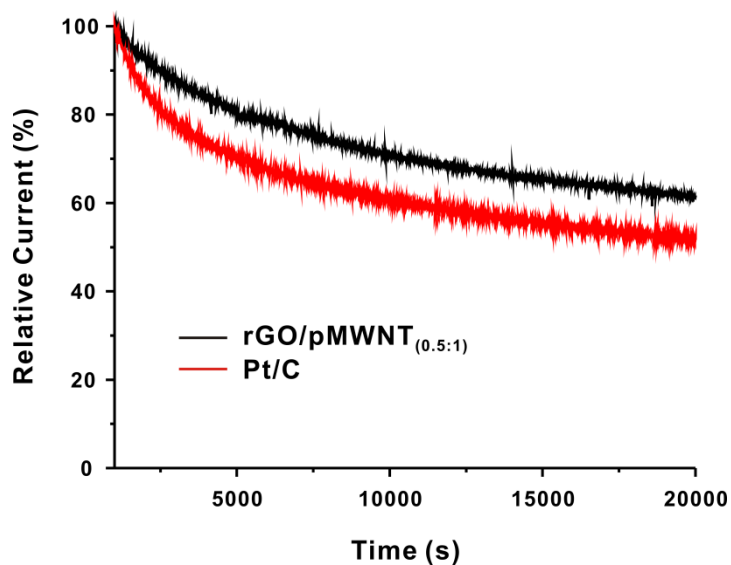
**Fig. S6** Linear sweep voltammetry (LSV) curves of (a) pMWNT, (b) rGO/pMWNT<sub>(0.5:1)</sub>, (c) rGO/pMWNT<sub>(1:1)</sub>, (d) rGO/pMWNT<sub>(2:1)</sub>, (e) rGO/pMWNT<sub>(5:1)</sub>, (f) rGO/pMWNT<sub>(10:1)</sub>, and (g) rGO measured in O<sub>2</sub>-saturated 0.1 M KOH solution.

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**Fig. S7** Current-time (*i-t*) chronoamperometric response of rGO/pMWNT<sub>(0.5:1)</sub> in O<sub>2</sub>-saturated 0.1 M KOH at -0.4 V (vs. SCE). 3 M of methanol was added at about 300 s to show crossover effect does not occur.

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**Fig. S8** The chronoamperometric durability response for 20000 s verified that the rGO/pMWNT<sub>(0.5:1)</sub> composite exhibited a very slow attenuation with high current retention of 61%, a value which is higher than that of Pt/C in the O<sub>2</sub>-saturated 0.1 M KOH solution at -0.25 V (vs. SCE). Electrode rotation rate: 1600 rpm.

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**Table S1.** ORR Catalytic Activity of Metal-free Catalyst according to method and components

Hybrid (Components)	Procedure (Different Components)	Voltage (vs Reference electrode)	Average Number of Electron Transferred (Procedure)	Reference (Journal/ Year)
Carbon Nitride (Graphene Oxide, Melamine)	600 °C Thermal Annealing	-0.8 V (vs Ag/AgCl)	3.4-3.6	S1 (ACS Nano/ 2011)
N-doped Graphene (Graphene Oxide, Cyanamide)	900 °C Thermal Annealing	-0.8 V (vs Ag/AgCl)	3.54	S2 (ACS Nano/ 2012)
PDAC functionalized CNT  (CNT, Vertically aligned CNT, PDAC)	A. Sonication (CNT)  B. 950 °C CVD growth (Vertically aligned CNT)	-0.8 V (vs SCE)	3.08 (A) 3.72 (B)	S3 (J. Am. Chem. Soc./ 2011)
S, N Dual-doped Mesoporous Graphene  (Graphene Oxide, Melamine, Benzyl disulfide)	900 °C Thermal Annealing, HF treatment	-0.6 V (vs Ag/AgCl)	3.6	S4 (Angew. Chem. Int. Ed./2012)
Macroporous Graphitic Carbon Nitride  (Carbon shell with Silica, Cyanamide,)	900 °C Carbonization	-0.75 V (vs Ag/AgCl)	3.17	S5 (Angew. Chem. Int. Ed./2012)
rGO/pMWNT	<b>Physical mixing</b> <b>100 °C Reduction</b>	-0.8 V (vs SCE)	3.6	<b>Our Work</b>

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- S2. K. Parvez, S. Yang, Y. Hernandez, A. Winter, A. Turchanin, X. Feng and K. Müllen, *ACS Nano*, 2012, **6**, 9541-9550.
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- S4. J. Liang, Y. Jiao, M. Jaroniec and S. Z. Qiao, *Angew. Chem. Int. Ed.*, 2012, **51**, 11496-11500.
- S5. J. Liang, Y. Zheng, J. Chen, J. Liu, D. Hulicova-Jurcakova, M. Jaroniec and S. Z. Qiao, *Angew. Chem. Int. Ed.*, 2012, **51**, 3892-3896.