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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.[S3] 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$_{(0.5:1)}$ thin films for contact angle measurement. rGO, pMWNT and rGO/pMWNT$_{(0.5:1)}$ 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$_{(0.5:1),}$ 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, 6μL 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 $\mu g_{Cat}/cm^2$ for rGO, 133 $\mu g_{Cat}/cm^2$ for pMWNT, 71.2 $\mu g_{Cat}/cm^2$ for rGO/pMWNT$_{(0.5:1)}$, and 20 $\mu g_{Pt}/cm^2$ for Pt, respectively. Before applying each catalyst, glassy carbon electrodes were polished with 0.05 µm 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 $K_3[Fe(CN)_6]$, 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.

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

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

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 (*ω*) and allows one to determine both kinetic current (i_k) and number of transferred electrons (*n*) involved in ORR.

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

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

$$i_{dl} = 0.62nFAC_{O_2}D_{O_2}{}^{2/3}v^{-1/6}\omega^{1/2} \text{ (Diffusion current)} \qquad (5)$$

$$= 0.620(\frac{2\pi}{60})^{1/2} nFAC_{O_2}(\omega' = \text{rpm number})^{1/2} D_{O_2}{}^{2/3} v^{-1/6}$$

$$= 0.2nFAC_{O_2}(\omega' = \text{rpm number})^{1/2} D_{O_2}{}^{2/3} v^{-1/6}$$

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 (7.06×10^{-6} 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^3 in 0.10 M KOH); v is the kinematic viscosity (1×10^{-6} m^2/s in 0.10 M KOH); D_{O_2} is the diffusion coefficient of O_2 in solution (1.87×10^{-9} m^2/s in 0.10 M KOH). ω and ω' 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.

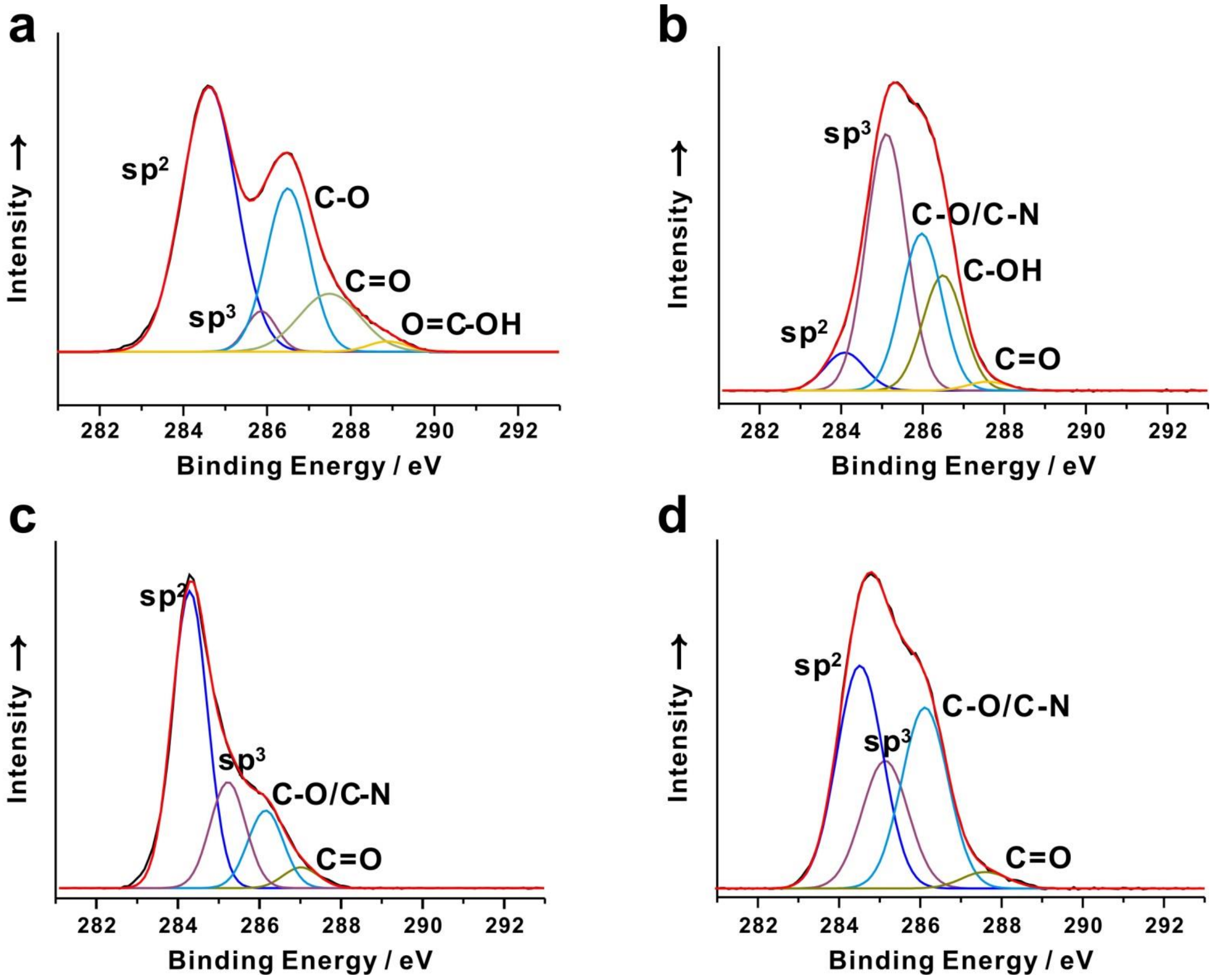

Fig. S1 High-resolution C 1s XPS spectra of all samples used in the study. (a) GO, (b) pMWNT, (c) rGO/pMWNT$_{(0.5:1)}$, and (d) rGO.

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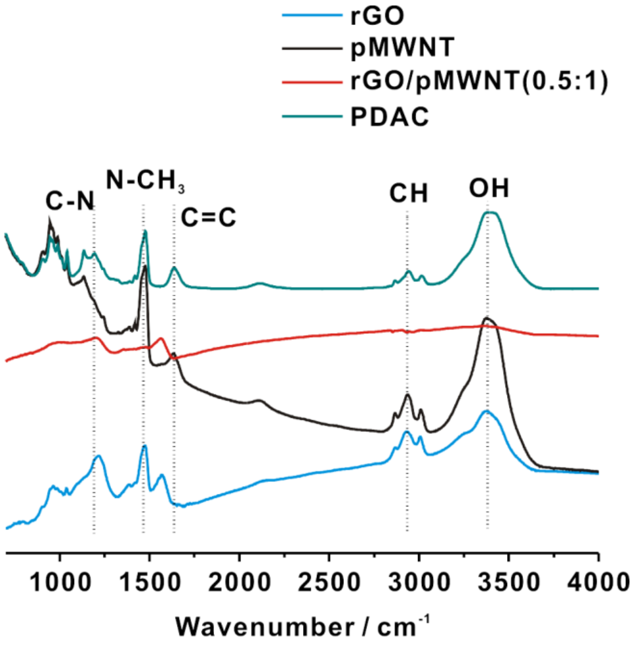

Fig. S2 FT-IR spectra of rGO, pMWNT, rGO/pMWNT$_{(0.5:1)}$, and pure PDAC. All peaks are assigned with the data of previous literature.[S3]

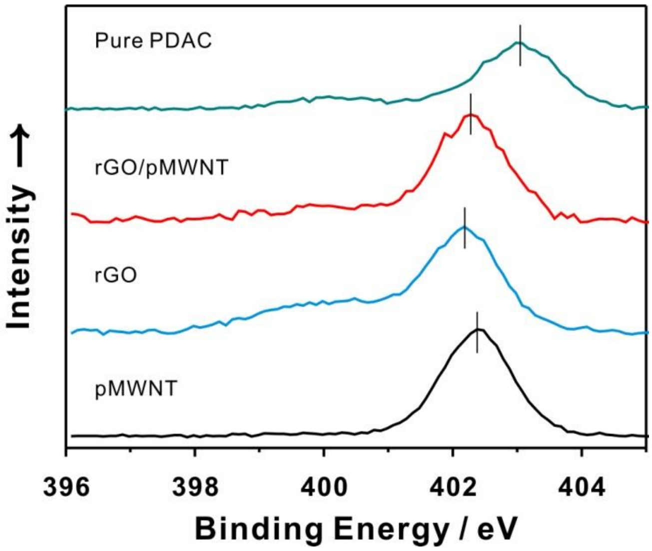

Fig. S3 High-resolution N 1s XPS spectra of all samples used in the study. Negative shift of N 1s peak from 402 eV (pure PDAC) to 401.5 eV (pMWNT) can be attributed to intermolecular charge-transfer of quaternary ammonium nitrogen.

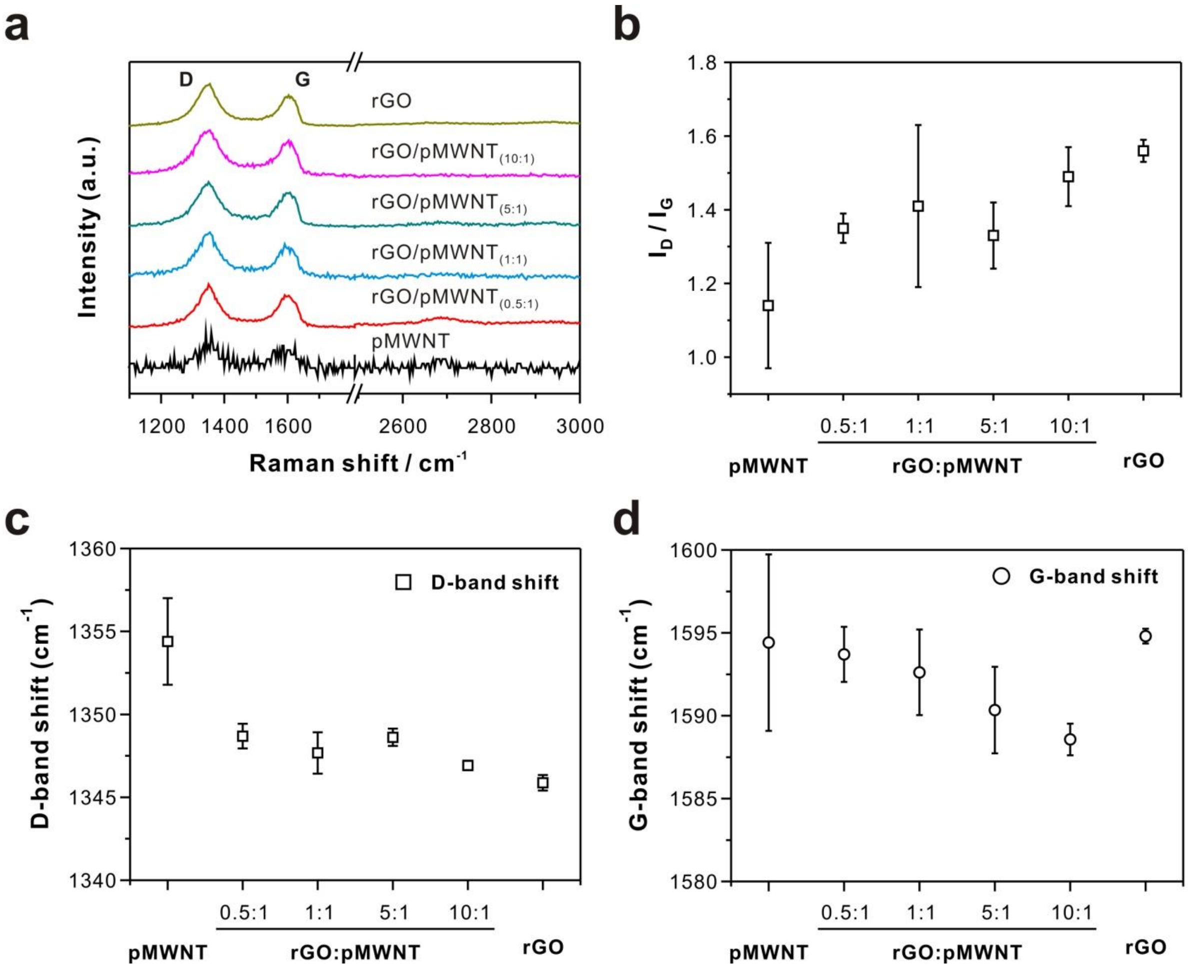

Fig. S4 (a) Raman spectra of all samples used in the study, (b) ratio of I_D/I_G, (c) D-band shift, and (d) G-band shift of all samples. The I_D/I_G ratio increased from 1.14 in pMWNT to 1.35 in rGO/pMWNT$_{(0.5:1)}$ and even to 1.49 in rGO/pMWNT$_{(10:1)}$, indicating the disordered graphitic structures 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 cm^{-1} in pMWNT to 1588.6 cm^{-1} in rGO/pMWNT$_{(10:1)}$ illustrated the charge transfer between rGO and pMWNT.

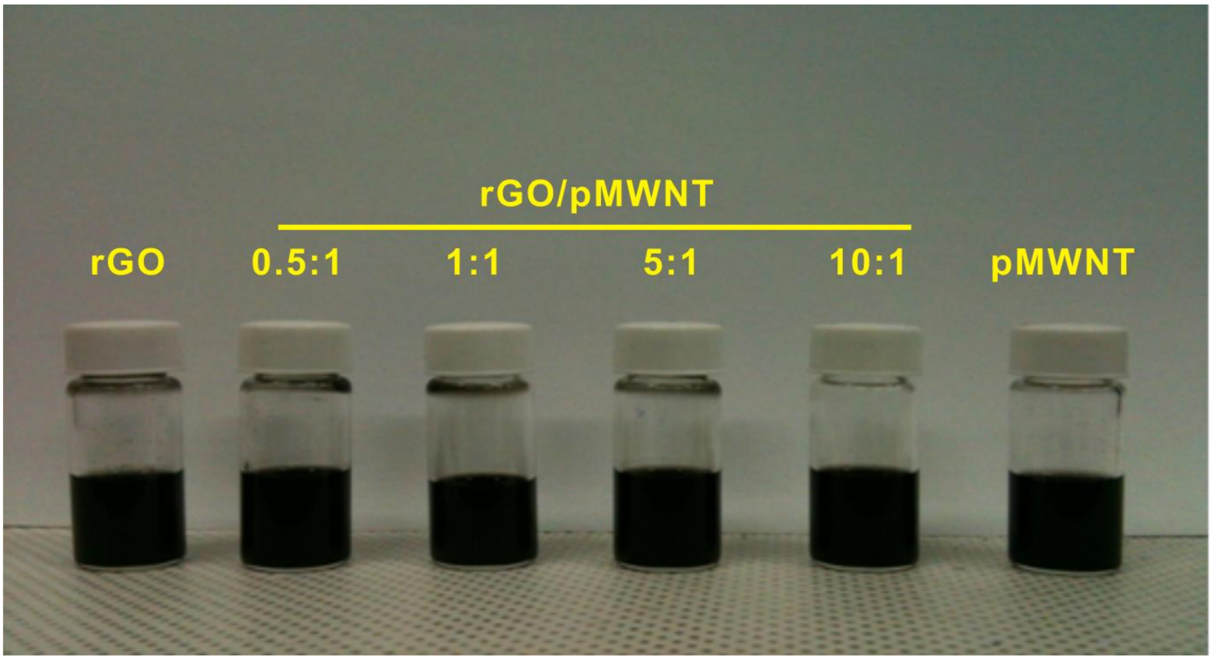

Fig. S5 Photograph of each suspension prepared in this study at a concentration of 0.50 mg/mL. The stability of the suspension remained over 8 months.

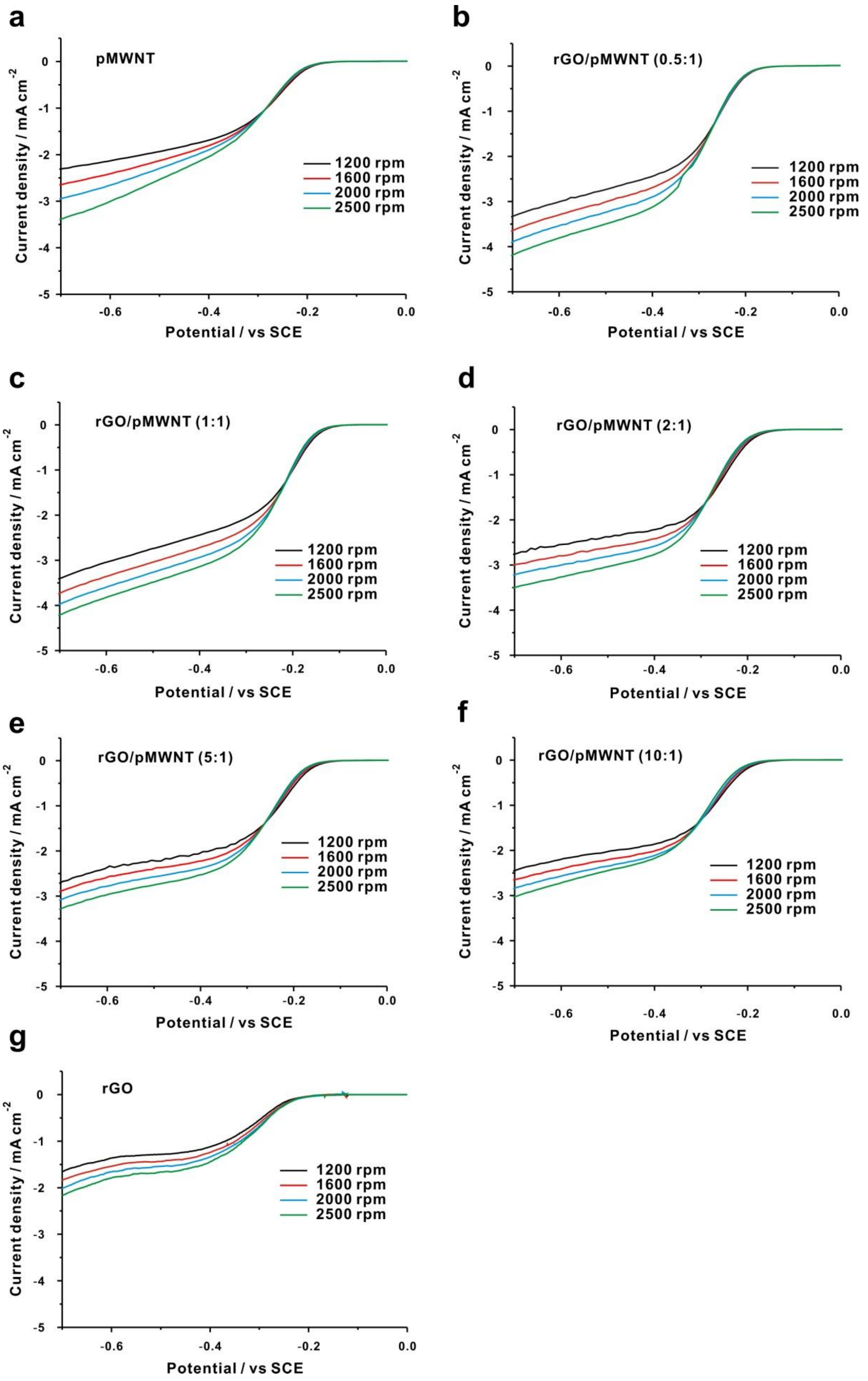

Fig. S6 Linear sweep voltammetry (LSV) curves of (a) pMWNT, (b) rGO/pMWNT$_{(0.5:1)}$, (c) rGO/pMWNT$_{(1:1)}$, (d) rGO/pMWNT$_{(2:1)}$, (e) rGO/pMWNT$_{(5:1)}$, (f) rGO/pMWNT$_{(10:1)}$, and (g) rGO measured in O_2-saturated 0.1 M KOH solution.

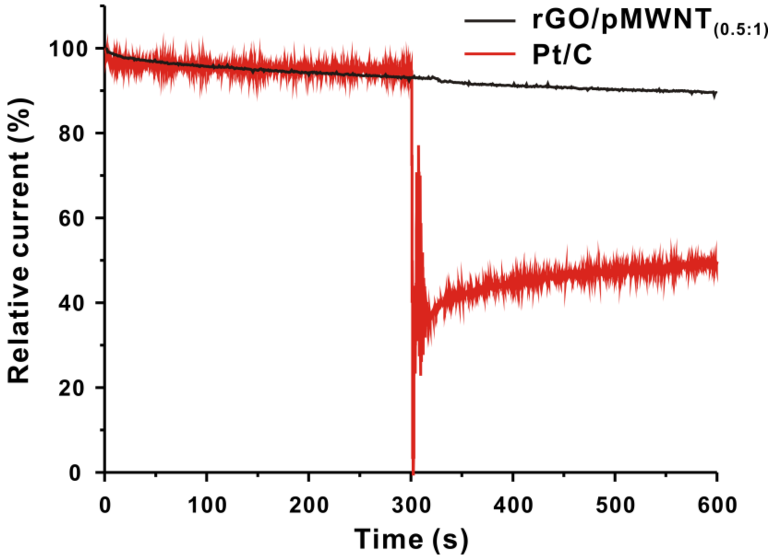

Fig. S7 Current-time (*i*-*t*) chronoamperometric response of rGO/pMWNT$_{(0.5:1)}$ in O_2-saturated 0.1 M KOH at -0.4 V (vs. SCE). 3 M of methanol was added at about 300 s to show crossover effect does not occur.

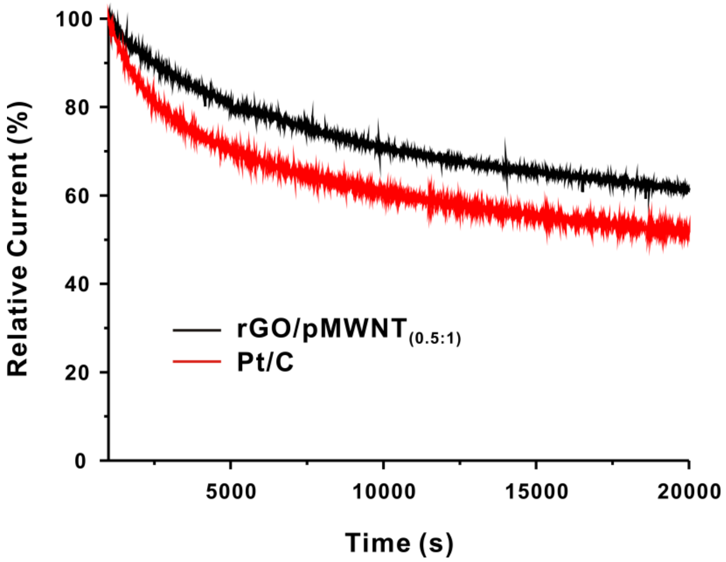

Fig. S8 The chronoamperometric durability response for 20000 s verified that the rGO/pMWNT$_{(0.5:1)}$ composite exhibited a very slow attenuation with high current retention of 61%, a value which is higher than that of Pt/C in the O_2-saturated 0.1 M KOH solution at -0.25 V (*vs*. SCE). Electrode rotation 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	**Physical mixing** **100 °C Reduction**	-0.8 V (vs SCE)	3.6	**Our Work**

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