Electronic Supplementary Information

Embedding activated carbon nanospheres into polymer-derived porous carbon networks to boost electrocatalytic oxygen reduction

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1. Experimental Section

1.1. Synthesis of TB

TB was synethisized via a one-step knitting method according to the literatures.¹⁻⁴ The 1,3,5triphenylbenzene (0.613 g) and benzene (0.47 g) were used as monomers. 1.36 g of dimethoxymethane was introduced as the cross-linker and then 2.9 g of FeCl₃ was added to the mixture as catalyst. The mixture was heated in 1,2-dichloroethane (DCE, 8 mL) solvent and reacted at 45 °C for 5 h to form a network and then heated at 80 °C for 19 hours to complete the condensation reaction. The resulting solid product was Soxhlet extracted by methanol until the filtrate was almost colorless and then dried in an oven at 80 °C.

1.2. Synthesis of Oxygen-Functionalization Activated Carbon/Porous Carbon

(AC/TBC(O)) Heterostructure

The resulted TB and activated carbon (commercial Vulcan XC-72) spheres were respectively acidified by refluxing in hydrochloric acid [HCl : water = 1:5 (volume ratio)] and 5 M nitric acid for 10 h. 20 mg of the acid treated AC and 180 mg of the acid treated TB were mixed by ultrasonication in 30 ml ethanol for 3 h. In the hydrothemal process, the dried powders were redispersed in 16 mL of 0.4 M glucose solution by ultrasonication for 4 h and then transferred to a 50 mL Teflon autoclave, maintaining at 120 °C for 10 h. The AC/TB(O)@glu composite was collected by centrifugation, washing and drying. Finally, the composite was calcined at 1000 °C at a rate of 20 °C min⁻¹ for 2 h in a N₂ atmosphere to yield the carbon heterostructure, which was labeled as AC/TBC(O). For comparison, the AC+TBC(O) catalyst was prepared in the similar procedure without adding glucose solution. And the single-component carbon, TBC, was obtained by direct pyrolysis of TB. The AC(O) and TBC(O) samples were synthesized in the same procedure in the absence of another one.

The AC/TBC(O) heterostructures with different composition were obtained by varing the adding amount of AC (10, 20, 30, 40 mg) when mixing with TB. The AC/TBC(O)-H₂ was prepared as a control through annealing the AC/TBC(O) heterostructure at 400 °C for 2 h in N_2/H_2 (95 %/5 %) with rate of 2 °C min⁻¹. Different pyrolysis temperature was set as 800 and 900 °C to produce AC/TBC(O)-T (T represented the pyrolysis temperature).

In order to testify the possible universality of the strategy, three kinds of N-doped carbon heterostructures (AC/gCN(O), AC/NTTC(O), and AC/TBC(O)+N) were fabricated by introducing N-containing precursors, graphitic carbon nitride (g-C₃N₄), 2,4,6-triphenyl-1,3,5-triazine (TT monomer), mixing melamine with AC/TBC(O) precursor. g-C₃N₄ was prepared by calcination of urea (15 g) in a muffle furnace at 550 °C for 4 h. The AC/gCN(O) sample was synthesized in the same procedure by adding 20 mg of the acid treated AC and 180 mg of g-C₃N₄. AC/NTTC(O) was prepared under the same method with AC/TBC(O) heterostructure by adding 0.618 g of 2,4,6-triphenyl-1,3,5-triazine (TT monomer) instead of TB monomer. AC/TBC(O)+N was obtained by mixing melamine with the AC/TB(O)@glu composite at a mass ratio of 1:2 by grinding and the following pyrolysis under identical condition. The descriptions of the mentioned samples are summarized in Table S1.

2. Material characterization

The morphology of the samples was examined by field emission scanning electron microscope (FESEM, SU8010) and high-resolution transmission electron microscopy (HRTEM, Talos, F200X). X-ray powder diffraction (XRD) patterns were collected on a PANalytical B.V. instrument equipped with Cu K α irradiation at an operation 40 kV voltage and 40 mA current. Raman spectra data were recorded using a 523 nm argon laser with a LabRAM HR800 (HORIBA Scientic, France). The fourier transform infrared (FT-IR) spectra were obtained under

ambient conditions in the wavenumber range of 4000-500 cm⁻¹ via a Bruker Vertex 70 Spectrometer using the KBr disk method. X-ray photoelectron spectroscopy (XPS) measurements were performed with an ESCALAB 250 X-ray photoelectron spectrometer using Al Ka radiation to analyze the surface of the obtained samples. The specific surface area was calculated Nonlocal density functional theory (NLDFT) method on Micromeritics TriStar II 3flex, the cylindrical model, was utilized to obtain the pore size distribution.

3. Electrochemical measurements

All the tests were operated on a CHI650E with a standard three-electrode electrochemical cell. Glassy carbon (GC, 5.0 mm in diameter) electrode works as the working electrode, an Ag/AgCl (3.5 M KCl) electrode as the reference electrode, and a carbon electrode as the counter electrode. 2 mg catalysts were dispersed in 0.4 mL mixed solution of 392 μ L alcohol and 8 μ L of 5wt% Nafion by 30 min sonication to obtain a catalyst "ink". 22 μ L sample suspensions were dropped on GC electrode with the catalyst loading 0.560 mg cm⁻² after drying at room temperature. For comparison, Pt(20 wt%)/C suspension was prepared as the same procedure with the Pt loading 15.28 μ g_{Pt} cm⁻².The Koutechy-Levich (K-L) plots were obtained by analyzing the RDE data at different electrode potentials. All potentials were referred to the RHE by following calculations: *E* (vs RHE) =*E* (vs Ag/AgCl) + 0.197V + 0.059 pH. The slopes of their linear fitting lines are used to calculate the electron transfer number (n) based on the following K-L equations:

$$1/J = 1/J_k + 1/Bw^{1/2} \tag{1}$$

$$B = 0.2nFAv^{-1/6}C_o D_o^{2/3}$$
⁽²⁾

Where *J* is the measured current density, $J_{\rm K}$ is the kinetic limiting current density, *w* is the electrode rotating rate, *F* is the Faraday constant (96500 C mol⁻¹), D_0 is the diffusion coefficient

of O₂ in 0.1 M KOH ($D_0 = 1.9*10^5 \text{ cm}^2 \text{ s}^{-1}$). C_0 is the bulk concentration of O₂ ($C_o = 1.2*10^6 \text{ mol} \text{ cm}^{-3}$), and *n* is the kinetic viscosity ($n = 0.01 \text{ cm}^2 \text{ s}^{-1}$). The constant 0.2 is adopted when the rotation rate is expressed in rpm.



Fig. S1 FSEM spectra of TB.



Fig. S2 N_2 adsorption and desorption isotherms and pore size distribution of of TB.



Fig. S3 SEM and FTEM images of contrast sample AC.



Fig. S4 FT-IR spectra comparison of TB and AC before and after acidification.

For TB sample, the peaks located at 1605, 1501, and 1439 cm⁻¹ were attributed to the aromatic ring skeleton vibrations which were consistent with the structure of monomers.¹ For AC sample, the peaks at 1388 and 1595 cm⁻¹ could be assigned to the aromatic C=C groups.^{5,6} After acidification, the newly appeared peak at 1737 cm⁻¹ corresponded to the C=O vibrations in the COOH group, suggesting the abundance of COOH groups in the carbon networks.⁵⁻⁷



Fig. S5 FSEM images of the oxygen-functionalized activated carbon/TB-derived porous carbon (AC/TBC(O)) heterostructure.



Fig. S6 a) XPS survey spectra of AC(O), TBC (O) and AC/TBC(O). High resolution XPS spectra of b) C1s and c) O1s of AC(O), TBC (O) and AC/TBC(O).

The high resolution C1s spectrum of AC/TBC(O) can be divided into four peaks cantered at 284.8, 285.8, 287.0 and 290.1 eV, which can be assigned to C-C/C=C, C-O, C=O and π - π * shake-up satellites, respectively (Fig. S6b).^{8,9} Correspondingly, the high resolution O1s spectrum after peak deconvolution contains C=O (531.7 eV) and C-O (533.4 eV) groups (Fig. S6c).¹⁰ The additional peak at 536.4 eV represents the chemisorbed oxygen or water (H-O-H) on the surface.



Fig. S7 a) XPS survey spectrum, b) high resolution spectrum of C1s and c) high resolution spectrum of O1s of TBC.



Fig. S8 Raman spectra for a) AC/TBC(O) and TBC, b) AC(O) and AC, c) TBC(O) and TBC, d) AC/TBC(O)-800 and AC/TBC(O)-900.

There are two strong peaks cantered at 1319 and 1572 cm⁻¹, corresponding to the sp³ defect sites (D band) and graphitic sp²-bonded carbon (G band), respectively. An obvious shift in the peak positions of Raman spectra can be observed between TBC and AC/TBC(O). Three couples of samples were compared to explain the difference, i.e. AC and AC(O), TBC and TBC(O), TBC and AC/TBC(O). Interestingly, there is no shift in the location of D and G bands between the carbon with and without oxygen functional groups. The functionalization caused the I_D/I_G values to be increased from 1.00 to 1.10 for AC and from 1.15 to 1.20 for TBC. The results indicate that the introduction of oxygenic groups did not change the positions of D and G bands but bring about the higher defect level.¹¹ In addition, the loss of 2D structure reflected the disordering of carbon structure by oxidation. Therefore, the shift only occurs in the formation of AC/TBC(O)

heterostructure, which further evidenced the interfacial interaction between two kinds of carbons. Generally, the elevated pyrolysis temperature should improve the graphitization degree of carbon materials,^{12,13} however, the I_D/I_G value increased with the temperature from 800 to 1000 °C. This abnormal change can also be found in many heteroatom-doped carbon materials mainly because the heteroatoms are inclined to escaping from the carbon network at the elevated temperature to produce more surface defects as exposed active sites for electrocatalysis.^{14,15}



Fig. S9 a) N₂ adsorption and desorption isotherms and b) pore size distribution of TBC(O) and AC/TBC(O).

Similar to TB polymer, the isotherms of the polymer-derived carbon displayed a typical type I curve, which is characteristic of microporous property.



Fig. S10 N₂ adsorption/desorption isotherms and pore size distribution of a, b) AC (O) and c, d) AC/TBC (O)-900,800.

The activated carbon materials exhibited a typical IV isotherm curve, indicating the existence of meso- and macroporosity. When elevating the temperature from 800 to 1000 °C, the surface area of the heterostructure increased while the proportion of micropores decreased (Table S4). It could be explained that the high temperature treatment induced the collapse of the polymer skeleton to produce ultrahigh specific surface area of 2042 m² g⁻¹ and large pore volume of 1.54 cm³ g⁻¹.



Fig. S11 LSV curves of samples prepared in the same procedure with or without adding glucose solution. The samples that prepared by similar procedure without adding glucose are labeled as AC-no glu., TBC(O)-no glu. and AC+TBC(O), respectively.



Fig. S12 XPS spectra of O1s of AC(O), TBC (O), AC/TBC(O) and AC+TBC(O).



Fig. S13 a) N₂ adsorption and desorption isotherms and b) pore size distribution of AC+TBC(O).

In comparison to the AC/TBC(O) heterostructure, the AC+TBC(O) catalyst possesses a much lower specific surface area (1070 m² g⁻¹) and pore volume (0.844 cm³ g⁻¹) (Table S4). Actually, its surface area is even lower than that of TBC(O) (1573 m² g⁻¹).



Fig. S14 EIS Nyquist plots of the samples.

The weak interfacial interactions in AC+TBC(O) catalyst were unfavorable for electron transfer and therefore decreasing the ORR efficiency. On the contrary, the embedding of conductive AC into TBC network effectively reduced the electron-transfer resistance of TBC electrode.



Fig. S15 LSV curves of AC/TBC(O)-X%, X% represents the mass percentage of AC (0%, 5%, 10%, 15%, 20%) when mixing with TB. The AC/TBC(O)-0% is the same as TBC(O) and the AC/TBC(O)-10% is AC/TBC(O).



Fig. S16 Comparison in LSV curves between the pristine carbon and oxygen-functionalized carbon.

In contrast to pristine carbons, AC and TBC, both AC(O) and TBC(O) exhibited greatly improved ORR efficiency, which verified that the local sites with oxygenic groups and defects were more catalytically active than those in pristine carbon network.



Fig. S17 Raman spectra of the AC/TBC(O) after N_2/H_2 reduction.



Fig. S18 ORR activities of AC/TBC(O) before and after N_2/H_2 reduction in O₂-saturated 0.1M KOH aqueous solutions with a scan rate of 10 mV s⁻¹ and a rotation rate of 1600 rpm.



Fig. S19 The contact angles and wetting behaviors of a) pristine AC spheres, b) AC(O), c) AC/TBC(O), and d) AC/TBC(O)-H₂.

The contact angles of pristine AC spheres, AC/TBC(O) and AC/TBC(O)-H₂ are 131.4°, 34.4° and 125.6°, respectively. The pristine AC spheres has typical hydrophobic property, whereas the introduction of oxygenic groups increases the surface hydrophilicity to be completely wettable. The reverse transform to hydrophobic surface further evidenced the removal of oxygenic groups after the reduction by H₂.



Fig. S20 ORR curves for different pyrolysis temperature samples in O_2 -saturated 0.1M KOH aqueous solutions with a scan rate of 10 mV s⁻¹ and a rotation rate of 1600 rpm.



AC/TBC(O)).



Fig. S22 a) RRDE measurements for AC/TBC(O) electrode at 1600 rpm in O₂-saturated 0.1M

KOH. b) Percentage of HO_2^- and electron-transfer number on the upper and lower halves of the graph, respectively.



Fig. S23 LSV curves of the AC/TBC(O) at different rotating speeds. The inset is the Koutecky-Levich plot at different potentials.

The Koutecky-Levich (K-L) plots (J^{-1} vs $\omega^{1/2}$) were derived from the LSV curves with the rotation speed varying from 400 to 2025 rpm to better understand the ORR kinetics on AC/TBC(O) catalyst. The good linearity indicates the first-order reaction kinetics toward the concentration of dissolved oxygen.



Fig. S24 Methanol tolerance experiments of AC/TBC(O), AC+TBC(O) and Pt/C with methanol injected at 400 s.



Fig. S25 N_2 adsorption and desorption isotherms and pore size distribution of g-C₃N₄.



Fig. S26 a) N₂ adsorption and desorption isotherms and b) pore size distribution of AC/gCN(O), AC/NTTC(O), and AC/TBC(O)+N.

Graphitic carbon nitride $(g-C_3N_4)$ has been widely used as N-doped carbon precursor owing to its high nitrogen content, however, its surface area (88 m² g⁻¹) is extremely low relative to TB. As a result, the assembly strategy greatly enriches the mesoporous structure in AC/gCN(O) to enlarge the surface area to 287 m² g⁻¹, which is still much lower than that of AC/TBC(O). The AC/NTTC(O) sample, prepared in a similar procedure with replacing TB monomer by 2,4,6triphenyl-1,3,5-triazine (TT monomer), possesses a high surface area of 1479 m² g⁻¹ and a large pore volume of 1.09 cm³ g⁻¹. Similar to AC/TBC(O), the steep N₂ uptake at low relative pressure $(p/p_0 < 0.001)$ and hysteresis loop in the medium and high-pressure region reflected the abundant micropores with coexistence of meso- and macropores. To introduce more doping sites into carbon networks, a nitrogen-rich compound (melamine) was mixed with AC/TBC(O) precursor. The following thermal treatment caused the condensation and carbonization of melamine to generate N-doped carbon, which partly blocked the micropores on the AC/TBC(O) surface. Meanwhile, the decomposition of melamine produced a large amount of gas to the formation of more meso- and macropores. Thus, the AC/TBC(O)+N sample shows a lower surface area (1127 $m^2 g^{-1}$) and pore volume (1.01 cm³ g⁻¹) in comparison to those of AC/TBC(O) sample (2042 m² g⁻¹) 1 and 1.54 cm³ g⁻¹).



Fig. S27 ORR activities of AC/gCN(O) and gCN(O) in O₂-saturated 0.1M KOH. The gCN(O) sample was synthesized in the same procedure in the absence of AC.

Sample	Description
AC/TBC (O)	Pyrolysis of AC/TB(O)@glu at 1000 °C
ТВ	Knitting 1,3,5-triphenylbenzene and benzene
TBC	Direct pyrolysis of TB
AC(O)	Similar procedure in the absence of TB
TBC(O)	Similar procedure in the absence of AC
AC/TB(O)@glu	Embedding AC(O) spheres into TBC(O) network with glucose linker
AC/TBC(O)-H ₂	Annealing AC/TBC(O) at 400 °C for 2 h in N ₂ /H ₂ (95 %/5 %)
AC/TBC (O)-800	Pyrolysis of AC/TB(O)@glu at 800 °C
AC/TBC (O)-900	Pyrolysis of AC/TB(O)@glu at 900 °C
AC/TBC (O)-5%	AC/TBC(O) with adding 10 mg of AC
AC/TBC (O)-10%	AC/TBC(O) with adding 20 mg of AC, i.e. AC/TBC(O)
AC/TBC (O)-15%	AC/TBC(O) with adding 30 mg of AC
AC/TBC (O)-20%	AC/TBC(O) with adding 40 mg of AC
AC/NTTC(O)	Similar procedure, replacing TB monomer by 2,4,6-triphenyl-1,3,5-triazine (TT monomer)
AC/TBC(O)+N	Similar procedure, mixing melamine with AC/TB(O)@glu for pyrolysis
AC/gCN(O)	Similar procedure, replacing TB by g-C ₃ N ₄
gCN(O)	AC/gCN(O) without adding AC

 Table S1 Summary and descriptions of the mentioned samples prepared in this study.

Sample	C-O/eV	C=O/eV	O/at%
TBC	533.0	531.3	3.75
TBC(O)	533.0	531.5	8.04
AC(O)	532.4	530.7	13.11
AC/TBC(O)	533.4	531.7	8.86

Table S2 The binding energy value and surface oxygen content of as-prepared samples from XPS analysis.

The O1s peak locations of TBC are close to that of TBC(O). However, both the C1s and O1s peaks of C=O and C-O components in AC(O) shifted to lower binding energy with respect to TBC(O). Such shift may be ascribed to the different carbon structure of commercial activated carbon and polymer-derived carbon.

Sample	O/C (molar ratio)	N/C (molar ratio)
AC/TBC(O)	0.079	-
TBC	0.027	-
AC/TBC(O)-H ₂	0.037	-
AC/gCN(O)	0.047	0.023
AC/TTC(O)	0.065	0.006
AC/TBC(O)+N	0.070	0.026

Table S3 Comparison of O:C, N:C (molar ratio) analyzed by EA.

The elemental composition of the carbon samples cannot be accurately measure by XPS technique because of the limitation in detected depth and the adventitious graphitic carbon for calibration. Element analysis (EA) was conducted to compare the oxygen composition of samples with and without surface acidification.

Sampla	S _{BET}	SL	PV	MPV ^d	
Sample	$(m^2 g^{-1})^{a)}$	$(m^2 g^{-1})^{b}$	$(cm^3 g^{-1})^{c}$		
TB	888	954	0.48	0.60	
TBC(O)	1573	1691	0.81	0.58	
AC	126	168	0.35	0.08	
AC(0)	231	243	0.29	0.04	
AC/TBC(O)-800	890	963	0.50	0.54	
AC/TBC(O)-900	1140	1239	0.67	0.47	
AC/TBC(O)	2042	2219	1.54	0.32	
AC+TBC(O)	1070	1165	0.84	0.42	
N-doped carbon electrocatalysts					
AC/TBC(O)+N	1127	1229	1.01	0.27	
AC/NTTC(O)	1479	1583	1.09	0.28	
AC/gCN(O)	287	287	0.58	0.10	

Table S4 Comparison of BET surface area and pore structure of different samples.

Surface area calculated using BET equation ^{a)} and Langmuir equation ^{b)}. ^{c)} Pore volume calculated at $p/p_0=0.995$. ^{d)} t-Plot micropore volume/Pore volume.

	Catalyst	$E_{1/2}(V)$ vs	$J_{\rm lim}$ (mA cm ⁻²)	Reference sample: Com. Pt/C		
Ref.				$E_{1/2}$ (V) vs	$J_{\rm lim}({\rm mA~cm^{-2}})$	
		КПЕ		RHE		
16	pentagon defects-carbon	0.780	-	0.843	-	
	pentagon defects/N-carbon	0.833	-	0.843	-	
i. carbo	on electrocatalysts without activ	e doping element	t (N, S, B or P)			
17	mesoporous fullerene C70	-0.260	6.50	-	5.50	
		(vs Ag/AgCl)				
18	carbon defect (DG)	0.760	-	-	-	
19	porous carbon (PC)	-	4.71	-	5.24	
20	plasma-treated graphene	0.737	-	-	-	
21	two-step-activated carbon	0.780	-	-	-	
	cloth					
22	carbon spheres(CSs)	0.835	4.17	0.855	5.15	
ii. N-doped and multi-heteroatom doped carbon electrocatalysts						
23	N-doped 3D-graphene	0.800	<3.0	~0.830	~5.75	
24	N-doped graphene	0.830	-	0.850	-	
25	N-doped carbon black	0.820	6.09	0.860	5.09	
26	N-doped carbon	0.840	-	0.810	-	
27	N-doped carbon@GO	0.850	6.10	0.820	6.00	
28	N,S co-doped granular	0.830	~5.80	-	-	
	carbon					
29	N,P-doped CNT/graphene	0.820	4.70	0.820	4.40	
30	N-doped holey carbon	0.780	4.60	0.830	5.44	
This	AC/TBC(O)	0.816	5.41	0.926	5 42	
work	AC/TBC(O)+N	0.860	5.50	0.820	5.45	

Table S5 Comparison of ORR electrocatalytic performance of AC/TBC(O) with the reported metal-free carbon electrocatalysts in recent literatures.

 $\overline{a} E_{1/2}$ is the half-wave potential. ^{b)} J_{lim} is the limiting current density. All the catalysts was tested in the 0.1M KOH solution.

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