Supplementary information

Article

Metallosupramolecular Polymer Precursor Design for Multi-element Co-doped Carbon Shells with Improved Oxygen Reduction Reaction Catalytic Activity

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Calculation of electron transfer number (*n*) for oxygen reduction reaction

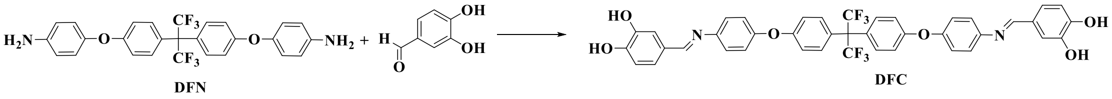
The electron transfer number (*n*) per oxygen molecule based on rotating disk electrode (RDE) data is calculated by K-L equations:

$$1/j = 1/j_k + 1/B\omega^{1/2} \quad (1)$$

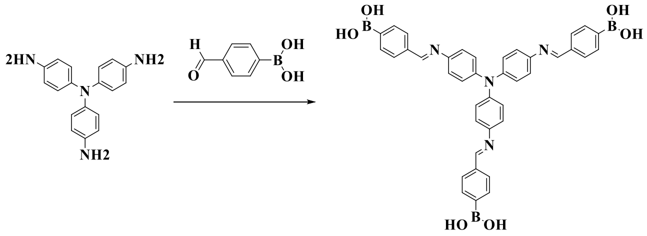
$$B = 0.2nF(D_{O_2})^{2/3} C_{O_2} \upsilon^{-1/6} \quad (2)$$

Where j is the measured current density, j_k is the kinetic-limiting current density, ω is the electrode rotation rate, F is Faraday constant (96485 C mol^{-1}), D_{O_2} is the diffusion coefficient of O_2 in 0.1 M KOH electrolyte (1.9×10^{-5} cm^{2}s^{-1}), C_{O_2} is the concentration of dissolved O_2 (1.2×10^{-6} molcm^{-3}), v is the kinematic viscosity of the 0.1 M KOH electrolyte (0.01 cm^{2}s^{-1}). The constant 0.2 is adopted when the rotation speed is expressed in rpm.[1]

Synthesis of DFC and TBB



Synthesis of DFC: To a solution of 4,4'-(((perfluoropropane-2,2-diyl)bis(4,1-phenylene))bis(oxy))dianiline (136.68 mg, 0.264 mmol) in anhydrous methanol (20 mL) was added 3,4-dihydroxybenzaldehyde (75.75 mg, 0.55 mmol). The clear yellow mixture was stirred and protected from light at room temperature overnight. The reaction mixture was concentrated into 3 mL, followed by filtering, washing with 100 mL of cold anhydrous methanol for 3 times, and drying in vacuum for 6 hours.[2] Yield: 60 %. Purity is 90 %. ^{1}H NMR (400 MHz, DMSO-D_6) δ (ppm): 9.56 (s, 2 H), 9.31 (s, 2 H), 8.41 (s, 2 H), 7.39 (s, 2 H), 7.36-7.35 (d, 4 H), 7.29-7.27 (d, 4 H), 7.19-7.18 (s, 2 H), 7.14-7.12 (d, 4 H), 7.10-7.08 (d, 4 H), 6.84-6.83 (s, 2 H). ^{13}CNMR (400 MHz, DMSO-D_6): 191.44, 160.41, 158.63, 153.33, 152.73, 149.87, 148.83, 146.45, 146.25, 131.92, 129.34, 128.47, 126.79, 124.98, 123.05, 121.03, 117.79, 115.98, 115.96, 114.68, 56.50. ESI/MS m/z 759.19225 $[M+H]^+$.



TBB

Synthesis of TBB: To a solution of Tris(4-aminophenyl)amine (96.8 mg, 0.276 mmol) in anhydrous ethanol (20 mL) was added 4-Formylphenylboronic acid (152 mg, 1.01 mmol). The clear red mixture was stirred and protected from light at room temperature overnight. The reaction mixture was concentrated into 5 mL. The cold methylene chloride (25.0 mL) was added into the above solution to get yellow precipitate, which was collected by filtering, washing with 100 mL of a cold solvent comprising anhydrous ethanol and methylene chloride (volume ratio : 5 : 1) for 3 times, and drying in vacuum for 6 hours.[3] Yield: 80 %. ^{1}H NMR (400 MHz, DMSO-D_6) δ (ppm): 8.68 (s, 3 H), 8.19 (s, 6 H), 7.95-7.87 (d, 6 H; d, 6 H), 7.33 (d, 6 H), 7.11 (d, 6 H). ^{13}CNMR (400 MHz, DMSO-D_6): 159.71, 146.64, 145.88, 138.01, 134.87, 134.69, 127.89, 124.79, 123.03. ESI/MS m/z 745.32 $[M+59]^-$.

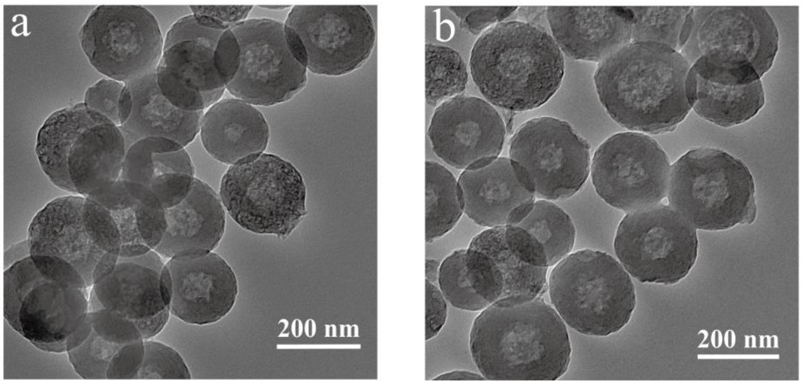


Figure 1. TEM images of (a) CS$_{12-550}$, (b) CS$_{12-750}$.

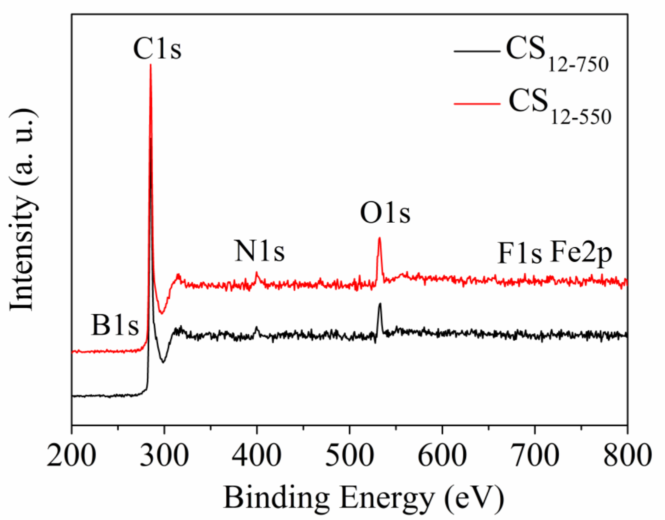


Figure S2. XPS survey spectra of CS$_{12-550}$ (a) and CS$_{12-750}$ (b).

Composition					
C %	N %	O %	B %	F %	Fe %
90.72	2.25	5.50	1.43	0	0.09

Table S1. Atomic percent of elements obtained from XPS analysis to CS$_{12-750}$.

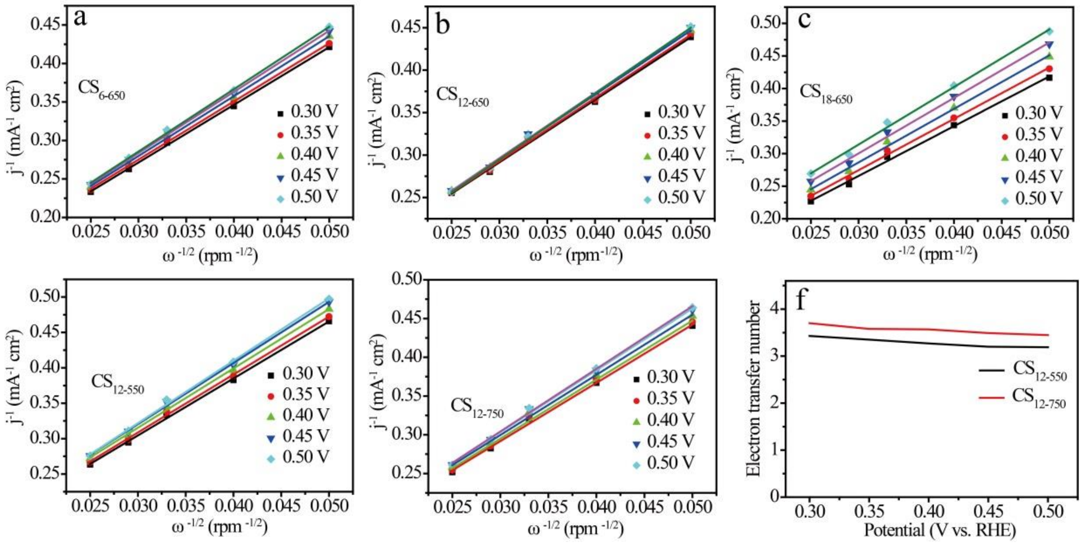


Figure S3. The corresponding K-L plots at various potentials of (a) CS_{6-650}, (b) CS_{12-650}, (c) CS_{18-650}, (d) CS_{12-550}, and (e) CS_{12-750}. Electron transfer numbers obtained from K-L plots of CS_{12-550} and CS_{12-750} (f).

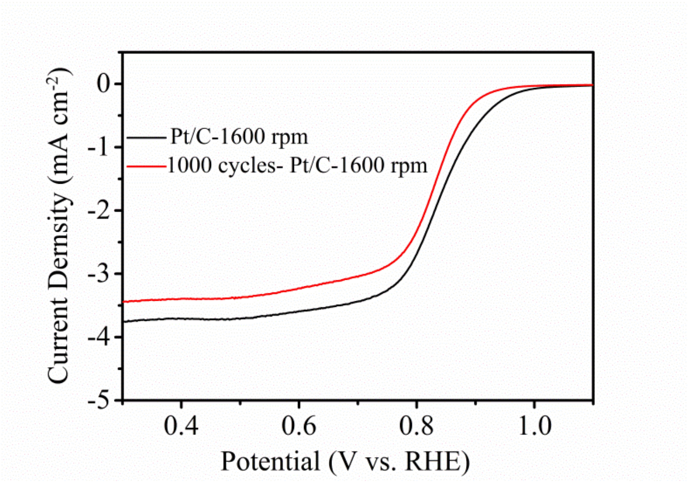


Figure S4. LSV curves of the commercial 20 wt% Pt/C at 1600 rpm in O_2-saturated 0.1 M KOH aqueous solution before and after 1000 cycles of CV curves with a scan rate of 50 mV/s.

References

1. Zhang, J. T.; Zhao, Z. H.; Xia, Z. H.; Dai. L. M. A metal-free bifunctional electrocatalyst for oxygen reduction and oxygen evolution reactions. *Nature Nanotechnology*. **2015**, *10*, 444-452.

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3. Chang, Y.; Yuan, C. H.; Li, Y. T.; Liu, C.; Wu, T.; Zeng, B. R.; Xu, Y. T.; Dai, L. Z. Controllable fabrication of a N and B co-doped carbon shell on the surface of TiO_2 as a support for boosting the electrochemical performances. *J. Mater. Chem. A*. **2017**, *5*, 1672-1678.