It is generally deemed that Fuel Cells including Proton exchange membrane fuel cell (PEMFC), direct methanol fuel cells (DMFC) and other cells, will be the most prospective and efficient energy generation and storage devices for their zero emissions and high-efficiency.1,2 In particular, PEMFC can produce as high as 1 W cm$^{-2}$ power density without any emission of pollutions.3 In PEMFC, H$_2$ is oxidized at the anode to produce protons and electrons, while O$_2$ is reduced to water and the sluggish ORR limits the energy output of PEMFC.4–7 For the maintenance of whole output efficiency, it is of practical significance in the commercialization of PEMFC to optimize the doping type and content of metal and non-metal heteroatoms in the frameworks.

Macrocyclic metal compounds such as phthalocyanines and porphyrins have special metal-N$_4$ chelate moieties, which can be partly inserted on the carbon surface after undergoing the appropriate thermal-treatment procedures. This special character equipped metal macrocyclic compound-derived carbons with highly active ORR electro-catalytic activities among various pH electrolytes.8–10 To develop advanced NPMCs by using macrocyclic metal compounds as precursors, the attractive route, but still faced some challenges. One is the effective enhancement of active site density for the macrocyclic compound-derived carbons. Metal-N$_4$ sites had effective ORR catalytic activity, but the larger molecule size made them a limited amount per unit surface of carbons.11 These planar π–π stacking in macrocyclic metal precursors always buried the metal-N$_4$ or other active sites into the carbon layers after pyrolysis, which further decreased the possible surface active site density of the derived carbons.12 Another is about the cost of macrocyclic compounds or polymers. For effectively increasing active site density of carbons, the macrocyclic compound precursors usually need to be specially designed and prepared for producing high porosity and considerable doping defects in the derived carbons.13 As a result, the thermal conversion of these expensive precursors to NPMCs is not cost effective, in contrast to Pt-based electrocatalysts. It is still a challenge to prepare high-efficiency ORR carbon-based electro-catalysts by hiring low-cost macrocyclic compounds as inexpensive precursors.

Herein, Co-Cu-N-S multi-doped hierarchical porous non-precious carbon catalysts were successfully synthesized by using inexpensive disulfonated Cu (II) phthalocyanine (CuD$_2$Pc) and tertrasulfonated Co (II) phthalocyanine (SCoPc) as the precursors. The prepared Co-Cu-N-S-Cs are cost-effective but efficient ORR catalyst in alkaline and acidic electrolytes. Its ORR half-wave potential reaches 0.85 V in 0.1 M KOH, higher than commercial Pt/C catalysts (JM, 20 wt%) and the previously reported Cu- and Co-based catalysts. The simultaneous doping of Cu- and Co on carbons was found to efficiently improve ORR performance of the derived carbons.

Experimental

**Synthesis process for Co-Cu-N-S-C.** — 1 g chitosan was dissolved into 100 mL 0.2 M HCl solution, and then 2 g SiO$_2$ monodispersed spheres (about 30 nm) and 0.1 g graphene oxides was added into the chitosan solution. The resultant mixture was heated to 60°C and kept stirring for 30 min. After cooling down to the room temperature, an aqueous solution of 1 M NaOH was added into the above mixture to adjust pH to 8. The resultant mixture was stirred for 30 min. After cooling down to the room temperature, an
ethanol–water solution (V/V = 1:1, 60 ml) containing tertrasulfonated copper phthalocyanine (CuDsPc, 0.3 g) and sulfonated cobalt (II) phthalocyanine (SCoPc, 0.1 g) were additionally added in the above mixture and were further stirred for 2 h at room temperature. After that, 25 mL 0.5 M NH₄H₂O was added and stirred for 30 min. The obtained mixtures were filtered and washed by deionized water and dried at 70°C overnight. The resulting samples were heated at 800–1000°C for 4 h under nitrogen atmosphere in quartz furnace. After the SiO₂ templates were etched in 5% HF solution for 12 h, the Co-Cu-N-S-C-n products (n is the calcining temperature) were finally obtained (Figure 1). In order to investigate the influence of metal, the CuDsPc and SCoPc were used separately during the synthesis process, called as Cu-N-S-C and Cu-N-S-C.

**Characterizations.**—A D/2500 X-ray diffractometer (Bruker AXS, Germany) with Cu Kα radiation (λ = 1.54 nm, V = 40 kV) was used to achieve powder X-ray diffraction patterns (XRD) patterns. Raman spectroscopy was performed on a GX-PT-1500 (150) instrument with a 532 nm excitation laser (1 mW). A QUANTA200 scanning electron microscope (SEM) was employed to determine the morphology and component. An AkTec 2000 transmission electron microscope (TEM) was used to record the transmission electron microscope images at an acceleration voltage of 200 kV. N₂ adsorption/desorption measurements were performed at 77 K on the QUADRASORBEVO Gas Sorption Surface Area and Pore Size Analyzer. A ThermoFisher ESCALAB 250Xi was conducted to gain X-ray photoelectron spectroscopy (XPS). The metal content was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES, IRIS Intrepid II, America).

**Electrochemical test.**—The ORR performance of as-mentioned catalysts was assessed by cyclic voltammetry (CV), linear sweep voltammetry (LSV) and rotating ring-disk electrode (RRDE) techniques. A commercial three-electrode cell system, including a working glass carbon RRDE (Pine, disk 0.2475 cm², Pt ring 0.1866 cm²), an Ag/AgCl, KCl (3 M) electrode as reference electrode, and a Pt electrode as counter electrode, was employed. The experiments were conducted in O₂-saturated 0.1 M KOH and 0.1 M HClO₄ solution. The working electrodes were prepared through dispersing 10 mg of carbon materials in 1.28 ml alcohol with 30 μL of 5 wt% Nafion solution by sonication before pipetting the catalyst suspension onto it. Catalyst suspension was pipetted onto a polished glassy carbon electrode surface and the electrode was dried at room temperature. A commercially available Pt/C catalyst (JM, 20 wt%) was used for comparison. The loading of as-achieved catalysts on the working electrode was 0.30 mg cm⁻² in alkaline solution and 0.60 mg cm⁻² in acidic solution. The catalyst loading of Pt/C on the electrode was 0.1 mg cm⁻² in both electrolytes. All the potentials were corrected to the reversible hydrogen electrode (RHE) potentials. The ORR current in both alkaline and acidic solutions were obtained by subtracting the current measured in N₂-saturated conditions from the current measured in O₂-saturated ones. The corresponding transferred electron number (n) and %H₂O₂ yield during the ORR were calculated by the following equations:

\[
    n = 4 \frac{I_d}{I_d + \frac{I_f}{N}} \quad \%\text{H}_2\text{O}_2 = 200 \times \frac{I_f/N}{I_d + \frac{I_f}{N}}
\]

where \(I_d\), \(I_f\), and \(N = 0.37\) are the disk current, ring current and collection efficiency, respectively, for the employed RRDE method.

**Results and Discussion**

**Synthesis of Co-Cu-N-S-Cs.**—Commercial sulfonated Cu and Co phthalocyanines were widely used as the desulfurization catalysts and dyes,28 which are cost-effective and economically available carbon precursors. Those two phthalocyanines are employed as the precursors of C, N, S and Cu or Co for the preparation of multi-doped carbons. However, the direct pyrolysis or heating them on carbon supports are often difficult to obtain high-efficiency ORR catalytic materials,25 because the sintering and agglomeration of precursors often stemmed the active sites on the derived carbon surface. In the present synthesis, commercial silica nano-spheres are hired as hard templates to avoid seriously sintering and stacking of the phthalocyanine-derived carbons. The additional mesopores were produced by the utilization of silica templates and more active sites were exposed on the surface of carbons. A few graphene oxides for enhancing the electron conductivity of the resulted carbons were also added in the precursors. Moreover, chitosan polymers dissolving in dilute hydrochloric acid

![Figure 1.](image-url) The illustration of synthesis procedure for preparing porous Co-Cu-N-S-C materials.
(HCl) could generate surface NH$_4^+$ cation ions, which connect with sulfonated phthalocyanine (-SO$_3^-$) anions and charged graphene oxides (-COO$^-$) to form salts. These were finally coated on silica spheres in one-pot synthesis. After undergoing the controlling pyrolysis and the following acid-etching, the obtained composites successfully converted to Co-Cu-N-S heteroatom-doped carbons.

**Structure, morphology and component.**—The morphology and porosity of Co-Cu-N-S-C were characterized by SEM, TEM and N$_2$-sorption analysis. Typically, the foam-like appearance and widely-dispersed porosity can be observed in SEM images of Co-Cu-N-S-C-900 (Figures 2A and 2B). The stacking of Co-Cu-N-S-C particles produced a lot of macropores, observed by SEM images. A more clear observation from TEM images showed a large amount of spherical pores (Figures 2C and 2D). These large-sized mesopores should be left after the removal of SiO$_2$ spheres. Few micropores can be found in the enlarged high-resolution TEM images. These results suggested the hierarchical porosity of Co-Cu-N-S-C prepared by the SiO$_2$ sacrificial template method.

N$_2$-sorption analysis was conducted to further investigate the porosity of the material. The isotherms of Co-Cu-N-S-Cs (Figure 3) could be classified as typical-IV isotherms, in terms of their enormous adsorption volume at relative low pressure then slowly increased in the middle relative pressure. The isotherms were parallel to each other, indicating the existence of similar porous structures. Insignificant hysteresis loops at 0.2–1.0 relative pressure represented for mesopores and macropores, consistent with the results of electron microscope. The porosity data of Co-Cu-N-S-Cs are shown in Table I, including S$_{BET}$ and total volume. The surface area of Co-Cu-N-S-C-900 reached 355.4 m$^2$ g$^{-1}$, which was larger than Co-Cu-N-S-C-800 and -1000.

The lower BET surface area for Co-Cu-N-S-C-800 was probably attributed to the incomplete carbonization of chitosan and macrocycle compounds. Higher heat-treatment at 1000$^\circ$C often caused the collapse of carbon frameworks and thus the decreased surface area. The pore size distribution curves of Co-Cu-N-S-Cs calculated by BJH or HK model revealed the wide pore distribution from micropores to macropores, in agreement with the results observed in SEM and TEM images. The hierarchical pore structures might effectively increase the exposure of ORR active sites and improve the transportation properties of Co-Cu-N-S-C in the electroreduction of O$_2$.

The carbon structure of Co-Cu-N-S-C samples has been confirmed by their large-angle XRD patterns. As shown in Figure 4, two remarkable diffraction peaks at 2$\theta$ = 25.5 and 43.2$^\circ$ can be generally observed in three samples prepared at different temperatures. These two peaks corresponded to the (002) and (101) diffraction of graphitic domains in the carbon frameworks. It is worth mentioning that there is an additional sharp peak at 2$\theta$ = 18$^\circ$ for Co-Cu-N-S-C-800. This peak was ascribed to the signals of crystalline GO in the precursors.

### Table I. Electrocatalytic performances of Co-Cu-N-S-C-n and their porosities.

| Sample         | Half-wave Potential (V)-KOH | Limiting Density (mA) | Half-wave Potential (V)-HClO$_4$ | Tafel Slope (mV dec$^{-1}$) | $S_{BET}$ (m$^2$ g$^{-1}$) | $V_{total}$ (cc g$^{-1}$) |
|----------------|-----------------------------|------------------------|----------------------------------|-----------------------------|---------------------------|---------------------------|
| Co-Cu-N-S-C-800| 0.85                        | 5.0                    | 0.58                             | 66                          | 211.4                     | 1.12                      |
| Co-Cu-N-S-C-900| 0.85                        | 5.4                    | 0.59                             | 63                          | 355.4                     | 1.55                      |
| Co-Cu-N-S-C-1000| 0.84                        | 4.7                    | 0.55                             | 70                          | 269.4                     | 1.47                      |
This result suggested that the GOs were incompletely merged into the graphitic carbons at the lower carbonization temperature. With the increase of pyrolysis temperature, the carbonization of GOs in the carbon frameworks was achieved.

The higher heat-treatment temperatures enhanced graphitization-degree of the resultant Co-Cu-N-S-C materials, confirmed by the increasing diffraction intensity of (002) and (101) peaks for Co-Cu-N-S-C-900 and -1000. The intensity ratio between D band (1360 cm\(^{-1}\)) and G band (1580 cm\(^{-1}\)) in Raman spectrum (Figure 5A) is also an evidence for graphitization-degree or defects in carbon frameworks.

The increased IG/ID values from 0.98 (Co-Cu-N-S-C-800), 0.99 (Co-Cu-N-S-C-900) to 1.03 (Co-Cu-N-S-C-1000) also indicated the enhancing graphitization-degree and the decreasing doping defects with higher pyrolysis temperature. However, the graphitization degree of carbon frameworks is not monotonously beneficial for the improvement of ORR catalytic performance. It should be desired that the amount of doping defects in carbon electro-catalysts should be as high as possible after maintaining the appropriate graphitization-degree of carbon frameworks. The selected area electron diffraction (SAED) of Co-Cu-N-S-C-900 (Figure 2F) exhibited a clear diffraction ring. It suggested that a good compromise between crystallinity and the amount of doping defects may be established in Co-Cu-N-S-C-900.

To investigate the elemental component and the doping defects of Co-Cu-N-S-C-900, EDS elemental mapping and XPS analysis were conducted. As observed in Figure 6, the SEM-mapping exhibited Co-Cu-N-S-C-900, EDS elemental mapping and XPS analysis were successfully bonded into carbon sheet. It is known that N species were always crucial to ORR performance for its ability to moderate the electron structure of adjacent C atoms. The high-resolution N 1s orbital spectrum (Figure 7C) was divided into four peaks at 398.2, 399.1, 399.8 and 401.0 eV, which were corresponding to pyridinic N, M-N\(_x\) (M = Co or Cu), pyrrolic and graphitic N, respectively. It has been suggested from previous studies that pyridinic N was often beneficial for onset potential while graphitic N could enlarge the current density of ORR. The Cu-N\(_x\) and Co-N\(_x\), whose peaks are too close to divide in N 1s spectrum, were presumably attributed by the decomposition and carbonization of CuDsPc and ScOpc at high pyrolysis temperature.

Table II. XPS elemental analysis for atomic percentage of Co-Cu-N-S-C-900.

| Element | C 1s | Cu 2p | Co 2p | O 1s | S 2p | N 1s |
|---------|------|-------|-------|------|------|------|
| Co-Cu-N-S-C-900 | 70.5 | 3.26  | 4.16  | 11.26| 0.61 | 10.21|

It was proved that Cu-N\(_x\) and Co-N\(_x\) play active roles for the promotion of ORR activity, formed from the coordination between metal ions and pyridinic or pyrrolic N. For S 2p spectrum in Figure 7D, the two remarkable peaks at 163.0 and 164.3 eV can be appointed to S 2p\(_{3/2}\) and S 2p\(_{1/2}\) of C-S-C covalent bond. The other peak at 167.0 eV represented the oxidized S in the form of C-SO\(_x\)-C. The Co 2p\(_{3/2}\) spectra (Figure 7E) revealed two peaks around 780.0 eV and 795.6 eV, which represented the coordinated Co(II) species and the corresponding satellite peak. The peak at 934.6 eV and Cu(0) in the high-resolution spectrum shows, indicating the insufficiency of metal particles in the surface of carbon catalysts, in accordance with the TEM results.

**Figure 6.** EDS elemental mapping (C, N, S, Cu and Co) of Co-Cu-N-S-C-900, scale bar 100 \(\mu\)m.

**Figure 5.** (A) Raman spectra of prepared Co-Cu-N-S-C-\(n\). (B) Raman spectra of Co-N-S-C-900, Cu-N-S-C-900 and Co-Cu-N-S-C-900.
undergoing acid-leaching were mostly encapsulated into carbon layers. The half-wave potential of Co-Cu-N-S-C-900 reached 0.85 V (Table I), 10 mV higher than that of 20 wt% Pt/C (0.84 V), among the best carbon-based ORR catalysts in 0.1 M KOH.

The catalytic activity of Co-Cu-N-S-C-900 was also investigated by CV technique in 0.1 M HClO₄ (Figure 8B). There was an obvious peak arose at 0.62 V in O₂-saturated electrolyte, suggesting effective ORR activity in acidic solution. The half-wave potential of Co-Cu-N-S-C-900 determined from the LSV curves reached 0.59 mV (Table I), more negative than that of 20 wt% Pt/C (0.84 mV) but similar to other Co- or Cu-based electro-catalysts.

The addition of Co into Fe-doped carbons has been demonstrated to enhance electrocatalytic activity and stability for ORR. Recently, Cu-doped carbons were also found to be very active for ORR, but the influence of adding Co in Cu-doped carbons on their ORR performance are still few reported. The LSV curves in Figure 8C showed that the half-wave potential of the derived catalysts only used CuDSpC or SCoPc in the synthesis (namely Cu-N-S-C-900 and Co-N-S-C-900) were lower than the catalyst with co-doped metal species. The limiting current density over Co-Cu-N-S-C-900 reached 5.4 mA cm⁻², which is larger than Co-N-S-C-900 and Cu-N-S-C-900. As shown in Figure 8D, the half-wave potential of Co-Cu-N-S-C-900 was 23 mV positive than Co-N-S-C-900 and 113 mV than Cu-N-S-C-900 in 0.1 M HClO₄ solution. These results suggested the higher ORR performance for co-doped Co-Cu-N-S-C-900 in two electrolytes, comparative to those similar catalysts reported previously (Table III). It may be attributed to the different catalytic carbon behaviors of Co and Cu species. It is well-known that Co species intensely catalyze the graphitization of organic precursor at thermolysis, which would tend to decrease the porosities and surface doping components of the derived carbons. Confirming by the lower D/G ratio of Cu-N-S-C-900 than Co-N-S-C-900 in Raman spectra (Figure 5B), the catalytic behavior for graphitization of Cu species are relative lower than Co species. However, it may facilitate the maintenance of ORR active sites at higher temperature heat-treatment process. Therefore, the mixed using of Cu- and Co-phthalocyanines could optimize the graphitization-related electron transportation and doping defects-related active site density in Co-Cu-N-S-Cs. Moreover, the carbonization temperature of precursors also exert important influence on the electron transportation and active site density of the prepared carbons. Figure 8E revealed the catalytic properties of Co-Cu-N-S-Cs obtained at different
Figure 8. CV curves for Co-Cu-N-S-C-900 in 0.1 M KOH solution (A) and 0.1 M HClO₄ solution (B), LSV curves for Co(x)-Cu(y)-N-S-C-900 in 0.1 M KOH solution (C) and 0.1 M HClO₄ solution (D), Co-Cu-N-S-C under different thermal treatment temperature in 0.1 M KOH solution (E) and 0.1 M HClO₄ solution (F) at a rotation rate of 1600 rpm.

Pyrolysis temperatures. The half-wave potential of different samples slightly changed (0.84 V-0.85 V). The diffusion limited current densities of Co-Cu-N-S-C-800 and Co-Cu-N-S-C-1000 are smaller than Co-Cu-N-S-C-900 in 0.1 M KOH.

In order to investigate the individual role of functional precursors, chitosan, graphene oxides and SiO₂ spheres were respectively excluded in the synthesis process. The achieved materials were assigned as Co-Cu-N-S-C-900-A (without chitosan), Co-Cu-N-S-C-900-B (without graphene oxides) and Co-Cu-N-S-C-900-C (without SiO₂ spheres). It was found that Co-Cu-N-S-C-900-C was sintered and became a rigid chunk after pyrolysis. Although difficult to accurately measure the electro-chemical ORR values owing to

| Sample                  | E½ KOH (vs.RHE) | J₁ KOH (mA) | E½ HClO₄ (mg cm⁻²) | Loading KOH (mg cm⁻²) | Loading HClO₄ (mg cm⁻²) | Ref. |
|-------------------------|----------------|-------------|--------------------|-----------------------|-------------------------|------|
| Co-Cu-N-S-C-800         | 0.85           | 5.0         | 0.58 (vs RHE)      | 0.3                   | 0.6                     | This work |
| Co-Cu-N-S-C-900         | 0.85           | 5.4         | 0.59 (vs RHE)      | 0.3                   | 0.6                     |       |
| Co-Cu-N-S-C-1000        | 0.84           | 4.7         | 0.55 (vs RHE)      | 0.3                   | 0.6                     |       |
| Co(N-HCO₃)              | 0.81           | 5.2         | /                  | 0.3                   | /                       | 41   |
| Cu₂Pc₂                  | /              | /           | 0.51 (Eo vs SCE)   | 0.106                 | /                       | 47   |
| Fe₃Pc₂                  | -0.14 (vs SCE) | 5.31        | /                  | 0.106                 | /                       | 48   |
| Zn₃Pc₂                  | -0.39 (vs SCE) | 3.66        | /                  | 0.106                 | /                       | 49   |
| Cu₂O nanocubes          | 0.80 (vs RHE)  | 3.6         | /                  | 0.2                   | /                       | 50   |
| Cu₂O nanocubes          | 0.72 (vs RHE)  | 2.9         | /                  | 0.6                   | /                       | 51   |
the impossible disperse of Co-Cu-N-S-C-900-C in alcohol, it can be deduced that the role of SiO$_2$ spheres is to increase the porosity and surface area of the resultant carbons and benefit the transportation of electrons and oxygen molecules. The LSV curves of Co-Cu-N-S-C-900-A and Co-Cu-N-S-C-900-B in both alkaline and acidic solution were shown in Figure 9. Compared with Co-Cu-N-S-C-900, the half-wave potential of Co-Cu-N-S-C-900-A is 20 mV lower in KOH electrolyte and 22 mV lower in HClO$_4$ electrolyte. Additionally, the limiting current density is much smaller. As expected, chitosan worked as the adhesives between macrocyclic compounds and silica, which facilitated the porosity of the prepared carbon and dispersion of active species on its surface. Co-Cu-N-S-C-900-B without graphene oxide precursors exhibited smaller limiting current density than Co-Cu-N-S-C-900. It indicated the important role of them in enhancing electron conductivity of the derived carbon frameworks.

The number of transferred electron and the yield for H$_2$O$_2$ during the catalytic process in KOH solution were calculated by RRDE results (Figure 10). The transferred electron number of Co-Cu-N-S-C-900 were counted to be 3.7–3.8 in the range of 0.2 ~ 0.6 V, suggesting a nearly four electron-transfer ORR over this material in 0.1 M KOH. The H$_2$O$_2$ yield for Co-Cu-N-S-C-900 (7.2–10.1%) in 0.2 ~ 0.6 V was slightly higher than that of commercial Pt/C catalyst (1.85–10.98%), but lower than other multi-doped catalysts prepared by us. The investigated electron transferred number in 0.1 M HClO$_4$ was calculated to about 3.8–3.9 between 0.05 and 0.3 V, indicating a similar nearly four electron-transfer ORR process in this potential range.

Tafel plots and corresponding slopes ascertained the kinetics parameters of the catalysts. As presented in Figures 11A and 11B, all slopes of Co-Cu-N-S-Cs in 0.1 M KOH were smaller than Pt/C catalyst (74 mV/dec), indicating stronger ability to reach larger current density.
at relative low overpotential in 0.1 M KOH solution. In comparison, the slopes were in accordance with the change for their half-wave potentials. 900°C was the most suitable heat-treatment temperature confirmed by its lowest Tafel slope (60 mV/dec) and the most positive half-wave potential.

The durability and methanol tolerance of non-precious metal catalysts in both alkaline and acidic solutions are crucial factors for practical application. After 20,000 s in the chronopotentiometric curves (i-t curves) in O2-saturated electrolytes, the current density remained 93% in 0.1 M KOH and 80% in 0.1 M HClO4, much superior to commercial Pt/C (75% and 69% at 10,000 s), indicating better stability of Co-Cu-N-S-C-900. Additionally, it is well-known that commercial Pt/C electrodes tend to be catalytically expired with the existence of methanol. The methanol crossover of Co-Cu-N-S-C-900 was also investigated with the addition of methanol at 400 s. As shown in Figures 12C and 12D, there is no significant decrease of ORR current after adding 6.2 mL methanol in 200 mL electrolytes. In comparison, the current of Pt/C were obviously declined in both solutions. With such superior catalytic performance and better stability, Co-Cu-N-S-C-900 can act as the promising electrocatalytic substitute of Pt/C especially in alkaline media.

Conclusions

In summary, low-cost commercial phthalocyanine and sulfonated cobalt (II) phthalocyanine were successfully converted into the efficient hierarchical porous multi-doped Co-Cu-N-S-C Pt-free catalytic materials for ORR. By optimizing the mass ratio during the synthesis process and the pyrolysis temperature, Co-Cu-N-S-C-900 was found to exhibit high-efficient ORR catalytic performance (0.85 V, 5.4 mA cm−2), better than that of Pt/C electrode and competitive to other non-precious metal electro-catalysts in 0.1 M KOH solution. The porous features, high surface area and the co-doping of N/S and Co/Cu species contributed to its enhanced ORR catalytic activity. This work provided a simple synthesis pathway for creating highly active multi-doped carbon-based ORR electro-catalysts by using low-cost macrocyclic compounds.

Acknowledgments

The authors are grateful to financial support from National Natural Science Foundation (No. 21303058) and Shanghai Municipal Natural Science Foundation (No. 13ZR1412400 and 11JC1403400).

ORCID

Aiguo Kong
https://orcid.org/0000-0003-4829-9454

References

1. S. Yang, R. Baezman, X. Feng, and K. Müllen, Acc. Chem. Res., 46, 116 (2013).
2. J. Stacy, Y. N. Regmi, B. Leonard, and M. Fan, Renew Sust Energy Rev., 69, 401 (2017).
3. L. Osmani, R. Escudero-Cid, M. Armandi, P. Ocoén, A. H. A. M. Videula, and S. Specchia, Electrochim. Acta, 266, 220 (2018).
4. S. Lu and Z. Zhuang, JACS, 139, 5156 (2017).
5. S. Fu, C. Zhu, J. Song, D. Du, and Y. Lin, Adv Energy Mater, 7(19), 1700363 (2017)
6. A. Holewinski, J. C. Idrobo, and S. Linic, Nat Chem, 6(9), 828 (2014).
7. M. D. Meganathan, S. Mao, T. Huang, and G. Sun, J Mater. Chem. A, 8(6), 2972 (2017).
8. J. Guo, Y. Li, Y. Cheng, L. Dai, and Z. Xiang, Acs Nano, 11(8), 8379 (2017)
9. G. Wu, G. More, C. M. Johnston, and P. Zelenay, Science, 322(6028), 443 (2011).
10. Y. Qian, I. A. Khan, and Z. Dan, Small, 13(37), 1701143 (2017).
11. T. Sun, Q. Wu, Y. Jiang, Z. Zhang, L. Du, L. Yang, X. Wang, and Z. Hu, Chemistry, 22(30), 10326 (2016).
12. S. U. Dar, M. A. Ud Din, M. U. Hameed, S. Ali, R. Akram, Z. Wu, and D. Wu, J Power Sources, 373, 61 (2018).
13. X. Wang, J. Wang, D. Wang, S. Dou, Z. Ma, J. Wu, L. Tao, A. Shen, C. Ouyang, Q. Liu, and S. Wang, Chem Commun, 50(37), 4839 (2014).
14. T. Zhou, Y. Zhou, R. Ma, Z. Zhou, G. Liu, Q. Liu, Y. Zhu, and J. Wang, Carbon, 114, 177 (2017).
15. K. Qu, Y. Zheng, S. Dai, and S. Z. Qiao, Nano Energy, 19, 373 (2016).
16. J. Liang, Y. Jiao, M. Jaroniec, and S. Z. Qiao, Angew. Chem. Int. Ed., 51(46), 11496 (2012).
