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Cobalt sulfide/N, S Co-doped porous carbon core-shell nanocomposites as superior bifunctional electrocatalysts for oxygen reduction and evolution reactions

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Exploring highly-efficient and low-cost bifunctional electrocatalysts for both oxygen reduction reaction (ORR) and oxygen evolution reactions (OER) in the renewable energy area has gained its momentum but still remains a significant challenge. Here we represent a simple but efficient way that utilizes ZIF-67 as the precursor and template for the one-step generation of homogeneous dispersed cobalt sulfide/N,S-codoped porous carbon nanocomposites as high-performance electrocatalysts. Due to the favourable molecular-like structural features and uniform dispersed active sites in the precursor, the resulting nanocomposites featured with unique core-shell structure, high porosity, homogeneous dispersion active components together with N and S-doping effect, not only show excellent electrocatalytic activity towards ORR with the high onset potential (around -0.04 V vs -0.02 V for benchmark Pt/C catalyst) and four-electron pathway, and OER with a small overpotential of 0.47 V for 10 mA cm⁻² current density, but also exhibit superior stability (92%) to commercial Pt/C catalyst (74%) in ORR and promising OER stability (80%) with good methanol tolerance. Our findings suggest that the transition metal sulfide-porous carbon nanocomposites derived from the one-step simultaneously sulfurization and carbonization of zeolitic imidazolate frameworks are excellent alternative bifunctional electrocatalysts towards ORR and OER in the next generation of energy storage and conversion technologies.

With the depletion of hydrocarbon-based energy resources and the increasing global energy demands, it is imperative to develop green and sustainable energy storage and conversion technologies as alternatives to currently widely used fossil fuels.¹⁻³ Electrocatalytic oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) play key roles in several important next-generation energy storage and conversion technologies, such as fuel cells, metal-air batteries and water splitting.⁴⁻¹³ Hitherto, most efficient electrocatalysts for ORR/OER contain precious metals including Pt or Ir; however, due to the prohibitive cost, poor stability of precious metals, the sluggish kinetics for ORR and the large polarisation, it is highly desirable to discover highly efficient and low-cost earth-abundant non-precious electroactive materials that can rival the performances of precious metal-based catalysts.¹⁴⁻¹⁷

Many efforts have, therefore, been devoted to transition metal oxides/sulfides based materials, as many transition metals like cobalt, manganese have been widely considered to

be electrochemically active for ORR and OER. Particularly, cobalt sulfides (Co_xS_y) with different phases have been previously investigated as ORR and OER electrode catalysts and exhibited attractive electrocatalytic performance among different non-precious and late transition metal chalcogenides.¹⁸⁻²³ For instance, CoS₂ is a good electrocatalyst for ORR and OER;²⁴ Co₃S₄ has excellent performance for ORR^{25, 26} and OER;²⁶ while Co_{1-x}S is a promising electrocatalyst for ORR^{18, 26} and OER,²⁶ Co₉S₈ is a good catalyst for ORR.²¹ However, the complicated preparation procedures coupled with the low electrical conductivities of cobalt sulfides usually result in the catalytic durability unsatisfactory. As alternatives, transition metal oxide/sulfide-carbon composites have been considered as promising electrocatalysts for ORR/OER since they hold a reasonable balance between catalytic activity, cost, and durability.²⁷ In particular, heteroatom (e.g., N, S, B, or P) doped carbon based materials have emerged and attracted great attention because heteroatom can tune the electronic and geometric properties of carbon, offering more active sites and enhancing the interaction between carbon structure and active sites.²⁷⁻³⁰ Remarkably, the combination of transition-metal metal oxide/sulfide with heteroatom-doped carbon can achieve high catalytic activity and improve durability because of the synergetic effect.²⁷

Metal organic frameworks (MOFs, including Zeolitic Imidazolate Frameworks (ZIFs)), a class of nanoporous materials assembled from metal ions and organic ligands,³¹⁻³³

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exhibit tuneable structures, versatile functionalities and fascinating properties. Owing to the molecular-like organic-inorganic crystal structure of MOFs, thermal treatment the parental MOFs can result in the formation of metal or metal oxide nanoparticles homogeneously dispersed within the nanoporous carbon matrices which frequently exhibit excellent electrochemical properties.³⁴⁻³⁹ Therefore, MOFs have emerged as excellent precursors or sacrificial templates for the preparation of porous carbon based nanocomposites, which offer a new approach to improve the catalytic activity and overcome the intrinsic limitations of the existing transition metal/metal oxide electrocatalysts.^{34, 35, 37-39} Metal sulfides derived from MOFs were recent reported;^{40, 41} however, to the best our knowledge, carbon-based metal sulfide composites derived from MOFs as highly efficient electrocatalysts for ORR/OER are rarely reported previously.

Herein, for the first time, we report the successful synthesis of atomically homogeneous dispersed cobalt sulfide/N,S-codoped porous carbon nanocomposites by a facile one-step sulfurization and carbonization of ZIF-67 simultaneously. ZIF-67 was chosen as a model precursor owing to its abundant Co–N moieties, rich organic resources and unique dodecahedral morphology.³³ Possessing unique core-shell structure, high porosity, homogeneous dispersion active components together with N and S-doping effect, the resulting composites exhibit excellent ORR and OER activities, superior durability, a four-electron pathway and high methanol tolerance in alkaline media, which outperformed the traditional Pt/C electrocatalyst. This may pave the way to further develop novel highly-efficient and low-cost composite electrocatalysts for the next generation of energy storage and conversion applications.

Experimental

Materials synthesis

ZIF-67 was synthesized from cobalt nitrate hexahydrate and 2-methylimidazole in water, following a modified procedure.⁴² The porous nanocomposites were prepared by a one-step direct carbonization and sulfurization process in the presence of hydrogen sulfide. In a typical synthesis, an alumina boat loaded with 0.25 g of dried ZIF-67 was placed in a flow-through quartz tube sitting in the centre of a tube furnace. The furnace was firstly heated to the target temperature (typically 600 – 1000 °C) with ramp rate 10 °C/min under pure argon atmosphere; when the furnace temperature reached the target temperatures, a 20 mL/min of hydrogen sulfide was then introduced in and maintained at the target temperature for 1 hour. The gas flow was then switched to argon only during the furnace cooled down to room temperature. The final product was collected from the quartz tube and labelled as Co_xS_y@C-z, where z stands for the sulfurization and carbonization temperature. Therefore the sample obtained from sulfurization temperature of 600, 800 and 1000 °C was labelled as Co_xS_y@C-600, Co_xS_y@C-800 and Co_xS_y@C-1000 respectively.

Materials characterization

X-ray diffraction (XRD) patterns were recorded with a Cu K α radiation (40 kV-40 mA) at a step time of 1 s and a step size of 0.02°. The Raman spectra of the samples were recorded in the backscattering arrangement, using a 532 nm laser excitation under laser power of 6 mW. Thermogravimetric analysis (TGA)/differential thermal analysis (DTA) was performed on a TA SDT Q600 instrument from the room temperature to 800 °C with a heating rate of 10 °C min⁻¹ under a continuous air flow of 100 mL min⁻¹. A Hiden QGA gas analysis mass spectrometer (MS) was coupled with the Q600 instrument to monitor and detect the gaseous compositions in the exhaust emission. Scanning electron microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDX) analyses were carried out on a Philips XL-30 machine in a high vacuum mode at an acceleration voltage of 20 kV. Samples were mounted using a conductive carbon double-sided sticky tape, then sputtered with a thin Au coating to reduce the effects of charging. Transmission electron microscopy (TEM) images were obtained on a JOEL-2100 at an acceleration voltage of 200 kV. The powder samples were first dispersed in absolute ethanol under moderate sonication, then pipetted onto a holey carbon Cu grid to obtain TEM specimens. N₂ gas sorptions were carried out on a Quantachrome Autosorb-iQ gas sorptometer via the conventional volumetric technique. Before gas analysis, the sample was evacuated for 3 hours at 200 °C under vacuum. The textural properties were determined via N₂ sorption at -196 °C. The surface area was calculated using the Brunauer-Emmett-Teller (BET) method based on adsorption data in the partial pressure (P/P_0) range of 0.02-0.22. The total pore volume was determined from the amount of nitrogen adsorbed at P/P_0 of ca. 0.99. X-ray photoelectron spectroscopy (XPS) was performed using a Kratos AXIS ULTRA spectrometer with a mono-chromated Al KR X-ray source (1486.6 eV) operated at 10 mA emission current and 15 kV anode potential. The analysis chamber pressure was better than 1.3×10⁻¹² bar. The take-off angle for the photoelectron analyzer was 90°, and the acceptance angle was 30° (in magnetic lens modes).

Electrocatalytic measurements

The electrocatalytic performance of the catalysts was evaluated by cyclic voltammograms (CV), linear sweep voltammograms (LSV) and chronoamperometry in a three-electrode electrochemical cell which was connected to a computer controlled potentiostat CHI 760D, coupled with a rotating disk electrode (RDE) system. A platinum wire and a Ag/AgCl/KCl (saturated solution) were used as the counter electrode and the reference electrode, respectively. A 3 mm in diameter bare glassy carbon electrode (GCE) or modified GCE with the studied material was used as the working electrode. Prior to use, GCE was hand-polished with chamois leather containing 0.05 μ m alumina slurry to obtain a mirror-like surface, washed with ethanol and distilled water by sonication for 5 min and allowed to dry. The modified GCE was prepared by casting a 5 μ L aliquot of the catalyst ink, which was obtained by ultrasonically dispersing 1 mg of the catalyst into 0.5 mL 0.05 wt% in alcohol Nafion solution, onto the fresh

surface of the pretreated GCE electrode and dried naturally to form a uniform thin film. The loading amount of each catalyst was kept to be $141.5 \mu\text{g cm}^{-2}$. The experiments were carried

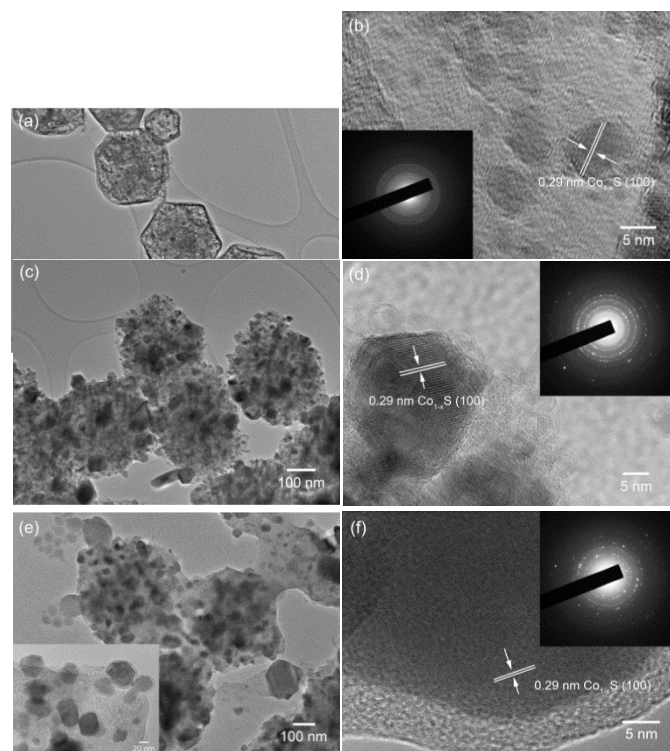


Fig. 1 TEM images of (a-b) $\text{Co}_x\text{S}_y@C-600$; (c-d) $\text{Co}_x\text{S}_y@C-800$ and (e-f) $\text{Co}_x\text{S}_y@C-1000$. Inset in (b), (d) and (f) is SAED patterns for corresponding sample.

out at room temperature in 0.1 M KOH solution, which was purged with high purity nitrogen or oxygen with a flow rate of 20 mL min^{-1} for at least 30 min prior to each measurement. All potentials were measured and reported vs the Ag/AgCl reference electrode.

Results and discussion

The structure and morphology of cobalt sulfide/N,S-codoped porous carbon composites samples are firstly investigated by transmission electron microscopy (TEM). The parental ZIF-67 precursor exhibits a typical rhombic dodecahedron with an average particle size of 350 nm (Fig. S1†).⁴² After sulfurization and carbonization process in hydrogen sulfide atmosphere at high temperatures, as presented in Fig. 1, the resulting cobalt sulfide/N,S-codoped porous carbon composites maintain the rhombic dodecahedron particles with a smaller size of 250 nm due to the shrinkage during the annealing process, and the particles tend to agglomerate and form larger particles at higher temperatures. Generally, all the composites are composed of numerous cobalt sulfides nanoparticles and continuous carbon networks, in which the cobalt sulfides nanoparticles are homogeneously embedded into the carbon matrix, with lattice fringes of $\sim 0.29 \text{ nm}$. The selected area electron diffraction (SAED) patterns shown in Inset of Fig. 1b, d

and f, clearly suggest that the bright scattered dots contribute from the crystalline cobalt sulfide nanoparticles while the dimmed diffraction rings are from the amorphous porous carbon matrix.¹⁸ In addition, the particle sizes for cobalt sulfide grow from 5 to 50 nm with the increase of annealing temperature from $600 \text{ }^\circ\text{C}$ to $1000 \text{ }^\circ\text{C}$, and the corresponding intensity of SAED patterns are also enhanced due to the increased annealing temperature resulting in the improved crystallization of cobalt sulfide particles. In particular, sample $\text{Co}_x\text{S}_y@C-600$ still maintains the original rhombic dodecahedron of the ZIF-67 precursor. Small cobalt sulfide nanoparticles (5 nm) are homogeneously dispersed into the carbon matrix. The surface of the sample $\text{Co}_x\text{S}_y@C-600$ is smooth (see the SEM in Fig. S2a†). While the sample $\text{Co}_x\text{S}_y@C-800$ shows slightly changed morphology because of the growing bigger cobalt sulfide crystals and its surfaces turn to rough (see Fig. S2b†), which is consistent with TEM results (Fig. 1c). Furthermore, high resolution TEM (Fig. 1d) indicates that onion-like carbon, which is formed due to the catalytic effect of metallic cobalt during the graphitization stage,^{36, 38} together with bigger cobalt sulfide particles (20 nm) can be observed. However, the sample $\text{Co}_x\text{S}_y@C-1000$ exhibit damaged or distorted rhombic dodecahedron morphology due to the higher annealing temperature, and cobalt sulfide crystals grow up to 50 nm (shown in Fig. 1e and Fig. S2c†). Interestingly, crystalline cobalt sulfide core and carbon shell structure is formed in the sample $\text{Co}_x\text{S}_y@C-1000$ (shown in Fig. 1e and f). This core-shell structure is also confirmed by using linear EDX analysis in STEM measurements (shown in Fig. S3†). The thickness of carbon shell is about 5 nm, which has tightly wrapped the cobalt sulfide crystals. Actually, core-shell structure has been proven to be beneficial to the improvement of electrocatalytic activities towards ORR and OER, where the core offers the catalytic active sites while the shell will provide facile electron transfer pathways and mass transport channels for the active cores due to the porous structures of carbon shell.^{27, 43}

Moreover, SEM combined with elemental mapping technique was used to ascertain the distribution of cobalt sulfide nanoparticles in the composite samples. As shown in Fig. S4†, element Co, S and C exhibit similar elemental mapping patterns to their selected area of SEM image, indicating the uniform dispersion of cobalt sulfide nanoparticles in the carbon matrix of sample $\text{Co}_x\text{S}_y@C-1000$. In addition, N is also observed in the elemental mapping, although N content is much less than that of C, possibly due to the high volatility of N species at high annealing temperature.

The crystal structures of the as-synthesized $\text{Co}_x\text{S}_y@C$ composites were further characterized by XRD (shown in Fig. 2a). Different from the Sodalite structure of ZIF-67 precursor (Fig. S1b†), the as-prepared composites show a broad XRD peak centred at 2θ of around 25° , representing the (002) diffraction of carbon.⁴⁴ Moreover, the XRD patterns of the composites indicate that they contain mainly Co_{1-x}S (ICDD PDF #42-0826) with the hexagonal structure in P63/mmc space group (no. 194).¹⁸ In addition, in sample $\text{Co}_x\text{S}_y@C-1000$, XRD peaks originated from Co_3S_4 (ICDD PDF #02-0825) can also be

observed, indicating the phase transition of cobalt sulfide crystals occurs at higher annealing temperature (1000 °C). Clearly, high sulfurization and carbonization temperature results in highly crystallized cobalt sulfide dispersed in carbon

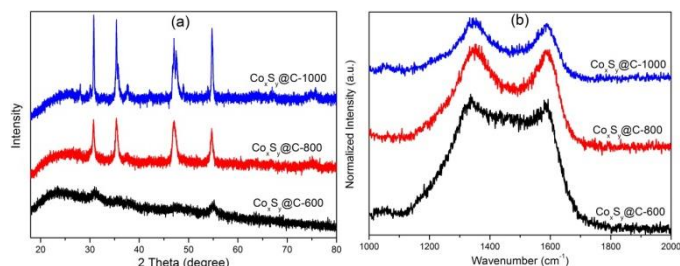


Fig. 2 (a) XRD patterns and (b) Raman spectra of the as-synthesized $\text{Co}_x\text{S}_y@C$ composites.

matrix. The XRD results are consistent with the lattice fringes of the Co_{1-x}S nanocrystals (Fig. 1b, d and f) and their electron diffraction patterns (the inset in Fig. 1d and Fig. 1f). Although it is ideal to achieve phase pure cobalt sulfide materials via control over the sulfurization temperature, it is actually difficult to achieve this using the proposed experimental procedure, which is consistent with the recent reports,^{45, 46} where the authors used sulfur for the sulfurization of ZIF-67 under different temperatures and the formation of the as-synthesized composites is complicated during the sulfurization and carbonization procedure. The XRD results clearly showed that with the increase of sulfurization temperatures, the XRD peaks for cobalt sulfide (mainly Co_{1-x}S phase) became more intense and sharper, accompanied with the appearing of Co_3S_4 , indicating the growth of crystallites and crystallinity improvement of cobalt sulfide. And both Co_{1-x}S and Co_3S_4 are regarded as good electrocatalysts for ORR and OER.^{18, 26} It is, however, worthy to understand the formation mechanism of cobalt sulfide in this relatively complicated system.

Raman spectroscopy is a powerful technique to investigate carbonaceous materials. As shown in Fig. 2b, all the composites clearly exhibit G band and D band in the Raman spectra, due to the bond stretching of all pairs of sp^2 atoms in both rings and chains and the breathing modes of sp^2 atoms in rings, respectively.^{47, 48} The G band at around 1590 cm^{-1} supports the presence of some nanocrystalline carbon and a high content of sp^2 -hybridized carbon atoms caused by the carbonization of the samples. The D band at around 1340 cm^{-1} is an indication of less disordered carbon. The appearance of both G band and D band in sample $\text{Co}_x\text{S}_y@C-600$, $\text{Co}_x\text{S}_y@C-800$, $\text{Co}_x\text{S}_y@C-1000$, suggests the formation of abundant defects and amorphous carbon in the composites during the sulfurization and carbonization process.

X-ray photoelectron spectroscopy (XPS) analysis was utilised to ascertain the structures of as-synthesized composites owing to the fairly complex phase diagram of cobalt sulphide.⁴⁹ Element survey by XPS (Fig. 3a) clearly suggests the presence of Co, S, C, N, and O in all the composites.^{27, 50} The spectrum of Co 2p (shown in Fig. 3b) for sample obtained at sulfurization temperature of 600 °C

($\text{Co}_x\text{S}_y@C-600$) exhibits two spin-orbit doublets at 781.2 and 796.9 eV, implying the existence of Co^{2+} oxidation state. However, except the spin-orbit doublets for Co^{2+} oxidation state, another doublets at 778.4 and 793.5 eV, which indicates the existence of Co^{3+} oxidation state,^{51, 52} can be found in the sample $\text{Co}_x\text{S}_y@C-800$ and $\text{Co}_x\text{S}_y@C-1000$, suggesting that a mixed Co^{2+} and Co^{3+} oxidation states are formed in these two samples.⁵¹⁻⁵³ In S 2p spectrum (shown in Fig. 3c), the first two peaks located at 161.4 and 162.5 eV were due to the spin-orbit coupling in metal sulfide,^{53, 54} while S 2p peak at 163.5 eV suggested the existence of covalent S-C bonds in the as-synthesized composites^{55, 56} indicating that S has been covalently inserted in N-doped porous carbon.⁴³ No peaks at around 164.5 eV corresponds to polysulfides (S_n^{2-}) can be found in all samples,⁵⁷⁻⁵⁹ and the peaks at 168.5 and 169.5 eV in S 2p spectrum indicate that inconsequential amount of Co_xS_y compounds were also formed during the thermal treatment process.^{60, 61} Moreover, the main peaks for N 1s spectra (shown in Fig. 3d) can be deconvoluted into four different types of nitrogen species: pyridinic-N (397.8 eV), Co-N (399.1 eV), pyrrolic-N (400.1 eV), and graphitic-N (401.8 eV), respectively.³⁹ The N species is widely considered to play an important role in the ORR and OER processes,^{62, 63} where pyridinic N could improve the onset potential and graphitic N determined the limiting current for ORR.^{27, 50} It is clear that high temperature results in low N content remaining in the samples, maybe due to the high volatility of N species under high temperature sulfurization process. From XPS results, the nitrogen doping level in sample $\text{Co}_x\text{S}_y@C-1000$ and $\text{Co}_x\text{S}_y@C-800$ is relatively low (2.51% and 3.64% respectively), sample $\text{Co}_x\text{S}_y@C-600$ possesses relatively high nitrogen content, and all the samples contain different level of sulfur content. However, it is not easy to evaluate the contribution of S doping to the catalytic activity separately in these complicated system. The C 1s spectrum of the composites (Fig. S5a†) exhibits a main peak at 284.6 eV suggesting the formation of sp^2 hybridized graphitic structure that can improve the electroconductivity of the samples, which is beneficial to fast electron transfer throughout the structural frameworks.²⁷ In addition, the C 1s can be further deconvoluted into peaks positioned at 284.8, 285.8, and 288.8 eV, which may attributed to C=C, C=N/C-O/C-S, and C-N, respectively.^{55, 64-66} Combining XPS analysis with XRD results, it is believed that the products derived from the sulfurization of ZIF-67 at high temperatures are basically Co_xS_y supported on N,S-codoped carbon composites.

The textural characteristics of the as-synthesised composites were analysed by N_2 sorption at $-196\text{ }^\circ\text{C}$. While sample $\text{Co}_x\text{S}_y@C-600$ exhibits a large hysteresis loop between its adsorption and desorption branches, implying the existence of mesoporous feature due to the voids between particles, the other two samples $\text{Co}_x\text{S}_y@C-800$, and $\text{Co}_x\text{S}_y@C-1000$ show largely reversible adsorption-desorption isotherms. These 3 samples exhibited specific surface area of 178, 238, and $248\text{ m}^2\text{ g}^{-1}$ and pore volume of 0.80, 0.35, and $0.31\text{ cm}^3\text{ g}^{-1}$, respectively (shown in Table S1), much lower than that of the ZIF-67 precursor (shown in Fig. 4 and Fig. S1c†), probably due

to the dominance of cobalt sulfide weight percentage in the as-synthesised composites. The relative large surface area of the composites is beneficial to provide more accessible active sites, which is likely to result in a higher electrocatalytic activity.³⁹

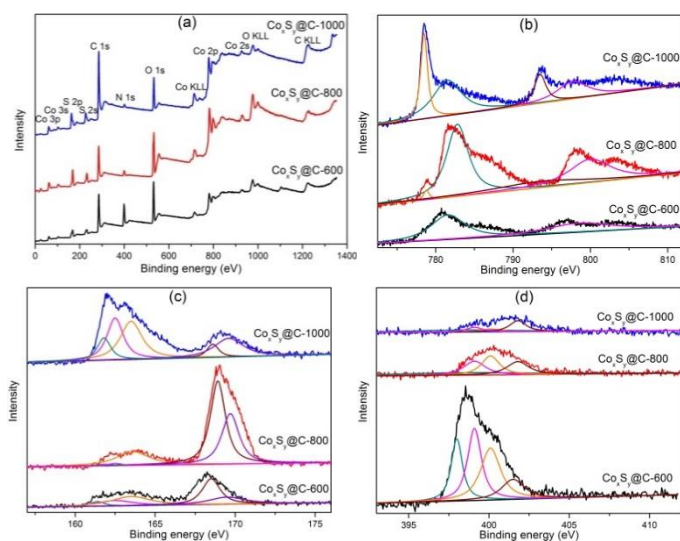


Fig. 3 (a) Element survey by XPS and high-resolution XPS spectrum of (b) Co 2p, (c) S 2p and (d) N 1s for the as-synthesised $\text{Co}_x\text{S}_y\text{@C}$ composites.

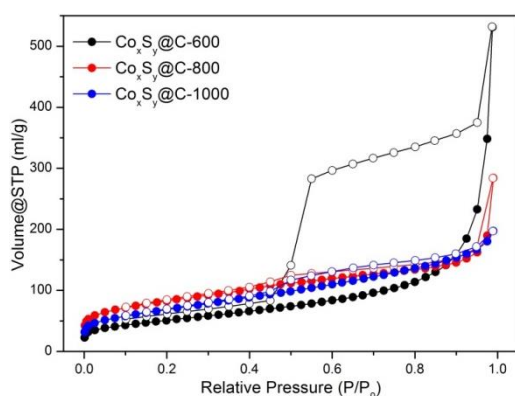


Fig. 4 Nitrogen adsorption-desorption isotherm curves of the as-synthesised $\text{Co}_x\text{S}_y\text{@C}$ composites.

The thermal stabilities of the composites in air were evaluated by TGA-MS. As shown in the TGA profiles (Fig. S6a[†]), all the as-synthesised composites exhibit a minor weight loss event below 100 °C due to the removal of adsorbed water from the composites (Fig. S6c[†]), followed by a small weight increase in the temperature range of 300–500 °C, due to the oxidation of cobalt sulfide to high valence state. There are then two major weight loss events at 450–500 and 790 °C for all the samples, corresponding to the burn off the N,S-codoped carbon species in air, as confirmed by the emission of CO_2 , NO_2 and SO_2 in their MS signals (see Fig. S6b, d and e[†]), and the decomposition and oxidation of cobalt sulfides (Fig. S6e[†]). It is worth noting that the sample $\text{Co}_x\text{S}_y\text{@C-600}$ shows different weight loss event in the temperature range of 300–500 °C,

accompanying the evolving CO_2 , NO_2 and SO_2 (see Fig. S6b, d and e[†]), maybe due to the oxidation of incomplete decomposition of organic ligands from the precursors.

The electrocatalytic activities of the as-prepared composites towards ORR are then evaluated by cyclic voltammetry (CV) measurements in 0.1 M KOH at 25 °C. Comparing the CV curves in O_2 -versus N_2 -saturated electrolyte solution, it clearly reveals that the composites are electrocatalytic active in ORR (Fig. 5a and Fig. S7[†]). As shown in Fig. 5a, no obvious redox peak is observed for $\text{Co}_x\text{S}_y\text{@C-1000}$ in N_2 -saturated solution. In contrast, when the electrolyte is saturated with O_2 , a well-defined cathodic peak clearly appears at -0.162 V, confirming the electrocatalytic activity for ORR.^{67, 68} Other samples $\text{Co}_x\text{S}_y\text{@C-600}$ and $\text{Co}_x\text{S}_y\text{@C-800}$ (Fig. S7[†]) show a cathodic peak at -0.425 and -0.156 V, respectively. Noticeably, the sample $\text{Co}_x\text{S}_y\text{@C-1000}$ shows a much higher peak current (2.94 mA cm^{-2}) than those of $\text{Co}_x\text{S}_y\text{@C-600}$ (0.735 mA cm^{-2}) and $\text{Co}_x\text{S}_y\text{@C-800}$ (1.48 mA cm^{-2}), implying that pronounced ORR catalytic activity for $\text{Co}_x\text{S}_y\text{@C-1000}$.

Rotating disk electrode (RDE) measurements were performed to gain further insight into the ORR kinetics of the $\text{Co}_x\text{S}_y\text{@C}$ composites. As shown in the polarization curves at 1600 rpm in 0.1 M KOH (Fig. 5b), $\text{Co}_x\text{S}_y\text{@C-1000}$ obviously holds the highest onset potential (around -0.04 V) and largest cathodic current density (-4.6 mA cm^{-2}), indicating its superior activity. The onset potential for $\text{Co}_x\text{S}_y\text{@C-1000}$ is close to that of the benchmark Pt/C catalyst (-0.02 V) while the half-wave potentials of them are very close, suggesting that $\text{Co}_x\text{S}_y\text{@C-1000}$ is a promising alternative catalyst for the cathodic ORR. In addition, the polarization curve of $\text{Co}_x\text{S}_y\text{@C-1000}$ is significantly different from that of $\text{Co}_x\text{S}_y\text{@C-600}$ and $\text{Co}_x\text{S}_y\text{@C-800}$ but resembles that of Pt/C, indicating that the ORR mechanism of $\text{Co}_x\text{S}_y\text{@C-1000}$ is different from those of the other $\text{Co}_x\text{S}_y\text{@C}$ composites but is more like that of Pt/C, which exhibited an efficient four-electron ORR pathway.^{69, 70} The mechanism of four-electron ORR pathway proceeds through two-oxygen atom side and/or bridge adsorption for oxygen dissociation simultaneously.⁷⁰

RDE measurements at different rotating speeds were carried out and the kinetic parameters were analysed with the Koutecky-Levich (K-L) equation. An increase in the rotation speed leads to an increase in the diffusion of oxygen at the surface of the electrode, which results in large current densities as shown in Fig. 5c. The good linearity and near parallelism properties of K-L plots for $\text{Co}_x\text{S}_y\text{@C-1000}$ indicates first-order reaction kinetics with regard to the concentration of dissolved oxygen and similar electron transfer numbers (n) for ORR at various potentials (Fig. 5d).⁷¹

The value of n and kinetic current density (J_k) can be respectively derived from the slope and intercept of the K-L plots (Fig. 5d and Fig. S8[†]) at various potentials,⁷² and the results are depicted in Fig. 5e. Obviously, the values of n for $\text{Co}_x\text{S}_y\text{@C-1000}$ varied from 3.69 to 3.78 in the potential range of -0.65 – -0.35V, suggesting that the ORR proceeded mainly through a four-electron pathway. This was further confirmed by the low HO_2^- yield (~12%) and high n value (> 3.7) measured by the RRDE tests as shown in Fig. S9c and 9d. The mechanism

of the four-electron transfer for ORR has been suggested to proceed through simultaneous two-oxygen atom side and/or bridge adsorption for oxygen dissociation.⁷⁰ In contrast, the n values for the other two composites decreased with the sulfurization temperature, and they are only 2.13–3.28 for the $\text{Co}_x\text{S}_y\text{@C-600}$, indicating that a two-electron pathway might dominate the $\text{Co}_x\text{S}_y\text{@C-600}$ catalysed ORR process. Moreover, the J_k values for $\text{Co}_x\text{S}_y\text{@C-1000}$ were always much higher than those for the other two composites, reflecting the enhanced electron transfer kinetics of oxygen reduction. Compared with other different previously reported catalysts (shown in Table S2), the ORR catalytic performance of $\text{Co}_x\text{S}_y\text{@C-1000}$ is competitive.

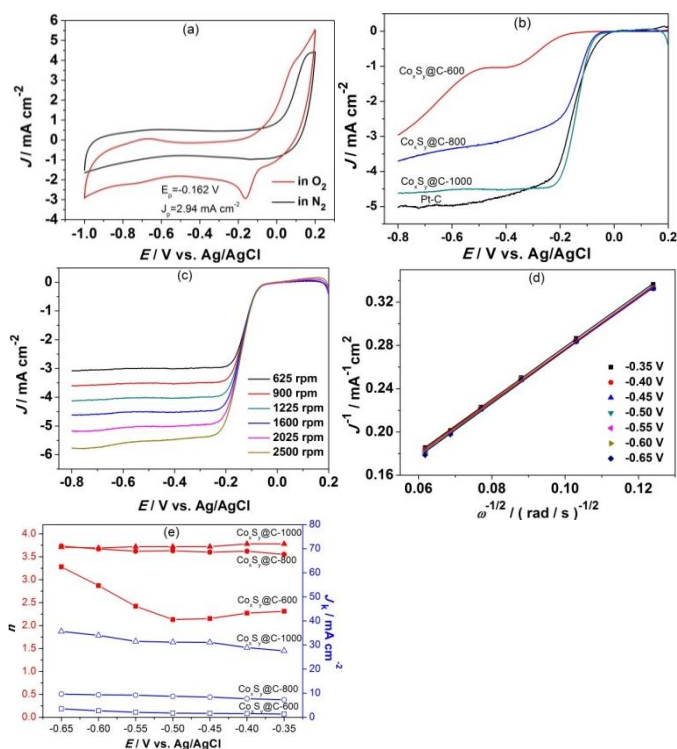


Fig. 5 (a) CV curves of $\text{Co}_x\text{S}_y\text{@C-1000}$ composite in N_2 - or O_2 -saturated 0.1 M KOH. (b) ORR polarization curves of $\text{Co}_x\text{S}_y\text{@C-600}$, $\text{Co}_x\text{S}_y\text{@C-800}$, $\text{Co}_x\text{S}_y\text{@C-1000}$, and Pt/C at 1600 rpm. (c) ORR polarization curves of $\text{Co}_x\text{S}_y\text{@C-1000}$ at different rotating speeds. (d) K-L plots of $\text{Co}_x\text{S}_y\text{@C-1000}$ at different potentials. (e) Electron transfer numbers (n) and the corresponding kinetic current density (J_k) of $\text{Co}_x\text{S}_y\text{@C-600}$, $\text{Co}_x\text{S}_y\text{@C-800}$, and $\text{Co}_x\text{S}_y\text{@C-1000}$ as a function of the electrode potentials.

The superior ORR activity of the $\text{Co}_x\text{S}_y\text{@C}$ -based composites is attributed to their novel structures. The pristine cobalt sulfides have major drawbacks in capacity fading and low conductivity. To overcome these obstacles, the cobalt sulfide nanoparticles can uniformly disperse into the heteroatom-doped carbon matrix, which formed a conducting network to the electrode and facilitate ORR through effective charge transport between oxygen molecules adsorbed on cobalt sulfide active sites and the electrode. The utilisation of molecular-like porous ZIF-67 as precursor not only enable the

generated cobalt sulfide nanoparticles homogeneously dispersed on porous carbon matrix, but also the porous carbons can serve as a substrate and good conductor that provide more accessible cobalt sulfide active sites, consequently further enhancement of the ORR activity can be realised. Specifically, for sample $\text{Co}_x\text{S}_y\text{@C-1000}$, the core-shell structure between the active cobalt sulfide nanoparticles and the porous carbon shells provides superior facile pathways for electron and mass transport.⁴³ In addition, heteroatom doped (N and S-doped) carbon also plays an important role in the ORR activity enhancement. By modifying the electronic and geometric properties of carbon matrix, N and S doping can not only provide more active sites, but also enhance the interaction between carbon structure and active catalytic sites.²⁷ The defects in carbon caused by N and S doping can result in much stronger adsorption of oxygen molecules and the higher activity for heterogeneous peroxide decomposition.²⁷

Besides the catalytic activities, the durability of the $\text{Co}_x\text{S}_y\text{@C-1000}$ composites and commercial Pt/C was tested at -0.15 V in 0.1 M KOH over 18000 s. It is observed that the sample $\text{Co}_x\text{S}_y\text{@C-1000}$ is more durable than commercial Pt/C (see Fig. 6a). The relative current of the sample $\text{Co}_x\text{S}_y\text{@C-1000}$, which was measured by chronoamperometry at a constant potential of -0.15 V after 18000 s, is 92%, but for Pt/C the value is only 74%. Such a high durability of $\text{Co}_x\text{S}_y\text{@C-1000}$ composite is due to the presence of the porous carbon matrix, which provides a conducting substrate and good electrochemical coupling between the substrate and oxygen molecules, and thus facilitates the ORR through the effective transportation of electrons between the oxygen molecules and the active sites of electrode. Moreover, the N and S co-doping on porous carbon shell may also play a role to form much stronger adsorption of oxygen molecules and the higher activity for heterogeneous peroxide decomposition. In addition, the unique core-shell structure of $\text{Co}_x\text{S}_y\text{@C-1000}$ composites also offers a better conducting substrate and excellent electrochemical coupling between the substrate and oxygen molecules.

Methanol crossover is one of the major disadvantages for Pt/C catalyst in ORR.^{23, 73} Thus, 1 M methanol was added into the 0.1 M KOH electrolyte solution to investigate the methanol tolerance for the as-synthesised composites under the same conditions as Pt/C. The results (see Fig. 6b) show that the introduction of methanol causes a sharp decrease in the current density for the Pt/C catalyst. In contrast, methanol has negligible effect on the performance of $\text{Co}_x\text{S}_y\text{@C-1000}$ composite at the cathode. The high durability and remarkable methanol tolerance give $\text{Co}_x\text{S}_y\text{@C-1000}$ superiority over the commercial Pt/C and thus it is a promising electrocatalyst for the cathodic ORR.

Excitingly, besides the high ORR activities, the $\text{Co}_x\text{S}_y\text{@C}$ composites also exhibit excellent electrocatalytic performances in OER (Fig. 7). Obviously, Pt/C is not a good catalyst for OER and much higher overpotential is required to achieve the current density of 10 mA cm^{-2} . Compared with sample $\text{Co}_x\text{S}_y\text{@C-600}$, $\text{Co}_x\text{S}_y\text{@C-800}$ and Pt/C, the higher OER

current density and an earlier onset of catalytic current are observed for sample $\text{Co}_x\text{S}_y\text{@C-1000}$, indicating that $\text{Co}_x\text{S}_y\text{@C-1000}$ is a highly active OER catalyst. As shown in Fig. 7a, an anodic peak of $\text{Co}_x\text{S}_y\text{@C-1000}$ is seen at around 0.3 V preceding the oxygen evolution, which can be attributed to the fact that cobalt sulfide nanoparticles in $\text{Co}_x\text{S}_y\text{@C-1000}$ are partly oxidized into cobalt oxide, forming the cobalt oxide/cobalt sulfide complex species.⁷⁴ The current density of 10 mA cm^{-2} can be achieved at a small overpotential of 0.47 V vs RHE for $\text{Co}_x\text{S}_y\text{@C-1000}$, much lower than that of $\text{Co}_x\text{S}_y\text{@C-800}$ (0.63 V vs RHE), but slightly higher than that of IrO_2 (0.45 V vs RHE). It is believed that the introduction of cobalt sulfide and N, S dopants results in the adjacent carbon atoms positively charged, which can not only facilitate the adsorption

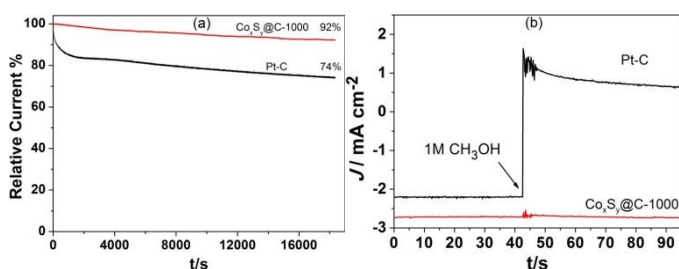


Fig. 6 (a) Current–time chronoamperometric responses of $\text{Co}_x\text{S}_y\text{@C-1000}$ and Pt/C at -0.15 V in O_2 -saturated 0.1 M KOH solution (1600 rpm). (b) Chronoamperometric responses of $\text{Co}_x\text{S}_y\text{@C-1000}$, and Pt/C at -0.15 V in O_2 -saturated 0.1 M KOH solution (1600 rpm) with the addition of 1 M methanol.

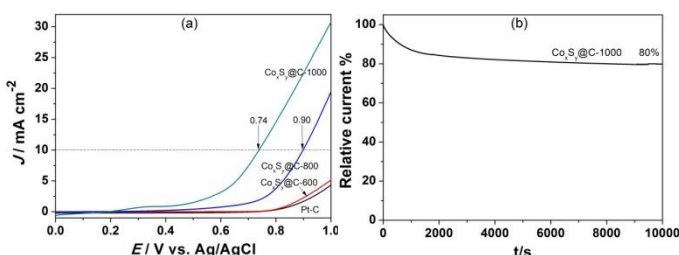


Fig. 7 (a) Linear sweep voltammetry (LSV) polarization curves of $\text{Co}_x\text{S}_y\text{@C-600}$, $\text{Co}_x\text{S}_y\text{@C-800}$, $\text{Co}_x\text{S}_y\text{@C-1000}$, and Pt/C at 5 mV s^{-1} in N_2 -saturated 0.1 M KOH solution. (b) Chronoamperometric response for $\text{Co}_x\text{S}_y\text{@C-1000}$ at 0.8 V vs Ag/AgCl.

of OH ions, but also promote the electron transfer between the catalyst surfaces and reaction intermediates.⁷⁵⁻⁷⁷ Significantly, the potential acquired for the current density of 10 mA cm^{-2} of $\text{Co}_x\text{S}_y\text{@C-1000}$ is comparable to those of other reported OER catalysts (as shown in Table S3). Furthermore, in the chronoamperometric test, the sample $\text{Co}_x\text{S}_y\text{@C-1000}$ can remain 80% its relative current after 10000 s (Fig. 7b), implying high durability of sample $\text{Co}_x\text{S}_y\text{@C-1000}$ in OER. Although oxidation may occur in Co-based OER catalyst,^{78, 79} it is believed that the surface property of the cobalt sulfide can be still maintained during the OER stability test, even though the cobalt sulfide was partly oxidized.²⁴ In the case of the sample $\text{Co}_x\text{S}_y\text{@C-1000}$, we believe the composite was largely maintained during the OER stability test since the unique core-

shell structures of the composites can protect the catalytic active cobalt sulfide from oxidation. It is likely that the a small amount of cobalt sulfide nanoparticles without carbon shell protections may be partly oxidized in the process of OER at 0.8 V vs Ag/AgCl for 2000 s which cause the slightly decay of catalytic performance.

In our work, the whole system of the cobalt sulfide/porous carbon materials is complicated as the as-synthesised composites containing different phases of cobalt sulfides, and nitrogen, sulfur (with different contents) co-doped porous carbons, and even the structure of the composites can affect the ORR and OER performance. Therefore, it is difficult to analyse each contribution of the materials separately. But it is believed that the higher electrocatalytic activity is led by the whole system.^{45, 46} Clearly, the sample $\text{Co}_x\text{S}_y\text{-1000}$ shows the best performance in ORR and OER. We believe that the main parameters that contribute to the higher electrocatalytic activity may be due to the highly crystallized cobalt sulfides combined with the synergistic effect between Co_xS_y and the porous carbons, the N and S doping may play the auxiliary roles. Moreover, the protective porous carbon substrate (for catalytic active Co_xS_y) and the unique core-shell structure of $\text{Co}_x\text{S}_y\text{@C-1000}$ may contribute to the excellent electrochemical stability.

Considering the easiness of preparation of $\text{Co}_x\text{S}_y\text{@C-1000}$ via a simple one-step sulfurization and carbonization of zeolitic imidazolate frameworks simultaneously, its cost-effective and much cheaper than the benchmarked Pt/C catalyst,³⁹ the remarkable features of excellent activities, favourable kinetics and high electrochemical stabilities, the current $\text{Co}_x\text{S}_y\text{@C-1000}$ sample may be one of the most promising alternative bifunctional electrocatalysts in both ORR and OER.

Conclusions

In summary, using ZIF-67 as a precursor, a facile one-step sulfurization and carbonization route has been successfully developed to synthesise atomically uniform dispersed cobalt sulfide nanocrystal particles embedded in N, S-codoped porous carbon matrices, which are promising advanced bifunctional electrocatalyst for ORR and OER. Due to the high porosity, unique core-shell structure, homogeneous dispersion and N and S-doping effect, the as-synthesised nanocomposite $\text{Co}_x\text{S}_y\text{@C-1000}$ not only exhibits exceptionally prominent electrocatalytic activity, good methanol tolerance and superior durability for ORR, but also offers promising catalytic performance for OER in alkaline medium. This work may open up a new avenue for the design and syntheses of highly homogeneous dispersed porous carbon-metal sulfides nanocomposite materials that display low-cost and efficient bifunctional electrocatalytic behaviours for the next generation of energy conversion and storage applications.

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