

CoSe₂/Co nanoheteroparticles embedded in Co, N co-doped carbon nanopolyhedra/nanotubes as an efficient oxygen bifunctional electrocatalyst for Zn–air batteries†

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Abstract

Transition metal selenide-based materials have been demonstrated as promising electrocatalysts for the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER), yet the actual design of a highly efficient and stable electro-catalyst based on these materials still remains a long and arduous challenge. Herein, a predesigned hybrid Zn/Co zeolitic imidazole framework was used to fabricate CoSe₂/Co nanoheteroparticles embedded within hierarchically porous Co, N co-doped carbonnanopolyhedra/nanotubes (CoSe₂/Co@NC-CNTs) through a facile approach involving controlled carbonization and selenization procedures. As expected, the optimized CoSe₂/Co@NC-CNT-1 displayed outstanding electrocatalytic performance for the ORR and OER, with an onset potential of 0.95 V *vs.* RHE, a half-wave potential of 0.84 V *vs.* RHE for ORR, and a potential of 1.69 V *vs.* RHE for OER at 10 mA cm^{−2}. It also exhibited excellent long-term stability and methanol resistance ability, which were superior to commercial IrO₂ and the commercial 20 wt% Pt/C catalyst. Notably, the assembled Zn–air battery with CoSe₂/Co@NC-CNT-1 showed a low charge–discharge voltage gap (0.696 V at 10 mA cm^{−2}) and a high peak power density (100.28 mW cm^{−2}) with long-term cycling stability. These superior performances can be ascribed to the synergistic effects of the highly active CoSe₂/Co nanoheterostructure, hierarchically porous structure with a large surface area, high electrical conductivity and uniform doping of the Co and N.

Introduction

On account of the increasingly serious environmental pollution globally, the replacement of traditional energy has become cumulatively more essential today. Relatively, electricity has been ubiquitously used as clean and environmentally friendly energy in our daily lives, and the demands for efficient energy conversion and storage have dramatically increased.^{1,2} In this case, fuel cells and metal–air batteries are gaining more and more attention among various energy devices because of their cleanness, high efficiency and environmental benignity.^{3,4} In these energy conversion devices, the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) are two significantly electrocatalytic reactions but they suffer from sluggish kinetics, which limit their commercialization, and therefore there is a need to find a new kind of low-cost and highly active electrocatalysts.^{5,6} Until now, Pt, Pt-based and IrO₂, IrO₂-based catalysts are still the best and most universal electrocatalysts for the ORR and OER. However, there are many existing problems with Pt-based catalysts, such as their high price, source shortage and limited stability.^{7–9} There is thus an urgent search for economical, abundant and highly active non-precious catalysts.

Among the many investigations on non-precious metal-based electrocatalysts, a lot of attention has been concentrated on developing transition-metal oxides/chalcogenides (M_xO_y, M_xS_y and M_xSe_y, *etc.*) due to their relatively low cost and expected long-term stability.^{10–14} Among these, CoSe₂, a kind of 3D transition metal chalcogenide, has demonstrated promise to potentially replace Pt-based catalysts.^{15,16} However, pure CoSe₂ still suffers from an intrinsic deficiency in terms of its low electron-transfer efficiency due to its low exposure of active sites and poor conductivity, making the electrocatalytic performance of CoSe₂ still far less than expected.^{17,18} Therefore, it is a huge challenge to prepare CoSe₂ catalysts with more exposed active sites and enhanced charge-transfer efficiency.

Recent studies have shown that heterostructures consisting of two constituents are beneficial for increasing the active sites and improving the electrocatalytic performance. Most studies have been focused on either the construction of heterostructures with noble metals or metal/metal and metal/metallic oxide systems.^{19,20} For instance, Chen^{21,22} produced AgPd/rGO catalysts and Pd₇₂Ce₂₈/C catalysts to enhance the electrocatalytic activity for the formate oxidation reaction, and through DFT studies, the relative crystallographic planes were verified to contribute to the electrocatalytic activity. However, study into metal/metallic selenide

heteroparticles remains quite rare and thus meaningful. Furthermore, loading active materials with a functional carbon matrix has been proven to be an effective means to improve the electrocatalytic performance of ORR and OER catalysts,^{23–25} in which the following factors are recognized to have an important role: (1) a high surface area with a hierarchical pore structure, which shortens the free diffusion path lengths of O₂ and the electrolyte to the catalytic active sites;²⁶ (2) a uniform decoration of heteroatoms (B, P, N, Co, Fe, *etc.*), which can usually modify the electronic properties and increase the structural and atomic defects, thus further enhancing the electrocatalytic performance of the catalysts;^{27,28} (3) a high density of valid active sites, as provided by M–N_x/C, for example, where the involvement of the Co–N_x moiety can effectively improve the electrocatalytic activity;²⁹ (4) high electrical conductivity, which can be enhanced by the incorporation of graphitized carbon and/or carbon nanotubes (CNTs), which are usually formed *via* catalysis over Fe, Co, *etc.*³⁰. Nevertheless, the realization of these strategies usually involves multi-step procedures, toxic reactants and rigorous experimental conditions. In this regard, discovering a universal and controllable way to combine transition metal materials with the multifunctional carbon skeleton is still quite desirable and challenging.

Metal–organic frameworks (MOFs), a kind of porous crystalline material that is constructed of metal units and organic ligands, have attracted tremendous attention in functional applications due to their extremely high surface area, variable pore structure and facile synthesis.^{31–33} The well-organized MOFs have been demonstrated as excellent precursors or sacrificial templates to prepare multifunctional carbon materials *via* a facile carbonization.^{34–36} In particular, zeolite imidazole frameworks (ZIFs), a subclass of MOFs that are constituted by bridging zinc or cobalt ions and nitrogen-rich imidazolate linkers within polyhedral frameworks, have been utilized as ideal precursors to prepare N-doped or graphitized carbon-based nanocomposites for energy storage and conversion applications.^{29,37}

Inspired by the above, in this work, we selected hybrid Zn and Co bimetallic zeolitic imidazole frameworks (Zn/Co-ZIFs) as the precursor to prepare hybrid electrocatalysts composed of CoSe₂/Co heterostructures and Co, N co-doped porous carbon nanopolyhedra/nanotubes through a facile and controllable calcination-selenization strategy. The Co ions within the synthesized ZIF precursor were first reduced to metallic cobalt and then further converted to CoSe₂/Co nanoheteroparticles in the subsequent reaction with selenium powder. Meanwhile, the organic ligands were *in situ* carbonized to a nitrogen-doped carbon matrix with high porosity and high electrical conductivity. The CoSe₂/Co nanoheteroparticles were uniformly dispersed in the carbon matrix, which had a strong and stable interfacial contact with the CoSe₂/Co nanoheteroparticles, significantly enhancing the mass transfer and the

exposure of active sites. The effects of selenization and the $\text{Zn}^{2+}/\text{Co}^{2+}$ molar ratios on the microstructure, composition and electrocatalytic activity were systematically studied.

As expected, the as-prepared hybrid electrocatalysts showed excellent electrocatalytic activity in alkaline media, and their stability as well as methanol tolerance were superior to a commercial Pt/C catalyst.

Results and discussion

The strategy to synthesize CoSe_2/Co -embedded Co, N-doped carbon nanopolyhedra/nanotubes involved three steps, as illustrated in Fig. 1. First, the hybrid Zn/Co-ZIFs with varied molar ratios of $\text{Zn}^{2+}/\text{Co}^{2+}$ were synthesized *via* the magnetically-stirred co-precipitation reaction of $\text{Zn}(\text{NO}_3)_2$ and $\text{Co}(\text{NO}_3)_2$ with 2-methylimidazole in methanol solution. Afterwards, the Zn/Co-ZIF precipitates were separated by centrifugation and further carbonized at 800 °C under a H_2/Ar atmosphere to obtain Co, N co-doped porous carbon nanopolyhedra/nanotubes (labelled $\text{Co@NC-CNT-}x$, where x indicates that the sample was derived from the corresponding Zn/Co-ZIFs with a $\text{Zn}^{2+}/\text{Co}^{2+}$ molar ratio value of x). It should be noted that the $\text{Co@NC-CNT-}x$ was strategically prepared to combine both the advantages of the Zn-ZIF-derived and Co-ZIF-derived carbon matrix, such as a high porosity with a large surface area and uniformly dispersed N species from the Zn-ZIF-derived carbon, a highly graphitized carbon structure, highly conductive CNTs and an active Co- N_x moiety from the Co-ZIF-derived carbon, with all these species conducive for a highly efficient oxygen reduction reaction.^{29,38,39} Finally, a thermal selenization procedure was performed to convert the Co metal into heterostructured CoSe_2/Co nanoparticles embedded within the highly porous Co, N co-doped carbon nanopolyhedra/nanotubes.

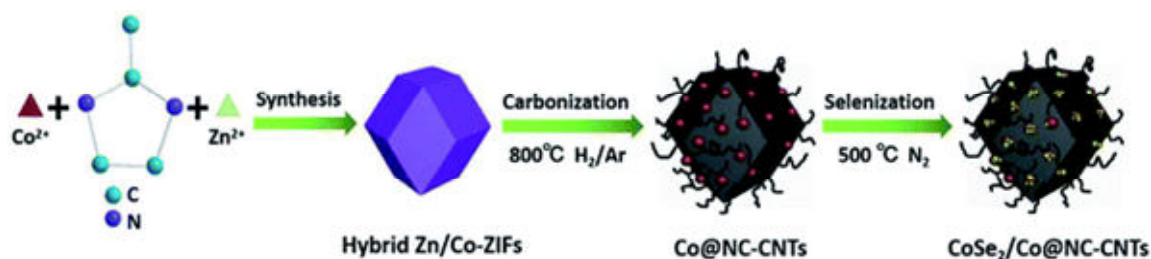


Fig. 1 Schematic illustration of the synthesis procedures of $\text{CoSe}_2/\text{Co@NC-CNTs}$.

The morphology and further detailed microstructure of the as-prepared samples were investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The crystalline features and composition were identified by powder X-ray diffraction (XRD). As shown in Fig. 2a and S2a–c,[†] the as-synthesized Zn/Co-ZIF nanoparticles showed a similar rhombic polyhedral shape with smooth surfaces and an increasing particle size (300–

500 nm) with the molar ratio of $\text{Zn}^{2+}/\text{Co}^{2+}$ increasing. After carbonization, the Zn/Co-ZIFs were transformed into porous Co, N co-doped carbon nanopolyhedra/nanotubes. As exhibited in Fig. S1 and S2d–f,[†] the XRD patterns of Co@NC-CNT-*x* corresponded well with those of the standard Co (PDF#15-0806), and the diffraction peaks of Co phase became more obvious with the Co content increasing. Furthermore, no peak of Zn was visible, indicating the complete evaporation of Zn metal at such a high temperature. Compared to the original Zn/Co-ZIFs, the ZIF-derived carbon particle size was decreased and the polyhedral structure was gradually unable to be maintained with the increase in the Co ratio, resulting from the degradation of organic linkers and the formation of more carbon nanotubes catalyzed from Co nanoparticles under high temperature treatment. After selenization with sufficient Se powder, some of the Co nanoparticles were transformed into CoSe₂. As exhibited in Fig. 3a, the characteristic peaks of CoSe₂/Co@NC-CNT-*x* corresponded well with those of standard CoSe₂ (PDF#53-0449) and Co (PDF#15-0806). Scanning electron microscopy (SEM) indicated that the larger particles (CoSe₂/Co) were distributed on the surface of CoSe₂/Co@NC-CNTs compared to with the Co@NC-CNTs (Fig. 2c–f). Detailed transmission electron microscopy (TEM) studies, taking CoSe₂/Co@NC-CNT-1 as an example, revealed that the carbon nanopolyhedra were embedded with a large number of well-dispersed CoSe₂/Co nanoparticles and highly porous textures existed throughout the whole particles (Fig. 2g and h). The carbon nanopolyhedra were also bridged by multi-walled carbon nanotubes (MWCNTs, with a diameter of about 12 nm). During the high-temperature carbonization process, graphitic carbon structures were formed under the catalyzation of Co metal nanoparticles (Fig. 2i). Besides, the high-magnification TEM image clearly shows interfaces of the embedded nanoparticles with crystal lattice spacings of 0.26 nm and 0.2 nm, which are in a good agreement with the (111) lattice plane of CoSe₂ and Co, respectively (Fig. 2j).

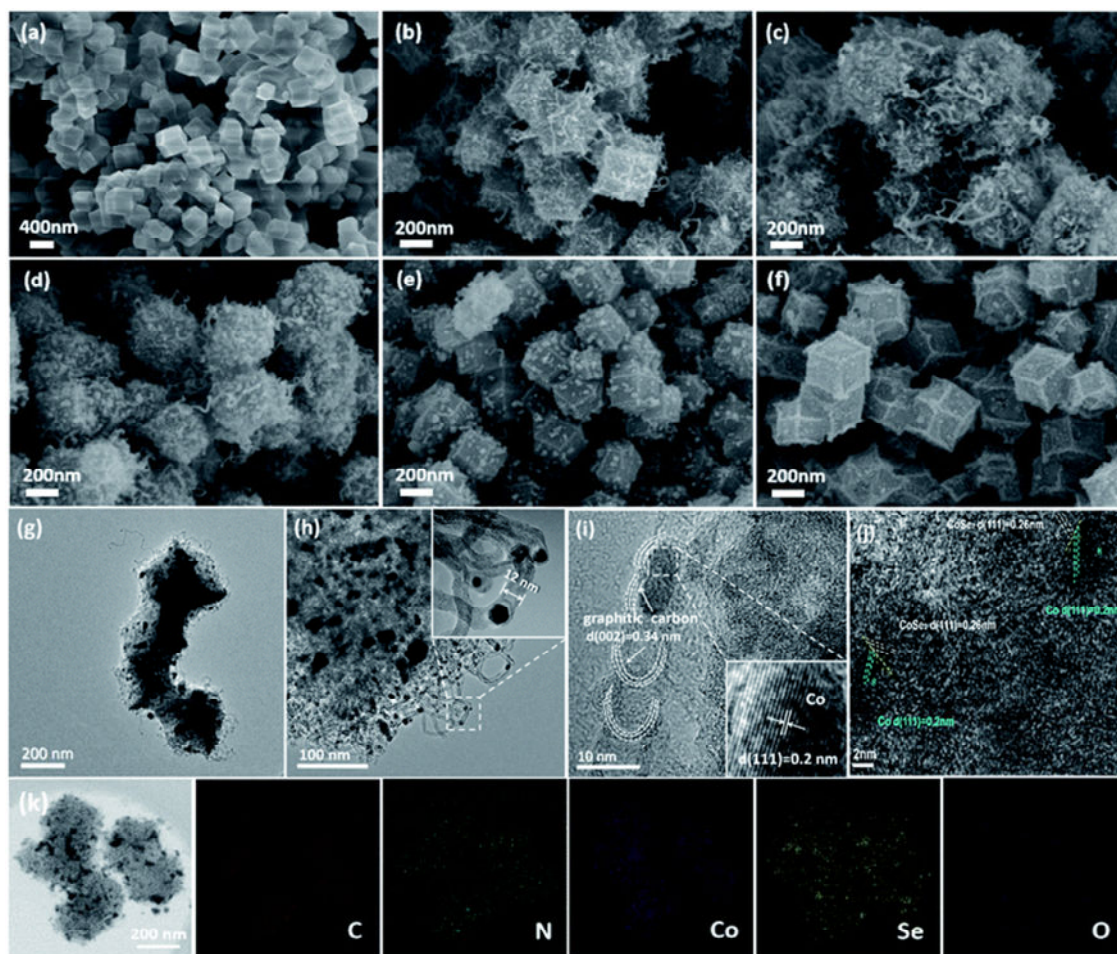


Fig. 2 SEM images of (a) Zn/Co-ZIF-1, (b) Co@NC-CNT-1, (c) CoSe₂/Co@NC-CNT-0.5, (d) CoSe₂/Co@NC-CNT-1, (e) CoSe₂/Co@NC-CNT-2, (f) CoSe₂/Co@NC-CNT-5. TEM images of (g and h) CoSe₂/Co@NC-CNT-1. HRTEM images of (inside of h) MWCNTs, (i) Co and (j) CoSe₂/Co nanoparticles. (k) Elemental mapping of CoSe₂/Co@NC-CNT-1.

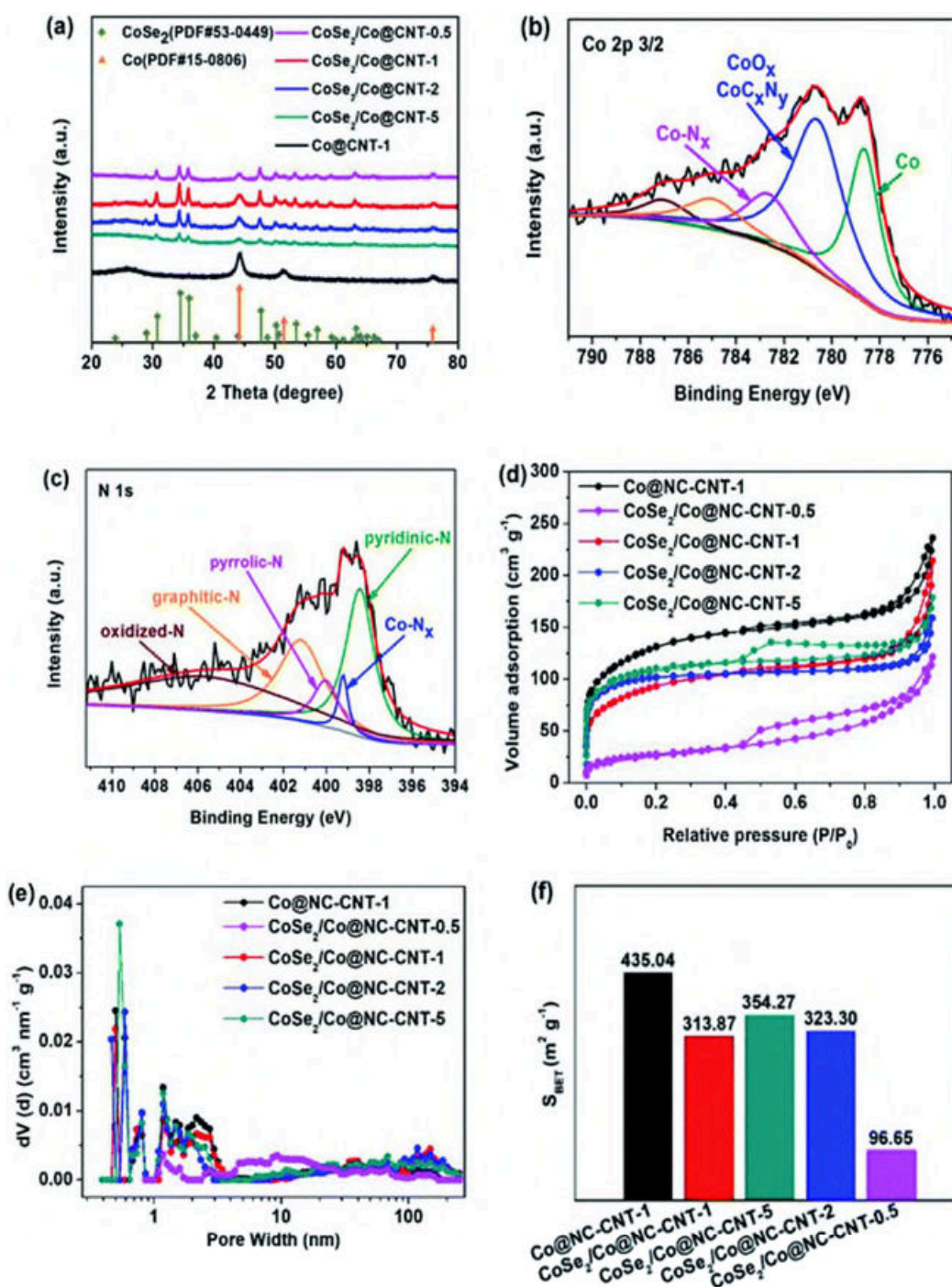


Fig. 3 (a) XRD pattern of Co@NC-CNT-1 and CoSe₂/Co@NC-CNT-*x* samples. High-resolution XPS spectra of (b) Co 2p 3/2 for CoSe₂/Co@NC-CNT-1, (c) N 1s for CoSe₂/Co@NC-CNT-1. (d) N₂ sorption isotherms for Co@NC-CNT-1 and CoSe₂/Co@NC-CNT-*x* samples. (e) Pore-size distributions of Co@NC-CNT-1 and CoSe₂/Co@NC-CNT-*x*. (f) BET surface areas of Co@NC-CNT-1 and CoSe₂/Co@NC-CNT-*x*.

Elemental mapping indicated that CoSe₂/Co@NC-CNT-1 was made mainly of Co, Se, N, C and O, among which Co, Se and N were uniformly distributed throughout the carbon matrix

(Fig. 2k). The other CoSe₂/Co@NC-CNT-*x* derived from Co@NC-CNT-*x* had similar structures with CoSe₂/Co@NC-CNT-1. Raman spectra were recorded to further study the carbon structure changes in the CoSe₂/Co@NC-CNTs. The two main peaks located at about 1350 cm⁻¹ (D band) and 1580 cm⁻¹ (G band) were related to disordered carbon and graphitic carbon, respectively. Here, the relative intensity ratio of the G band to the D band (I_G/I_D) is usually used to evaluate the graphitization degree of carbon materials.^{40,41} As exhibited in Fig. S3,[†] the values of I_G/I_D increased with the increase in Co contents, indicating the increase in graphitized carbon structures.

To look further into the chemical compositions and elemental valence states, X-ray photoelectron spectroscopy (XPS) measurements of CoSe₂/Co@NC-CNT-1 were carried out. As exhibited in Fig. S4a,[†] the survey scan spectrum of CoSe₂/Co@NC-CNT-1 clearly confirmed the presence of Co, Se, N, C and O elements. The high-resolution spectrum of C 1s was fitted and divided into three peaks: graphitic sp² carbon at 284.6 eV, C=N bonds at 285.9 eV and C–N bonds at 287.6 eV, respectively (Fig. S4b[†]). The fitting results confirmed the graphitic carbon layers were introduced with nitrogen atoms during the carbonization process. The high-resolution spectrum of Co 2p_{3/2} exhibited three important peaks at 778.6, 780.6 and 782.6 eV (Fig. 3b), which were related to the metallic Co, CoO_{*x*}/CoC_{*x*}N_{*y*} and Co–N_{*x*}, respectively. The Co–N_{*x*} moieties, which have been demonstrated to be among the best active sites for ORR, play an important role in improving the ORR performance. The high-resolution spectrum of N 1s was fitted and divided into five peaks at 398.4, 399.2, 400.1, 401.1 and 405.6 eV, which were in agreement with the pyridinic-N, Co–N_{*x*}, pyrrolic-N, graphitic-N and oxidized-N, respectively (Fig. 3c). All these N species have been proven to make a great contribution towards the ORR activity except for oxidized-N. Additionally, as illustrated in Fig S4c and 4d,[†] the O 1s spectrum was deconvoluted into four peaks at 530.5, 531.1, 532.4 and 53.8 eV, associated with the Co–O, C=O, Se–O and H–O–H bonds, respectively. The high-resolution spectrum of Se 3d was deconvoluted into three main peaks at 54.1, 55.1 and 58.8 eV, corresponding to Co–Se, Se–Se and Se–O–Se, respectively.

The ORR and OER are types of interfacial reactions, for which abundant porous structures and a large surface area are beneficial. So, nitrogen adsorption/desorption measurements were employed to obtain more detailed information about the porous texture of Co@NC-CNT-1 and CoSe₂/Co@NC-CNT-*x* (*x* = 0.5, 1, 2, 5). As displayed in Fig. 3d, all the samples exhibited type IV isotherms with a significant rise at the beginning with loading nitrogen and hysteresis loops appearing at a moderate relative pressure ($P/P_0 > 0.4$), revealing the coexistence of microporous and mesoporous structures in the body. As conformed by the pore-size

distributions (Fig. 3e), the microporous structure was centred at 0.6 nm while the mesoporous structure was centred at 2.5 nm. Fig. 3f gives the BET surface areas of Co@NC-CNT-1 and CoSe₂/Co@NC-CNT-*x* (*x* = 0.5, 1, 2, 5): 435.04, 96.65, 313.87, 323.30 and 354.27 m² g⁻¹, respectively. It could be obviously observed that the BET surface area of Co@NC-CNT-1 (435.04 m² g⁻¹) was larger than that of CoSe₂/Co@NC-CNT-1 (313.87 m² g⁻¹), while CoSe₂/Co@NC-CNT-1 had the best ORR and OER performance. It was revealed that the electrocatalytic activity is not entirely determined by the specific surface area and active CoSe₂/Co heterostructures can efficiently improve the electrocatalytic performance in ORR and OER. In addition, CoSe₂/Co@NC-CNT-5 had the largest BET surface area (354.27 m² g⁻¹) among the CoSe₂/Co@NC-CNT-*x* electrocatalysts, while CoSe₂/Co@NC-CNT-0.5 had the least specific surface area (96.65 m² g⁻¹), suggesting that the increase in Co content causes a decrease in the specific surface area. Such high BET surface areas and hierarchically porous structures can provide more active sites and reaction locations to improve the ORR and OER performance of the electrocatalyst.

With the various bits of structural information mentioned above, we studied the electrocatalytic properties of CoSe₂/Co@NC-CNT-*x* (*x* = 0.5, 1, 2, 5) in alkaline media (0.1 M KOH and 1 M KOH). Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) curves were first recorded by the rotation disk electrode (RDE) and L-type glassy carbon electrode measurements. As a comparison, commercial 20 wt% of Pt/C, commercial IrO₂ (Ir ≥ 84.5%) and the corresponding Co@NC-CNT-1 electrodes were measured under the same conditions, respectively. As shown in Fig. 4a, b and S6,[†] the CV curves for all the electrocatalysts exhibited a nearly rectangular shape and no reduction peak appeared in the Ar-saturated solution in the ORR. On the contrary, all the electrocatalysts, except for the contrastive Pt/C, exhibited a well-defined reduction peak from 0.7 V to 0.9 V vs. RHE in O₂-saturated solution, confirming their obvious electrocatalytic activities for ORR. The ORR performances for all the electrocatalysts were further evaluated using the LSV technique at a rotation speed of 1600 rpm. As displayed in Fig. 4c and Table S1,[†] compared to the other CoSe₂/Co@NC-CNT-*x* (*x* = 0.5, 2, 5), it could be obviously observed that CoSe₂/Co@NC-CNT-1 possessed the best electrocatalytic performance, which was even comparable to that of Pt/C. The values for CoSe₂/Co@NC-CNT-1 and Pt/C for the diffusion-limited current density, onset potential and half-wave potential were 6.82 and 6.52 mA cm⁻², 0.95 and 1.06 V (vs. RHE), 0.84 and 0.86 V (vs. RHE), respectively. Those are superior to the other CoSe₂/Co@NC-CNT-*x* electrocatalysts (*x* = 0.5, 2, 5), especially for Co@NC-CNT-1 (diffusion-limited current density of 5.47 mA cm⁻², onset potential of 0.9 V vs. RHE, and half-wave potential of 0.82 V vs. RHE), confirming

the superiority of the active CoSe₂/Co-embedded porous carbon structure. Furthermore, the Tafel slopes of CoSe₂/Co@NC-CNT-*x* (*x* = 0.5, 1, 2, 5) were all smaller than for Pt/C in [Fig. 4d](#), but the Tafel slope of CoSe₂/Co@NC-CNT-1 was the smallest among these samples, and it also had the best ORR performance. Therefore, it is clear that a smaller Tafel slope could confirm a better ORR performance in electrocatalysts.

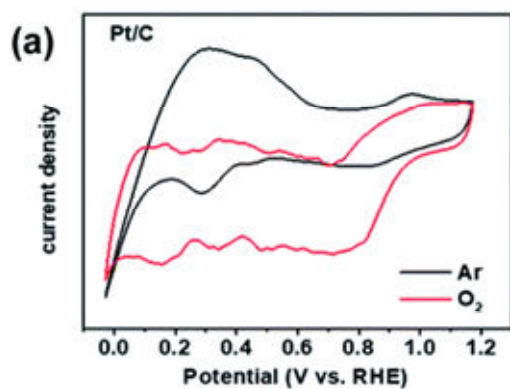
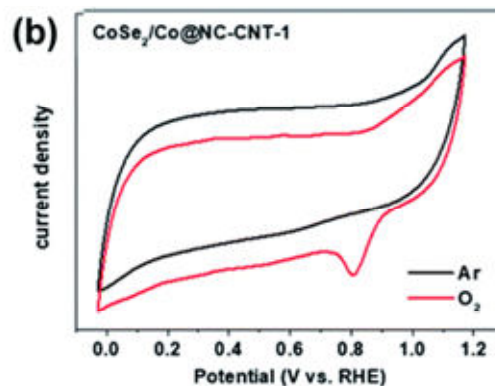
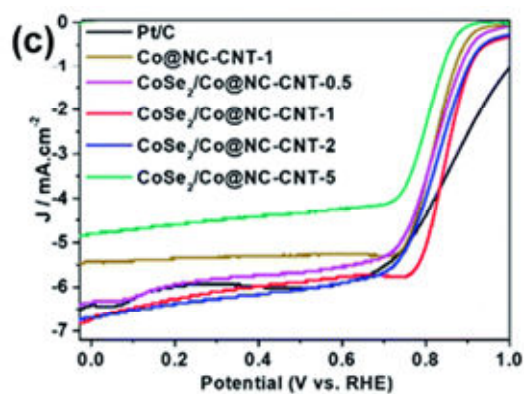
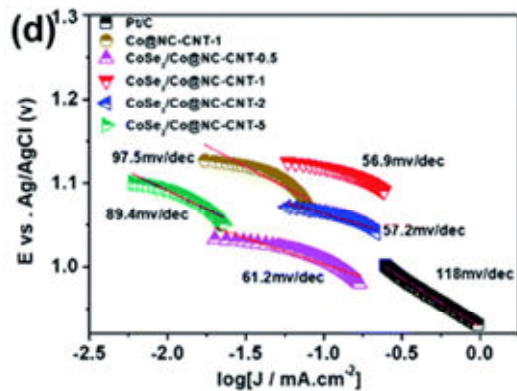
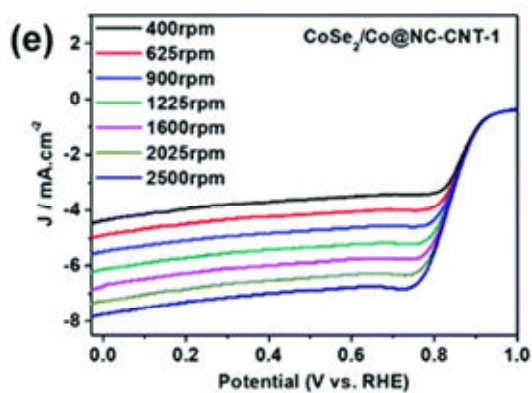
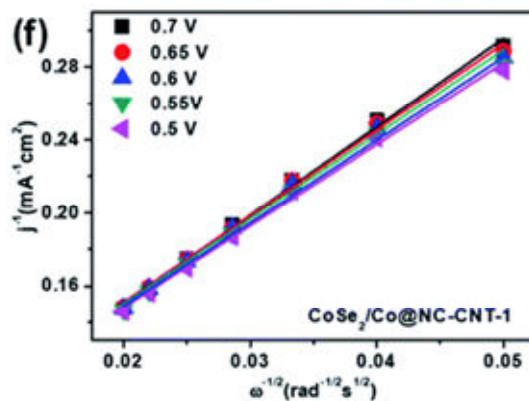
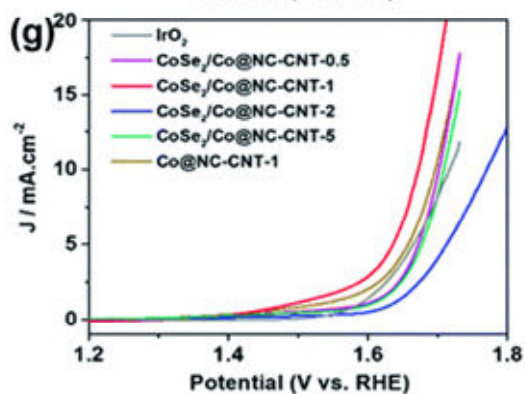
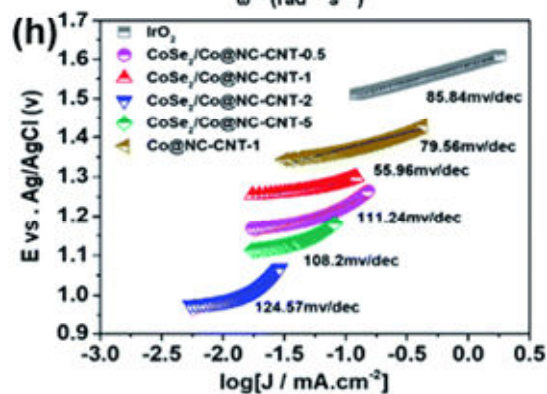


Fig. 4 CV curves of (a) commercial Pt/C and (b) CoSe₂/Co@NC-CNT-1 in Ar-saturated and O₂-saturated 0.1 M KOH. (c) LSV curves of different samples for ORR in O₂-saturated 0.1 M KOH at a rotation rate of 1600 rpm. (d) Tafel plots of different samples for ORR. (e) LSV curves of CoSe₂/Co@NC-CNT-1 for ORR at different rotation speeds. (f) Koutecky–Levich plots of CoSe₂/Co@NC-CNT-1 at different potentials. (g) LSV curves of different samples for OER in O₂-saturated 1 M KOH. (h) Tafel plots of different samples for OER.

To gain more insights into the ORR activity and the reaction kinetics, the ORR polarization curves of the CoSe₂/Co@NC-CNT-*x* and Pt/C electrocatalysts were measured at different rotation speeds from 400 to 2500 rpm in O₂-saturated 0.1 M KOH. As shown in [Fig. 4e](#) and [S7,†](#) the diffusion-limited current density increased with the rotation speed increasing due to the shorter diffusion paths at high speed. The electron-transfer number (*n*) in the reaction path was calculated based on the Koutecky–Levich (K–L) equation. As displayed in [Fig. 4f](#) and [S8,†](#) the K–L plots at various potentials displayed great linearity and close slope values, which indicated that these electrocatalysts have similar electron-transfer numbers for the ORR. The electron-transfer number of CoSe₂/Co@NC-CNT-1 was calculated to be 3.8–4.0 at a potential range from 0.5–0.7 V (*vs.* RHE), suggesting the ORR activity was catalyzed by CoSe₂/Co@NC-CNT-1 mainly through a four-electron transfer process. In [Fig. 4g](#), CoSe₂/Co@NC-CNT-*x* (*x* = 0.5, 1, 2, 5) displayed better OER electrocatalytic performance than IrO₂, and CoSe₂/Co@NC-CNT-1 possessed outstanding electrocatalytic property, with a potential of 1.69 V *vs.* RHE at 10 mA cm^{−2}. Additionally, the Tafel slope of CoSe₂/Co@NC-CNT-*x* (*x* = 0.5, 1, 2, 5) and IrO₂ are displayed in [Fig. 4h](#), and it could be seen that the Tafel slope of CoSe₂/Co@NC-CNT-1 was the smallest among these samples. In the meantime, CoSe₂/Co@NC-CNT-1 also had the best OER performance among these samples and IrO₂, confirming the Tafel slope was lower and the OER performance was better.

To evaluate the electrochemical active surface area (ECSA), the double layer capacitance (*C_{dl}*) was measured to assess the value of ECSA. Finally the ECSA value of CoSe₂/Co@CNT-1 was roughly calculated to 1472.19 cm², which was the largest ECSA value among these five samples and implied it had the most electrocatalytic active sites for ORR.

In addition to the electrocatalytic activity, the long-term stability and methanol tolerance ability are also important factors to evaluate the electrocatalytic performance of OER and ORR electrocatalysts. To evaluate the long-time stability, all the electrocatalysts were cycled in a voltage range from −0.4 V to 0 V (*vs.* Ag/AgCl) at a scan speed of 50 mV s^{−1} in O₂-saturated 0.1 M KOH for ORR, in which they can both be involved in reduction reaction processes. After a continuous 10 000 CV cycles, the LSV curves of all the electrocatalyst were tested again. As

shown in [Fig. 5a, b](#) and S9a–f,[†] the half-wave potential of CoSe₂/Co@NC-CNT-1 remained almost unchanged with only a little negative movement of 11 mV, while the Pt/C electrocatalyst suffered from a larger negative movement of about 42 mV, indicating the superb stability compared to Pt/C and the other electrocatalysts. Furthermore, the methanol resistance of CoSe₂/Co@NC-CNT-1 was also measured by adding 3 M methanol at 300 s, and it was observed that there was almost no variation in the LSV curves of CoSe₂/Co@NC-CNT-1, while the Pt/C electrocatalyst appeared to show a continuous decrease in activity due to the methanol poisoning reaction ([Fig. 5c and d](#)). In addition, the OER LSV curves of all the electrocatalysts were tested, with the results shown in [Fig. 5e, f](#) and S9h–l,[†] where after a continuous 10 000 CV cycles, the potential gap of CoSe₂/Co@NC-CNT-1 was narrower than IrO₂, which indicated CoSe₂/Co@NC-CNT-1 was more stable than Pt/C in alkaline solution. The results here demonstrate that CoSe₂/Co@NC-CNT-1 has a strong resistance against cross-over effects, making it a promising electrocatalyst for direct methanol fuel cells.

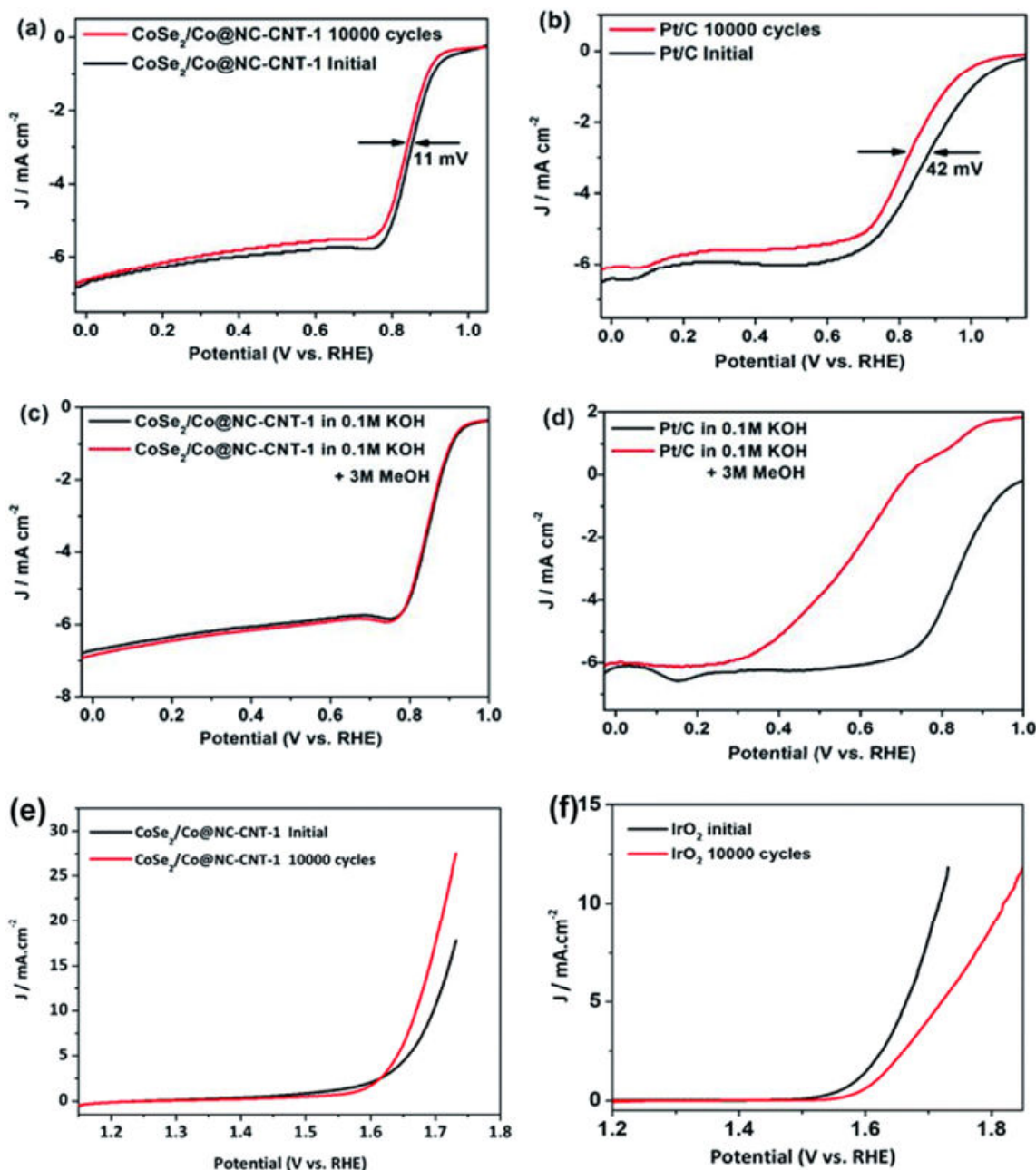


Fig. 5 LSV curves of (a) CoSe₂/Co@NC-CNT-1 and (b) commercial Pt/C for ORR before and after 10 000 potential cycles in O₂-saturated 0.1 M KOH. LSV curves of (c) CoSe₂/Co@NC-CNT-1 and (d) commercial Pt/C in O₂-saturated 0.1 M KOH without and with 3 M MeOH. LSV curves of (e) CoSe₂/Co@NC-CNT-1 and (f) commercial IrO₂ for OER before and after 10 000 potential cycles in O₂-saturated 1 M KOH.

To explore the practical application of CoSe₂/Co@NC-CNT-1, a conventional liquid Zn–air battery (Fig. 6a) was assembled by using carbon paper coated with CoSe₂/Co@NC-CNT-1 as the air cathode and polished Zn sheet as the anode, respectively, with an aqueous solution of 6 M KOH and 0.2 M Zn(Ac)₂ utilized as the electrolyte. For comparison, the commercial 20 wt% Pt/C + IrO₂ electrocatalyst was also prepared as a Zn–air battery for further tests. As

shown in Fig. 6b, the open circuit voltage of the rechargeable Zn–air battery with CoSe₂/Co@NC-CNT-1 was measured to be 1.405 V, which was close to that of the Pt/C + IrO₂ air cathode (1.462 V). Fig. 6c exhibits the discharge polarization curves and the corresponding power density plots of a single battery, where the maximum power density of the Zn–air battery with CoSe₂/Co@NC-CNT-1 was calculated to be 100.28 mW cm⁻², which was higher than that of the Pt/C + IrO₂ electrocatalyst (75.9132 mW cm⁻²). The excellent electrocatalytic performance of CoSe₂/Co@NC-CNT-1 is due to the appropriate number of CoSe₂/Co nanoheteroparticles and the porous carbon matrix, which enhance the diffusion of O₂ and the association among the active sites.

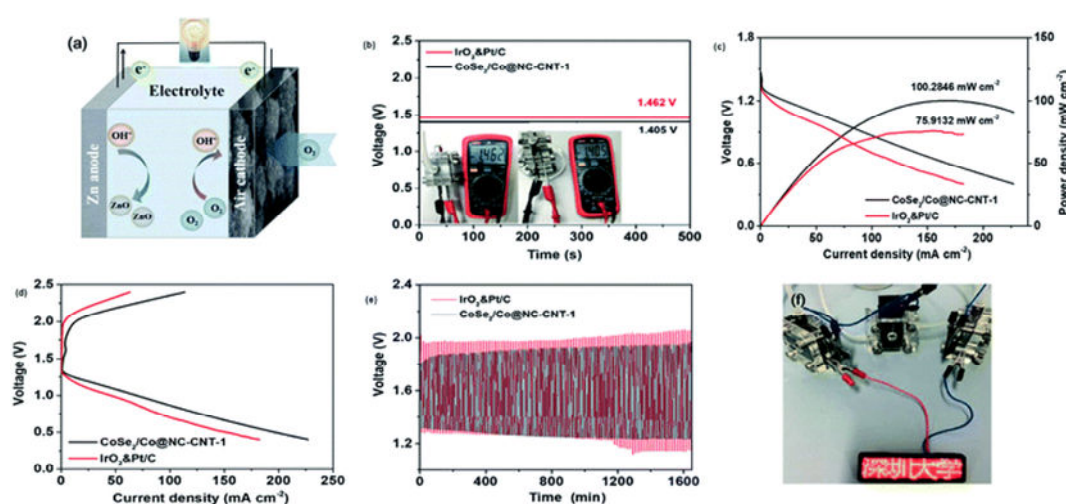


Fig. 6 (a) Schematic illustration of the liquid Zn–air battery. (b) Open circuit plots of the Zn–air battery with CoSe₂/Co@NC-CNT-1 and IrO₂&Pt/C served as the air cathode, respectively, inset: the corresponding digital photo of the Zn–air battery based on CoSe₂/Co@NC-CNT-1 catalyst with an open circuit voltage of 1.405 V. (c) Discharge polarization curves and corresponding power density curves of the Zn–air batteries equipped with CoSe₂/Co@NC-CNT-1 and IrO₂&Pt/C air cathodes. (d) Charge and discharge polarization curves of Zn–air batteries with CoSe₂/Co@NC-CNT-1 and Pt/C air cathode, respectively. (e) Long-term cycling stability at 10 mA cm⁻² with 10 min per cycle. (f) Digital photo of a glowing red LED panel powered by three Zn–air batteries.

For a rechargeable Zn–air battery, a small difference value between the charge and discharge voltage are also critical.^{5,6} Fig. 6d displays the charge and discharge polarization curves, as expected, where the charge–discharge voltage gap of the Zn–air battery with the CoSe₂/Co@NC-CNT-1 cathode (696 mV) was lower than that of the Pt/C + IrO₂ cathode (905 mV) at a current density of 10 mA cm⁻², which implied that the CoSe₂/Co@NC-CNT-1 cathode could improve the recharge ability of the Zn–air battery. Furthermore, the cyclic

stability of CoSe₂/Co@NC-CNT-1 for the Zn–air battery was also measured by galvanostatic charge and discharge tests at a current density of 10 mA cm⁻² (with 5 min for charging, 5 min for discharging and 1 min break after each assignment). As demonstrated in Fig. 6e, during 1700 min (140 cycles), the charge–discharge voltage gap of the CoSe₂/Co@NC-CNT-1-based air cathode was always smaller than that of the Pt/C + IrO₂-based air cathode in the Zn–air battery. Additionally, the CoSe₂/Co@NC-CNT-1-based Zn–air battery exhibited a better cycling stability than the Pt/C + IrO₂-based Zn–air battery. The remarkable duration of CoSe₂/Co@NC-CNT-1 in the oxygen reaction benefited from its stable porous structure and appropriate number of CoSe₂/Co nanoheteroparticles. Furthermore, a red LED panel with the Chinese words “Shenzhen University” could be lit up by three Zn–air batteries connected in series (Fig. 6f), demonstrating the materials promise in practical applications in Zn–air batteries.

Experimental

Reagents

Zinc nitrate hexahydrate [Zn(NO₃)₂·6H₂O, 99.99%], cobalt nitrate hexahydrate [Co(NO₃)₂·6H₂O, 99.99%], Se powder (99.9%) and methanol (MeOH, 99.5%) were purchased from Aladdin Industrial Corporation (CHN). A commercial 20 wt% Pt/C catalyst was purchased from Alfa Aesar (USA). A commercial IrO₂ (Ir > 84%) catalyst was purchased from Aladdin Industrial Corporation (CHN). Nafion solution (5 wt%) and 2-methylimidazole (98.0%) were acquired from Sigma-Aldrich (USA). All these reagents were used without any further purification.

Synthesis of hybrid Zn/Co-ZIFs

The synthesis of hybrid Zn/Co-ZIFs was based on a modified procedure reported in the previous literature.²⁹ Typically, solution A was first prepared by dissolving Zn(NO₃)₂·6H₂O and Co(NO₃)₂·6H₂O with the desired molar ratio of Zn²⁺/Co²⁺ (0.5, 1, 2, 5, equal to 1 : 2, 1 : 1, 2 : 1, 5 : 1, respectively) in 200 mL methanol, with the total molar amount of Zn²⁺ and Co²⁺ fixed at 30 mmol. solution B was made of 2-methylimidazole (9.84 g) with 200 mL methanol and was added to solution A with moderate stirring for 24 h at room temperature. Then the resulting precipitate was separated by centrifugation and washed thoroughly with methanol twice, and finally dried at 70 °C for 12 h. The resulting purple product was named as Zn/Co-ZIF-*x*, where *x* represents the molar ratio of Zn²⁺/Co²⁺.

Synthesis of Co@NC-CNTs

First, 800 mg of hybrid Zn/Co-ZIFs were heated to 800 °C with a heating rate of 2 °C min⁻¹ and held at 800 °C for 3 h under a mixed H₂/Ar flow (5 vol% H₂) of 100 mL min⁻¹, in a vacuum

tube furnace. Then the Co@NC-CNT- x were obtained after cooling down to room temperature naturally, where x means the sample is derived from hybrid ZIFs with a $\text{Zn}^{2+}/\text{Co}^{2+}$ molar ratio of x .

Synthesis of CoSe₂/Co@NC-CNTs

Here, 100 mg of Co@NC-CNT- x obtained above and 500 mg of Se powder were separately added into both ends of a quartz boat. Then this quartz boat was put into a vacuum tube furnace with the Se powder and placed at the upstream side of the carrier N_2 flow (100 mL min^{-1}), and annealed at 500°C for 3 h with a heating rate of 5°C min^{-1} . The resulting product was collected and denoted as CoSe₂/Co@NC-CNT- x , where $x = 0.5, 1, 2, 5$, respectively, which indicates that the sample was prepared from the selenization of Co@NC-CNT- x .

Materials characterization

X-ray diffraction (XRD) patterns were recorded on a SmartLab instrument using $\text{Cu K}\alpha$ radiation (20 kV , 200 mA , $\lambda = 1.54178 \text{ \AA}$). Scanning electron microscopy (SEM) images were obtained by using an Hitachi SU-70 field emission scanning electron microscopy system with a voltage of 5 kV . Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were acquired on a Joel JEM-2100F instrument at an acceleration voltage of 200 kV . N_2 sorption isotherms were investigated on a Micromeritics ASAP 2020 instrument, and the Brunauer–Emmett–Teller (BET) surface areas were calculated from the N_2 isotherm curves ranging from a relative pressure of 0 to 0.3, and the pore-size distributions (PSDs) were calculated using a density functional theory (DFT) method. The valence states of the samples were measured by using a MicroLab 350 X-ray photoelectron spectrometer (XPS).

Electrode preparation and electrochemical tests

All the electrocatalytic measurements were performed on an electrochemical workstation (VMP-300, Bio-Logic Science Instruments) using a three-electrode system in 0.1 M aqueous KOH electrolyte solution for ORR and 1 M aqueous KOH electrolyte solution for OER. A Pt wire and an Ag/AgCl (filled with 3.5 M KCl solution) electrodes were used as the counter and reference electrodes, respectively. A surface-coated glassy carbon (CG) rotating disk electrode (RDE) was employed as the ORR working electrode (disc area of 0.19625 cm^2) and an L-type glassy carbon electrode was used as the OER working electrode (disc area of 0.19625 cm^2). The catalyst ink was made by weighing 1 mg of as-prepared samples to disperse in a mixed solution that included $4 \text{ }\mu\text{L}$ of Nafion solution ($5 \text{ wt}\%$) and $196 \text{ }\mu\text{L}$ of ethanol, and then the mixture was ultrasonicated for about 30 min to get an homogenous solution. After that, $10 \text{ }\mu\text{L}$ of the catalyst ink was cast onto the surface of the working electrode, followed by drying at

room temperature for 30 min. A commercial 20 wt% Pt/C-loaded RDE and a commercial IrO₂-loaded L-type glassy carbon electrode were prepared by the same procedure. Specially, before the electrochemical tests, the electrolyte was saturated by a pure O₂ or Ar gas flow for at least 30 min.

For ORR, the cyclic voltammetry (CV) experiments were performed in saturated Ar and O₂ in 0.1 M KOH by applying a voltage range from −1 V to 0.2 V (*vs.* Ag/AgCl) with a scan rate of 50 mV s^{−1}, and the linear sweep voltammetry (LSV) measurements were conducted in O₂-saturated 0.1 M KOH by applying a voltage range from −1 V to 0.2 V (*vs.* Ag/AgCl) with a scan rate of 10 mV s^{−1} and varied rotating speed (400–2500 rpm). In the OER, the cyclic voltammetry (CV) experiments and the linear sweep voltammetry (LSV) measurements were performed in saturated O₂ 1 M KOH, applying a voltage range from −1 V to 0.2 V (*vs.* Ag/AgCl) with a scan rate of 5 mV s^{−1}. All the electrochemical measurements were carried out at room temperature.

All the potentials were measured *vs.* Ag/AgCl (3.5 M KCl) reference electrode referring to the reversible hydrogen electrode (RHE) scale according to the Nernst equation:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + E_0 + 0.059\text{pH} \quad (1)$$

where E_{RHE} is the converted potential *vs.* RHE, $E_{\text{Ag/AgCl}}$ is the experimental potential measured *vs.* Ag/AgCl and E_0 is the standard potential of Ag/AgCl at 25 °C (0.205 V).

Moreover, the cyclic voltammetry was carried out to assess the electrochemical double-layer capacitance (C_{dl}) at 50 mV s^{−1}.

$$C_{\text{dl}} = \frac{1}{2sv(V_a - V_b)} \int_{V_b}^{V_a} I(V) dV \quad (2)$$

where s is defined as the area of activity for the materials in the glassy carbon electrode (cm²), V_a is defined as the final electropotential (V) and V_b is the initial electropotential (V), v is the scan rate (V s^{−1}) and $I(V)$ is the measuring current (A).

Also, a specific capacitance (20–60 μF cm^{−2}) of 40 μF cm^{−2} was applied to calculate the electrochemical active surface area (ECSA).

$$ECSA = \frac{C_{dl}}{40 \mu F cm^{-2}} cm_{ECSA}^2 \quad (3)$$

The corresponding number of electrons transferred (n) could be calculated by the following Koutecky–Levich (K–L) equations:

$$\frac{1}{j} = \frac{1}{j_K} + \frac{1}{j_L} = \frac{1}{j_K} + \frac{1}{B\omega^{1/2}} \quad (4)$$

$$B = 0.2nFC_0(D_0)^{2/3}\nu^{-1/6} \quad (5)$$

$$j_K = nFkC_0 \quad (6)$$

where j represents the measured current density, j_L and j_K represent the diffusion-limiting current density and kinetic current density, respectively, and ω is the disk angular speed ($\nu = 2\pi N$, N is the linear rotating speed). Also, F is the Faraday constant equal to $96485 C mol^{-1}$ and n represents the overall number of transferred electrons. Other parameters are defined as follows: C_0 is the molar concentration of O_2 ($1.2 \times 10^{-6} mol cm^{-3}$); D_0 is the diffusion coefficient of O_2 in 0.1 M KOH ($1.9 \times 10^{-5} cm^2 s^{-1}$); ν is the kinematic viscosity for the electrolyte ($0.01 cm^2 s^{-1}$), and k is the electron-transfer rate constant.

Conclusions

In conclusion, we successfully designed and prepared CoSe₂/Co nanoparticles embedded in hierarchically porous Co, N co-doped carbon nanopolyhedra/nanotubes through a two-step high-temperature process. The optimized CoSe₂/Co@NC-CNT-1 was exploited as an ORR and OER electrocatalyst in alkaline medium, and exhibited superior electrocatalytic performance through a nearly four-electron process. In the ORR, the values of the diffusion-limited current density, onset potential and half-wave potential for CoSe₂/Co@NC-CNT-1 were $6.82 mA cm^{-2}$, $0.95 V$ (vs. RHE), and $0.84 V$ (vs. RHE) respectively, while it also had a potential of $1.69 V$ vs. RHE for the OER at $10 mA cm^{-2}$. CoSe₂/Co@NC-CNT-1 also possessed extraordinary long-term stability and a methanol tolerance ability in comparison to a commercial Pt/C catalyst or commercial IrO₂ catalyst. The outstanding ORR and OER performances of CoSe₂/Co@NC-CNT-1 should be ascribed to the close combination of CoSe₂/Co nanoheteroparticles with the doped carbon matrix, which possessed a high surface area, a highly graphitized and porous carbon structure, conductive CNTs and uniform Co and N

doping. Those characteristics are beneficial to the transfer of electrons and the transport of the electrolyte. Herein, those superior structures and an appropriate number of CoSe₂/Co nanoheteroparticles enabled CoSe₂/Co@NC-CNT-1 to show the best catalytic performance among the series CoSe₂/Co@NC-CNT-*x* (*x* = 0.5, 1, 2, 5). In addition, a fabricated Zn–air battery equipped with the CoSe₂/Co@NC-CNT-1 cathode also exhibited a higher peak power density and discharge stability than Pt/C. Considering the activity of CoSe₂/Co@NC-CNTs in this study, this material also has promise for use in advanced electrodes in other areas of energy storage and conversion, such as water splitting and lithium-ion batteries.

Conflicts of interest

There are no conflicts to declare.

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