Journal of Materials Chemistry A



View Article Online

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Cite this: J. Mater. Chem. A, 2018, 6, 24071

Received 6th September 2018 Accepted 6th November 2018

DOI: 10.1039/c8ta08668k

rsc.li/materials-a

Apically Co-nanoparticles-wrapped nitrogendoped carbon nanotubes from a single-source MOF for efficient oxygen reduction⁺

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Metal-organic framework (MOF)-derived transition metal/carbon nanotubes composites (TM/CNTs) have been developed as a promising oxygen electrocatalyst for energy conversion devices. However, relatively complicated synthesis limits current research to a handful of MOFs precursors. Herein, we used a single-source dicyanamide-based Co-MOF to prepare cobalt nanoparticles-wrapped bamboo-like nitrogen-doped carbon nanotubes (Co@BNCNTs) by a short-term (3 h) one-step pyrolysis at a lower temperature (as low as 700 °C). Organic dicyanamide linkers on the framework of Co-MOF not only served as the nitrogen source but also conduced to the formation of CNTs, and inorganic Co nanoparticles are enclosed in situ in graphitic carbon shells. Co@BNCNTs exhibited comparable oxygen reduction electrocatalytic activity and enhanced stability to commercial 20 wt% Pt/C catalyst in alkaline solution. Remarkably, rechargeable Zn-air batteries based on Co@BNCNTs as the air cathode demonstrated excellent cycling stability with no increase in polarization even after 65 h. The single-source MOF as precursor offers more facile and designable method for highly active and durable catalysts for various specific reactions.

The oxygen reduction reaction (ORR) is a cornerstone reaction in the cathode of regenerative fuel cells and metal–air batteries for the direct conversion of chemical energy to electricity.^{1,2} The intrinsically sluggish kinetics of the ORR highly calls for efficient electrocatalysts to accelerate the performance.^{3–5} To date, noble metal (*e.g.*, platinum group metal) based nanomaterials are the most efficient commercial ORR electrocatalysts. Yet, their prohibitive cost, scarcity and serious intermediate tolerance severely hinder their large-scale implementation to meet the growing energy demands of large-scale application.^{6,7}

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Transition metal/carbon nanotubes composites hold great promise as alternatives of noble metal-based catalysts for ORR,⁸⁻¹³ and further doping N-heteroatom into the CNTs could introduce abundant defects in the walls of nanotubes and modulate electronic structure, thus promoting oxygen adsorption and ORR activity.^{8,14}

Recently, intensive efforts have also been devoted to developing efficient strategies to prepare TM/CNTs hybrids for oxygen electrocatalysis.¹⁵⁻²⁵ Metal–organic frameworks (MOFs) have captured great attention as novel self-sacrificed templates and precursors for fabricating hybrid electrocatalysts19,21 because of their exceptionally large pore volumes, extraordinary tunability of inorganic nodes and organic linkers and their unique spatial connections.²⁶⁻²⁹ Classic ZIF (ZIF-67 ^{11,18}/ZIF-9 ³⁰) and MIL-101³¹ have been extensively used. However, to obtain distinctive N-doped carbon nanotubes, the addition of auxiliary agents such as dicyandiamide^{18,32,33} and melamine^{11,31} is required, which served as both the inducer of the graphitic structure and an extra N source during the pyrolysis of MOFs.12 Using N-rich MOFs as single self-sacrificed templates and precursors to prepare CNT-based materials demonstrated great advantages.^{19,34} The currently developed methods need longer pyrolysis time³⁴ and reductive gas,¹⁹ which probably is related to the inherence of the selected MOFs. Seeking for available MOFs as single precursors to manufacture N-doped carbon nanotubes for cost-effective yet efficient ORR electrocatalysts remains a formidable challenge.

Herein, we elaborately selected a novel dicyanamide-based Co-MOF (Co(dca)₂pyz, dca = dicyanamide, pyz = pyrazine)³⁵ as the single precursor to fabricate N-doped carbon nanotubes. Dicyanamide linkers on the MOF not only could serve as a nitrogen source but also favor the formation of NCNTs due to their inducing effect for graphitic structure upon calcination.^{33,36} On this basis, the inorganic Co nodes could form Co nanoparticles, which could be *in situ* encapsulated in N-doped CNTs. Thus, TM/CNTs hybrids, which have demonstrated excellent ORR catalytic activity, could be designed from the object MOFs. After optimization, a one-step synthesis with

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[†] Electronic supplementary information (ESI) available. See DOI: 10.1039/c8ta08668k

a shorter pyrolysis time (merely 3 h) pyrolysis process at a lower temperature (700 °C) under N₂ atmosphere was developed, which easily produced the resultant Co@BNCNTs. The hybrid possesses hierarchically porous structure and bamboo-like tubular N-doped CNTs (NCNT), at the endpoint of which, the cobalt nanoparticles are encapsulated in graphitic layers. Co@BNCNTs exhibits comparative ORR activity and enhanced durability as well as methanol tolerance when benchmarked with a commercial Pt/C electrocatalyst under identical testing conditions. Impressively, the assembled Zn–air battery based on optimized Co@BNCNTs displays an open-circuit potential of 1.48 V and a high power density of 90 mW cm⁻². In addition, the developed method here can be generalized to other MOFs with different metal nodes.

The overall fabrication process of Co@BNCNTs is schematically illustrated in Fig. 1. First, well-defined twofold interpenetrated nanostructured Co(dca)₂pyz was constructed by a facile and scalable method in accordance with the preceding literature.³⁵ In Co(dca)₂pyz, each metal center is octahedrally coordinated to four $N(CN)_2^{-}$ anions and two pyrazine ligands, resulting in the overall Co-N₆ moiety, which is believed to be favorable for incorporating cobalt nanoparticles into the carbon network, promoting the uniform in situ doping of N active sites into the whole carbon matrix (Fig. S1, ESI†). Thus, the abundant Co-N₆ centers and the introduction of dca in Co-MOF encourage us to pyrolyze Co-MOF under different conditions to obtain N-doped carbon nanotubes with enveloped Co nanoparticles (Co@BNCNTs-700/800/900/1000, the numbers representing the calcination temperatures). As demonstrated in Fig. S2a (ESI[†]), the powder X-ray diffraction (PXRD) pattern of as-synthesized Co(dca)₂pyz could be unambiguously assigned to the pattern simulated from the single-crystal data of the Co-MOF.35 Combined with the results of elemental analysis and infrared spectra, all were indicative of the high crystallinity and purity of the synthetic Co-MOF precursor (Fig. S2b, Table S1, ESI[†]). The as-synthesized Co-MOF was then calcined in N₂ atmosphere to prepare the porous carbon nanotube materials. The photographs in Fig. S3 (ESI[†]) demonstrate that the tight pink powder switched to loosened black carbon materials after calcination due to numerous intertwined carbon nanotubes growing in situ. The main diffraction peaks at about 44.2° and 51.5° shown in Fig. 2a and S4 (ESI[†]) are attributed to the characteristic (111) and (200) crystal planes of cubic metallic

cobalt (JCPDS no. 89-4307), respectively. The sharp peak centered at about 26.2° is related to carbon species, which indicates that the cobalt/carbon hybrid material has been successfully synthesized by the current strategy. The carbon species are further confirmed by Raman spectroscopy. Fig. S5 (ESI[†]) illustrates a typical Raman spectrum of Co@BNCNTs, in which three distinct peaks at 1340, 1585, and 2570 cm^{-1} can be assigned to the D band, G band and 2D band of NCNTs, respectively. The D band is related to the disordered structures on the graphitic plane and defects in carbon materials, while the G band suggests the degree of graphitization.37 Another 2D band implies a relatively high degree of graphitization and the existence of few-layer graphene-like structures.8,38 The intensity ratio of the D-band to the G-band (I_D/I_G) is applied to qualitatively assess the graphitic ordering.39 The results also indicate that an enhanced temperature of calcination resulted in a higher graphitization degree of the resultant Co@BNCNTs. The improved graphitization of these materials should be beneficial for electrical conductivity and catalytic activity.40

Field-emission scanning electron microscopy (FESEM) was performed to study the morphology and microstructure of Co-MOF and Co@BNCNTs. As demonstrated in Fig. S6, ESI† a panoramic view by scanning electron microscopy reveals that the as-prepared Co-MOF exhibits a rod-shaped morphology with an average size of about 15 µm. Through direct pyrolysis of the precursor at different temperatures, the Co-MOF transformed into numerous typical bamboo-shaped CNTs with high density (Fig. 2b, c and S7, ESI[†]). The SEM observed in Fig. 2c distinctly reveals the vertical NCNT arrays. Interestingly, as depicted in Fig. 2d and e, the metal nanoparticles are observed within the apexes of the carbon nanotubes. The phase composition of the resultant sample was further characterized by highresolution TEM (HRTEM) analysis. Typical HRTEM (Fig. 2f) shows that a single nanoparticle with a clear lattice distance of 0.20 nm corresponds to the (111) plane of cubic metallic Co, which matches the XRD result as well. The high-resolution image also reveals that CNTs are crystalline and that the lattice fringes with an inter-planar distance of ~0.34 nm correspond to the C (002) plane. The size of the metal nanoparticles are in the range of 20-100 nm, and the diameters of the nanotubes are in the range of 50-200 nm (Fig. S8, ESI[†]). Meanwhile, this is especially apparent for the graphene layers directly surrounding the Co nanocrystals. These Co



Fig. 1 Schematic illustration of the preparation of Co@BNCNTs as an electrocatalyst for the oxygen reduction reaction.



Fig. 2 (a) PXRD patterns for the Co@BNCNTs materials compared to the simulated pattern of cubic cobalt. (b-d) SEM images of Co@BNCNTs; (e, f) TEM and HRTEM images of Co@BNCNTs; (g) SAED pattern of Co@BNCNTs; (h-k) elemental mapping images of Co@BNCNTs clearly showing the encapsulated Co nanoparticle and the uniform presence of N and C in carbon nanotubes.

nanoparticles encased in carbon nanotubes are protected by the carbon layer from being leached in the extremely harsh environment, while the encapsulated cobalt metals can activate O2 through the outer carbon surface.41 Moreover, it is fascinating to observe that the graphitic layers with interlayer spacings in the walls are not perfectly parallel to the axial direction of the CNTs, exhibiting more defects and edges in the NCNTs, which would be beneficial to the enhanced electrocatalytic property.³⁴ The SEM and HRTEM images show that the Co@BNCNTs are several 5 µm long and 7-8 nm thick multi-walled CNTs (MWCNTs). The selected-area electron diffraction (SAED) patterns in Fig. 2g also suggests several rings which correspond to the (111), (200) diffractions of metallic Co and the (002) diffractions of graphite carbon.11 The corresponding TEM elemental mappings seen in Fig. 2h-k clearly express the encapsulated Co nanoparticle and the uniform distribution of N and C elements within the skeleton of the carbon nanotubes. Based on the above results, it is noteworthy that the hybrid prepared from a lower temperature (700 °C) displays the same morphology of the compact bamboo-like NCNTs with wrapped Co nanoparticles as those from higher temperatures (Fig. S7 and S9, ESI[†]), which is encouraging in consideration of energy consumption. More surprisingly, Co@BNCNTs-700 possesses comparable catalytic activity to those of higher temperatures as discussed in detail later.

To further clarify the surface chemical information of the Co@BNCNTs, X-ray photoelectron spectroscopy (XPS) measurements were conducted, which clearly showed distinct signals of N, C, O, and Co elements without any other impurities (Fig. 3 and S10, ESI[†]). Peak deconvolution of the Co 2p_{3/2} core level region shows one main peak at 780.1 eV and one satellite peak at 783.4 eV, while the Co $2p_{1/2}$ region shows one main peak at 795.6 eV accompanied with a satellite peak at 804.6 eV (Fig. 3b and S11, ESI[†]). The peaks at 783.4 and 795.6 eV are assigned to the Co-C bond and oxidized Co species, respectively.34,42 The oxidized Co species on the Co@BNCNTs surface is probably due to the oxidation of the active cobalt surface in ambient air.43 The intense satellite peaks observed in the Co 2p spectra can be ascribed to the shakeup excitation of high-spin Co²⁺ ion.¹³ As demonstrated in Fig. 3c, the high-resolution XPS spectra of N 1s is deconvoluted into three subpeaks, including pyridinic N (398.6 eV), pyrrolic N (400.8 eV), and graphitic N (404.1 eV).44 As exhibited in Fig. S12 (ESI⁺), the highest content of pyrrolic N in Co@BNCNTs-900 might contribute to the positive onset potential for ORR.37,45 Meanwhile, the appropriate graphitic N was believed to promote the adsorption of oxygen atoms by withdrawing electrons from adjacent carbon atoms, which generally played a key role in ORR electrocatalytic activity.46 It is worth noting that the pyrrolic N proportion of Co@BNCNTs-900 is the highest, but



Fig. 3 (a) XPS survey spectrum of Co@BNCNTs-900, (b–d) the corresponding high-resolution XPS spectra for Co 2p, N 1s and C 1s, respectively; (e) FTIR spectroscopy of the Co@BNCNTs catalysts; (f) N_2 sorption isotherms of the Co@BNCNTs catalysts at 77 K.

the total N content is relatively low (1.63%, Table S2, ESI[†]), which means that the total pyrrolic N content of Co@BNCNTs-900 is not the highest in all samples. The main peak at approximately 284.6 eV in the high-resolution C 1s spectrum (Fig. 3d and S11, ESI^{\dagger}) is attributed to graphitic sp² carbon, while carbon bonding with nitrogen (C-N) centered at 285.3 eV further verifies the successful nitrogen doping of Co@BNCNTs.11 As exhibited in Tables S2 and S3,† the nitrogen concentration of the materials gradually decreased with increasing pyrolysis temperature.47 Fourier transform infrared spectroscopy (FTIR) was also used to characterize the bonding configurations in the Co@BNCNTs materials, and strong peaks at 1232 cm⁻¹ were observed, which were assigned to C-N stretching.48 The identification of the C-N bond again confirms the N doping in Co@BNCNTs (Fig. 3e). The specific surface areas and porous natures of the Co@BNCNTs-700, 800, 900, 1000 materials were carried out by N2 adsorption at 77 K (Fig. 3f). The isotherms for the four samples are similar in shape and can be identified as type IV isotherms according to IUPAC classifications, with a very distinct hysteresis loop of typical H2. Combining the pore size distributions results (Fig. S13, ESI⁺), it can be confirmed that Co@BNCNTs possess hierarchical porous structure. The specific surface areas for Co@BNCNTs-700, 800, 900, 1000 were 145.89, 146.74, 147.08, 97.117 m² g^{-1} , respectively, based on Brunauer-Emmett-Teller (BET) calculations. The reduced BET value under 1000 °C is probably due to the increased graphitization degree of the materials (Fig. S4 and S5, ESI⁺).⁴⁴ The hierarchically porous NCNTs

combined with their nanotubular structures could promote the transportation of reactants and products and expose more accessible active sites for the electrocatalytic energy conversion process.⁴⁹

The heteroatom-activated carbon nanotubes are claimed to be the active sites for ORR, which inspired us to investigate the ORR performance of Co@BNCNTs. CV measurements were first performed in O₂- or N₂-saturated 0.1 M KOH aqueous solution in a three-electrode electrochemical cell. As shown in Fig. 4a, a distinct oxygen reduction peak (~0.83 V vs. RHE) was observed in the O₂-saturated electrolyte but was not observed in the N₂saturated electrolyte. The cathodic peak approaches that of commercial Pt/C (0.84 V, Fig. S14, ESI[†]), suggesting the outstanding ORR catalytic activity of the Co@BNCNTs materials.^{50,51} The linear scan voltammogram (LSV) curves for different catalysts were obtained at 5 mV s⁻¹ and compared with those of the commercial 20 wt% Pt/C catalyst. The corresponding ORR polarization curves at 1600 rpm (Fig. 4b and Table S4, ESI[†]) show that the four samples have close half-wave potentials (0.81 \pm 0.01) and onset potentials (0.91 \pm 0.02), revealing that the Co@BNCNTs materials derived from dca-MOF under different temperatures all exhibit outstanding ORR catalytic activity. Notably, Co@BNCNTs-900 has the highest electrocatalytic activity with an onset potential of ca. 0.93 V (vs. RHE), a half-wave potential $(E_{1/2})$ of *ca.* 0.82 V at 1600 rpm, and a diffusion limiting current density at 0.3 V is 5.30 mA cm⁻², which are comparable to those of the 20 wt% Pt/C catalyst $(0.84 \text{ V}, 5.35 \text{ mA cm}^{-2})$. Different from most reported results,19,34,44,52-55 the electrocatalysts prepared at different temperatures possess similar ORR activity, which may be attributed to the unique structural advantage of compact bamboo-like NCNTs wrapping Co nanoparticles for the four samples, thus facilitating electron diffusion from well-defined nanotubes directionality to the metal centers. The result demonstrates that a class of efficient ORR electrocatalysts derived from single-source dca-MOF in lenient operational conditions under a non-reducing atmosphere express excellent electrocatalytic activity, which is comparable to those of the materials obtained from harsh conditions. The methodology could shed new light on the rational design and exploration of TM/CNTs hybrids (Table S5, ESI†).

Another critical parameter for evaluating ORR catalytic activity was the electron transfer number (n) per oxygen molecule. Thus, LSV measurements at different rotation rates (400-2500 rpm) were recorded to evaluate the ORR kinetics and reaction pathways of the Co@BNCNTs. As shown in Fig. 4c and S15-S17 (ESI[†]), the limited diffusion current densities of the Co@BNCNTs catalysts linearly increase with increasing rotation rates, as the O2 diffusion distance in the electrolyte is shortened at high rotation rates, revealing that ORR on the Co@BNCNTs catalysts is a kinetics-controlled process.56-58 The number of electrons transferred during the ORR process was calculated with the Koutecky-Levich (K-L) equation and compared at different potentials. Fig. 4d and S15-S17 (ESI[†]) showed linear and parallelism relationships of different samples between i^{-1} and $\omega^{-1/2}$, manifesting the presence of first-order reaction kinetics in regard to the oxygen concentration, and a similar



Fig. 4 (a) CV curves of Co@BNCNTs-900 in O₂- and N₂-saturated 0.1 M KOH electrolyte at a scan rate of 20 mV s⁻¹; (b) LSV curves of Co@BNCNTs-700, 800, 900, 1000 and Pt/C in O₂-saturated 0.1 M KOH with a sweep rate of 5 mV s⁻¹ at 1600 rpm; (c) ORR polarization curves of Co@BNCNTs-900 materials at different rotating speeds; (d) the corresponding K–L plots at different potentials; (e) chronoamperometric response and (f) methanol tolerance test for Co@BNCNTs-900 and Pt/C at 0.6 V in O₂-saturated 0.1 M KOH solution at 1600 rpm.

electron transfer number (n) toward ORR at various potentials. When the potential ranged between 0.4 and 0.6 V, the calculated electron-transfer numbers for Co@BNCNTs (3.92-4.04 for Co@BNCNTs-700, 3.98-4.07 for Co@BNCNTs-800, 3.91-4.01 for Co@BNCNTs-900 and 3.90-4.01 for Co@BNCNTs-1000), based on eqn (1) and (2) (ESI⁺), approached the Pt/C's value of 4.00 measured in the same environment (Fig. S18, ESI[†]). This suggests that the catalysts can catalyze oxygen reduction in an efficient 4e dominant process under alkaline conditions, with water as the product.²¹ The rotation ring-disk electrode (RRDE) measurements were further carried out to monitor the hydrogen peroxide yield (% H₂O₂), revealing that the H₂O₂ yield over Co@BNCNTs remained below 12% over the potential range of 0.40-0.80 V with a corresponding electron transfer number of about 3.85 according to eqn (3) and (4) (Fig. S19, ESI[†]). These values are in good agreement with the reported n values from the K-L plots. These results affirm that the catalytic process at the Co@BNCNTs electrode underwent a four-electron ORR pathway, confirming its high ORR catalytic efficiency and selectivity.

Aside from the catalytic activity, the durability and tolerance to methanol crossover effects of the ORR catalyst at the cathode are two other important parameters in the practical application. The chronoamperometric curve (*i*–*t*) at 0.6 V was collected for evaluation, and the results in Fig. 4e show that after 40 000 s of continuous operation, Pt/C shows a remarkable loss of *ca.* 40% current, while Co@BNCNTs-900 yields a much slower decay of <5%. Meanwhile, we measured LSV curves of Co@BNCNTs-900 before and after 5000 cycles at the potential window of 0.4– 1.0 V, which displays the maintained limiting current density with only a small negative shift of 5 mV for $E_{1/2}$. No significant changes in morphology, phase structure, or N-doping distribution were observed for Co@BNCNTs after the long-time cycle testing, also indicating an excellent ORR stability (Fig. S20-S22, ESI[†]). Moreover, the crossover effect caused by methanol and the stability of the ORR electrocatalysts was also investigated by chronoamperometric measurement in an O2-saturated 0.1 M KOH solution at 1600 rpm. The introduction of methanol led to a sharp drop in current density for Pt/C, whereas no apparent performance decay was observed for Co@BNCNTs (Fig. 4f and S23, ESI[†]), indicating that Co@BNCNTs presents a strong tolerance to methanol crossover.53,59 The above results highlight the excellent stability of Co@BNCNTs, which could be ascribed to the robust framework structure composed of crystalline NCNTs embedded with Co nanoparticles. Therefore, the Co@BNCNTs show comparable performance to that of the Pt/C catalyst and remarkable stability as well as methanol tolerance and could be further applied to energy conversion devices (Table S7, ESI[†]). Meanwhile, the ORR catalytic activity in 0.1 M HClO4 for Co@BNCNTs was evaluated, which also exhibited catalytic activities for ORR in the acidic electrolyte (Fig. S24, S25 and Table S6, ESI[†]).⁶⁰ Furthermore, their OER activities were first observed by linear sweep voltammetry (LSV) measurements in 1 M KOH solution (Fig. S26, ESI[†]). The result revealed that the materials possess significant activity and stability for OER.

To evaluate the practical applicability of Co@BNCNTs, a homemade Zn–air battery was assembled (Fig. 5), in which 6 M KOH with 0.2 M zinc acetate served as the electrolyte, and a polished zinc plate and Co@BNCNTs catalyst loaded on nickel foam served as the anode and the air cathode, respectively.⁶¹ The fabricated battery exhibits an open circuit voltage of 1.48 V in the static ambient atmosphere without external gas purging,



Fig. 5 (a) Graphical illustration of the homemade Zn–air battery; (b) photograph of the assembled battery with an open-circuit voltage of 1.48 V and red LED (~2 V) powered by two-series batteries; (c) open-circuit plots of a homemade Zn–air battery; (d) polarization and corresponding power density curves of the assembled battery; (e) long-term cycling tests of the Zn–air battery using Co@BNCNTs-900 as air cathode at the charging and discharging current density of 5 mA cm⁻² (10 min for each cycle).

which maintains high stability for up to 20 h (Fig. 5b, c). And the device connected with two batteries in series is capable of lighting a red light emitting diode (LED) in the actual application (Fig. 5b and S27, ESI†). The maximum power density was calculated as 90 mW cm⁻² at 145 mA cm⁻² (Fig. 5d). Furthermore, the cycling tests of the rechargeable Zn–air battery with the 6 M KOH and 0.2 M Zn(Ac)₂ electrolyte demonstrated the strong stability and reversibility of the battery (Fig. 5e and Table S8, ESI†). The long-term cycling performance at a constant current density of 5 mA cm⁻² in a short interval (10 min per cycle) further reveals its long lifetime, in which nearly invariable charge and discharge potentials (2.03 and 1.07 V with a small voltage gap of 0.96 V) can be observed over a duration of 65 h.

Conclusions

In summary, we report a facile and convenient strategy for the direct formation of bamboo-shaped N-doped carbon nanotubes decorated with Co nanocrystals by calcining a novel dca-based Co-MOF without an extra precursor. Thanks to the synergetic interaction between the NCNTs matrix and Co nanoparticles wrapped in NCNTs, the Co@BNCNTs composite demonstrated excellent ORR catalytic activity with high catalytic efficiency, selectivity and long-term durability. Furthermore, the catalyst Co@BNCNTs was used as an air cathode to construct the stable Zn-air battery for energy conversion. More strikingly, the electrocatalysts derived at different temperatures possessed comparative ORR activity, which may be attributed to the unique structural advantage of the compact bamboo-like

NCNTs wrapping Co nanoparticles. The lenient synthetic conditions for the architecture of these unique composites are very exciting in terms of reducing energy consumption. Thus, our study will encourage the development of metallic nanoparticles in situ wrapped in fascinating N-doped carbon nanotubes (M@NCNTs) derived from single-source dicyanamidebased MOF for energy conversion applications. Furthermore, it would expand the toolbox for the adequate usage of the diversity of metal-organic frameworks to construct desirable carbon-based functional materials. And it can be anticipated that this methodology could be a versatile route for synthesizing varied unique graphitic carbon features with other active earthabundant metal nanoparticles embedded for efficient and Pt-alternative durable catalysts in renewable energy technologies.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This study was supported by the National Science Fund for Distinguished Young Scholars (No. 21825106); National Natural Science Foundation of China (No. 21671175); Program for Science & Technology Innovation Talents in Universities of Henan Province (164100510005); Program for Innovative Research Team (in Science and Technology) in Universities of Henan Province (19IRTSTHN022).

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