An easy synthesis of Ni-Co doped hollow C-N tubular nanocomposites as excellent cathodic catalysts of alkaline and neutral zinc-air batteries

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ABSTRACT Exploring high-activity electrocatalyst for oxygen reduction reaction (ORR) is of great significance for a variety of renewable energy conversion and storage technologies. Herein, we fabricated novel ORR electrocatalysts derived from Ni-Co nanoparticles encapsulated in hollow tubular C-N composites (ht-CN) through an easy and scalable pyrolysis route utilizing nickel acetate and cobalt acetate as metal precursors, 2-cyanoguanidine as the nitrogen source, and sucrose as the carbon source. Among the prepared nanocomposite catalysts with different molar ratios of Ni/Co, the catalyst Ni₂Co₃@ht-CN exhibits an outstanding ORR electroactivity comparable to Pt/C catalyst both in alkaline and neutral media. Home-made zinc-air battery with the Ni₂Co₃@ht-CN as cathode electrocatalyst presents excellent performance and superior durability either in neutral or alkaline medium. The Ni₂Co₃@ht-CN battery delivers an open circuit voltage of 1.08 V and a maximum power density of 47 mW cm⁻² in 0.5 mol L⁻¹ KNO₃ solution, while 1.51 V and 314 mW cm⁻² in 6 mol L⁻¹ KOH solution. In addition, whether in neutral or alkaline solution, the constant current discharge curves of the Ni₂Co₃@ht-CN battery at different current densities exhibit higher voltage plateau and stability than the Pt/C battery. Results demonstrate the potential application of the catalysts of the present investigation to Zn-air batteries both in alkaline and neutral media.

Keywords: oxygen reduction reaction, Zn-air battery, NiCo catalyst, carbon nanotube

INTRODUCTION

As one of the most promising electrical energy storage devices, zinc-air battery has received great attention due

to its high specific energy density (about 1,084 W h kg⁻¹), safety and reliability, and plays an ever increasing important role in addressing the emerging environmental issue and meeting with the future energy requirements [1–5]. However, the slow oxygen reduction reaction (ORR) of the cathode is a major block that hinders zinc-air batteries' large-scale applications [6]. Therefore, extensive research in exploration of low-cost, high-activity, and durable alternative electrocatalysts for ORR has been done in order to achieve high operational performance of the Zn-air battery.

Pt-based catalysts are generally considered to be the most effective catalysts for ORR. Unfortunately, a range of issues including high cost, scarcity of natural resources and insufficient durability still limit the large-scale commercialization of Pt-based electrocatalysts [7]. So far, a variety of non-Pt-based catalysts have been developed as alternatives to Pt-based electrocatalysts [8,9], and porous nanotubular carbon materials (nt-CMs) have been widely studied due to their extensive applications to catalysis, adsorption and energy in the recent decades [10–12]. To further enrich the application of the nt-CMs in the field of electrochemical research, they are usually doped with other atoms like nitrogen. N-doped nanotubular carbon composites (nt-CNs) not only improve the dispersion of nt-CMs, but also change the local charge density of nanotubes, improve the electron transport properties of nanotubes, and reduce the resistivity [13,14]. The synthesis and application of nt-CNs as ORR electrocatalysts have become one of the hotspots in recent years [15]. The first method for preparing nt-CNs was the so-called arc evaporation using a graphite rod as the electrode. Its main

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advantage is that the synthesized nt-CNs are highly graphitized. Later, the development of chemical vapor deposition (CVD) provides a feasible approach for synthesizing nt-CNs [16,17]. Another technique for preparing nt-CNs is laser evaporation [17]. These traditional methods are called “synchronous *in-situ* doping”, which are generally time-consuming, high-cost and environmentally unfriendly [18,19]. Therefore, other simple ways for synthesizing nt-CNs have been developed like the high-temperature carbonization of nitrogen-containing polymers, which is carried out by pyrolysis under atmosphere of nitrogen-containing gaseous molecules [20–25]. Metal-coordinated nanotubular C-N composites (M-nt-CNs) materials have been established as one of the best alternatives to Pt/C because of their excellent catalytic activity [26]. As non-precious metals, Ni and Co nanoparticles have been widely explored and show great potential applications in energy conversion and storage devices due to their abundant resources and environmental friendliness [27,28]. As for the carbon-supported Ni/Co nanocatalysts, nickel and cobalt particles were favorable in activating the outer graphitic layers, contributing to the enhancement of active site density toward ORR [29]. Ni-Co-coordinated nanotubular C-N composites (Ni-Co-nt-CNs) have been therefore paid much attention due to their large surface areas, uniform hetero atom geometric distributions and the presence of porous defects [30], which could provide more catalytic active sites, playing a key role in electrocatalysis.

Herein, we report a low-cost and facile approach for the synthesis of NiCo-hollow tubular C-N composite nanocatalysts (NiCo@ht-CN) through direct pyrolysis of the mixture composed of 2-cyanoguanidine, sucrose and metal Ni/Co salt, without introducing extra complex procedures in addition to high temperature pyrolysis. NiCo@ht-CN particles were formed by using NiCo as the growth catalyst of the hollow nanotube, and 2-cyanoguanidine and sucrose as the C-N source. The as-formed ht-CN composites are intertwined with each other to form a crimped structure. This unique feature provides the prepared samples with high intrinsic activities, fast electron transfer and high density of active sites. Among the as-prepared samples, the $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ shows impressive catalytic performances toward ORR in either neutral or alkaline electrolyte. Zn-air batteries in alkaline and neutral media were assembled with Zn as the anode and carbon paper coated by the prepared samples as the air electrode (cathode) and reveals much better performance compared to that with the commercial Pt/C.

EXPERIMENTAL SECTION

Materials

2-Cyanoguanidine, sucrose, cobalt acetate, nickel acetate, potassium hydroxide and potassium nitrate purchased from Sinopharm Group Chemical Reagent Co. Ltd, were analytical purity grade and used as received without further purification. Commercial Pt/C (40%, Johnson Matthey Corp.) was from Shanghai Qunyi Energy Equipment Co. Ltd. (Shanghai, China). Water used was from a Nanopure water system (18.2 MΩ cm).

Preparation of $\text{Ni}_x\text{Co}_y\text{@ht-CN}$ electrocatalysts

A mixture of nickel acetate and cobalt acetate (0.3 g), sucrose (0.3 g), and 2-cyanoguanidine (3.0 g) were added to H_2O (50 mL), and the obtained mixture was well stirred to form a homogeneous solution. After being dried in vacuum oven at 80°C, the solid was transferred into a tube furnace and heated to 600°C at a rate of 4°C min⁻¹ under N_2 . After being held at 600°C for 2 h, the furnace was heated to 800°C and kept at this temperature for 2 h again. The as-obtained black powder was collected and marked as $\text{Ni}_1\text{Co}_1\text{@ht-CN}$, $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ and $\text{Ni}_3\text{Co}_2\text{@ht-CN}$ corresponding to Ni/Co atomic ratio of 1:1, 2:3 and 3:2, respectively. For the preparation of Ni or Co sample (Ni@ht-CN or Co@ht-CN), nickel acetate (0.3 g) or cobalt acetate (0.3 g) was used instead of their mixture.

Characterization and measurement

Characterization of the catalysts was performed by a field emission scanning electron microscope (SEM, Zeiss Merlin compact-61-78), a transmission electron microscope (TEM, JEM-2100F, Japan), a X-ray diffractometer (XRD, Ultima Multipurpose X-Ray Diffraction System IV, Rigaku, Japan), energy dispersive spectra (EDS, Oxford Instruments, Britain), X-ray photoelectron spectroscopy (XPS, K-Alpha 1063), Brunauer-Emmett-Teller (BET, 3H-2000PM2, China), Raman spectra (Andor SR-500i), and Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, Agilent ICGOES730). A conventional three-electrode system controlled with the AutoLab PGSTAT30/FRA electrochemical system was used for the electrochemical measurements, where glassy carbon (GC) or carbon paper modified with a film of catalyst ink, Pt foil and Ag/AgCl in saturated KCl were used as the working, counter and reference electrodes respectively. All potentials reported in this work were *versus* the reversible hydrogen electrode (RHE). The catalyst ink was prepared by blending the catalyst powder

(5 mg) with 5 wt% Nafion solution (50 μL) and ethanol (950 μL) in an ultrasonic bath. Catalyst ink (10 μL) was then pipetted onto the GC surface (0.1256 cm^2), leading to a catalyst loading of 0.4 mg cm^{-2} . As for the GC electrode coated with Pt/C, it was prepared by pipetting the Pt/C catalyst ink (5 μL) onto the GC surface. The mass loading of the Pt/C was 0.2 mg cm^{-2} (pure Pt loading was 0.08 mg cm^{-2}). Performances of Zn-air batteries were tested in homemade electrochemical cells, where carbon paper coated with the prepared catalysts or Pt/C was used as the air cathode (catalyst loading 2 mg cm^{-2} for all NiCo@ht-CN catalysts and 0.5 mg cm^{-2} for Pt/C) and zinc plate was used as the anode. The electrolyte was 0.5 mol L^{-1} KNO_3 for neutral Zn-air battery and 6.0 mol L^{-1} KOH for alkaline Zn-air battery. All measurements were carried out at room temperature ($20 \pm 2^\circ\text{C}$).

RESULTS AND DISCUSSION

Fig. 1a–e shows the morphological texture of the catalysts Ni_1Co_1 @ht-CN, Ni_2Co_3 @ht-CN, Ni_3Co_2 @ht-CN, Co@ht-CN and Ni@ht-CN, where dense and thin nanotubes with a curly state can be discerned. The white metallic particles are mainly distributed at the epitaxial ends of the nanotubes. This is consistent with the possible formation

mechanism of C-N hollow nanotubes [31], where metal (Ni or Co) nanoparticles produced during pyrolysis act as the growth catalyst of the nanotubes. Fig. 1 also shows that NiCo@ht-CN catalysts (Fig. 1a–c) generally produce less amorphous carbon than single metal catalysts. The nanotubes formed by Ni_2Co_3 @ht-CN are relatively more evenly distributed, and there is little agglomeration. On the basis of these SEM images, diameter distribution histograms of nanotubes are shown in the inset of Fig. 1. As for the single Ni sample Ni@ht-CN (Fig. 1e), large diameters of the nanotubes were observed, and the diameter of the nanotubes mostly exceeds 26 nm. In addition, the single Co sample Co@ht-CN (Fig. 1d) displays short nanotubes with smaller diameter. Results show that as a growth catalyst of nanotubes, Ni/Co nanoparticles with an appropriate atomic ratio play a key role in the formation of uniform C-N nanotubes.

The morphological features of the Ni_2Co_3 @ht-CN were further observed using TEM. From Fig. 2a, b, the metal nanoparticles are encased in the top end of nanotubes and coated by several graphitic layers (002) (Inset image of Fig. 2b) [31]. The corresponding lattice fringes of the NiCo nanoparticles are shown in Fig. 2b, which is characterized with high-resolution TEM (HRTEM). The lattice fringe of 0.2088 nm is close to the standard lattice

Figure 1 SEM images of Ni_1Co_1 @ht-CN (a), Ni_2Co_3 @ht-CN (b), Ni_3Co_2 @ht-CN (c), Co@ht-CN (d) and Ni@ht-CN (e). Inset is diameter distribution histograms of nanotubes.

Figure 2 TEM and HRTEM images (a, b) (Inset image of b shows lattice fringes of NiCo) and the distribution histogram for Ni/Co particles of $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ (c).

fringes of Ni (0.2034 nm, PDF#04-0850) and Co (0.2047 nm, PDF#15-0806), which are corresponding to the (111) lattice planes of pure Ni and Co [32]. And the lattice fringe of 0.1776 nm is close to the standard lattice fringes of Ni (0.1762 nm, PDF#04-0850) and Co (0.1772 nm, PDF#15-0806), which are related to the (200) lattice planes of Ni and Co [33]. Thus, the TEM analysis consolidates that the nanoparticles distributed on carbon nanotubes are NiCo alloy. Fig. 2c reveals that the diameter distribution of NiCo alloy nanoparticles is mostly in 8–20 nm. There are also some smaller particles (4–8 nm) that may not be involved in the formation of nanotubes.

Based on these considerations, we propose a possible mechanism for forming ht-CN as shown in Scheme 1. It is widely believed that the formation of ht-CN requires three key steps of nucleation, migration and growth [34,35]. At high temperatures, 2-cyanoguanidine decomposes to form graphitic nanosheets, sucrose acts as a

primary carbon source to form carbon nanoparticles, and metal nanoparticles are formed by the thermal reduction process. The metal nanoparticles act as the catalytic center for nanotube growth, and subsequently, the graphitic nanosheets and carbon nanoparticles migrate toward the catalytic centers and deposit on the surface of the metal nanoparticles to become the nuclei of nanotube growth. As other nanosheets and carbon particles continue to migrate to the surface of the core, the long hollow tubular composites are formed. The anisotropic growth rate of the tubular composites leads to the distorted patterns. Based on this formation mechanism, metal nanoparticles are usually located at the opening ends of the CNTs. This can be strongly supported by the TEM images as shown in Fig. 2.

XRD pattern in Fig. 3a shows the weak and broad characteristic diffraction peak centered at ca. 26.5° is corresponding to the (002) plane of graphite carbon, which is consistent with HRTEM results, demonstrating the existence of several graphitic layers in the as-prepared catalysts [36]. When C-N is doped with Ni and Co, three distinctive peaks located at 44.32° , 51.62° and 76.10° could be seen for $\text{Ni}_1\text{Co}_1\text{@ht-CN}$, $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ and $\text{Ni}_3\text{Co}_2\text{@ht-CN}$ catalysts. These three peaks are right located in between those of Co (PDF#15-0806) and Ni (PDF#04-0850), which could be attributed to the (111), (200) and (220) lattice planes for a metallic Co or Ni face-centered cubic structure [37]. Combined with the analysis of HRTEM above, it can be further confirmed that the nanoparticles decorated on N-doped carbon nanotubes are NiCo alloy [38–41]. The corresponding EDS mappings (Fig. 3b) indicate that the NiCo@ht-CN is composed of homogeneously dispersed C, N, Ni and Co elements.

Nitrogen-sorption measurement (Fig. 3c) shows all samples display a type-IV isotherm with a distinct hys-

Scheme 1 Illustration of the formation of the hollow tubular C-N composites (ht-CN).

Figure 3 XRD patterns (a), EDS spectra (b), N₂-adsorption/desorption isotherms (c), PSD curves calculated from the adsorption branch of the isotherms by the DFT method (d), and Raman spectra (e) of the samples.

teresis loop at a relative pressure P/P_0 of 0.4–1.0, which is normally related to capillary condensation in mesopores, while the sharp increase at low pressures ($P/P_0 = 0-0.4$) indicates the existence of micropores [42]. The calculated surface areas of Ni₁Co₁@ht-CN, Ni₂Co₃@ht-CN and Ni₃Co₂@ht-CN are 354.94, 368.35 and 335.76 m² g⁻¹, respectively. Ni₂Co₃@ht-CN catalyst can provide a larger surface area to expose more active sites, and thus lead to the enhanced electrocatalytic activity [43,44]. The pore-size distribution (PSD), analyzed by density functional theory (DFT) (Fig. 3d), shows that the pores of three NiCo@ht-CN are mostly smaller than 1 nm, that is, the high surface areas of the NiCo@ht-CN can be mainly attributed to microporosity. Raman spectra of NiCo@ht-CN samples in Fig. 3e exhibit two peaks in the range of 1,300–1,650 cm⁻¹ corresponding to the D and G bands as well as a weak peak at about 2,700 cm⁻¹ assigned to 2D bands [45]. The G band corresponds to the bond stretching of all sp²-bonded pairs, including C=C, N=C, N=O and C=O, while the D band is associated with the sp³ defect sites. The values of I_D/I_G between 1.003–1.006 for NiCo@ht-CN prove the certain graphitization carbon structure and defect sites in the materials [46]. The Ni-Co atomic ratio, obtained by ICP-OES, in the Ni₁Co₁@ht-CN, Ni₂Co₃@ht-CN and Ni₃Co₂@ht-CN is 1.08, 0.67 and

1.49, respectively, which is very close to their stoichiometric ratios.

XPS confirms the existence of C, N, Ni and Co elements in the Ni₂Co₃@ht-CN (Fig. 4a). The C 1s peak (Fig. 4b) is concentrated at around 283.7 (C=C), 284.2 (N=C) and 285.1 eV (C–C), indicating the successful synthesis of graphitic carbon. The presence of asymmetric C–N peak suggests the doping of N in the graphitic carbon sheet [47]. The high-resolution N 1s spectrum (Fig. 4c) is deconvoluted into three dominant peaks at 398.0, 399.9 and 401.1 eV, which can be assigned to pyridinic-N (63%), pyrrolic-N (24%) and graphitic-N (13%), respectively. It is generally considered that the pyridinic-N and graphitic N play a crucial role in ORR [48,49]. Pyridinic N, due to its electron-donating properties, can serve as metal anchoring sites for Ni and Co atoms [50]. The core level spectrum of Co 2p (Fig. 4d) can be deconvoluted into six peaks, of which the peaks at 781.6 and 797.2 eV are attributed to Co²⁺, while those at 779.6, 794 and 795.9 eV are ascribed to Co³⁺. The high-resolution Co 2p_{3/2} spectrum is deconvoluted into three peaks centered at 777.5, 779.6 and 781.6 eV, which can be attributed to the existence of metallic Co, Co–N, and Co–C, respectively [51–53]. The presence of such catalytically active groups increases the electronic interactions be-

Figure 4 XPS spectra of (a) all elements, (b) C 1s, (c) N 1s, (d) Co 2p, (e) Ni 2p in $\text{Ni}_2\text{Co}_3\text{@ht-CN}$.

tween Co and nitrogen-doped graphitic carbon, and improves the electrocatalytic performance of the catalyst toward ORR [54,55]. For the case of Ni 2p spectrum (Fig. 4e), the peak located at about 852.1 eV can be assigned to Ni metal, and the fitting peaks at 853.5 and 854 eV are assigned to Ni^{2+} , while the other two fitting peaks at 855.1 and 871.3 eV can be indexed to Ni^{3+} , and the peak at 877.8 eV located aside Ni $2p_{1/2}$ is ascribed to its satellite peak [56]. According to the XPS results of the Co and Ni, it can further confirm the presence of the chemical bonding between metal-metal and metal-N in the $\text{Ni}_2\text{Co}_3\text{@ht-CN}$. It is generally accepted that carbon-nitrogen complexes can be significantly formed after Ni and Co doping, which can produce catalytic active surfaces that weakly bind oxygenated intermediates, resulting in higher ORR activity [57].

To assess the electrocatalytic activities of the prepared samples toward ORR, cyclic voltammetric (CV) measurements were performed in $0.5 \text{ mol L}^{-1} \text{ KNO}_3$ (Fig. 5) and $0.1 \text{ mol L}^{-1} \text{ KOH}$ (Fig. 6). CVs of the samples in N_2 and O_2 -saturated $0.5 \text{ mol L}^{-1} \text{ KNO}_3$ at a scan rate of 50 mV s^{-1} shown in Fig. 5a display that all the prepared catalysts exhibit a distinct increment of cathodic current in O_2 -saturated electrolyte, which is caused by ORR on the catalysts. No significant cathodic peak can be observed between the potential of -0.2 and 0.8 V in N_2 -

saturated electrolyte. The ORR peak potential on the $\text{Ni}_1\text{Co}_1\text{@ht-CN}$, $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ and $\text{Ni}_3\text{Co}_2\text{@ht-CN}$ catalysts is ca. 0.52, 0.53 and 0.47 V, respectively (Fig. 5b). In view of the important role of the electrochemical surface areas (ECSAs) in electroactivity, ECSAs of the $\text{Ni}_1\text{Co}_1\text{@ht-CN}$, $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ and $\text{Ni}_3\text{Co}_2\text{@ht-CN}$ catalysts were obtained by the CVs at 0.705–0.805 V (vs. RHE) at different scan rates in $0.5 \text{ mol L}^{-1} \text{ KNO}_3$ (Fig. 5c–e). The slope of the linear curve derived from the dependence of the current at 0.755 V upon the scan rate reveals a double layer capacitance (C_{DL}) (Fig. 5f). The surface area of the prepared catalysts can be obtained by using a specific capacitance (C_s) of $60 \mu\text{F cm}^{-2}$ reported according to our recent work [31]. ECSA is calculated by the following formula: $\text{ECSA} = C_{\text{DL}}/C_s$.

The ECSA for $\text{Ni}_1\text{Co}_1\text{@ht-CN}$, $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ and $\text{Ni}_3\text{Co}_2\text{@ht-CN}$ on glassy carbon (GC) electrode was calculated to be 44.03, 59.60 and 12.41 cm^2 , respectively (Inset of Fig. 5f), indicating the much larger active surface area of the $\text{Ni}_2\text{Co}_3\text{@ht-CN}$. The large ECSA value also makes contribution to ORR electroactivity.

CV data in $0.1 \text{ mol L}^{-1} \text{ KOH}$ were also obtained as indicated in Fig. 6. Similarly, the CV curves of the $\text{Ni}_1\text{Co}_1\text{@ht-CN}$, $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ and $\text{Ni}_3\text{Co}_2\text{@ht-CN}$ in N_2 -saturated alkaline media display a featureless voltammetric profile (Fig. 6a). In O_2 -saturated media,

Figure 5 CV curves of NiCo₁@ht-CN, NiCo₃@ht-CN and NiCo₂@ht-CN in O₂-saturated and N₂-saturated 0.5 mol L⁻¹ KNO₃ at a scan rate of 50 mV s⁻¹ (a); CV curves of NiCo₁@ht-CN, NiCo₃@ht-CN and NiCo₂@ht-CN in O₂-saturated 0.5 mol L⁻¹ KNO₃ at a scan rate of 50 mV s⁻¹ (b); C_{DL} obtained by measuring the charging currents for the cyclic voltammograms shown in the catalyst NiCo₁@ht-CN (c), NiCo₃@ht-CN (d) and NiCo₂@ht-CN (e) at various scan rates. The effect of the scan rate on the anodic and cathodic charging current taken from center of each CV at 0.755 V vs. RHE (f).

Figure 6 CV curves of NiCo₁@ht-CN, NiCo₃@ht-CN and NiCo₂@ht-CN in O₂-saturated and N₂-saturated 0.1 mol L⁻¹ KOH at a scan rate of 50 mV s⁻¹ (a). CV curves of NiCo₁@ht-CN, NiCo₃@ht-CN and NiCo₂@ht-CN in O₂-saturated 0.1 mol L⁻¹ KOH at a scan rate of 50 mV s⁻¹ (b). C_{DL} obtained by measuring the charging currents for the cyclic voltammograms shown in the catalyst NiCo₁@ht-CN (c), NiCo₃@ht-CN (d) and NiCo₂@ht-CN (e) at various scan rates. Effect of scan rate on the anodic and cathodic charging current taken from center of each CV at 1.10 V vs. RHE (f).

however, a more positive shift of ORR peak potential for $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ than that of the other two catalysts is observed (Fig. 6b). And the $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ presents a more positive ORR onset potential (0.77 V vs. RHE) than that of $\text{Ni}_1\text{Co}_1\text{@ht-CN}$ (0.75 V vs. RHE) and $\text{Ni}_3\text{Co}_2\text{@ht-CN}$ (0.73 V vs. RHE). Results indicate that the $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ is more beneficial to ORR in O_2 -saturated 0.1 mol L^{-1} KOH media. Similarly, the ECSA of the prepared catalysts in alkaline media can be obtained by changing the potential interval of the CV to 1.05–1.15 V in alkaline solution. The ECSA for $\text{Ni}_1\text{Co}_1\text{@ht-CN}$, $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ and $\text{Ni}_3\text{Co}_2\text{@ht-CN}$ on GC electrode in 0.1 mol L^{-1} KOH media was calculated to be 26.12, 32, and 21.88 cm^2 respectively (Inset of Fig. 6f), further suggesting that the $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ possesses the larger ECSA in alkaline media.

To further investigate the electrochemical performances of the $\text{Ni}_1\text{Co}_1\text{@ht-CN}$, $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ and $\text{Ni}_3\text{Co}_2\text{@ht-CN}$ catalysts in neutral and alkaline media, the linear scanning voltammogram (LSV) curves were recorded on a rotating disk electrode (RDE) at a rotation speed of 1,600 rpm (Fig. 7a, c). In neutral 0.5 mol L^{-1} KNO_3 (Fig. 7a), the half wave potential of $\text{Ni}_1\text{Co}_1\text{@ht-CN}$,

$\text{Ni}_2\text{Co}_3\text{@ht-CN}$, $\text{Ni}_3\text{Co}_2\text{@ht-CN}$ and Pt/C is 0.53, 0.51, 0.50 and 0.62 V, respectively. Their limiting diffusion current densities at -0.18 V are 5.26, 6.63, 4.09 and 4.36 mA cm^{-2} , respectively. Although the half-wave potential of the catalysts is less than that of Pt/C, the $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ displays a much larger diffusion current density than Pt/C. In alkaline electrolyte (Fig. 7c), the half wave potential of $\text{Ni}_1\text{Co}_1\text{@ht-CN}$, $\text{Ni}_2\text{Co}_3\text{@ht-CN}$, $\text{Ni}_3\text{Co}_2\text{@ht-CN}$ and Pt/C is 0.80, 0.84, 0.79 and 0.87 V, respectively, showing that the $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ presents almost the same ORR half wave potential and limiting diffusion current as the Pt/C. Results prove the much higher electrocatalytic activity of the $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ than the other catalysts. ORR kinetics polarization curves of the $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ under different rotation rates are displayed in Fig. 7b (neutral electrolyte) and Fig. 7d (alkaline electrolyte). A well-defined current plateau arises in these two electrolytes, and the limiting current density at 2,000 rpm reaches almost 7 mA cm^{-2} in neutral solution or 5.3 mA cm^{-2} in alkaline solution. Corresponding Koutecky-Levich (K-L) plots obtained at different potentials are shown in inset of Fig. 7b and 7d [58]. The electron transfer number (n) of ORR on the $\text{Ni}_2\text{Co}_3\text{@ht-CN}$

Figure 7 (a) RDE polarization curves of the prepared catalysts and Pt/C in O_2 -saturated 0.5 mol L^{-1} KNO_3 at 1,600 rpm at 5 mV s^{-1} . (b) RDE polarization curves of $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ at different rotation rates in O_2 -saturated 0.5 mol L^{-1} KNO_3 at 5 mV s^{-1} . Inset image is the corresponding K-L plots for $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ at different potentials. (c) RDE polarization curves of the prepared catalysts and Pt/C in O_2 -saturated 0.1 mol L^{-1} KOH at 1,600 rpm at 5 mV s^{-1} . (d) RDE polarization curves of $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ at different rotation rates in O_2 -saturated 0.1 mol L^{-1} KOH at 5 mV s^{-1} ; inset is the corresponding K-L plots for $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ at different potentials. (e) Polarization curves of $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ in O_2 -saturated 0.5 mol L^{-1} KNO_3 at 1,600 rpm before and after 5,000 cycles (inset: chronoamperometric response of $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ at 0.4 V). (f) Polarization curves of $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ in O_2 -saturated 0.1 mol L^{-1} KOH at 1,600 rpm before and after 5,000 cycles (inset: chronoamperometric response of $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ at 0.7 V).

CN was calculated to be in the range of 3.7–3.9 in neutral media or 3.6–3.9 in alkaline media, based on the K-L equation and the parameters in the literature [59,60], indicating that the ORR process on the $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ is nearly a four-electron pathway in both neutral and alkaline media. These results imply that the decoration of NiCo alloy nanoparticles on ht-CN composites could result in more active sites and easier reduction of oxygen into water due to the special novel structure. One of the active sites is derived from the metal- N_4 structure, which can be easily formed from nitrogen source, metal source and carbon carrier at 600–800°C [61]. Also, carbon-nitrogen complexes can be significantly formed after Ni and Co doping, which can produce catalytic surfaces that weakly bind oxygenated intermediates, resulting in higher ORR activity [62,63]. In addition, the homogeneous distribution of abundant Co@N active sites on the surface of the mesoporous carbon can greatly promote electron penetration to enhance the ORR catalytic activity, and the presence of a high proportion of Co is generally more helpful to promote the oxygen reduction process [64]. Therefore, the ORR electroactivity order of the catalysts follows $\text{Ni}_2\text{Co}_3\text{@ht-CN} > \text{Ni}_1\text{Co}_1\text{@ht-CN} > \text{Ni}_3\text{Co}_2\text{@ht-CN}$. To verify the stability of the catalyst for oxygen reduction, 5,000 times consecutive linear scanning tests were carried out in neutral and alkaline media, as shown in Fig. 7e and 7f. Results reveal that both in neutral and alkaline media, no noticeable change of the polarization curves on the

$\text{Ni}_2\text{Co}_3\text{@ht-CN}$ was observed before and after 5,000 cycles. Chronoamperometric data also show a negligible current degradation at 7,200 s (the insets of Fig. 7e, f), which demonstrates excellent long-term stability of the catalyst in neutral and alkaline electrolyte.

To further verify the practicability of the catalyst as an air cathode for a zinc-air battery, we investigated the ORR polarization curves of the prepared catalysts in the half-cell model (Fig. 8a), where the working electrode (air electrode) is fabricated by coating the catalyst on carbon cloth. Corresponding polarization curves are manifested in Fig. 8b (neutral solution) and Fig. 8d (alkaline solution). A nearly linear increase of the ORR current with the negative shift of potential arises for all the catalysts in both neutral and alkaline media when the potential is lower than the onset potential. Although the onset potential of ORR on the prepared catalysts in the neutral electrolyte is lower than that of Pt/C, the current generated by the $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ exceeds that of Pt/C. In alkaline solution (Fig. 8d), the $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ reveals better performance than other catalysts and even Pt/C. The effect of potential sweeping rate on polarization curve was also investigated and the results are shown Fig. 8c (neutral) and Fig. 8e (alkaline). In the range of 5 to 100 mV s^{-1} , the sweeping rate has little effect on current density, showing that oxygen gas can reach the three-phase interface of electrolyte/catalyst/gas in time through the gas diffusion layer of the carbon cloth. Results con-

Figure 8 (a) Schematic diagram of a half-cell test to measure ORR performance of the air electrode. (b) Polarization curves of all prepared catalysts coated in carbon cloth in $0.5 \text{ mol L}^{-1} \text{KNO}_3$ at 100 mV s^{-1} . (c) Polarization curves of the catalyst $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ coated in carbon cloth at different scan rates in $0.5 \text{ mol L}^{-1} \text{KNO}_3$. (d) Polarization curves of all prepared catalysts coated in carbon cloth in $0.1 \text{ mol L}^{-1} \text{KOH}$ at 100 mV s^{-1} . (e) Polarization curves of the catalyst $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ coated in carbon cloth at different scan rates in $0.1 \text{ mol L}^{-1} \text{KOH}$.

firm that the prepared catalysts are excellent electrocatalysts for ORR and the corresponding carbon cloth coated with the catalysts is the reliable air electrode as the cathode of Zn-air battery.

To investigate the practical application of the as-developed catalysts in neutral and alkaline electrolyte, we assembled zinc-air batteries with the prepared catalyst loading on carbon cloth as the cathode and a Zn sheet as anode in $0.5 \text{ mol L}^{-1} \text{ KNO}_3$ and $6.0 \text{ mol L}^{-1} \text{ KOH}$ (Fig. 9a). For comparison, the commercial Pt/C as cathode catalyst was also inspected. Fig. 9b presents the polarization and power density curves of Zn-air battery with different cathodic catalysts in $0.5 \text{ mol L}^{-1} \text{ KNO}_3$. The

$\text{Ni}_2\text{Co}_3\text{@ht-CN}$ exhibits a larger current density of around 225 mA cm^{-2} and a maximum power density of about 47 mW cm^{-2} , about 21% higher than that ($\sim 37 \text{ mW cm}^{-2}$) of the Pt/C. The power density of the $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ (47 mW cm^{-2}) also exceeds the results obtained in neutral zinc-air battery reported recently [65–67]. The $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ displays an open-circuit voltage (V_{OC}) of 1.08 V, which is slightly lower than that of the Pt/C (1.12 V) but higher than the other two catalysts. This is consistent with the result in Fig. 7a. In addition, discharge curves of the battery under different current densities (25, 50, 100 and 150 mA cm^{-2}) were also tested in $0.5 \text{ mol L}^{-1} \text{ KNO}_3$ for both the $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ and Pt/C cathodic catalysts

Figure 9 (a) Zinc-air battery test device schematic. (b) Polarization and power density curves of the Zn-air battery using the prepared catalysts and Pt/C as cathode catalysts in $0.5 \text{ mol L}^{-1} \text{ KNO}_3$. (c) Discharge curves of the $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ battery and Pt/C battery in $0.5 \text{ mol L}^{-1} \text{ KNO}_3$ under different current densities. (d) Polarization and power density curves of the Zn-air battery using the prepared catalysts and Pt/C as cathode catalysts in $6.0 \text{ mol L}^{-1} \text{ KOH}$. (e) Discharge curves of the $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ battery and Pt/C battery in $6.0 \text{ mol L}^{-1} \text{ KOH}$ under different current densities. (f) Continuous discharge (38 h) of the $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ battery and Pt/C battery in $0.5 \text{ mol L}^{-1} \text{ KNO}_3$ under 150 mA cm^{-2} current density. (g) Continuous discharge (38 h) of the $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ battery and Pt/C battery in $6.0 \text{ mol L}^{-1} \text{ KOH}$ under 150 mA cm^{-2} current density. (h) Photograph of eight LEDs connected to two neutral batteries with the cathode catalyst $\text{Ni}_2\text{Co}_3\text{@ht-CN}$.

(Fig. 9c). A well-defined voltage plateau develops at any discharge current, and the $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ battery always shows a higher plateau than the Pt/C. This reveals that the neutral Zn-air battery with the cathodic catalyst $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ possesses a persistent and stable discharge performance even at a high current density of 150 mA cm^{-2} . As for the polarization and power density curves in alkaline solution (Fig. 9d), the $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ battery also exhibits an outstanding performance compared with the Pt/C. The maximum power density on the $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ is 314 mW cm^{-2} , about 1.6 times larger than that of the Pt/C (198 mW cm^{-2}). When the test is cut off to 0.6 V, corresponding discharge current density still reaches 500 mA cm^{-2} , showing superior performance over those in recent work [68–70]. A surprising result can be clearly seen from the dependence of the battery voltage upon discharge time as indicated in Fig. 9e, where the plateau voltage of the $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ battery drops by only 0.08 V after 240 min of stepped constant current discharge, while the plateau voltage of the Pt/C battery drops by 0.21 V. Constant current discharge curves at 150 mA cm^{-2} in $0.5 \text{ mol L}^{-1} \text{ KNO}_3$ and $6.0 \text{ mol L}^{-1} \text{ KOH}$ are shown in Fig. 9f and Fig. 9g, respectively. The discharge time of $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ battery and Pt/C battery in the neutral electrolyte can last for about 10 h when the test is cut off to 0.1 V. As can be seen from the whole discharge curve (Fig. 9f), the battery voltage of the $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ is slightly higher than that of the Pt/C. In alkaline solution (Fig. 9g), however, the $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ battery reveals much higher and more stable discharge voltage than the Pt/C even at a high discharge current density of 150 mA cm^{-2} . After ~25 h continuous discharge, the cell voltages of the $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ and Pt/C batteries are 1.160 and 1.035 V respectively, showing a voltage difference of 0.125 V. This further indicates the better performance of the $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ for ORR in alkaline medium than in neutral solution. The high ORR catalytic activity and stability of the $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ is responsible for advanced Zn-air batteries and other related fuel cells as an excellent cathodic catalyst. As exemplified in Fig. 9h, eight light-emitting diodes (LEDs) can be easily lightened by two series $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ battery in neutral solution.

The superior electrochemical performances of the $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ catalyst for ORR can be attributed to its novel morphological structure and special compositions: i) the combination of Co-Ni alloy with N can modulate the electronic properties and surface polarities, thus providing more ORR active sites and improving the activity of the catalyst; ii) the “synergistic effect” between

Ni and Co caused by their same crystal structure (face centered-cubic) and similar cell parameters enhances the ORR activity; iii) hollow tubular structure and porous surface of the catalyst also promote the ORR due to lots of ORR active sites in the interior of carbon shells; iv) large active surface area of ht-CN, as well as the presence of graphitization carbon structure and defects sites in the material, can efficiently enhance the transfer speed for both electrons and oxygen; and v) the higher content of pyridine-N and graphite-N provides a significant amount of ORR-related active sites.

CONCLUSIONS

In summary, we have developed a facile and cost-effective method to prepare NiCo doped hollow tubular C-N nanocomposites (NiCo@ht-CN) by directly pyrolyzing a mixture of Ni/Co salt, 2-cyanoguanidine and sucrose. Such hollow C-N nanotubes exhibit a bamboo-like shape with a tube diameter as small as 12 nm. In addition, the prepared $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ catalyst possesses excellent ORR activity and enhanced discharge performance (compared with the Pt/C) in alkaline and neutral solutions. We have shown that the newly-developed catalyst can be successfully implemented as a highly efficient cathode in Zn-air battery operating in different pH electrolytes. Whether in neutral or alkaline medium, the $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ battery presents higher discharge current density and power density, more importantly, much higher discharge voltage plateau and stability, compared with the Pt/C battery. The facile procedure and scalability for the synthesis of the $\text{Ni}_2\text{Co}_3\text{@ht-CN}$ may open up a promising avenue for the development of cathode catalysts applied to various fuel cells and metal-air batteries.

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Conflict of interest The authors declare no conflict of interest.

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Ni-Co掺杂空心C-N管状复合物作为锌-空气电池阴极催化剂的性能研究

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摘要 氧还原反应(ORR)高活性电催化剂的研究对于可再生能源转化和储存技术具有重要意义. 我们通过一种简单的热解途径利用乙酸镍和乙酸钴作为金属前体, 双氰胺作为氮源, 蔗糖作为碳源, 将Ni-Co纳米颗粒封装在中空管状C-N复合物(ht-CN)中制备了新型ORR电催化剂. 其中, Ni/Co摩尔比为2:3的催化剂Ni₂Co₃@ht-CN在碱性和中性介质中均表现出与Pt/C接近的优异ORR电活性, 以Ni₂Co₃@ht-CN为阴极的锌-空气电池无论在中性还是碱性中都表现出优异放电性能: 在0.5 mol L⁻¹ KNO₃溶液中的开路电压和最大功率密度分别为1.08 V和47 mW cm⁻², 而在6 mol L⁻¹ KOH溶液中分别为1.51 V和314 mW cm⁻²; 无论是在中性还是碱性溶液中, Ni₂Co₃@ht-CN电池在不同电流密度下的恒流放电曲线都表现出比Pt/C电池更高的电压平台和稳定性. 结果表明本文研究的催化剂是碱性和中性Zn-空气电池优异的阴极材料.