Atomic cobalt anchored on covalent triazine frameworks with ultra-high performance towards oxygen reduction reaction

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ABSTRACT Single cobalt atom is promising non-precious metal catalyst instead of Pt in the oxygen reduction reaction (ORR). However, it is still a great challenge to develop a cost-effective, ultrastable and efficient single-atom cobalt catalyst for ORR, requiring efficient fabrication strategies and robust support to stabilize the single cobalt atom. Here, we prepared a highly active and stable atomically isolated cobalt catalyst *via* covalent triazine framework (CTF) support with Ketjen Black (KB) hybridization in scale. The prepared single Co catalyst (Co-CTF/KB) possesses high metal loading over 4 wt% and shows superior ORR performance with a half-wave potential ($E_{1/2}$) of 0.830 V and a limiting current density of 6.14 mA cm⁻² as well as high tolerance of methanol in an alkaline medium, which outperforms commercial Pt/C and most non-precious-metal catalysts reported to date. Benefitting from strong stabilization of Co atoms on CTF, Co-CTF/KB shows outstanding stability with only 5 mV negative shifts after 10,000 cycles. Moreover, it also displays high catalytic activity for oxygen evolution reaction (OER), suggesting it is an efficient ORR/OER bifunctional catalyst. The present work provides a facile strategy for preparing single-atom catalysts in bulk quantity and contributes to development of catalysts for electrochemical conversion and storage devices.

Keywords: single-atom cobalt, non-precious metal catalysts, oxygen reduction reaction (ORR), covalent triazine framework (CTF) support, cost-effective scalable preparation

INTRODUCTION

The increasing energy crisis and rising environmental concerns call for the urgent development of renewable energy technologies, such as fuel cells and metal-air bat-

teries [1–3]. Benefitting from high energy density and environment-friendly features, fuel cells and metal-air batteries are promising candidates for next generation of energy conversion and storage devices. However, their efficiencies strongly depend on the sluggish kinetics of oxygen reduction reaction (ORR) at the cathode [4,5]. To date, Pt-based materials are the most effective and available commercial ORR catalysts, but severely unavoidable disadvantages, such as high cost, serious deficiency, limited durability and fast deactivation by CO, impede their scalable applications in practice [6–15]. Consequently, it has been the foremost topic of this field that exploring high-performance, durable, and earth-abundant non-precious ORR electrocatalysts over the past few years [16–18]. Among all the reported non-precious metal catalysts, including transition metal sulfides/oxides [19], nitrides [20], carbon materials [9], and perovskites [21], transition metal-coordinating nitrogen-doped carbon single-atom catalysts (SACs) (M-N-C, M = Fe or Co) have emerged as the most promising alternatives to Pt for ORR [22–26], because of their superior electrocatalytic activity, stability and low-cost scalable synthesis. In SACs, the smallest metal particles, i.e., single atoms, are distributed on the surface of support material, which are beneficial to boost their catalytic activities with the maximized atom utilization [27–31]. Both Fe-N-C and Co-N-C SACs exhibit high ORR activity, but Fe-N-C SACs always promote decomposition of H₂O₂ to produce hydroxyl and hydroperoxyl radical species, which will induce an deteriorated activity along with their decomposition of the active sites, membranes and carbon supports [32,33]. In contrast, Co-N-C SACs do not suffer from this problem and thus are

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more promising durable ORR catalysts. As isolated metal atoms tend to aggregate during the preparation and catalytic process due to their high surface energy, the stability and ORR activity of Co-N-C SACs are mostly determined by the supports, which can anchor and expose the isolated active metal atoms to prevent them from aggregating, and modulate their morphology and electronic structures to boost their ORR activity. Therefore, to improve the ORR activity of isolated cobalt atoms, several N-doped carbon supports (N-C) for cobalt SACs have been fabricated, such as hollow N-doped carbon spheres prepared by SiO₂ template-assisted pyrolysis of cobalt porphyrines [34,35], hierarchically porous N-doped carbons fabricated by template-assisted pyrolysis of cobalt salts and small molecules [36,37], N-doped carbons derived from pyrolysis of metal-organic frameworks (MOFs) [33,38], N-doped carbon nanofibers synthesized by pyrolysis of nanofibers consisting of cobalt salts and carbon and nitrogen sources [32], and porphyrinic triazine-based frameworks prepared by trimerization of cobalt cyanoporphyrine monomers [39]. With these supports, impressive improvement of ORR activity has been achieved, but such pyrolysis under high temperature usually leads to aggregation of unstable metallic compounds enclosed in carbon shells or inhomogeneous distribution of single metal atoms [33]. Thus, it is highly desirable to develop suitable supports with well-defined sites to anchor single cobalt atoms under moderate temperature, affording SACs with homogeneous distribution of atomically isolated cobalt in bulk quantity.

Recently, covalent triazine frameworks (CTFs) obtained from the trimerization of aromatic nitriles have emerged as suitable novel platforms for the synthesis of electrocatalysts [40–43] because of the following merits: 1) CTFs possess abundant pyridinic nitrogen atoms with lone pairs of electrons, which can efficiently bond with single metal atoms [44,45]; 2) CTFs feature porous structure with uniform nano pores, which are ideal sites to anchor single atoms and thus benefit exposing the active sites; 3) The covalently bonded framework of CTFs endows them with strong mechanical property, which might contribute to the stability of SACs; 4) CTFs synthesized by the ionothermal methods possess good electrical conductivity because partial graphitization will inevitably occur during the synthesis process [46]. Nevertheless, the role of CTFs in supporting single cobalt atoms towards ORR has not been explored, although they have worked as catalysts or support material for various applications, such as separation and storage of gases, energy storage, photocatalysis and heterogeneous catalysis [46,47].

Herein, we prepared highly reactive and stable isolated single cobalt atoms supported by covalent triazine frameworks with Ketjen Black (KB) hybridization (Co-CTF/KB) for ORR. The as-fabricated Co-CTF/KB features conductive networks, unique porous structures, and high specific surface area as well as the abundance of atomically dispersed highly active Co-N-C sites. Consequently, Co-CTF/KB exhibits superior ORR activity with an onset potential of 0.940 V, a half-wave potential of 0.830 V, a high limiting current density of 6.14 mA cm⁻² and a low Tafel slope of 65 mV dec⁻¹, which outperform commercial Pt/C and most non-precious-metal catalysts reported to date. Furthermore, Co-CTF/KB shows long-term stability with little ORR polarization curve shift after 10,000 cycles. In addition, it also displays superior methanol tolerance with negligible current change in the presence of 3.0 mol L⁻¹ methanol. This work presents large-scale preparation of a low-cost, ultrastable and efficient single-atom Co electrocatalyst with high metal loading content for ORR.

EXPERIMENTAL SECTION

Sample preparation

Synthesis of CTF: 0.5 g of 2,6-dicyanopyridine and 5.28 g of ZnCl₂ were mixed in a glove box (99.99% argon with 0.1 ppm water). The mixture was transferred into a glass ampoule pipe and the pipe was evacuated, sealed, heated at the rate of 5°C min⁻¹ and maintained at 400°C for 21 h. The resulting powder was washed with 0.1 mol L⁻¹ HCl, water and tetrahydrofuran in sequence, and then dried under vacuum at 80°C for 12 h, giving a dark powder.

Synthesis of CTF/KB: 0.5 g of 2,6-dicyanopyridine, 0.5 g of KB EC600JD and 5.28 g of ZnCl₂ were mixed in a glove box (99.99% argon with 0.1 ppm water). The mixture was transferred into a glass ampoule pipe and the pipe was evacuated, sealed, heated at the rate of 5°C min⁻¹ and maintained at 400°C for 21 h. The resulting powder was washed with 0.1 mol L⁻¹ HCl, water and tetrahydrofuran in sequence, and then dried under vacuum at 80°C for 12 h, giving a dark powder.

Synthesis of Co-CTF/KB: 100 mg of CTF/KB and 100 mg of cobalt (II) acetate tetrahydrate were put into 50 mL of methanol, respectively, and treated with sonication for 1 h. Then, cobalt (II) acetate tetrahydrate solution was injected to the suspension of CTF/KB in methanol and kept at 60°C for 4 h. The as-obtained product was centrifuged and washed with methanol thrice. Finally, the Co-CTF/KB was obtained after drying in an oven at 80°C for 12 h.

Sample characterization

The X-ray diffraction (XRD) was tested by X-ray diffraction (Rigaku D/max-2500B2+/PCX system). The transmission electron microscopy (TEM) images and high-resolution images were observed with Field-emission transmission electron microscopy (FE-TEM, Tecnai G2 F20 U-TWIN). Scanning transmission electron microscopy (STEM) and elemental mapping images were collected from high-angle annular dark-field STEM (HAADF-STEM). The HAADF-STEM images were carried out in an aberration-corrected JEOL ARM-200F system equipped with a cold field emission gun and an ASCOR probe corrector at 60 kV. The cobalt concentrations of the samples were conducted on the inductively coupled plasma atomic emission spectroscopy (ICP-AES). The X-ray photoelectron spectroscopy (XPS) experiments were performed on an ESCALAB250Xi system with a monochromatic Al K α X-ray source. Nitrogen adsorption and desorption isotherms were determined by nitrogen physisorption at 77 K on a Micromeritics ASAP 2020 analyzer. The samples were degassed under vacuum at 150°C for 10 h (10^{-5} bar) before analysis. The specific surface area (SBET) was calculated by the Brunauer-Emmet-Teller (BET) approach. Pore size distribution data was calculated based on the density functional theory (DFT) model.

Electrochemical measurements

All the electrochemical measurements were carried out in a conventional three-electrode system using the CHI760E electrochemical station (Shanghai Chenhua Instrument Factory, China), in which saturated calomel electrode (SCE, 1.015 vs. reversible hydrogen electrode (RHE) in 0.1 mol L $^{-1}$ KOH) and platinum net (0.1 cm 2) were regarded as the reference electrode and the counter electrode, respectively, with 0.1 mol L $^{-1}$ KOH aqueous solution as the electrolyte. Rotating disk electrode (RDE) and rotating ring-disk electrode (RRDE) tests were both detected by American Pine Instruments device. Five milligram of catalyst was ultrasonically dispersed in 1 mL ethanol for about 30 min, and then 50 μ L of 0.5 wt% Nafion solution was added. The mixture was sonicated for 1 h to form a homogeneous catalyst ink. Then, 10 μ L of the as-prepared catalyst ink was dropped on the RDE, giving loading of 0.255 mg cm $^{-2}$. The commercially available carbon-supported Pt/C electrode was prepared according to the above procedure with loading of $\sim$ 0.255 mg cm $^{-2}$. Before testing, O $_2$ flow was carried out through the electrolyte in the cell for about 30 min to achieve the O $_2$ -saturated solution. The cyclic voltammetry

(CV) tests were measured in O $_2$ -saturated 0.1 mol L $^{-1}$ KOH solution with a scan rate of 50 mV s $^{-1}$. RDE/RRDE tests were conducted in O $_2$ -saturated 0.1 mol L $^{-1}$ KOH at different rotation rates with a sweep rate of 10 mV s $^{-1}$ at room temperature. The electron transfer number (n) and hydrogen peroxide yield (H $_2$ O $_2$ %) were calculated by the following equations:

$$n = 4 \times \frac{I_d}{I_d + I_r/N}, \quad (1)$$

$$\text{H}_2\text{O}_2(\%) = 200 \times \frac{I_r/N}{I_d + I_r/N}, \quad (2)$$

where I_d is the disk current, I_r is the ring current, and $N = 0.37$ is the current collection efficiency of the Pt ring [9].

The polarization curves were collected at various disk rotation rates of 400, 625, 900, 1225, 1600, 2025 and 2500 rpm, respectively, for the RDE examination. Thus, the number of electrons transferred (n) was calculated using Koutecky-Levich equations to analyze the kinetic parameters on the basis of the following equations:

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K}, \quad (3)$$

$$B = 0.62nFC_0D_0^{2/3}\nu^{-1/6}, \quad (4)$$

where J is the measured current density, and J_K and J_L are the kinetic-limiting current densities and diffusion-limiting current densities, respectively. Where, ω is the angular velocity. n is the number of electrons transferred per oxygen molecule. F is the Faraday constant (96,500 C mol $^{-1}$). C_0 is the bulk concentration of O $_2$ in 0.1 mol L $^{-1}$ KOH (1.2×10^{-3} mol L $^{-1}$). D is the diffusion coefficient of O $_2$ in 0.1 mol L $^{-1}$ KOH (1.9×10^{-5} cm 2 s $^{-1}$). ν is the kinematic viscosity of the electrolyte (0.01 cm 2 s $^{-1}$).

RUSULTS AND DISCUSSION

As an ideal support for single-atom Co, the proposed CTF should have binding sites and well-defined pores to anchor and accommodate single cobalt atoms. Thus, 2,6-dicyanopyridine was chosen as the monomer to prepare the target CTF as it provides extra binding sites for Co atoms besides triazine frameworks. And KB was hybridized with the target CTF to increase the conductivity of this composite. As shown in Fig. 1, CTF/KB was obtained by *in situ* polymerization of 2,6-dicyanopyridine in-molten ZnCl $_2$ containing KB, and then was functionalized with Co atoms within a solution of cobalt(II) acetate in methanol through an impregnation strategy, obtaining Co-CTF/KB.

The morphology of Co-CTF/KB and CTF/KB was examined by TEM. The TEM images of KB, CTF and CTF/

Figure 1 Schematic diagram of synthesis and structure of Co-CTF/KB and its application in ORR (blue: N, red: Co and black: C).

KB (Fig. S1) show no large CTF bulks in CTF/KB, implying that CTF is well mixed with KB during the polymerization. High-resolution TEM of Co-CTF/KB reveals that no metal nanoparticles (>1 nm) aggregate on Co-CTF/KB (Fig. 2a). The existing form and atomic distribution of Co atoms were also verified *via* HAADF-STEM with sub-angstrom resolution, which is a powerful tool for identifying individual metal atoms. As shown in Fig. 2c, numerous evenly distributed white bright dots at atomic scale are observed on the surface of Co-CTF/KB (highlighted by red circles), while no clusters and nanoparticles of Co species are observed, suggesting that the Co is atomically dispersed on the support. And the corresponding energy-dispersive X-ray spectroscopy (EDX) elemental mappings show that Co and N atoms are uniformly distributed over the entire architecture of Co-CTF/KB as well (Fig. 2b).

Furthermore, the XRD spectrum of Co-CTF/KB only shows one broad carbon peak at $\sim 24^\circ$ and no other peaks of metallic Co and/or Co compounds can be observed (Fig. S2), meaning that there is only atomic cobalt on CTF/KB support, which is consistent with the HR-TEM result. The ICP-AES analysis shows that Co-CTF/KB possesses a bulk Co content of ~ 4.16 wt% (Table S1). All these results strongly suggest high dispersion of single cobalt atoms in the CTF/KB.

To investigate the cobalt coordination in Co-CTF/KB, CTF/KB was chosen as the reference. The wide-range XPS analysis reveals that there are C, N and O in both CTF/KB and Co-CTF/KB, but only Co-CTF/KB contains Co (Fig. S3). Moreover, the nitrogen species and chemical environments of nitrogen in CTF/KB and Co-CTF/KB were explored by high-resolution C 1s and N 1s analysis. In the C 1s XPS spectrum of Co-CTF/KB (Fig. S4), there are two peaks at ~ 284.7 and 285.7 eV in C 1s region, which can be assigned to carbon atoms neighbored with

carbon and nitrogen atoms, respectively, revealing that nitrogen atoms are anchored within a carbon backbone. As shown in Fig. S5, four peaks at 398.7, 399.4, 400.7 and 402.0 eV corresponding to pyridinic N, pyrrolic N, graphitic N, oxidized N, respectively, can be observed in the high-resolution N 1s spectra of CTF/KB [48]. In contrast, there is a new peak around 399.6 eV in the N 1s spectrum of Co-CTF/KB (Fig. 2d) with 1 eV upshift compared with the pristine pyridinic N (~ 398.7 eV) [49], which could be ascribed to the energy of pyridinic N that binds cobalt in Co-N_x as the literature reported [50], but not that of pyrrolic N that binds cobalt because if Co is bound to pyrrolic N, like in porphyrins, the peak will appear at a lower binding energy of ~ 398.5 eV [51]. Moreover, theoretical calculation by DFT also predicted that the position of Co-N_x peak should be in the range of 399.3–400.9 eV [52]. The formation of Co-N_x was further confirmed by the Co 2p XPS analysis (Fig. S6). In the Co 2p XPS spectrum (Fig. S6), there are two distinct peaks at ~ 782.1 and 780.5 eV, which can be ascribed to cobalt in Co-N_x and Co-C_x-N_y, respectively [53]. The above analysis indicates that Co atoms are anchored by nitrogen atoms of CTF in Co-CTF/KB and atomically dispersed on the nitrogen-doped framework of CTF, giving Co-N-C moieties. Additionally, Co-CTF/KB also possesses high BET specific surface area of 734.2 m² g⁻¹ and large pore volume of 0.71 cm³ g⁻¹ (Fig. S7 and Table S2), which will benefit the exposure of rich active sites to oxygen and mass-transport of oxygen and electrolyte.

The electrocatalytic activities of Co-CTF/KB for ORR were investigated by CV and linear sweep voltammetric (LSV) measurements on an RDE in O₂-saturated 0.1 mol L⁻¹ KOH solution at 20°C . As shown in Fig. 3a, distinct cathodic peaks are observed for both Co-CTF/KB and CTF/KB in the O₂-saturated electrolyte. However, the ORR peak current density for Co-CTF/KB (0.820 V) is

Figure 2 (a) High-resolution transmission electron microscopy (HR-TEM) images of Co-CTF/KB. (b) HAADF-STEM image and the corresponding element mapping of Co-CTF/KB: Co (red), C (purple), N (cyan). (c) HAADF-STEM image of Co-CTF/KB (isolated bright dots marked with red circles are cobalt atoms) and (d) N 1s XPS spectrum of Co-CTF/KB.

obviously more positive than that of CTF/KB (0.680 V). The LSV further reveals that Co-CTF/KB has an outstanding ORR activity in terms of the limiting current density and half-wave potential ($E_{1/2}$). As shown in Fig. 3b, the limiting current density of Co-CTF/KB is 6.14 mA cm^{-2} , higher than that of CTF/KB (4.5 mA cm^{-2}) and Pt/C (5.6 mA cm^{-2}), and the $E_{1/2}$ for Co-CTF/KB (0.830 V) is more positive than that of CTF/KB (0.70 V) and Pt/C (0.810 V), indicating that Co-N-C species give rise to much better ORR activity compared with N-C sites and consequently highlighting the critical role of metal center (Co-N-C) in ORR catalytic activity. Moreover, Co-CTF/KB shows the lowest Tafel slope of 65 mV dec^{-1} compared with CTF/KB (71 mV dec^{-1}) and Pt/C (75 mV dec^{-1}), suggesting that Co-CTF/KB is an excellent ORR catalyst with superior kinetics. The distinct Tafel slope values for Co-CTF/KB and CTF/KB further reveal that the rate limiting step are improved after incorporating Co-N-C active sites. Theoretical calculation has also proven that singly dispersed cobalt sites could

significantly increase the hydrogenation of OH^* species in the process of ORR [35].

The ORR kinetics of Co-CTF/KB was also evaluated by an RDE system at different rotation rates (400–2500 rpm) in $0.1 \text{ mol L}^{-1} \text{ KOH}$ (Fig. 3d). Based on the Koutecky-Levich (K-L) equation, the electron transfer number (n) of Co-CTF/KB calculated from the diffusion-controlled region to the kinetics-controlled region (0.2 to 0.75 V) is approximately 4 (Fig. 3e), while the electron transfer number of CTF/KB is smaller than 3.7 (Fig. S8). The electron transfer number (n) and peroxide percentage of CTF/KB and Co-CTF/KB were also evaluated by the RRDE (Fig. 3f). The RRDE analysis indicates that the n value of Co-CTF/KB is 3.92–4.0 in the whole potential range, which is well consistent with the result of RDE. Simultaneously, the H_2O_2 yield of Co-CTF/KB in alkaline condition is below 10% at all potentials, meaning that Co-CTF/KB possesses high selectivity towards 4-electron pathway in the ORR process. All these above results confirm that the catalytic process at the Co-CTF/KB

Figure 3 (a) CV curves of CTF/KB and Co-CTF/KB at a scan rate of 50 mV s⁻¹. (b) LSV curves and (c) the corresponding Tafel plots of Pt/C, CTF/KB and Co-CTF/KB at a scan rate of 10 mV s⁻¹ with 1600 rpm. (d) LSV curves at different rotating rates and (e) the corresponding K-L plots and electron transfer numbers of Co-CTF/KB. (f) The electron transfer numbers of ORR and H₂O₂ production on the ring electrode during ORR reaction for CTF/KB, Co-CTF/KB and Pt/C, respectively. The catalyst loading was about 0.255 mg cm⁻² for all tests.

electrode undergoes a 4-electron ORR pathway in alkaline medium, implying an excellent ORR catalytic efficiency.

To identify the distinguished performance between Co-CTF/KB and CTF/KB, their electrochemical surface areas (ECSAs) were investigated, which is an important standard parameter to evaluate the ORR activity. According to the CV plots in Ar-saturated 0.1 mol L⁻¹ KOH, ECSAs of the two electrodes were calculated by electrochemical double-layer capacitances (EDLCs) between 0.964 and 1.166 V (*versus* RHE) at various scan rates (Fig. S9). Obviously, the Co-CTF/KB exhibits the C_{dl} (electrical double-layer capacitance) of 12.1 mF cm⁻², which is about 29% higher than that of CTF/KB (9.4 mF cm⁻²), demonstrating that Co-CTF/KB possesses much more exposed active sites than CTF/KB and thus contributing to its superior ORR activity (Fig. 4a).

The long-term stability of Co-CTF/KB was evaluated by CV between 0.5 and 1.0 V at a scan rate of 50 mV s⁻¹ in O₂-saturated 0.1 mol L⁻¹ KOH. After 10,000 continuous cycles, Co-CTF/KB retains a similar LSV curve to the initial one with ~5 mV negative shift for $E_{1/2}$ (Fig. 4b) and only 3 mV dec⁻¹ negative shift for Tafel slope (Fig. S10), which are lower than most reported values of non-precious metal catalysts [35], showing the outstanding stability in alkaline media. Furthermore, in order to examine

the fuel crossover effect, the chronoamperometric response (*i*-*t*) of Co-CTF/KB and commercial 20% Pt/C were compared in 0.1 mol L⁻¹ KOH + 3 mol L⁻¹ methanol solutions (Fig. 4c). There is no obvious oscillation in the current density on Co-CTF/KB after injecting 3 mol L⁻¹ methanol into the electrolyzing solution, while the current density of 20% Pt/C catalyst decreases about 20% under the same condition, suggesting that Co-CTF/KB has outstanding tolerance to methanol crossover. The above results highlight the remarkable ORR electrocatalytic performance of Co-CTF/KB that outperforms commercial Pt/C and most reported single-atom electrocatalysts (Fig. S11 and Table S3). The SCN⁻ poison experiment was also carried out to further confirm the role of Co-N_x in ORR (Fig. S12). After the introduction of SCN⁻, the $E_{1/2}$ and diffusion-limited current density of Co-CTF/KB is found to be decreased, further manifesting that the Co-N_x is the active site for ORR.

Besides ORR activity, Co-CTF/KB also shows electrocatalytic oxygen evolution reaction (OER) activity, which was investigated in O₂-saturated 0.1 mol L⁻¹ KOH at 1600 rpm. Co-CTF/KB displays lower onset potential and much higher current density as compared with 20% Pt/C and RuO₂ (Fig. 4d), exhibiting that Co-CTF/KB possesses superior OER activity to Pt/C. The overall oxygen elec-

Figure 4 (a) The electrical double-layer capacitance at 1.1 V with various scan rates for CTF/KB and Co-CTF/KB, respectively. (b) LSV curves of Co-CTF/KB before and after 10,000 cycles, respectively. (c) The methanol tolerance of Co-CTF/KB and Pt/C by chronoamperometric response (i - t) in O_2 -saturated 0.1 mol L^{-1} KOH solution with and without methanol. (d) LSV curves of different catalysts (10 mV s^{-1}), showing the bifunctional ORR/OER catalytic activity.

trode performance was evaluated by ΔE ($E_{\text{OER}} - E_{\text{ORR}}$) between the OER potential at 10.0 mA cm^{-2} and the ORR potential at $E_{1/2}$. Co-CTF/KB has a low potential difference around 0.95 V, validating that Co-CTF/KB possesses good ORR/OER bifunctional activities, which arise from its unique features, including abundant atomically dispersed highly active Co-N-C sites, conductive networks, unique hierarchical porous structure, and high specific surface area.

CONCLUSIONS

In conclusion, we presented scalable preparation of a cost-effective, highly active and stable single-atom cobalt catalyst supported by CTF hybridized with KB. Featured by the defined nitrogen active sites and porous structure along with high specific surface area, Co atoms can be strongly anchored with nitrogen atoms and well dispersed on the CTF/KB skeleton. Consequently, Co-CTF/KB exhibits excellent activities for ORR in alkaline media. It also shows extraordinary long-term stability and excellent methanol tolerance. In addition, Co-CTF/KB also exhibits good OER catalytic activity, suggesting that Co-CTF/KB

can work as a bifunctional catalyst for ORR and OER. This work opens up an avenue for developing high-efficiency and stable noble-metal-free single-atom cobalt catalysts for reversible energy conversion and storage devices.

Received 29 November 2020; accepted 6 January 2021;
published online 24 March 2021

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Acknowledgements This work was supported by the Ministry of Science and Technology of China (2012CB933403), the National Natural Science Foundation of China (51425302 and 51302045), and the Chinese Academy of Sciences.

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Conflict of interest The authors declare no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

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具有高效氧还原反应催化活性的共轭三嗪骨架材料负载的单原子钴催化剂

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摘要 单原子钴是一种理想的代替铂催化氧还原反应(ORR)的非贵金属催化剂, 然而制备低成本、高稳定性且高效的此类催化剂仍面临挑战。这需要高效的制备策略以及强健的支撑材料以稳定单原子钴。因此, 我们提出了一种适于大量制备的三嗪骨架材料负载的单原子钴ORR催化剂(Co-CTF/KB)。其单原子钴负载量达4 wt%, 在碱性介质中ORR催化性能超过商用Pt/C和大部分已报道的非贵金属催化剂: 半波电位($E_{1/2}$)达0.830 V, 截止电流为6.14 mA cm⁻², 且具有极高的甲醇耐受性。得益于CTF对钴单原子的强稳定性, Co-CTF/KB催化循环10000圈后, 电位偏移仅5 mA, 展现出极好的循环稳定性。此外, Co-CTF/KB还能催化析氧反应(OER), 是一种高效、高稳定的ORR/OER双功能催化剂。此工作为规模化制备高质量单原子催化剂提供了新思路。