Bacterial cellulose-regulated synthesis of metallic Ni catalysts for high-efficiency electrosynthesis of hydrogen peroxide

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ABSTRACT The decentralized production of H₂O₂ via a two-electron oxygen reduction reaction (2e[−] ORR) has emerged as a promising alternative to the energy-intensive anthraquinone (AQ) process. However, its practical application requires 2e[−] ORR electrocatalysts with high activity and selectivity. Herein, we report the synthesis of metallic Ni nanoparticles anchored on bacterial cellulose-derived carbon fibers (Ni-NPs/BCCF) via a facile impregnation-pyrolysis method as efficient electrocatalysts for 2e[−] ORR to H₂O₂. By tuning the amount of Ni precursor, the best electrocatalytic performance toward 2e[−] ORR was achieved for Ni-NPs/BCCF-20.7, affording a high H₂O₂ selectivity of ~90% and an onset potential of 0.75 V vs. reversible hydrogen electrode (RHE) in an alkaline electrolyte. Ni-NPs/BCCF-20.7 achieved the largest H₂O₂ yield rate of 162.7 ± 13.7 mmol g_{cat}^{−1} h^{−1} and the highest Faradaic efficiency of 93.9% ± 4.2% at 0.2 and 0.5 V vs. RHE from the bulk ORR system, respectively. Theoretical calculations revealed the more favorable “end-on” adsorption configuration of molecular oxygen on the exposed Ni(111) plane, which can effectively suppress the O–O bond dissociation, resulting in high selectivity for H₂O₂ generation.

Keywords: bacterial cellulose, nickel nanoparticles, two-electron oxygen reduction reaction, hydrogen peroxide

INTRODUCTION

H₂O₂ has various applications, such as a bleaching agent, disinfecting agent, oxidant, and propellant agent [1]. Over the last century, H₂O₂ has primarily been produced at the industrial scale using the indirect anthraquinone (AQ) process [2], which involves the sequential hydrogenation and oxidation of AQ molecules, followed by extraction and distillation to remove substantial organic wastes and obtain highly concentrated H₂O₂. This process is both energy-intensive and causes safety-related issues regarding the transport and storage of high-purity H₂O₂ [3]. The direct synthesis of H₂O₂ using O₂ and H₂ seems to be a promising alternative [4,5]; however, the risk of explosion and an unsatisfactory efficiency limit its practical applications. The considerable global demand for H₂O₂ has led to an urgent requirement for more cost-efficient and environmentally friendly synthetic approaches; consequently, in this field,

researchers have recently focused on electrochemical routes for the on-site production of H₂O₂. The electrochemical synthesis of H₂O₂ proceeds via the two-electron oxygen reduction reaction (2e[−] ORR), which enables green, on-site, and decentralized production of H₂O₂ at ambient conditions [3,6,7]. However, this promising route is extremely challenging because of the highly sluggish kinetics of 2e[−] ORR and the competitive four-electron (4e[−]) reaction pathway [8–12]. Thus, the design and fabrication of extremely active and selective electrocatalysts for the electrosynthesis of H₂O₂ via 2e[−] ORR is extremely desirable.

Recently, many studies have focused on developing high-efficiency 2e[−] ORR electrocatalysts such as noble metal alloys [13–15], transition metal-based materials [16–18], and carbonaceous materials [19–21]. Transition metal-based materials show improved activity compared with their carbonaceous counterparts and are extremely cheaper compared with noble metal alloys; therefore, the former have gradually become the predominant electrocatalysts for H₂O₂ electrosynthesis. Ma *et al.* [22] reported a catalyst based on Ni₃B nanoparticles, exhibiting an H₂O₂ selectivity of >90% and an onset potential of ~0.7 V vs. reversible hydrogen electrode (RHE) in 0.1 mol L^{−1} KOH. Their theoretical calculations suggested the important role of the inner B atoms for the optimization of the binding energy of OOH*. Wang *et al.* [23] developed a liquid-liquid interfacial synthesis method to fabricate two-dimensional Ni metal-organic framework (MOF) nanosheets. By tuning the ratio of metal precursors and organic linkers, Ni MOF nanosheets reached 98% H₂O₂ selectivity with a H₂O₂ production rate of 80 mmol g_{cat}^{−1} h^{−1} in 0.1 mol L^{−1} KOH. Byeon *et al.* [24] reported a nonprecious metal electrocatalyst composed of MnO and Mn–N_x nanostructures, thus affording a H₂O₂ selectivity of ~80% in 0.1 mol L^{−1} HClO₄. These authors demonstrated that MnO and Mn–N_x in porous carbon were active sites for producing H₂O₂. Sheng *et al.* [25] reported that CoS₂ was both active and selective toward 2e[−] ORR in an acidic solution with ~70% H₂O₂ selectivity and a cumulative H₂O₂ yield of 13 μmol after 60 min of electrolysis. Despite the progress in the development of transition metal-based electrocatalysts, pure transition metal nanoparticles anchored on carbon supports have been rarely investigated as 2e[−] ORR electrocatalysts for H₂O₂ generation. Therefore, obtaining a deep understanding of this type of electrocatalysts, particularly on their structure-property relationships, is important. Further-

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more, carbon substrates anchored metal nanoparticles are usually fabricated *via* cumbersome synthetic processes that involve the carbonization of MOFs or organic molecules, which limits the synthesis of electrocatalysts in large quantity [26–28]. Thus, biomass has become a promising alternative for the large-scale synthesis of carbon-supported electrocatalysts with $2e^-$ ORR activity because of its abundance, cheapness, and tunability [29–31]. Owing to the multiple functional groups (e.g., N and O functional groups) of biomass, which can readily coordinate with transition metals, the use of biomass-based precursors to synthesize transition-metal electrocatalysts offers a promising route toward the $2e^-$ ORR production of H_2O_2 .

Herein, Ni nanoparticles supported on bacterial cellulose (BC)-derived carbon fibers (denoted as Ni-NPs/BCCF) were synthesized using a facile impregnation-pyrolysis method. BC with abundant oxygen functional groups not only regulates Ni^{2+} impregnation but also serves as a precursor of the carbon substrate to anchor Ni nanoparticles *via* a carbothermal reduction process. To optimize the electrocatalytic property, a number of samples named as Ni-NPs/BCCF-17.3, Ni-NPs/BCCF-20.7, Ni-NPs/BCCF-23.1, and Ni-NPs/BCCF-24.6 were fabricated by changing the amount of Ni^{2+} precursor in the adsorption solution. According to the electrochemical measurements, Ni-NPs/BCCF-20.7 possesses improved electrocatalytic performance toward $2e^-$ ORR, thus exhibiting a high H_2O_2 selectivity of ~90% and an onset potential of 0.75 V *vs.* RHE in 0.1 mol L⁻¹ KOH. Moreover, Ni-NPs/BCCF-20.7 has the largest H_2O_2 yield rate of 162.7 ± 13.7 mmol g_{cat}⁻¹ h⁻¹ and the highest Faradaic efficiency (FE) of $93.9\% \pm 4.2\%$ at 0.2 and 0.5 V (*vs.* RHE) in the bulk $2e^-$ ORR system, respectively. The intrinsic catalytic mechanism was explained by performing theoretical calculations, revealing that the more favorable “end-on” adsorption configuration of O_2 on the exposed Ni(111) plane can effectively suppress O–O bond dissociation, resulting in high H_2O_2 selectivity.

EXPERIMENTAL SECTION

Materials and reagents

Commercial BC was supplied by Guilin Qihong Technology Co., Ltd. $NiCl_2 \cdot 6H_2O$, $HClO_4$, KOH, and H_2SO_4 were purchased from Sinopharm Chemical Reagent Co., Ltd. $Ce(SO_4)_2$ and $K_3[Fe(CN)_6]$ were obtained from Aladdin Chemical Reagent Co., Ltd. Commercial carbon cloth (CC) and Nafion solution (5 wt%) were obtained from Shanghai Hesen Electric Co., Ltd. All chemical reagents used in the synthesis were of analytical grade and did not require purification.

Fabrication of Ni-NPs/BCCF

BC (1.0 g) was immersed in 400 mL of solution containing 40 mmol of $NiCl_2 \cdot 6H_2O$ overnight. BC with adsorbed Ni^{2+} was subsequently frozen in liquid nitrogen and freeze-dried in a bulk tray dryer (LGJ-12, Beijing Songyuanhuaxing Technology Develop Co., Ltd.) for 48 h. Then, the product obtained was transferred to a tube furnace and heated to 360°C with a ramp rate of 2°C min⁻¹ for 2 h and then to 700°C with a ramp rate of 5°C min⁻¹ for 2 h under Ar atmosphere. After cooling down naturally to room temperature, the collected solid product was ground with a mortar, washed with deionized water and ethanol several times, and then dried for further use. By changing the amount of Ni source (20, 60, and 80 mmol) in the adsorption solution, various Ni-NPs/BCCF samples with different Ni con-

tents were fabricated. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analyses revealed that Ni content in the contrast samples was 17.3, 20.7, 23.1, and 24.6 wt%, respectively (Table S1). A BCCF sample without Ni was synthesized by pyrolyzing the BC precursor at 360°C for 2 h and then at 700°C for 2 h under Ar atmosphere.

Characterizations

The crystalline structures of samples were identified by X-ray diffraction analysis (XRD, Philips X'pert PRO) using Ni-filtered monochromatic Cu K α radiation ($\lambda = 1.5418$ Å) at 40 kV and 40 mA. Scanning electron microscopy (SEM) images of samples were obtained using an SU8020 microscope (Hitachi, Japan) with an accelerating voltage of 10.0 kV. Transmission electron microscopy (TEM) images were obtained using a JEMARM 200F microscope operated at an accelerating voltage of 200 kV. Raman spectra were measured on a Renishaw Micro-Raman Spectroscopy (Renishaw inVia Reflex) using 532 nm laser excitation. Fourier transform infrared (FT-IR) spectra were obtained on a Nicolet-Nexus spectrometer (Thermo Nicolet Corporation) using the KBr pellet technique. Nitrogen adsorption-desorption isotherms were obtained using an automated gas sorption analyzer (Autosorb-iQ-Cx). Ni contents in Ni-NPs/BCCF were determined using an ICP-AES ICP-6300 (Thermo Fisher Scientific). X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB 250 XPS (Thermo, America) equipped with Al K $\alpha_{1,2}$ monochromatized radiations at 1486.6 eV X-ray source. Absorbance data were obtained on an SHIMADZU UV-2700 ultraviolet-visible (UV-vis) spectrophotometer.

Electrochemical measurements

Electrochemical measurements were performed on a CHI 760E electrochemical workstation (CH Instrumental Corporation, Shanghai, China) with a three-electrode cell and a rotating ring-disk electrode setup (RRDE, Pine Instruments Corporation) under ambient conditions. An RRDE electrode with a glassy carbon electrode (area = 0.247 cm²) and a Pt ring electrode (area = 0.186 cm²) was used as the working electrode. Before these measurements, the electrode was polished with 0.3- and 0.05- μ m alumina suspensions on a polishing cloth and rinsed with deionized water several times. A Ag/AgCl or Hg/HgO electrode and Pt wire were used as the reference and counter electrodes, respectively. Three electrolytes were used, specifically, 0.1 mol L⁻¹ KOH (pH ~ 12.93), 0.1 mol L⁻¹ phosphate-buffered saline (pH ~ 6.31), and 0.1 mol L⁻¹ $HClO_4$ (pH ~ 1.27). The catalyst ink was prepared by dispersing 5 mg of the as-synthesized Ni-NPs/BCCF into 980 μ L of ethanol and 20 μ L of Nafion solution (5.0 wt%), followed by ultrasonication for 1 h to obtain a homogeneous ink. Then, 10 μ L of catalyst ink was drop-casted on the disk electrode and naturally dried. The catalyst loading amount was 0.2 mg cm⁻². The potentials of electrochemical measurements were converted into RHE using the following equations:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \times \text{pH} + 0.197, \quad (1)$$

$$E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.059 \times \text{pH} + 0.098. \quad (2)$$

All catalysts were activated first by performing cyclic voltammetry (CV) at 100 mV s⁻¹ and 1600 r min⁻¹ for 40 cycles. Linear sweep voltammetry (LSV) curves were obtained in O_2 -saturated condition with a scan rate of 10 mV s⁻¹ at 1600 r min⁻¹,

and the potential of Pt ring electrode was held at 1.2 V vs. RHE to detect H_2O_2 generated on the disk electrode. The H_2O_2 selectivity, electron transfer number (n), and H_2O_2 production on RRDE were calculated using the following equations:

$$\text{Selectivity (\%)} = 200 \times (I_r / N_c) / (I_d + I_r / N_c), \quad (3)$$

$$n = 4I_d / (I_d + I_r / N_c), \quad (4)$$

$$\text{H}_2\text{O}_2 \text{ production} = 1/2 \times I_r / N_c \times M_r \times 3600 / (F \times A), \quad (5)$$

where I_r and I_d are the ring current and the disk current, respectively, N_c is the collection efficiency of the ring electrode (0.365 after calibration by the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox system), M_r is the molecular weight of H_2O_2 , F is the Faraday constant, and A is the area of the disk electrode.

The RRDE measurements were conducted at different rotation speeds, and the n value was calculated as per the following Koutecky-Levich (K-L) equations:

$$1/j = 1/j_k + 1/j_d = 1/j_k + 1/(B\omega^{1/2}), \quad (6)$$

$$B = 0.62nFD^{2/3}\nu^{-1/6}C, \quad (7)$$

where j_k and j_d are the kinetic and diffusion-limited current density, respectively; ω is the angular velocity of the electrode (rad s^{-1}); F is the Faraday constant ($96,485 \text{ C mol}^{-1}$); D is the diffusion coefficient of O_2 in the electrolyte ($1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$); ν is the kinematic viscosity of the electrolyte ($0.01 \text{ cm}^2 \text{ s}^{-1}$); and C is the concentration of O_2 ($1.2 \times 10^{-6} \text{ mol cm}^{-3}$).

Bulk ORR electrolysis and detection of H_2O_2

The electrosynthesis of H_2O_2 and the quantification of the H_2O_2 concentration were conducted in a two-compartment three-electrode H-cell system separated by a Nafion 117 membrane. Each compartment was filled with 40 mL of electrolyte. The CC ($1.0 \text{ cm} \times 1.0 \text{ cm}$) supporting the Ni-NPs/BCCF-20.7 catalyst (0.5 mg) was used as the working electrode with Hg/HgO and Pt mesh as reference and counter electrodes, respectively. Before these measurements, the electrolyte in the cathode compartment was purged with O_2 for at least 30 min to reach saturation and vigorously stirred to facilitate the mass transport of O_2 . Then, bulk ORR electrolysis was performed at different potentials for 2 h, and the electrolyte was subsequently neutralized with an equal volume of $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ for spectrophotometric determination. The H_2O_2 yield in the electrolyte was quantified according to the ceric sulfate titration method using the following reaction:

where yellow-colored Ce^{4+} was reduced by H_2O_2 to colorless Ce^{3+} , which was detected by UV-vis spectroscopy. A typical concentration-absorbance curve was calibrated by linearly fitting the absorbance values at 317 nm for various known concentrations of Ce^{4+} . The H_2O_2 yield was subsequently determined on the basis of the reduced concentration of Ce^{4+} using the following equation:

$$C_{\text{H}_2\text{O}_2} = 2 \times \left[V_{\text{Ce}^{4+}} \times C_{\text{Ce}^{4+}}^{\text{before}} - (V_{\text{Ce}^{4+}} + V_{\text{electrolyte}}) \times C_{\text{Ce}^{4+}}^{\text{after}} \right] / (2 \times V_{\text{electrolyte}}), \quad (8)$$

where $C_{\text{Ce}^{4+}}$ is the volume of added $\text{Ce}(\text{SO}_4)_2$; $C_{\text{Ce}^{4+}}^{\text{before}}$ and $C_{\text{Ce}^{4+}}^{\text{after}}$ are the concentrations of Ce^{4+} before and after the reaction, respectively; and $V_{\text{electrolyte}}$ is the volume of added

electrolyte after neutralization.

The FE value was calculated using the following equation:

$$\text{FE (\%)} = (2 \times C \times V \times F) / Q \times 100\%, \quad (9)$$

where F is the Faraday constant ($96,485 \text{ C mol}^{-1}$), C is the concentration of H_2O_2 , V is the volume of electrolyte, and Q is the total charge during the ORR.

Computational details

Spin-polarized first-principle calculations were performed with density functional theory (DFT) using the projector augmented wave method [32,33] in the Vienna *Ab initio* Simulation Package (VASP) [34]. The electronic exchange-correlation effects were described with the Perdew-Burke-Ernzerhof generalized gradient approximation functional [35]. A $p(4 \times 4)$ supercell of Ni (111) slab of three layers with one bottom layer fixed was constructed. A cutoff energy of 400 eV and a vacuum of 15 Å in the z -direction were used. Gamma-centered $3 \times 3 \times 1$ Monkhorst-Pack k -point sampling was conducted. All relaxations were performed until the force of the energy convergence threshold reached $10^{-5} \text{ eV atom}^{-1}$ and the force converged to 0.02 eV Å^{-1} . Symmetrization was closed during the adsorption calculations. The adsorption energy (E_{ads}) was calculated as follows:

$$E_{\text{ads}} = E_{(\text{a+slab})} - E_{\text{slab}} - E_{\text{a}}, \quad (10)$$

where $E_{(\text{a+slab})}$, E_{slab} , and E_{a} are the optimized energies of the total system, the clean surface, and the adsorbate in the gas phase, respectively.

RESULTS AND DISCUSSION

Fig. 1a shows the two-step synthetic procedure for the Ni-NPs/BCCF catalyst. Briefly, BC with rich -OH groups was used as an adsorption regulator to adsorb Ni^{2+} , followed by pyrolysis first at 360°C for 2 h and then at 700°C for another 2 h under Ar atmosphere to obtain metallic Ni nanoparticles anchored on BCCFs. By tuning the amount of Ni^{2+} precursor in the adsorption solution, the following contrast samples were fabricated: Ni-NPs/BCCF-17.3, Ni-NPs/BCCF-20.7, Ni-NPs/BCCF-23.1, and Ni-NPs/BCCF-24.6. For comparison, pure BCCF was synthesized under the same conditions used for fabricating Ni-NPs/BCCF but without the Ni source. The crystalline phase compositions of samples were examined by XRD, and the corresponding patterns are shown in Fig. 1b. The XRD pattern of BCCF exhibits only a broad characteristic diffraction peak at 25° , corresponding to the (002) plane of graphitic carbon. The XRD patterns of Ni-NPs/BCCF samples show the same crystal phase and characteristic diffraction peaks at 44.5° , 51.8° , and 76.4° , which can be indexed to the (111), (200), and (220) lattice planes of cubic Ni phase, respectively, which results from the carbothermal reduction of Ni^{2+} at high temperatures. The microstructure of products was characterized by SEM and TEM. The SEM image of BCCF shows a well-defined carbon fiber morphology with a three-dimensional (3D) network structure (Fig. 1c). In Ni-NPs/BCCF, Ni nanoparticles are uniformly distributed on the carbon fibers and have an average size of $\sim 85 \text{ nm}$ (Fig. S1), as shown by TEM images (Fig. 1d and Fig. S2), and the carbon fibers and Ni nanoparticles tend to gradually aggregate as the concentration of the Ni precursor increases. The high-resolution TEM (HRTEM) image of Ni-NPs/BCCF-20.7 shows a clear lattice fringe with an interplanar spacing of 0.198 nm corresponding to the (111) plane of metallic Ni (Fig. 1e). The high-angle annular dark-field scanning TEM

Figure 1 (a) Schematic of the synthetic procedure for Ni nanoparticles supported on BCCFs (Ni-NPs/BCCF). (b) XRD patterns of BCCF and Ni-NPs/BCCF. (c) SEM image of BCCF. (d) TEM and (e) high-resolution TEM images of Ni-NPs/BCCF-20.7. (f) High-angle annular dark-field scanning TEM image and the corresponding elemental mapping images of Ni-NPs/BCCF-20.7.

(HAADF-STEM) image and the corresponding elemental mapping images display a homogenous distribution of C, O, and Ni over the entire sample (Fig. 1f). These results confirm the successful synthesis of metallic Ni nanoparticles anchored on BCCF with the exposed (111) plane.

The composition of BCCF and Ni-NPs/BCCF were investigated using Raman and FTIR techniques. The Raman spectra clearly show two peaks corresponding to the D and G bands at ~ 1340 and 1590 cm^{-1} , respectively (Fig. S3). The intensity ratio of the D and G bands (I_D/I_G) is generally used to assess the degree of graphitization in carbon-based materials. The I_D/I_G values of BCCF, Ni-NPs/BCCF-17.3, Ni-NPs/BCCF-20.7, Ni-NPs/BCCF-23.1, and Ni-NPs/BCCF-24.6 were determined to be 0.91, 0.89, 0.93, 0.95, and 0.95, respectively, suggesting the dominant graphitic carbon structures with improved conductivity. As per FTIR results, all Ni-NPs/BCCF samples possess

abundant oxygen functional groups, including $-\text{OH}$, $-\text{COOH}$, and $\text{C}-\text{O}-\text{C}$, which stem from BC (Fig. S4). These oxygen functional groups are beneficial to tuning the $2e^-$ ORR selectivity, as has been described previously [8,19,36]. The Brunauer-Emmett-Teller surface areas of the Ni-NPs/BCCF catalysts were determined as per the nitrogen adsorption isotherms, which demonstrate high values ranging from 363 to $526\text{ m}^2\text{ g}^{-1}$ with porous structures (Fig. S5 and Table S1) that provide many active sites for the $2e^-$ ORR process. The porous structure facilitates mass transport during electrocatalysis, thereby allowing the immediate release of the generated H_2O_2 , which improves H_2O_2 selectivity.

The composition and chemical state of Ni-NPs/BCCF-20.7 were examined by XPS. As expected, the XPS survey spectrum shows the existence of Ni (7.34 at%), O (63.31 at%), and C (29.35 at%) in Ni-NPs/BCCF-20.7 (Fig. 2a). The high-resolution

C 1s spectrum presented in Fig. 2b can be deconvoluted into three peaks assigned to C–C/C=C (284.8 eV), C–O (286.4 eV), and O–C=O (289.8 eV) [19]. The O 1s spectrum shows the presence of Ni–O–C (529.3 eV) [37], as shown in Fig. 2c. The O species stem from BC, which can effectively coordinate with Ni atoms to form Ni–O bonds that anchor the Ni nanoparticles. Both C 1s and O 1s spectra confirm the presence of rich oxygen functional groups, which is consistent with the FT-IR results. Furthermore, the high-resolution Ni 2p spectrum (Fig. 2d) shows two primary peaks of Ni 2p_{3/2} (855.6 eV) and Ni 2p_{1/2} (873.1 eV) with two broad satellite peaks at 861.4 and 879.3 eV, confirming the existence of Ni²⁺ [37,38]. Recent reports reported that Ni²⁺ centers behave as the active sites for 2e[−] ORR, thus playing an important role in enhancing the ORR activity and tuning the selectivity [39].

The electrocatalytic performance of Ni-NPs/BCCF toward 2e[−] ORR was first evaluated using an RRDE setup in O₂-saturated 0.1 mol L^{−1} KOH. The ring electrode was maintained at a constant potential of 1.2 V vs. RHE to selectively oxidize H₂O₂ produced on the disk electrode. Before measurements, the collection efficiency of the ring electrode was calibrated using K₃[Fe(CN)₆] and the value was determined to be 0.365, which is extremely close to the theoretical value (i.e., 0.37) (Fig. S6). Fig. 3a shows the LSV curves, which show different disk and ring current densities for the Ni-NPs/BCCF catalysts, thus suggesting their diverse activity and selectivity for 2e[−] ORR. The current densities were normalized by the corresponding geometric area of the disk and ring electrode. Fig. 3b shows the H₂O₂ selectivity calculated from RRDE measurements. For Ni-NPs/BCCF-17.3, the H₂O₂ selectivity was ~84% and increased to ~90% with an increase in the amount of Ni source to 40 mmol. However,

increasing the Ni amount to 60 and 80 mmol, the H₂O₂ selectivity decreased to ~74% and ~75%, respectively. *n* values of Ni-NPs/BCCF during the reaction were calculated. The Ni-NPs/BCCF-20.7 exhibited a dominant 2e[−] pathway, whereas Ni-NPs/BCCF-17.3, Ni-NPs/BCCF-23.1, and Ni-NPs/BCCF-24.6 displayed a mixture of 2e[−] and 4e[−] pathways. The additional evaluation of the activity of catalysts revealed that Ni-NPs/BCCF-20.7 delivered a high onset potential of 0.75 V vs. RHE at −0.1 mA cm^{−2} and a large diffusion-limiting disk current density of 2.88 mA cm^{−2} at 0.2 V vs. RHE, thus approaching the theoretical limit for 2e[−] ORR. However, the diffusion-limiting disk current densities of Ni-NPs/BCCF-17.3, Ni-NPs/BCCF-23.1, and Ni-NPs/BCCF-24.6 were as low as 1.97, 2.59, and 2.69 mA cm^{−2} at 0.2 V vs. RHE, indicating that Ni-NPs/BCCF-20.7 afforded the best activity and selectivity for 2e[−] ORR. Nevertheless, the H₂O₂ selectivity of BCCF was only ~60% with a considerably lower diffusion-limiting disk current density of 1.41 mA cm^{−2} at 0.2 V vs. RHE, thus revealing the important role of Ni nanoparticles in the H₂O₂ electrosynthesis.

The fast ORR kinetics of Ni-NPs/BCCF-20.7 was demonstrated by a lower Tafel slope of 79.3 mV dec^{−1} compared with that of Ni-NPs/BCCF-17.3 (92.9 mV dec^{−1}), Ni-NPs/BCCF-23.1 (94.5 mV dec^{−1}), and Ni-NPs/BCCF-24.6 (101.5 mV dec^{−1}) (Fig. S7). Furthermore, a sufficient H₂O₂ production was achieved by Ni-NPs/BCCF-20.7, with a H₂O₂ output of 1.32 mg cm^{−2} h^{−1} at 0.45 V vs. RHE, as shown in Fig. S8. Moreover, the double-layer capacitance (*C*_{dl}) of Ni-NPs/BCCF catalysts was investigated using CV at different scan rates (Fig. S9), which is normally proportional to the electrochemically active surface area. The *C*_{dl} of Ni-NPs/BCCF-20.7 was determined to be 7.42 mF cm^{−2}, which is proportional to the 2e[−] ORR perfor-

Figure 2 (a) Survey XPS of Ni nanoparticles supported on BCCFs (sample Ni-NPs/BCCF-20.7). High-resolution (b) C 1s, (c) O 1s, and (d) Ni 2p XPS spectra of Ni-NPs/BCCF-20.7.

Figure 3 (a) LSV curves of Ni nanoparticles supported on BCCFs (Ni-NPs/BCCF) at 1600 r min⁻¹ in 0.1 mol L⁻¹ KOH. (b) H₂O₂ selectivity and electron transfer number (*n*) calculated from RRDE measurements. (c) Stability measurement of Ni-NPs/BCCF-20.7 at a constant potential of 0.5 V vs. RHE. (d) LSV curves of Ni-NPs/BCCF-20.7 after stability measurement and (e) the corresponding H₂O₂ selectivity and *n*. (f) Comparison of the H₂O₂ selectivity of Ni-NPs/BCCF-20.7 and other recently reported electrocatalysts.

mance and larger than that of BCCF (0.23 mF cm⁻²), Ni-NPs/BCCF-17.3 (3.62 mF cm⁻²), Ni-NPs/BCCF-23.1 (4.48 mF cm⁻²), and Ni-NPs/BCCF-24.6 (4.86 mF cm⁻²) (Fig. S10). Because the Ni amount increased to 40 mmol, the electrocatalytic 2e⁻ ORR performance underwent an increase owing to an increase in

catalytic active sites. However, on increasing the Ni amount, the 2e⁻ ORR performance decreased possibly because excess active sites that were not saturated by the oxygen flux prompted certain side reactions under high overpotentials, such as 4e⁻ ORR, decomposition, or additional reduction of H₂O₂ [25]. These

results demonstrate that Ni-NPs/BCCF-20.7 is the optimal electrocatalyst for $2e^-$ ORR with superior activity and selectivity. The stability of Ni-NPs/BCCF-20.7 was evaluated using RRDE measurements as per the chronoamperometric response at a constant disk potential of 0.5 V vs. RHE for 10 h (Fig. 3c). Ni-NPs/BCCF-20.7 maintained 87.2% of initial disk current after continuous reaction for 10 h. However, the ring current and H_2O_2 selectivity increased after 2 h of reaction, possibly because of the accumulation of H_2O_2 with low concentration in the electrolyte [40]. Subsequently, the electrolyte was refreshed and purged with O_2 to reach saturation, and the LSV curves were remeasured. Compared with the fresh catalyst, the Ni-NPs/BCCF-20.7 sample demonstrated negligible decay of current densities after 10 h of reaction, and the H_2O_2 selectivity remained $\sim 89\%$, indicating excellent stability (Fig. 3d, e). The high H_2O_2 selectivity, activity, and stability of Ni-NPs/BCCF-20.7 catalyst render it superior to recently reported catalysts, including certain noble metal and single-atom catalysts (Fig. 3f and Table S2).

To probe optimal operating conditions of Ni-NPs/BCCF-20.7 for H_2O_2 electrosynthesis, the effect of the loading amount of the catalyst on the ORR activity and selectivity was investigated in 0.1 mol L^{-1} KOH. As the catalyst loading amount increased, the disk current density became larger because of the larger amount of catalytic active sites, and the onset potential showed a slightly positive shift (Fig. S11a). However, the ring current decreased on increasing the catalyst loading amount, resulting in lower H_2O_2 selectivity (Fig. S11b). This may be attributed to the thickening of the catalyst layer with increasing loading amount, which

increases the residence time of the reaction intermediates in the catalyst layer, leading to an additional reduction of H_2O_2 and the consequent decrease in the H_2O_2 selectivity. Hence, the catalyst loading amount is an important parameter for electrocatalytic H_2O_2 generation, and the optimal loading amount of Ni-NPs/BCCF-20.7 was reported to be 0.2 mg cm^{-2} . The measurements were conducted at different rotation speeds using Ni-NPs/BCCF-20.7 as the electrocatalyst, and the n value of the ORR was determined using the K-L equations (Fig. 4a). The n value was close to that obtained using the RRDE method, thus further demonstrating the occurrence of a primary $2e^-$ pathway with H_2O_2 as the final product (Fig. 4b). To focus on the $2e^-$ ORR activity and selectivity of Ni-NPs/BCCF-20.7, the electrocatalytic performance was investigated in electrolytes with different pH values. As shown by the LSV curves in Fig. 4c, decreasing the pH value caused a gradual decrease in the diffusion-limiting disk and ring current densities and an increase in the overpotentials. The H_2O_2 selectivity gradually decreased from $\sim 90\%$ to $\sim 78\%$ and to $\sim 61\%$ when changing the electrolyte from alkaline to neutral and to acidic, respectively (Fig. 4d). This pH-dependent activity and selectivity decrease can be attributed to the more difficult desorption of H_2O_2 from the catalyst surface at lower pH values and higher overpotentials, in accordance with previous reports [40,41]. The results demonstrate that Ni-NPs/BCCF-20.7 possesses better activity and selectivity for $2e^-$ ORR to H_2O_2 in an alkaline solution.

RRDE measurements only allow instantaneous detection of the H_2O_2 intermediate, which can be oxidized at the Pt ring electrode. To accurately determine the on-site production of

Figure 4 (a) LSV curves of the Ni nanoparticles supported on BCCFs (sample Ni-NPs/BCCF-20.7) at different rotation speeds in 0.1 mol L^{-1} KOH. (b) K-L plots and the calculated electron transfer number (n) value. (c) LSV curves of Ni-NPs/BCCF-20.7 in O_2 -saturated electrolytes with different pH values. (d) H_2O_2 selectivity and n of Ni-NPs/BCCF-20.7 in different electrolytes.

H_2O_2 , bulk ORR electrolysis was performed in O_2 -saturated 0.1 mol L^{-1} KOH using a two-compartment three-electrode H-cell setup under ambient conditions. As the working electrode, the Ni-NPs/BCCF-20.7 electrocatalyst was drop-casted on CC (Ni-NPs/BCCF-20.7/CC) at a loading amount of 0.5 mg cm^{-2} , and the yield of H_2O_2 was quantified using the ceric sulfate titration method. Fig. S12 shows the UV-vis spectra of the Ce^{4+} solution with various concentrations and the corresponding linear calibration curves. Fig. S13 shows the chronoamperometric curves at different applied potentials, which suggests that current density decreased as the potentials shifted to positive values. Then, the electrolyte operating at each applied potential was injected into the Ce^{4+} solution with a known concentration, and the UV-vis spectra were obtained to determine the H_2O_2 yield (Fig. S14). The H_2O_2 concentration varied with the given potential. Fig. 5a shows that the largest H_2O_2 yield rate of $162.7 \pm 13.7 \text{ mmol g}_{\text{cat}}^{-1} \text{ h}^{-1}$ and the highest FE of $93.9\% \pm 4.2\%$ were attained at 0.2 and 0.5 V vs. RHE *via* bulk ORR electrolysis, respectively. Therefore, the high-efficiency H_2O_2 electrosynthesis can be achieved using Ni-NPs/BCCF-20.7 as the catalyst, outperforming most of the recently reported 2e^- ORR catalysts (Table S3).

Subsequently, consecutive recycling tests were conducted in O_2 -saturated 0.1 mol L^{-1} KOH at 0.5 V vs. RHE for eight cycles of 2 h reaction to examine the reusability of the catalyst (Fig. S15). The H_2O_2 yield and FE determined were maintained during the recycling tests, thus confirming the superior reusability of Ni-NPs/BCCF-20.7/CC (Fig. 5b). Moreover, a bulk electrolysis experiment was performed using bare CC without depositing the

catalyst. An extremely low H_2O_2 yield was obtained, revealing that the CC support has limited influence on the H_2O_2 production *via* 2e^- ORR (Fig. S16). Furthermore, long-term bulk electrolysis was performed under 0.5 V vs. RHE for 10 h to generate H_2O_2 (Fig. S17). With a negligible decay of the current density, $572.92 \mu\text{mol H}_2\text{O}_2$ was produced with an FE of $\sim 83.8\%$, further confirming the excellent stability of Ni-NPs/BCCF-20.7/CC (Fig. 5c). Because the structural stability of the catalyst is another significant parameter toward an efficient 2e^- ORR, Ni-NPs/BCCF-20.7 was characterized by XRD and HRTEM after use (post-ORR). No crystal phase change was observed in the XRD pattern after 10 h of electrolysis (Fig. S18a). Furthermore, the HRTEM image of post-ORR Ni-NPs/BCCF-20.7 revealed a lattice fringe with an interplanar spacing of 0.201 nm, indicating that the exposed (111) plane of metallic Ni was well maintained, which demonstrates the brilliant structural stability of Ni-NPs/BCCF-20.7 (Fig. S18b). As per the Ni 2p XPS spectrum after electrocatalysis (Fig. S19), the catalyst remained at the +2 valence state without significant changes compared with the fresh catalyst, thus confirming that the Ni^{2+} atoms behave as the active sites in the electrochemical H_2O_2 synthesis [39].

To gain more insight into the 2e^- ORR mechanism at the Ni nanoparticles with the exposed (111) plane, theoretical calculations were subsequently performed. First, the $\text{p}(4 \times 4)$ Ni(111) slab model was constructed and two different oxygen configurations, namely, “side-on” and “end-on” adsorption configurations, were considered because the adsorption of O_2 is the first step in the ORR process [42]. The “side-on” adsorption refers to the combination of the two O atoms of the oxygen

Figure 5 (a) H_2O_2 yield rate and the corresponding FE of the Ni nanoparticles supported on BCCFs drop-casted on CC (sample Ni-NPs/BCCF-20.7/CC) at each applied potential after 2 h of reaction. (b) Recycling stability measurements of Ni-NPs/BCCF-20.7/CC at 0.5 V vs. RHE for eight cycles. (c) Chronoamperometric curve of Ni-NPs/BCCF-20.7/CC at 0.5 V vs. RHE for 10 h of reaction.

Figure 6 (a) Surface of the slab models. (b) Top view of the OOH* scission. (c) Top view of the defect Ni(111) slab with the adsorbed OOH* molecule. (d) Difference charge density of the OOH* via "end-on" configuration. The yellow and cyan colors represent electron accumulation and depletion, and the blue, red, and pink spheres correspond to Ni, O, H atoms, respectively.

molecule with the catalyst, for which a weak adsorption energy of 0.673 eV was determined. Furthermore, the "end-on" adsorption corresponds to the vertical interaction of one O atom with the catalyst with the adsorption energy of −2.121 eV. The selectivity for 2e[−] or 4e[−] ORR primarily depends on whether the O–O bond is broken. Then, the amount of the adsorbed O₂* that captured the first pair (H⁺ + e[−]) to form OOH* was calculated. In both cases, the O–O bond was cleaved during the first hydrogenation process, indicating that the flat Ni(111) was not beneficial to OOH* formation. As per a previous report, the defect site would be conducive to stabilizing the intermediates [43]. Hence, the atom defect Ni(111) (Fig. 6a) was theoretically reconstructed. As shown in Fig. 6b, the O₂ parallel adsorption was not beneficial to the 2e[−] process because the OOH* species may split into O* and OH*. However, the O₂ vertical configuration would enable the 2e[−] ORR process because of the stability of the OOH* optimized configuration (Fig. 6c and Fig. S20). These results agree with previous reports [44,45]. Furthermore, since the electronic properties of the catalyst are an important factor affecting the adsorption and activation of O₂ and the intermediates, the difference charge density was calculated to analyze the electron transfer between the surface and adsorbed OOH* molecules. As shown in Fig. 6d, the accumulated negative charge of Ni defect sites would be beneficial to the subsequent OOH* hydrogenation process, resulting in H₂O₂ desorption.

CONCLUSIONS

In summary, Ni-NPs/BCCF were synthesized using a simple impregnation-pyrolysis method as efficient electrocatalysts for 2e[−] ORR. In 0.1 mol L^{−1} KOH, Ni-NPs/BCCF-20.7 possesses superior electrocatalytic performance toward 2e[−] ORR, thus exhibiting a H₂O₂ selectivity of ~90% and an onset potential of 0.75 V vs. RHE. Moreover, this catalyst achieves a large H₂O₂

yield rate of 162.7 ± 13.7 mmol g_{cat}^{−1} h^{−1} at 0.2 V vs. RHE and a high FE of 93.9% ± 4.2% at 0.5 V vs. RHE in bulk ORR electrolysis. DFT calculations revealed the more favorable "end-on" adsorption configuration of O₂ on the exposed Ni(111) plane, which can effectively suppress O–O bond dissociation and thus enhance the selectivity toward H₂O₂ generation. This work provides new insights for the design and development of high-efficiency 2e[−] ORR electrocatalysts for H₂O₂ generation.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

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细菌纤维素调控合成金属镍催化剂用于高效电合成过氧化氢

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摘要 通过两电子氧化还原反应($2e^-$ ORR)原位分散生产过氧化氢(H_2O_2)是一种很有前途的、能替代传统的能源密集型蒽醌法的过氧化氢生产方法. 然而, 其实际应用高度依赖于高活性、高选择性的两电子氧还原电催化剂的设计与合成, 并且仍面临挑战. 本文利用生物质材料细菌纤维素调控合成金属镍纳米颗粒, 通过简单的浸渍-热解法得到锚定在细菌纤维素衍生的碳纤维上的镍纳米颗粒催化剂. 通过调控镍前驱体的用量, 发现Ni-NPs/BCCF-20.7催化剂具有优异的两电子氧化还原催化性能, 其表现出~90%的 H_2O_2 选择性且起始电位为0.75 V(相对于可逆氢电极(RHE)). 通过H-Cell恒电位电解, 该催化剂分别在0.2和0.5 V(相对于RHE)得到最高的 H_2O_2 生成速率($162.7 \pm 13.7 \text{ mmol g}_{\text{cat}}^{-1} \text{ h}^{-1}$)和法拉第效率($93.9\% \pm 4.2\%$). 进一步理论计算表明, 氧气分子在暴露的Ni(111)晶面上具有更有利的“垂直”吸附构型, 可以有效抑制O-O键的解离, 从而具有较高的 H_2O_2 选择性.