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Electrocatalyst derived from fungal hyphae and its excellent activity for electrochemical production of hydrogen peroxide



Hai-Xia Zhang ^{a, 1}, Shi-Chao Yang ^{b, 1}, Yun-Lu Wang ^{a, 1}, Jian-Chao Xi ^a, Jing-Cheng Huang ^a, Jiang-Feng Li ^c, Ping Chen ^{a, d, *}, Rong Jia ^{b, e, **}

^a School of Chemistry and Chemical Engineering, Anhui University, Hefei, Anhui, 230601, PR China

^b School of Life Science, Anhui University, Hefei, Anhui, 230601, PR China

^c Department of Chemistry, Lishui University, Lishui, 323000, PR China

^d Institute of Physical Science and Information Technology, Anhui University, PR China

^e Anhui Key Laboratory of Modern Biomanufacturing, Anhui University, Hefei, 230601, People's Republic of China

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ABSTRACT

Producing hydrogen peroxide (H_2O_2) by electrochemical O_2 reduction is a promising process, although developing high-performance carbon-based electrocatalysts at a low-cost with high-volume production remains a great challenge. We report a novel method to prepare the excellent electrocatalysts for the H_2O_2 production derived from the fungal hyphae (with bioconcentrated dye), which was used as the main sources of C, N, O, and P. The optimizational electrocatalyst had a large surface area with many nanopores, which exhibited excellent activity, selectivity, and stability towards O_2 reduction when producing H_2O_2 in an alkaline media and good activity, selectivity, and stability in neutral media. A flow cell with the optimizational electrocatalyst as cathode and IrO₂ as anode exhibited exceptionally high Faradaic efficiency and H_2O_2 productivity when driven by commercial dry battery (1.5 V) or by solar-energy battery (2.5 V or 3.0 V). This is helpful in developing an electrocatalyst for H_2O_2 production and practical industrial application of O_2 reduction to H_2O_2 by electrocatalyst for other electrochemical reactions, such as hydrogen evolution reactions, oxygen evolution reactions, and CO₂ reduction reactions. © 2019 Elsevier Ltd. All rights reserved.

1. Introduction

Hydrogen peroxide (H_2O_2) is used in various industries, such as paper bleaching, textiles, and wastewater treatment [1,2]. H_2O_2 is currently commercially generated via the anthraquinone oxidation process. This is a multi-step and complex method requiring many large-scale devices. The waste organic byproducts produced during this process, the storage, and the transportation of large-scale products are problematic [2]. Another alternative route is to synthesize H_2O_2 directly from hydrogen and oxygen with the help of catalysts. This is potentially hazardous, as the hydrogen/oxygen

¹ These authors have the equal contribution to this paper.

mixture could explode [3,4]. Researchers have found a method to produce H_2O_2 by means of electrochemistry, which boasts lower energy consumption, higher productivity, and is environmentally friendly [5]. The high yield H_2O_2 requires the presence of electrocatalysts with high performances, such as high selectivity and activity. Developing the catalysts remains an essential challenge in this field [6–12].

Previous reports have used the noble metal nanomaterials (for example: platinum (Pt), palladium (Pd) and gold (Au)) and their alloys (Pd-Hg and Pd-Au) as electrocatalysts for the H_2O_2 generation, demonstrating that these catalysts are efficient and boast excellent electrocatalytic properties (such as small overpotential and high selectivity to H_2O_2) [13–15]. The scarcity and high cost of these materials, as well as the toxicity of Hg could affect their practical application to a certain degree. It is necessary to explore other materials, including non-precious metals and carbon-based materials.

Carbon materials have advantages in their resources and are



^{*} Corresponding author. School of Chemistry and Chemical Engineering, Anhui University, Hefei, Anhui, 230601, PR China.

^{**} Corresponding author. School of Life Science, Anhui University, Hefei, Anhui, 230601, PR China.

E-mail addresses: chenping@ahu.edu.cn (P. Chen), ahujiarong@163.com (R. Jia).

cheaper than the noble-metal materials [16–18]. The ingredient and structure of these materials have a decisive impact on the electrosynthesis of H₂O₂. Some studies regarding heteroatomdoped carbon materials that use N-doped carbons with high 2e⁻ selectivity as oxygen reduction electrocatalysts have been reported. The presence of heteroatom influences the chemical structure of the catalyst, which improves the H₂O₂ productivity and selectivity [6.8.19.20]. The carbon-based materials have become more popular. thanks to their super high surface area and numerous exposed active sites. Many methods aim to achieve enough surface area, although these methods are not perfected [21–24]. Fungal hyphae is the typical biomass material that is formed by the germination of fungal spores. Fungus hyphae is cheap, obtained easily, and does not generate pollution. Growth of fungus hyphae requires essential nutrients, such as carbon and nitrogen sources, making it a candidate for preparing heteroatom-doped carbon materials. Irpex lacteus is a cosmopolitan fungus that is widespread in Europe, North America, and Asia [25,26]. Irpex lacteus F17 is a forest mushroom, a type strain of lignin degrader fungus, belonging to the class Basidiomycetes. Very recently, we reported the high-quality draft genome sequence of Irpex lacteus F17, which was isolated from a decaying hardwood tree in the vicinity of Hefei, China [27].

Here, we used the fungal hyphae from *lrpex lacteus* F17 as sources of N-, O-, and P to prepare the N-, O-, and P-tridoped nanoporous carbon. The typical product exhibited excellent activity, selectivity, and stability towards oxygen reduction for producing H_2O_2 in both alkaline and neutral media.

2. Experimental section

2.1. Chemicals

 K_2SO_4 , C_2H_5OH , KOH, and fuchsin basic were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The above chemicals were analytical reagent and used without further purification.

2.2. Preparation of the N-, O- and P-tridoped nanoporous carbon derived from fungal hyphae

2.2.1. Preparation of the fungal hyphae with dye

Irpex lacteus F17 was isolated from a decayed wood chip pile in Hefei, China, which was then stored in the China Center for Type Culture Collection (CCTCC AF 2014020). The fungus was cultured on a PDA solid medium (200 g/L of potato extract, 20 g/L of glucose, and 20 g/L of agar) for 5 days at 28 °C. Then the grown mycelial mat was dug up from the agar-plate and was inoculated into 120 ml liquid PDA medium for the formation of mycelial pellets. Incubation was carried out at 28 °C on a rotary shaker at 120 rpm for 6 days. These mycelial pellets were used for the subsequent experiments. To ensure inoculum size of the fungus was the same, 1 mL of the mycelia suspension obtained by crushing the mycelial pellets in a Waring blender was inoculated into a Erlenmeyer flask containing a new liquid PDA medium, and grown at 28 °C in a constant temperature shaker. When new mycelial pellets occurred in the flasks after 5 days, 0.6 mL fuchsin basic solution (6 mg/mL) was added and incubated continuously for 2 days. The control group did not have the fuchsin basic solution. After the culture, separation, deionized water washing to fastness, and freeze-drying, the dried fungal hyphae with dye were obtained. The experiments were performed in the sterile operation and all media were sterilized at 121 °C for 20 min before inoculation.

2.2.2. Preparation of the N-, O- and P-tridoped nanoporous carbon derived from fungal hyphae

The dried fungal hyphae with dye were calcined in the N₂ atmosphere (at 750 °C, 800 °C, and 850 °C) for 1 h at a heating rate of 5 °C/min and a cooling rate of 5 °C/min. The N-, O-, and P-tridoped nanoporous carbon derived from fungal hyphae were obtained. They were denoted as N-O-P-C-750, N-O-P-C-800, and N-O-P-C-850. We also prepared the N-, O- and P-tridoped nanoporous carbon derived from fungal hyphae without the dye according to the same steps as typical N-, O-, and P-tridoped nanoporous carbon. The fungal hyphae did not have dye. The material was N-O-P-C-800-C.

Fig. 1 shows the preparation of typical N-, O-, and P-tridoped nanoporous carbon from fungal hyphae (N-O-P-C-800).

2.3. Characterization

SEM images were obtained on a scanning electron microscopy (SEM) with a field emission scanning electron microanalyzer (Hitachi SU8010) and energy-dispersive X-ray spectroscopy (EDX) analytical system. The SEM samples were prepared by drop-drying the samples from their aqueous suspensions onto silicon substrates. The X-ray photoelectron spectroscopy (XPS) data was collected using an ESCALAB MKII X-ray photoelectron spectrometer (Thermo VG Scientific Ltd., East Grinstead, Sussex, UK). The BET surface area and the pore size distribution of all samples were analyzed on a Micrometrics ASAP2020 analyzer (USA). The micropore size distribution was calculated using the Horvath-Kawazoe method. An inVia-Reflex spectrometer (Renishaw) was used to obtain the Raman spectra.

2.4. Rotating ring-disk electrode (RRDE) measurements

We prepared the catalyst ink according to pervious literature [16,21]. For each catalyst, the powder (15 mg) was dispersed in 3 mL of mixed solvent (1:3 v/v isopropanol/deionized water) with Nafion (wt.0.8%). The obtained mixture was ultrasonicated for 30 min to obtain the catalyst ink. The ink (10-µL volume) was uniformly deposited onto the glassy carbon ring-disk (Pine Research Instrumentation, Durham, NC, USA) and air dried. A glassy carbon ring-disk was used as the working electrode, a platinum



Fig. 1. Illustrated diagram of the N-O-P-C-800 preparation. (a) fungal hyphae; (b) fungal hyphae containing dye; (c) dried fungal hyphae with dye; and (d) N-O-P-C-800.

plate was used as counter electrode, and an Ag/AgCl was used as reference electrode in an O₂-saturated 0.1 M KOH and in an O₂-saturated 0.1 M K₂SO₄ solution.

The working electrode was scanned at a rate of 5 mVs^{-1} with a rotating speed of 1600 rpm. The ring current (i_R) was achieved using a Pt ring electrode separately in the alkaline and neutral media. The selectivity for H₂O₂ yield was evaluated using the RRDE voltammogram of each sample, according to the following equation [6,16]:

$$\%(H_2O_2) = 200 \times \frac{IR/N}{ID + IR/N}$$
(1)

where i_D denotes the disk current, i_R is the ring current, and N stand for the current collection efficiency of the Pt ring. N was 0.33 from the reduction of K₃Fe[CN]₆ and the corresponding result (the RRDE voltammograms for the determination of current collection efficiency) is shown in Fig. S1.

2.5. H₂O₂ production in a flow electrochemical cell

Catalyst-coated gas diffusion electrode (GDE) was prepared by depositing 150 µL of catalyst ink onto a pre-cut strip $(2.0 \text{ cm} \times 2.0 \text{ cm})$ of GDE and was immediately dried. H₂O₂ production for the samples were investigated by a three-electrode and two-electrode method on a CHI750e electrochemical workstation (Shanghai Chenhua Instrument Co., Shanghai, China). The experiments were performed in a flow electrochemical cell with two compartments separated by a Nafion 117 membrane. (The experimental device was shown in Fig. S2). On the side of the cell there was the electrolyte of 0.1 M KOH or K₂SO₄. The GDE, a IrO₂/C, and an Ag/AgCl electrode were used as the working electrode, counter electrode, and reference electrode. Before the measurement, the cathodic compartment of the cell was saturated with high-purity O_2 (99.999%) for at least 30 min. The O_2 was continuously bubbled into the cathodic chamber at a rate of 40 mL/min during the reduction.

2.6. Determination of the H_2O_2 concentration

Determination of the H_2O_2 concentration was as follows: the H_2O_2 concentration was measured by ultraviolet—visible (UV—Vis) spectrophotometry according to the yellow Ce⁴⁺ solution that could be reduced to colorless Ce³⁺ by H_2O_2 . A UV-3600 UV—Vis spectrophotometer (Shimadzu Scientific Instruments Inc., Kyoto, Japan) was used. The H_2O_2 concentration was calculated according to the reduced Ce⁴⁺ amount and equations (2) and (3) [6].

$$2Ce^{4+} + H_2O_2 \rightarrow 2Ce^{3+} + 2H^+ + O_2$$
(2)

$$M = 2.5 \times M_{Ce4+} \tag{3}$$

where M denotes the concentration of $H_2O_2(M)$ and M $_{Ce4+}$ was the molarity of consumed Ce⁴⁺.

A standard curve for measurement of the Ce^{4+} concentration was established by various concentrations of the corresponding $Ce(SO_4)_2$ standard solution. The sample in the potentiostatic electrolysis used a 1 mL sample that was mixed with 4 mL of the standard solution and the selected $Ce(SO_4)_2$ standard solution was transferred to the quartz glass UV cell for testing.

2.7. Calculations for productivity, faradic efficiency of the produced H_2O_2 and energetic efficiency of the flow cell

The faradaic efficiency (F.E.) for the produced H₂O₂ was

calculated for the chronoamperometric measurements by determining the charge required to produce the measured product concentration and dividing the, by the total charge passed. The productivity of the produced H_2O_2 was calculated by the produced hydrogen peroxide concentration in 100 mL solution. The reaction time and the area of the GDE was supported by the catalyst. The energetic efficiency (E.E.) of the flow cell was calculated by the following equation:

$$\eta_{energetic,H_2O_2} = \frac{E_{H_2O_2}^0 F E_{H_2O_2}}{V_{in}}$$
(4)

where $E_{H_2O_2}^0$ is the standard thermodynamic potential of H₂O₂, $FE_{H_2O_2}$ is the faradaic efficiency of H₂O₂, and V_{in} is the total cell voltage.

3. Results and discussion

Fig. 2a—b shows the typical product (N-O-P-C-800) with a sheet shape. The elemental mapping (Fig. 2d—f and Fig. S3) exhibited four types of elements C, N, O, and P that were uniformly dispersed in the carbon nanosheets. The EDS data proved the existence of C, N, O, and P elements. Fig. S4 shows the SEM images of the N-O-P-C-750, N-O-P-C-850, and N-O-P-C-800-C.

Fig. 3a-b shows the results of the BET of the N-O-P-C-800, where the typical product had a large quantity of nanopores (mesopores and micropores). The BET specific surface area, total pore volume, and micropore volume of the N-O-P-C-800 was $350 \text{ m}^2 \text{ g}^{-1}$, 0.30 cm³ g⁻¹, and 0.12 cm³ g⁻¹. Table S1 shows the details of the element content ratio, the BET surface area, the total pore volume, and the micropore volume of the samples. Fig. S5 and Table S1 show that with the increased annealing temperature, the BET surface area became higher and the pore size distribution changed. The BET specific surface area, the total pore volume, and the micropore volume of N-O-P-C-800-C were $281 \text{ m}^2 \text{ g}^{-1}$, 0.18 cm³ g⁻¹, and 0.12 cm³ g⁻¹. The N-O-P-C-800 had higher BET specific surface area and total pore volume than the N-O-P-C-800-C. During the preparation of N-, O-, and P-tridoped nanoporous carbon, the bioconcentrated dye (fuchsin basic) in fungal hyphae was helpful in promoting the BET specific surface area and total pore volume.

Table S1 shows that the N-O-P-C-800 had an atomic content of C, N, O, and P of 74.7 at%, 2.7 at%, 18.9 at%, and 3.7 at%. Fig. 3c-f exhibit the high-resolution C1s, N1s, O1s, and P2p XPS spectra of the N-O-P-C-800. Fig. 3c shows a strong peak at 284.8eV and two weak peaks at 285.9eV and 287.8eV. The peak of 284.8 eV represents the sp² hybridized graphite carbon. The peaks at 285.9 eV and 287.8 eV corresponded to the carbon-oxygen single bond (C–OH) and the carbon doubly bound to oxygen (C=O) [23]. Fig. 3d shows that the three types of nitrogen atoms (pyridinic nitrogen, pyrrolic nitrogen and graphite nitrogen) were doped in the carbon materials. The peak at 398.3 eV belonged to the pyridinic nitrogen, the peak at 399.7 eV was pyrrolic nitrogen, and the peal at 401.0 eV was attributed to the graphitic nitrogen with the highest peak area [16]. Content of graphitic-, pyrrolic- and pyridinic- N in different samples was shown in Table S2. Fig. 3e shows the O=C-O bond (corresponding to the peak of 531.8 eV), O=C bond (corresponding to the peak of 532.8 eV), and the C–O–C bond (corresponding to the peak of 533.4 eV) in N-O-P-C-800. Content of different type oxygen in different samples was listed in Table S3. Fig. 3f shows that the N-O-P-C-800 contained the P-C bond (corresponding to a peak of 132.8 eV), the P-N bond (corresponding to a peak of 133.6 eV), and the P–O bond (corresponding to a peak of 134.4 eV) [21]. The XPS spectra of N-O-P-C-750, N-O-P-C-850 and N-O-P-C-800-C were



Fig. 2. (a) SEM image of N-O-P-C-800; (b-f) STEM image and mapping of C, N, O, and P of N-O-P-C-800.



Fig. 3. (a-b) Nitrogen adsorption-desorption isotherm curve and pore distribution of N-O-P-C-800. (c-f) high-resolution C1s, N1s, O1s, and P2p XPS spectra of the N-O-P-C-800.

also tested (Figs. S6-S8). The C, N, O, and P contents in the N-O-P-C-800-C were 73.6 at%, 3.0 at%, 19.3 at%, and 4.1 at%. These materials had C, N, O, and P elements, with various elements existing in the same form. We also tested the Raman spectra of the samples. Fig. S9 shows that the samples have two strong peaks at the G band and D band, the positions of the two main peaks concentrated around 1335 cm⁻¹ and 1593 cm⁻¹, with one weak 2D peak appearing at 2850 cm [16]. According to the above results and discussion, the N-, O-, and P-tridoped nanoporous carbon was prepared using the fungal hyphae (from *Irpex lacteus* F17) as N-, O-, and P- sources.

We investigated the electrocatalytic activity of the samples toward oxygen reduction to H_2O_2 by RRDE measurements in alkaline and neutral media. The RRDE voltammograms in the O_2 -saturated 0.1 M KOH are shown in Fig. 4a. The N-O-P-C-800 exhibited the highest overall catalytic reactivity for oxygen reduction (disk current density, j_{disk} , up to -2.5 mA/cm^2), and the largest HO₂ specific productivity (ring current, i_{ring} , up to 0.73 mA/cm²) at 0.3 V (Fig. 4a). The H₂O₂ selectivity from the RRDE voltammograms are shown in Fig. 4b. The H₂O₂ selectivity depended on the applied potential. The N-O-P-C-800 revealed that the selectivity was around 93.0–97.0% at potentials ranging from 0.25 V to 0.68 V (vs RHE), indicating that it followed the 2-electron reduction pathway. As a control, the N-O-P-C-800-C showed lower H₂O₂ selectivity (14.5–29.5% from 0.25 V to 0.68 V). The N-O-P-C-800 had the best performance. In addition, for further comparison, the dye has been carbonized under the optimal conditions (800 °C, 5 °C/min) and the product was denoted



Fig. 4. (a-b) Polarization curves (solid lines), simultaneous H₂O₂ detection currents at the ring electrode (dashed lines) and H₂O₂ selectivity of the samples in the 0.1 M KOH solution (rotational speed of 1600 rpm); (c-d) Polarization curves (solid lines), simultaneous H₂O₂ detection currents at the ring electrode (dashed lines) and H₂O₂ selectivity of samples in 0.1 M K₂SO₄ solution (rotational speed of 1600 rpm).

as dye-800. The activity of dye-800 tested by RRDE (Fig. S10) indicated that there is not ideal performance for oxygen reduction to H₂O₂. Fig. 4c shows the RRDE voltammograms in the O₂-saturated 0.1 M K₂SO₄. The N-O-P-C-800 exhibited the highest overall catalytic reactivity for oxygen reduction. When the potential was 0 V (vs RHE), the j_{disk} reached up to -2.2 mA/cm^2 and the *i*_{ring} approached 0.30 mA/cm², revealing the largest HO₂ specific productivity. In 0.1 M K₂SO₄, the H₂O₂ selectivity of the samples depended on the applied potential. N-O-P-C-800 showed the selectivity of 53.1–60.4% from -0.14 V to 0.41 V (vs RHE), indicating the N-O-P-C-800 had the best performance in the neutral media than other samples. The results in acidic media are shown in Fig. S11, the electrochemical performance in acid solution was not ideal compared to alkaline and neutral solutions (the selectivity of N-O-P-C-800 catalyst was only less than 50%).

To further investigate the catalytical activity, the H₂O₂ faradaic selectivity and productivity during bulk electrolysis were tested by a flow cell with a GDE (containing N-O-P-C-800) cathode and a GDE (containing IrO₂) anode. The H₂O₂ faradaic selectivity and productivity were both important factors to evaluate the performance of the catalyst. The H₂O₂ faradaic selectivity was calculated according to the real amount of H₂O₂ produced in the reduction reaction. The amount of H₂O₂ faradaic selectivity and the amount of H₂O₂ produced in alkaline (0.1 M KOH) solution by N-O-P-C-800 catalyst for 18 cycles at the applied potentials of 0.15 V, 0.25 V, and 0.35 V(vs RHE). Fig. 5a–b shows that when the applied potential shifted negatively, the H₂O₂ production rate increased. The H₂O₂ production rate of the 1470 mmol $g_{catalyst}^{-1}$ at 0.25 V (Fig. 5a) and the faradaic selectivity of up to 97.0% (Fig. 5b) were obtained. N-O-

P-C-800 catalyst exhibited the both high H₂O₂ production rate and high faradaic selectivity. Previous literature revealed that the catalytical activity of the N-O-P-C-800 was superior to most of the reported catalysts, including nitrogen-doped carbon, transitionmetal-based, and metal catalysts (Table S4) [6,11,28-30]. Fig. 5a shows that the N-O-P-C-800 catalyst exhibited excellent stability in the successive H₂O₂ production. The electrocatalyst should have ideal durability, which is considered one of the most important issues [6,7,31,32]. Fig. 5c-d shows the H₂O₂ production rate of 435 mmol $g_{catalyst}^{-1}$ h⁻¹ at 0.1 V and faradaic selectivity of up to 65.0% was obtained in the 0.1 M K₂SO₄ solution, which indicated the N-O-P-C-800 catalyst exhibited good catalytical activity and stability in the neutral solution. The results indicated that the N-O-P-C-800 catalyst was a promising electrocatalyst for H₂O₂ production by the ORR process. In the alkaline solution, the N-O-P-C-800 catalyst exhibited the H₂O₂ production rate (0.25 V, 1470 mmol $g_{catalyst}^{-1} h^{-1}$) and faradaic selectivity (97.0%), which was remarkably higher than the 0.1 M K_2SO_4 (0.10 V, 435 mmol $g_{catalyst}^{-1}$ h⁻¹, faradaic selectivity 65.0%). The concentrated basic solution containing H_2O_2 could be used in many fields, including the pulp and paper industries [6,11].

We investigated the catalytical activity of the N-O-P-C-800 catalyst by a two-electrode method in the flow cell in an alkaline solution (0.1 M KOH) and a neutral solution (0.1 M K₂SO₄) [33]. The H₂O₂ Faradaic efficiency and productivity during bulk electrolysis at different cell voltage are shown in Fig. 6. Fig. 6a shows that the H₂O₂ started to generate at a cell voltage of 0.73 V (with iR-free correction) and reached a current of 15.0 mA at a voltage of 1.5 V. Fig. 6b-c shows that the H₂O₂ production rate of 540 mmol $g_{catalyst}^{-1}$ h⁻¹ at cell voltage of 1.3 V and Faradaic efficiency reached 93.1% in 0.1 M KOH. Fig. 6e-h shows the results in 0.1 M K₂SO₄.



Fig. 5. (a-b) Faradaic efficiency and H₂O₂ productivity for the N-O-P-C-800 catalyst as a function of cycle number at 0.15 V, 0.25 V, and 0.35 V(vs RHE) in 0.1 M KOH; (c-d) Faradaic efficiency and H₂O₂ productivity for N-O-P-C-800 catalyst as a function of cycle number at -0.10, 0.10 and 0.30 V(vs RHE) in 0.1 M K₂SO₄.

Fig. 6e shows that the H_2O_2 started to generate at a cell voltage of 1.18 V (with iR-free correction) and reached a current of 15.0 mA at a voltage of 2.0 V. The H_2O_2 production rate of 220 mmol $g_{catalyst}^{-1}$ at cell voltage of 2.1 V and Faradaic efficiency of up to 35% were obtained (Fig. 6e–h). The H_2O_2 production rate and Faradaic efficiency of the flow cell in the alkaline solution were higher than in the neutral solution. The flow cell in the alkaline solution exhibited a high H_2O_2 production rate and Faradaic efficiency, which was due to the cathode (excellent N-O-P-C-800 catalyst) and the anode (containing IrO₂).

The electrochemical conversion efficiency (energetic efficiency) for H_2O_2 was discussed according to its standard thermodynamic potential, Faradaic efficiency, and the total input cell voltage. This measurement method accounts for the potential losses (including the overpotentials of cathode and anode and resistance losses) and accurately defines the overall electrochemical cell efficiency. The energetic efficiency and current values are two key indexes in the practical industrial application of the electrochemical cell [19,33]. As shown in Fig. 6d and h, when the cell voltage increased, the energetic efficiency decreased, and reduction current and H_2O_2 production rate increased. In the 0.1 M KOH, the overall energetic efficiency for H_2O_2 reached up to 29.0% when the total current was 21 mA/cm². The exceptional energetic efficiency and total current density values were two key advantages for the practical industrial application of H_2O_2 [33].

We investigated the H_2O_2 production rate and the Faradaic efficiency by the two-electrode cell driven by a commercial dry battery (1.5 V) and a solar-energy battery (2.5 and 3.0 V) (shown in Fig. 7a–b). Fig. 7c–d shows the Faradaic efficiency of 85.0% and 662 mmol $g_{catalyst}^{-1}h^{-1}$ H_2O_2 that was achieved via a dry battery in

15 min. The 804 mmol g $_{catalyst}^{-1} h^{-1} H_2O_2$ (Faradaic efficiency of 94.0%) and 921 mmol g $_{catalyst}^{-1} h^{-1} H_2O_2$ (Faradaic efficiency of 95.0%) was obtained in 15 min via a solar-energy battery with 2.5 V and 3.0 V. These results revealed that the two-electrode cell was driven by the commercial dry battery (1.5 V) and has potential application in O₂ reduction to H₂O₂ via only the solar-energy battery and not by the electricity power from the fossil fuels [34].

From the above discussion, in the preparation, addition of dye (fuchsin basic) plays an important role in the excellent activity. The N-O-P-C-800 had higher BET specific surface area and total pore volume than the N-O-P-C-800-C. The carbon sheets in N-O-P-C-800 had large surface areas with many nanopores, so that many catalytic sites on the surface of the catalyst were exposed for the reaction [16,21,35]. These catalysts contained the doped-nitrogen and oxygen. From Tables S2 and S3, the content of different type nitrogen and oxygen of the samples are different. The addition of dye (fuchsin basic) can also change the content of different type of N element and the content of different type of O. Some DFT studies have shown that the doped N or O play an important role in the H₂O₂ production by the ORR process [6,10,20,36,37]. In addition, the carbon sheets in the material may form an interpenetrated network structure, which was helpful to accelerate the reactant and the electron transport [22,23].

4. Conclusions

We proposed fungal hyphae as the main sources of C, N, O, and P to prepare the electrocatalyst to produce H_2O_2 by the ORR process. The electrocatalyst was the N-, O-, and P-tridoped nanoporous carbon that had a large surface area with many nanopores. It



Fig. 6. (a) I-V curve of the flow cell with a GDE (containing N-O-P-C-800) cathode and a GDE (containing IrO₂) anode in 0.1 M KOH; (b) I-t curves of the flow cell at the different applied potentials in 0.1 M KOH; (c) H₂O₂ productivity and Faradaic efficiency at the different applied potentials in 0.1 M KOH; (d) energetic efficiency at the different applied potentials in 0.1 M KOH; (e) I-V curve of the flow cell with a GDE (containing N-O-P-C-800) cathode and a GDE (containing IrO₂) anode in 0.1 M KOH; (d) energetic efficiency at the different applied potentials in 0.1 M KOH; (e) I-V curve of the flow cell with a GDE (containing N-O-P-C-800) cathode and a GDE (containing IrO₂) anode in 0.1 M K₂SO₄; (f) I-t curves of the flow cell at the different applied potentials in 0.1 M K₂SO₄; (g) H₂O₂ productivity and Faradaic efficiency at the different applied potentials in 0.1 M K₂SO₄; and (h) energetic efficiency at the different applied potentials in 0.1 M K₂SO₄; and (h) energetic efficiency at the different applied potentials in 0.1 M K₂SO₄; and (h) energetic efficiency at the different applied potentials in 0.1 M K₂SO₄.



Fig. 7. (a-b) Illustration of the H_2O_2 production by ORR process driven by dry cells and solar cells; and (c-d) Faradaic efficiency and H_2O_2 productivity for N-O-P-C-800 catalyst by dry cell and solar cells (2.5 V and 3.0 V) in 0.1 M KOH.

exhibited excellent activity, selectivity, and stability towards O_2 reduction for producing H_2O_2 in alkaline media and showed good activity, selectivity, and stability with neutral media. In the preparation, addition of dye (fuchsin basic) plays an important role in the excellent activity. A flow cell with a GDE (containing the typical electrocatalyst) cathode and a GDE (containing IrO₂) anode exhibited exceptionally high Faradaic efficiency, H_2O_2 productivity, and energetic efficiency in alkaline media. The Faradaic efficiency and H_2O_2 productivity were maintained when it was driven by a commercial dry battery (1.5 V) or by a solar-energy battery (2.5 V or 3.0 V), which indicated that these excellent electrocatalyst may have potential application in the O_2 reduction to H_2O_2 . This work provides insights in developing the new electrocatalyst for H_2O_2 production to H_2O_2 by electrocatalysis.

Conflicts of interest

The authors declare no conflict of interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.electacta.2019.04.011.

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