Fungi residue derived carbon as highly efficient hydrogen peroxide electrocatalyst

Zhu Meng [a], Juntao Li [b], Feng Huo [c], Yan Huang [a,*], Zhonghua Xiang [a,*]

[a] State Key Laboratory of Organic-Inorganic Composites, College of Chemical Engineering, College of Energy, Beijing University of Chemical Technology, Beijing 100029, China
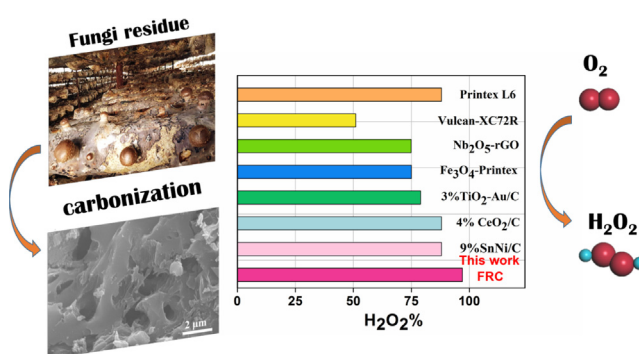[b] Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK
[c] Beijing Key Laboratory of Ionic Liquids Clean Process, State Key Laboratory of Multiphase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China

HIGHLIGHTS

- Highly efficient biocarbon catalyst was first developed with fungiresidue biomass.
- This work provides a facile way to produce excellent low-cost H_2O_2 electrocatalyst.
- The selectivity of FRC exceeds state of the art catalysts with Max H_2O_2% 98%.

GRAPHICAL ABSTRACT

ABSTRACT

In electrochemical devices, the reduction of dissolved oxygen in electrolyte can achieve on-site production of hydrogen peroxide. The industrial viability of the process strongly depends on cathode electrocatalyst. However, current catalysts rely on rare, noble metals and their composite. Thus, it remains a great challenge of cost-effective catalyst with both high activity and selectivity. Herein, we made use of extremely low-cost fungi residue biomass, developing a multi-non-precious metal doped carbon catalyst (named as FRC) for H_2O_2 electrogeneration by facile in-situ synthesis. The one-step prepared FRC balances the performance of different metal oxides and exhibits not only high activity but also high selectivity at a spacious potential range. Specifically, the current density for ring reaches 0.45 mA cm^{-2} at -0.5 V (vs SCE). Besides, the selectivity achieves 98% and remain above 91% in wide potential range ($-0.7 \sim -0.3$ V), which exceeds almost all metal contained carbon materials to our knowledge. As the first study of fungi residue towards H_2O_2 electrogeneration, this novel approach provides a highly promising and low cost electrocatalyst for real production, moreover, exploring a new direction for H_2O_2 electrocatalyst development.
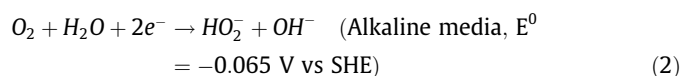
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1. Introduction

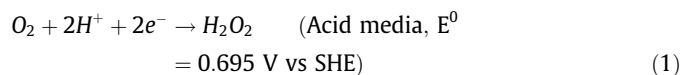Hydrogen peroxide is commonly used in pulp bleaching (Bianchi et al., 1999) and propylene oxide production (Kertalli et al., 2016; Zuwei et al., 2001). Recently, it attracts numerous attention in environmental field since it can effectively conduct

many environmental processes without secondary pollution, for example, water purification (Asghar et al., 2015; Chen et al., 2014; Yao et al., 2013) and flu gas denitrification (Zhou et al., 2015).

Because of economic cost and process inherent complexity (Campos-Martin et al., 2006), the present state-of-art *i.e.*, the anthraquinone method produce hydrogen peroxide in a large scale and high concentration way. There is a general call for on-site production where hydrogen peroxide is producing closer to the point of consumption, direct synthesis H_2O_2 in electrochemical devices is an attractive and promising way. On the one hand, H_2O_2 synthesis through H_2 and O_2 is an exergonic reaction, electrogeneration H_2O_2 can recover that Gibbs free energy as electronic energy thus reduce the energy consumption. On the other hand, electrosynthesis produces hydrogen peroxide in a safety way and avoids the explosion danger of H_2 and O_2 putting together. This is a vital problem in other alternative producing method like under plasma (Yi et al., 2013) or sorts of catalyst (Edwards and Hutchings, 2008; Freakley et al., 2016; Shibata et al., 2013).

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad \text{(Acid media, E}^0$$
$$= 0.695 \text{ V vs SHE)} \quad (1)$$

$$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^- \quad \text{(Alkaline media, E}^0$$
$$= -0.065 \text{ V vs SHE)} \quad (2)$$

*SHE refers to standard hydrogen electrode.

In real process, oxygen reduction reaction (ORR) occur through $2e^-$ or $4e^-$ pathways, the electro transfer number of reaction depends on the employed electrocatalyst. For H_2O_2 production, an ideal catalyst should possess high activity to optimize energy efficiency and catalyst loading, besides, high selectivity to ensure the high yields of hydrogen peroxide (Verdaguer-Casadevall et al., 2014). As clearly seen from the Eqs. (1) and (2), the shift in potential for alkaline media is low with respect to acidic medium, which means the production process need less energy in alkaline media than in acid media. Therefore, we focus on developing high activity and selectivity catalyst under alkaline medium in this study.

Carbon materials are widely used as either electrocatalysts or supports due to its great activity (Hu et al., 2013; Wang et al., 2013; Yang et al., 2007). However, catalyst with both high selectivity and activity is still a challenge. To overcome such limitation, there are already some improvements, e.g., heteroatoms doping and porous structure manipulation (Fellinger et al., 2012; Liu et al., 2015). Among them, introducing hetero-metal or metal oxides into carbon materials can promote the ORR activity and make it prone to $2e^-$ pathway. Some researchers have reported the good catalytic performance of different metals like Fe_3O_4 (Barros et al., 2015), WO_3 (Assumpcao et al., 2013a) and W-Au (Antonina et al., 2017) dispersing on diverse supports, e.g., carbon fibers (Hu et al., 2013) and graphite (Wang et al., 2008). However, the scarcity of these metals increases the expense of catalyst. Moreover, these active metal species grown by post decoration are possibly detached from the conductive carbon support interface during continuous oxygen gas bubbling, which may lead to significant decay of catalytic performance (Cheng et al., 2017). Thus, it is still important to develop facial method to prepare cost-effective and stable catalyst.

Nature owns numerous biomass in high abundance as economic, renewable and green carbon precursors. Fungi residue is composed of sawdust, cottonseed hull, gypsum and residual mushroom hyphae. As the waste of mushroom cultivation, it naturally contains cellulose, semicellulose and lignin, accompanied with various metals, e.g., Al, Si, Ca, Mg. Using these metals that originally existed in the raw material can avoid the using of exterior metal source and effectively reduce the cost. Therefore, fungi residue gives us an opportunity to develop electrocatalyst with high activity and selectivity.

Here, we used low cost fungi residue biomass which possess intrinsic metal oxides, developing an in-situ synthesized multi-non-precious metal doped carbon catalyst (named as FRC) for H_2O_2 electrogeneration. The one-step prepared FRC balances the performance of different metal oxides and exhibits not only high activity (0.45 mA cm^{-2} at -0.5 V) but also high selectivity (maximum of 98%) under operating medium. The high selectivity exceeds almost all the similar type catalysts under alkaline medium to our knowledge. Besides, we performed comprehensive characterizations to elucidate the possible active sites and origin of great performance.

2. Material and methods

2.1. Fungi residue-biocarbon electrocatalyst preparation

Fungi residue used in this experiment was obtained from Ruizhao edible fungus waste processing company that located at Pingquan, China. The target electrocatalyst was prepared by one-step annealing which avoiding the complexity and was easy to replicate. Specifically, as shown in Fig. 1, the raw material was first pretreated, i.e., shattering and sieving to even brown powder, then air-dried under 105 °C until constant weight. After that, the brown powder was putted in a temperature programmable tube for annealing step. The final as-synthesized material denote as FRC. Specific annealing parameters are shown as following: heating from room temperature to 350 °C in 50 min and maintained 2 h, after that keep heating until the final temperature (800, 900, 1000 °C) and maintained for another 2 h, the process was proceeding under Ar atmosphere with the flux fixed at 100 sccm.

2.2. Chemical and physical characterization

The morphology of FRC material was characterized by scanning electron microscopy (SEM) using a HITACHI-S4700 instrument, apart from that, information about metal category was provided by the equipped energy dispersive X-ray spectrometer (EDS).

X-ray photoelectron spectroscopy (XPS) analysis was carried out using a commercial spectrometer (ThermoFisher Scientific USA). The twin anode Al Ka line was used as X-ray source and the analyzer pass energy was set to 100 eV for survey and 30 eV for high-resolution scans. The inelastic background of the spectra was subtracted using Shirley's method. The spectra were fitted without placing constraints using XPS peak software. The width at half maximum (FWHM) varied between 0.8 and 2.2 eV, and the accuracy of the peak positions was ±0.1 eV.

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) was performed in a Spectro Ciros CID ICP optical emission spectrometer (software), ICP-OES and Inductively coupled plasma mass spectrometry (ICP-MS) are both determined at the Analytical Instrumentation Center of Beijing University of Chemical Technology. A 201.265 nm line was employed for acquisition, and a five-point calibration curve with a correlation coefficient $R^2 > 99.9$ was prepared from analytical grade chemicals.

2.3. Electrochemical characterization

The rotating ring-disk electrode (RRDE) measurements described in this study were performed under three-electrode system, with Pt wires and SCE (Hg/Hg_2Cl_2) as counter and reference electrode, respectively, the commercial electrode from Pine Instru-