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Generating more Mn^{4+} ions on surface of nonstoichiometric MnO_2 nanorods via microwave heating for improved oxygen electroreduction

Kebin Xu[a], Xiuxia Lin[a], Xiufang Wang[a], Ligui Li[b,c,*], Zaisheng Zhu[a,*], Yong Tian[a,*]

[a] Guangdong Engineering & Technology Research Center of Topic Precise Drug Delivery System, School of Pharmacy, Guangdong Pharmaceutical University, 280 Waihuan Dong Road, University Town, Guangzhou 510006, China
[b] Guangzhou Key Laboratory for Surface Chemistry of Energy Materials, New Energy Research Institute, School of Environment and Energy, South China University of Technology, 382 Waihuan Dong Road, University Town, Guangzhou 510006, China
[c] Guangdong Provincial Key Laboratory of Atmospheric Environment and Pollution Control, College of Environment and Energy, South China University of Technology, 382 Waihuan Dong Road, University Town, Guangzhou 510006, China

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ABSTRACT

Catalytic activities of transition metal oxides are usually influenced by their surface states. Herein, microwave heating is exploited as a fast and economic alternative approach to conventional postsynthesis calcination to effectively tune the surface states of nonstoichiometric MnO_2 nanorods. After heating with microwave for 30 min, although the crystalline phase and morphology of nonstoichiometric MnO_2 nanorods are largely reserved, the content of high-valent Mn cations, i.e. Mn^{4+}, on the surface of nonstoichiometric MnO_2 is maximized, which leads to a remarkably reduced charge transfer resistance for ORR, and the corresponding catalytic activity of oxygen reduction reaction (ORR) is markedly enhanced and becomes close to that of commercial Pt/C catalyst, within the context of onset potential, diffusion-limiting current density and average electron transfer number. The present work not only enriches the way to tune the ORR activity of catalysts, but also provides a deeper insight into the influence of surface state on electrochemically catalytic activity of manganese oxides.

1. Introduction

Oxygen reduction reaction (ORR) is a pivotal process in several emerging green energy storage and conversion technologies, such as alkaline fuel cells, microbial fuel cells and metal-air batteries [1–5]. Due to its complex reaction pathways and sluggish electron-transfer kinetics, ORR requires catalysts to generate a sufficiently high current density for practical applications, of which noble metals (Pt, Pd, etc.) based nanomaterials are of the universal choice due to their remarkable performance [6–9]. However, the intrinsic disadvantages of noble metals, such as high cost and scarcity, necessitate either an efficient utilization of noble metals or exploration of completely disruptive alternatives, for example, noble-metal-free electrocatalysts [10–15].

Recently, manganese oxides are considered as one of the potential alternatives to noble metal-based electrocatalysts because of their considerable activities, low cost, earth-abundance as well as low impact to environment [16–21]. Compared with the extensively used commercial Pt/C catalyst, manganese oxide catalysts generally are less active, showing much larger overpotentials and lower electron transfer numbers [17,22–25]. Therefore, many strategies have been developed to increase the electrocatalytic activity of manganese oxides, including anchoring on conductive materials [26–29], coating with metals [30], hydrogenation [31], doping with other metal cations to form multimetal oxides [27,32–35], etc. Although these pioneer approaches are indeed proven to be effective, they are relatively complicated, and hence novel methods for tailoring the electrocatalytic activity of intrinsic manganese oxides are still highly demanded, from the viewpoints of academic research and industrial application.

The surface electronic states of intrinsic manganese oxides are reported to significantly influence on the corresponding electrochemical catalytic activities. For example, after carefully monitoring the surface intermediates of electrochemical oxygen evolution reaction (OER), a reversable reaction of ORR, on rutile MnO_2 with different facet orientations, Nakamura et al. [36] recently found that the coverage of the Mn^{3+} intermediate is about 11-fold higher on the metastable (1 0 1) surfaces as compared with that on (1 1 0) surfaces, eventually

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[*] Corresponding authors at: Guangdong Engineering & Technology Research Center of Topic Precise Drug Delivery System, School of Pharmacy, Guangdong Pharmaceutical University, 280 Waihuan Dong Road, University Town, Guangzhou 510006, China (Z. Zhu and Y. Tian); Guangzhou Key Laboratory for Surface Chemistry of Energy Materials, New Energy Research Institute, School of Environment and Energy, South China University of Technology, 382 Waihuan Dong Road, University Town, Guangzhou 510006, China (L. G. Li)

E-mail addresses: esguili@scut.edu.cn (L. Li), 1036981937@qq.com (Z. Zhu), tian_yong_tian@163.com (Y. Tian).

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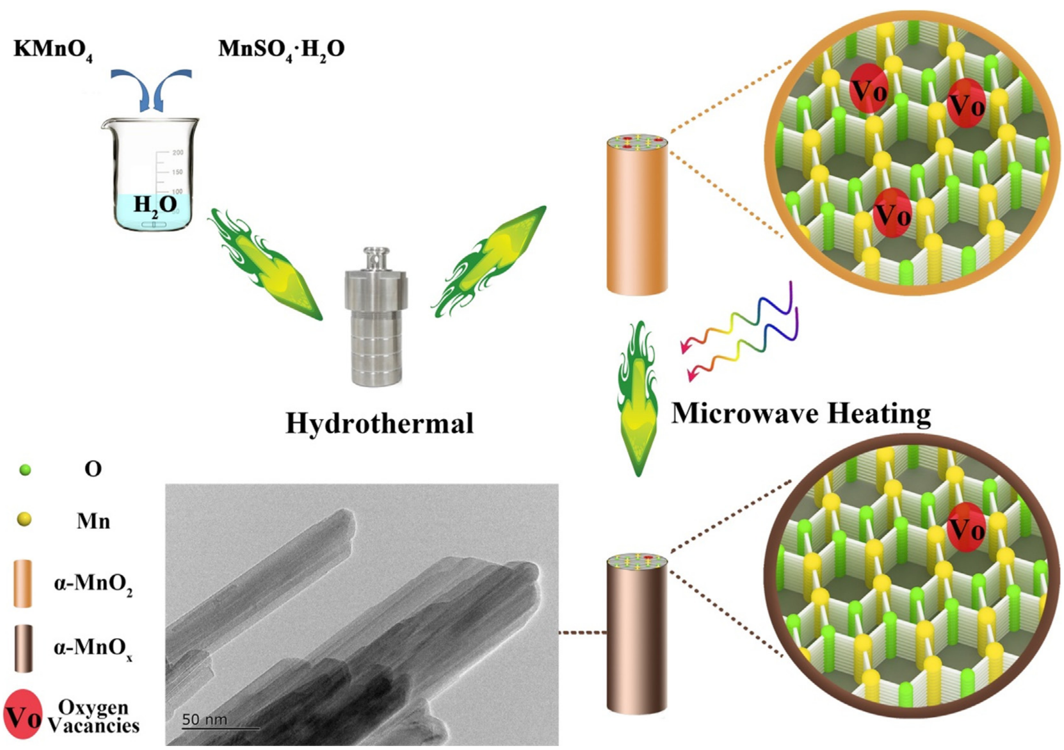

Scheme 1. Schematic illustration of the synthesis process of MnO_2-t sample.

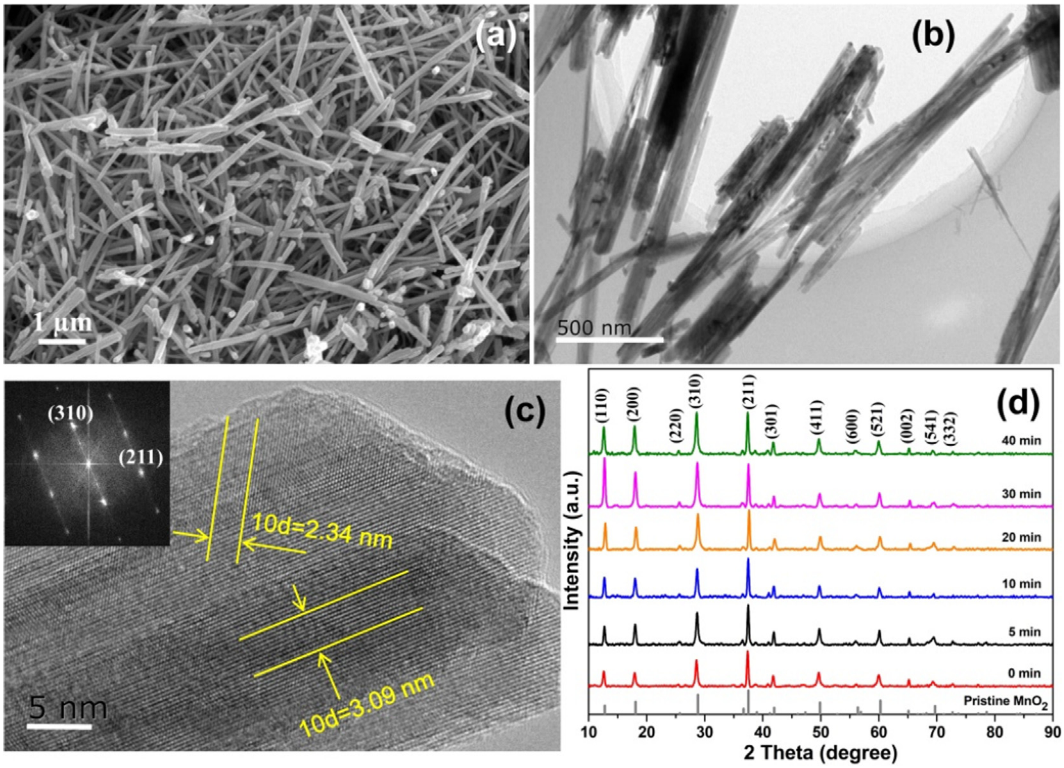

Fig. 1. (a) Representative SEM, (b) TEM and (c) high-resolution TEM image of MnO_2-30 sample. Inset to panel (c) is the corresponding FFT patterns. (d) The XRD profiles of MnO_2-t samples after heating with microwave for varied time.

contributing to a superior OER activity on (1 0 1) surfaces. As a facile method, post-synthesis calcination treatments are widely used to tune the surface states of manganese oxides to optimize the corresponding ORR catalytic activity [16,19]. For instance, Chen et al. [16,17] reported that oxygen vacancies were generated on MnO_2 surface after post-synthesis calcination for about 2 h, which led to markedly enhanced ORR activity in alkaline electrolyte. Recently, Sun et al. [19] utilized an electrochemical method to successfully increase the content of high-valent Mn, i.e. Mn^{4+} cations, on manganese oxides surface, and consequently the ORR catalysis was indeed substantially improved.