

# Boosting oxygen reduction performance of manganese oxide in alkaline media by three-dimensional highly ordered conductive porous framework

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## I. Experimental Section

### 1.1 Materials

Boric acid,  $\text{NiCl}_2$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , Nickel sulfamate, saccharin, sodium (SDS) dodecyl sulfate, KOH (99.99 %), Nafion solution (5 wt %), Pt/C (20 wt %),  $\text{MnSO}_4$ ,  $\text{CH}_3\text{COONa}$  were purchased from Aladdin. Methanol was obtained from Guangzhou Chemical Reagents. All of the chemicals were used without further purification. High-purity water ( $18.25 \text{ M}\Omega \text{ cm}$ ) supplied by a UP Water Purification System was used in all the experiments.

### 1.2 Materials Synthesis

#### Fabrication of 3D Highly Ordered Bicontinuous Porous Ni Scaffold (Ni-pc)

Firstly, the PS colloidal crystals were prepared by vertically growth method. The -OOC-terminated PS latex particles with diameter of 450 nm were dispersed in water to form stable suspensions with a concentration of  $3 \text{ mg mL}^{-1}$ . Followed by allotting into 10 mL vials, the conducting glass slice was put vertically into each vial. After 5-7 days in  $25^\circ\text{C}$ , the ethanol was volatilized completely and obtained PS colloidal crystal on both sides of the glass slices. Then the ordered PS opal templates on conducting glass slice were annealed at different temperature ( $101^\circ\text{C}$ ,  $102^\circ\text{C}$ ,  $103^\circ\text{C}$  and  $104^\circ\text{C}$ ) for 1 h. The 3D Ni inverse opal template was synthesized by galvanostatically electrodeposition with a constant current density of  $1 \text{ mA cm}^{-2}$ . The PS opal template, Ni plate ( $1 \times 4 \text{ cm}$ ) and Ag/AgCl electrode were employed as the working, counter and reference electrode, respectively. After nickel electrodeposition, PS was removed by immersing the template in chloroform for 30 minutes with oscillation. The 3D Ni inverse opal was further polished by 10 minutes oxygen plasma etching to remove the residual polymer and got Ni-pc.

#### Fabrication of $\text{MnO}_2$ @Ni-pc Electrodes

MnO<sub>2</sub> was incorporated on the 3D Ni scaffold by anodic pulse deposition in the aqueous solution of 0.5 M MnSO<sub>4</sub> and 0.5 M CH<sub>3</sub>COONa at 35 °C. Here Pt plate was used as the counter electrode. Various mass loading of MnO<sub>2</sub> was controlled by different deposition cycles of 150, 300 and 450 segments. The mass loading of MnO<sub>2</sub> was calculated by ICP-AES, which was about 0.056 mg cm<sup>-2</sup> for 300 segments.

### 1.3 Structural Characterization

Powder X-ray diffraction (PXRD) patterns of the samples were recorded on a Bruke D8 Advance powder X-ray diffractometer with a Cu K source ( $\lambda = 0.15406$  nm). 2-theta was run from 10° to 70° with a scan speed of 0.12° s<sup>-1</sup>. The morphology and microstructure of products were characterized by scanning electron microscopy (SEM, S4800). X-ray photoelectron spectroscopy (XPS) measurements were executed using an ESCALAB 250 instrument. Element composition was analyzed using a VISTA-MPX EL02115765 inductive coupled plasma atomic emission spectrometer (ICP-AES).

### 1.4 Electrode preparation and electrochemical tests

#### Preparation of catalysts electrode:

Firstly, rotating disk electrode (RDE, diameter: 5 mm, Pine) was polished by Al<sub>2</sub>O<sub>3</sub> powder and ultrasonic washed by ethanol and water, respectively. Then, in order to test the performance, MnO<sub>2</sub>@3D Ni-pc was stripped off from the conductive glass by a very thin scalpel. Afterwards, the MnO<sub>2</sub>@3D Ni-pc was stick on the polished RDE by 1  $\mu$ L of Nafion (5 wt %) and dried at room temperature. The loading amount of the MnO<sub>2</sub> catalyst is about 0.056 mg cm<sup>-2</sup>.

#### Electrochemical measurements:

All the electrochemical measurements were performed on a CHI 760 electrochemical workstation (CH Instruments Inc., Shanghai) equipped with a Pine Instrument (model AFMSRCE). A standard three-electrode cell was used to measure the performance with a Pt plate (1 cm  $\times$  3 cm) as the counter electrode, and a HgO/Hg electrode as the reference electrode. RDE covered with a thin catalyst film was used as the working electrode.

Linear-sweep voltammetry measurements were performed at different rotation speeds ranging from 400 to 1600 rpm at a scan rate of 10 mV s<sup>-1</sup>. Cyclic voltammograms (CVs) were conducted at a scan rate of 50 mV s<sup>-1</sup>. All the measurements were performed in N<sub>2</sub> or O<sub>2</sub>-saturated 0.1 M KOH.

The overall electron transfer numbers involved in the ORR process can be calculated using the Koutecky-Levich equation as following:

$$\frac{1}{|J|} = \frac{1}{|J_L|} + \frac{1}{|J_k|} = \frac{1}{B\sqrt{\omega}} + \frac{1}{|J_k|} \quad (1)$$

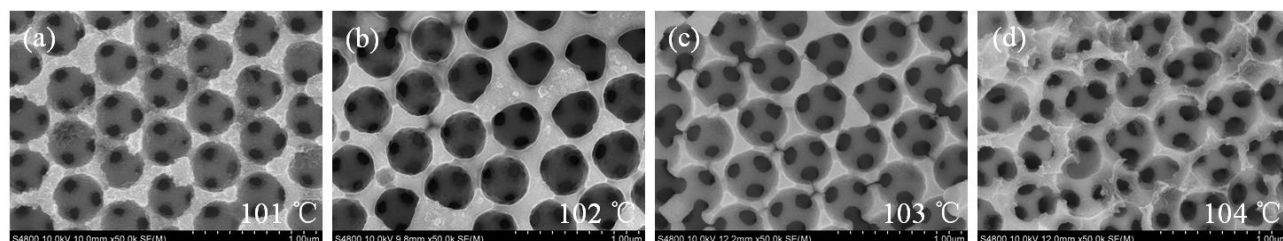
$$B=0.2nFC_0(D_0)^{2/3}\nu^{-1/6} \quad (2)$$

Where  $J$  is the measured current density,  $J_L$  is the diffusion-limiting current density and  $J_K$  is kinetic-limiting current density.  $B$ ,  $\omega$  and  $n$  are the reciprocal of the slope, electrode rotating speed in rpm and electron transfer number per oxygen molecule, respectively.  $F$  is the Faraday constant ( $F = 96485 \text{ C mol}^{-1}$ ),  $C_0$  is the concentration of  $O_2$ ,  $D_0$  is the diffusion coefficient of  $O_2$ ,  $\nu$  is the kinematic viscosity of the electrolyte, and  $k$  is the electron transfer rate constant. The electrolyte used for this research was  $O_2$  saturated 0.1 M KOH, so  $C_0$ ,  $D_0$  and  $\nu$  were used as  $1.2 \times 10^{-3} \text{ M}$ ,  $1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  and  $0.01 \text{ cm}^2 \text{ s}^{-1}$ , respectively. The constant 0.2 was adopted when the rotating speed is expressed in rpm.

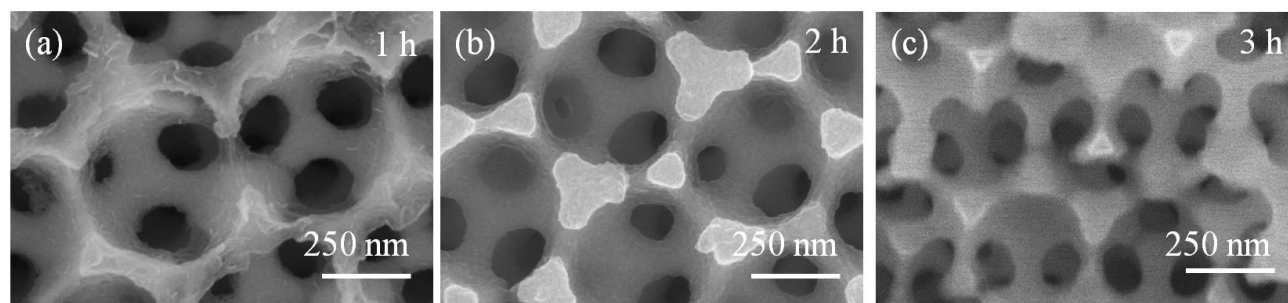
All potentials reported in this work were calibrated vs. reversible hydrogen electrode (RHE) based on the standard calculation method:

$$E(\text{RHE}) = E(\text{HgO}/\text{Hg}) + 0.098 + 0.059 \times \text{pH} \quad (3)$$

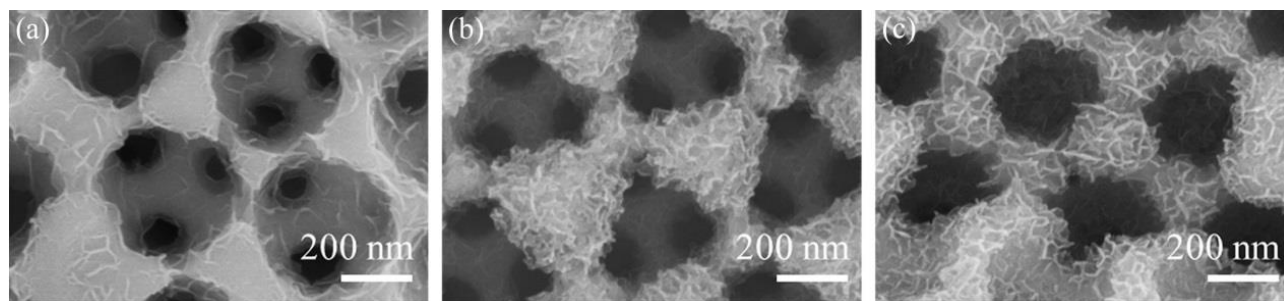
## II. Supplementary Figures



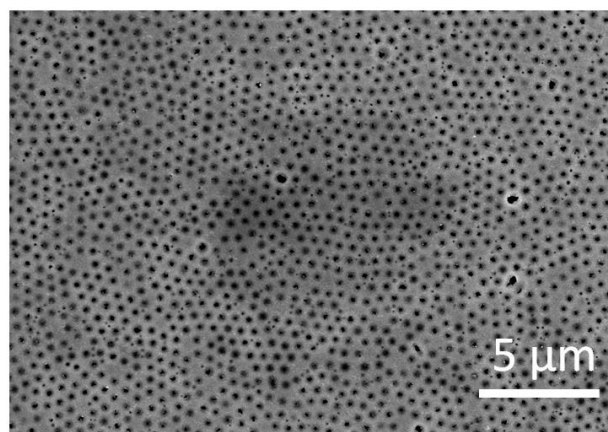
**Figure S1** SEM images of 3D Ni scaffolds with the PS opal templates annealed under different temperature (101 °C, 102 °C, 103 °C and 104 °C) for the same annealing time (1 h).



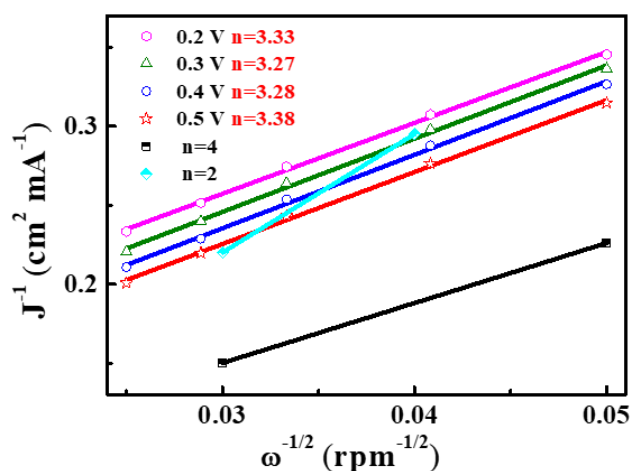
**Figure S2** SEM images of 3D Ni scaffolds with the PS opal templates annealed for different electrodeposition time (1 h, 2 h and 3 h) at the same temperature and annealing time (104 °C, 1h).



**Figure S3** SEM images of MnO<sub>2</sub>@3D Ni scaffold with different MnO<sub>2</sub> mass loading, which electrodeposited for 150, 300 and 450 segments, respectively. (the PS opal templates were annealed at 104 °C for 1 h, and electrodeposited Ni scaffold with 1 h).



**Figure S4** SEM image of the reverse side for MnO<sub>2</sub>@Ni-pc (electrodepositing MnO<sub>2</sub> with 300 segments).



**Figure S5** The K-L plots of MnO<sub>2</sub>@Ni-pc corresponding to Figure 3c.