Supporting Information

γ-MnOOH Nanowires Hydrothermally Reduced by Leaves for High-efficiency Electrocatalysis of the Glucose Oxidation Reaction

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Supporting Information contains:

Supplementary Discussions
Number of Figures: 10 (Figure S1 – S10)
Number of Tables: 1 (Table S1)
Number of Page: 16 (S1 – S16)
Supplementary Discussions

Experimental section

γ-MnOOH nanowires: Sapless leaves from a Magnolia grandiflora Linn tree were preprocessed with the sequence of deionized water washing, ultrasonic cleaning with ethanol and drying in air. Then, the leaves were cut into pieces as tiny as possible with clean scissors. KMnO₄ (5.0 mg) was dissolved in 10.0 mL deionized water under stirring for 10 min at room temperature. Subsequently, the solution was transferred into a Teflon-lined stainless-steel autoclave (25 mL) with the addition of 1.0 mg leaf pieces under hydrothermal conditions of 180 °C for 12 h and then naturally cooled to room temperature. The resulting precipitate was easily separated from the remaining organic compounds because of the different densities and finally was thoroughly washed with deionized water and ethanol several times.

Characterization of γ-MnOOH nanowires

X-ray diffraction (XRD) patterns are recorded on a Bruker D8 Advanced X-ray Diffractometer under the following conditions: 40 kV, 40 mA, Cu Kα radiation (λ = 0.154 nm).

X-ray photoelectron spectroscopy (XPS) measurements were performed with monochromatized Al Kα exciting X-radiation (PHI Quantera SXM).

Scanning electron microscopy (SEM) images are obtained using a Zeiss-Supra 55.

High-resolution transmission electron microscopy (HRTEM) images and energy dispersive X-ray (EDX) analytical data are collected on a Tecnai G2 F30 instruments electron microscope operating at 200 kv acceleration voltage, TEM equipped with an EDX detector.

Fourier transform infrared (FTIR) spectroscopy was collected on a TENSOR 27 with samples prepared as KBr pellets at wavenumbers ranging from 4000 to 400 cm⁻¹.

Thermogravimetric (TG) analyses are performed on a PerkinElmer TGA instrument heating from room temperature to 800°C in air atmosphere at the rate of 5°C min⁻¹.
Preparation of the modified electrodes. First, 5 mg of the as-prepared $\gamma$-MnOOH nanowires was suspended in a Nafion solution with a concentration of approximately 20 mg mL$^{-1}$. Before modification, GCEs (3 mm in diameter) were polished with a 0.3 $\mu$m Al$_2$O$_3$ slurry and later ultrasonically cleaned with ethanol and water. Then, 5 $\mu$L of the above suspension was dropped onto the GCE surface and dried in air. The modified electrode was later washed with deionized water three times to avoid the possible influence of residual Nafion for the subsequent tests.

Electrochemical characterization on the modified electrodes. Electrochemical performance measurements were carried out on a CHI 660e electrochemical workstation (CH Instruments, Shanghai, China). All the electrochemical measurements were based on a conventional three-electrode system, which consisted of a modified GCE electrode serving as the working electrode, a Ag/AgCl (in saturated KCl) electrode as the reference electrode, and platinum foil as the counter electrode.
Supplementary Figures

Figure S1. SEM images of the samples synthesized for 12 h at different temperatures. a, b) 140 °C; c, d) 160 °C; e, f) 200 °C.
Figure S2. SEM images of the samples synthesized at 180 °C for different reaction time. a, b) 6 h; c, d) 8 h; e, f) 10 h; g, h) 24 h.
Figure S3. FTIR spectrum of the $\gamma$-MnOOH nanowires.
Figure S4. Raman spectra of the $\gamma$-MnOOH nanowires.
Figure S5. TG curve of the γ-MnOOH nanowires.
Figure S6. SEM images of the γ-MnOOH nanowires after 4000 s for GOR. a) Samples modified on the GCE; b-d) High-magnification images of the selected area in a).
Figure S7. The electrochemical impedance spectra of the γ-MnOOH nanowires before and after GOR cycling at room temperature.
Figure S8. CV curves in NaOH (0.1 M) when adding different concentrations of Glu with different mass loadings. a) 4 mg mL\(^{-1}\); b) 3 mg mL\(^{-1}\); Current-time response with the addition of 20 μM Glu at different potentials of 0.40, 0.50 and 0.60 V in 0.1 M NaOH with different mass loadings. c) 4 mg mL\(^{-1}\); d) 3 mg mL\(^{-1}\).
Figure S9. Electrochemical performances of the $\gamma$-MnOOH nanowires with different mass loadings (4 and 3 mg mL$^{-1}$). a) Current-time response curves at 0.60 V with successive addition of different amounts of Glu in 0.1 M NaOH; b) Current-time response curves with successive addition of 100 $\mu$M Glu for 10 times into 0.1 M NaOH at 0.60 V; c) Current-time response curves with addition of 100 $\mu$M Glu, 5 $\mu$M AA, 5 $\mu$M UA, 5 $\mu$M DA, 5 $\mu$M NaCl, and 100 $\mu$M Glu into 0.1 M NaOH at 0.60 V. d) Plots of the electrocatalytic current of Glu vs its concentrations in the range of 0.5 $\mu$M to 265.5 $\mu$M.
Figure S10. The stability of the response current for the $\gamma$-MnOOH nanowires after the addition Glu solution (100 $\mu$M) during 4000 s with different mass loadings.
### Supplementary Table

**Table S1.** Comparison of electrochemical performance of as-prepared $\gamma$-MnOOH nanowires with other Mn-based materials from literature.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Detection limit (μM)</th>
<th>Linear range (μM)</th>
<th>Sensitivity (μA mM$^{-1}$ cm$^{-2}$)</th>
<th>Ref.</th>
</tr>
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<tr>
<td>$\alpha$-MnO$_2$/Co$_3$O$_4$</td>
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<td>up to 7000</td>
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<tr>
<td>MnO$_2$ nanowires</td>
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<td>5-2000</td>
<td>—</td>
<td>2</td>
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<tr>
<td>Pt/Au-MnO$_2$</td>
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<td>100-3000</td>
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<td>$\gamma$-MnOOH nanowires</td>
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<td><strong>0.5-6065</strong></td>
<td><strong>6.936</strong></td>
<td><strong>This work</strong></td>
</tr>
</tbody>
</table>

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*a) TMB: 3,3′,5,5′-tetramethylbenzidine  
*b) CNFs: carbon nanofibers*
Supplementary References

References


