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Supporting information

Hydrothermal synthesis of *γ*-MnOOH nanowires using sapless leaves as the reductants: an effective catalyst for the regio-specific epoxidation of *β*-ionone

Yuqing Luo[1], Xiaotian Guo[1], Wenjie Lu[1], Yong Liu[2,3], Lei Yu*[1] and Huan Pang*[1]

1. School of Chemistry and Chemical Engineering, Institute for Innovative Materials and Energy, Yangzhou University, Yangzhou, 225009, Jiangsu, P. R. China.

2. Collaborative Innovation Center of Nonferrous Metals of Henan Province, Henan Key Laboratory of High-Temperature Structural and Functional Materials, School of Materials Science and Engineering, Henan University of Science and Technology, Luoyang, China.

3. Henan Key Laboratory of Non-Ferrous Materials Science & Processing Technology, Henan University of Science and Technology, Luoyang, China.

1. Materials

Reagents were purchased with purities of more than 98% and used as received. Solvents were of analytical purity (AR) and used without any special treatment. All the reagents and solvents were purchased from Shanghai Sinopharm Chemical Reagent Co., and the sapless leaves were collected from the *Magnolia grandiflora* Linn tree in the campus. All aqueous solutions were freshly prepared with high purity water (18 MΩ cm).

2. Experimental Section

2.1 Synthesis of the γ-MnOOH nanowires

5.0 mg of $KMnO_4$ with 1.0 mg of natural leaves (from a *Magnolia grandiflora* Linn tree; the sapless leaves were washed with deionized water and ethanol, dried naturally in air, then cut into tiny pieces with scissors), were mixed with 10.0 mL deionized water. The solution mixture was subsequently transferred into a 25 mL of Teflon-lined stainless-steel autoclave through a mild hydrothermal process (180 °C for 12 h) and then cooled to room temperature naturally. According to different densities, the resulting precipitate was easily separated from the remaining organic compounds. Finally, the product was thoroughly washed with deionized water several times, and dried in air.

2.2 Method of γ-MnOOH nanowires-catalyzed selective epoxidation of β-ionone

In a glass reaction tube, 1 mmol of *β*-ionone (192.3 mg), 2 mg of *γ*-MnOOH nanowires, a piece of magnetic bar and EtOAc (1 mL) were added successively. The tube was then charged with O_2 (the O_2 from oxygen cylinder was introduced into the tube via a glass pipe putting at its bottom at the speed of 0.8 cm^3/s for one mininute) and sealed by a Teflon plug. The resultant mixture was stirred at 80 °C for 48 h. After cooled to room temperature, the solvent was removed by distillation under vacuum with a rotary evaporator and the residue was separated by preparative thin-layer chromatography on silica gel GF254 (eluent: petroleum ether/EtOAc, 10 : 1) to give 104.2 mg of epoxide **3** (50% yield).

*2.3 Characterization data of epoxide **3***

Oil; IR (film): 2935, 1752, 1674, 1626, 1462, 1429, 1361, 1301, 1252, 1171, 1046, 985, 940, 909, 834, 788 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 6.98 (d, *J* = 15.6 Hz, 1H), 6.24 (d, *J* = 15.6, 1H), 2.24 (s, 3H), 1.90-1.85 (m, 1H), 1.75-1.70 (m, 1H), 1.46-1.38 (m, 3H), 1.21 (s, 6H), 1.10-1.02 (m, 1H), 0.89 (s, 3H).

*2.4 Details for the control experiment testing the stability of the epoxide **3***

In a glass reaction tube, 1 mmol of epoxide **3**, 2 mg of *γ*-MnOOH nanowires, a piece of magnetic bar and EtOAc (1 mL) were added successively. The tube was then charged with O_2 (the O_2 from oxygen cylinder was introduced into the tube via a glass pipe putting at its bottom at the speed of 0.8 cm^3/s for one mininute) and sealed by a Teflon plug. The resultant mixture was stirred at 80 °C for 48 h. After cooled to room temperature, the solvent was removed by distillation under vacuum with a rotary evaporator and the residue was separated by preparative thin-layer chromatography on silica gel GF254 (eluent: petroleum ether/EtOAc, 10 : 1) to give 154.3 mg of epoxide **3** (74% yield, i.e. 26% decomposition).

3. Material characterization

3.1 The characterization of γ-MnOOH nanowires

The morphological features were characterized by field emission scanning electron microscopy (FESEM, Zeiss-Supra55), high resolution transmission electron microscopy (HRTEM, Tecnai G2F30 S-TWIN), and energy dispersive X-ray spectrometry (EDS) mapping. X-ray diffraction (XRD) patterns were examined on a Bruker D8 Advanced X-ray Diffractometer (Cu-Kα radiation: λ = 0.15406 nm). The chemical states were measured using an Axis Ultra X-ray photoelectron spectroscope (XPS, Kratos Analytical Ltd., UK) equipped with a standard monochromatic Al-Kαsource (hv = 1486.6 eV). Fourier transform infrared (FTIR) transmission spectra were obtained on a BRUKER-EQUINOX-55 IR spectrophotometer. Thermogravimetric measurements were determined via a PerkinElmer Pyris 1 TGA thermogravimetric analysis (TGA) instrument.

*3.2 The characterization of epoxide **3***

IR spectra were measured on a Bruker Tensor 27 Infrared spectrometer. ^{1}H NMR spectrum was recorded on a Bruker Avance instrument (400 MHz) using $CDCl_3$ as the solvent and Me_4Si as the internal standard. Chemical shifts for ^{1}H NMR were referred to internal Me_4Si (0 ppm) and *J*-values were shown in Hz.

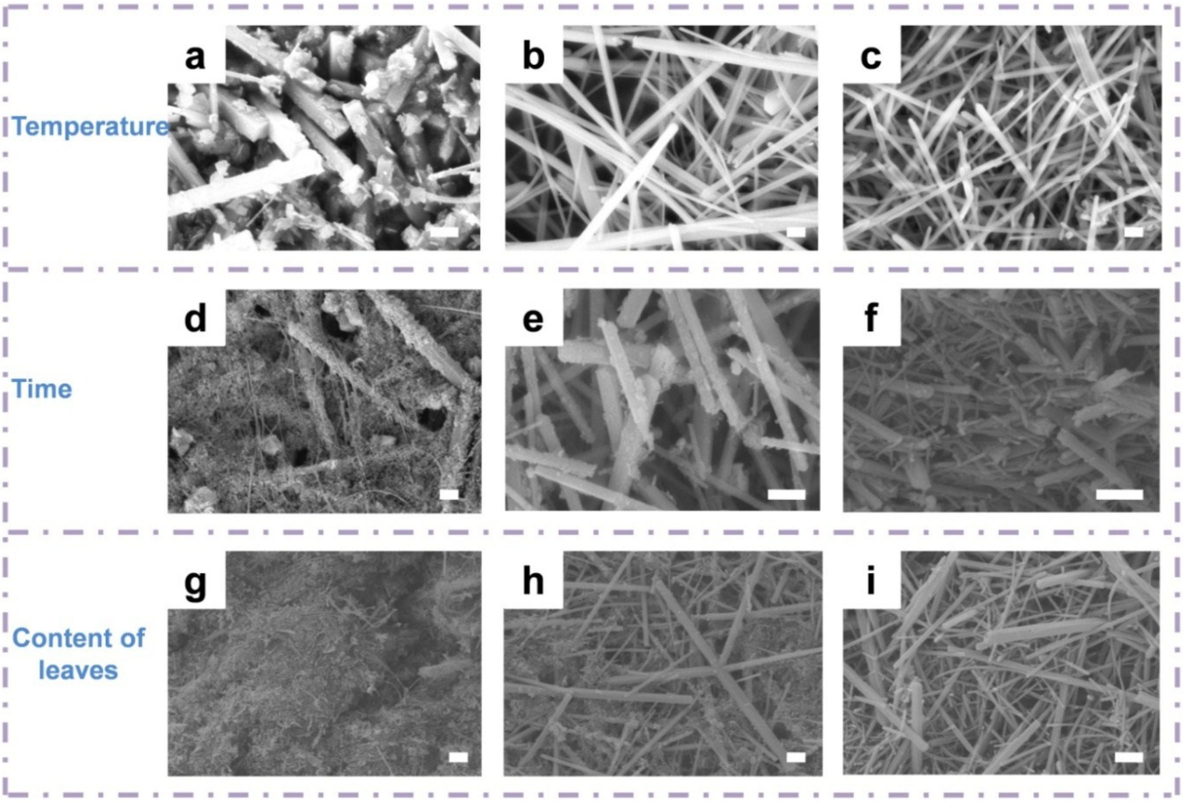

Figure S1. a-c) SEM images of the samples synthesized at different temperatures (140 °C, 160 °C, 200 °C, respectively) for 12 h with 1.0 mg of leaves; d-f) SEM images of the samples synthesized at 180 °C for different reaction times (8 h, 10 h, 24 h, respectively) with 1.0 mg of leaves; g-h) SEM images of the samples synthesized at 180 °C for 12h with different content of the added content of sapless leaves (0.5 mg, 2.0 mg, 4.0 mg, respectively). (scale bar: 200 nm)

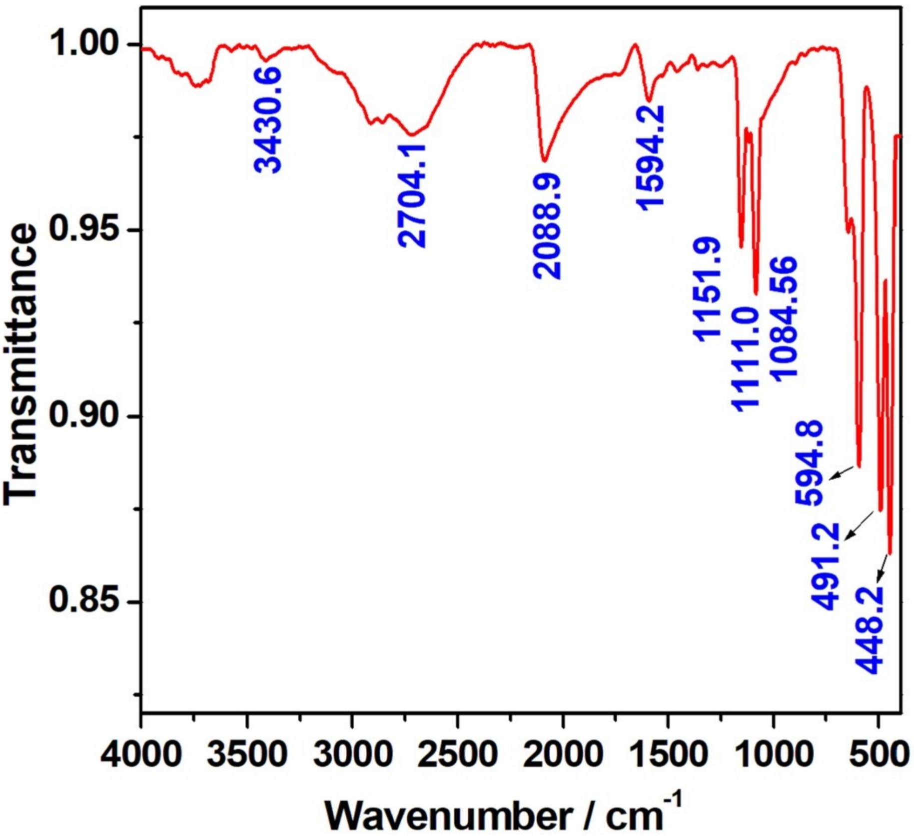

Figure S2. FTIR spectrum of the sample.

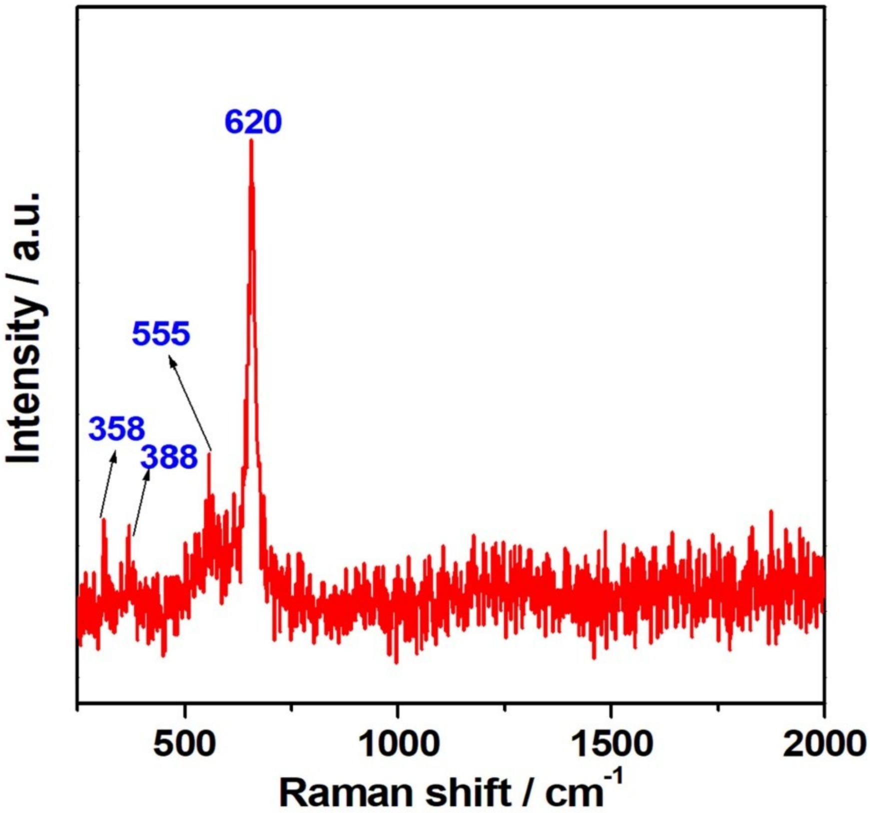

Figure S3. Raman spectra of the *γ*-MnOOH nanowires.

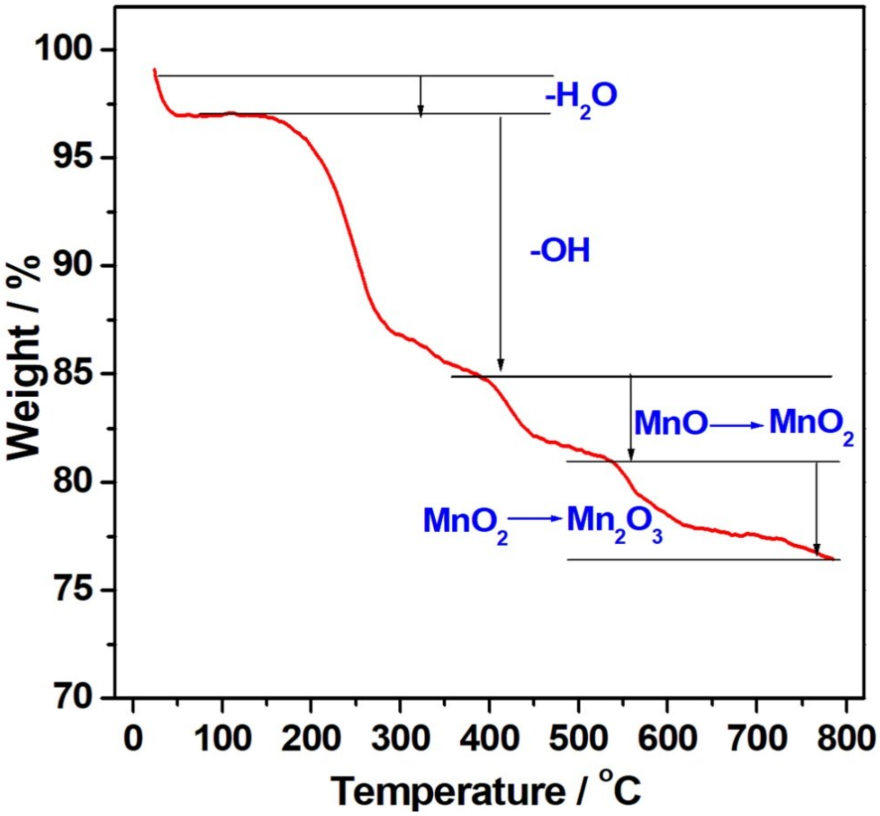

Figure S4. TGA curve of the sample in air atmosphere (50-800 °C).

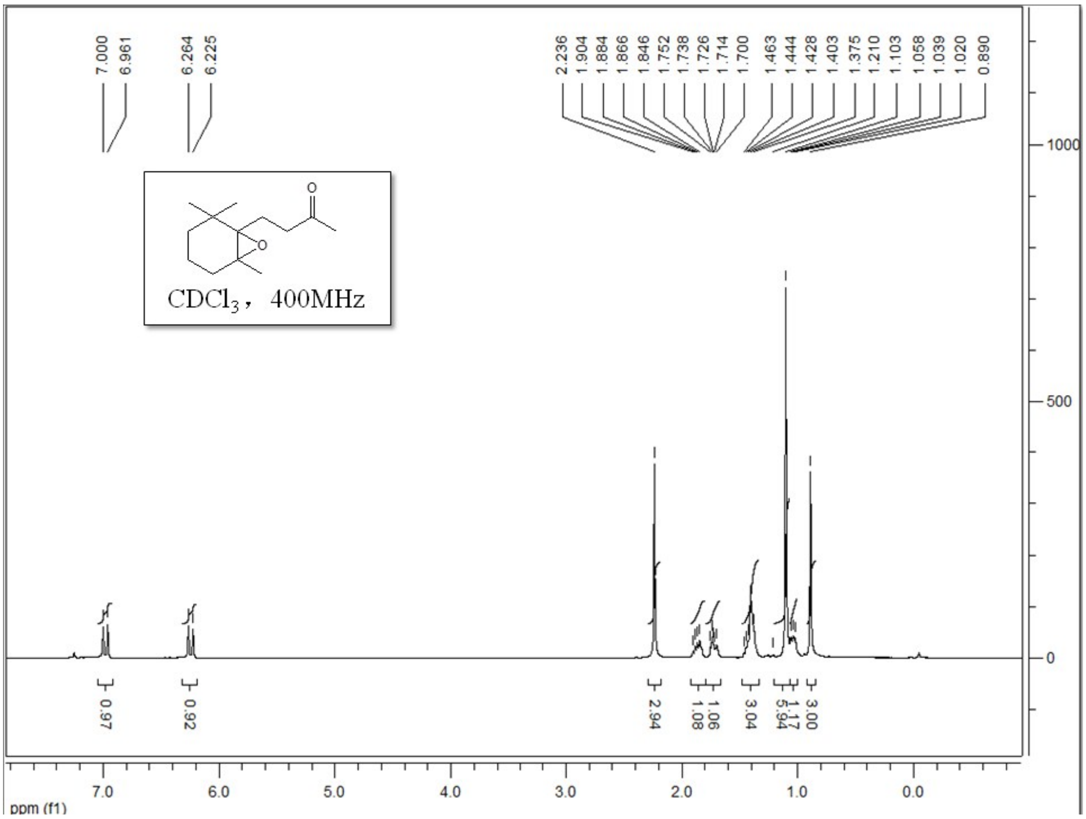

Figure S5. The ^{1}H NMR spectrum of epoxide **3**.

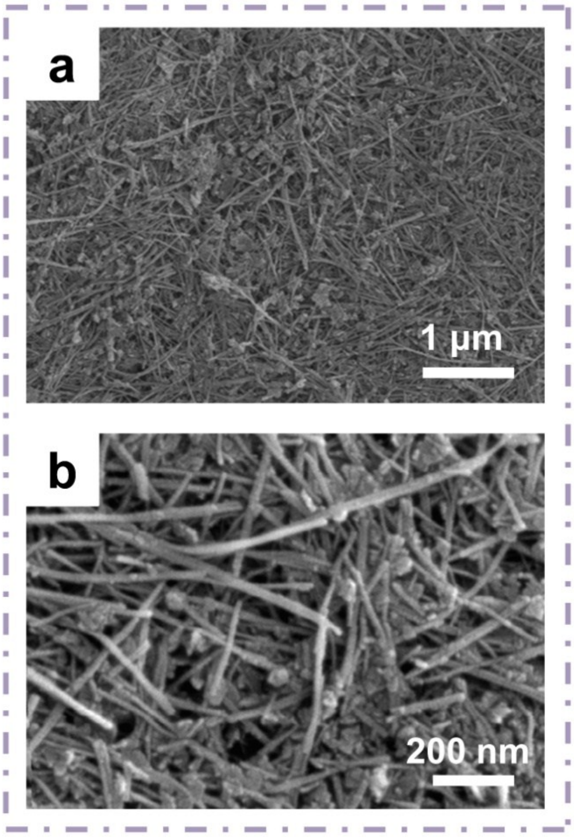

Figure S6. a) Low-magnification and b) high-magnification SEM images of the *γ*-MnOOH nanowires after the reaction.

As demonstrated in the SEM images (**Figure S6**), the *γ*-MnOOH samples well maintain their initial morphologies after the organic reaction, indicating good structural integrity. It is obvious that the nanowires become thinner (below 25 nm in diameter) and shorter when compared to the nanowires prior to the reaction, and the substance adhered to the wire surfaces may be the reaction intermediates or the partly collapsed nanowires.

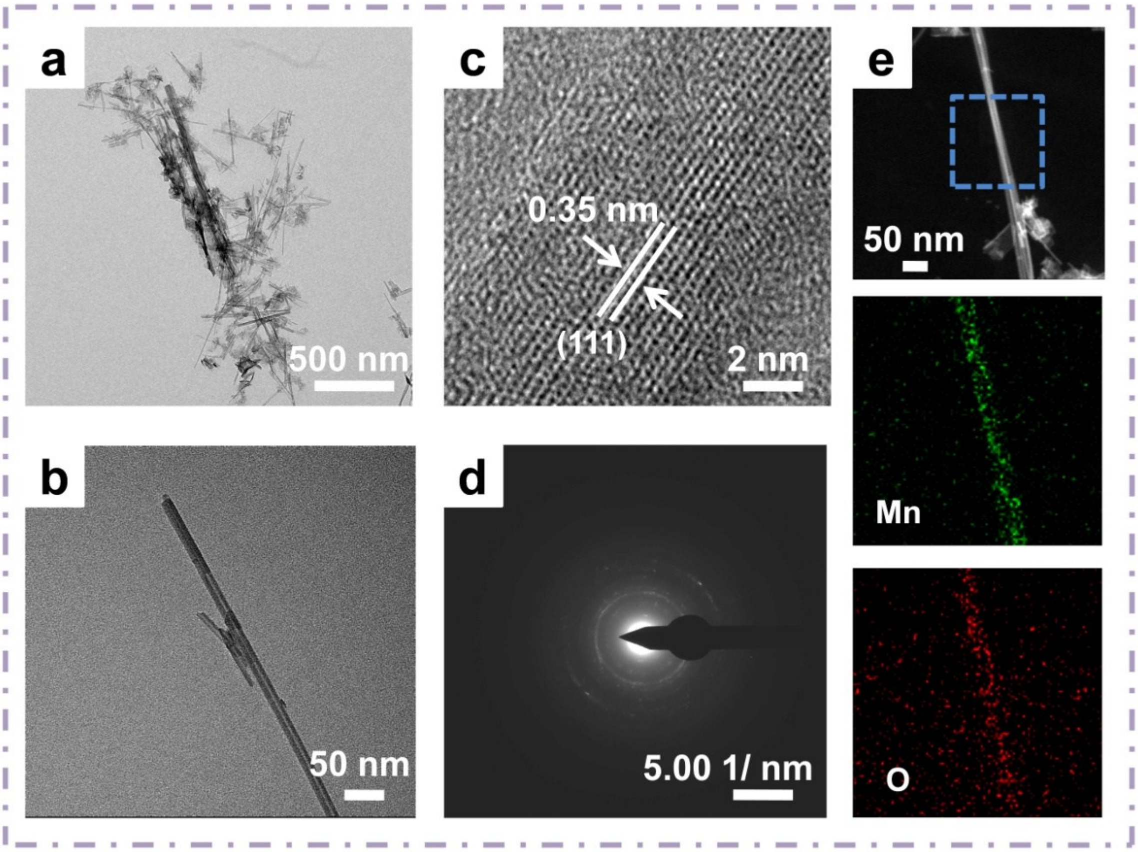

Figure S7. a, b) TEM images; c) HRTEM image; d) the SAED pattern; e) EDX-elemental mapping images of Mn and O from the chosen area of the *γ*-MnOOH nanowires after the catalytic reaction.

TEM images show moderate aggregation of the used catalyst in **Figure S7**a and b, which corresponds with the results of the morphologies shown in the SEM images. Meanwhile, the lattice fringes in **Figure S7**c are still relatively clear, with interlayer spacings of approximately 0.35 nm in average. In addition, the SAED pattern in **Figure S7**d demonstrates that the nanowires keep their monoclinic nature after the reactions. EDX-elemental mapping images (**Figure S7**e) reveal the distribution of Mn and O on the surface of the nanowires.

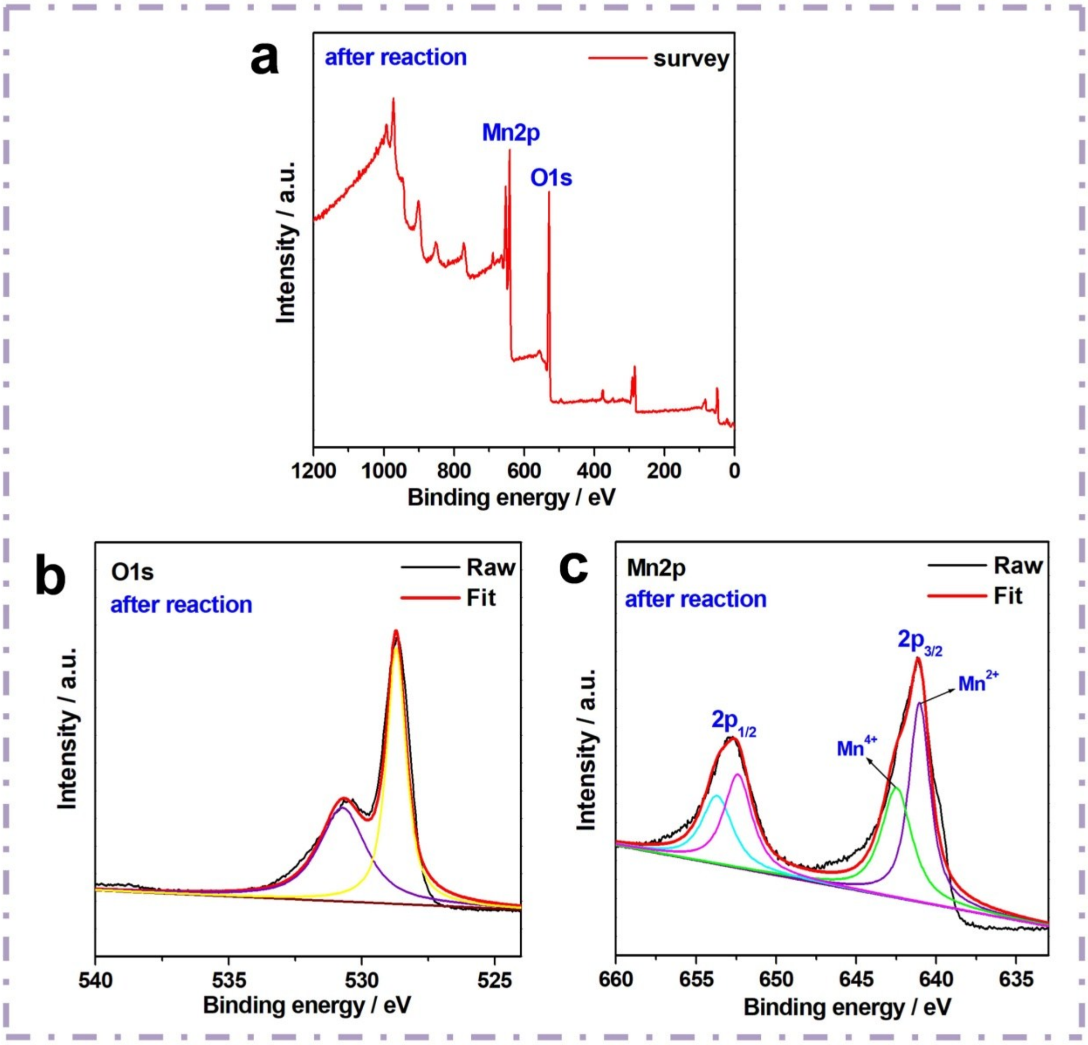

Figure S8. a) XPS survey spectrum of the *γ*-MnOOH nanowires; high-resolution spectra of b) O 1s and c) Mn 2p for the *γ*-MnOOH nanowires after the reaction.

In **Figure S8**a, the XPS survey spectrum displays that Mn and O are still the main elements existing in the sample after the catalytic reaction. The high-resolution XPS spectra of O1s and Mn2p, respectively, in **Figure S8**b and c resemble those of the initial *γ*-MnOOH nanowires, and the average state of Mn is kept at Mn(III).

Catalyst	Oxidant	Solvent	Condition (T, t)[a)]	Yield (%)	Ref.
Se/C	H_2O_2	EtOAc	80 °C, 24 h	62	[1]
Se/C	O_2	EtOAc	80 °C, 24 h	26	[1]
$[3,5\text{-}(CF_3)_2C_6H_3Se]_2$	H_2O_2	MeCN	80 °C, 24 h	70	[2]
Pt/MCM-41	O_2	$CHCl_3$	80 °C, 22 h	73	[3]
Au/ZSM-5	O_2	$CHCl_3$	50 °C, 22 h	48	[4]
γ-MnOOH nanowires	**O_2**	**EtOAc**	**80 °C, 48 h**	**50**	**This work**
— (blank experiment)	O_2	EtOAc	80 °C, 48 h	8	This work

a) T, t: temperature, time

Table S1. Comparison of the performance of different catalysts for the regio-specific epoxidation of *β*-ionone.

References

1 Y. Yang, X. Fan, H. Cao, S. Chu, X. Zhang, Q. Xu and L. Yu, *Catal. Sci. Technol.*, 2018, **8**, 5017–5023.

2 L. Yu, Z. Bai, X. Zhang, X. Zhang, Y. Ding and Q. Xu, *Catal. Sci. Technol.*, 2016, **6**, 1804–1809.

3 Z. Peng and G. Lu, *Catal. Letters*, 2007, **117**, 126–129.

4 Z. Peng and G. Lu, *Chinese J. Catal.*, 2007, **3**, 239–245.