

Electronic Supplementary Information (ESI)

Nanostructured MnO₂: an efficient and robust water oxidation catalyst

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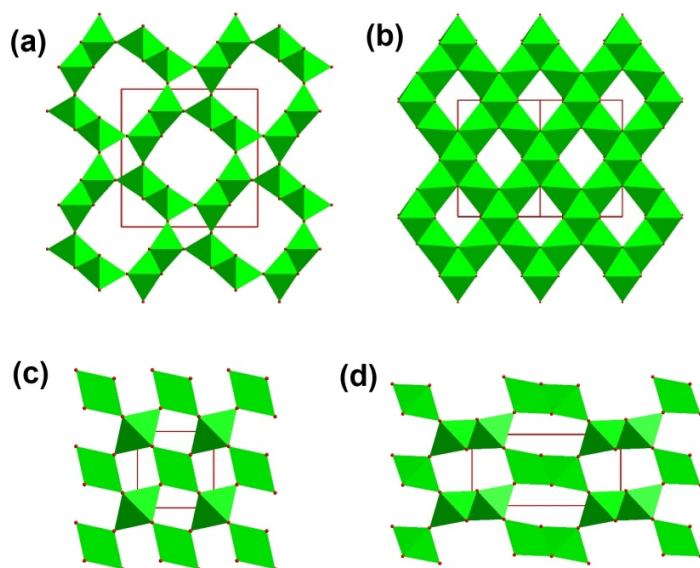


Figure S1: Four polymorphs of MnO₂: (a) α -MnO₂, (b) λ -MnO₂, (c) β -MnO₂, and (d) γ -MnO₂.

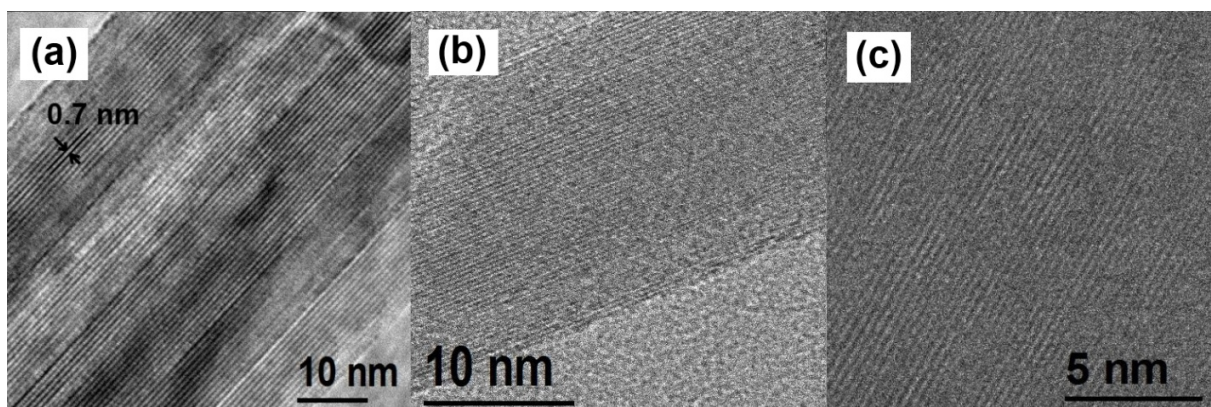


Figure S2: HRTEM images for (a) α -MnO₂ nanotubes, (b) α -MnO₂ nanowires, and (c) β -MnO₂ nanowires.

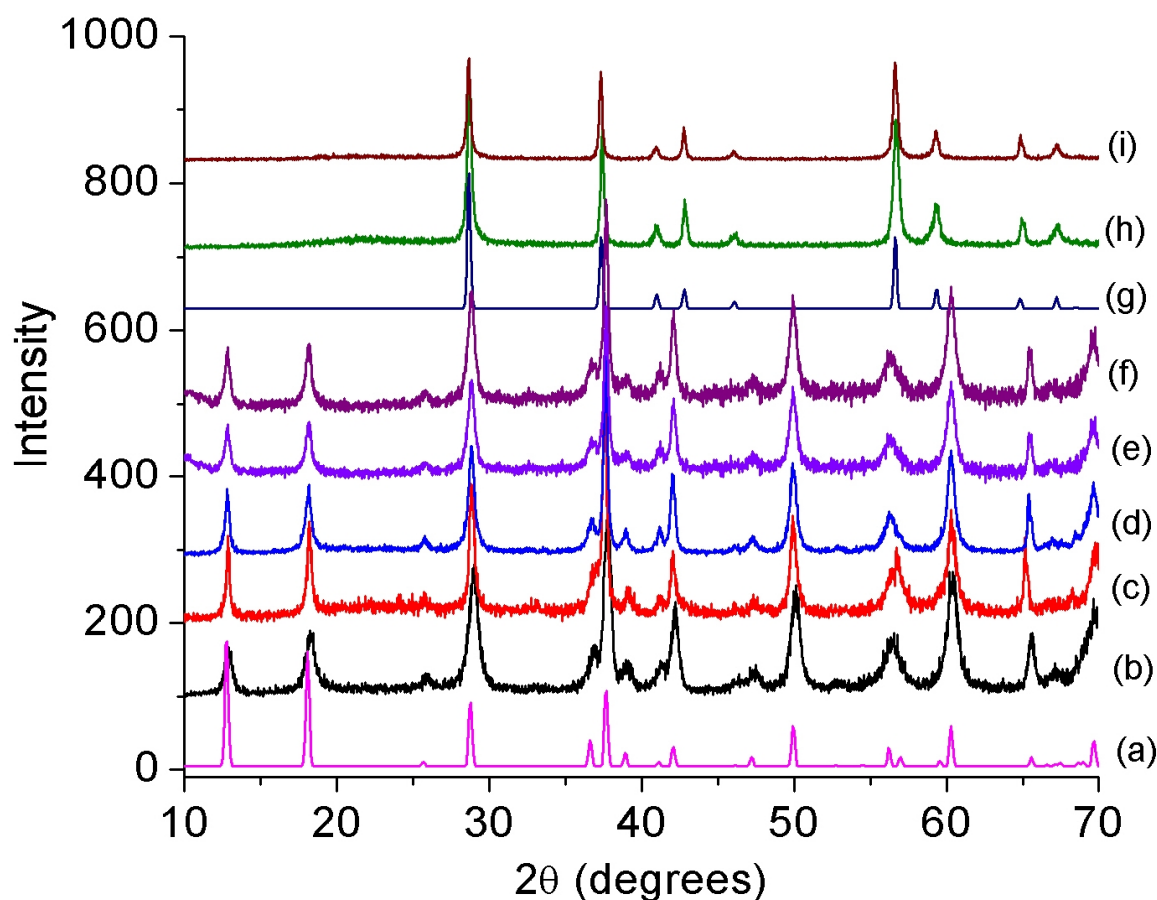


Figure S3: PXRD patterns for (a) α - MnO_2 standard, (b) as-synthesized α - MnO_2 nanotubes, (c) as-synthesized α - MnO_2 nanowires, (d) bulk α - MnO_2 particles, (e) α - MnO_2 nanotubes after acid treatment, (f) α - MnO_2 nanotubes after grinding, (g) β - MnO_2 standard, (h) β - MnO_2 nanowires, and (i) β - MnO_2 nanowires after acid treatment.

Experimental details for synthesis of α - MnO_2 nanotubes:

The synthesis of α - MnO_2 nanotubes containing 10% K^+ was adapted from a recent report.¹ In a typical synthesis, 0.3 g of KMnO_4 was dissolved in water and 0.8 g of concentrated hydrochloric acid was added under stirring. The mixture was transferred and sealed in a hydrothermal bomb with PTFE liner, followed by a thermal treatment in an oven at 140 °C for 12 h. After cooling to room temperature, the resulting mixture was filtered, washed by water, and dried at 60 °C.

1. Luo, J. *et al.* Synthesis of single-crystal tetragonal α - MnO_2 nanotubes. *Journal of Physical Chemistry C* **112**, 12594-12598, doi:10.1021/jp8052967 (2008).

Experimental details for synthesis of α - MnO_2 nanowires:

The synthesis of α -MnO₂ nanowires was adapted from a recent report.² In a typical synthesis, 0.394 g of KMnO₄ was dissolved in 35 mL of water and 0.17 g of MnSO₄·H₂O was added under stirring. The mixture was transferred and sealed in a hydrothermal bomb with PTFE liner, followed by a thermal treatment in an oven at 180 °C for 16 h. After cooling to room temperature, the resulting mixture was filtered, washed by water, and dried at 60 °C.

2. Wang, X., Li, Y. D. Synthesis and formation mechanism of manganese dioxide nanowires/nanorods. *Chem. Eur. J.* 2003, 9, 300.

Experimental details for synthesis of β -MnO₂ nanowires:

The synthesis of β -MnO₂ nanowires was adapted from a recent report.³ In a typical synthesis, 0.21 g of KMnO₄ was dissolved in 35 mL of water and 0.23 g of MnSO₄·H₂O was added under stirring. The mixture was transferred and sealed in a hydrothermal bomb with PTFE liner, followed by a thermal treatment in an oven at 160 °C for 16 h. After cooling to room temperature, the resulting mixture was filtered, washed by water, and dried at 60 °C.

3. Wang, X., Li, Y. D. Synthesis and formation mechanism of manganese dioxide nanowires/nanorods. *Chem. Eur. J.* 2003, 9, 300.

Experimental details for synthesis of bulk α -MnO₂ particles:

To synthesize bulk α -MnO₂ the general procedure prepared by C.S. Johnson et al. was followed.⁴ 10g of Mn₂O₃ (Sigma-Aldrich ~325mesh) was mixed with 100mL of a 6M H₂SO₄. The flask was attached to a reflux column to prevent water evaporation, and the solution was heated at 105 °C overnight. Afterwards the product was filtered and washed via vacuum filtration with water and ethanol. The material was then heated for 8 hours at 250 °C in a tube furnace under vacuum to remove any remaining moisture. The tube was then opened in an argon filled glovebox to ensure no water was able to absorb to the material.

4. Johnson, C. S.; Dees, D. W.; Mansuetto, M. F.; Thackeray, M. M.; Vissers, D. R.; Argyriou, D.; Loong, C. K.; Christensen, L., Structural and electrochemical studies of alpha-manganese dioxide (α -MnO₂). *Journal of Power Sources* **1997**, 68 (2), 570-577.

Experimental details for acid treatment of α -MnO₂ nanotubes and β -MnO₂ nanowires:

The acid treatment was carried out as follows: 1 g of as-synthesized nanostructured MnO₂ was dispersed in 100 mL of 1M HNO₃ aqueous solution and stirred 24 h at room temperature. The mixture was filtered, washed with water, and dried at 60 °C.

Experimental Details:

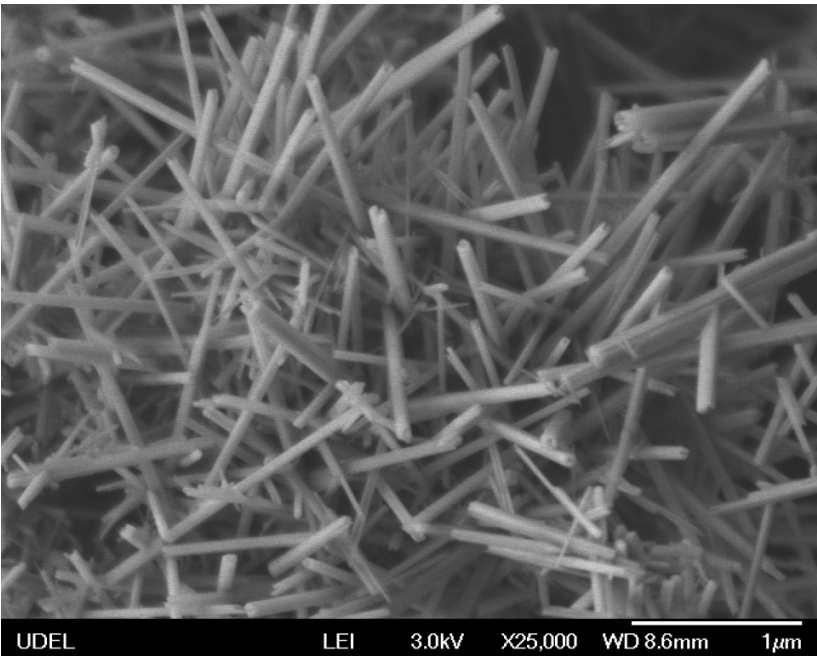
Scanning electron microscope (SEM) images were recorded on a JEOL JSM7400F microscope with a field emission gun capable of 1.5 nm resolution. The imaging using the SEM and elemental analysis using energy dispersive analysis (EDX) was done at a voltage of 3 kV and 15 kV, respectively. Transmission electron microscope (TEM) images were recorded on a field emission transmission electron microscope JEM-2010F FasTEM. Powder X-ray diffraction (PXRD) results were collected on a Philips X'pertdiffractometer using a Cu K α source. N₂ adsorption isotherms were collected on a Micromeritics ASAP 2010 at 77 K. All the samples were degassed at 423 K under vacuum before the measurements. The Clack electrode system, Oxygraph from Hansatech Instruments Ltd, was used for oxygen detection. The light source utilized is a 300W Xe Lamp (Newport Oriel) fitted with a 400 nm cut-off filter.

Surface Mn atom calculations:

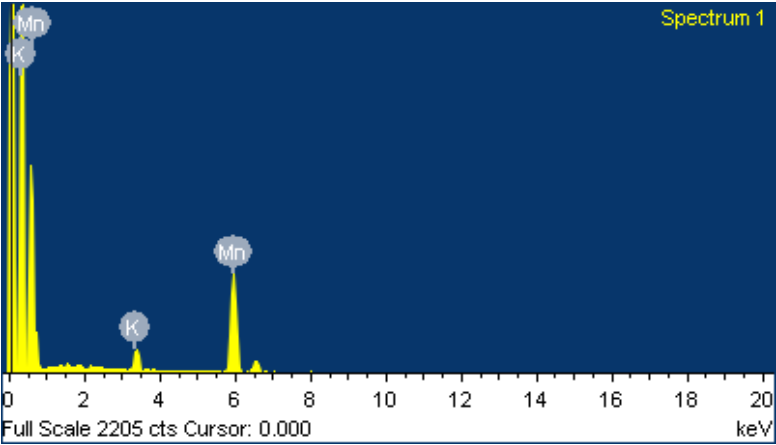
α -MnO₂: Using the unit cell of length 9.8Å with 8Mn atoms on a face, the density of surface Mn atoms was estimated to be 8.3×10^{18} atoms/m². By using BET surface area, we could obtain the TOF per surface Mn.

β -MnO₂: Using the unit cell of length 4.3Å with 2 Mn atoms on a face, the density of surface Mn atoms was estimated to be 1.08×10^{19} atoms/m². By using BET surface area, we could obtain the TOF per surface Mn.

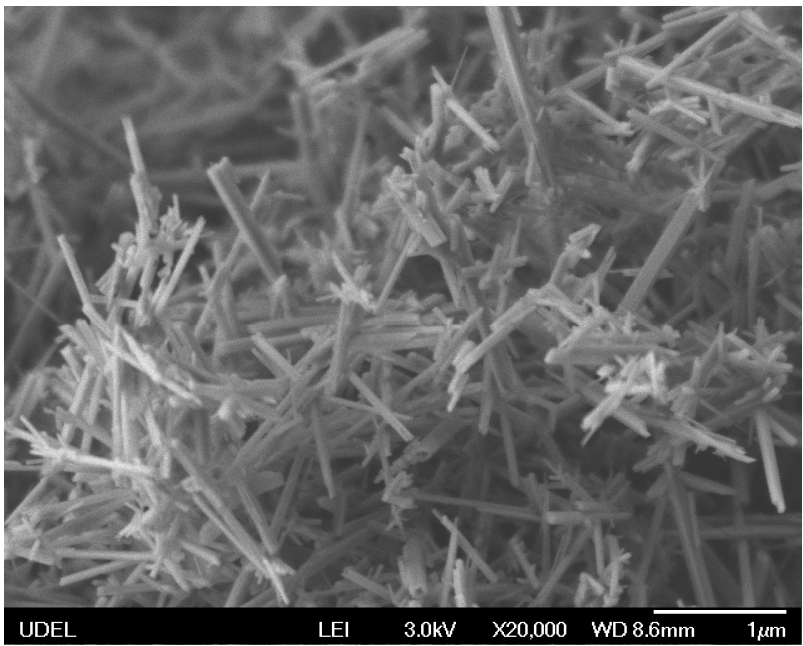
SEM images and EDX results of as-synthesized α -MnO₂ nanotubes:



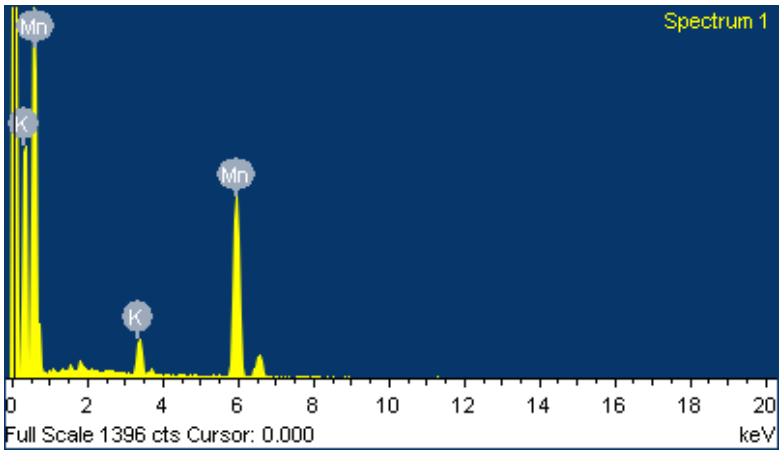
Element	Weight%	Atomic%
K K	7.71	10.51
Mn K	92.29	89.49
Totals	100.00	



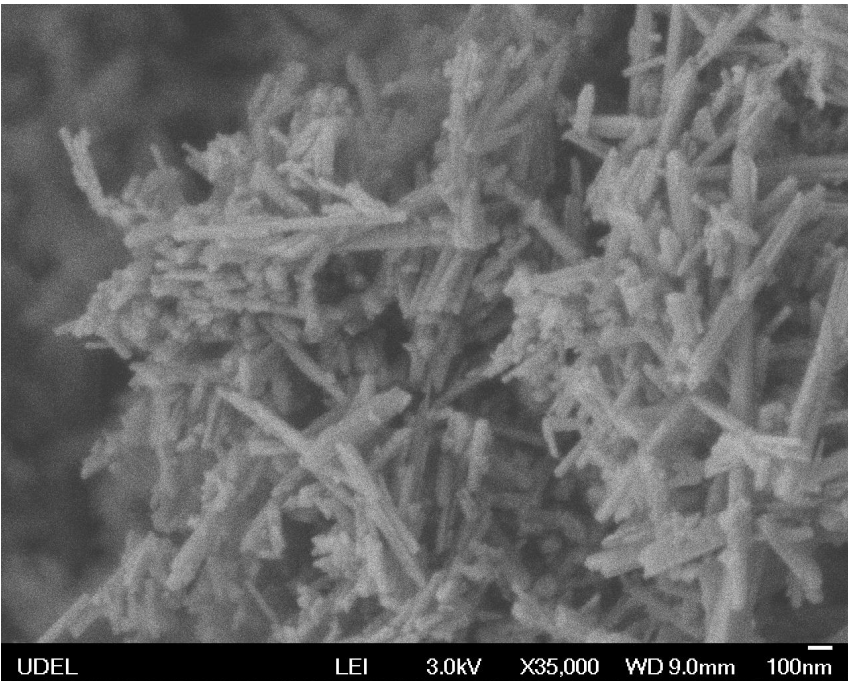
SEM images and EDX results of acid treated α -MnO₂ nanotubes:



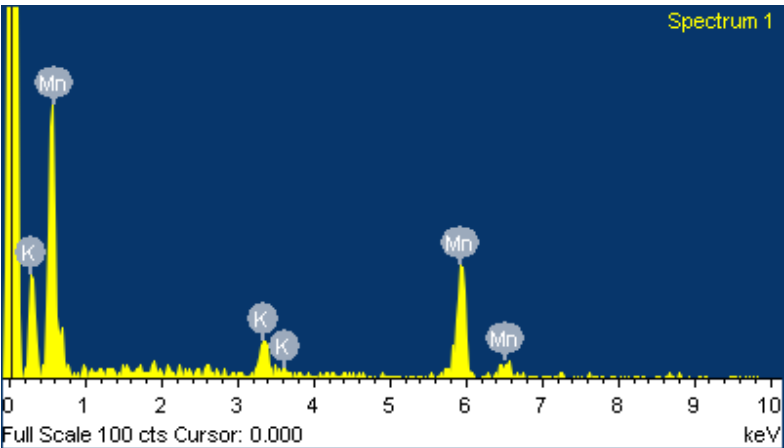
Element	Weight%	Atomic%
K K	7.06	9.64
Mn K	92.94	90.36
Totals	100.00	



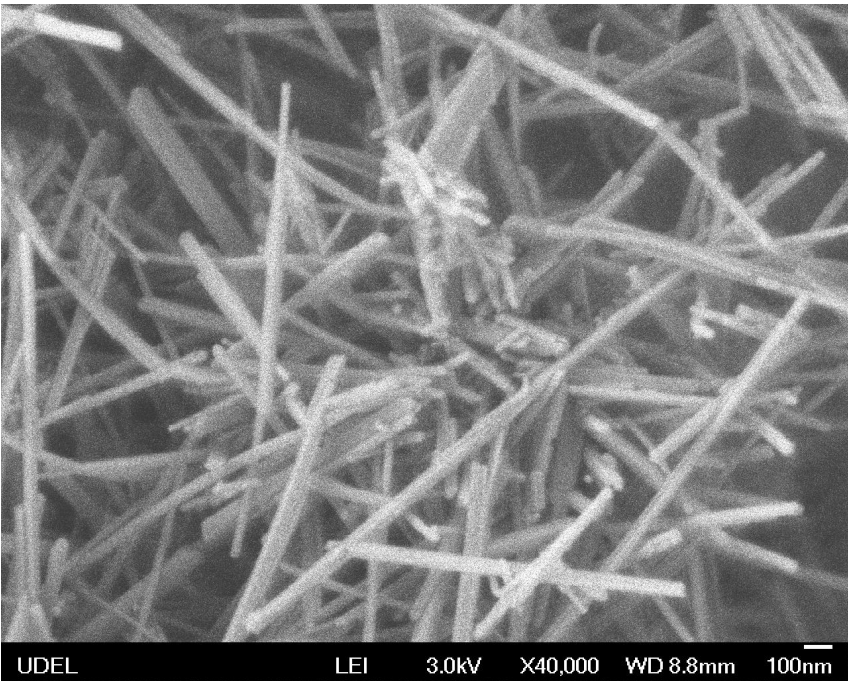
SEM images and EDX results of crushed α -MnO₂ nanotubes:



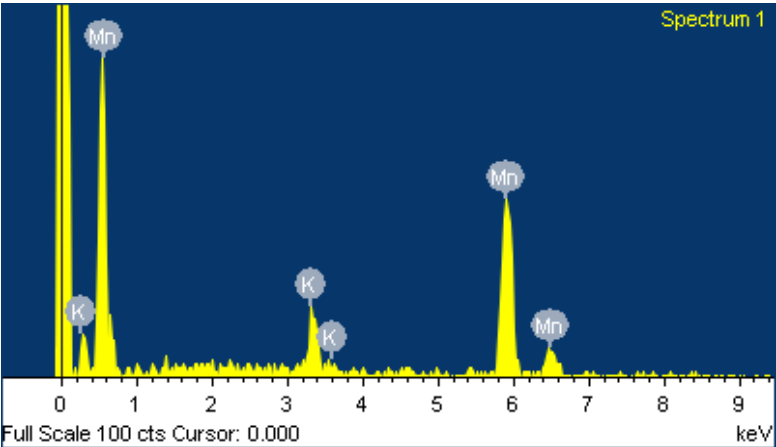
Element	Weight%	Atomic%
K K	8.07	10.98
Mn K	91.93	89.02
Totals	100.00	



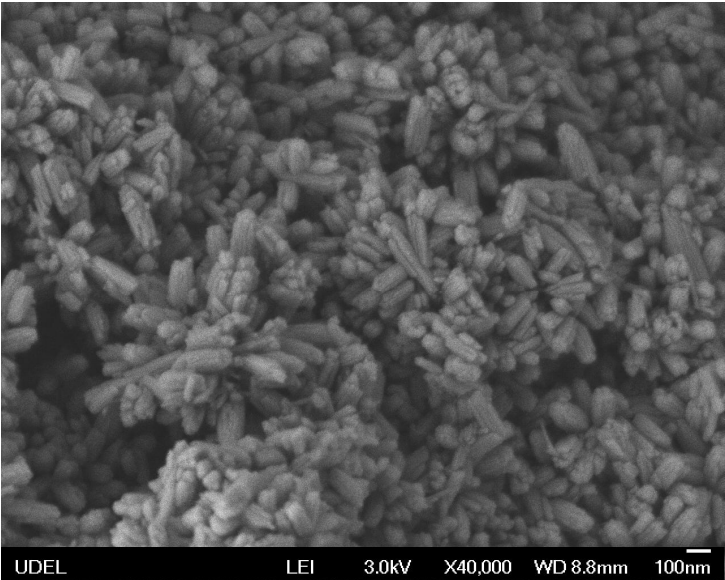
SEM images and EDX results of α -MnO₂ nanowires:



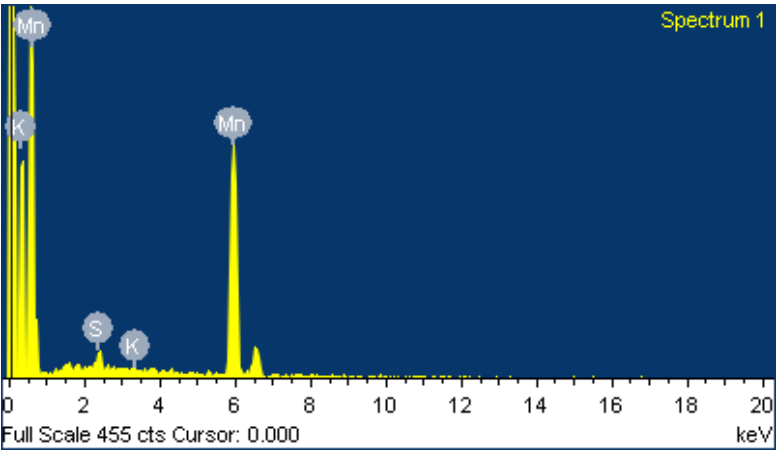
Element	Weight%	Atomic%
K K	8.01	10.90
Mn K	91.99	89.10
Totals	100.00	



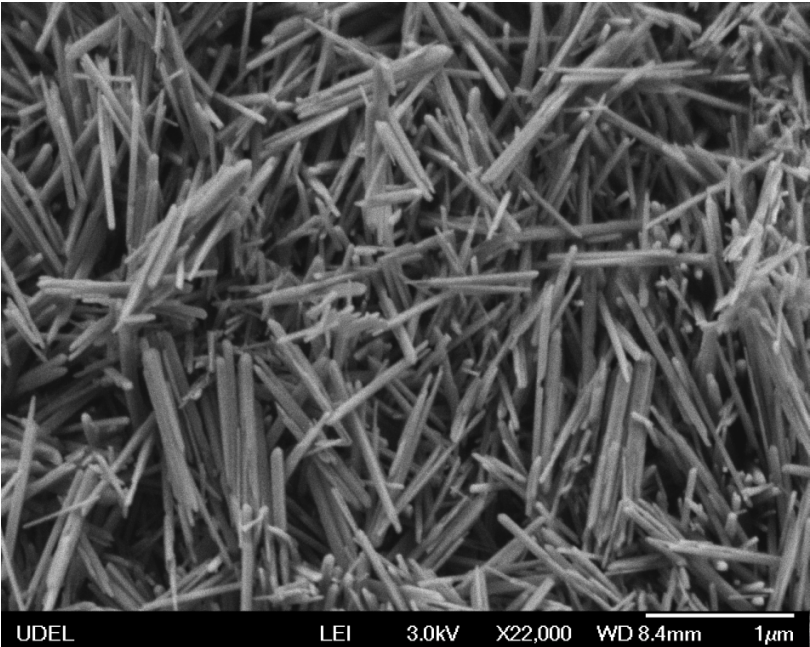
SEM images and EDX results of bulk α -MnO₂ particles:



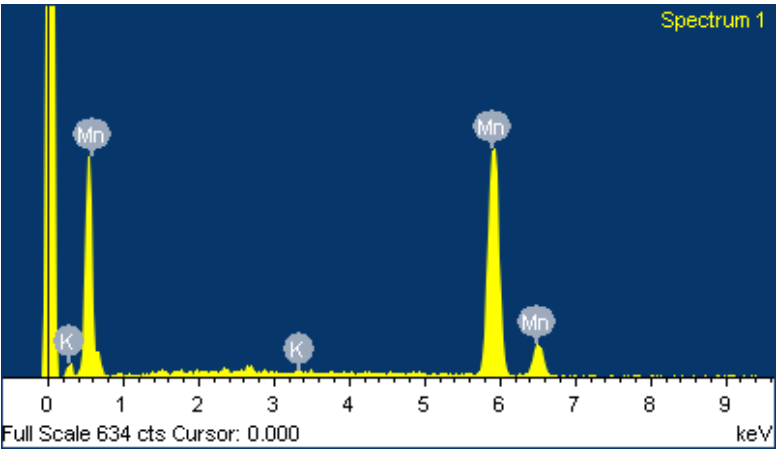
Element	Weight%	Atomic%
S K	2.30	3.87
K K	-0.15	-0.20
Mn K	97.85	96.33
Totals	100.00	



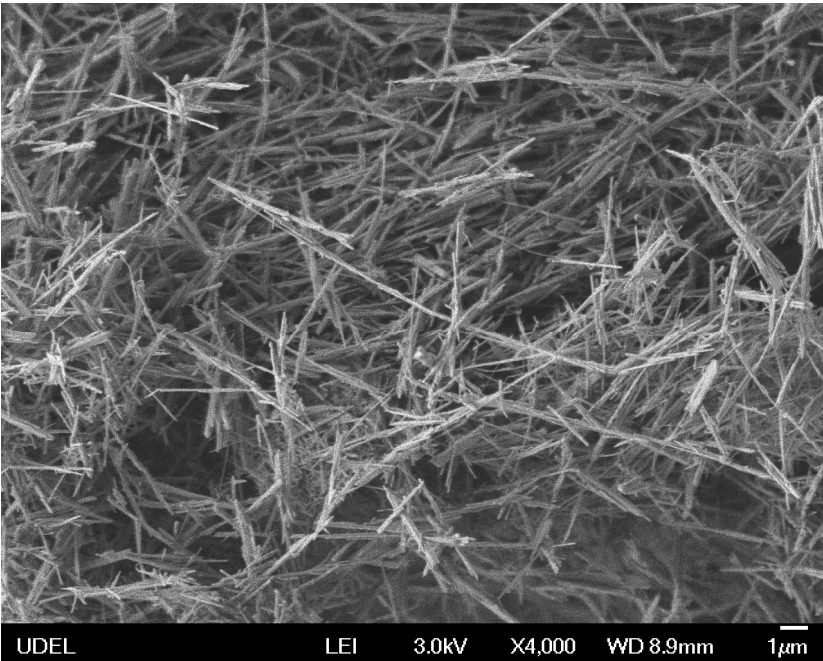
SEM images and EDX results of as-synthesized β -MnO₂ nanowires:



Element	Weight%	Atomic%
K K	0.07	0.10
Mn K	99.93	99.90
Totals	100.00	



SEM images and EDX results of acid treated β -MnO₂ nanowires:



Element	Weight%	Atomic%
K K	0.78	1.10
Mn K	99.22	98.90
Totals	100.00	

