Supporting Information for

Facile synthesis of single-crystalline MnO_2 nanowire arrays with high photothermal catalytic activity

Tetsuro Soejima,[a, b]* Haruki Inoue,[b] Keigo Egashira,[b] Yaozong Yan[b] and Hiroaki Tada[a, b]*

[a] Department of Applied Chemistry, Faculty of Science and Engineering, Kindai University, 3-4-1, Kowakae, Higashi-Osaka, Osaka 577-8502, Japan.

[b] Graduate School of Science and Engineering, Kindai University, 3-4-1, Kowakae, Higashi-Osaka, Osaka 577-8502, Japan.

E-mail: soejima@apch.kindai.ac.jp, h-tada@apch.kindai.ac.jp

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Materials.

All aqueous solutions were prepared with distilled water. Glass slides (18 mm × 32 mm × 0.13-0.17 mm) as the substrate to grow TiO_2 nanocorals and MnOOH and MnO_2 nanowire arrays (NWA) were purchased from Matsunami Glass Ind., Ltd. Acetonitrile, phenazine-2,3-diamine, and hydrochloric acid (HCl) were purchased from FUJIFILM Wako Pure Chemical Corporation. Hydrogen peroxide for the photothermal catalytic reaction, sodium carbonate (Na_2CO_3), and hexamethylenetetramine (HMT) were purchased from KISHIDA CHEMICAL Co.,Ltd. Manganese(II) nitrate hexahydrate ($Mn(NO_3)_2 \cdot 6H_2O$) and β-MnO_2 nanoparticles were purchased from KANTO CHEMICAL CO.,INC. *o*-Phenylenediamine and hydrogen peroxide (35%, H_2O_2) for the syntheses of TiO_2 and manganese oxide nanostructures were purchased from Tokyo Chemical Industry Co., Ltd. Titanium(IV) oxysulfate hydrate ($TiOSO_4 \cdot nH_2O$, $n \sim 5$) was purchased from NACALAI TESQUE, INC.

Growth of TiO_2 nanocorals on glass substrate

71.25 mg of $TiOSO_4 \cdot nH_2O$ and 60 µL of 35% H_2O_2 aqueous solution were added to 19 mL of water, and then the pH was adjusted to 1.30 with the addition of concentrated HCl. After $TiOSO_4$ was completely dissolved, 42.0 mg of Na_2CO_3 was added to the aqueous solution of $TiOSO_4$–H_2O_2. The obtained aqueous solution was poured in glass vials with polypropylene screw caps. A glass slide was immersed and placed against the inside wall. The sample was heated at 80 °C for 15 h in a constant-temperature drying oven. The obtained thin films were washed with water, and dried in air at room temperature. The as-prepared film was calcined at 400 ºC for 2 h in an electric furnace to improve adhesion between TiO_2 nanocorals and the glass substrate. The TiO_2 nanocoral consists of a rutile overlayer with 400-500 nm thickness and an anatase underlayer with 50-100 nm thickness.

Growth of γ-MnOOH and β-MnO_2 nanowire arrays on TiO_2 nanocorals

45 µL of $Mn(NO_3)_2·6H_2O$ and 60 µL of H_2O_2 aqueous solution were added to 19 mL of water, and then 0.04 g of HMT was added to the aqueous solution of $Mn(NO_3)_2–H_2O_2$. The obtained aqueous solution was poured in a glass vial with a polypropylene screw cap after HMT has been dissolved. A substrate was immersed and placed against the inside wall. The sample was heated at 85 °C for 5 h. The obtained thin film was washed with water and dried in air at room temperature. The as-prepred film was calcined at 400 ºC for 2 h in an electric furnace to convert the as-grown γ-MnOOH into β-MnO_2.

Analysis of the prepared nanocrystals

X-ray diffraction (XRD) was performed using a Shimadzu XD-D1. Field-emission scanning electron microscopy (SEM) was performed using a Hitachi S-5000 and a Hitachi S-4800 type II. UV-vis-near infrared diffuse reflectance spectra were measured using a JASCO V-670 UV-Vis spectrophotometer with an integrating sphere. X-ray photoelectron spectroscopy (XPS) was performed using a Shimadzu KRATOS-AXIS Nova spectrometer (X-ray source operated at 15 kV) and a ULVAC-PHI VersaProbe 4 (X-ray source operated at 15 kV). The observed sample was sputtered using Pt-Pd alloy before SEM observation. The measured binding energies by the XPS were referenced to the C 1s line at 284.6 eV. TEM observations was performed using a JEOL JEM-4000EX (acceleration voltage, 400 kV). The photoluminescence (PL) spectra were collected by means of a JASCO FP-6000 spectrofluorometer with varying excitation wavelengths at -196ºC.

Catalytic and photothermal catalytic reactions

The oxidative coupling of OPD to DAP was carried out using a double jacket-type reaction cell in the dark and under illumination of simulated sunlight (PEC-L12-S17, Peccell technologies, Inc.) (AM 1.5 one sun, $\lambda > 660$ nm). The light intensity at the place of the reaction cell was adjusted to 100 mW cm^{-2}, and then the light was irradiated through an optical filter (AGC TECHNO GLASS Co., R-68). A H_2O-acetonitrile solution (20 mL, 9 : 1 v/v) of 5 mM *o*-phenylenediamine (OPD) with or without H_2O_2 (10 mM) was placed in the reaction cell, and then, β-MnO_2 NWA-grown glass substrate (2 cm × 2.5 cm) was immersed into the solution. For comparison, commercial β-MnO_2 NPs (Kanto Chemicals) were used as the catalyst in the place of β-MnO_2 NWA. In this case, the amounts of MnO_2 contained in both the systems were made the same (1.5 mg). At a given time, an aliquot of the reaction solution was taken to be diluted ten times with water. The concentraiton of 2,3-diaminophenazine (DAP) was determined by the absorption intensity at 420 nm by using a UV-vis spectrophotometer (Shimadzu Corporation, UV-1800).

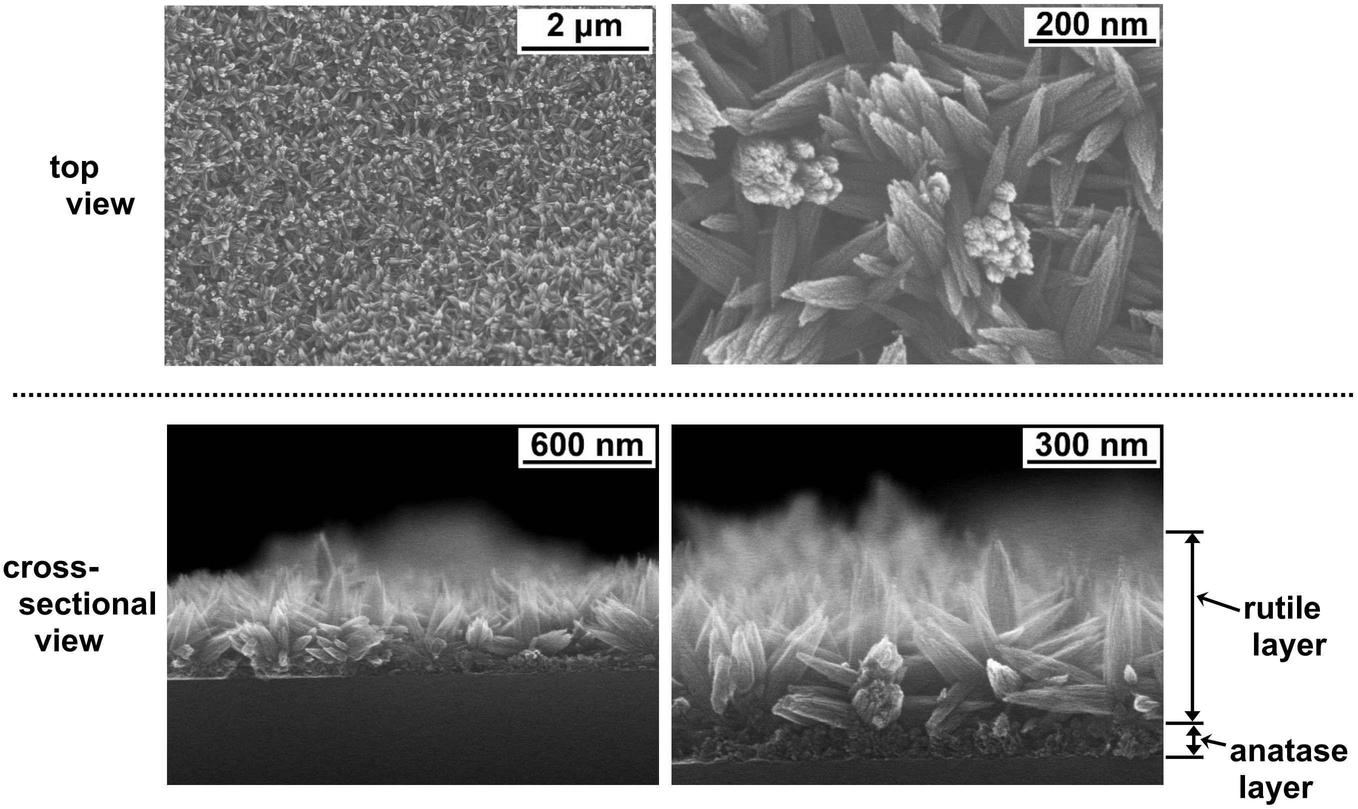


Fig. S1. SEM images of TiO_2 nanocoral substrates for the growth of γ-MnOOH NWA. TiO_2 nanocorals consist of anatase base film and rutile nanocoral layer.

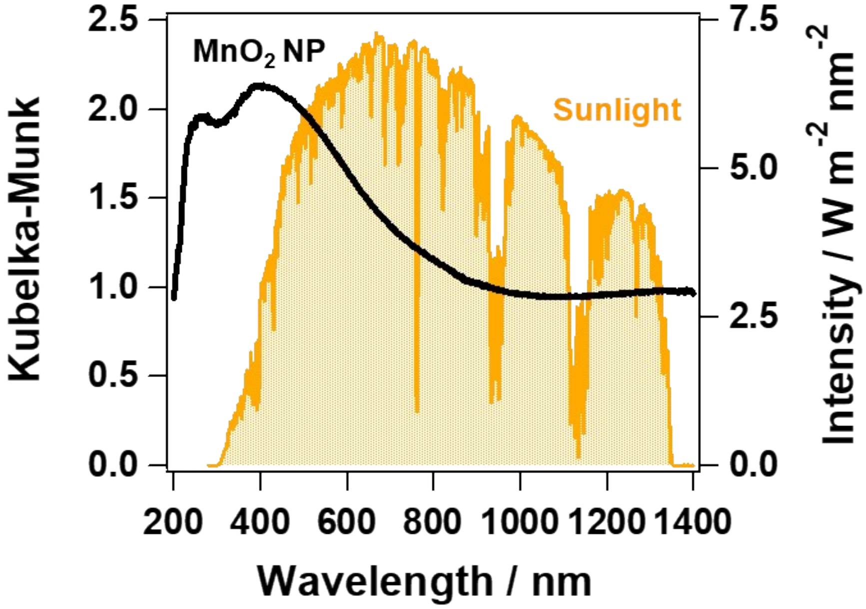


Fig. S2. Kubelka-Munk-transformed absorption spectrum of β-MnO_2 NPs, and the solar spectrum for comparison. Diffuse reflectance spectrum of β-MnO_2 NPs was measured by diluting them to 30% with $BaSO_4$.

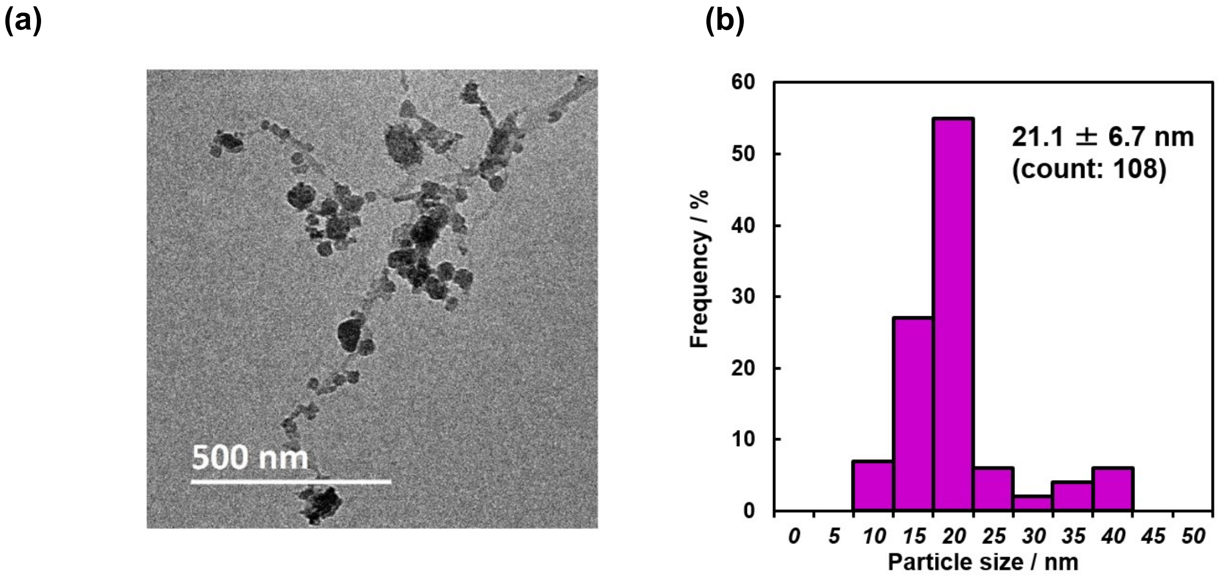


Fig. S3. TEM image (a) and particle size distribution (b) of β-MnO_2 NPs.

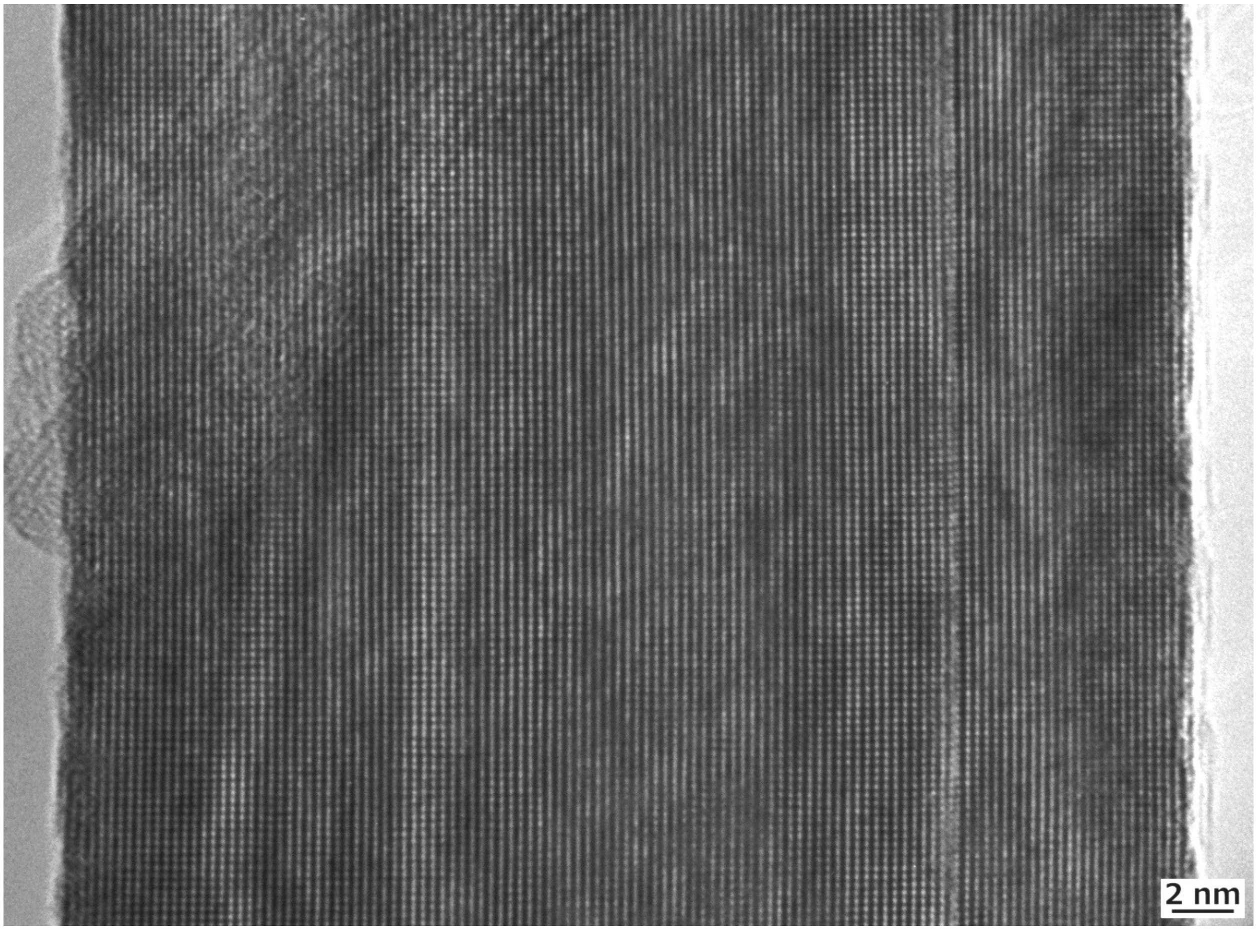


Fig. S4. A large scale HRTEM image of a γ-MnOOH nanowire.

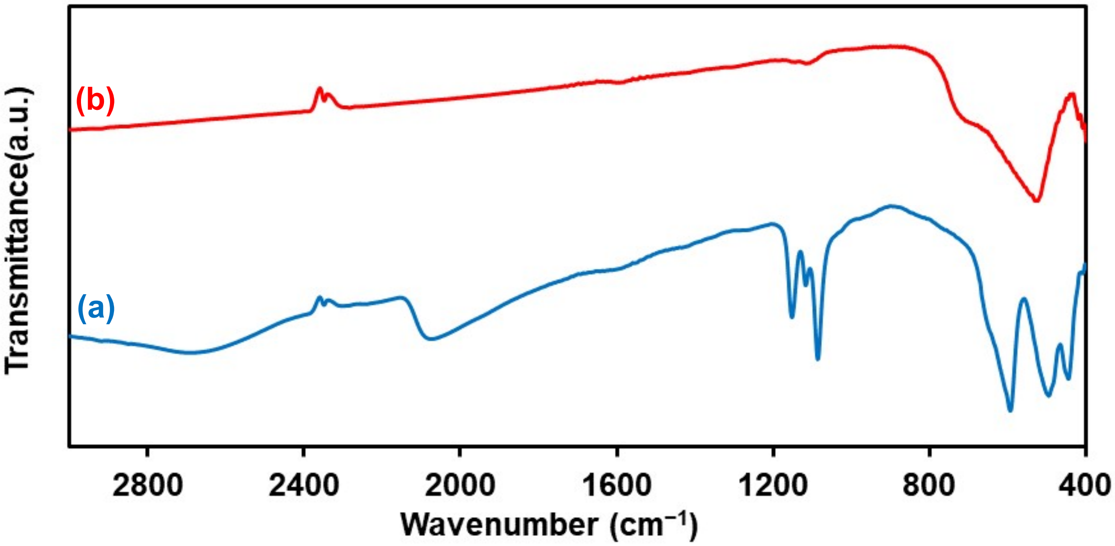


Fig. S5. FT-IR spectra of (a) γ-MnOOH and (b) β-MnO_2 NWA.

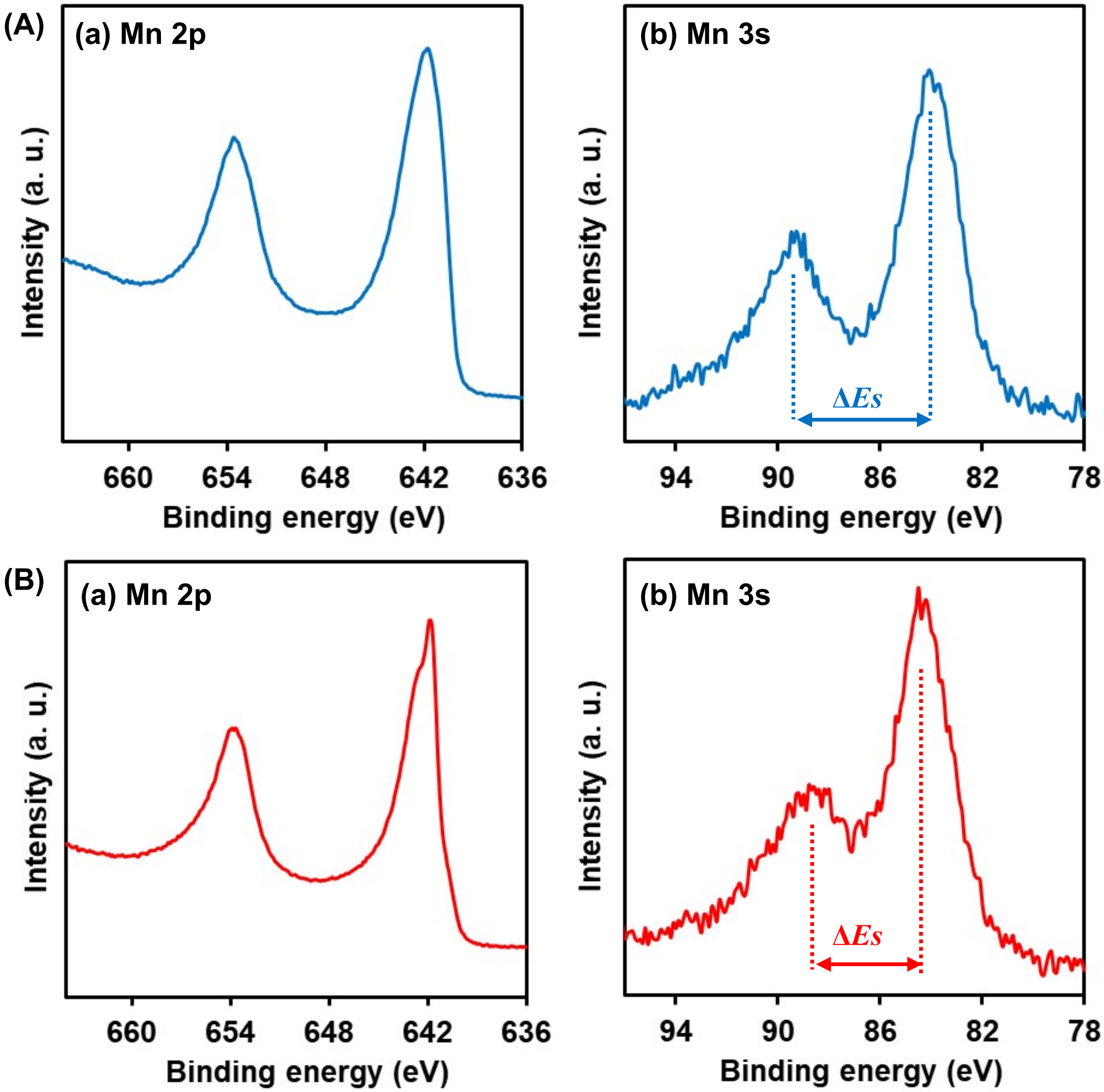


Fig. S6. High-resolution (a) Mn 2p and (b) Mn 3s XPS spectra of (A) γ-MnOOH and (B) β-MnO_2 NWA.

The average oxidation state (AOS) of manganese was calculated by using the magnitude of Mn3s multiplet splitting (ΔEs), according to the following relationship;

$$\text{AOS} = 8.95 - 1.13\Delta Es$$

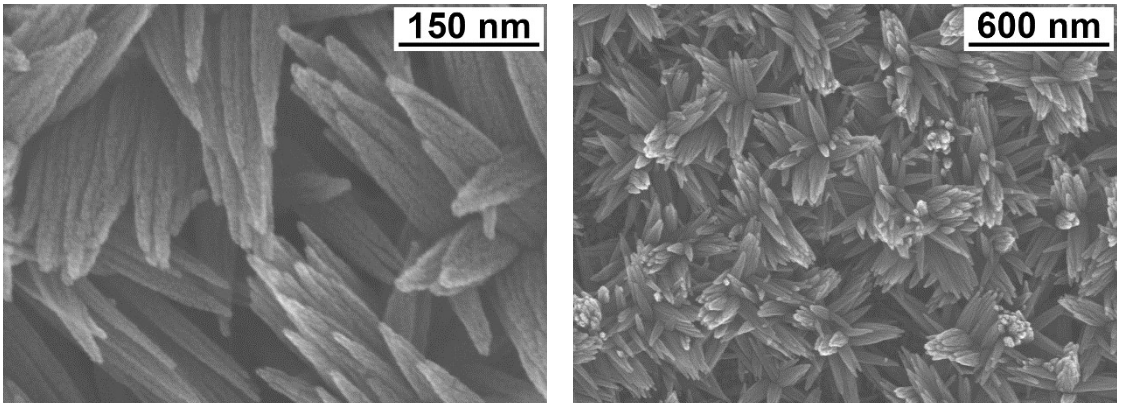
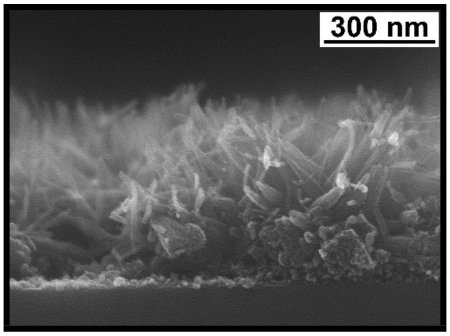
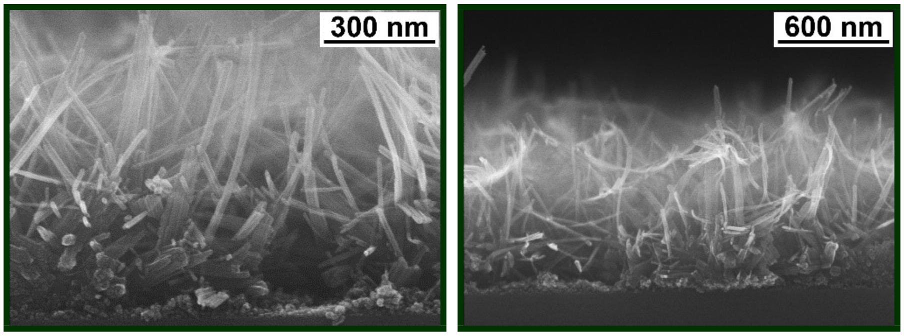


Fig. S7. SEM images of a film sample. TiO_2 nanocoral substrates were placed in an aqueous solution containing $Mn(NO_3)_2$ and H_2O_2 at an angle against the wall of glass vials and were kept at 85 °C.

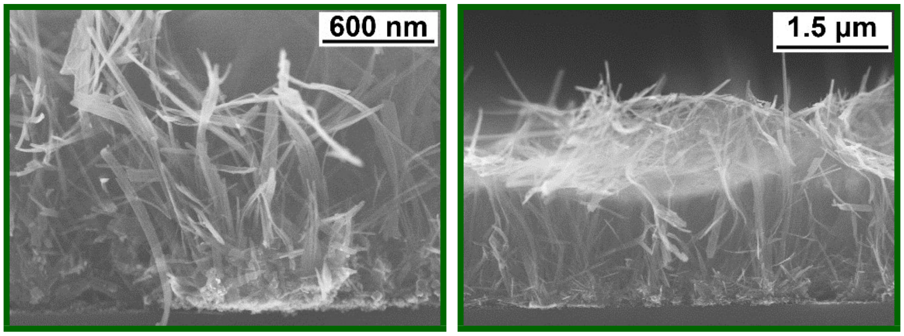
(a) 40 °C



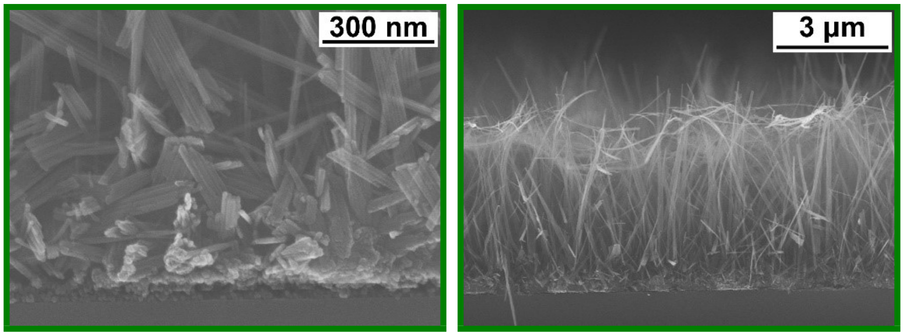
(b) 50 °C

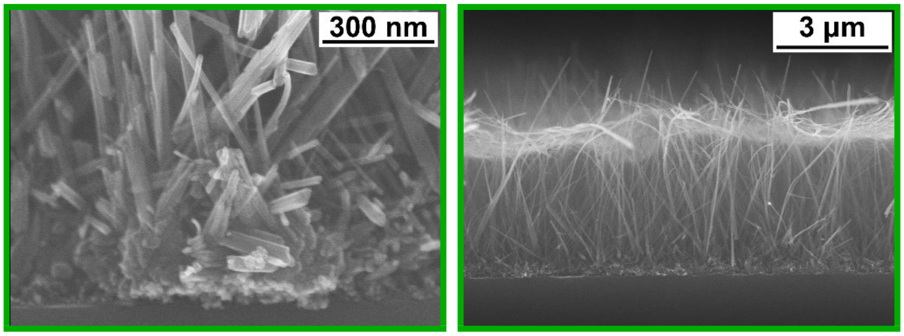


(c) 60 °C



(d) 70 °C




(e) 80 °C

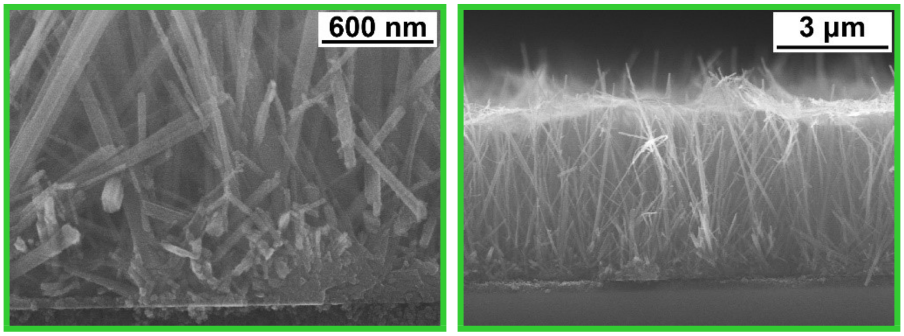

(f) 90 °C

Fig. S8. SEM images of γ-MnOOH NWA obtained at various reaction temperatures; (a) 40 °C, (b) 50 °C, (c) 60 °C, (d) 70 °C, (e) 80 °C, (f) 90 °C.

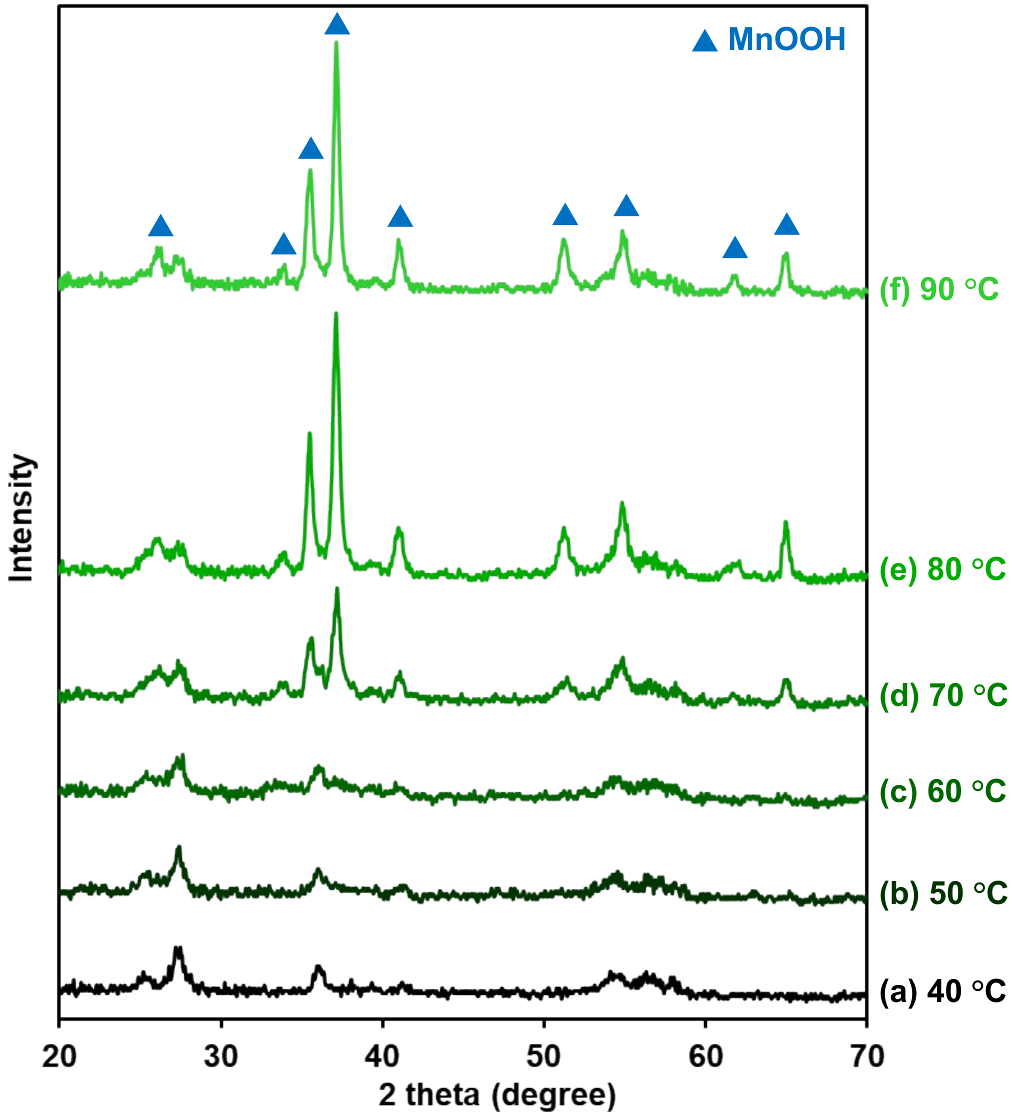


Fig. S9. XRD patterns of γ-MnOOH NWA obtained at various reaction temperatures; (a) 40 °C, (b) 50 °C, (c) 60 °C, (d) 70 °C, (e) 80 °C, (f) 90 °C.

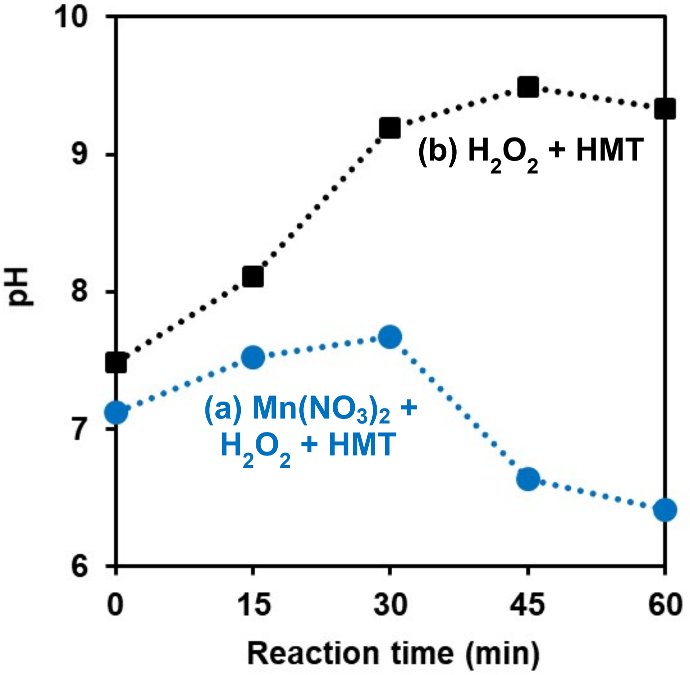


Fig. S10. Time-course changes in pH on the growth solutions of γ-MnOOH NWA with or without $Mn(NO_3)_2$.

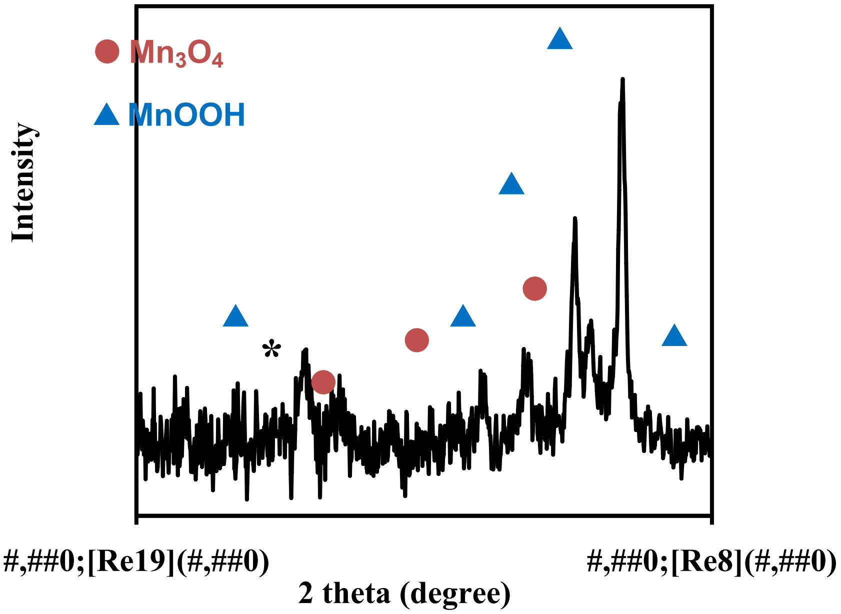
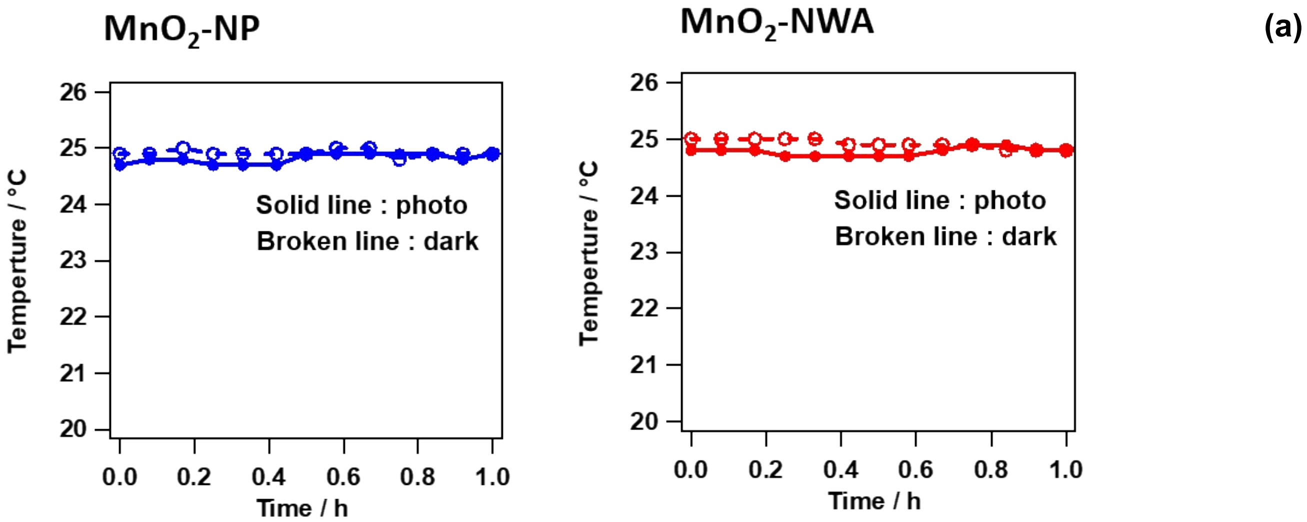


Fig. S11. XRD pattern of the as-prepared film sample. TiO_2 nanocoral substrates were placed in an aqueous solution containing $Mn(NO_3)_2$ and HMT at an angle against the wall of glass vials and were kept at 85 °C.



S12. Temperature change in the bulk reaction solution during the photothermal reaction in the β-MnO_2 NP and β-MnO_2 NWA catalyst systems. The temperature was directly measured by thermometer while taking care to avoid its direct light exposure.

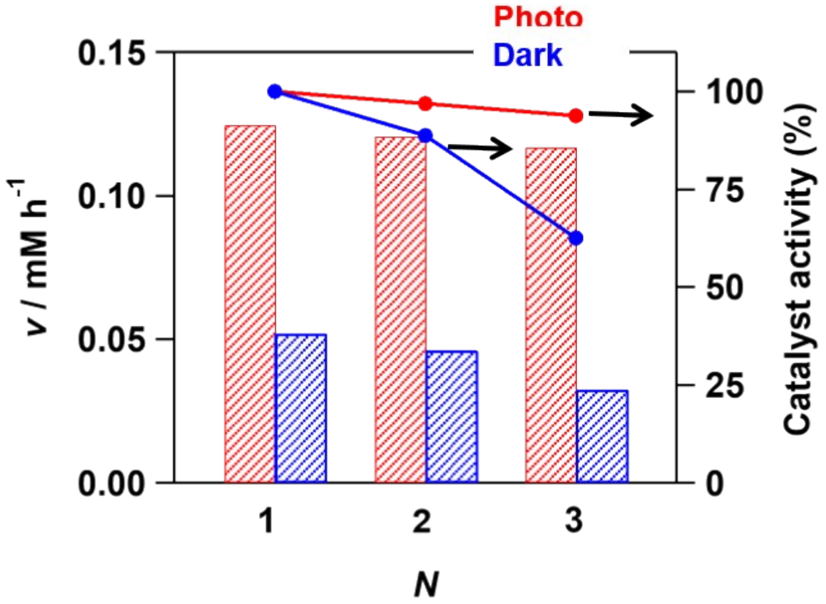
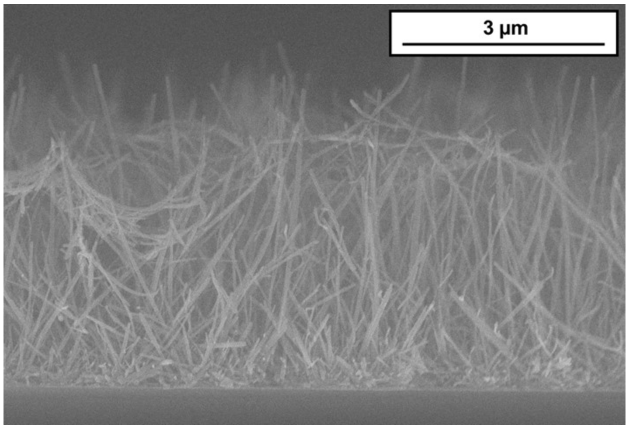


Fig. S13. Stability of β-MnO_2 NWA during the repeated dark (blue) and photothermal (red) reactions. *N* denotes the repetition number of the reaction.

(a) photo



(b) dark

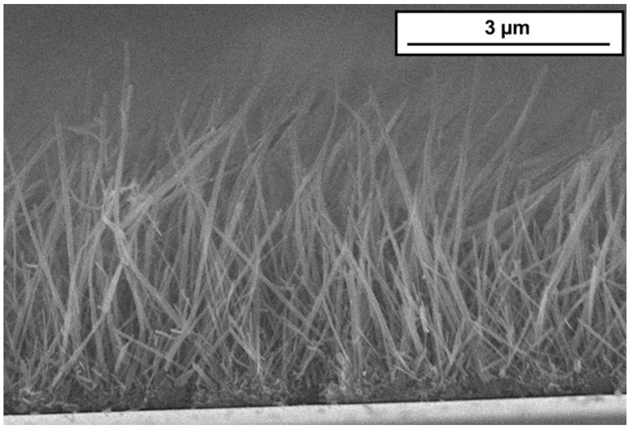


Fig. S14. SEM image of the β-MnO_2 NWA catalyst used after the repeated photothermal reaction.

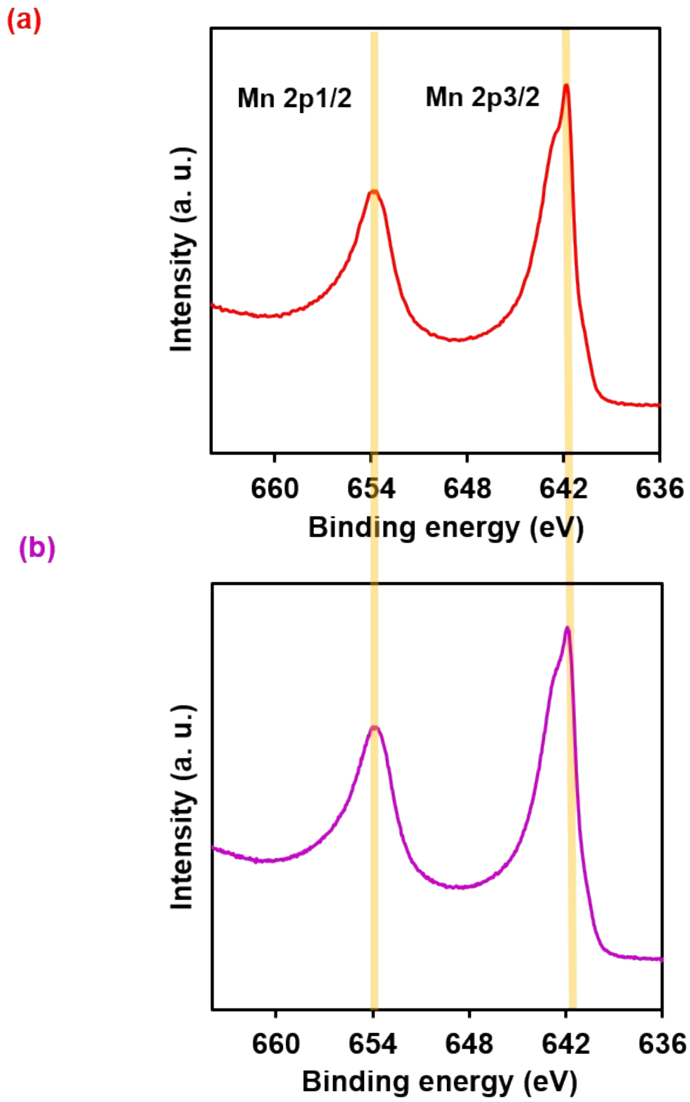


Fig. S15. Mn 2p XPS spectra of the β-MnO_2 NWA catalyst used (a) before and (b) after the repeated photothermal reaction.