Electronic Supplementary Information

Carboxymethyl cellulose-templated synthesis of hierarchically structured metal oxides

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Experimental Details

Materials: $CeCl_3 \cdot 7H_2O$ (trace metal basis, 99.9%), $Ca(NO_3)_2 \cdot 4H_2O$ (99.0%), $Mn(NO_3)_2 \cdot 4H_2O$ (purum p.a., > 97.0%), carboxymethyl cellulose (fibers), ZnO nanoparticles (< 50 nm), and other reagents were purchased from Sigma-Aldrich (St. Louis, USA) and used without purification.

Preparation of CeO_2 fibers: For synthesis of CeO_2 fibers, 2 g of carboxymethyl cellulose (CMC) was immersed in 50 ml of different concentrations of $CeCl_3 \cdot 7H_2O$ solution (1 ~ 4 mM). After 30 minutes of incubation under ambient condition, CMC was separated, washed with deionized water, and calcinated at different temperatures (800 ~ 1000 ℃) for 2 hours.

Synthesis of ZnO fibers: ZnO fibers was prepared 5 g of CMC and 50 ml of $Zn(NO_3)_2 \cdot 6H_2O$ solution (0.2 mM). Mixture solution was incubated under ambient condition for 30 minutes. The CMC was separated, washed with deionized water and calcinated at 500 ℃ for 2 hours.

Preparation of $CaMn_2O_4$ fibers: $CaMn_2O_4$ fibers were prepared with a different amount of CMC (0.05 ~ 4 g) and a solution of 40 ml of $Ca(NO)_3 \cdot 4H_2O$ (25 mM) and $Mn(NO)_3 \cdot 4H_2O$ (62.5 mM). $CaMn_2O_4$ fibers were obtained by calcinating CMC at 1000 ℃ under air atmosphere for 2 hours.

Synthesis of g-C_3N_4 powder: g-C_3N_4 was prepared according to the previous literature. Briefly, 3 g of dicyandiamide in alumina crucible was calcinated at 600 ℃ under air for 4 hours.

Characterization: The morphologies of each sample were observed using a S-4800 field emission scanning electron microscopy (Hitachi Co., Japan) at an electron acceleration voltage of 5 ~ 10 kV. The X-ray diffraction patterns were recorded using a D/MAX-RB X-ray diffractometer (Rigaku Co., Japan) with a scan rate of 4 °/min, range of 10 °~ 70 °, and a Cu Kα radiation wavelength of 1.5418 Å. Absorbance spectra were obtained using a UV-visible spectrophotometer (Jasco Inc., Japan) with a diffuse-reflectance mode. The mass change as a function of temperature in the isothermal mode was measured using a Setsys 16/18 thermal analyzer (Setaram, France) with a heating rate of 10 ℃/min and a temperature range of 25 ~ 800 ℃ under air. The surface charges of Ce^{3+}-CMC fibers dispersion in deionized water at pH 7.0 were investigated by zeta-potential measurements using a Zetasizer nano zs (Malvern, UK). The FT-IR spectra of Ce^{3+}-CMC fibers, HCl and NaOH treated CMC fibers were obtained using a FT-IR 200 spectrophotometer (Jasco Inc., Japan). The amount of adsorbed metal ions in CMC fibers was measured using an Agilent ICP-MS 7700S inductively coupled with a plasma mass spectrometer (Agilent, USA). A spectrofluorometric study was conducted using an RF-5301PC (Shimadzu Co., Japan) with an excitation wavelength of 320 nm. X-ray photoelectron spectroscopic analysis was carried out using a K-alpha (Thermo VG Scientific, UK) in the range of 0 – 1300 eV. We measured pore size and surface area of CeO_2 fibers by Brunauer-Emmett-Teller (BET) method using ASAP 2020 N_2 gas sorption analyzer (Micromeritics, USA).

Methylene blue (MB) degradation test: A reactive solution was prepared by mixing 30 mg of CeO_2 samples (CeO_2 fibers and bulk CeO_2) in a 30 mL of MB solution (26.7 μM). The reactive solution was incubated and stabilized in the dark for 4 hours with vigorous stirring to complete the equilibrium of adsorption-desorption of MB molecules on the surface of CeO_2 samples before visible light irradiation. The solution was irradiated by a xenon lamp (450 W) with a 420 nm cut-off filter. To analyze the degree of MB degradation, the absorbance of the reaction solution at 665 nm was measured after removing CeO_2 samples by centrifugation.

Preparation of g-C_3N_4/ZnO nanoparticle and g-C_3N_4/ZnO fiber: Hybridization of g-C_3N_4 and ZnO was carried out with different amount of g-C_3N_4. g-C_3N_4 were dispersed in DI water by sonication (20 mg in 50 ml). ZnO was also dispersed in DI water (100 mg in 10 ml), and different amounts of g-C_3N_4 (1, 3, 5, and 10 wt% of g-C_3N_4) were added to the ZnO dispersed aqueous solution. The mixture solution was incubated at 70 °C for overnight to evaporate DI water. We conducted photochemical NADH regeneration with different g-C_3N_4/ZnO nanoparticles (fibers) (1, 3, 5, and 10 wt%), and figured out the optimized g-C_3N_4 content (3 wt%) (data not shown).

Photochemical nicotineamide adenine dinucleotide (NADH) regeneration and photoenzymatic synthesis of ʟ-glutamate: The photochemical regeneration of NADH was conducted visible light irradiation with a xenon lamp (450 W) at room temperature. The reaction solution was prepared by dissolving 1 mM of NAD^+ and 250 µM of $[Cp^*Rh(bpy)H_2O]^{2+}$ (**M**) in 3 mL of phosphate buffer (100 mM, pH 7.0) containing 15 w% triethanolamine. ZnO fiber (100 mg), g-C_3N_4/ZnO nanoparticles (100 mg), g-C_3N_4 powder (3 mg), and g-C_3N_4/ZnO fibers (100 mg) were dispersed in the reactive solution. The concentration of NADH in reactive solution was measured by analyzing its absorbance at 340 nm using UV-visible spectrophotometer (Jasco Inc., Japan). For the photoenzymatic synthesis of ʟ-glutamate was coupled with photoregeneration of NADH using g-C_3N_4/ZnO (100 mg) fiber. The reaction solution for the photoenzymatic reaction consisted of NAD^+ (1 mM), $[Cp^*Rh(bpy)H_2O]^{2+}$ (250 µM), α-ketoglutarate (5 mM), $(NH_4)_2SO_4$ (100 mM) and GDH (40 U) in 3 mL of phosphate buffer (100 mM, pH 7.0) containing 15 w% triethanolamine.

Photocurrent measurement: Photo-electrodes were prepared by drop casting of each samples (10 µg) on ITO glass (1 x 1 cm^2). Photocurrent responses were measured with prepared photo-electrodes as working electrodes, a platinum wire as a counter electrode, Ag/AgCl reference electrode, and $NaSO_4$ (0.5 M) solution (as electrolyte) using WMPG 1000 potentiostat (WonATech, Korea). An applied potential for photo-electrodes against Ag/AgCl was set to 0.3 V.

Electrochemical analysis of $CaMn_2O_4$*:* Cyclic voltammetry (CV) was conducted using WMPG 1000 potentiostat (WonATech, Korea) with $CaMn_2O_4$ samples-Nafion (40 µg in 20 µL) deposited on glassy carbon electrode as a working electrode, a platinum wire as a counter electrode, and an Ag/AgCl reference electrode. The electrochemical reaction was performed in an O_2 saturated sodium phosphate solution (100 mM, pH 7.0) at room temperature with a scan rate of 50 mV s^{-1}.

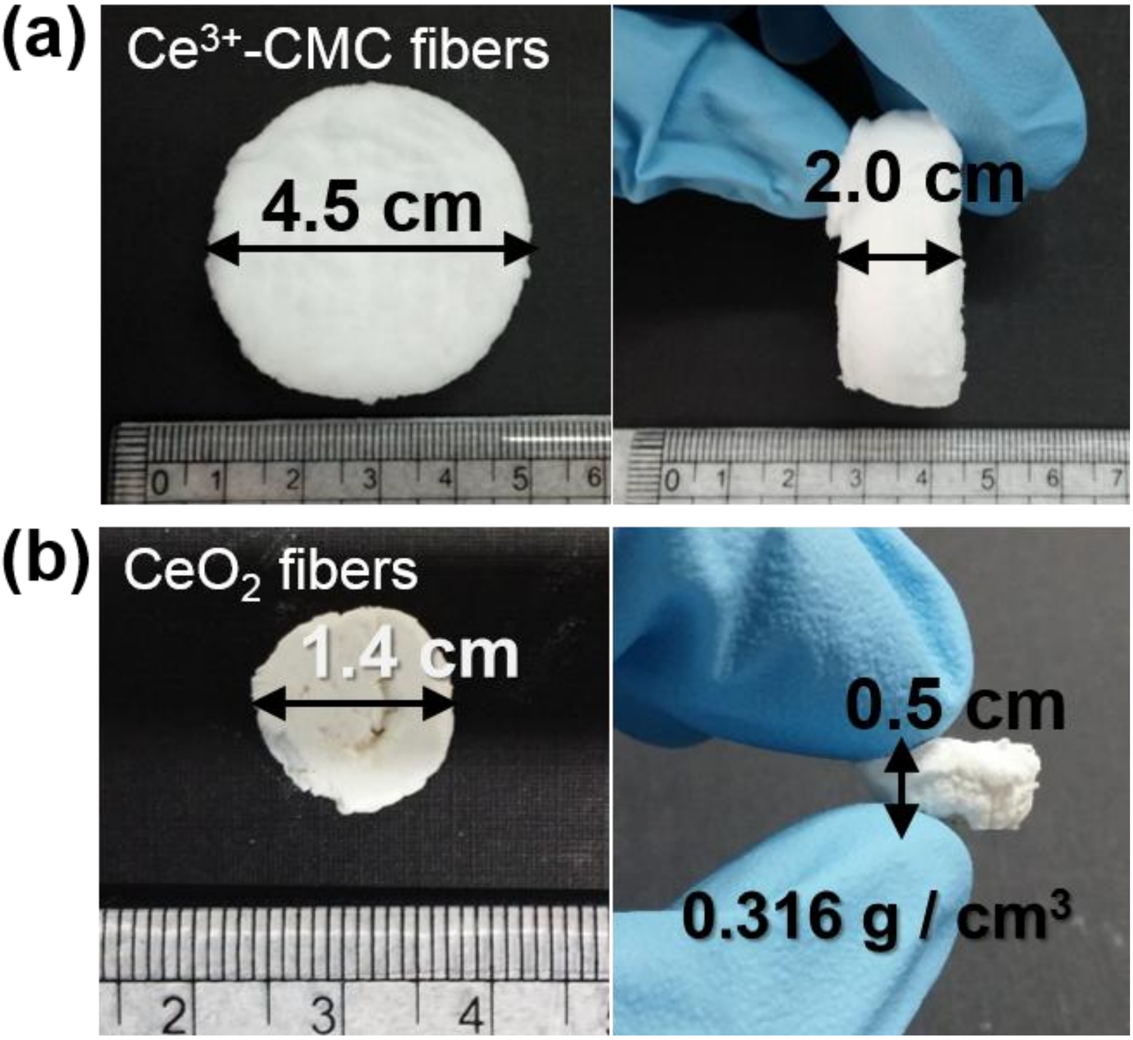


Figure S1. Photographs of Ce^{3+}-CMC fibers and free-standing CeO_2 synthesized from Ce^{3+}-CMC fibers.

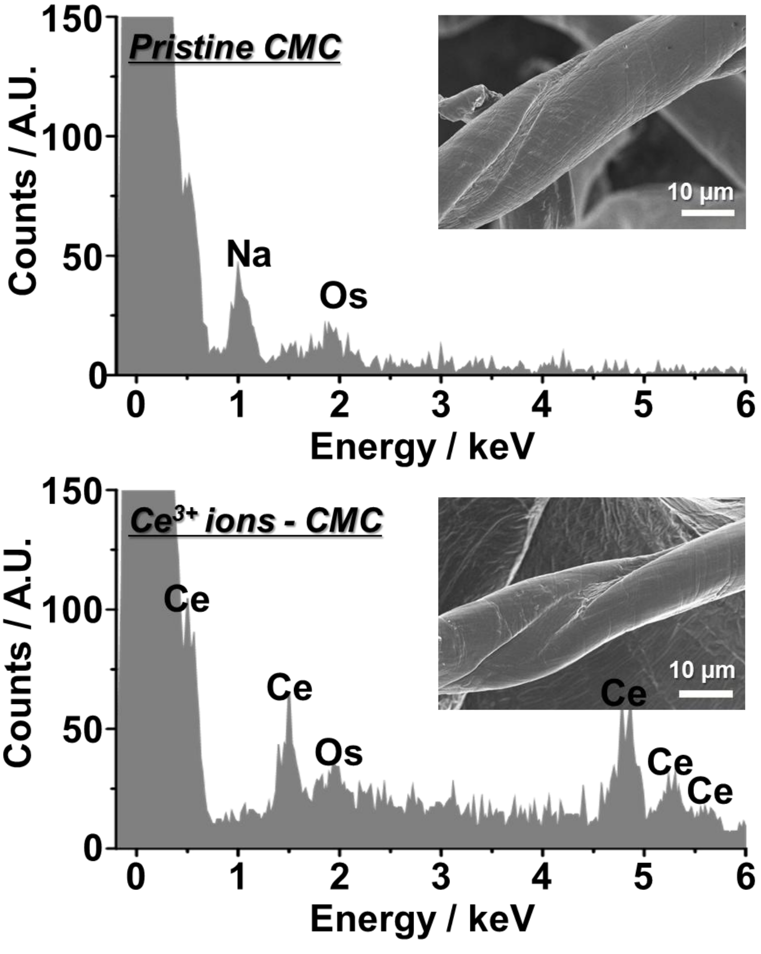


Figure S2. Surface analysis by EDX demonstrates that metal ions in the CMC fibers.

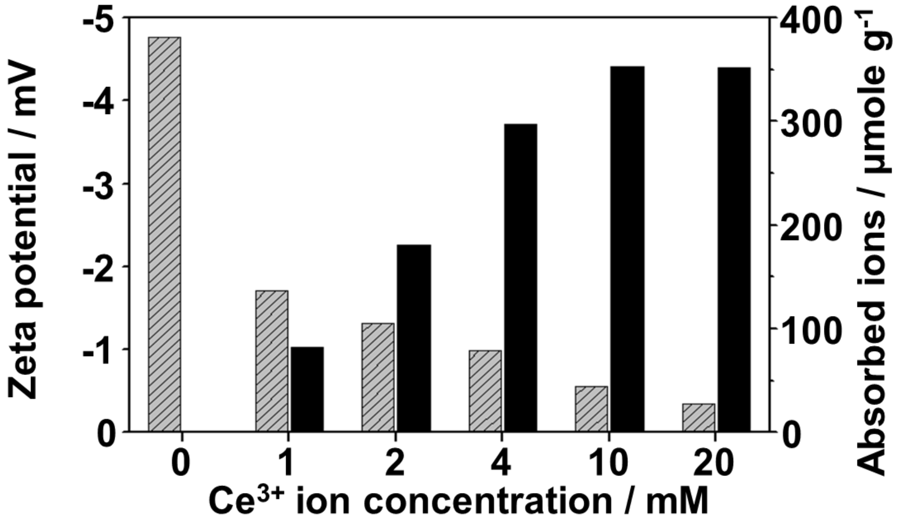


Figure S3. Zeta potential analysis of Ce^{3+} ion-adopted CMC fibers with the measured amount of Ce^{3+} ions in CM-cellulose.

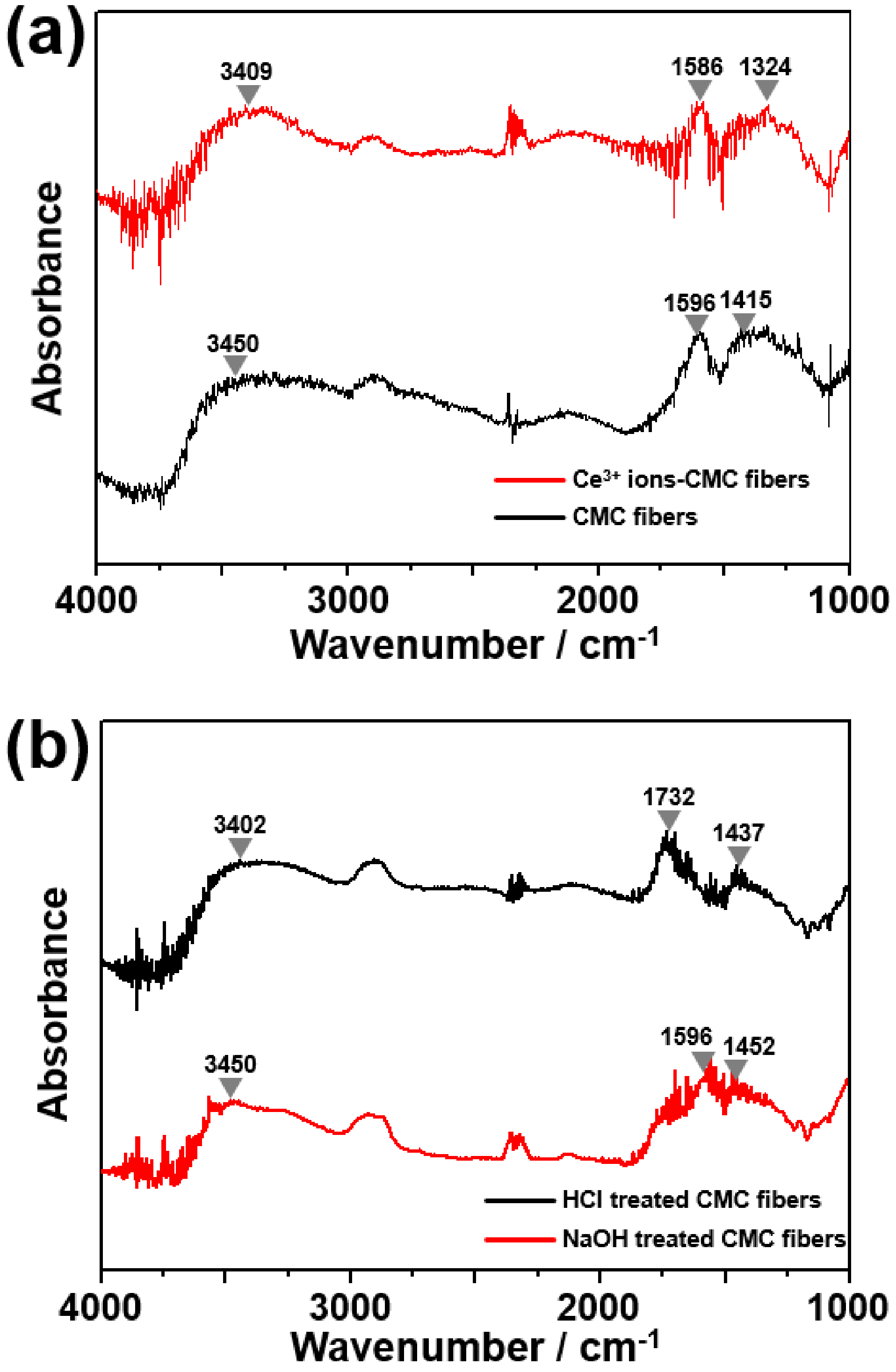


Figure S4. (a) FT-IR spectra of pristine CMC fibers and Ce^{3+}-CMC fibers. FT-IR absorption peaks corresponding to the stretching vibration modes of hydroxyl groups (~3400 cm^{-1}) and carboxyl groups (~1400 cm^{-1}). (b) FT-IR spectra of HCl (acid) and NaOH (basic) treated CMC fibers.

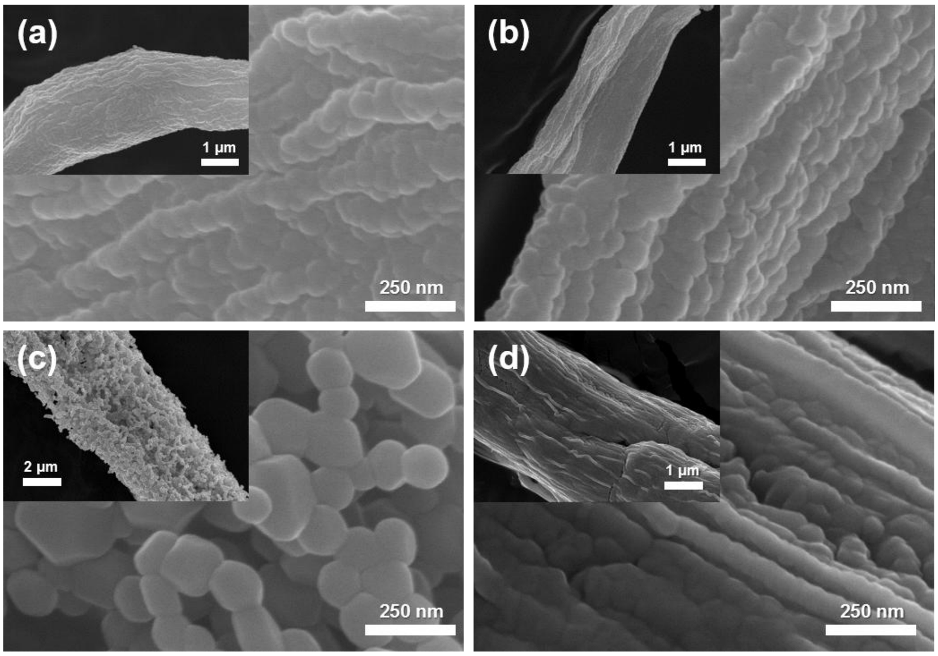


Figure S5. SEM images of CeO$_2$ fibers synthesized with different conditions [(a) 1 and (b) 4 mM of CeCl$_3$ solution and calcination temperature of 800 ℃ with HCl treated CMC, (b) 1 and (c) 4 mM of CeCl$_3$ solution and calcination temperature of 800 ℃ with NaOH treated CMC].

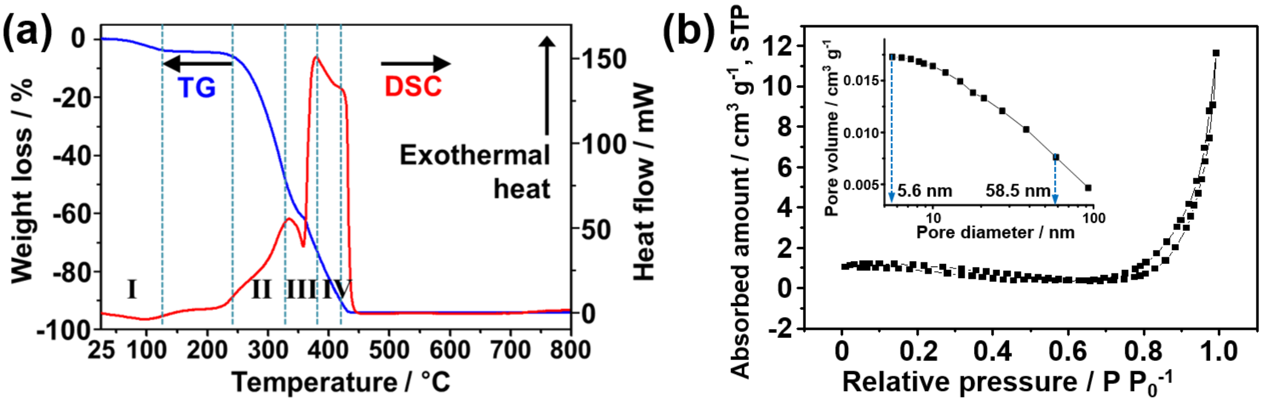


Figure S6. (a) Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) curves of Ce^{3+}-adopted CMC fibers [(I) evaporation of water; (II) decomposition of cellulose fiber; (III) formation of CeO$_2$ phase; (IV) burn out of carbon backbone]. (b) Nitrogen adsorption-desorption isotherms and Barrett-Joyner-Halenda (BJH) pore size distribution (inset) of CeO$_2$ fibers.

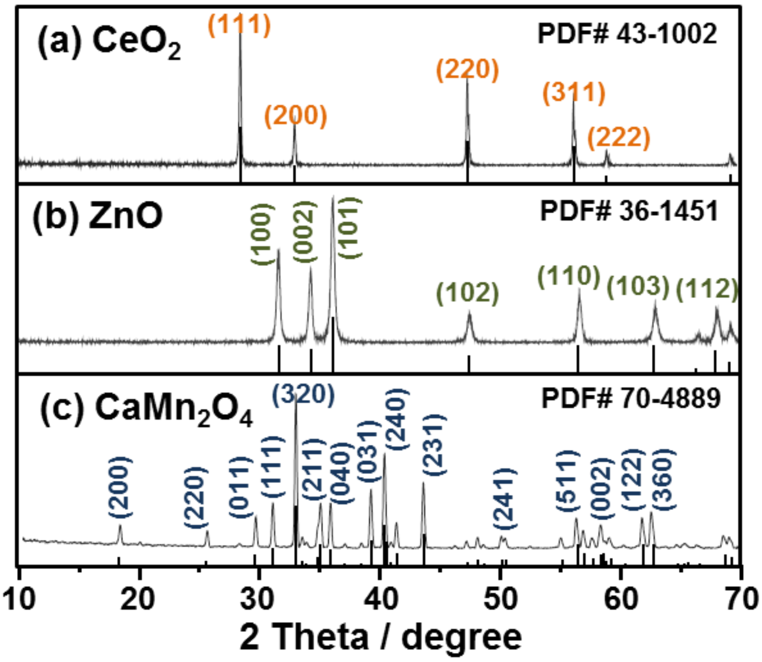


Figure S7. XRD spectra of the (a) CeO_2, (b) ZnO, and (c) $CaMn_2O_4$ fibers.

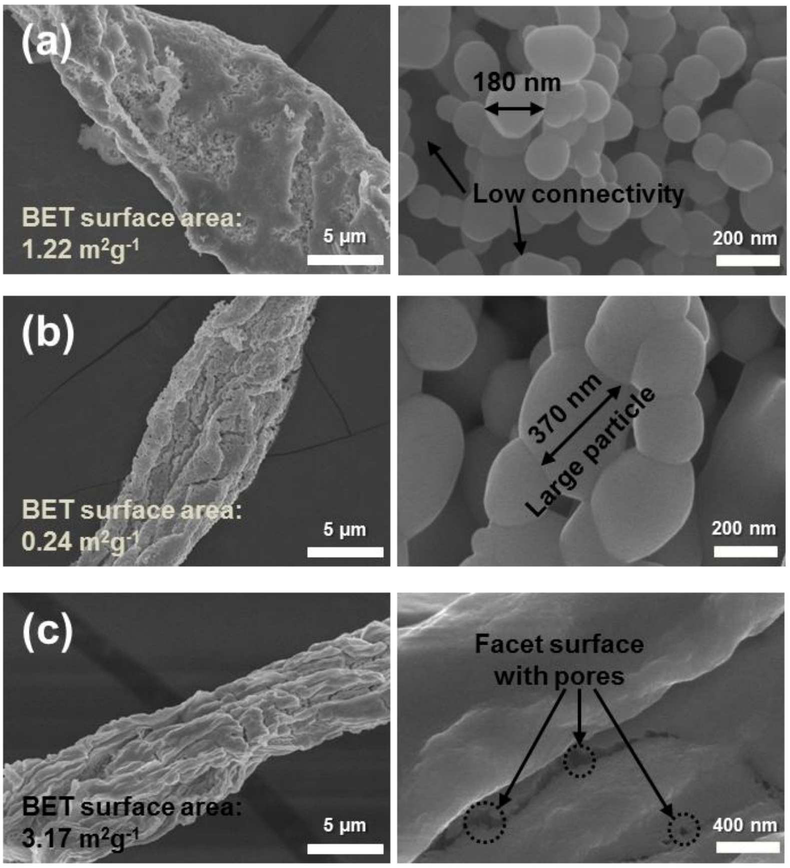


Figure S8. SEM images of CeO_2 fibers synthesized with different conditions [(a) 1 mM of $CeCl_3$ solution and calcination temperature of 800 ℃, (b) 4 mM of $CeCl_3$ solution and calcination temperature of 1000 ℃, and (c) 20 mM $CeCl_3$ solution with 800 ℃ calcination temperature].

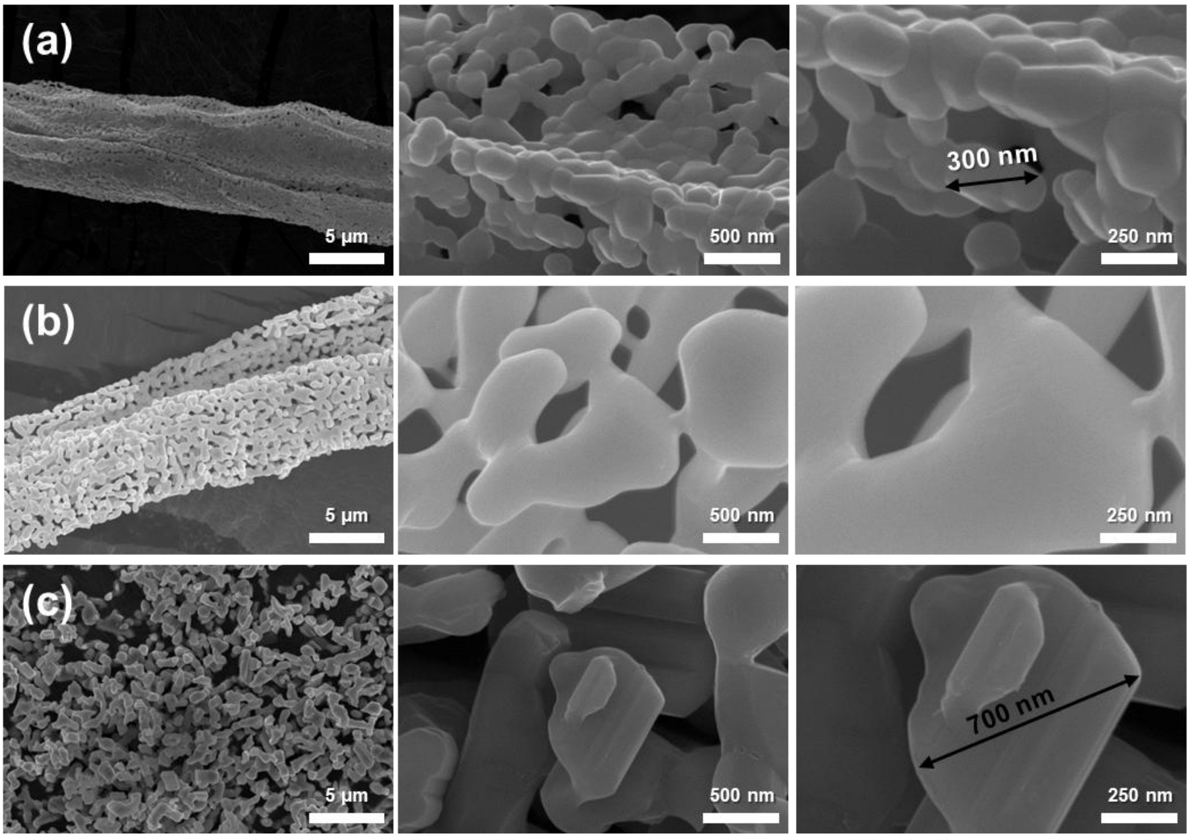


Figure S9. SEM images of $CaMn_2O_4$ synthesized with different amount of CM-cellulose; (a) 0.5 g, (b) 4 g, and (c) 6 g under identical experimental condition of precursor concentration and calcination temperature [1 mmole of $Ca(NO)_3{\cdot}4H_2O$ and 2.5 mmole of $Mn(NO)_3{\cdot}4H_2O$ in 40 ml of deionized water and calcination temperature of 1000 ℃ under the air].

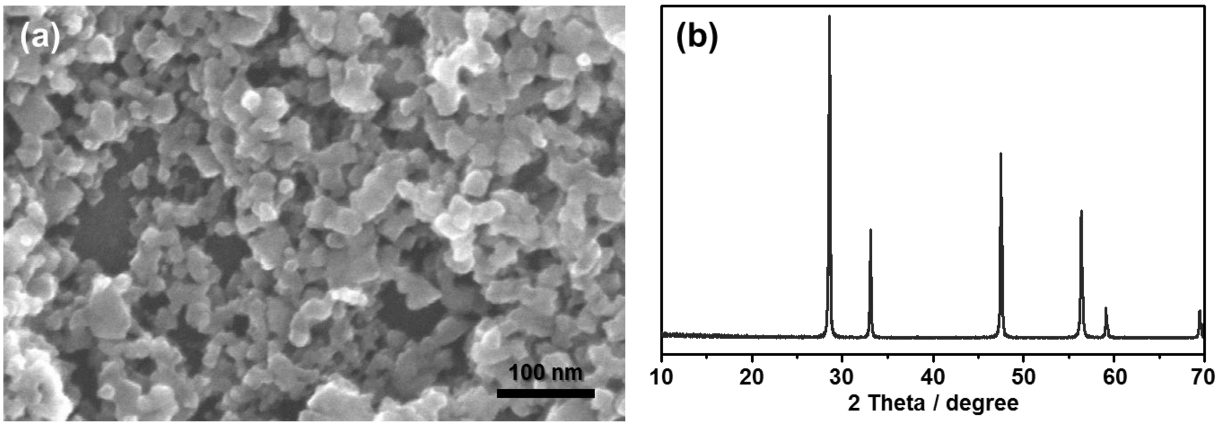


Figure S10. (a) SEM image of CeO_2 nanoparticles (purchased from Sigma-Aldrich Co., < 25 nm). (b) XRD spectrum showing the corresponding X-ray diffraction pattern of crystalline CeO_2.

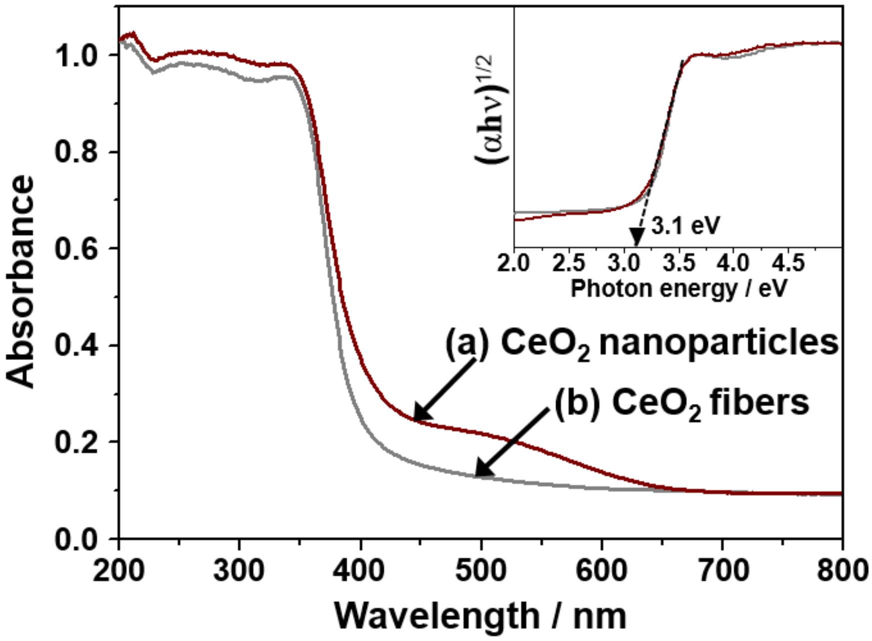


Figure S11. UV-visible absorbance spectra of (a) CeO_2 nanoparticles and (b) CeO_2 fibers synthesized using CMC. The inset spectra shows the relationship between the transformed Kubelka-Munk function versus photon energy for CeO_2 samples.

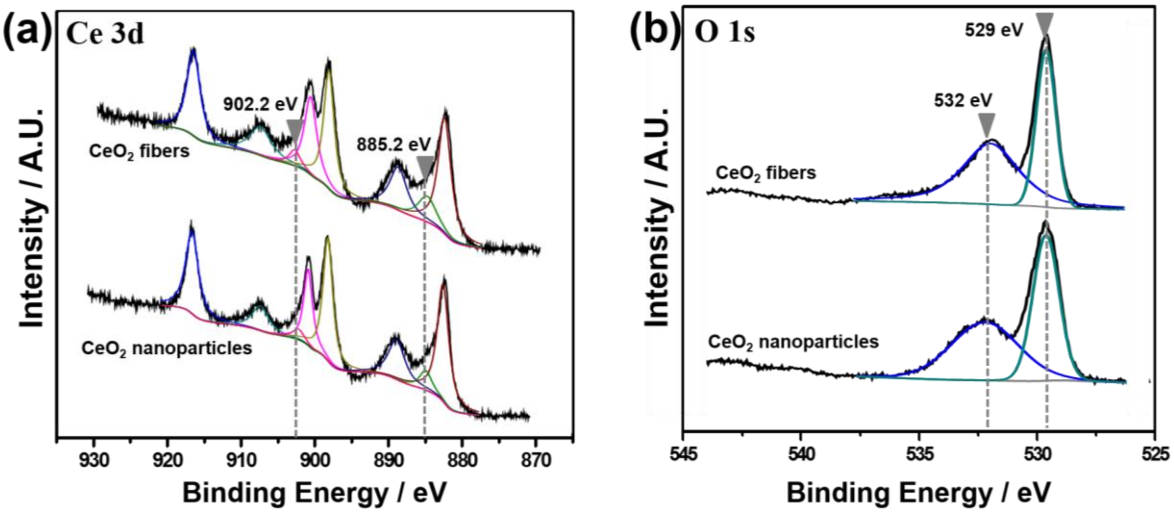


Figure S12. XPS spectra of CeO_2 fibers (synthesized with 4 mM of $CeCl_3$ solution and calcination temperature of 800 ℃), and CeO_2 nanoparticles (< 25 nm, purchased from Sigma Aldrich): (A) Ce 3d, and (B) O1s. The concentrations of Ce^{3+} ions on the surface of CeO_2 fibers and CeO_2 nanoparticles were calculated as 10.4% and 6.8%, respectively.

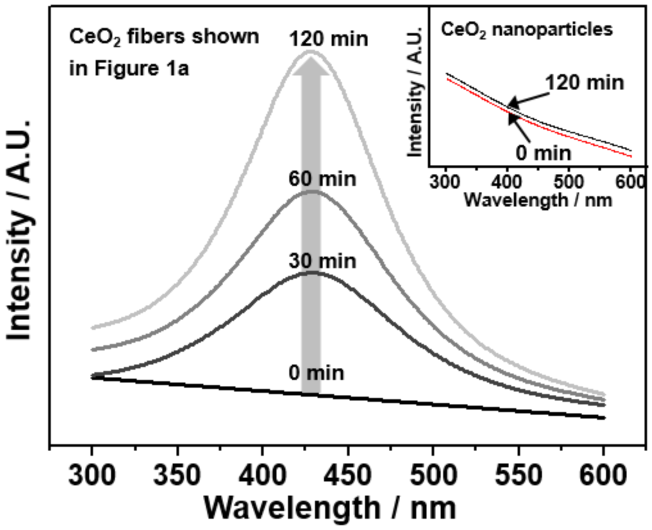
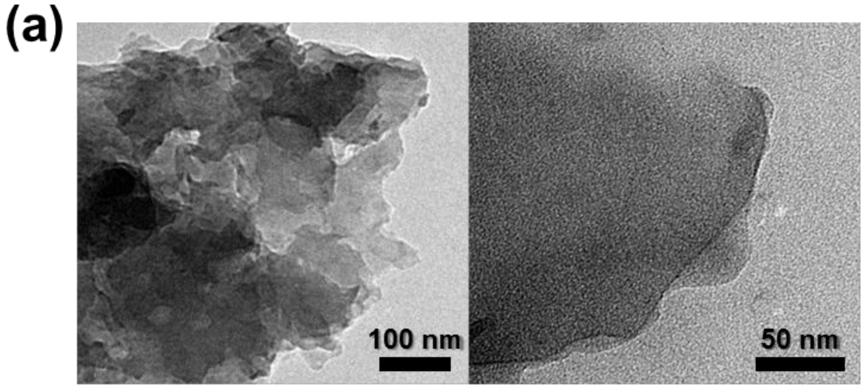


Figure S13. Fluorescence spectra of 2-hydroxyl terephthalate (TA-OH$^{\cdot}$) produced by MB and CeO_2 fibers (shown in Figure 1a) during photocatalytic reaction. In the case of CeO_2 nanoparticles, TA-OH$^{\cdot}$ was not generated (inset).



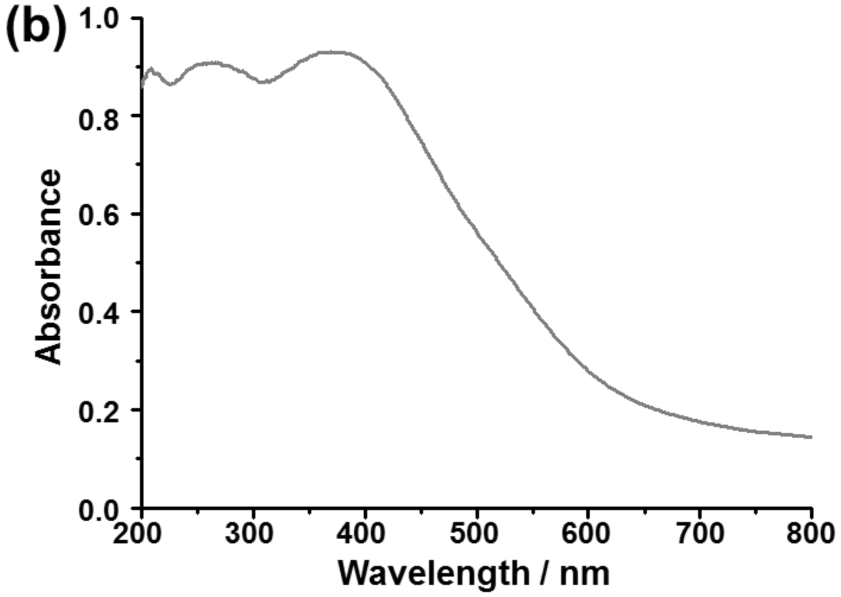


Figure S14. Characterizations of prepared g-C_3N_4 powder using TEM and UV-visible spectrophotometer. (a) TEM images of g-C_3N_4 powder exhibit a sheet-like two dimensional sheet-like structures in different magnifications. (b) UV-visible spectrum of g-C_3N_4 powder shows the strong absorption band in the range of 400-600 nm.

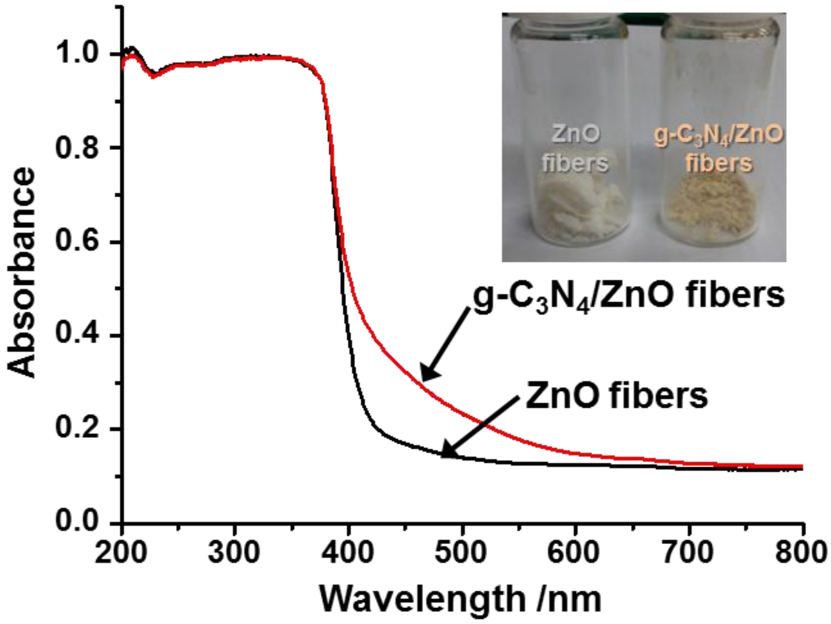


Figure S15. DRS spectra of ZnO fibers and g-C_3N_4/ZnO fibers, and a photograph of ZnO fibers and g-C_3N_4/ZnO fibers (inset). ZnO fiber had no absorbance in the visible light range. [black solid line] After hybridization with g-C_3N_4, g-C_3N_4/ZnO fibers exhibit increased absorbance in the range of 400-600 nm. [red solid line]

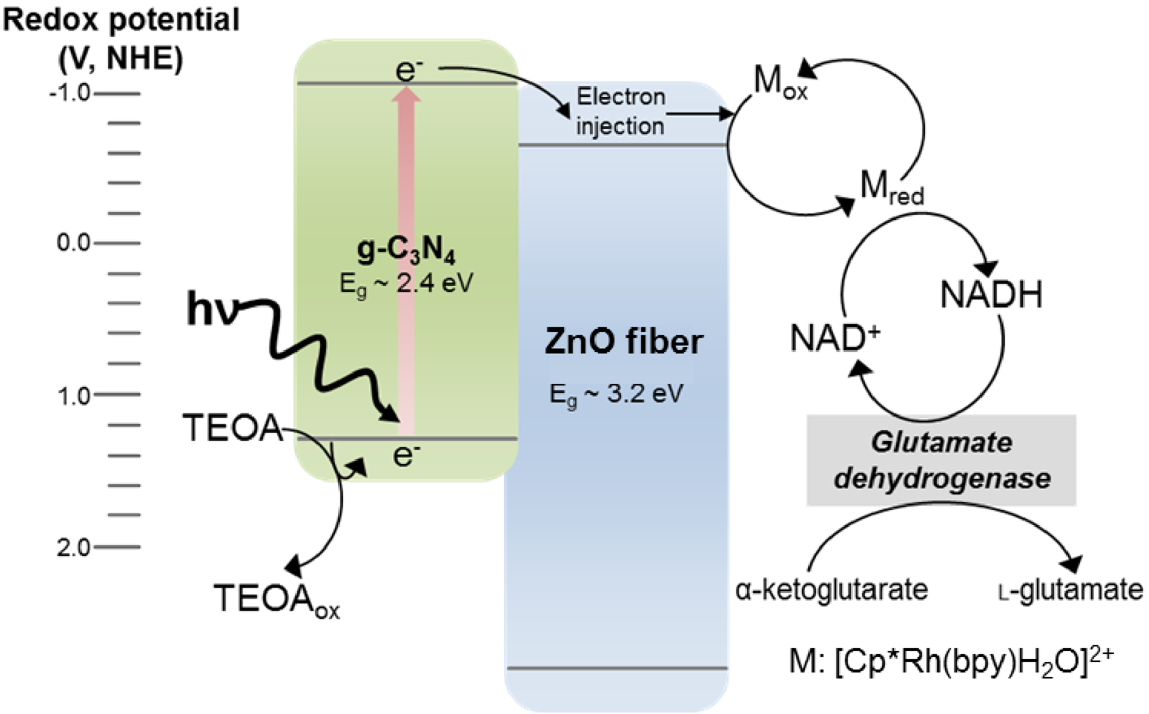


Figure S16. Proposed mechanism of an electron transfer between g-C_3N_4 and ZnO fiber, and photochemical NADH regeneration with gC_3N_4/ZnO fiber through an electron mediator (**M** = $[Cp^*Rh(bpy)H_2O]^{2+}$].

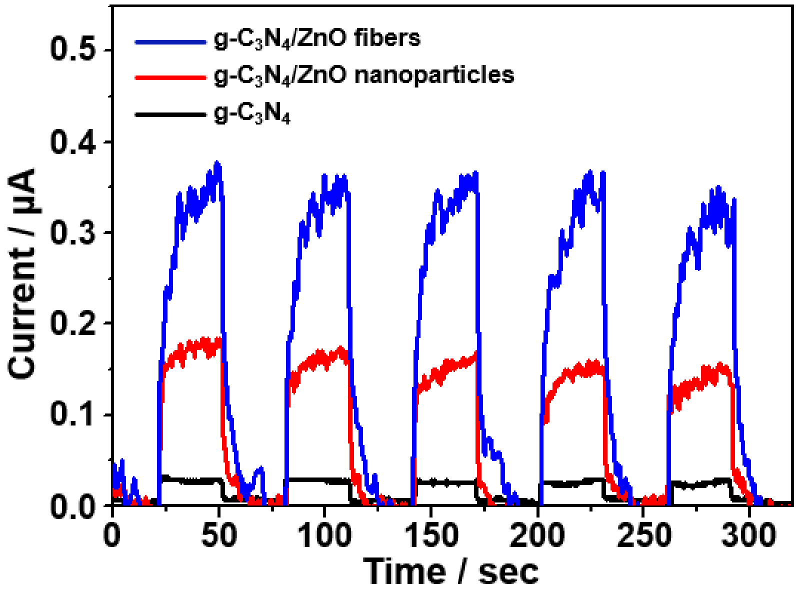


Figure S17. Photocurrent response for bare g-C_3N_4, g-C_3N_4/ZnO nanoparticles, and g-C_3N_4/ZnO fibers under visible light irradiation.

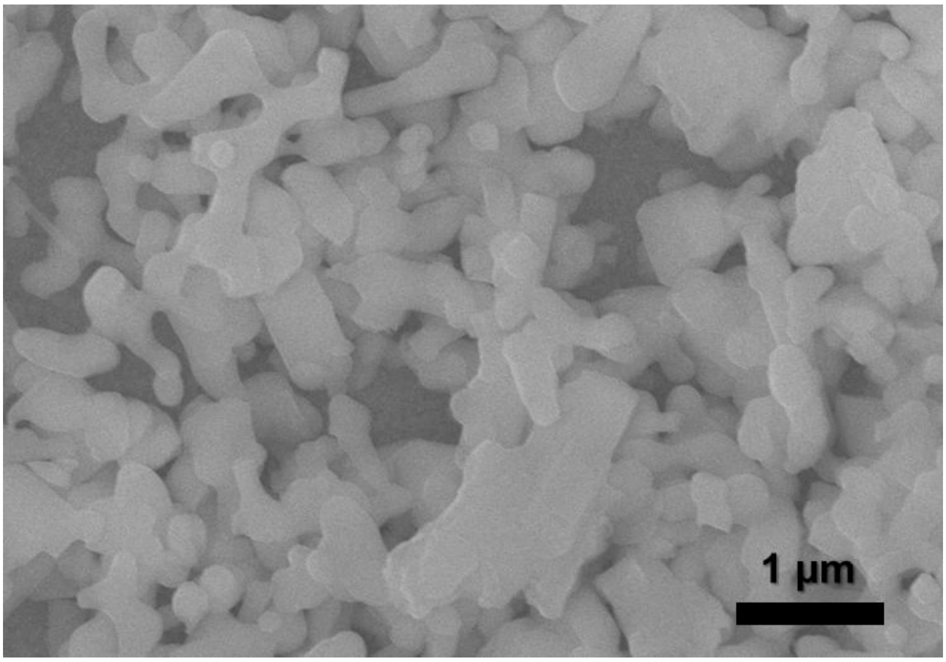


Figure S18. SEM image of bulk $CaMn_2O_4$ synthesized using conventional hydrothermal method.

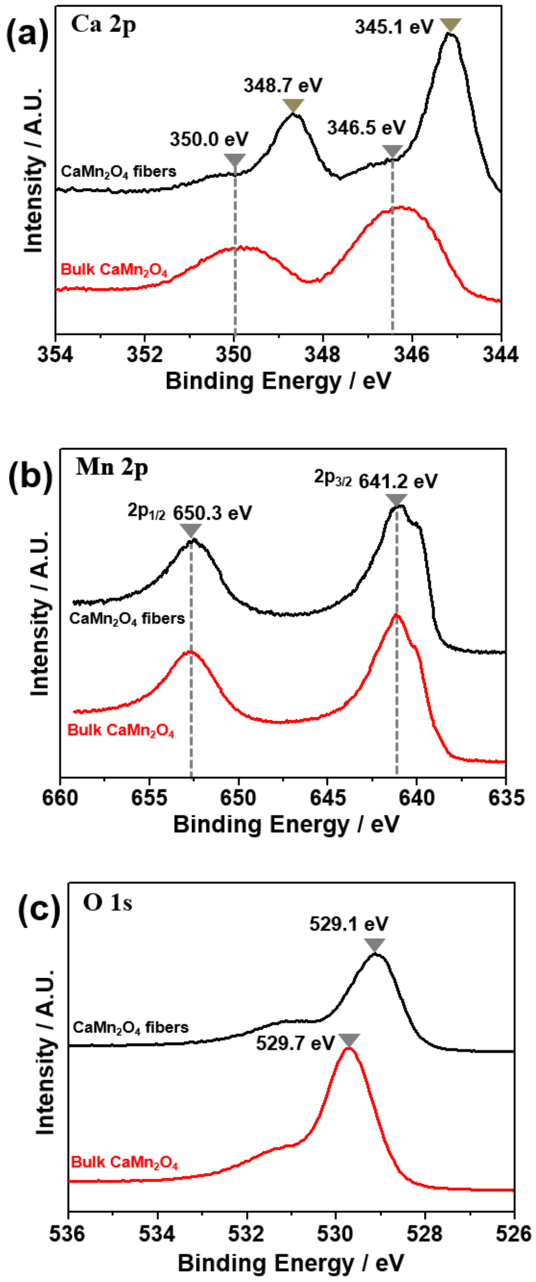


Figure S19. XPS spectra of Ca 2p, Mn 2p, and O 1s of $CaMn_2O_4$ fibers and Bulk $CaMn_2O_4$.