

## Electronic Supplementary Information

### **Porous $\beta$ -MnO<sub>2</sub> nanoplates derived from MnCO<sub>3</sub> nanoplates as highly efficient electrocatalysts toward oxygen evolution reaction**

Jun Kim,<sup>‡ab</sup> Ju Seong Kim,<sup>‡c</sup> Hionsuck Baik,<sup>d</sup> Kisuk Kang<sup>c\*</sup> and Kwangyeol Lee<sup>ab\*</sup>

<sup>a</sup> Center for Molecular Spectroscopy and Dynamics, Institute for Basic Science (IBS), Seoul 02841, Korea

<sup>b</sup> Department of Chemistry and Research Institute for Natural Sciences, Korea University, Seoul 02841, Republic of Korea

<sup>c</sup> Department of Materials Science and Engineering, Research Institute of Advanced Materials, Seoul National University, 599 Gwanak-ro, Gwanak-gu, Seoul 08826, Republic of Korea

<sup>d</sup> Korea Basic Science Institute (KBSI), Seoul 02841, Republic of Korea

<sup>‡</sup> These authors contributed equally to this work.

\* To whom all correspondence should be addressed to K. Kang (email: matlgen1@snu.ac.kr) and K. Lee (email: kylee1@korea.ac.kr).

**Material Characterizations.** Transmission Electron Microscopy (TEM) and high-Resolution TEM (HRTEM) were carried out in Tecnai G2 20 S-Twin microscope operated at 200 kV and Tecnai G2 F30ST microscope operated at 300 kV. X-ray diffraction (XRD) patterns were collected to understand the crystal structures of MnCO<sub>3</sub> nanoplate, porous MnO<sub>2</sub> nanoplate, and porous Au/MnO<sub>2</sub> nanoplate with Rigaku Ultima III diffractometer system using graphite-monochromatized Cu-K $\alpha$  radiation at 40 kV and 30 mA.

**Electrode preparation.** The working electrode was prepared by drop-casting method on the carbon paper using catalyst homogeneous ink. To form homogeneous ink, 5 mg of active materials were dispersed in 1 ml of deionized water with 0.1 ml of neutralized Nafion solution and sonicated for 30 min. The prepared ink was

dropped onto the carbon paper with a loading amount of  $0.4 \text{ mg cm}^{-2}$  and the prepared electrode was dried at  $80 \text{ }^{\circ}\text{C}$  oven for 30 minutes.

**Electrochemical characterizations.** Electrochemical characterizations were measured using a conventional three-electrode cell configuration in  $1 \text{ M KOH}$  electrolyte with an electrochemical potentiostat (CHI 608C, CH Instruments). Ag/AgCl electrode with saturated KCl solution and Pt plate were used as a reference electrode and a counter electrode, respectively. All potential are shown the reversible hydrogen electrode (RHE) according to following equation,  $E(\text{RHE}) = E(\text{Ag/AgCl}) + 0.059 \times \text{pH} + 0.197 \text{ V}$ . Ohmic drop of all data were compensated. Cyclic voltammetry (CV) measurement was carried out in  $1 \text{ M KOH}$  solution at a scan rate of  $10 \text{ mV s}^{-1}$ . In addition, capacitive current was removed by averaging of forward and backward scan. All electrochemical measurements were performed at ambient temperature.

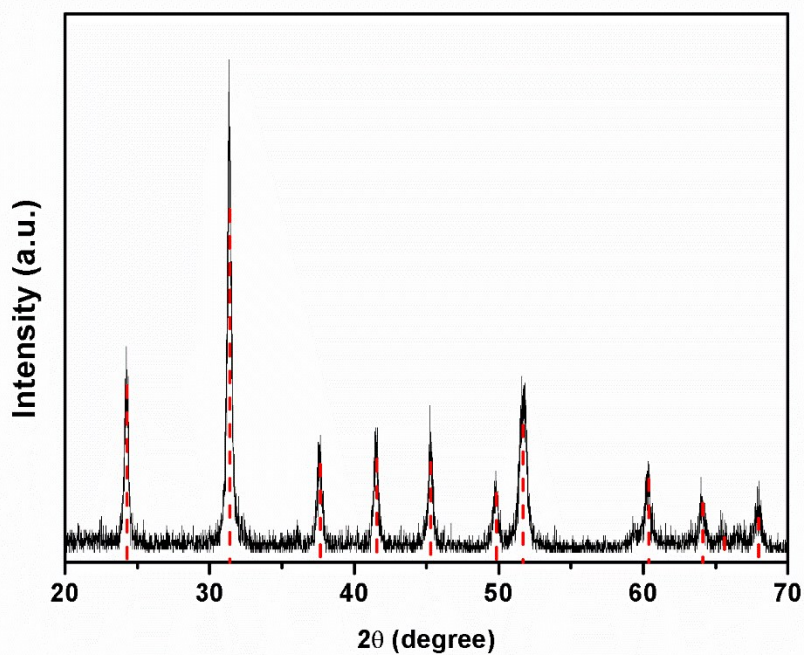
## Experimental Condition

**Preparation of  $\text{MnCO}_3$  nanoplate (MCP).** A slurry of  $\text{Mn}(\text{OAc})_2$  ( $2.50 \text{ mmol}$ ), NaOA ( $2.50 \text{ mmol}$ ) and oleylamine ( $5.00 \text{ mmol}$ ) was prepared in a  $100 \text{ mL}$  Schlenk tube equipped with a bubbler. The tube containing the slurry was evacuated for  $10 \text{ min}$  at room temperature, and then the reaction mixture was maintained at  $290 \text{ }^{\circ}\text{C}$  under  $\text{CO}_2$  flow with magnetic stirring for  $1 \text{ h}$ . The white product was cooled down to room temperature, and washed with copious amount of hexane, ethanol and water to remove any excess reagents. Finally, the white product was treated with dilute acetic acid ( $5\% \text{ v/v}$ ) for  $30 \text{ min}$ , and washed several times with ethanol. The final product was dried in an oven at  $45 \text{ }^{\circ}\text{C}$ .

**Preparation of porous  $\text{MnO}_2$  nanoplate (PMOP).**  $300 \text{ mg}$  of MCP powder was heated in a tube furnace under  $\text{O}_2$  ( $40\%$ ) flow at  $400 \text{ }^{\circ}\text{C}$  for  $2 \text{ h}$ . The black product was collected and washed with ethanol, and then dried in an oven at  $45 \text{ }^{\circ}\text{C}$ .

**Preparation of Au deposited porous  $\text{MnO}_2$  nanoplate (Au/PMOP).** In a typical synthesis of low, medium and high (L-, M- and H-) Au/PMOP, a  $20 \text{ mM}$  stock solution of Au in distilled water was prepared. Three portions of  $50 \text{ mg}$  of

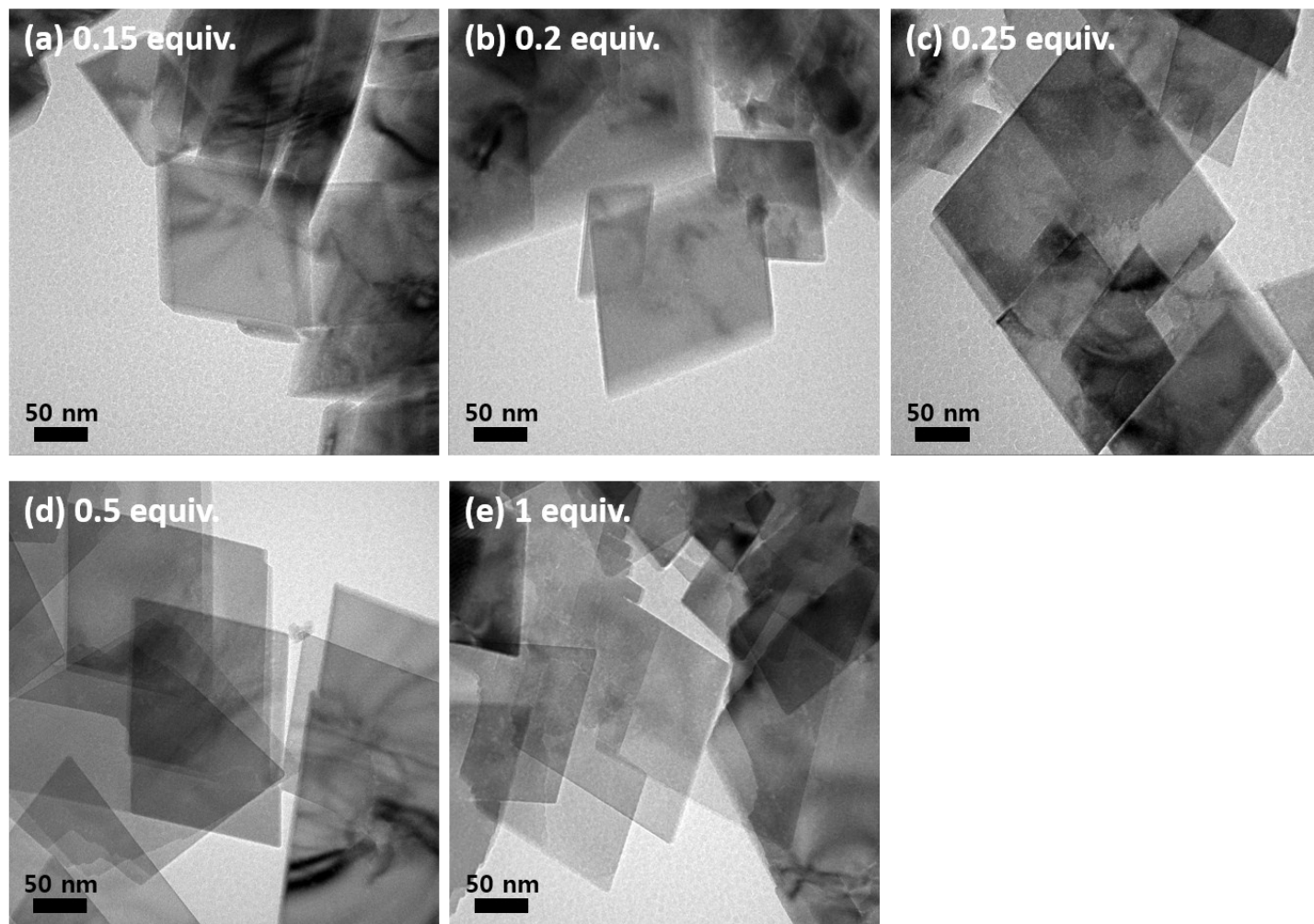
MnO<sub>2</sub> powder were placed in three separate 20 mL vials with 10 mL of distilled water, and 1.0681 g (L), 2.2043 g (M) and 3.4155 g (H) of urea were added to each vial, respectively. The mixtures were sonicated for 10 min for uniform dispersion. Then, three aliquots, 0.89 mL (L), 1.84 mL (M) and 2.84 mL (H) of the Au stock solution, were injected into each vial and the reaction mixtures were maintained at 80 °C for 8 h with magnetic stirring. Finally, each product was collected and washed with copious amount of water and ethanol. The final products were dried in an oven at 45°C.



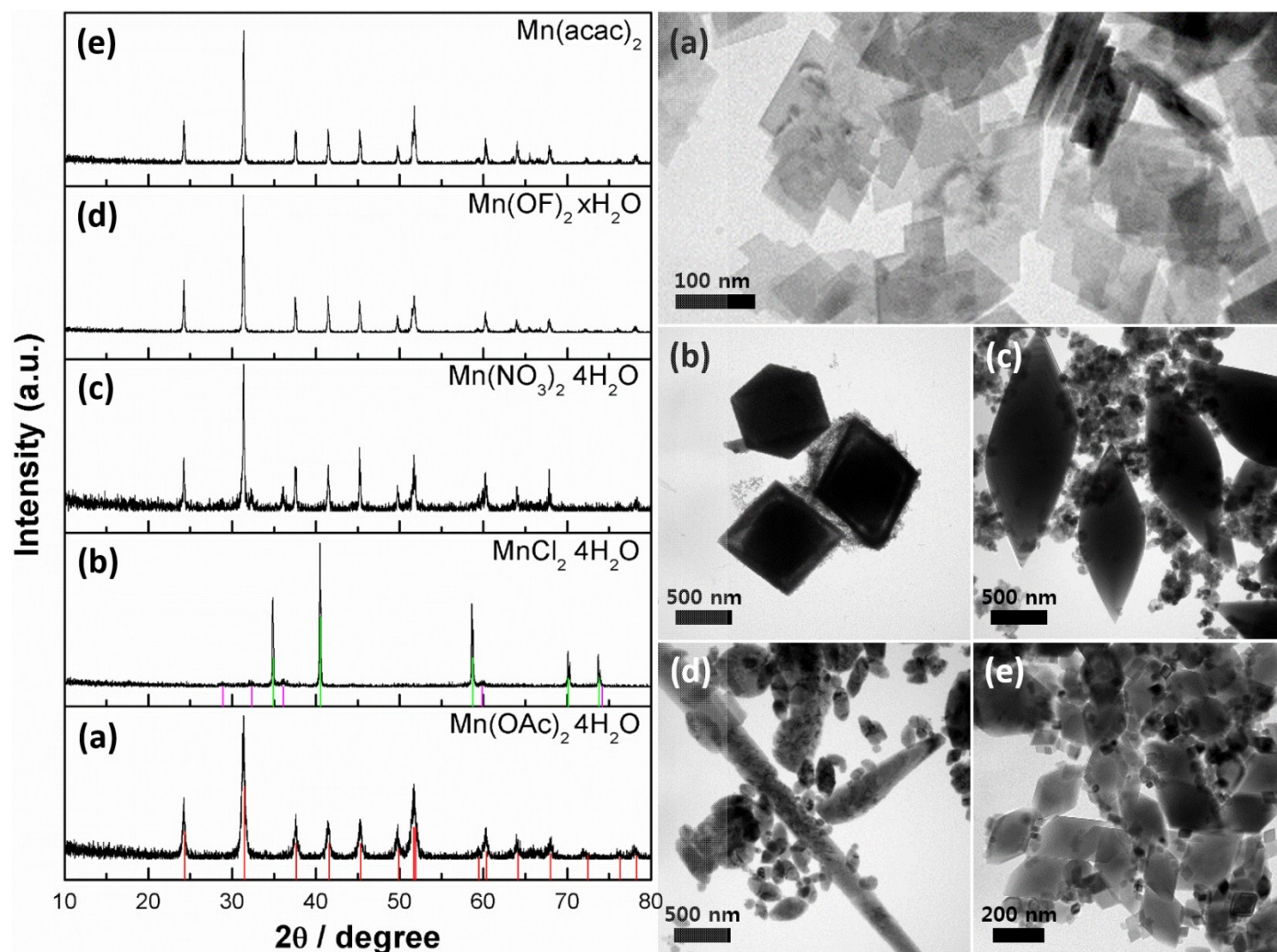
**Fig. S1.** XRD pattern of MCP (red:  $\text{MnCO}_3$ , JCPDS #01-086-0172)

Precursor	Surfactant	Solvent	Gas	Product
$\text{Mn}(\text{OAc})_2$	X	Oleylamine	Ar	MnO
	NaOA	Oleylamine	Ar	MnO
	X	Oleylamine	$\text{CO}_2$	MnO
	NaOA	Oleylamine	$\text{CO}_2$	$\text{MnCO}_3$
	NaOA	1-octadecene	$\text{CO}_2$	$\text{MnCO}_3$

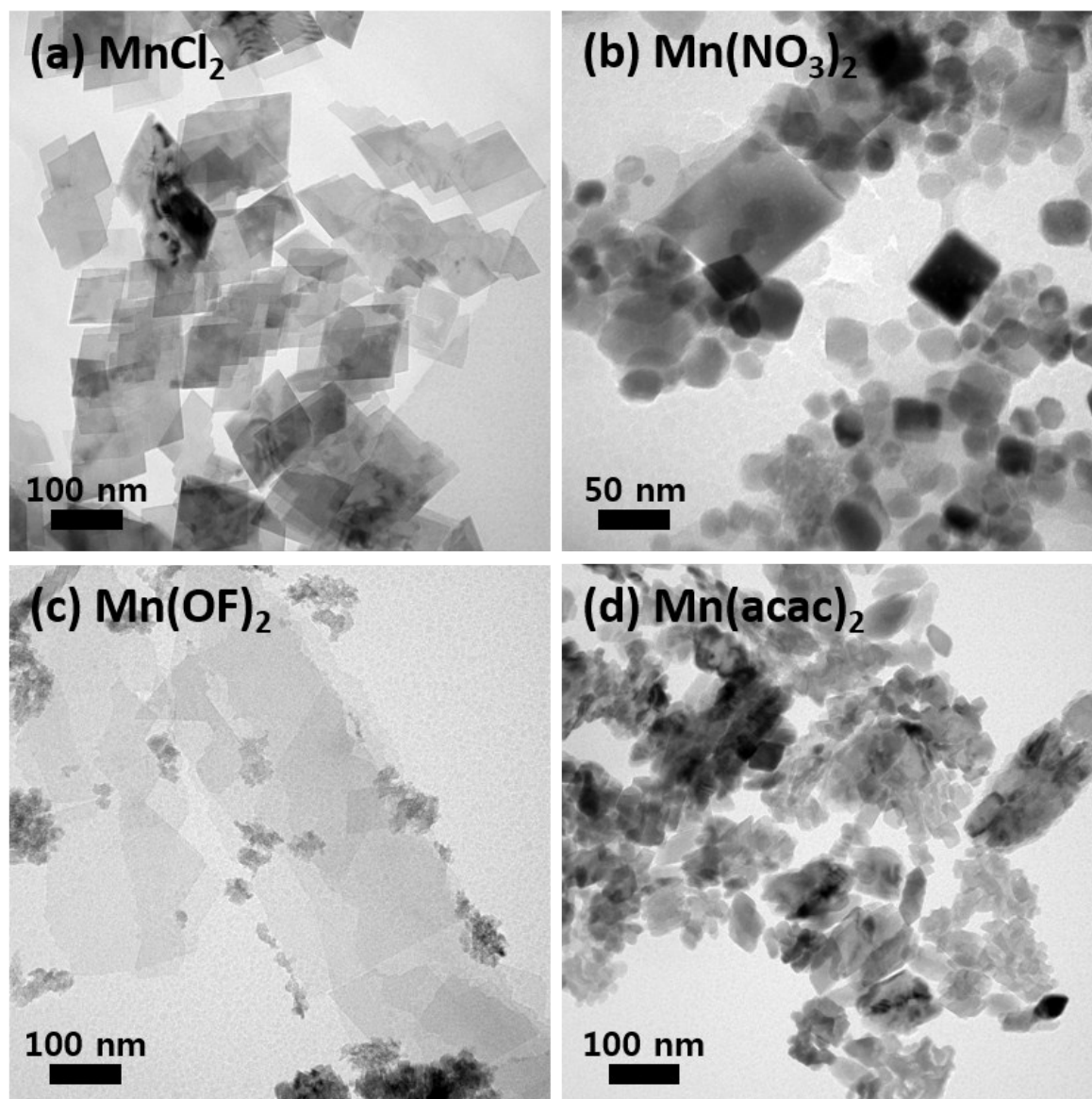
**Table S1.** Testing the role of reagents used in the synthesis of  $\text{MnCO}_3$



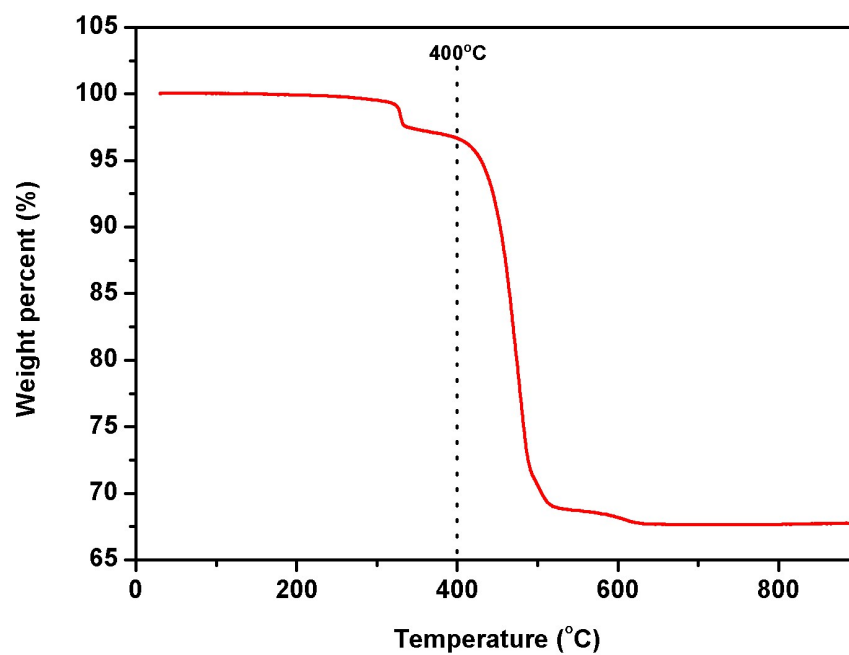
**Fig. S2.** TEM images for MCP showing the changes in nanoplate thickness depending on the different amounts of NaOA.



**Fig. S3.** TEM images and XRD patterns of the products synthesized from (a) Mn(II) acetate tetrahydrate, (b) Mn(II) chloride tetrahydrate, (c) Mn(II) nitrate tetrahydrate, (d) Mn(II) formate hydrate and (e) Mn(II) acetylacetonate (red:  $\text{MnCO}_3$ , green:  $\text{MnO}$ , pink:  $\text{Mn}_3\text{O}_4$ )

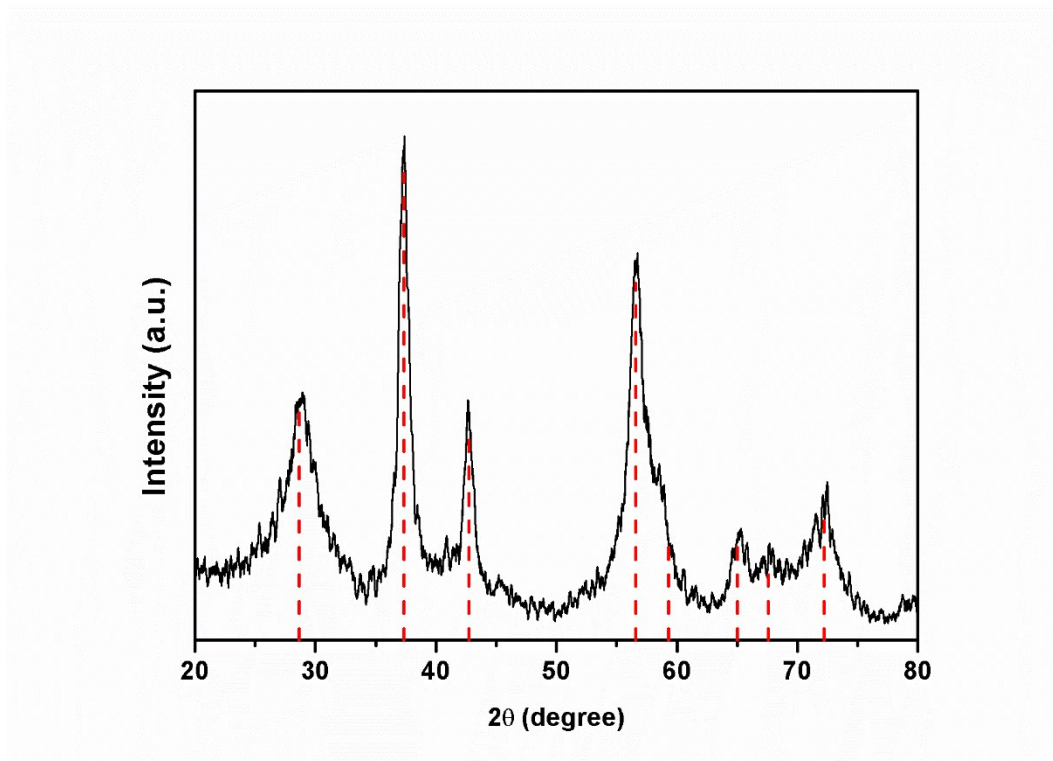


**Fig. S4.** TEM images of the products synthesized from (a) Mn(II) chloride, (b) Mn(II) nitrate, (c) Mn(II) formate and (d) Mn(II) acetylacetonate with sodium acetate.

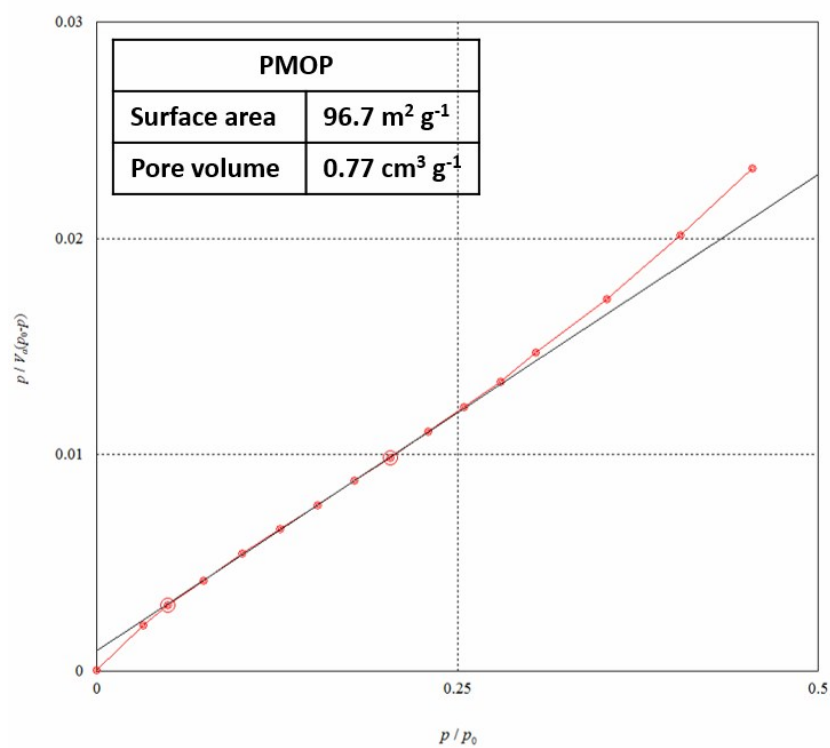
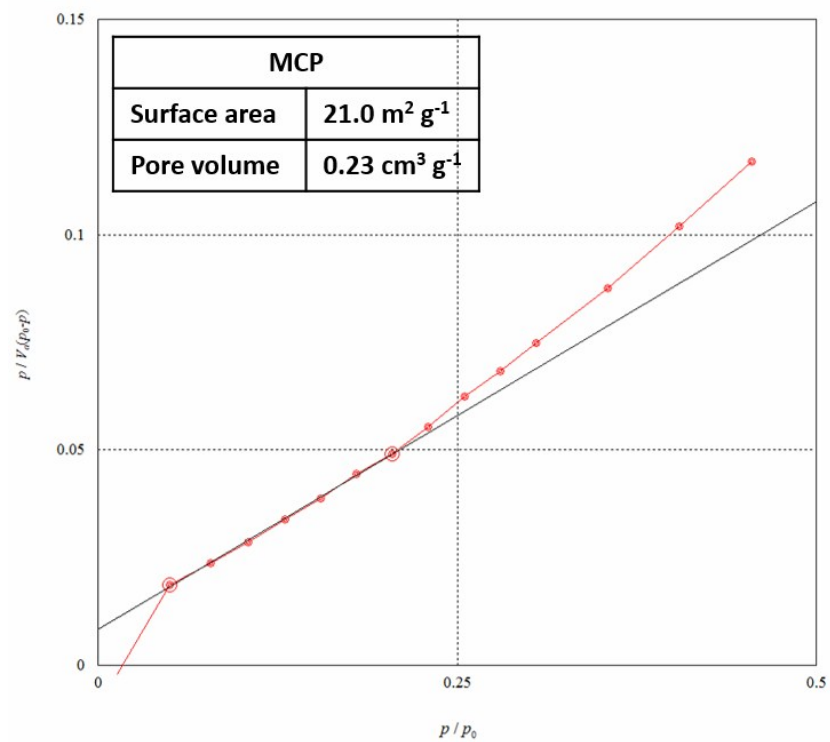


**Fig. S5.** Thermogravimetric analysis of MCP under O<sub>2</sub>

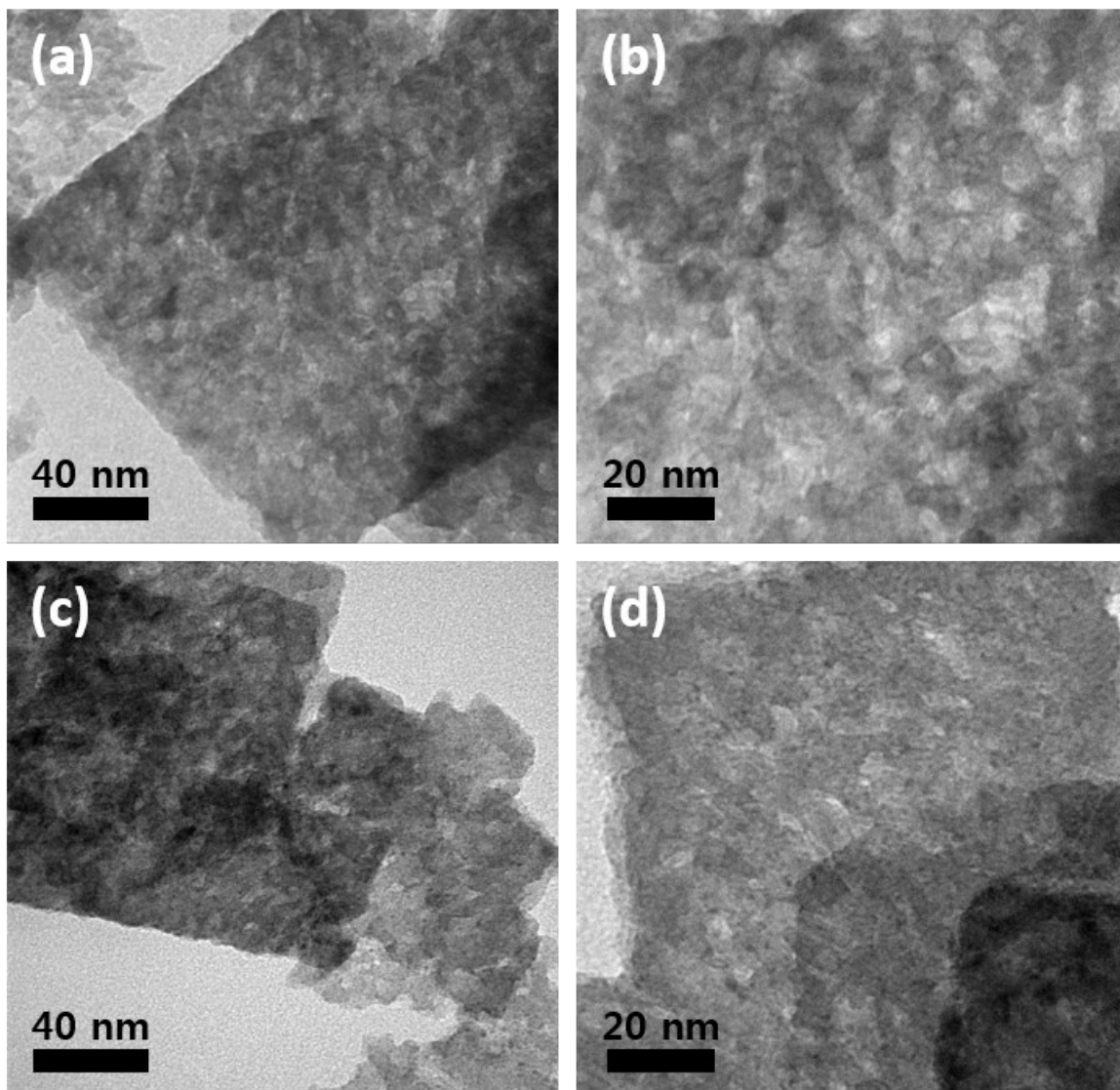




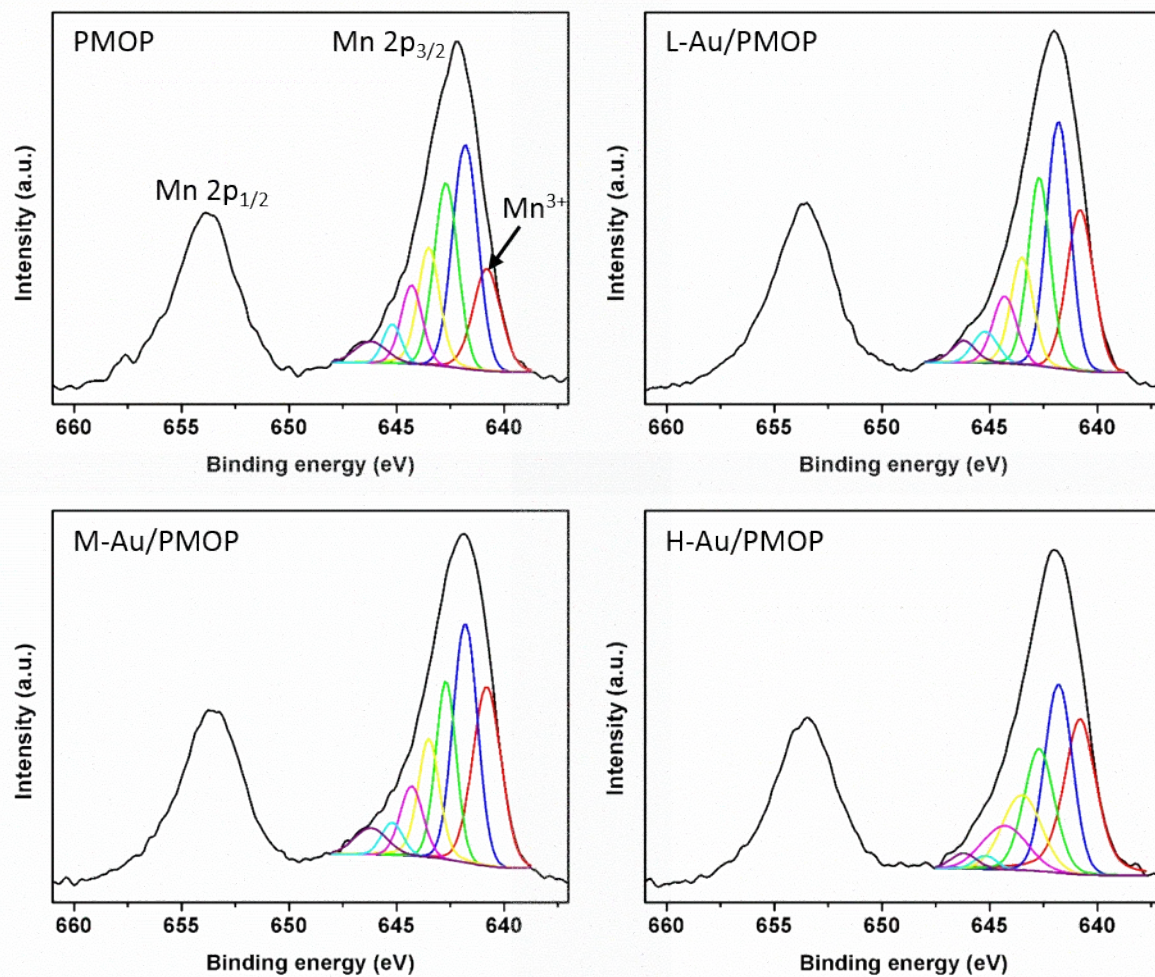
**Fig. S6.** XRD pattern of PMOP (red:  $\beta$ -MnO<sub>2</sub>, JCPDS #01-071-4824)



**Fig. S7.** BET measurements of MCP and PMOP

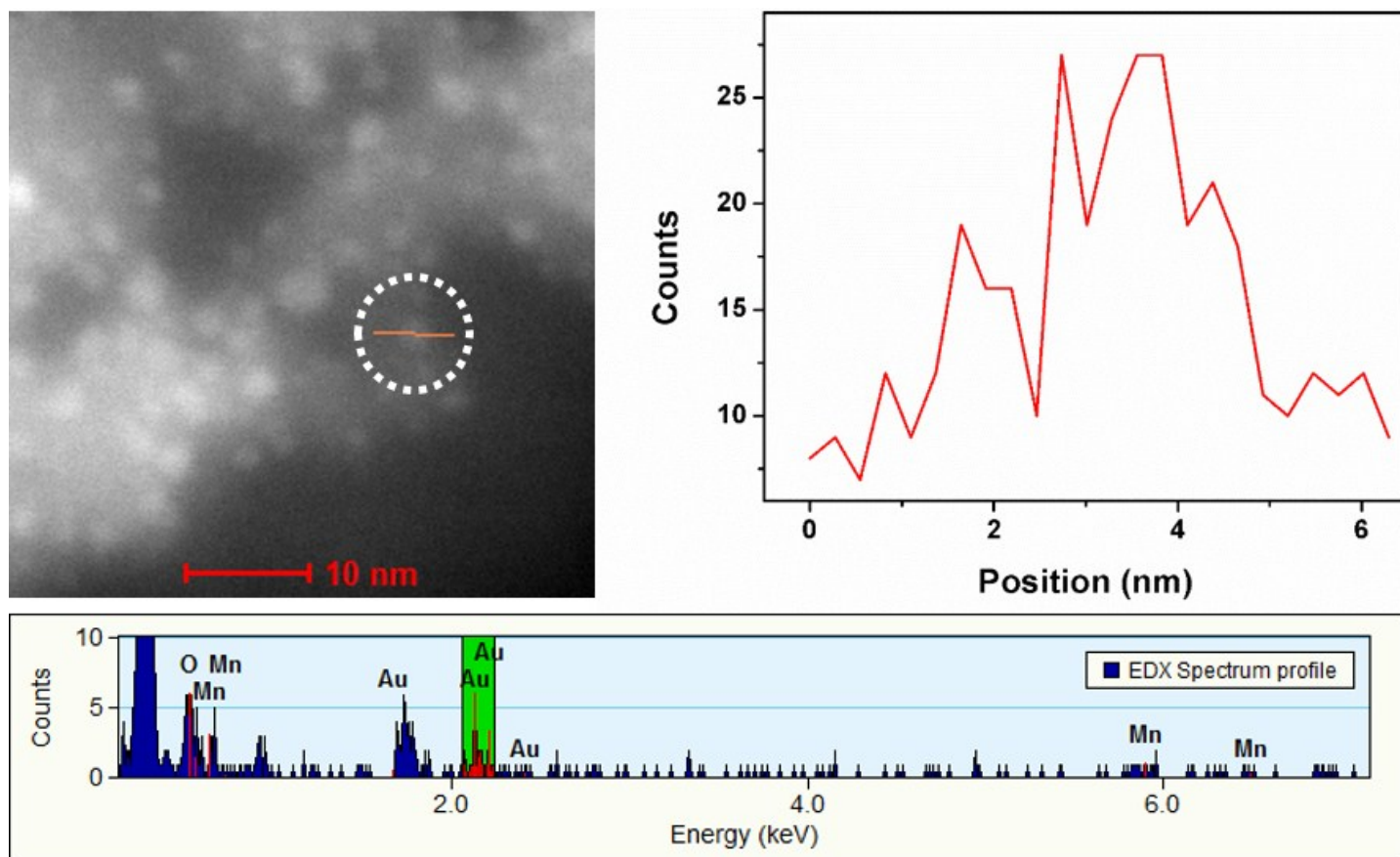


**Fig. S8.** TEM images of (a,b) L-Au/PMOP and (c,d) M-Au/PMOP

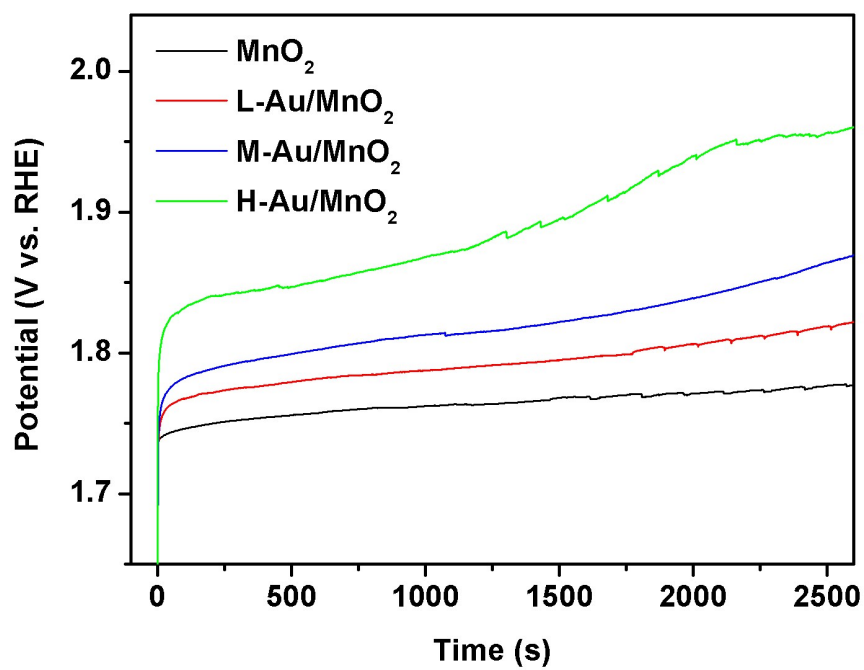


	Peak 1 (blue)	Peak 2 (green)	Peak 3 (yellow)	Peak 4 (magenta)	Peak 5 (neon blue)	Peak 6 (purple)	Mn <sup>3+</sup> peak (red)
Binding energy (eV)	641.8	642.7	643.5	644.3	645.2	646.2	640.8

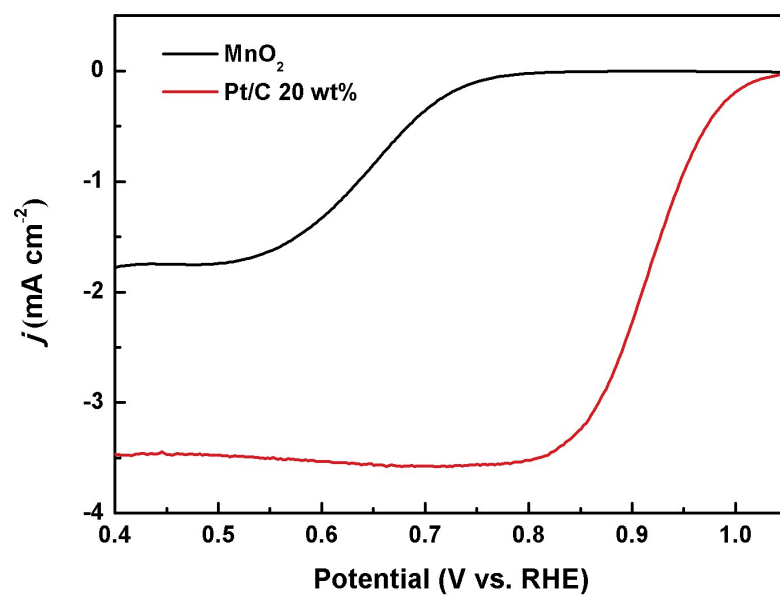
**Fig. S9.** XPS spectra of Mn 2p<sub>3/2</sub> of PMOP and Au/PMOP catalysts



**Fig. S10.** Line profile analysis of Au nanoparticle on porous MnO<sub>2</sub> nanoplate (H-Au/PMOP sample)



**Fig. S11.** Chronopotentiometry at 5 mA cm<sup>-2</sup> for long-term stability test of the catalysts



**Fig. S12.** Voltammograms of PMOP toward oxygen reduction reaction using RDE in 1 M KOH saturated with  $\text{O}_2$ .