Supporting Information

Mechanistic Investigation with Kinetic Parameters on Water Oxidation Catalyzed by Manganese Oxide Nanoparticles Film

Hongmin Seo[†], Kyoungsuk Jin[†], Sunghak Park[†], Kang Hee Cho[†], Heonjin Ha[†], Kang-Gyu Lee[†], Yoon Ho Lee[†], Dang Thanh Nguyen[‡], Hyacinthe Randriamahazaka[#], Jong-Sook Lee*[,‡], and Ki Tae Nam*[,†]

[†]Department of Materials Science and Engineering, 1 Gwanak-ro, Gwanak-gu, Seoul 08826, Korea

[‡]School of Materials Science and Engineering, Chonnam National University, 77 Yongbong-ro, Buk-gu, Gwangju, 61186, Korea

[#]Université Paris Diderot, Sorbonne Paris Cité, ITODYS, UMR 7086 CNRS, SIELE Group, 15 rue Jean Antoine de Baïf, 75013 Paris, France

Supporting Information Content

Pages: S1-S9

Figures: S1-S4

Table: S1

E-mail: jongsook@jnu.ac.kr, nkitae@snu.ac.kr

1. Materials and basic characterization

1. Materials

$Mn(CH_3COO)_3$-$4H_2O$ (99 %), 1-octadecene (90%), myristic acid ($CH_3(CH_2)_{12}COOH$) (99%), decanol ($CH_3(CH_2)_9OH$), Na_2HPO_4-$7H_2O$ (ACS reagent, 98.0-102.0 %), and NaH_2PO_4-$2H_2O$ (99.0 %) were purchased from Sigma Aldrich and used as received without further purification. Fluorine-doped-tin-oxide-coated glass (FTO, TEC-8) with the surface resistivity of 15 Ω sq^{-1} was manufactured by Pilington Company.

2. Scanning electron microscopy (SEM)

The morphology of the p-MnO NPs films on the FTO substrates was characterized with a high resolution scanning electron microscope (Supra 55VP, Carl Zeiss, Germany). After deposition of the MnO NPs, the substrate was gently rinsed in deionized water at least 3 times and dried with nitrogen gas. Images were taken with an acceleration voltage of 2 kV, and EDX spectra with a 15 kV.

3. Transmission electron microscopy (TEM)

TEM images and selected area electron diffraction (SAED) patterns were obtained using a high resolution transmission electron microscope (JEM-3000F, JEOL, Japan) with the acceleration voltage of 300 kV. To prepare TEM samples, the MnO NPs dispersed in hexane were dropped on the TEM grid and dried in air.

2. Estimation of turnover frequency (TOF) for 300 nm-thickness p-MnO NPs

The number of active sites for 300 nm-thickness p-MnO NPs film was calculated with the assumption that all Mn atoms on the surface of nanoparticles serve as the active sites. The number of active sites for 300 nm-thickness Mno NPs film was calculated by the following equation with assumption that the surface of p-MnO NPs was (100) facet. The crystal structure and lattice parameter for MnO were face-centered cubic structure and 4.43×10^{-8} cm.

$$\begin{aligned}(\text{The number of active sites}) &= (ECSA) \times (the\ moles\ of\ Mn\ atoms\ /\ cm^2) \\ &= (147.8)\ \times \left(\frac{2}{(4.43 \times 10^{-8})^2\ \times (6.02\ \times 10^{23})}\right) \\ &= 2.502\ \times 10^{-7}\ \text{moles}\ /\ cm^2 \end{aligned} \quad \text{(S1)}$$

TOF at 1.35 V vs. NHE can be calculated by calculated by the following equation based on the above values.

$$\begin{aligned}(\text{TOF}) &= \frac{(current\ denistiy\ at\ 1.35\ V\ vs.NHE)}{4 \cdot F \cdot (the\ number\ of\ active\ sites)} \\ &= \frac{0.00496\ A/cm^2}{4 \cdot (96485\ A \cdot s\ /mol) \cdot (2.502 \times 10^{-7}\ \text{moles}\ /\ cm^2)} = 0.052\ s^{-1} \end{aligned} \quad \text{(S2)}$$

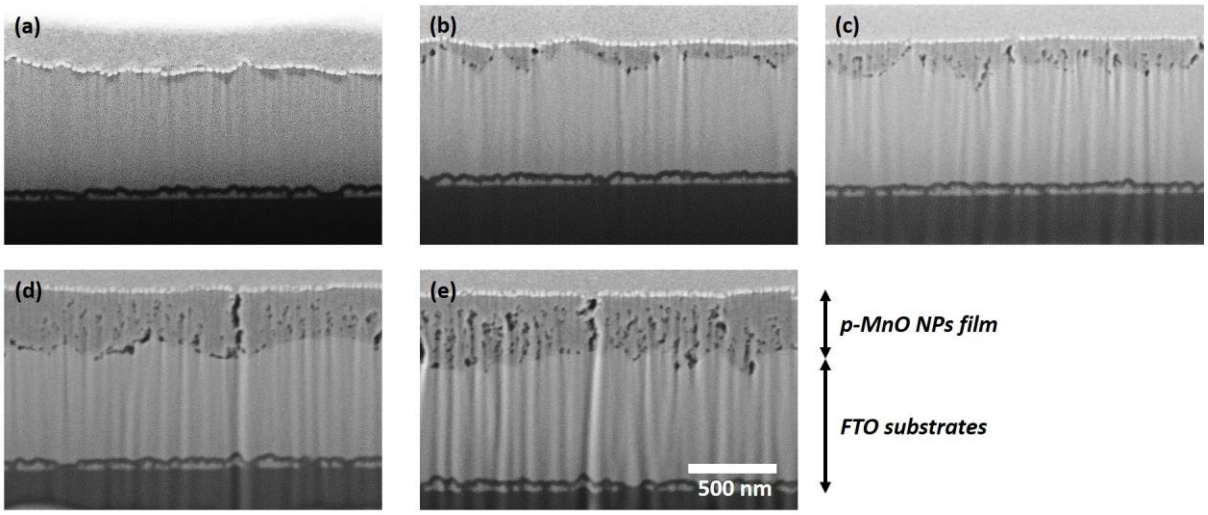


Figure S1. Cross-sectional scanning electron microscopy (SEM) images for p-MnO NPs films on FTO substrates for (a) 20 nm- (b) 70 nm- (c) 150 nm- (d) 300 nm- and (e) 500 nm-thickness

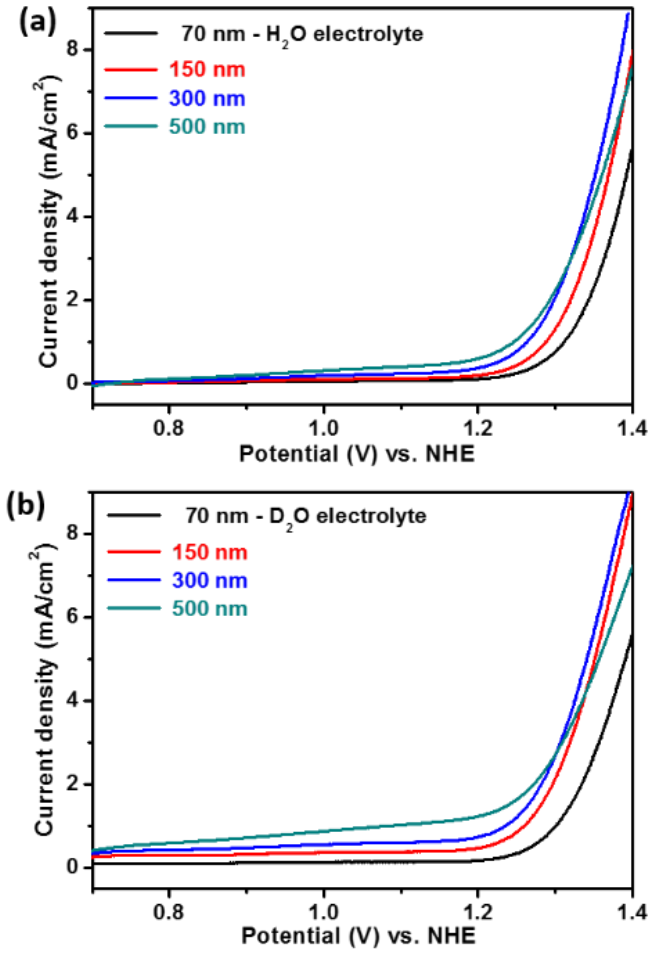


Figure S2. Polarization-corrected cyclic voltammetry curves from 0.7 V to 1.4 V vs. NHE for p-MnO NPs film of various thicknesses (70, 150, 300 and 500 nm) at 0.5M phosphate buffer solution under pH 7. (a) H_2O electrolyte (b) D_2O electrolyte

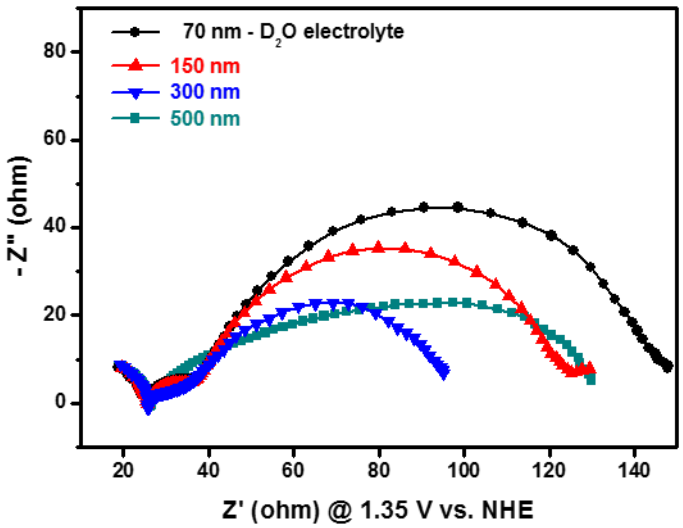
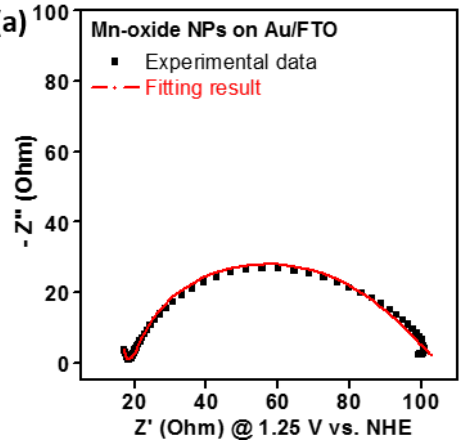


Figure S3. Nyquist plots for several thickness (70, 150, 300 and 500 nm) of p-MnO NPs film at 1.35 V vs. NHE in D_2O electrolyte. The black, red, blue and dark cyan spectra were for 70, 150, 300 and 500 nm-thickness, respectively

(a)



(b)

Physical parameters	Fitting results
R_{tr}	**7.65 Ω**
R_{int}	84.42 Ω
C_{int}	0.036 mF

Figure S4. (a) Nyquist plot for 150 nm-thickness Mn-oxide NPs film on Au/FTO substrates at 1.25 V vs. NHE in 0.5 M phosphate buffer solution. The black dots and red line indicated experimental data and fitting result using our proposed circuit model. (b) The values for physical parameters (R_{tr}, R_{int} and C_{int}) from fitting with our circuit model.

Nature of Mn-oxide	Preparation method	Mass of electroactive materials (mg/cm^2)	Electrolyte	Capacitance (F/g)	Reference
p-MnO NPs	**Spin-coating**	**0.24**	**0.5 M PBS**	**8.97**	**This work**
Mn_3O_4 film	Electrostatic spray deposition	0.116	0.1 M Na_2SO_4	150	Ref. 1
Mn_3O_4 film	Chemical bath deposition	0.57	1 M Na_2SO_4	193	Ref. 2
MwCNT/Mn_3O_4 film	Dip-casting method	10.1	0.5 M Na_2SO_4	143	Ref. 3
Graphene/Mn_3O_4 powder	Hydrothermal	2.0	1 M Na_2SO_4	114	Ref. 4
	Precipitation from MnO_2 organosol	0.75	1 M Na_2SO_4	175	Ref. 5

Table S1. Summary for reported capacitance for several Mn-oxide electrodes.

References

1. Nam, K.-W.; Kim, K.-B., Manganese oxide film electrodes prepared by electrostatic spray deposition for electrochemical capacitors. *J. Electrochem. Soc.* **2006,** *153* (1), A81-A88, DOI 10.1149/1.2131821.
2. Jang, K.; Lee, S.-w.; Yu, S.; Salunkhe, R. R.; Chung, I.; Choi, S.; Ahn, H., Facile Low-temperature Chemical Synthesis and Characterization of a Manganese Oxide/multi-walled Carbon Nanotube Composite for Supercapacitor Applications. *Bull. Korean Chem. Soc* **2014,** *35* (10), 2975, DOI 10.5012/bkcs2014.35.10.2974.
3. Cui, X.; Hu, F.; Wei, W.; Chen, W., Dense and long carbon nanotube arrays decorated with Mn_3O_4 nanoparticles for electrodes of electrochemical supercapacitors. *Carbon* **2011,** *49* (4), 1225-1234, DOI 10.1016/j.carbon.2010.11.039.
4. Lee, J. W.; Hall, A. S.; Kim, J.-D.; Mallouk, T. E., A facile and template-free hydrothermal synthesis of Mn_3O_4 nanorods on graphene sheets for supercapacitor electrodes with long cycle stability. *Chem. Mater.* **2012,** *24* (6), 1158-1164, DOI 10.1021/cm203697w.
5. Wang, B.; Park, J.; Wang, C.; Ahn, H.; Wang, G., Mn_3O_4 nanoparticles embedded into graphene nanosheets: preparation, characterization, and electrochemical properties for supercapacitors. *Electrochimica Acta* **2010,** *55* (22), 6812-6817, DOI 10.1016/j.electacta.2010.05.086.