Electronic Supplementary Information for

Catalytic activity of $NiMnO_3$ for visible light-driven and electrochemical water oxidation

Dachao Hong,[a] Yusuke Yamada,[a] Akifumi Nomura[a] and Shunichi Fukuzumi*[,a,b]

[a] *Department of Material and Life Science, Graduate School of Engineering, ALCA, Japan Science and Technology Agency, Osaka University, Suita, Osaka 565-0871, Japan*
[b] *Department of Bioinspired Science, Ewha Womans University, Seoul, 120-750, Korea*

* To whom correspondence should be addressed.
E-mail: fukuzumi@chem.eng.osaka-u.ac.jp; Fax: +81-6-6879-7370; Tel: +81-6-6879-7368

Experimental Methods

Materials. All chemicals used for synthesis were obtained from a chemical company and used without further purification. Manganese(II) nitrate hexahydrate, Mn_2O_3 (mesh 325) and Mn_3O_4 (mesh 325) were purchased from Sigma-Aldrich Co. Nickel(II) nitrate hexahydrate, nickel(II) acetate tetrahydrate, cobalt(II) acetate, $Na_2S_2O_8$, $NaHCO_3$, ethylene glycol (EG), phosphate buffer powder (pH 7.0) and Ag_2SO_4 were obtained from Wako Pure Chemical Industries, Ltd. $[Ru(bpy)_3]Cl_2$ was obtained from Tokyo Chemical Industry Co., Ltd. $[Ru(bpy)_3]SO_4$ was synthesised by adding one equivalent of Ag_2SO_4 to an aqueous solution of $[Ru(bpy)_3]Cl_2$. Purified water was provided by a Millipore MilliQ water purification system where the electronic conductance was 18.2 MΩ cm. $NiMnO_3$, α-MnO_2, NiO and Co_3O_4 were synthesised by following reported methods.

Synthesis of $NiMnO_3$ and α-MnO_2.[S1] An aqueous solution (10 mL) containing nickel(II) nitrate hexahydrate (2.5 mmol, 0.73 g) and manganese(II) nitrate hexahydrate (2.5 mmol, 0.72 g) was slowly added to $NaHCO_3$ aqueous solution (1.0 M, 50 mL) with magnetic stirring at room temperature (RT). The resulting precipitates were collected by centrifugation and washed with water and ethanol for several times, and finally dried *in vacuo*. The precursor was heated with a rate of 10 ºC/min up to 450 ºC in air, maintaining the temperature for 5 h, and finally rapid cooling to RT. α-MnO_2 was prepared by addition of an aqueous solution (10 mL) containing manganese(II) nitrate hexahydrate (5.0 mmol, 1.4 g) to $NaHCO_3$ aqueous solution (1.0 M, 50 mL) and followed by the same procedure of $NiMnO_3$.

Synthesis of NiO.[S2] Ethylene glycol (EG) (24 mL) was added to an aqueous solution (24 mL) containing nickel(II) acetate tetrahydrate (5.0 mmol, 1.24 g) with magnetic stirring at RT. The solution was then transferred into a Teflon-lined stainless-steel autoclave of 140 mL capacity. The sealed autoclave was heated to and maintained at 200 ºC for 3.0 h in an oven and cooled to RT. The resulting emerald green precipitates $[Ni(OH)_2]$ were collected by filtration and washed with water and ethanol for several times, and dried *in vacuo*. NiO was prepared by calcination of the obtained $Ni(OH)_2$ in an oven at 300 ºC in air for 3.0 h.

Synthesis of Co_3O_4.[S3] An aqueous solution of cobalt(II) acetate (80 mM, 73 mL) was slowly added to an aqueous ammonia solution (25%, 7.3 mL) with vigorous stirring by a magnetic stirrer. After 20 min stirring, the obtained pale pink slurry was transferred to a Teflon-lined stainless-steel autoclave of 140 mL capacity. The sealed autoclave was heated to and maintained at 150 ºC for 3.0 h in an oven and cooled to RT. The obtained particles were collected by filtration and washed with water for several times and dried at 65 ºC for several hours.

Characterisation of Catalysts. X-ray diffraction patterns were recorded by a Rigaku Ultima IV. Incident X-ray radiation was produced by Cu X-ray tube, operating at 40 kV and 40 mA with Cu $K\alpha$ radiation of 1.54 Å. The scanning rate was 2 °/min from 10° to 70° in 2θ. Scanning electron microscope images of metal oxides were observed by a FE-SEM (JSM-6701F) operating at 3.0 kV. X-ray fluorescence analysis was performed with a ZSX-100e (Rigaku). Nitrogen adsorption-desorption at 77 K was performed with a Belsorp-mini (BEL Japan, Inc.) within a relative pressure range from 0.01 to 101.3 kPa. A sample mass of ~200 mg was used for adsorption analysis after pretreatment at 150 ºC for ~3.0 h under vacuum conditions and kept in N_2 atmosphere until N_2-adsorption measurements. The sample was exposed to a gas mixture of He and N_2 with a programmed ratio and adsorbed amount of N_2 was calculated from the change of pressure in a cell after reaching the equilibrium (at least 5 min).

Light-driven Water Oxidation. Light-driven water oxidation was performed as follows. A catalyst (0.10 or 0.50 g L^{-1}) was added to a phosphate buffer solution (50 mM, pH 7.0, 2.0 mL) containing $Na_2S_2O_8$ (5.0 mM) and $[Ru(bpy)_3]SO_4$ (0.25 mM) flushed with Ar gas. The solution was then irradiated with a xenon lamp (Ushio Optical, Model X SX-UID 500X AMQ) through a colour filter glass (Asahi Techno Glass) transmitting $\lambda > 420$ nm at room temperature. Evolved oxygen gas in a headspace was quantified by a Shimadzu GC-17A gas chromatograph [Ar carrier, a capillary column with molecular sieves (Agilent Technologies, 19095PMS0, 30 m × 0.53 mm) at 313 K] equipped with a thermal conductivity detector.

Electrochemical Water Oxidation. Electrochemical water oxidation was performed on an ALS 630B electrochemical analyzer using a carbon paste electrode modified with 5% of a metal oxide catalyst as a working electrode, a saturated calomel reference electrode (SCE) and a Pt wire as a counter electrode. Linear sweep voltammograms were recorded by applying the voltage from 0 V to 1.5 V to the working electrode in a phosphate buffer (50 mM, pH 7.0) at room temperature with a scanning rate of 100 mV s^{-1}.

S1. D. Mehandjiev, A. Naydenov and G. Ivanov, *App. Catal.*, *A*, 2001, **206**, 13.

S2. L.-X. Yang, Y.-J. Zhu, H. Tong, Z.-H. Liang, L. Li and L. Zhang, *J. Solid State Chem.* 2007, **180**, 2095.

S3. Y. Yamada, K. Yano, Q. Xu and S. Fukuzumi, *J. Phys. Chem. C*, 2010, **114**, 16456.

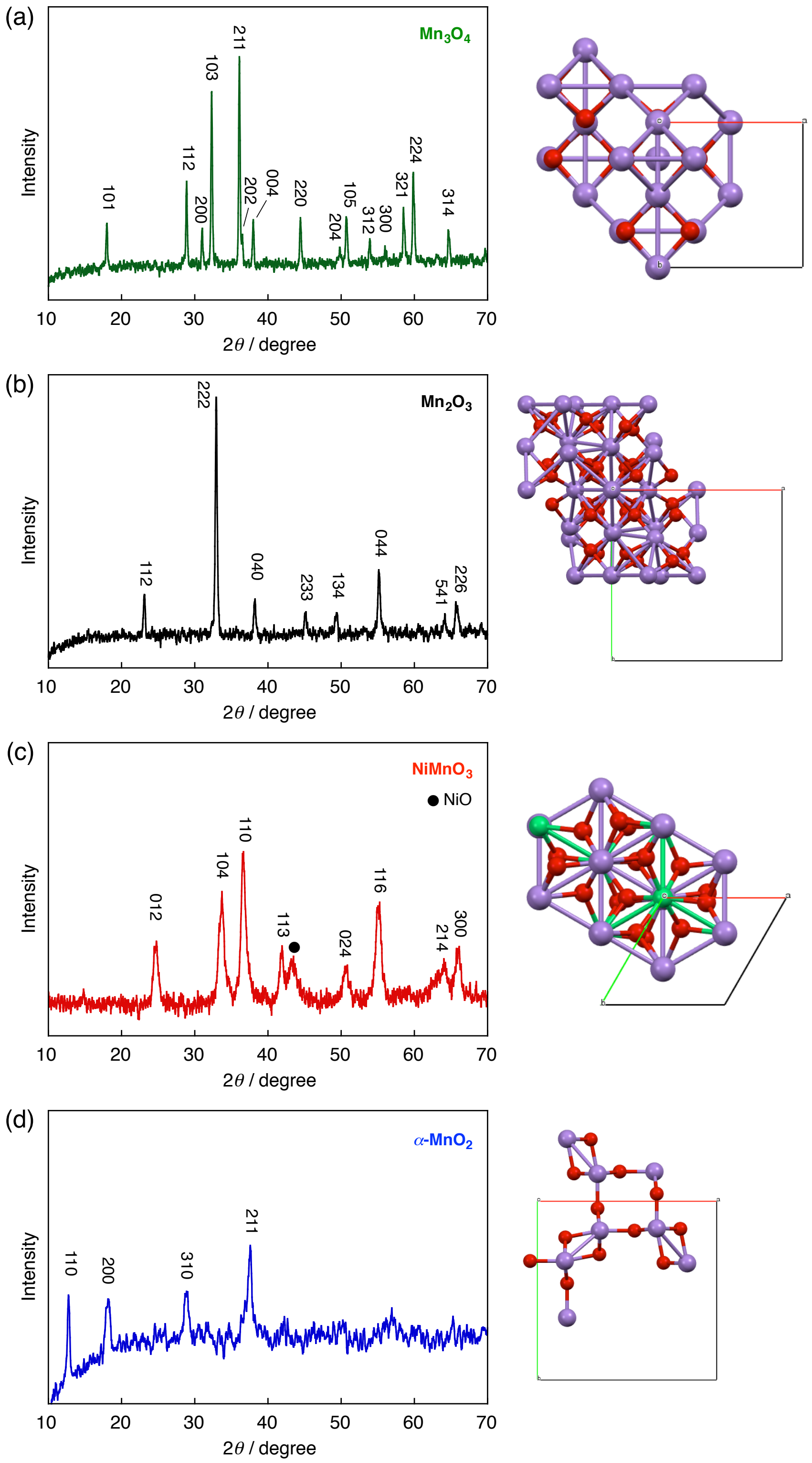

Fig. S1 Powder XRD patterns of (a) Mn_3O_4, (b) Mn_2O_3 (c) $NiMnO_3$ and (d) α-MnO_2 with the Miller indexes. The sizes of crystallites determined by using the Scherrer's equation were 33 nm for Mn_3O_4, 26 nm for Mn_2O_3, 8.8 nm for $NiMnO_3$ and 21 nm for α-MnO_2.

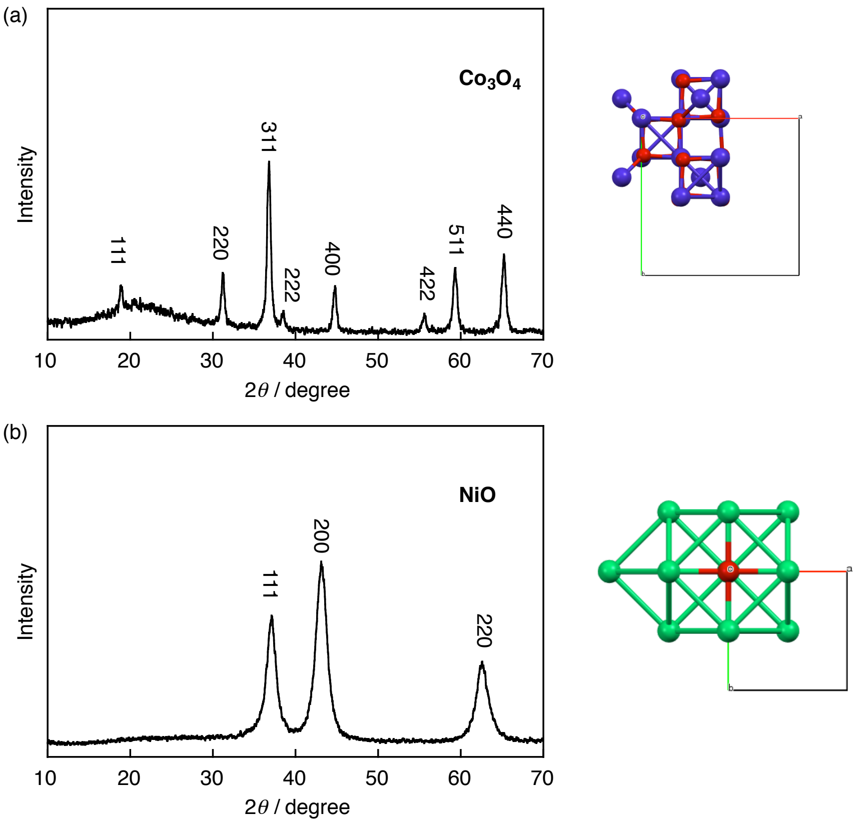

Fig. S2 Powder XRD patterns of (a) Co_3O_4 and (b) NiO with the Miller indexes. The sizes of crystallites determined by using the Scherrer's equation were 15 nm for Co_3O_4 and 5.0 nm for NiO.

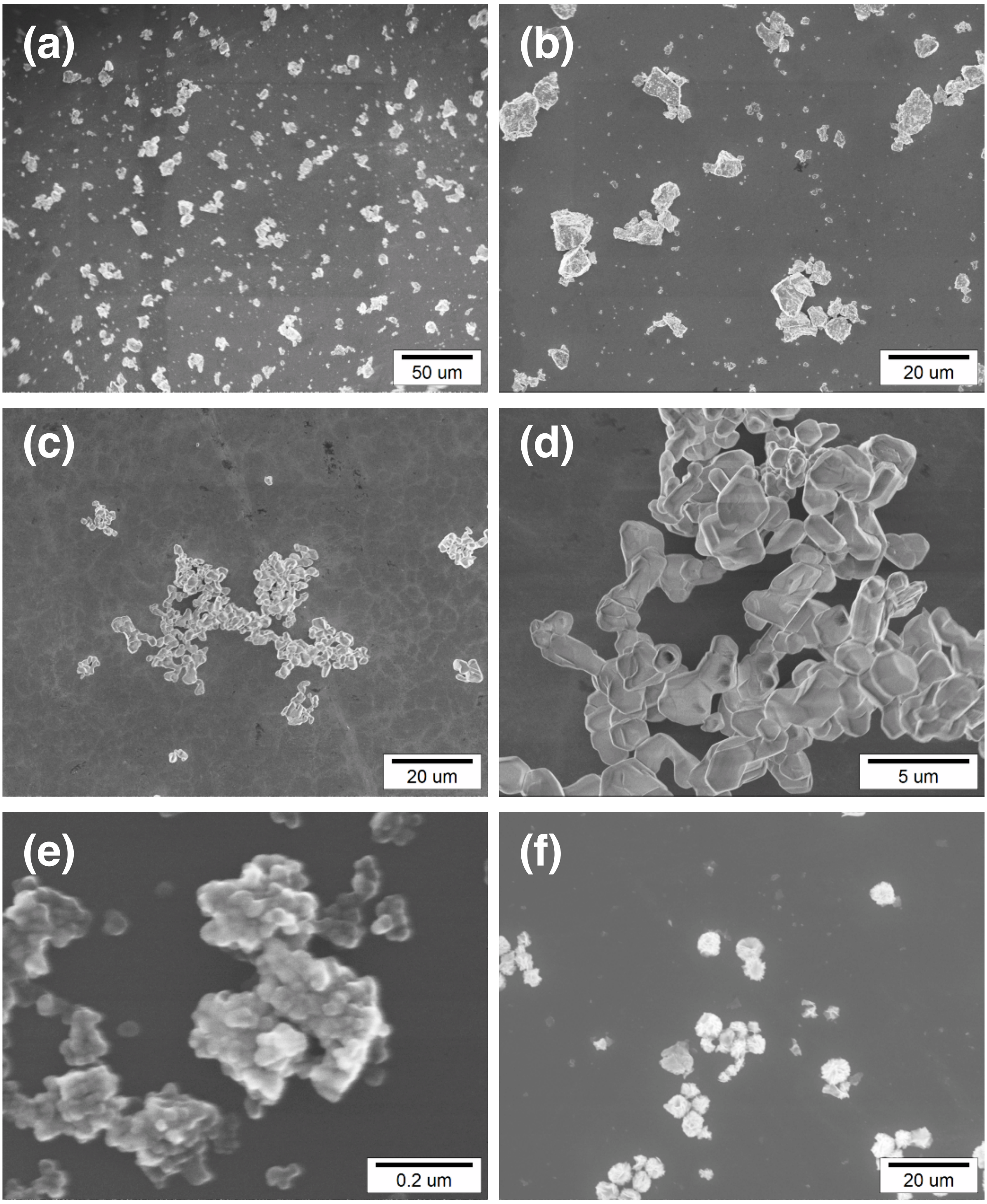

Fig. S3 SEM images of (a and b) Mn_2O_3, (c and d) Mn_3O_4, (e) Co_3O_4 and (f) NiO.

Table S1 Overpotential of various catalysts for electrochemical water oxidation.

Catalyst	Onset potential, V (*vs.* SCE)	pH	Standard potential, V (*vs.* SCE)	Overpotential, V	ref.
$NiMnO_3$	1.0	7.0	0.58	0.42	this work
Co phosphate	0.99	7.0	0.58	0.41	S4
Ni borate	0.89	9.2	0.45	0.44	S5
Nickel ferrite	0.95	8.0	0.52	0.43	S6

S4. M. W. Kanan and D. G. Nocera, *Science*, 2008, **321**, 1072.

S5. D. K. Bediako, B. Lassalle-Kaiser, Y. Surendranath, J. Yano, V. K. Yachandra and D. G. Nocera, *J. Am. Chem. Soc.*, 2012, **134**, 6801.

S6. D. Hong, Y. Yamada, T. Nagatomi, Y. Takai and S. Fukuzumi, *J. Am. Chem. Soc.*, 2012, **134**, 19572.