Electronic Supplementary Information for

Boosting Photocatalytic Overall Water Splitting by Co doping into Mn₃O₄ Nanoparticles as Oxygen Evolution Cocatalyst

Taizo Yoshinaga,[a] Masaki Saruyama,*[b] Anke Xiong,[c] Yeilin Ham,[c] Yongbo Kuang,[c] Ryo Niishiro,[d,e] Seiji Akiyama,[e,f] Masanori Sakamoto,*[b] Takashi Hisatomi,[c] Kazunari Domen,[c] and Toshiharu Teranishi*[b]

[a] Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8571, Japan

[b] Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan

[c] Department of Chemical System Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

[d] Mitsui Chemicals, Inc., 580-32 Nagaura, Sodegaura 299-0265, Japan

[e] Japan Technogical Research Association of Artificial Photosynthetic Chemical Process (ARPChem), 5-1-5 Kashiwanoha, Kashiwa 277-6589, Japan

[f] Mitsubishi Chemical Group Science and Technology Research Center, Inc., 1000 Kamoshida-cho, Aoba-ku, Yokohama 227-8502, Japan
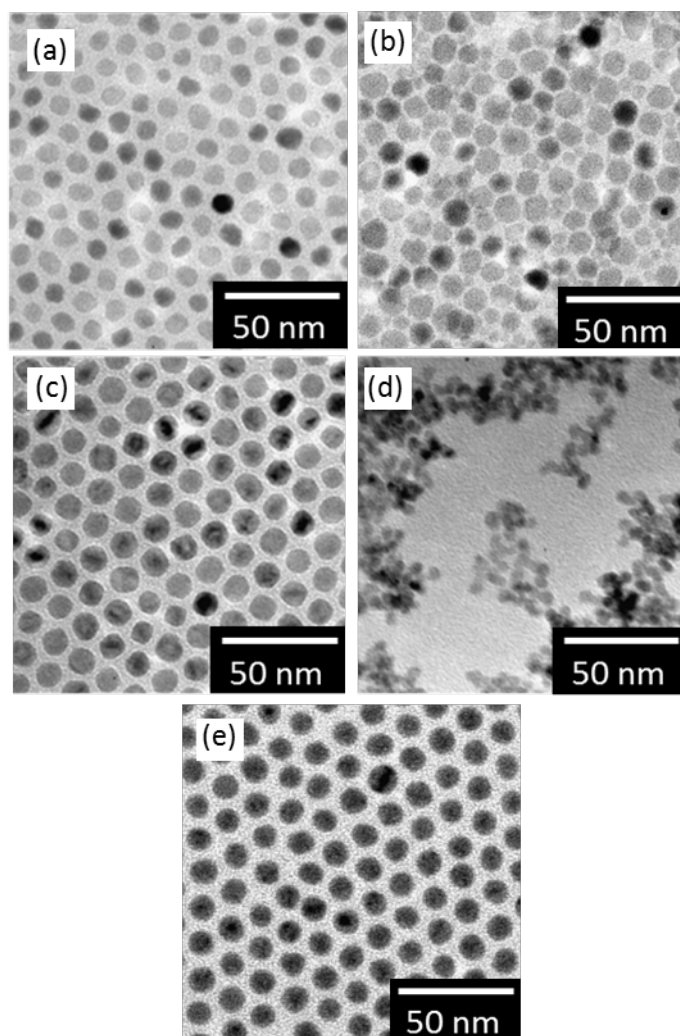
Contents

Fig. S1 TEM images of $Co_yMn_{1-y}O$ NPs synthesized in different conditions. (a) 50 mol%Co using Co(II) stearate (9.7±0.9 nm), (b) 60 mol%Co using Co(II) stearate (9.8±1.8 nm), (c) 10 mol%Co using Co(II) acetate (10.9±0.8 nm), and (d) 10 mol%Co using Co(II) acetylacetonate. (e) TEM image of Co NPs (11.3±0.6 nm).
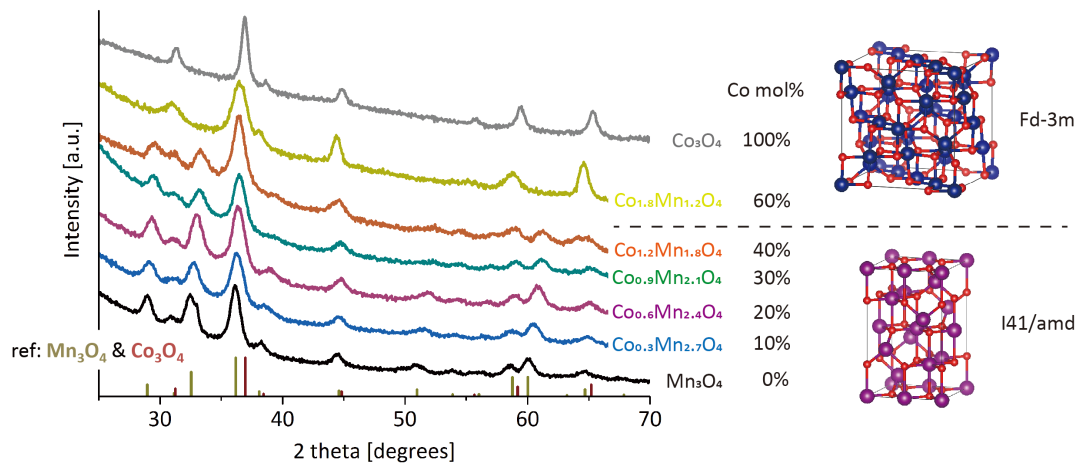
Fig. S2 XRD patterns of Co$_x$Mn$_{3-x}$O$_4$ NPs with x of 0, 0.3, 0.6, 0.9, 1.2, 1.8 and 3. Crystal phase transition from tetragonal spinel (I41/amd) to cubic spinel (Fd-3m) occurred when x became larger than 1.2.
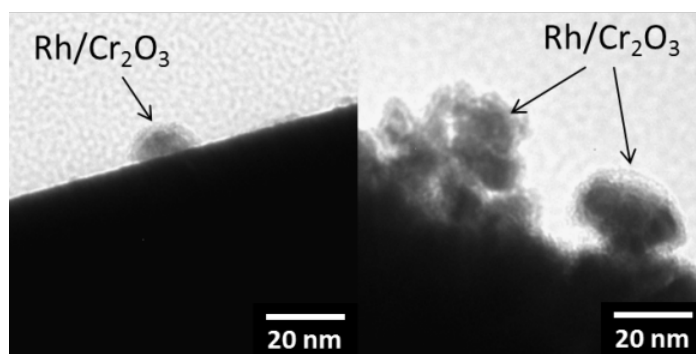
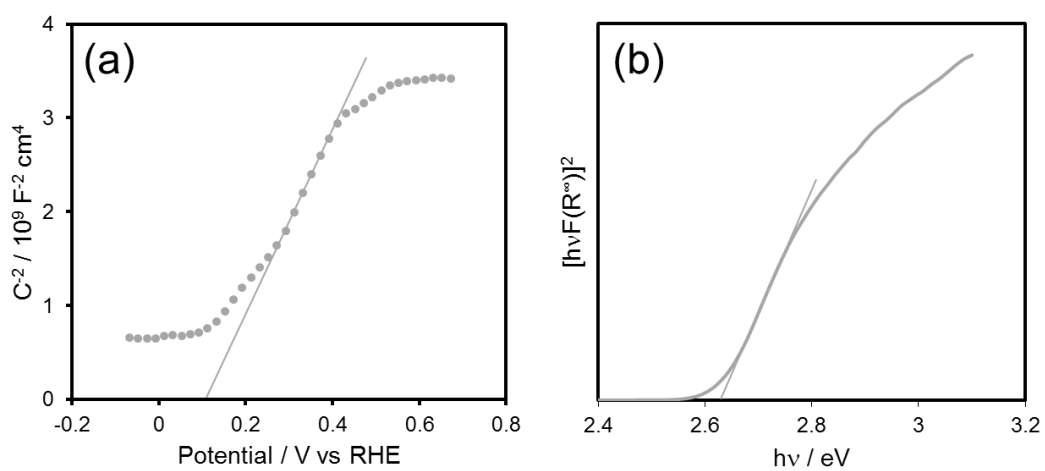**Fig. S3** TEM images of Rh@Cr_2O_3 NPs on $Co_xMn_{3-x}O_4$ (Co 40 mol%) loaded $SrTiO_3$.

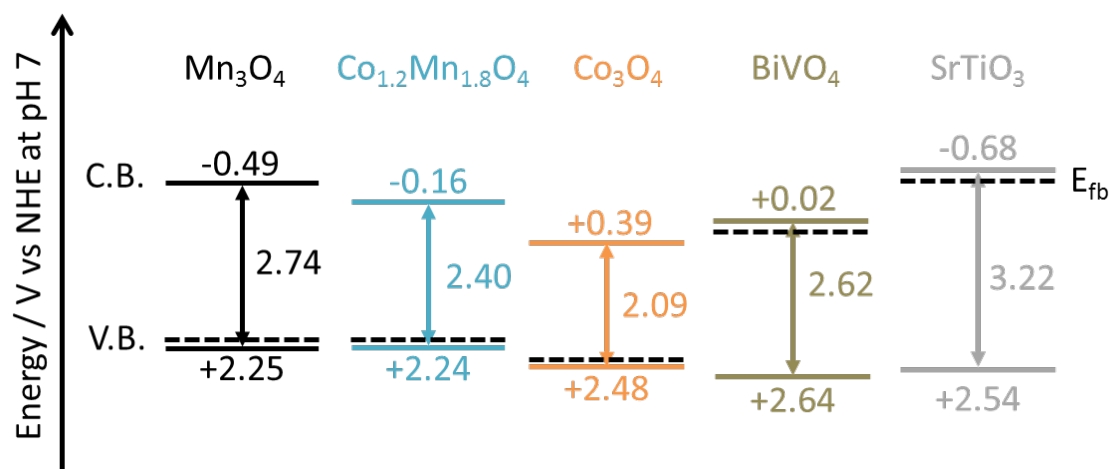**Fig. S4** (a) Mott-Schottky plot and (b) Tauc plot of $BiVO_4$ film.

Fig. S5 Schematic of calculated band structures of $Co_xMn_{3-x}O_4$, $BiVO_4$, and $SrTiO_3$.

Table S1 Calculated Mulliken electron negativity (χ), measured band gap energy (E_g), isoelectric point (IEP), energy level of conduction band edge (E_{cb}) and valence band edge (E_{vb}) of $Co_xMn_{3-x}O_4$, $BiVO_4$, and $SrTiO_3$.

	χ	E_g (measured) / eV	IEP / pH	E_{cb} / eV vs NHE at pH 7	E_{vb} / eV vs NHE at pH 7
Mn_3O_4	5.57	2.74	3.8 [a]	-0.49	+2.25
$Co_{1.2}Mn_{1.8}O_4$	5.70	2.40	4.2 [b]	-0.16	+2.24
Co_3O_4	5.90	2.09	7.5 [c]	+0.39	+2.48
$BiVO_4$	6.04	2.62	3.5 [d]	+0.02	+2.64
$SrTiO_3$	5.34	3.22	8.5 [e]	-0.68	+2.54

χ was calculated by using ionization energy and electron affinity of each atom.[f]

IEP of $Co_{1.2}Mn_{1.8}O_4$ is assumed to be the same as that of $CoMn_2O_4$.[b]

E_{cb} and E_{vb} were estimated by using an equation below[f]:

$$E_{cb} = \chi - E^c - 0.5 \times E_g + 0.059 \times (IEP - 7)$$
$$E_{vb} = E_{cb} + E_g$$

where E^c is the energy of free electrons on the hydrogen scale (4.5 eV vs NHE).

References

[a] Z. Wang, J. Li, Y. Weng, M. Feng, Z. Zhuang and Y. Yu, *J. Mater. Chem. A*, 2017, **5**, 15650.

[b] M. Y. Nassar and S. Abdallah, *RSC Adv.*, 2016, **6**, 84050.

[c] C. Pirovano and S. Trasatti, *J. Electroanal. Chem.* 1984, **180**, 171.

[d] R. Li, F. Zhang, D. Wang, J. Yang, M. Li, J. Zhu, X. Zhou, H. Han and C. Li, *Nat. Commun.* 2013, **4**, 1432.

[e] M. Kosmulski, *J. Colloid Interface Sci.*, 2011, **353**, 1.

[f] J. Wang, F. E. Osterloh, *J. Mater. Chem. A*, 2014, **2**, 9405.