Supporting Information for

Complex Impedance Analysis on Charge Accumulation Step of Mn₃O₄ nanoparticles during Water Oxidation

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Figure S1. Cross-sectional scanning electron microscopy (SEM) images for Mn_3O_4 nanoparticles (NPs) films on FTO substrates with (a) 20 nm- (b) 70 nm- (c) 150 nm- and (d) 300 nm-thickness.



Figure S2. Stability experiments on $10 \text{ nm } \text{Mn}_3\text{O}_4$ NPs using chronoamperometry analysis. The experiment was performed under 0.5 M phosphate condition, pH 7.



Figure S3. XPS spectrum of the 10 nm Mn_3O_4 nanoparticles (NPs) before and after the electrolysis. (a) Mn2p and (b) P 2p spectrum of Mn_3O_4 NPs before and after electrolysis (1.3 V vs. NHE) in 0.5 M phosphate buffer (pH 7). The slight shift of the Mn 2p spectrum indicates that the surface state was a little oxidized during the electrolysis. However, there was no observable P 2p spectrum as shown in Figure S3b.



Figure S4. Post characterization of 10 nm Mn_3O_4 nanoparticles (NPs). (a) Comparison of the Raman spectra of Mn_3O_4 NPs before and after the electrolysis clearly indicate that no additional phase was newly formed after the electrolysis. (b) SEM and (c) TEM images of Mn_3O_4 NPs after the electrolysis (1.3 V vs. NHE) in 0.5 M phosphate condition, pH 7.



Figure S5. Cyclic voltammetry curves for Mn_3O_4 NPs on FTO substrates with (a) 20 nm- (b) 70 nm- (c) 150 nm- and (d) 300 nm-thickness in 0.5 M phosphate buffer solution (pH 7).



Figure S6. Linear sweep voltammetry (LSV) curves for Mn_3O_4 NPs on FTO substrates with 20 nm-, 70 nm-, 150 nm- and 300 nm-thickness, respectively in 0.5 M phosphate buffer solution (pH 7).



Figure S7. (a) Mn K-edge XANES spectra of Mn_3O_4 NPs at different anodic potential in 0.5 M phosphate buffer solution (pH 7). (b) Mn K-edge XANES spectra of various reference powders with different average valence states. (c) Mn average valence state of Mn_3O_4 NPs film according to the applied potentials.



Figure S8. Nyquist plots (Z' vs Z'') for (a) 20 nm- (b) 150 nm- (c) 300 nm-thickness Mn_3O_4 NPs film at open circuit potential, 0.8, 1.0, 1.2, 1.25, 1.3 and 1.35 V vs. NHE.



Figure S9. Complex capacitance plots (C' vs C'') for (a) 20 nm- (b) 150 nm- (c) 300 nmthickness Mn_3O_4 NPs film at open circuit potential, 0.8, 1.0, 1.2, 1.25, 1.3 and 1.35 V vs. NHE.



Figure S10. Complex conductance plots (G' vs G'') for (a) 20 nm- (b) 70 nm- (c) 150 nm- and (d) 300 nm-thickness Mn_3O_4 NPs film at open circuit potential, 0.8, 1.0, 1.2, 1.25, 1.3 and 1.35 V vs. NHE.