Supporting Information

Enhanced Photo-Electrochemical Water Oxidation on MnO_x in Buffered Organic/Inorganic Electrolytes

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Titration of H₂O₂

In order to investigate whether the butylamine is oxidized by permanganate during the titration, a control experiment was conducted by permanganate titration of the commercial H_2O_2 with and without the presence of the BAN/BA as shown in figuer S16. The two electrolytes show same end point within error. In other words there is no additional consumption of MnO_4^- in the presence of the amine.



Figure S1. Absorbance of MnO_4^- at 565 nm added to the solutions with the same amount of commercial H_2O_2 : (a) in 0.10 M Bi + 1.0 M BAN and (b) in pure water.



Figure S2. SEM secondary electron (SE) images, acquired at 30 kV at a working distance of 6 mm, show the morphology of the MnO_x film on FTO (deposition for 10 mins). (a) as-grown; (b) after long term running under illumination (~9 suns); c) the side view of MnO_x on FTO glass. d) Raman spectra of MnO_x before and after PEC measurement. In the Raman spectra, it can be observed three main peaks at 503, 570 and 642 cm⁻¹, which has been related to the Mn-O vibrations.[1] The positions of these are the same in the MnO_x before and after the PEC measurement, indicating that the material is stable during PEC testing.



Figure S3. Dependence of film thickness on the deposition time. The line shows the linear fit of the data, where the thickness exhibits linear relationship with increasing deposition time.



Figure S4. Dark current density of MnO_x films with different deposition times, measured in 0.10 M Bi + 0.50 M BAN electrolyte at pH9.



Figure S5. LSVs of MnO_x film deposited for 10 mins on FTO (black) and Au (red), measured in Bi (0.20 M) with BAN (1.0 M) electrolyte at pH9 in dark current (dashed line) and under light (solid line).



Figure S6. CVs of MnO_x film deposited for 30 mins, measured in Bi (0.10 M) with BAN (0.50 M) electrolyte at pH9 under illumination (~9 suns) from the front side (blue) and back side (red), as well as in dark condition (black). In order to illiminate the FTO glass effect, a slide of FTO glass was placed in front of the film for the front illumination condition.



Figure S7a. Tafel plot of MnO_x film deposited for 5 mins (blue) and 30 mins (red), measured in 0.20 M Bi at pH9 in dark conditions.



Figure S7b. Tafel plot of MnO_x film deposited for 5 mins (blue) and 30 mins (red), measured in 0.10 M Bi + 0.50 M BAN at pH9 in dark conditions.



Figure S8. Dark current density of MnO_x films (30 mins deposition) in different electrolytes at pH9.



Figure S9. LSV plots of MnO_x films in different electrolytes at pH9 in dark (dashed line) and under light (solid line): 1.0 M BAN (black), 1.0 M BAN with 0.20 M NaNO₃ (blue), 1.0 M BAN with 0.20 M Bi (red).



Figure S10. Dark currents (filled bar with grid) and photocurrents (filled bar without grid) on MnO_x measured at different potentials obtained from LSV plots, in 1.0 M BAN + 0.20 M Bi at pH9 (cyan), 1.0 M EAN +0.20 M Bi at pH9 (pink).



Figure S11. CPE measurements on MnO_x films in Bi+BAN at different potentials under chopped light (~9 suns). Arrows show the turning of the light on and off.



Figure S11d. CPE measurement on MnO_x film in Bi+BAN at 1.0 V vs SCE under light (~9 suns). Arrows show the turning of the light on and off.

Electrochemical Impedance Spectroscopy

Figures S12 show the Nyquist plots of MnO_x films in different electrolytes at pH9, the equivalent circuit model used for fitting the data and the fitted results is shown in **table S1**. The experimental results could be fitted well with an equivalent circuit model which contains one resistor and two RC circuits. In this model, R_s is the series resistance of the cell, R_1 is the semiconductor and electrolyte resistances in parallel with cell, capacitance, CPE_1 . R_p and CPE_2 represent the charge transfer resistance and capacitance, respectively, and W_o is the Warburg diffusion impedance.

In the high frequency range, one semicircle is observed for the three electrolytes at all applied potentials. The position and the radius of this semicircle for a particular electrolyte does not change by varying the applied potential, but decreases a little on illumination (illuminated and dark EIS are compared in figure S12 a, b, c). The semicircles in the high frequency range are usually related to the resistance of the film, electrolyte and contacts in the circuit.[1,2] The fitted parameters show that the resistance R_1 is smaller in the mixture and BAN solution than that in Bi buffer (table S1), which is due to the better conductivity when higher concentration of electrolytes are used.

At low frequencies, another semicircle appears and its radius under illumination is smaller than that in the dark at higher potentials. This semicircle varies with applied potential (figure S12a, b, c) and is understood to be associated with the water oxidation reaction.[1,3] As indicated in figure S12a, the radius of the second semicircle decreases significantly above 0.8 V in Bi, while it exhibits a remarkable decrease above 0.6 V in the presence of BAN (figure S12b, c). This indicates that, above 0.8 V, illumination significantly decreases the charge transfer resistance for water oxidation in all three electrolytes. A comparison of the Nyquist plots at 1.0 V, see figure 12d, shows that the radius of the semicircle at low frequencies is much smaller (under illumination) in the Bi buffer and BAN/Bi mixture than in BAN. The fitted parameters indicate a higher charge transfer resistance (Rp) for the water oxidation reaction in the BAN electrolyte, as expected from the LSV plot at this potential (figure 1). The BAN/Bi mixture exhibits the smallest Rp indicating a significant decrease in the water oxidation charge transfer resistance, as expected from the higher photocurrents shown in figures 1 and 2.



Figure S12a. Impedance spectroscopy (Nyquist plots) of MnO_x films in 0.20 M Bi at pH9 at bias of 0.4-1 V vs. SCE in dark (black) and under illumination (red).



Figure S12b. Impedance spectroscopy (Nyquist plots) of MnO_x films in 1.0 M BAN at pH9 at bias of 0.4-1 V vs. SCE in dark (black) and under illumination (red).



Figure S12c. Impedance spectroscopy (Nyquist plots) of MnO_x films in 0.10 M Bi +1.0 M BAN at pH9 at bias of 0.4-1 V vs. SCE in dark (black) and under illumination (red).



Figure S12d. (i) Impedance spectroscopy (Nyquist plots) of MnO_x films in different electrolytes at pH9 at a bias of 1.0 V vs. SCE under illumination: 0.20 M Bi (black squares), 1.0 M BAN (red dots), and 0.10 M Bi +1.0 M BAN (blue triangles). Symbols represent the experimental data and the solid lines represent the fitting data base on the equivalent circuit model as shown in figure S12d (ii). (ii) Equivalent circuit model used for fitting the experimental data in figure S11d(i).

Table S1. Fitting results of the EIS data in figure S12d(ii) to the equivalent model in figure S12d(ii).

	R₁/ Ω	CPE₁-T/ F	CPE ₁ -P/ F	R_p/Ω	CPE ₂ -T/ F	CPE ₂ -P/ F	W₀-R/ Ω
Bi	64	1.2E-6	0.80	89	0.0007	0.80	
BAN	40	8.8E-7	0.81	2119	0.0008	0.81	
Bi+BAN	35	6.5E-7	0.93	49	0.0015	0.81	49



Figure 12e. Impedance spectroscopy (Nyquist) of MnO_x films in 1.0 M BAN (black squares) and 0.10 M Bi +1.0 M BAN (red dots) at pH10 at a bias of 0.8 V vs. SCE under illumination. Symbols represent the experimental data and the solid lines represent the fitting data base on the equivalent circuit as shown in figure S12d(ii).

UV-Vis Spectra

Figure S13 Shows the transmittance spectra of MnO_x.



Figure S13.UV-Vis Transmittance spectra of MnO_x films deposited for different time.

The absorption coefficient $\alpha(\lambda)$ was calculated from the transmittance of film by the equation:[4]

 $T = e^{-\alpha d}$

Where T is the transmittance and d is the thickness of films.

NMR spectra

The NMR spectra do not show significant difference after long-term electrochemical measurement under illumination.



Figure S14. NMR spectra of electrolyte (0.10 M Bi+1.0 M BAN in D₂O at pH9) before and after water oxidation reaction under illumination.

Effect of H₂O₂ on the LSV plot

A controlled measurement by adding H_2O_2 into 0.20 M Bi was conducted and the result is shown below. The onset for the oxidation of H_2O_2 (~0.1 V vs. SCE) is much lower than those for the O_2 evolution (~ 0.8 V vs. SCE) or the H_2O_2 production (~ 0.6 V vs. SCE) on MnO_x.



Figue S15. LSVs of MnO_x film measuring in Bi buffer (black) and Bi+BAN (blue) at pH9 with and without H_2O_2 .

Faradaic efficiency



Figure S16. Oxygen and H_2O_2 measurement results in dark. Conditions: applied a constant current of 0.5 mA for 90 min in a gas-tight setup. The electrolyte is 0.10 M Bi +1.0 M BAN at pH9 and the volume is 6 ml. The head space is 26 ml and the oxygen is measured by fluoresce probe. The measured overall efficiency of the water oxidation (O_2 and H_2O_2 production) in dark is 94±7%.

H ₂ O ₂ production	H ₂ O ₂ production	O ₂ production	O ₂ production	Overal Faradic
(µmol)	efficiency (%)	(µmol) ^b	efficiency (%)	efficiency
2.5±0.2	27±2	3.5+0.1	75±2	102 ± 4%

^a The experiment was conducted at a constant current o 0.5 mA for 60 min in a gas-tight setup. ^b the oxygen production measurement was conducted by measuring the oxygen level in the gas before and after the PEC experiment.



Figure S17. The concentration of H_2O_2 with time in 1.0 M BAN in dark (blue) and under light (red). The solution contained 0.01 g of commercial MnO₂ and 50 ul of H_2O_2 (3%) in 4 ml of electrolyte, and the experiment is conducted with constant stirring. The concentration of H_2O_2 is determined by UV-Vis titration as detailed in the experimental section.

Reference

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