Supporting information for:

Photo-assisted electrodeposition of manganese oxide on TaON anodes: effect on water photooxidation capacity under visible light irradiation

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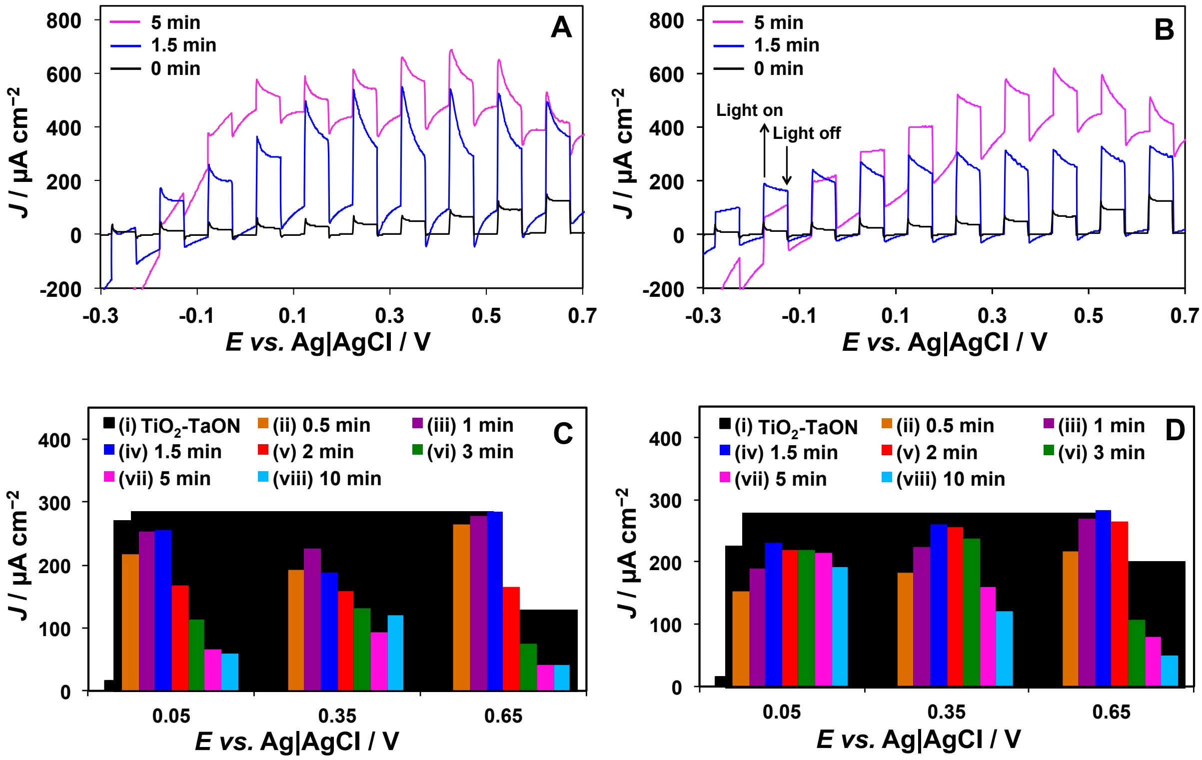

Figure S1. (A, B) Voltammograms (scan rate, v = 0.025 V s^{-1}) for water oxidation by TiO_2-TaON (black) and MnO_x/TiO_2-TaON films (t_{dep} = 1.5 (blue) and 5 min (magenta)) in contact with aqueous 0.1 M Na_2SO_4 (pH = 6) under chopped visible light irradiation (1 sun, $\lambda > 400$ nm). (C, D) Photooxidation current densities at different potentials derived from voltammograms (exemplified in panels A and B) for (i) TiO_2-TaON and (ii-viii) MnO_x/TiO_2-TaON prepared using defined t_{dep}. Currents are normalised to the geometric surface area of the films. MnO_x was electrodeposited (A, C) in dark and (B, D) under continuous visible light irradiation (1 sun, $\lambda > 400$ nm) from aqueous 0.01 M $Mn(CH_3COO)_2$ with 0.1 M Na_2SO_4 (pH = 5) at J_{dep} = 250 μA cm^{-2} for the defined t_{dep}.

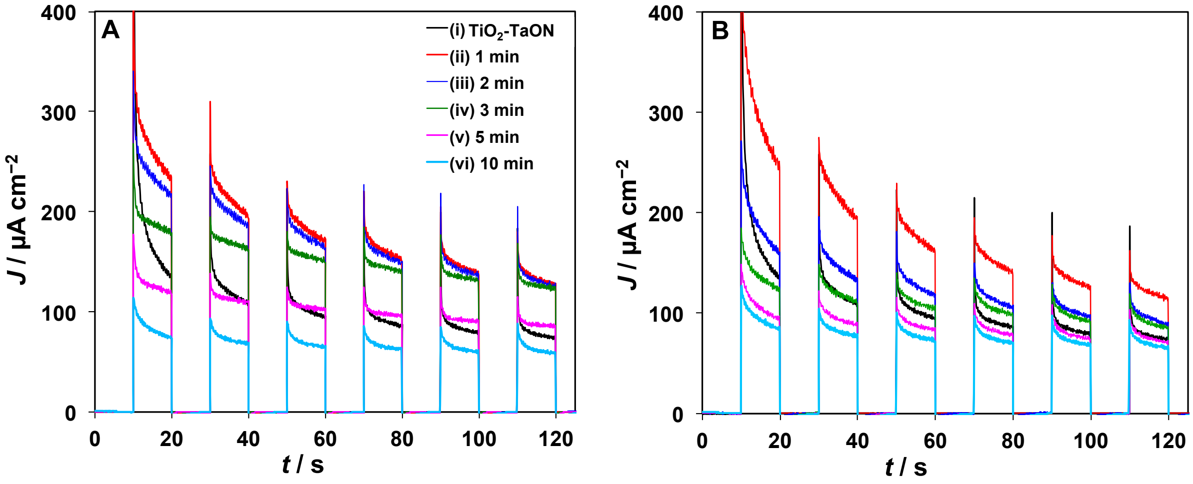

Figure S2. Chronoamperograms obtained for water photooxidation at 1 V (*vs.* Ag|AgCl) by (i) TiO_2-TaON and (ii-vi) MnO_x/TiO_2-TaON films in contact with aqueous 0.1 M Na_2SO_4 (pH = 6) under chopped visible light irradiation (1 sun, $\lambda > 400$ nm). MnO_x was electrodeposited (A) in dark and (B) under continuous visible light irradiation (1 sun, $\lambda > 400$ nm) for defined t_{dep} and under conditions defined in Fig. S1.

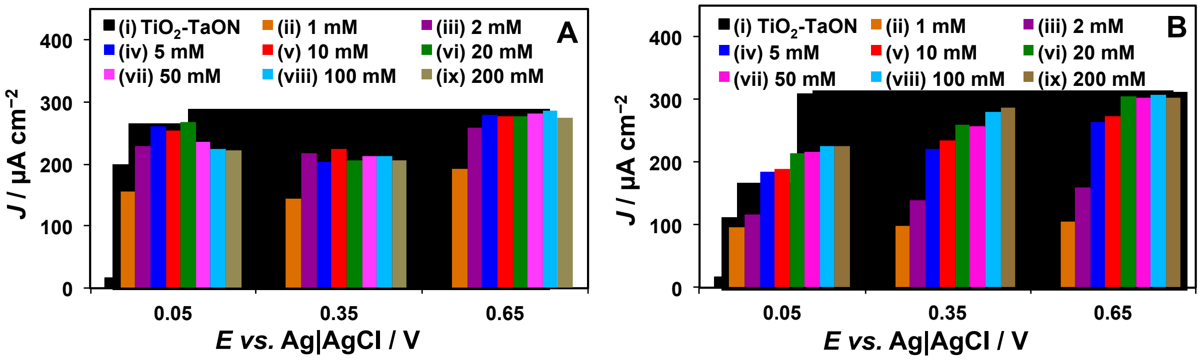

Figure S3. Photooxidation current densities at different potentials derived from voltammograms (scan rate, $v = 0.025$ V s^{-1}) obtained under chopped visible light irradiation for (i) TiO_2-TaON and (ii-ix) MnO_x/TiO_2-TaON films prepared using different c_{Mn} in contact with aqueous 0.1 M Na_2SO_4 (pH = 6). MnO_x was electrodeposited for t_{dep} = 1 min (A) in dark and (B) under continuous visible light irradiation (1 sun, λ > 400 nm) and other conditions as defined in Fig. S1.

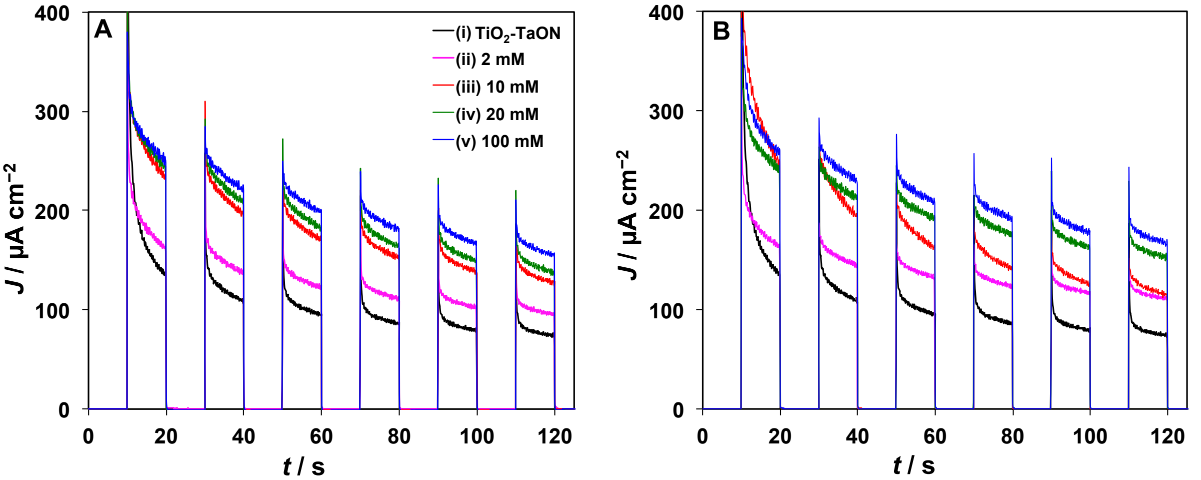

Figure S4. Chronoamperograms obtained for water photooxidation at 1 V (*vs.* Ag|AgCl) by (i) TiO_2-TaON and (ii-v) MnO_x/TiO_2-TaON films in contact with aqueous 0.1 M Na_2SO_4 (pH = 6) under chopped visible light irradiation (1 sun, $\lambda > 400$ nm). MnO_x was electrodeposited for t_{dep} = 1 min (A) in dark and (B) under continuous visible light irradiation (1 sun, λ > 400 nm) using defined c_{Mn} and under conditions defined in Fig. S3.

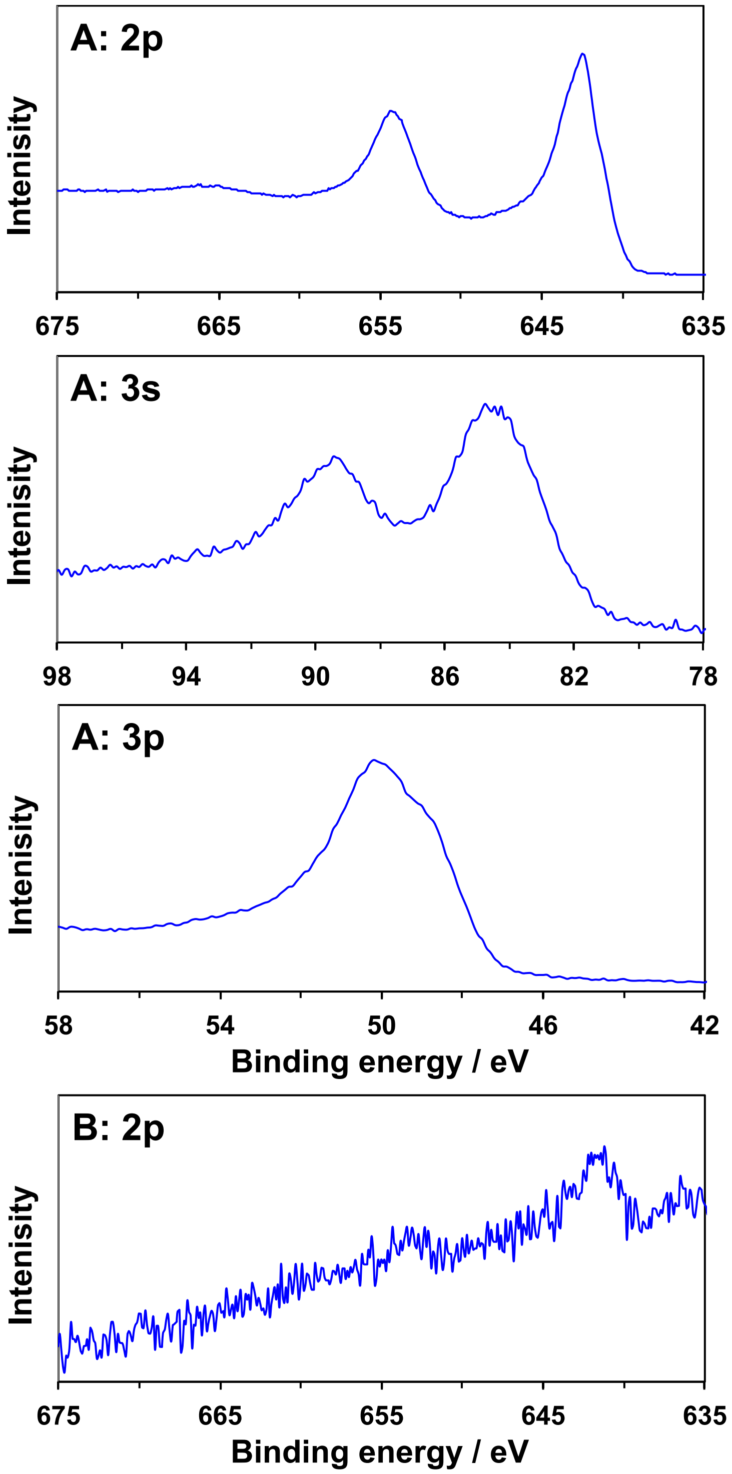

Figure S5. Mn 2p, 3s and 3p core level spectra of the (A) MnO_x/FTO and (B) MnO_x/TiO_2-TaON electrodes. MnO_x was electrodeposited (A) in dark at J_{dep} = 250 μA cm^{-2} and (B) under continuous visible light irradiation (1 sun, λ > 400 nm) at E_{dep} = 0.7 V vs. Ag|AgCl|KCl(sat.) for t_{dep} = 1.33 min and under other conditions defined in Fig. S1.

Table S1. Peak positions in the Mn 2p, 3s and 3p core level spectra for MnO$_x$/FTO. MnO$_x$ was electrodeposited under conditions defined in Fig. S5.

Signal	Binding energy / eV
Mn 2p (1)	642.43
Mn 2p (2)	654.20
Mn 3p	49.98
Mn 3s (1)	84.45
Mn 3s (2)	89.40
Mn 3s splitting	4.95
Mn 2p - O 1s	112.39

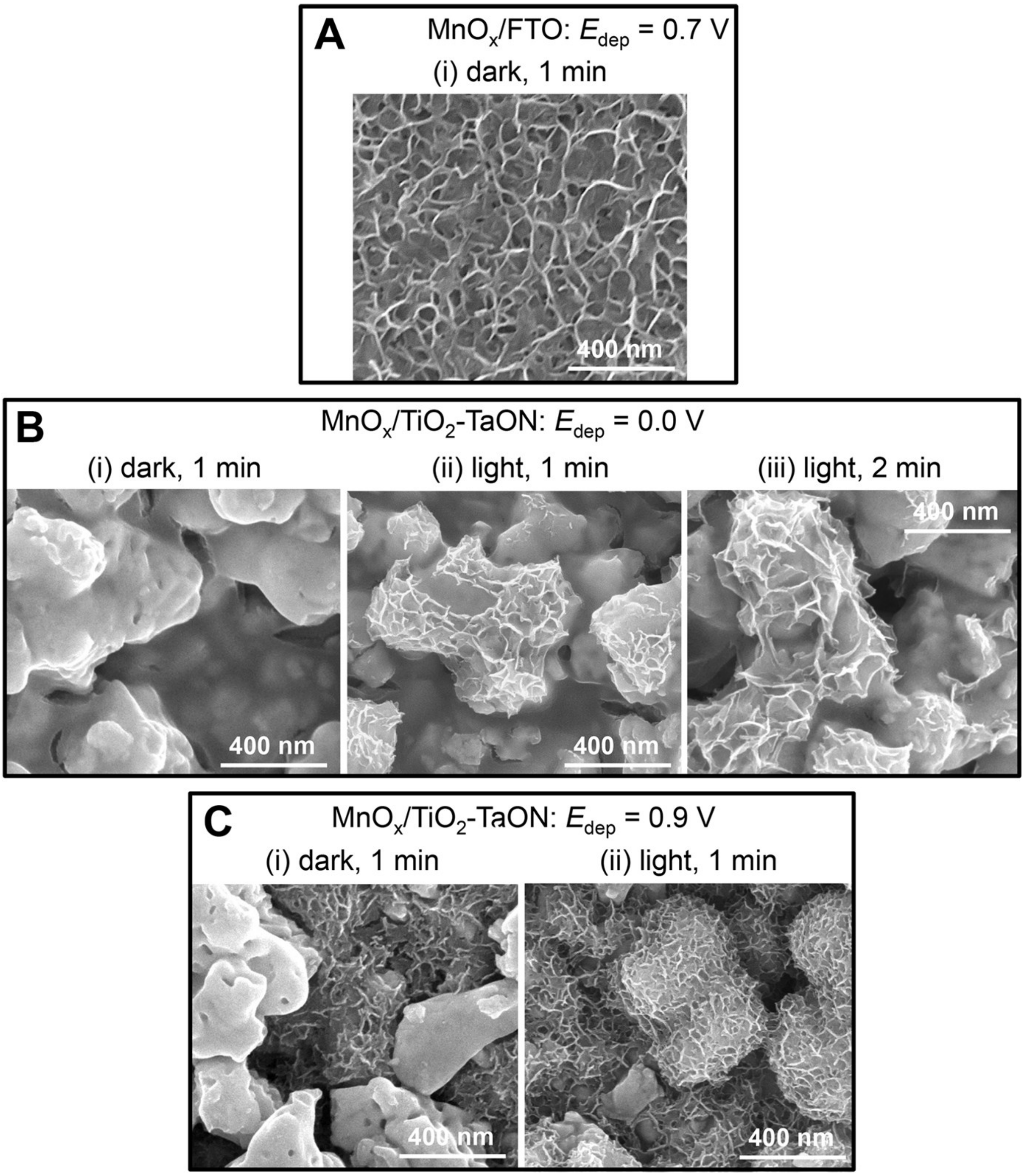

Figure S6. SEM images obtained for the MnO_x/FTO (A) and MnO_x/TiO_2-TaON films (B and C). MnO_x was electrodeposited over a bare FTO substrate at E_{dep} = 0.7 V (*vs.* Ag|AgCl) (A), and over TiO_2-TaON films at E_{dep} = 0.0 V (B) or at E_{dep} = 0.9 V (C) under conditions defined in the figure using aqueous 0.01 M $Mn(CH_3COO)_2$ with 0.1 M Na_2SO_4 (pH = 5) as a deposition solution.

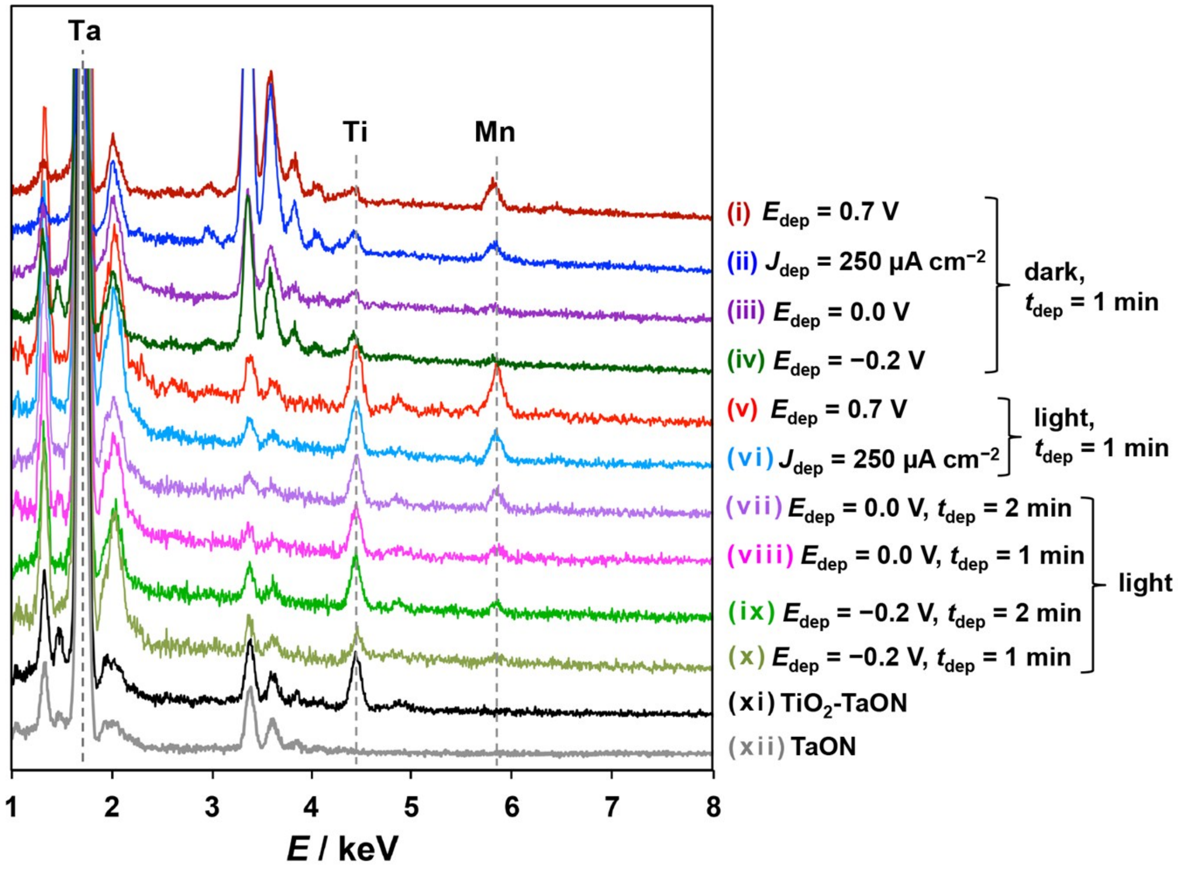

Figure S7. Comparison of EDX spectra obtained for (i-x) MnO_x/TiO_2-TaON, (xi) TiO_2-TaON and (xii) TaON films. MnO_x was electrodeposited over TiO_2-TaON films using an aqueous solution of 0.01 M $Mn(CH_3COO)_2$ with 0.1 M Na_2SO_4 (pH = 5) at E_{dep} = −0.2 (d, i and j), 0.0 (c, g and h) or 0.7 V (*vs.* Ag|AgCl) (a and e) or at J_{dep} = 250 µA cm^{-2} (b and f) using defined t_{dep} in dark or under illumination (1 sun, λ > 400 nm).

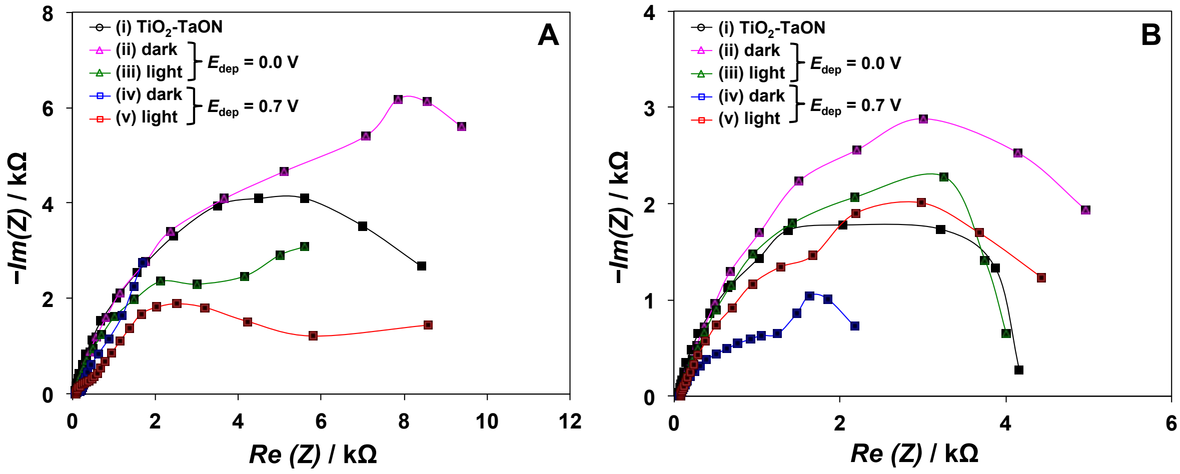

Figure S8. Nyquist plots at (A) 0.65 V and (B) 1.05 V *vs.* Ag|AgCl for TiO_2-TaON (i, *black*) and MnO_x/TiO_2-TaON (ii-v). EIS data were obtained under illumination (1 sun, $\lambda > 400$ nm) using aqueous 0.1 M Na_2SO_4 (pH = 6). Symbols show the experimental data, lines are guides to an eye. MnO_x was electrodeposited for 1 min over TiO_2-TaON films using an aqueous solution of 0.01 M $Mn(CH_3COO)_2$ with 0.1 M Na_2SO_4 (pH = 5) at $E_{dep} = 0.0$ (*green*, *magenta*) or 0.7 V (*blue*, *red*) in dark (*magenta*, *blue*) or under illumination (1 sun, $\lambda > 400$ nm) (*green*, *red*).

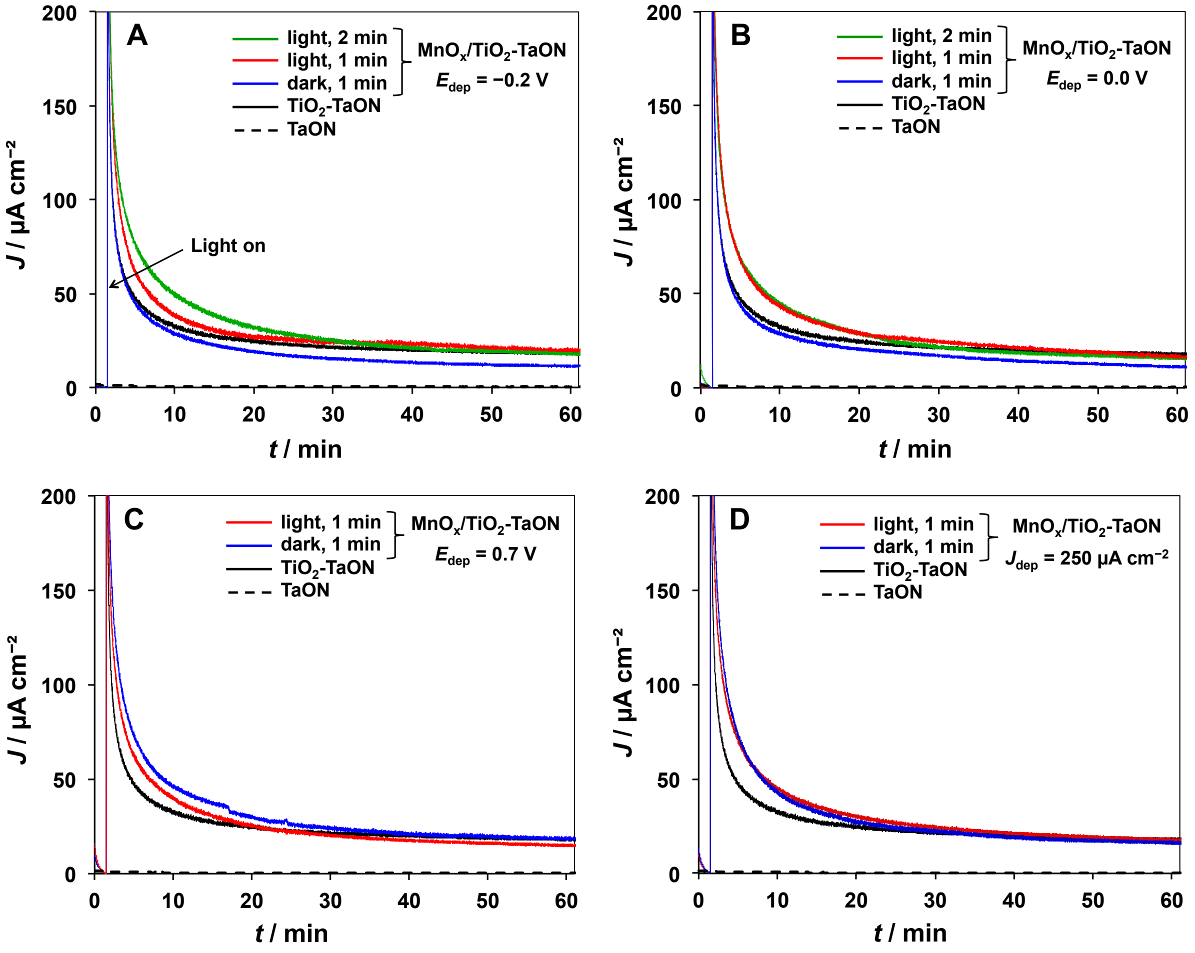

Figure S9. Chronoamperograms obtained for MnO$_x$/TiO$_2$-TaON (*green*, *red* and *blue*), TiO$_2$-TaON (*black*) and TaON (*black* - broken lines) at 1 V *vs.* Ag|AgCl under continuous visible light irradiation (1 sun, $\lambda > 400$ nm) in contact with aqueous 0.1 M Na$_2$SO$_4$ (pH = 6). MnO$_x$ was electrodeposited over TiO$_2$-TaON films using an aqueous solution of 0.01 M Mn(CH$_3$COO)$_2$ with 0.1 M Na$_2$SO$_4$ (pH = 5) at $E_{dep} = -0.2$ (A), 0.0 (B) or 0.7 V *vs.* Ag|AgCl (C), or at $J_{dep} = 250$ µA cm^{-2} (D) for the defined amount of time in dark or under illumination (1 sun, $\lambda > 400$ nm).

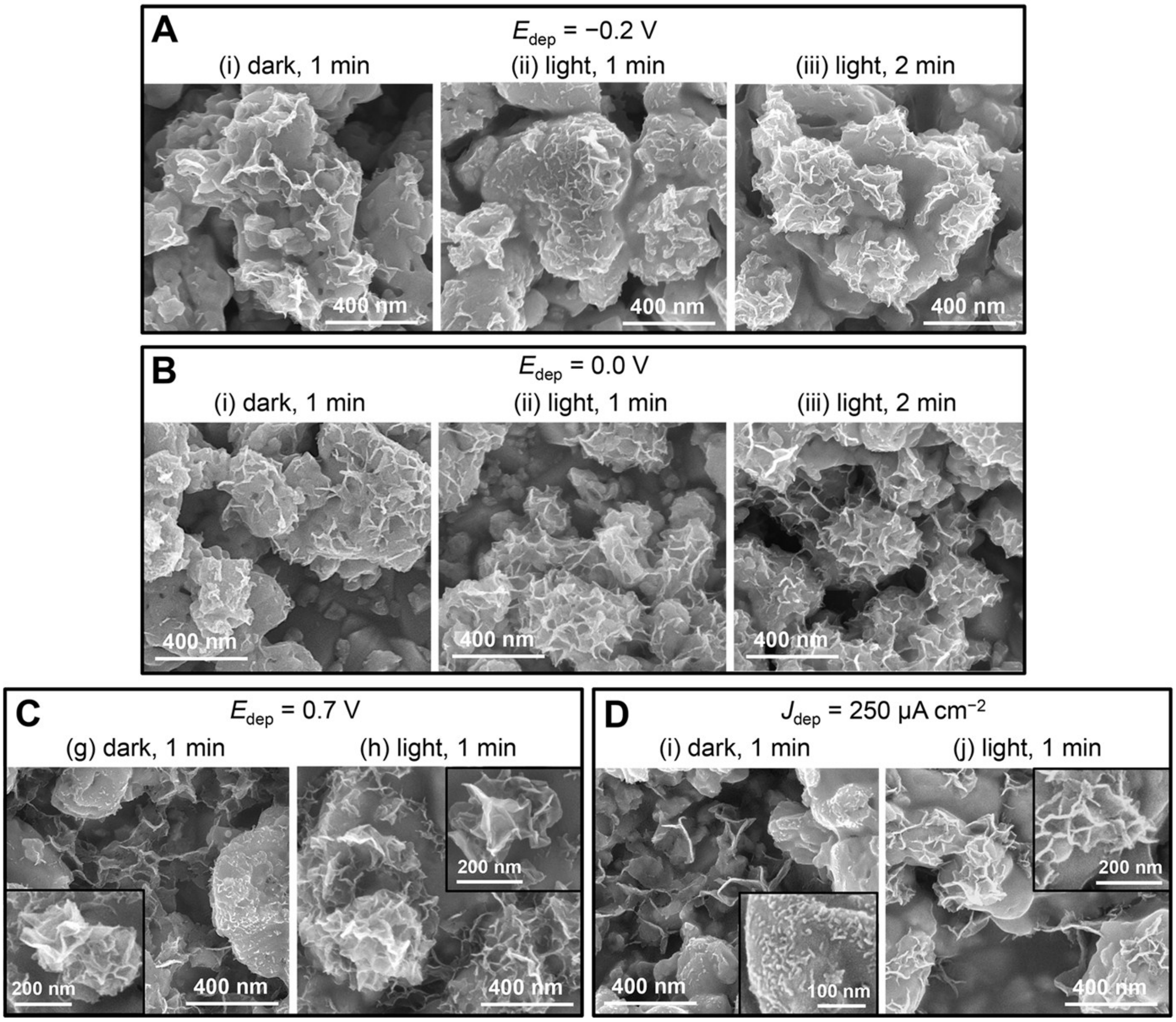

Figure S10. SEM images obtained for MnO_x/TiO_2-TaON after 60 min of potentiostatic water photooxidation at 1.0 V (*vs.* Ag|AgCl) under continuous visible light irradiation (1 sun, $\lambda > 400$ nm) using aqueous 0.1 M Na_2SO_4 (pH = 6). Electrodeposition of MnO_x was carried out under conditions defined in figure using aqueous 0.01 M $Mn(CH_3COO)_2$ with 0.1 M Na_2SO_4 (pH = 5).

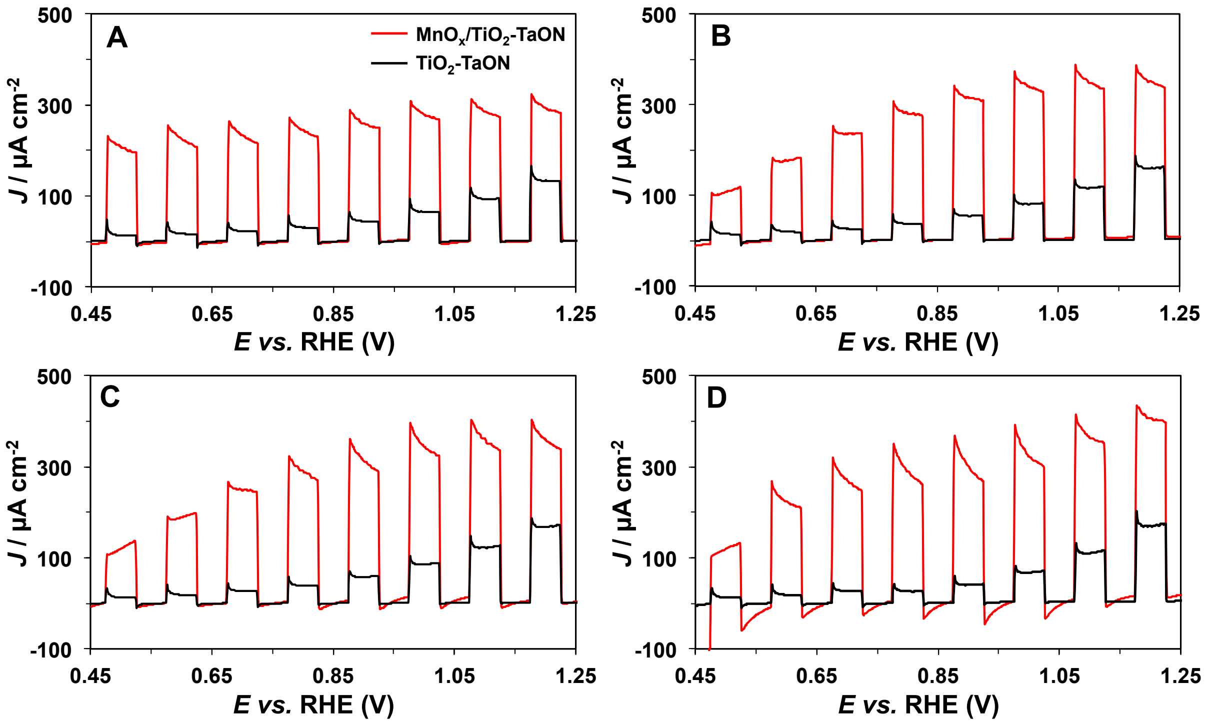

Figure S11. Voltammograms ($v = 0.025$ V s^{-1}) obtained under chopped visible light irradiation (1 sun, $\lambda > 400$ nm) for MnO_x/TiO_2-TaON (*red*) and TiO_2-TaON (*black*) in contact with (A) 0.1 M Na_2SO_4 solution, pH = 6.0, (B) 0.1 M phosphate buffer, pH = 7.0, (C) 0.1 M borate buffer, pH = 9.2 and (D) 0.1 M Na_2SO_4 solution + NaOH, pH 12. Note that the potentials are referred to the reversible hydrogen electrode (RHE), not Ag|AgCl. MnO_x was electrodeposited over TiO_2-TaON films using an aqueous solution of 0.01 M $Mn(CH_3COO)_2$ with 0.1 M Na_2SO_4 (pH = 5) at $E_{dep} = 0.7$ V *vs.* Ag|AgCl for 1 min under illumination (1 sun, $\lambda > 400$ nm). Each voltammogram has been corrected for the corresponding dark current at 0.65 V *vs.* RHE to facilitate comparisons of the photocurrents.

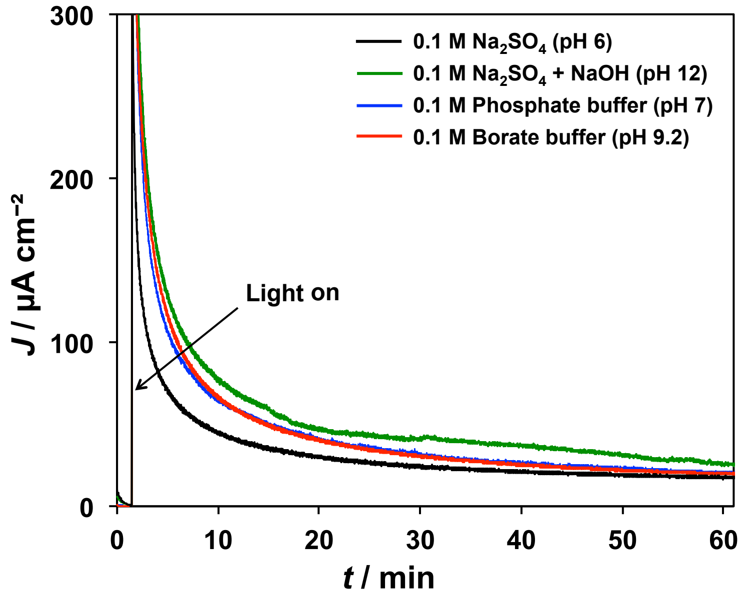

Figure S12. Chronoamperograms obtained for MnO_x/TiO_2-TaON films at 1.55 V *vs.* RHE under continuous visible light irradiation (1 sun, $\lambda > 400$ nm) in contact with 0.1 M Na_2SO_4 solution, pH = 6.0 (*black*), 0.1 M phosphate buffer, pH = 7.0 (*blue*), 0.1 M borate buffer, pH = 9.2 (*red*) and 0.1 M Na_2SO_4 + NaOH, pH 12 (*green*). MnO_x was electrodeposited over TiO_2-TaON films using an aqueous solution of 0.01 M $Mn(CH_3COO)_2$ with 0.1 M Na_2SO_4 (pH = 5) at E_{dep} = 0.7 V *vs.* Ag|AgCl for 1 min under continuous illumination (1 sun, $\lambda > 400$ nm).

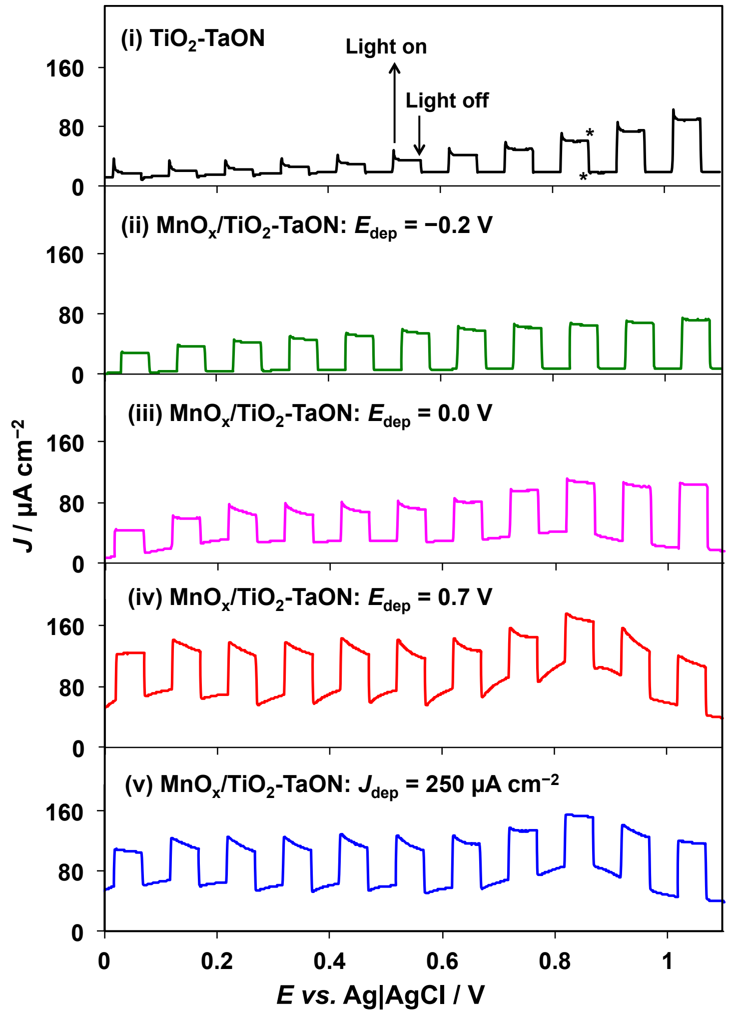

Figure S13. Voltammograms used for the calculation of IPCE were obtained at $v = 0.005$ V s^{-1} under chopped monochromatic light irradiation with λ = 410 nm for (i) TiO_2-TaON (light intensity 5.75 mW cm^{-2}) and (ii-v) MnO_x/TiO_2-TaON (light intensity 2.4 mW cm^{-2}) in contact with aqueous 0.1 M Na_2SO_4 (pH = 6). MnO_x was electrodeposited over TiO_2-TaON films using an aqueous solution of 0.01 M $Mn(CH_3COO)_2$ with 0.1 M Na_2SO_4 (pH = 5) at $E_{dep} = -0.2$ (ii), 0 (iii) or 0.7 V *vs.* Ag|AgCl (iv), or at J_{dep} = 250 μA cm^{-2} (v) for 1 min under illumination (1 sun, $\lambda > 400$ nm). Asterisks in top plot exemplify the data points used for calculation of the photocurrent density, which was further used for calculation of IPCE. Contribution of the reduction processes upon ceasing the irradiation observed for $E_{dep} = 0.70$ V might result in overestimation of the true water oxidation photocurrent densities. However, this effect is negligible for other samples used for IPCE measurements.

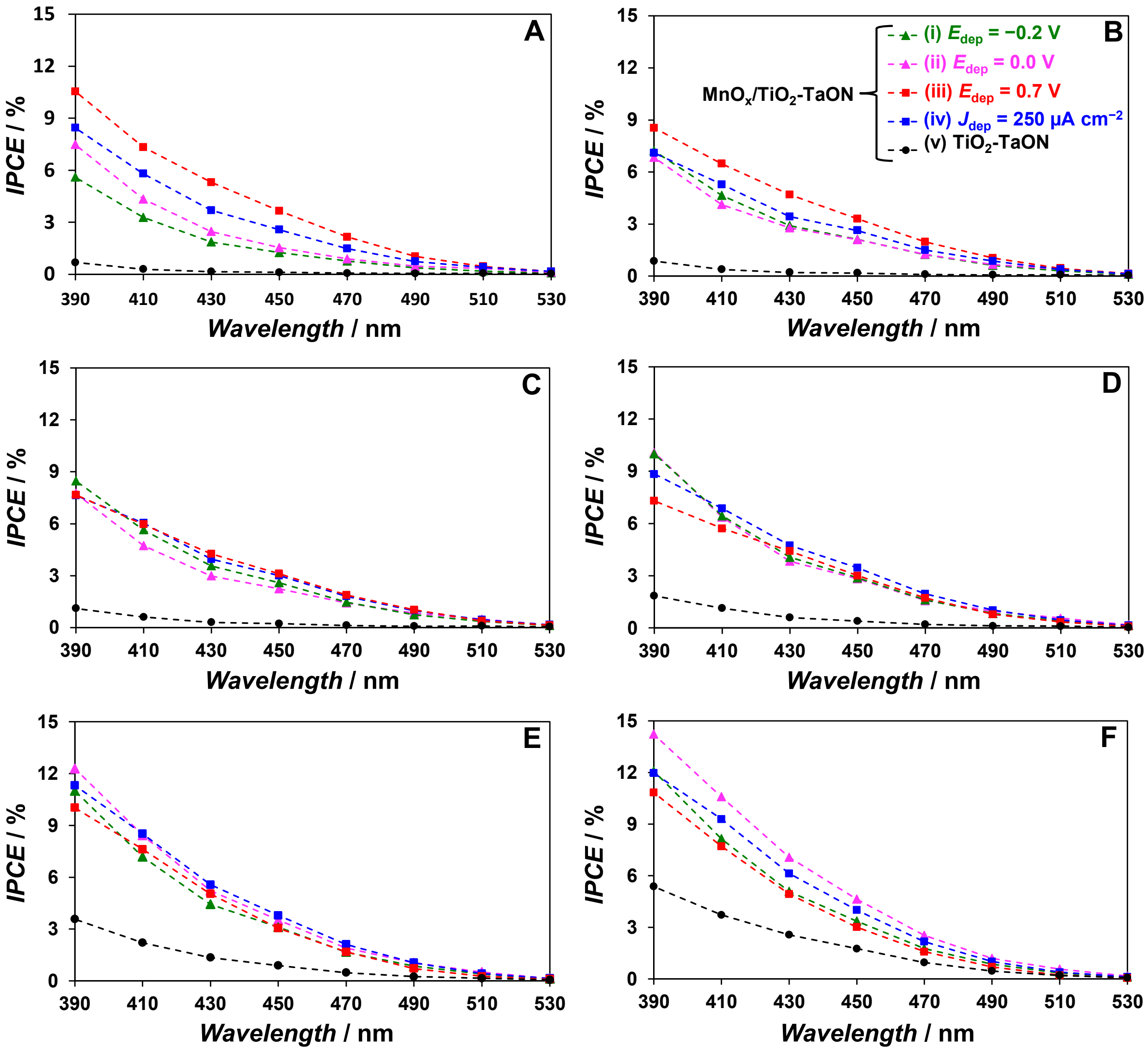

Figure S14. IPCE spectra obtained at (A) 0.05 V, (B) 0.25 V, (C) 0.45 V, (D) 0.65 V, (E) 0.85 V and (F) 1.05 V *vs*. Ag|AgCl for (i - iv) MnO_x/TiO_2-TaON and (v) TiO_2-TaON films in contact with aqueous solution of 0.1 M Na_2SO_4 (pH = 6) under irradiation. MnO_x was electrodeposited over TiO_2-TaON films using an aqueous solution of 0.01 M $Mn(CH_3COO)_2$ with 0.1 M Na_2SO_4 (pH = 5) at $E_{dep} = -0.2$ (i), 0.0 (ii) or 0.7 V *vs.* Ag|AgCl (iii), or at $J_{dep} = 250$ µA cm^{-2} (iv) for 1 min under illumination (1 sun, $\lambda > 400$ nm).