Supporting Information (SI)

Synthesis of Three-layer Perovskite Oxynitride $K_2Ca_2Ta_3O_9N \cdot 2H_2O$ and Photocatalytic Activity for H_2 Evolution under Visible Light

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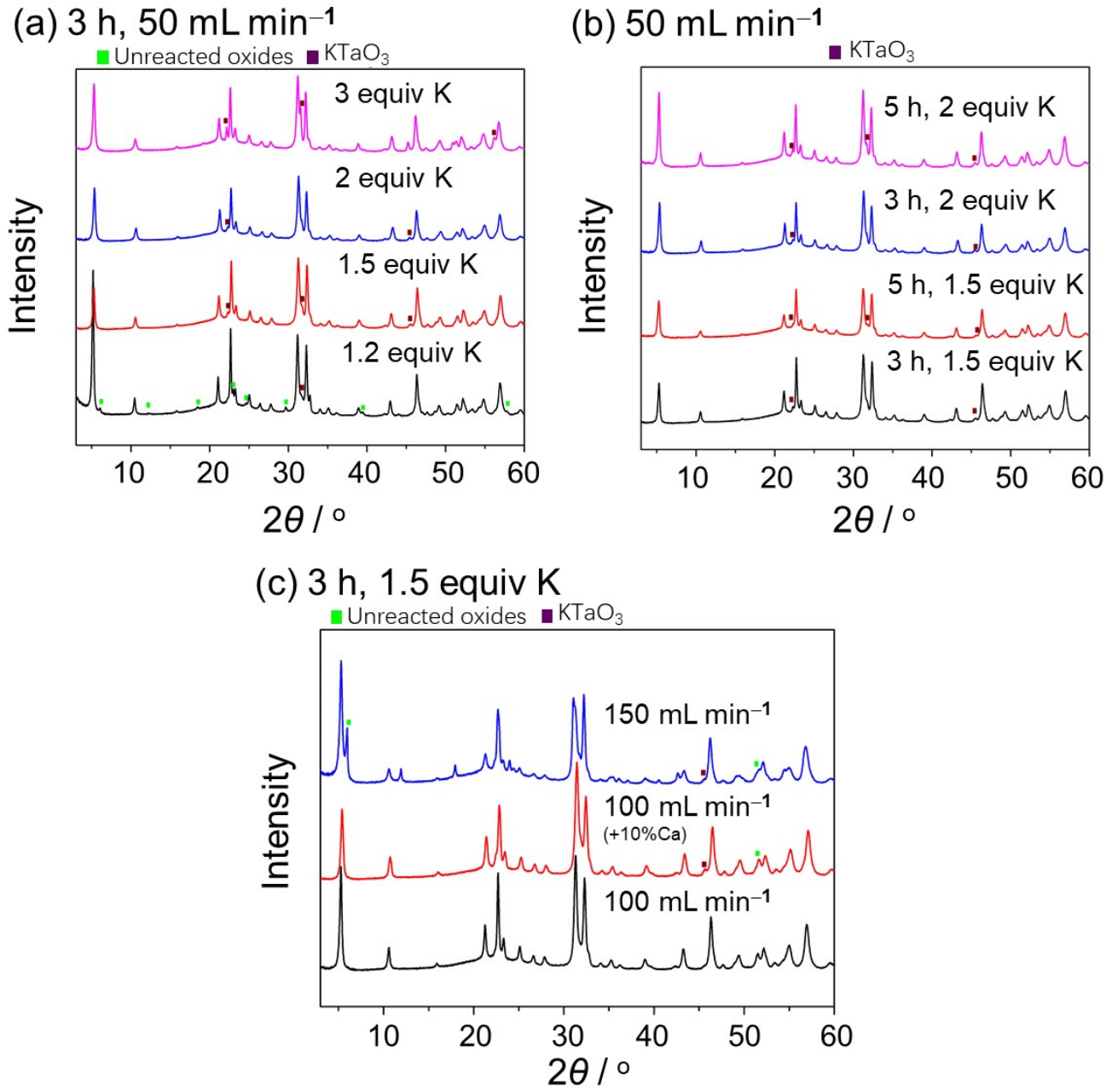

Figure S1. XRD patterns for nitridation products of $KCa_2Ta_3O_{10}$ under various reaction conditions (at 1173 K); (a) different amounts of K_2CO_3 at 50 mL min^{-1} of NH_3 flow, (b) different reaction times at 50 mL min^{-1} of NH_3 flow, and (c) different NH_3 flow rates. The best reaction conditions for $K_2Ca_2Ta_3O_9N{\cdot}2H_2O$ synthesis were finally confirmed to be 1173 K, 3 h, 100 mL min^{-1} NH_3 flow, and 1.5 mol equiv of potassium (from K_2CO_3).

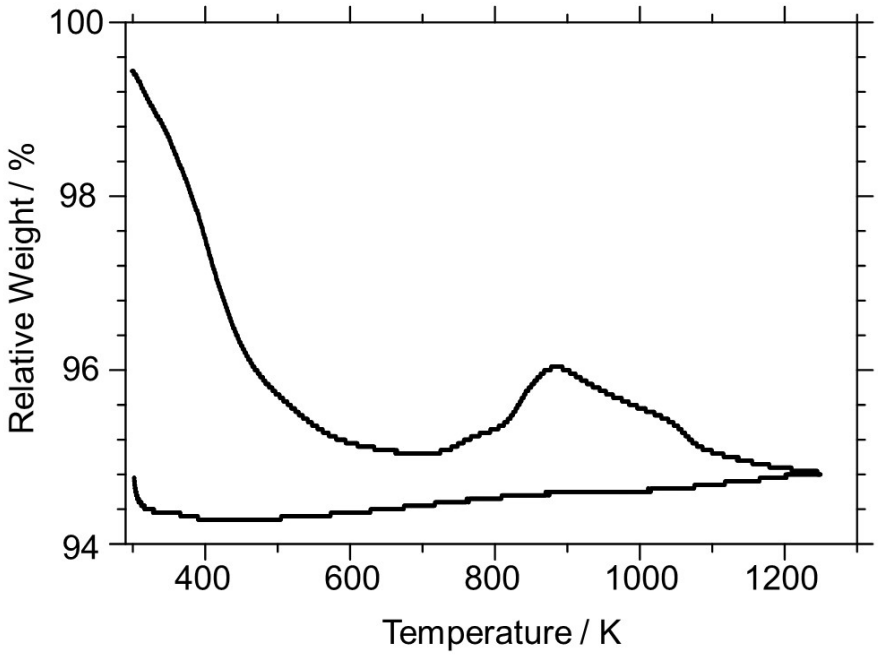

Figure S2. TGA profile for $K_2Ca_2Ta_3O_9N{\cdot}nH_2O$ under air flow. Conditions: temperature range, 298–1273 K; heating/cooling rate, 5 K min^{-1}.

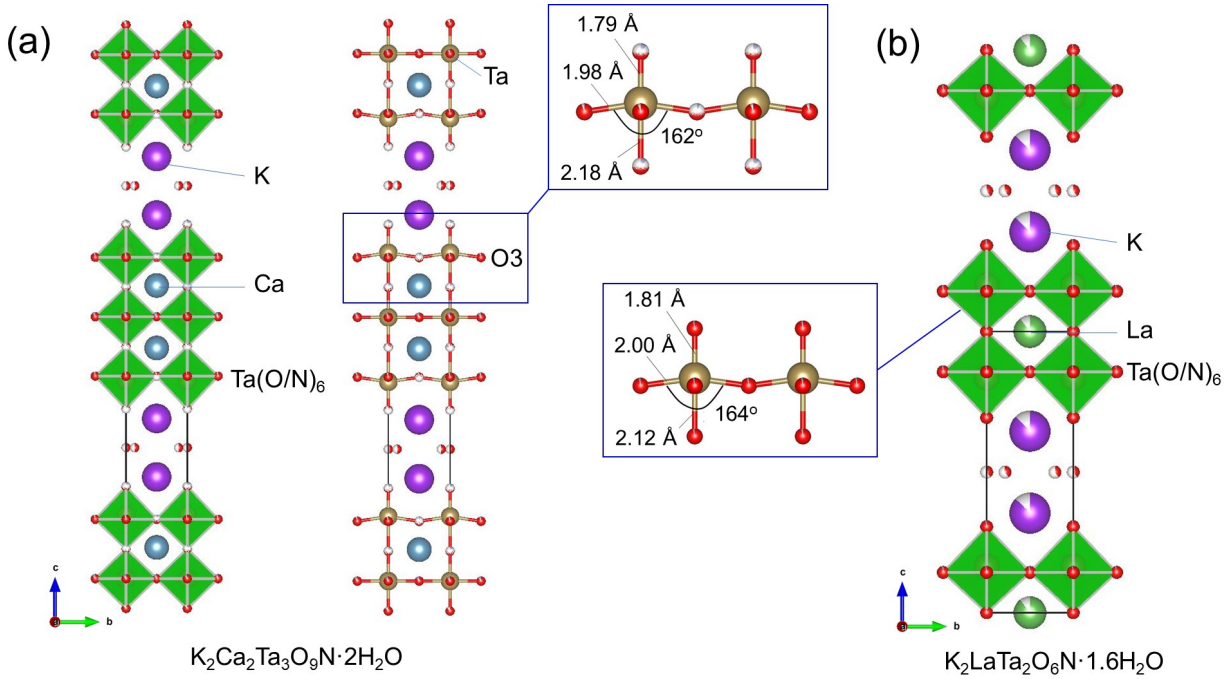

Figure S3. Comparison of the crystal structures of (a) $K_2Ca_2Ta_3O_9N{\cdot}2H_2O$; (b) $K_2LaTa_2O_6N{\cdot}1.6H_2O$. The inset is the coordination geometry around Ta, band length and angle were calculated from the results of Rietveld refinement.

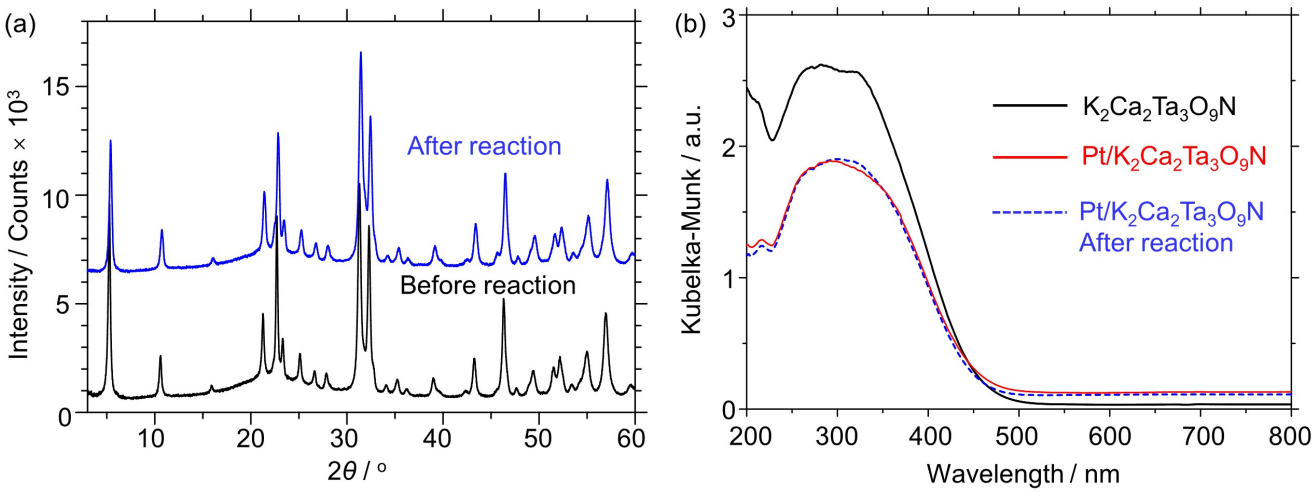

Figure S4. (a) XRD patterns for $Pt/K_2Ca_2Ta_3O_9N$ before and after reaction. (b) DRS for the photocatalysts before and after reaction.

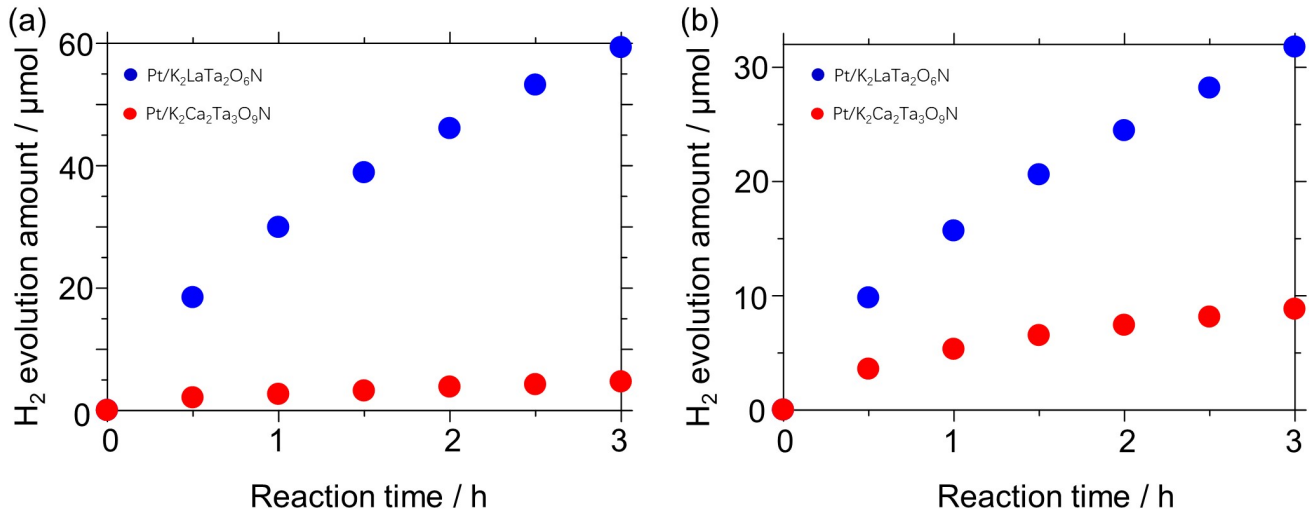

Figure S5. Time courses of H_2 evolution over $Pt/K_2Ca_2Ta_3O_9N{\cdot}2H_2O$ and $Pt/K_2LaTa_2O_6N{\cdot}1.6H_2O$ in (a) aqueous NaI solution (5 mM, pH = 2.5), and (b) aqueous methanol solution (10 vol%). Reaction conditions: catalyst, 50 mg; light source, 300 W Xe lamp without cutoff filter ($\lambda > 350$ nm).

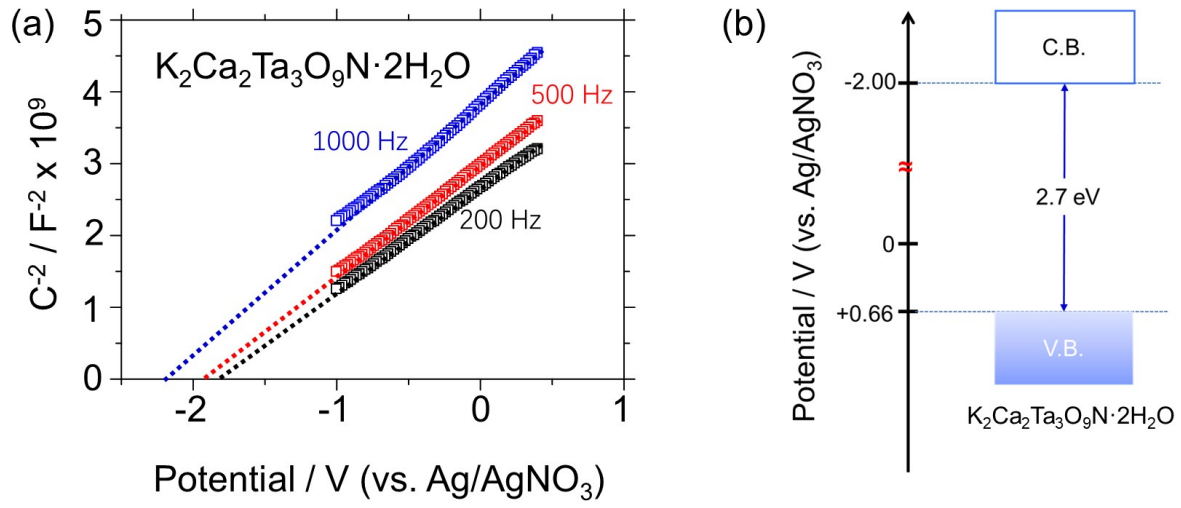

Figure S6. (a) Mott-Schottky plots for $K_2Ca_2Ta_3O_9N{\cdot}2H_2O$ with different frequencies in a MeCN solution containing 0.1 M Et_4NBF_4. (b) Proposed band gap structure for $K_2Ca_2Ta_3O_9N{\cdot}2H_2O$.

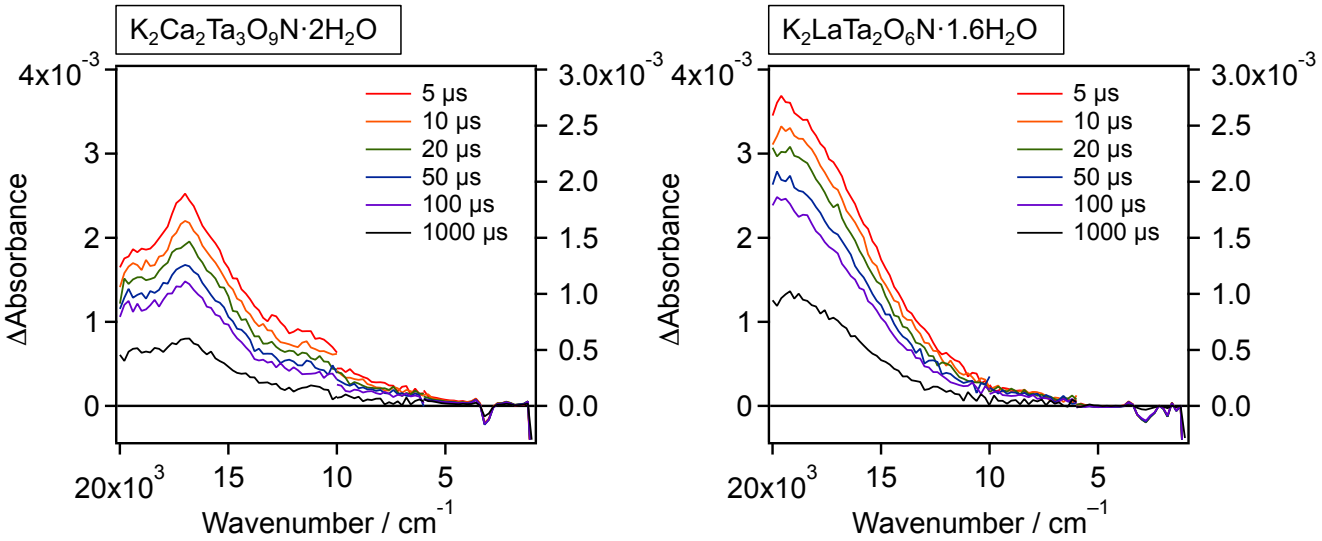

Figure S7. Transient absorption spectra for $K_2Ca_2Ta_3O_9N{\cdot}2H_2O$ and $K_2LaTa_2O_6N{\cdot}1.6H_2O$ recorded with 480 nm laser pulse excitation under a N_2 atmosphere (20 Torr).

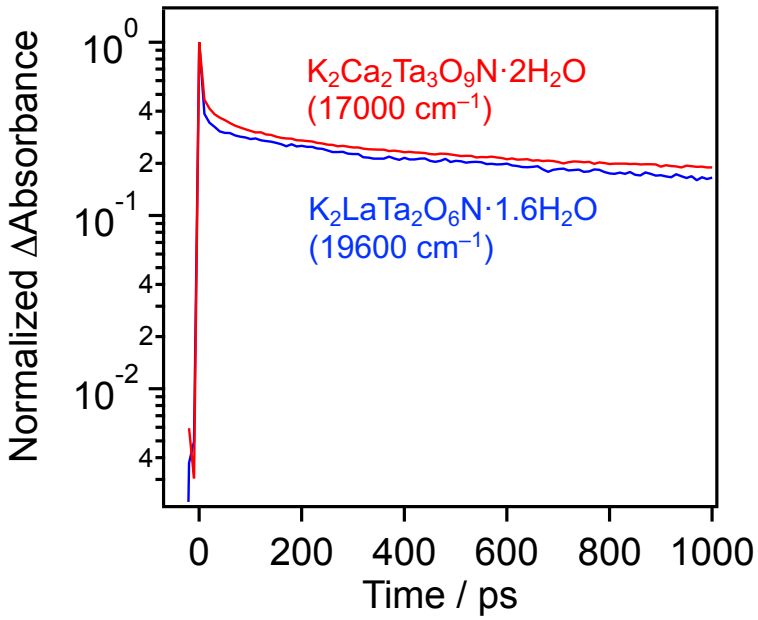

Figure S8. Decay curves of transient absorption intensity for $K_2Ca_2Ta_3O_9N·2H_2O$ and $K_2LaTa_2O_6N·1.6H_2O$ recorded at 17000 or 19600 cm^{-1}. Excitation: 480 nm, atmosphere: air.

Table S1. Refined structural parameters and reliability factors for synchrotron XRD data for $K_2Ca_2Ta_3O_9N·2H_2O$ measured at 297 K.

Atom	Coordinates			Occupancy	Uiso / Å^2	Site
	x	*y*	*z*			
K	1/2	1/2	0.37970	1	0.045(6)	2h
Ca	1/2	1/2	0.12850	1	0.008(2)	2h
Ta	0	0	0	1	0.004(8)	1a
Ta	0	0	0.24408	1	0.004(8)	2g
O1/N1[a]	0	1/2	0	0.875/0.125	0.073(9)[b]	2f
O2/N2[a]	0	0	0.10938	0.875/0.125	0.073(9)[b]	2g
O3/N3[a]	0	1/2	0.22248	0.938/0.063	0.073(9)[b]	4i
O4/N4[a]	0	0	0.34738	0.875/0.125	0.073(9)[b]	2g
O5[c]	0.12422	0	1/2	1/2	0.073(9)[b]	4m

[a] The ratio was decided in order to retain charge neutrality. Nitrogen was assumed to be equally located in each site. [b] Atomic displacement parameters for anions were assumed to be the same. [c] The O(5) is from intercalated H_2O and H atoms were not included for the analysis.