Supplementary Information

Sensitization of Wide Band Gap Photocatalysts to Visible Light by a Molten CuCl treatment

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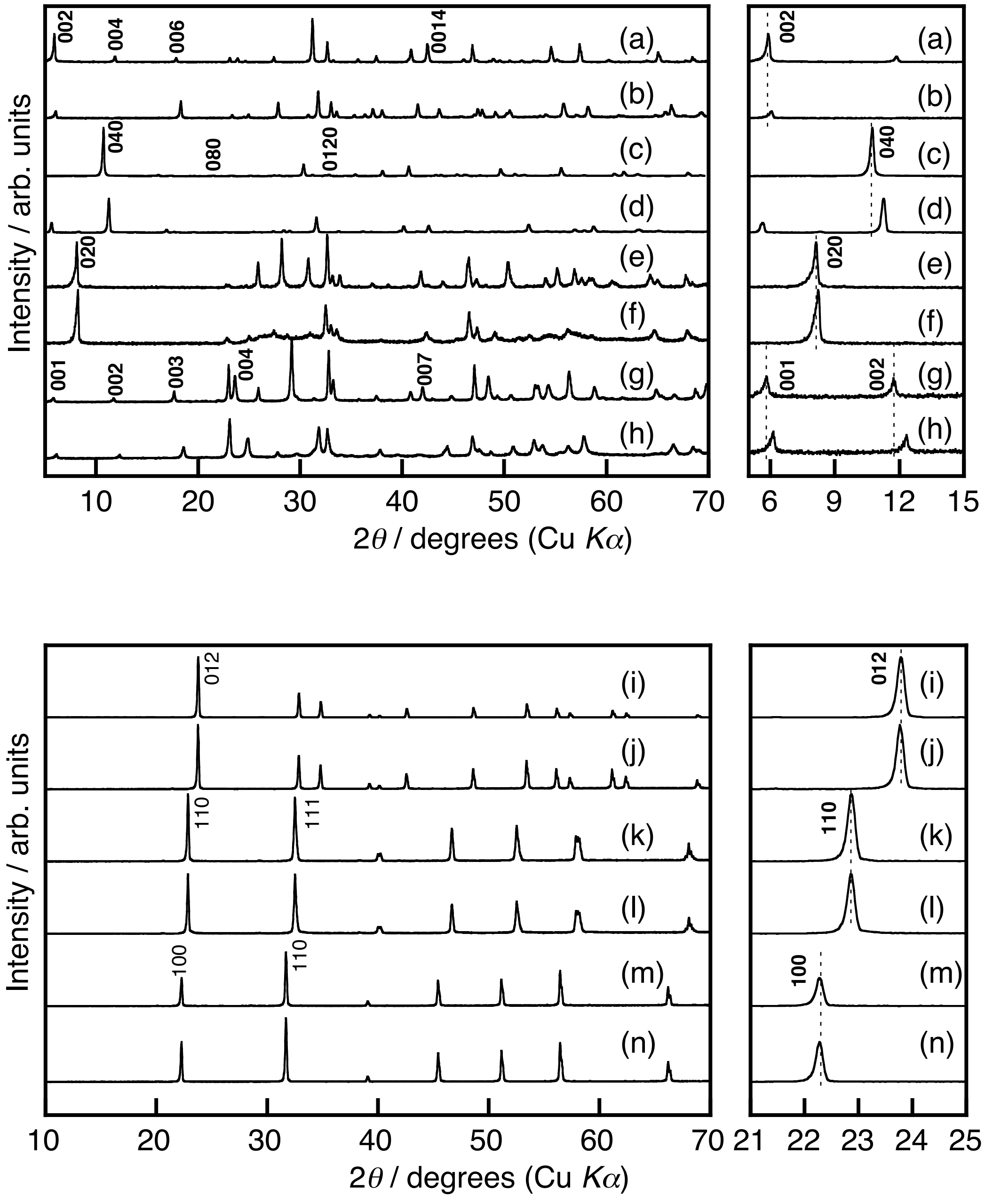

Figure S1. X-ray diffraction patterns of (a) $K_2La_2Ti_3O_{10}$, (b) Cu(I)-$K_2La_2Ti_3O_{10}$, (c) $K_4Nb_6O_{17}$, (d) Cu(I)-$K_4Nb_6O_{17}$, (e) $KLaNb_2O_7$, (f) Cu(I)-$KLaNb_2O_7$, (g) $RbCa_2Ta_3O_{10}$, (h) Cu(I)-$RbCa_2Ta_3O_{10}$, (i) $LiTaO_3$, (j) Cu(I)-$LiTaO_3$, (k) $NaTaO_3$, (l) Cu(I)-$NaTaO_3$, (m) $KTaO_3$ and (n) Cu(I)-$KTaO_3$.

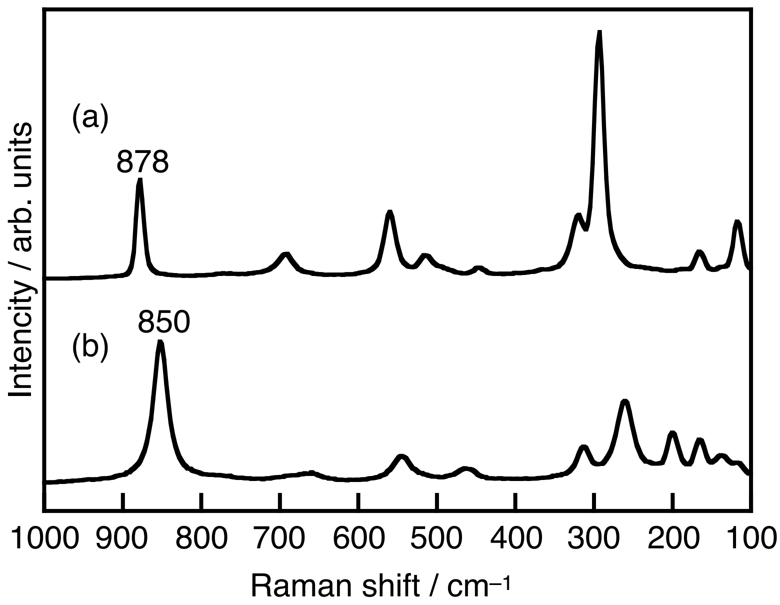

Figure S2. Raman spectra of (a) $K_2La_2Ti_3O_{10}$ and (b) Cu(I)-$K_2La_2Ti_3O_{10}$. Excitation wavelength: 532 nm.

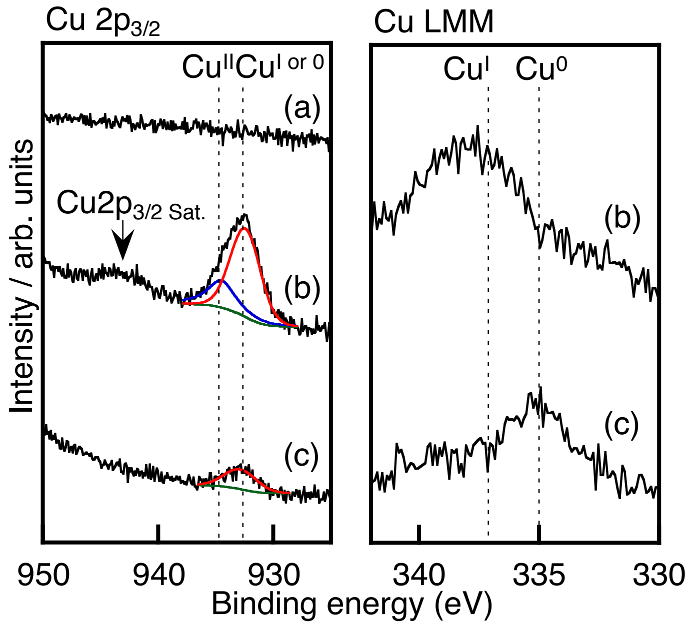

Figure S3. X-ray photoelectron and Auger spectra of (a) $LiTaO_3$, (b) Cu(I)-$LiTaO_3$ and (c) 60s Ar-etched Cu(I)-$LiTaO_3$. Assigned by ref. 20.

Determination of the Cu(I)-exchange ratio

ICP-AES

The calibration curves were obtained using potassium, lanthanum, titanium and copper standard solutions for ICP-AES analysis (Wako Pure Chemical). After mixing a standard solution of germanium as internal standard to correct flame intensity and the each standard solution, the mixture solutions were diluted to 100 mL with distilled water for the ICP-AES analysis. The emission wavelengths used for determinate quantity were 769.896 nm for K, 379.487 nm for La, 323.452 nm for Ti, 213.598 nm for Cu and 209.426 nm for Ge.

Figure S4 shows the calibration curves for K, La, Ti and Cu. The y-axis represents the intensity of K, La, Ti or Cu normalized by an internal standard of Ge. All calibration curves had correlation coefficients larger than 0.999.

0.02 g of $K_2La_2Ti_3O_{10}$ and Cu(I)-$K_2La_2Ti_3O_{10}$ were completely dissolved in ca. 0.2 mL of an aqua regia. The solutions were diluted to 100 mL with distilled water for the ICP-AES analysis, after adding 0.5 mL of germanium standard solution (1000 ppm).

Table S1 shows the signal intensity and calculated molar number of $K_2La_2Ti_3O_{10}$ and Cu(I)-$K_2La_2Ti_3O_{10}$. No K^+ ions were observed in Cu(I)-$K_2La_2Ti_3O_{10}$, indicating 100% of Cu(I)-exchange ratio.

XRF

Photocatalyst of $K_4Nb_6O_{17}$, $KLaNb_2O_7$, $RbCa_2Ta_3O_{10}$, $LiTaO_3$ and $NaTaO_3$ were mixed with CuO in the ratio of alkaline:Cu = 1:0, 1:0.25, 1:0.5, 1:0.75 and 1:1 to prepare calibration curves. The used emission X-ray source was Ge. The energy of X-ray used for determinate quantity was 8.094 keV for Cu $K\beta$, 16.581 keV for Nb $K\alpha$ and 9.342 keV for Ta $L\beta$.

Figure S5 shows the calibration curves of Cu(I)-$K_4Nb_6O_{17}$, Cu(I)-$KLaNb_2O_7$, Cu(I)-$RbCa_2Ta_3O_{10}$, Cu(I)-$LiTaO_3$ and Cu(I)-$NaTaO_3$. Calibration curves had correlation coefficients larger than 0.9980.

Table S2 shows the signal intensity, calculated ratio of Cu to either Nb or Ta and Cu(I)-exchange ratio of Cu(I)-$K_4Nb_6O_{17}$, Cu(I)-$KLaNb_2O_7$, Cu(I)-$RbCa_2Ta_3O_{10}$, Cu(I)-$LiTaO_3$ and Cu(I)-$NaTaO_3$. Ratio of Cu to Nb or Ta of Cu(I)-$K_4Nb_6O_{17}$, Cu(I)-$KLaNb_2O_7$, Cu(I)-$RbCa_2Ta_3O_{10}$, Cu(I)-$LiTaO_3$ and Cu(I)-$NaTaO_3$ are 46.0, 32.3, 30.0, 2.2 and 8.9%, respectively. Cu(I)-exchange ratio of Cu(I)-$K_4Nb_6O_{17}$, Cu(I)-$KLaNb_2O_7$, Cu(I)-$RbCa_2Ta_3O_{10}$, Cu(I)-$LiTaO_3$ and Cu(I)-$NaTaO_3$ can be calculated to be 69, 65, 90, 2 and 9%, respectively.

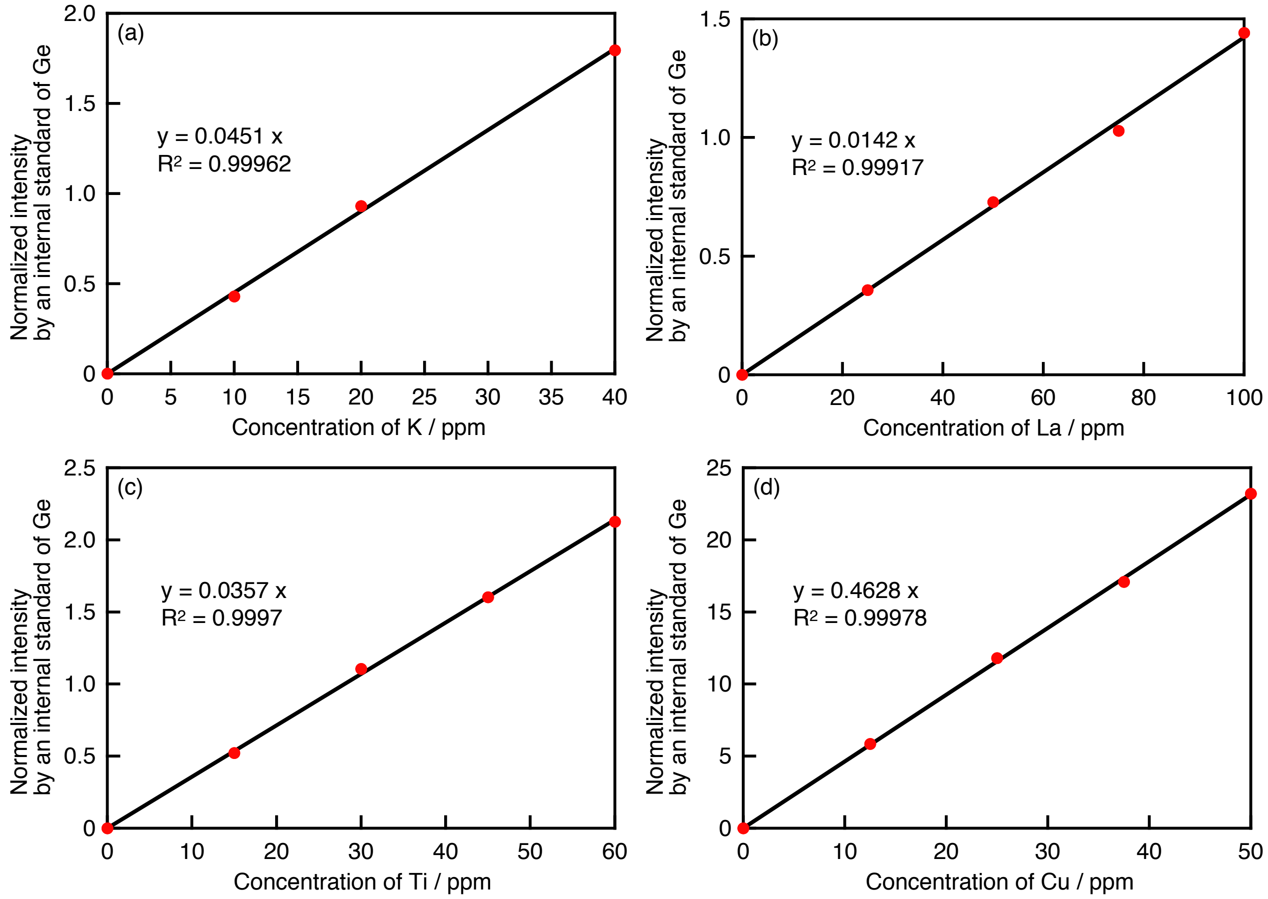

Figure S4. Calibration curves of (a) K, (b) La, (c) Ti and (d) Cu in ICP-AES analysis.

Table S1. ICP signal intensity and calculated element contents of $K_2La_2Ti_3O_{10}$ and Cu(I)-$K_2La_2Ti_3O_{10}$

Element	$K_2La_2Ti_3O_{10}$		Cu(I)- $K_2La_2Ti_3O_{10}$	
	Signal intensity	Calculated molar number/μmol	Signal intensity	Calculated molar number/μmol
K	45301	58.9	0	0
La	48992	57.0	46503	54.6
Ti	65504	87.3	61022	82.2
Cu	5796	0.07	606204	47.4
Ge	43572	–	43116	–

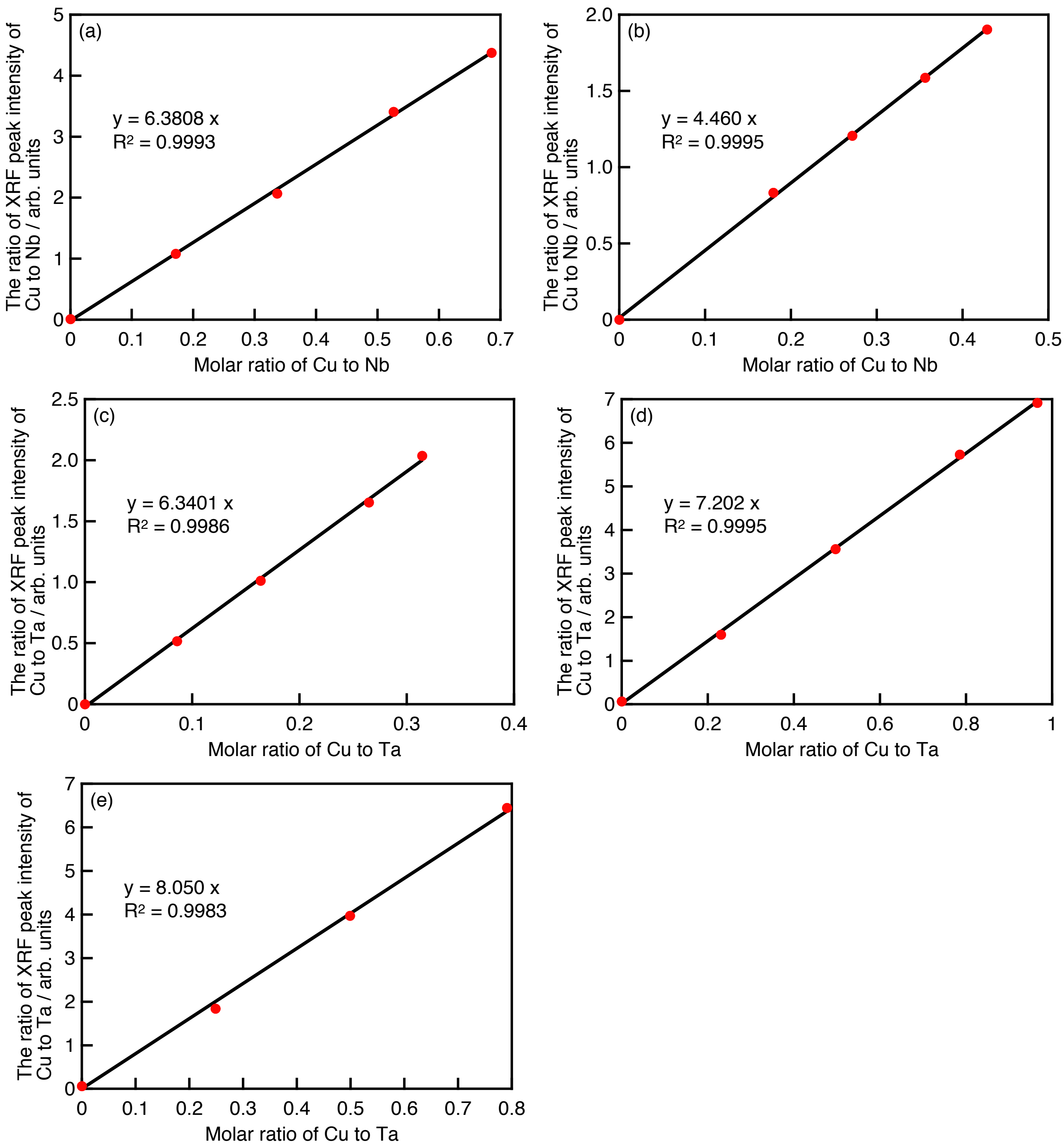

Figure S5. Calibration curves of (a) Cu(I)-$K_4Nb_6O_{17}$, (b) Cu(I)-$KLaNb_2O_7$, (c) Cu(I)-$RbCa_2Ta_3O_{10}$, (d) Cu(I)-$LiTaO_3$ and (e) Cu(I)-$NaTaO_3$ in XRF analysis.

Table S2. XRF signal intensity, calculated ratio of Cu to either Nb or Ta and Cu(I)-exchange ratio of Cu(I)-$K_4Nb_6O_{17}$, Cu(I)-$KLaNb_2O_7$, Cu(I)-$RbCa_2Ta_3O_{10}$, Cu(I)-$LiTaO_3$ and Cu(I)-$NaTaO_3$

Photocatalyst	XRF peak intensity			Ratio of Cu to either Nb or Ta %	Cu(I)-exchange ratio %
	Cu	Nb	Ta		
Cu(I)-$K_4Nb_6O_{17}$	28.03	9.54	–	46.0	69
Cu(I)-$KLaNb_2O_7$	13.03	9.04	–	32.3	65
Cu(I)-$RbCa_2Ta_3O_{10}$	10.17	–	5.15	30.0	90
Cu(I)-$LiTaO_3$	1.17	–	7.31	2.2	2
Cu(I)-$NaTaO_3$	4.17	–	5.81	8.9	9