Supporting information

Development of visible-light-responsive Ir and La-codoped $KTaO_3$ photocatalyst for water splitting

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Experimental details

Preparation of Ir and La-codoped $ATaO_3$ (A=Li, Na, K)

$ATaO_3$ (A=Li, Na, K) doped with Ir(0.1%) and La(0.2%) (denoted as $ATaO_3$:Ir,La) was prepared by a solid-state reaction. Starting materials of Li_2CO_3 (Kanto Chemical, 99.0%), Na_2CO_3 (Kanto Chemical, 99.8%), K_2CO_3 (Kanto Chemical, 99.5%), Ta_2O_5 (Rare Metallic, 99.99%), and IrO_2 (Kojundo Chemical) were mixed at atomic ratios of Li/Ta/Ir/La=1.05:0.999:0.001:0.002 for $LiTaO_3$:Ir,La, Na/Ta/Ir/La=1.05:0.999:0.001:0.002 for $NaTaO_3$:Ir,La, and K/Ta/Ir/La=1.1:0.999:0.001:0.002 for $KTaO_3$:Ir,La. The excess amounts of Li, Na, and K were added to the starting materials to compensate for volatilization during synthesis. The mixture was calcined in air at 1173 K for 1h and then at 1423 K for 10 h in an alumina crucible. The excess alkali metal ions were removed by rinsing with water after the calcination.

A $RhCrO_3$ cocatalyst was impregnated on the $KTaO_3$ codoped with Ir and La photocatalyst in advance to demonstrate water splitting. The $KTaO_3$ powder and an aqueous solution containing desired amounts of $Rh(NO_3)_3$ (Kanto Chemical, >80% as anhydrous) and $Cr(NO_3)_3$ (Kanto Chemical, 98.0%–103.0%) were placed in a porcelain crucible and dried on a hot plate. The impregnated powder was calcined in air at 623 K for 1 h.

Characterization

The crystal phase of the prepared powder was analyzed on an X-ray diffractometer (Rigaku, MiniFlex). Diffuse reflectance spectra were obtained using a UV-vis-NIR spectrometer (JASCO, V-650) equipped with an integrating sphere, and were converted from reflection to K-M function by the Kubelka-Munk method. Morphology and particle size of the photocatalyst powder were observed using a scanning electron microscope (JEOL, JSM-7600F).

Photocatalytic reactions

Sacrificial H_2 and O_2 evolution and overall water splitting were carried out in a gas-closed circulation system with a top-irradiation cell with a Pyrex window. Photocatalyst powder (0.3 g) was dispersed in an aqueous solution (120 mL) containing methanol (10 vol%) and $H_2[PtCl_6]$ (0.3 wt% Pt with respect to the photocatalyst) for the sacrificial H_2 evolution. Meanwhile, photocatalyst powder (0.3 g) was dispersed in an aqueous solution (120 mL) containing $AgNO_3$ (0.02 mol L^{-1}) for the sacrificial O_2 evolution. Overall water splitting was also demonstrated using $RhCrO_3$-loaded $KTaO_3$ codoped with Ir and La (0.3 g) dispersed in water (120 mL). A 300 W Xe lamp (PerkinElmer, Cermax PE300BF) was used as a light source, and the wavelength of the irradiated light was controlled to visible light using long-pass filters (HOYA L42, Y48, Y50, Y52, O54, O56, R60), if necessary. The amounts of evolved gases were determined using an online gas chromatograph (Shimadzu, GC-8A, TCD detector, MS-5A column, Ar carrier). Apparent quantum yields (AQY) for the sacrificial H_2 and O_2 evolution were estimated using the following equation.

[AQY%] = 100 × [the number of reacted electrons or holes] / [the number of incident photons]

= 100 × [the number of evolved H_2 molecules] × 2 / [the number of incident photons]

= 100 × [the number of evolved O_2 molecules] × 4 / [the number of incident photons]

The photon flux of the monochromatic light through a band-pass filter (Asahi Spectra, HMZ0420, λ=420 nm) was measured using a silicon diode head (Ophir Optoronics, PD300-UV head and NOVA display).

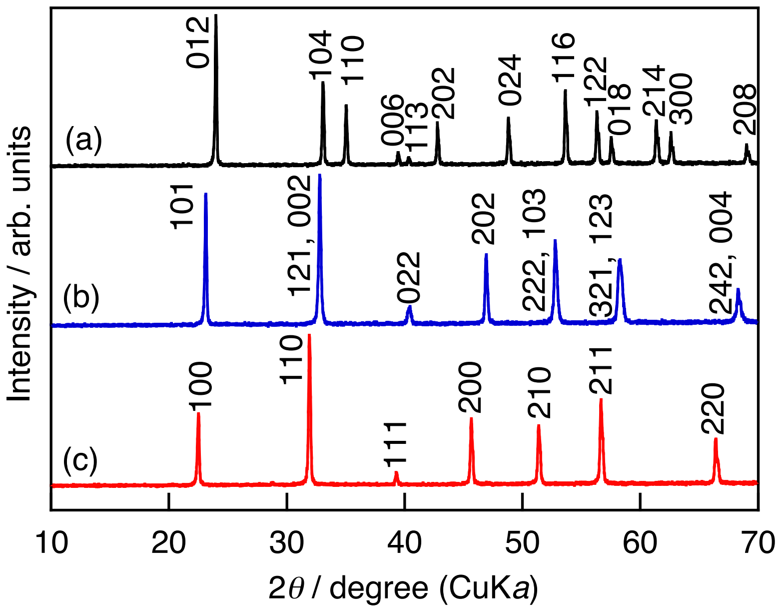

Figure S1. XRD patterns of (a) $LiTaO_3$:Ir(0.1%),La(0.2%), (b) $NaTaO_3$:Ir(0.1%),La(0.2%), and (c) $KTaO_3$:Ir(0.1%),La(0.2%).

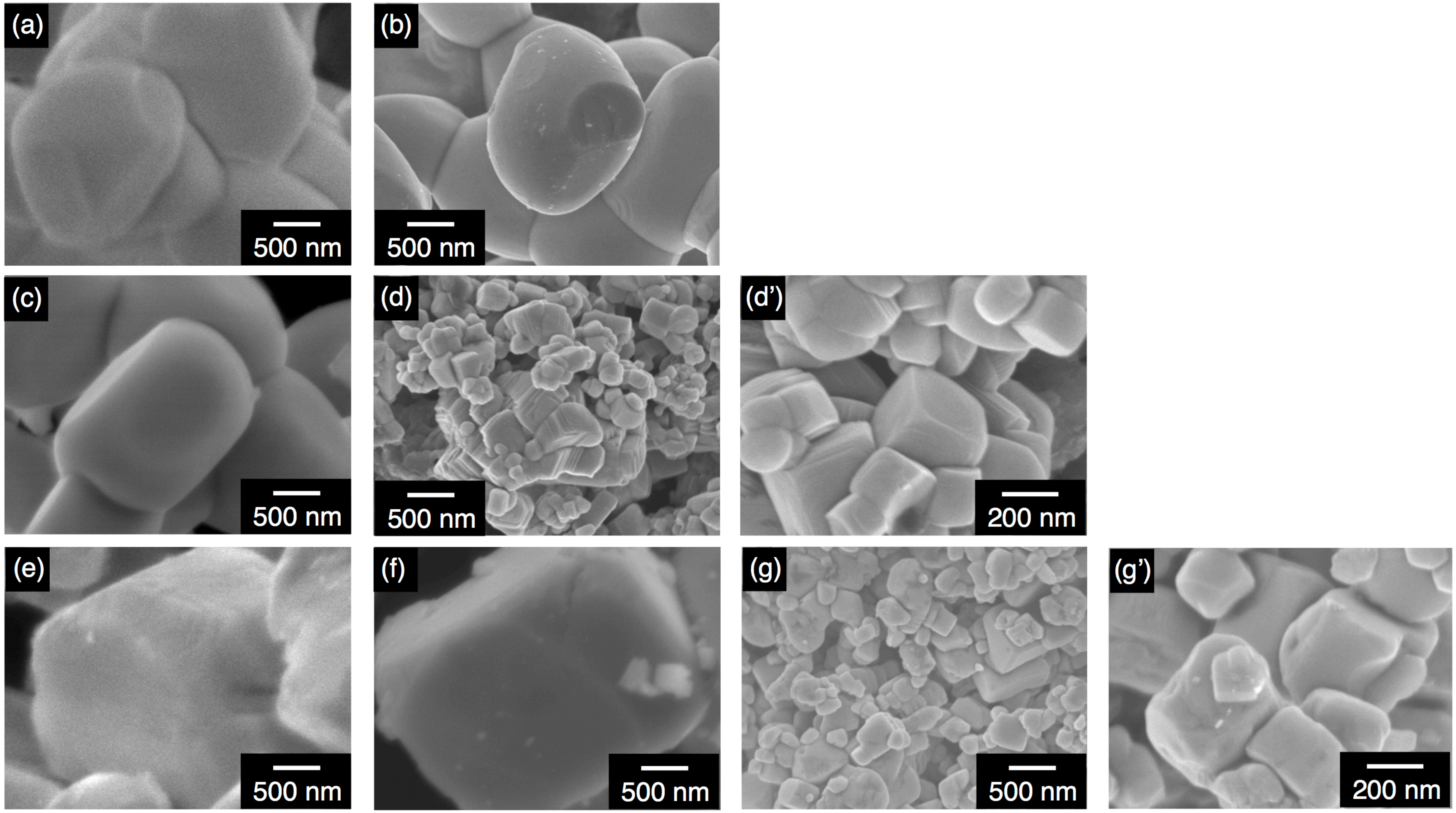

Figure S2. SEM images of (a) non-doped $LiTaO_3$, (b) $LiTaO_3$:Ir(0.1%),La(0.2%), (c) non-doped $NaTaO_3$, (d, d') $NaTaO_3$:Ir(0.1%),La(0.2%), (e) non-doped $KTaO_3$, (f) $NaTaO_3$:Ir(0.1%), and (g, g') $KTaO_3$:Ir(0.1%),La(0.2%).

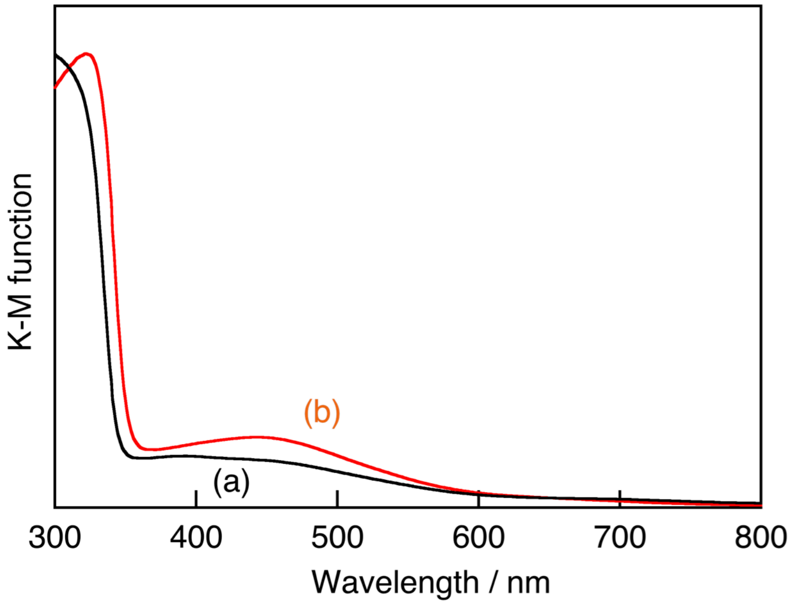

Figure S3. Diffuse reflectance spectra of (a) $KTaO_3$:Ir(0.1%),La(0.2%) and (b) $KTaO_3$:Ir(0.1%).

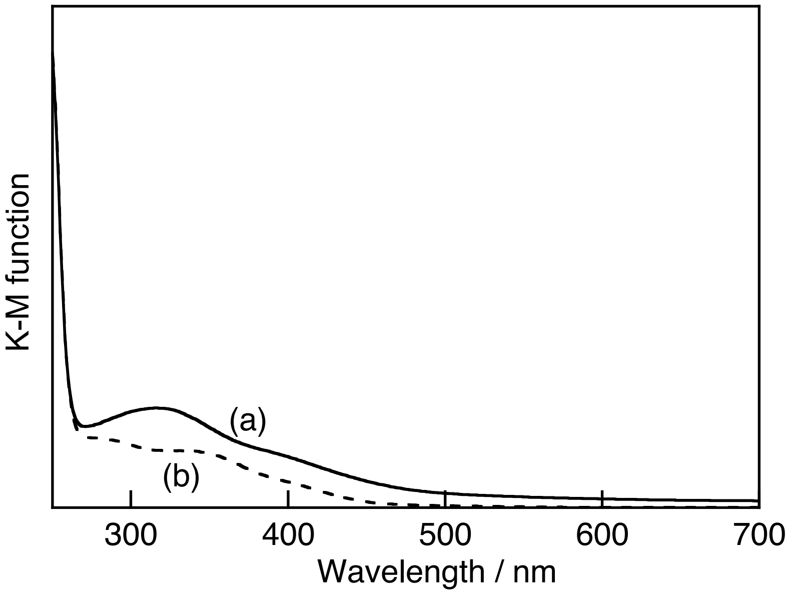

Figure S4. Diffuse reflectance spectra of $LiTaO_3$:Ir(0.1%),La(0.2%) (a) with and (b) without H_2 reduction at 673 K.