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Supporting Information

Development of Ir and La-codoped $BaTa_2O_6$ photocatalysts using visible light up to 640 nm as an H_2-evolving photocatalyst for Z-schematic water splitting

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Experimental

Preparation of ATa_2O_6 (A= Ca, Sr, and Ba) photocatalysts codoped with iridium and La ions

Ir and Ta-codoped ATa_2O_6 (A= Ca, Sr, and Ba) was prepared by a borate-flux method. Starting materials of $CaCO_3$, $SrCO_3$, $BaCO_3$, Ta_2O_5, IrO_2, and La_2O_3, and a flux agent of H_3BO_3 (Kanto Chemical; 99%) were mixed with a molar ratio of (Ca, Sr, or Ba)/Ta/Ir/La/B = 1.1:2:0.02:0.04:0.2. The mixture was calcined at 1373K for 10h in an alumina crucible. The obtained powder was washed with 0.02mol L^{-1} HCl to remove borate flux agents. Ir and Ta-codoped $BaTa_2O_6$ was also prepared by a solid-state reaction and a NaCl-flux method. The materials of $BaCO_3$, Ta_2O_5, IrO_2, and La_2O_3 were mixed with a molar ratio of Ba/Ta/Ir/La = 1:2:0.02:0.04 for the solid-state reaction. The mixture was calcined in air at 1173K for 1h and then 1423K for 10h in an alumina crucible. The materials of $BaCO_3$, Ta_2O_5, IrO_2, and La_2O_3, and a flux agent of NaCl were mixed with a mole ratio of Ba/Ta/Ir/La/Na = 1:2:0.02:0.04:0.2 for the NaCl-flux method. The mixture was calcined at 1373K for 10h in an alumina crucible. The obtained powder was washed with water to remove NaCl flux agents.

Characterization of photocatalysts

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; Ubest-570) equipped with an integrating sphere, and were converted from reflection to absorbance by the Kubelka-Munk method. Morphology of the photocatalyst powder was observed using a scanning electron microscope (Jeol; JSM-6700F).

Photocatalytic reactions

Sacrificial H_2 evolution and Z-schematic water splitting were carried out using a gas-tight circulation system. The photocatalyst powder (0.1–0.3g) was dispersed in an aqueous solution (120 mL) containing methanol (10 vol%) and $H_2[PtCl_4]_2$ (0.3 wt% Pt with respect to photocatalysts) for sacrificial H_2 evolution. H_2 evolution as a half reaction of Z-scheme system was also demonstrated using aqueous solutions containing $FeCl_2$ (2 mmol L^{-1}, pH 2.4), and $[Co(bpy)_3]SO_4$ 1 mmol L^{-1}, pH 3.7) of electron mediators. H_2SO_4 was used for the pH adjustment of the solutions. Pt(0.3 wt%)- and Ru(0.5 wt%)-cocatalysts were photodeposited on the H_2-evolving photocatalyst from $H_2[PtCl_4]_2$ and $RuCl_3$ in an aqueous methanol solution in advance. For the Z-schematic water splitting, Ru-loaded $BaTa_2O_6$ doped with Ir and La (0.05 g) and $BiVO_4$ (0.05 g) were dispersed in a 1 mmol L^{-1} aqueous $[Co(bpy)_3]SO_4$ solution (pH 3.7). A top-irradiation reaction cell with a Pyrex window and a 300 W Xe lamp (Parkin Elmer, CERMAX PE300BF) with a long-pass filter (L42) were used. Amounts of evolved H_2 and O_2 were determined using an online gas chromatograph (Shimadzu, GC-8A, TCD, MS-5A column, Ar carrier).

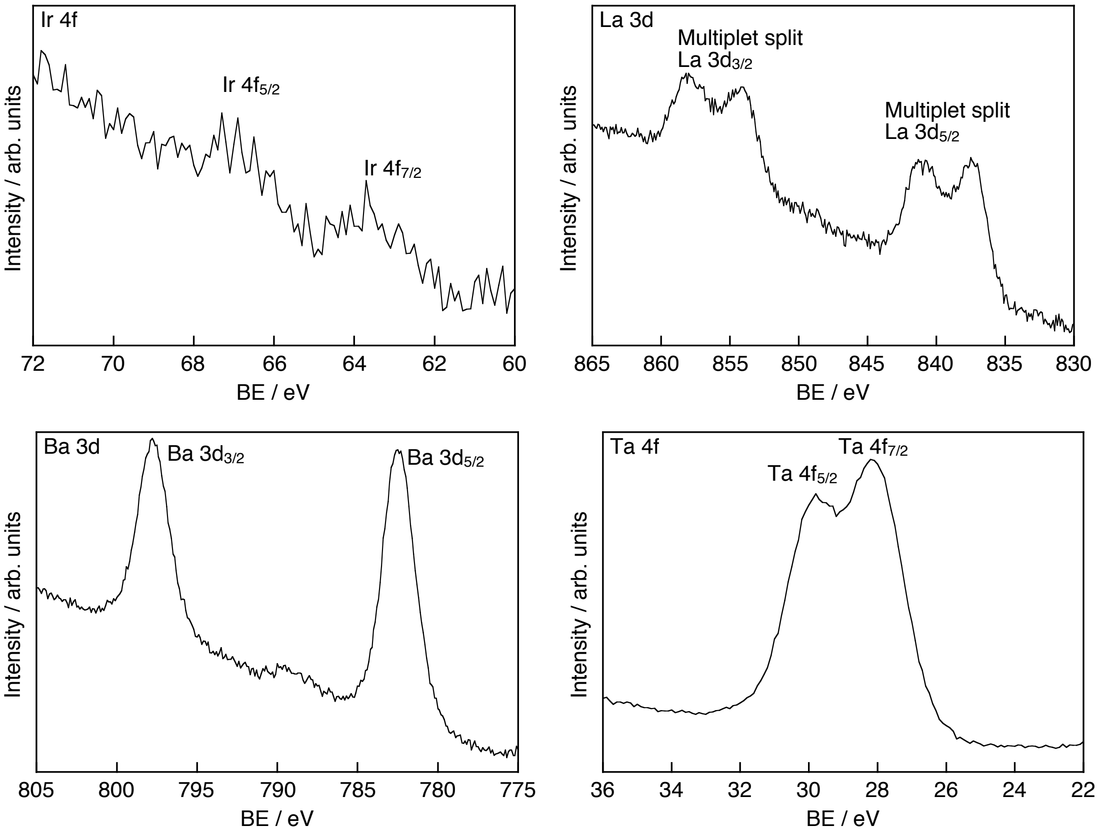

Figure S1 XPS peaks of Ir4f, La3d, Ba3d, and Ta4f peaks for $BaTa_2O_6$:Ir(1%),La(2%) prepared by a borate-flux method at 1373K.

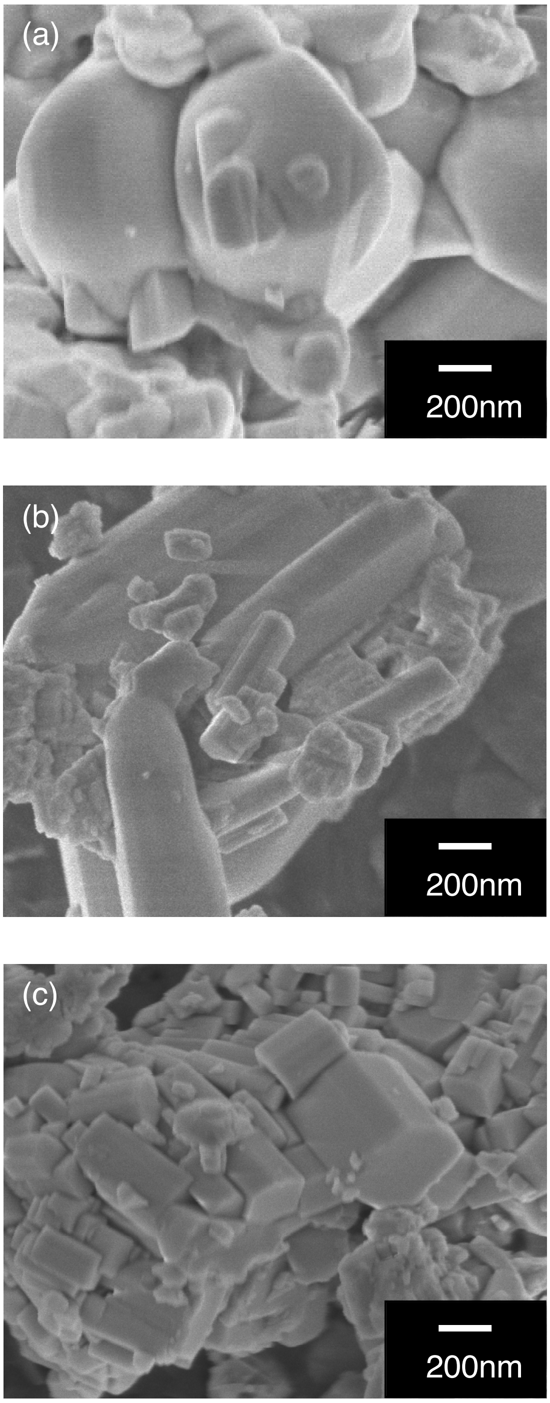

Figure S2 SEM images of $BaTa_2O_6$:Ir(1%),La(2%) synthesized by (a) a solid-state reaction (1423 K), (b) a NaCl-flux method (1373 K), and (c) a borate-flux method (1373 K).

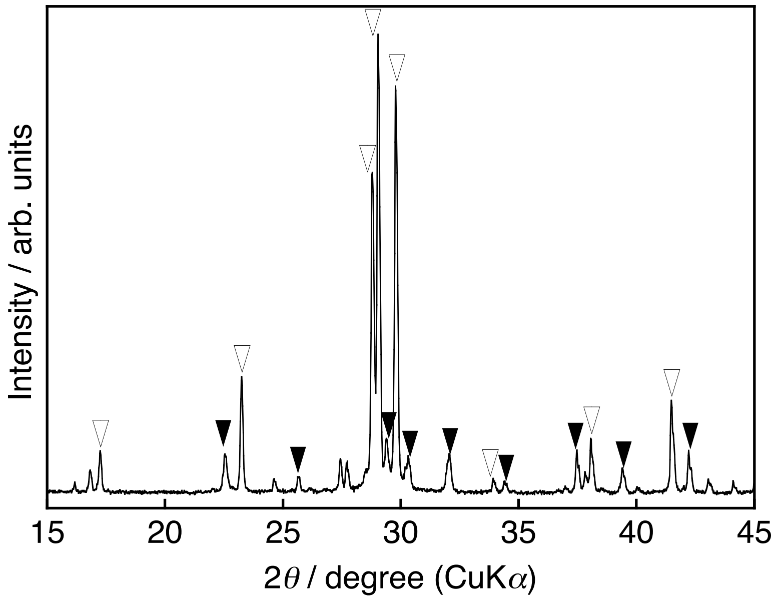

Figure S3 XRD pattern of $BaTa_2O_6$:Ir(1 at%) prepared by a borate-flux method at 1373 K.

Closed mark: tungsten bronze type tetragonal system (PDF: 50-1706), open mark: $CaTa_2O_6$ type orthorhombic system (PDF: 20-146).

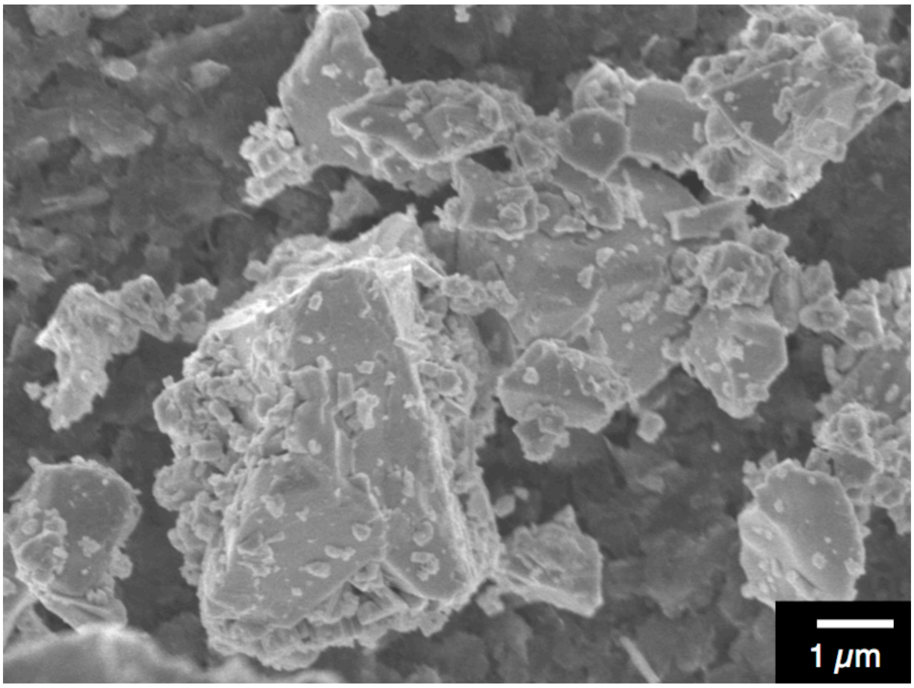

Figure S4 SEM image of $BaTa_2O_6$:Ir(1 at%) prepared by a borate-flux method at 1373 K.

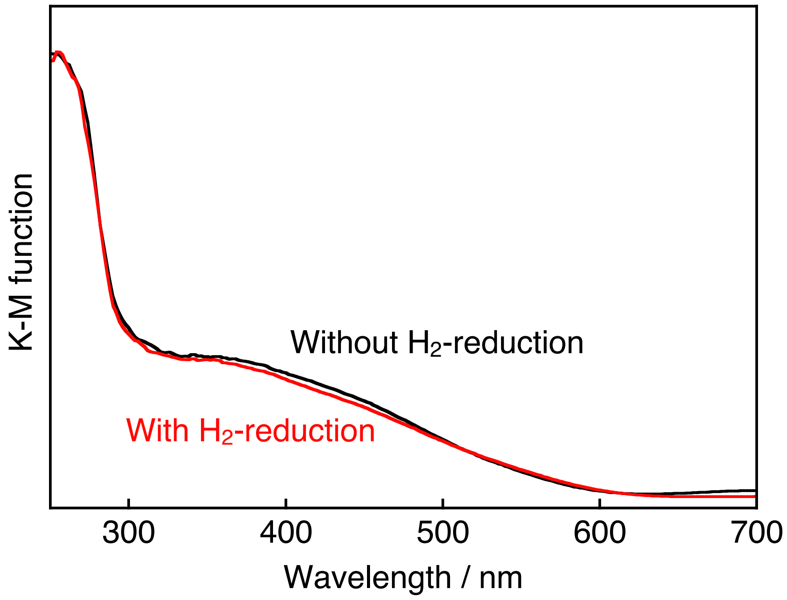

Figure S5 Diffuse reflectance spectra of $BaTa_2O_6$:Ir(1 at%) prepared by a borate-flux method at 1373 K. H_2 reduction was carried out at 473K.