

## Supporting information

### Development of Ir and Sr-codoped KNbO<sub>3</sub> photocatalysts as an O<sub>2</sub>-evolving photocatalyst for Z-schematic water splitting under visible light irradiation

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#### Experimental details

##### Preparation of photocatalysts

KNbO<sub>3</sub> doped with Ir(x at%) and Sr(5x at%) was prepared by a solid-state reaction. Starting materials of K<sub>2</sub>CO<sub>3</sub> (Kanto Chemical, 99.5%), Nb<sub>2</sub>O<sub>5</sub> (Kojundo Chemical, 99.9%), IrO<sub>2</sub> (Kojundo Chemical), and SrCO<sub>3</sub> (Kanto Chemical, 99.9%) were mixed at atomic ratios of K/Nb/Ir/Sr=1.1:1-0.01x:0.01x:0.05x. The excess amount of K was added to the starting materials to compensate for volatilization during synthesis. For example, 0.7602 g of K<sub>2</sub>CO<sub>3</sub>, 1.3284 g of Nb<sub>2</sub>O<sub>5</sub>, 0.00112 g of IrO<sub>2</sub>, and 0.00369 g of SrCO<sub>3</sub> were used for KNbO<sub>3</sub> doped with Ir(0.05 at%) and Sr(0.25 at%) with an atomic ratio of K/Nb/Ir/Sr=1.1:0.9995:0.0005:0.0025. The mixture was calcined in air at 1173 K for 1h and subsequently at 1173 K for 10 h in an alumina crucible. The excess K ions were removed by rinsing with water after the calcination.

SrTiO<sub>3</sub> doped with Rh(1 at%) (SrTiO<sub>3</sub>:Rh) as a H<sub>2</sub>-evolving photocatalyst for a Z-scheme system was prepared by a solid-state reaction, as previously reported.<sup>1</sup> Starting materials of SrCO<sub>3</sub> (1.5796 g), rutile TiO<sub>2</sub> (Kojundo Chemical, 99.99%, 0.7907 g), and Rh<sub>2</sub>O<sub>3</sub> (Wako Chemical, 0.0127 g) were mixed at atomic ratios of Sr/Ti/Rh=1.07:0.99:0.01. The mixture was calcined in air at 1173 K for 1h and then at 1273 K for 10 h in an alumina crucible. A Ru(0.7 wt%)-cocatalyst was photodeposited on SrTiO<sub>3</sub>:Rh (0.5 g) from RuCl<sub>3</sub> (32.0 mmol L<sup>-1</sup>, 1.08 mL) in an aqueous methanol solution (10 vol%, 120 mL).

##### 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 spectrometer (JASCO, V-650) equipped with an integrating sphere, and were converted from reflection to K-M function by the Kubelka-Munk method. The specific surface area of the prepared powder was determined by N<sub>2</sub> adsorption using the Brunauer-Emmett-Teller (BET) method (MicrotracBEL, BELSORP MINI X). Morphology and particle size of the photocatalyst powder were observed using a scanning electron microscope (JEOL,

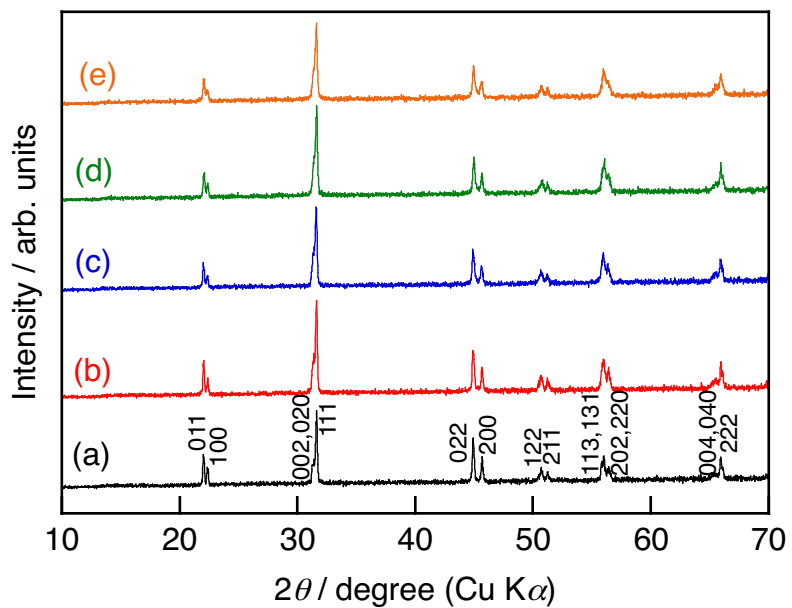
JSM-7600F).

### **Photocatalytic reactions**

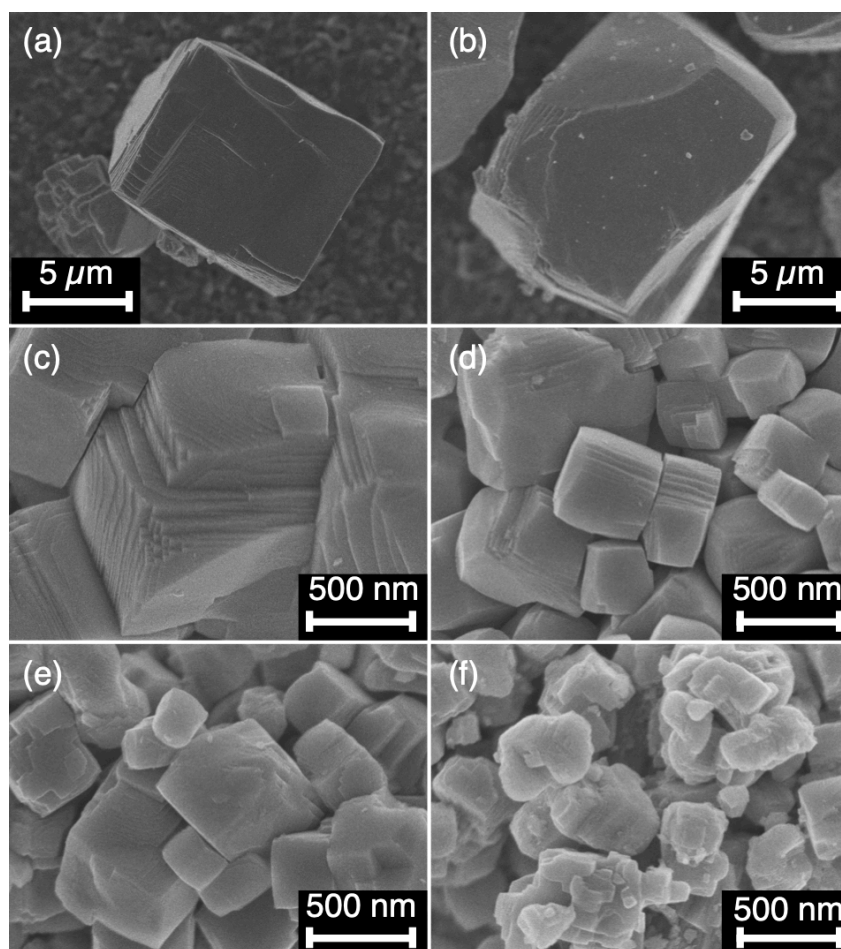
Sacrificial O<sub>2</sub> evolution and overall water splitting were carried out in a gas-closed circulation system with a top-irradiation cell with a Pyrex window. Photocatalyst powder (0.3 g) was dispersed in an aqueous solution (120 mL) containing AgNO<sub>3</sub> (0.02 mol L<sup>-1</sup>) for the sacrificial O<sub>2</sub> evolution. Z-schematic water splitting was also demonstrated using Ru-loaded SrTiO<sub>3</sub>:Rh (0.05 g) as a H<sub>2</sub>-evolving photocatalyst and KNbO<sub>3</sub>:Ir(0.05 at%),Sr(0.25 at%) (0.05 g) as an O<sub>2</sub>-evolving photocatalyst dispersed in water (120 mL, pH 3.5 adjusted by H<sub>2</sub>SO<sub>4</sub>). 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, O54, O56, R58, R62), if necessary. The amounts of evolved gases were determined using an online gas chromatograph (Shimadzu, GC-8A, TCD detector, MS-5A column, Ar carrier).

### **References**

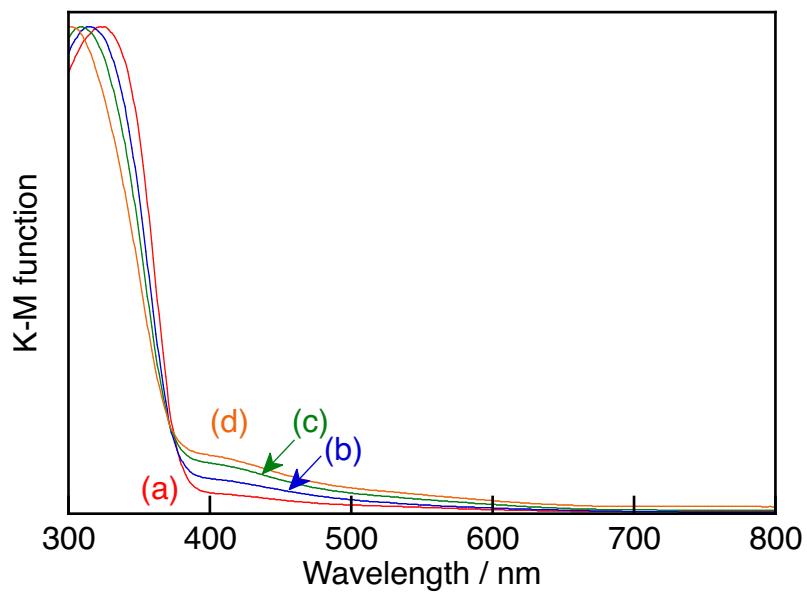
1. Y. Sasaki, H. Nemoto, K. Saito and A. Kudo, *J. Phys. Chem. C*, 2009, **113**, 17536.



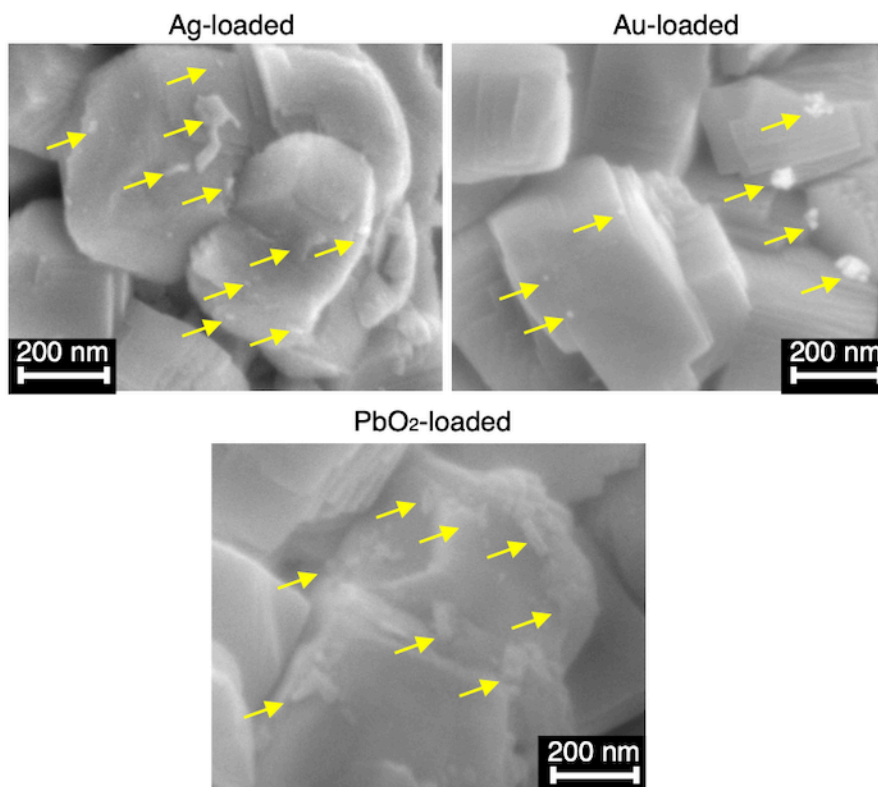
**Figure S1** XRD patterns of KNbO<sub>3</sub> doped with (a) Ir(0.05 at%), (b) Ir(0.01 at%),Sr(0.05 at%), (c) Ir(0.05 at%),Sr(0.25 at%), (d) Ir(0.1 at%),Sr(0.5 at%), and (e) Ir(0.3 at%),Sr(1.5 at%).



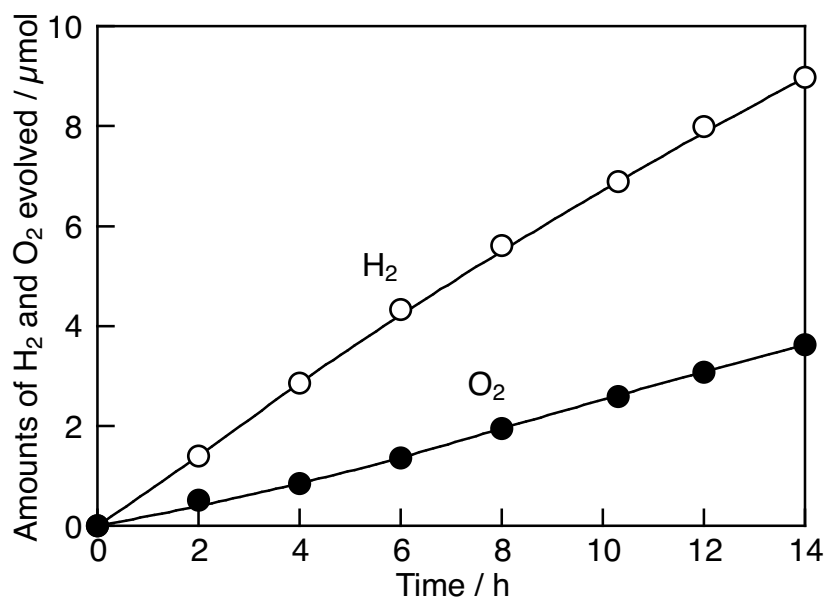
**Figure S2** SEM images of (a) non-doped KNbO<sub>3</sub> and KNbO<sub>3</sub> doped with (b) Ir(0.05 at%), (c) Ir(0.01 at%),Sr(0.05 at%), (d) Ir(0.05 at%),Sr(0.25 at%), (e) Ir(0.1 at%),Sr(0.5 at%), and (f) Ir(0.3 at%),Sr(1.5 at%).



**Figure S3** Diffuse reflectance spectra of KNbO<sub>3</sub> doped with (a) Ir(0.01 at%),Sr(0.05 at%), (b) Ir(0.05 at%),Sr(0.25 at%), (c) Ir(0.1 at%),Sr(0.5 at%), and (d) Ir(0.3 at%),Sr(1.5 at%).



**Figure S4** SEM images of KNbO<sub>3</sub>:Ir(0.05 at%),Sr(0.25 at%) loaded with Ag, Au, and PbO<sub>2</sub> by a photodeposition method.



**Figure S5** Z-schematic solar water splitting using Ru(0.7 wt%)-loaded SrTiO<sub>3</sub>:Rh(1 at%) and KNbO<sub>3</sub>:Ir(0.05 at%),Sr(0.25 at%) under simulated sunlight irradiation (AM-1.5G, 100 mW cm<sup>-2</sup>). Photocatalyst: 0.05 g each, reactant solution: H<sub>2</sub>SO<sub>4</sub> aq. 120 mL (pH 3.5), light source: solar simulator, cell: top-irradiation cell with a Pyrex window, irradiation area: 32 cm<sup>2</sup>.