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Supporting Information

First example of oxide semiconductor photocatalyst consisting of heptavalent cation: Visible-light-induced water oxidation on M_3ReO_8

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Experimental

(a) Characterization of catalyst

The prepared samples were characterized by powder X-ray diffraction (XRD; D8 ADVANCE, Bruker AXS; Cu Kα), scanning electron microscopy (SEM; NVision 40, Carl Zeiss-SIINT or VE-9800, KEYENCE), and UV-visible diffuse reflectance spectroscopy (V-650, Jasco). The surface area was measured using a BELSORP-mini (Microtrac BEL) at liquid nitrogen temperature (77 K).

(b) Electrochemical measurement

A paste was prepared by mixture of Y_3ReO_8 and water (Milli-Q grade), coated on conductive substrate (FTO), and then dried at room temperature. The Mott-Schottky plots were measured using an electrochemical analyzer (VersaSTAT 4, Princeton Applied Research). The electrochemical cell consisted of Y_3ReO_8/FTO electrode, a counter electrode (Pt wire), a Ag/AgCl reference electrode, and a phosphate buffer solution (0.1 M, pH = 6). AC amplitude and frequency were 10 mV and 1~2 kHz, respectively.

(c) Calculation

We calculated the electronic structures of the materials examined in this study using the Cambridge Serial Total Energy Package (CASTEP)[1]. The exchange and correlation energy was evaluated within the generalized gradient approximation (GGA) of density functional theory (DFT), as proposed by Perdew, Burke, and Ernzerhof (PBE). The electronic states were expanded using a plane-wave basis set with a cutoff energy of 1000 eV. The k-point set was 5×5×5. Geometry optimization was performed before calculating the electronic structures using the Broaden–Fletcher–Goldfarb–Shanno (BFGS) algorithm.

(d) Photocatalytic reactions

Photocatalytic reactions were carried out using a Pyrex glass reactor connected to a closed gas–circulation system. Photocatalyst powder (0.1 g) was suspended in 250 mL of an aqueous $AgNO_3$ solution (10 mM) in the reactor by using a set of magnetic stirrer and bar. After thorough degassing the suspension, the reaction system was filled with Ar gas (ca. 9 kPa). The suspension was irradiated using 300 W Xe lamp fitted with L-42 cut-off filter. The evolved gases were analyzed by on-line gas chromatography (detector; TCD, column packing; molecular sieve 5 A, Ar carrier).

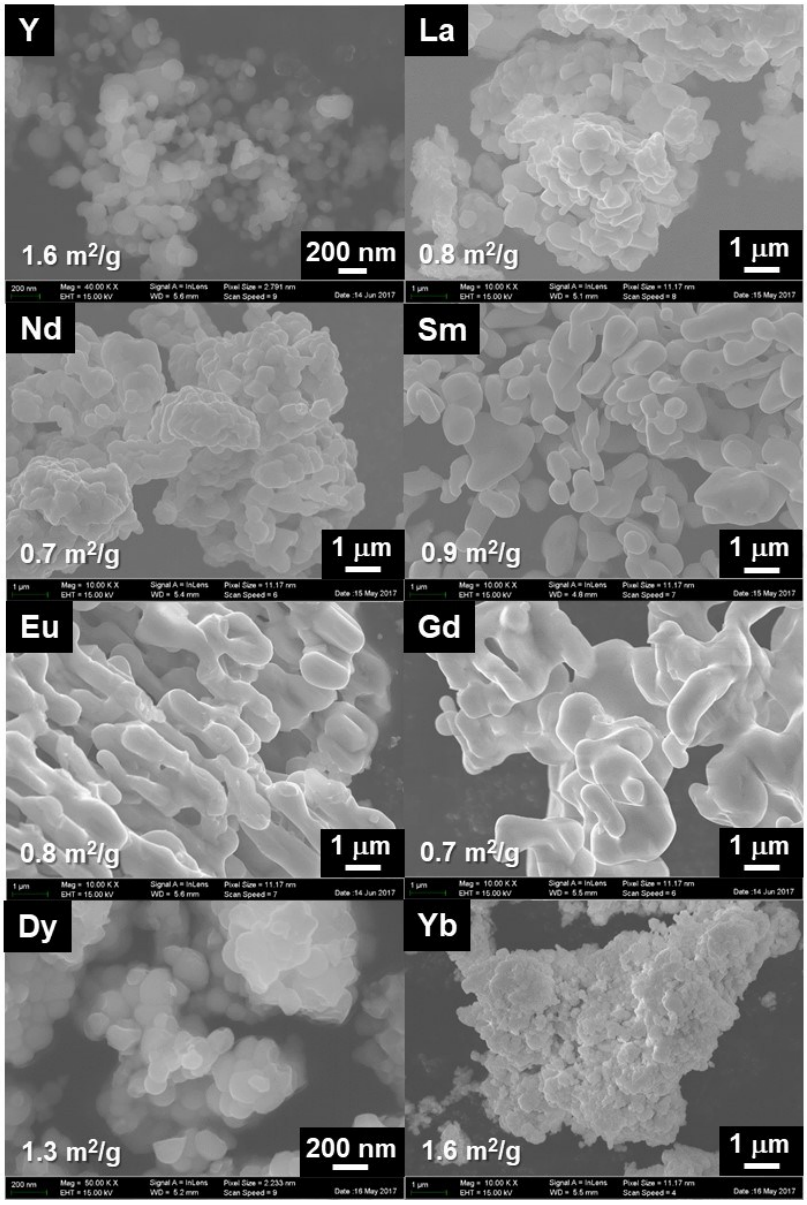

Figure S1. SEM images of M_3ReO_8 (M = Y, La, Nd, Sm, Eu, Gd, Dy, and Yb).

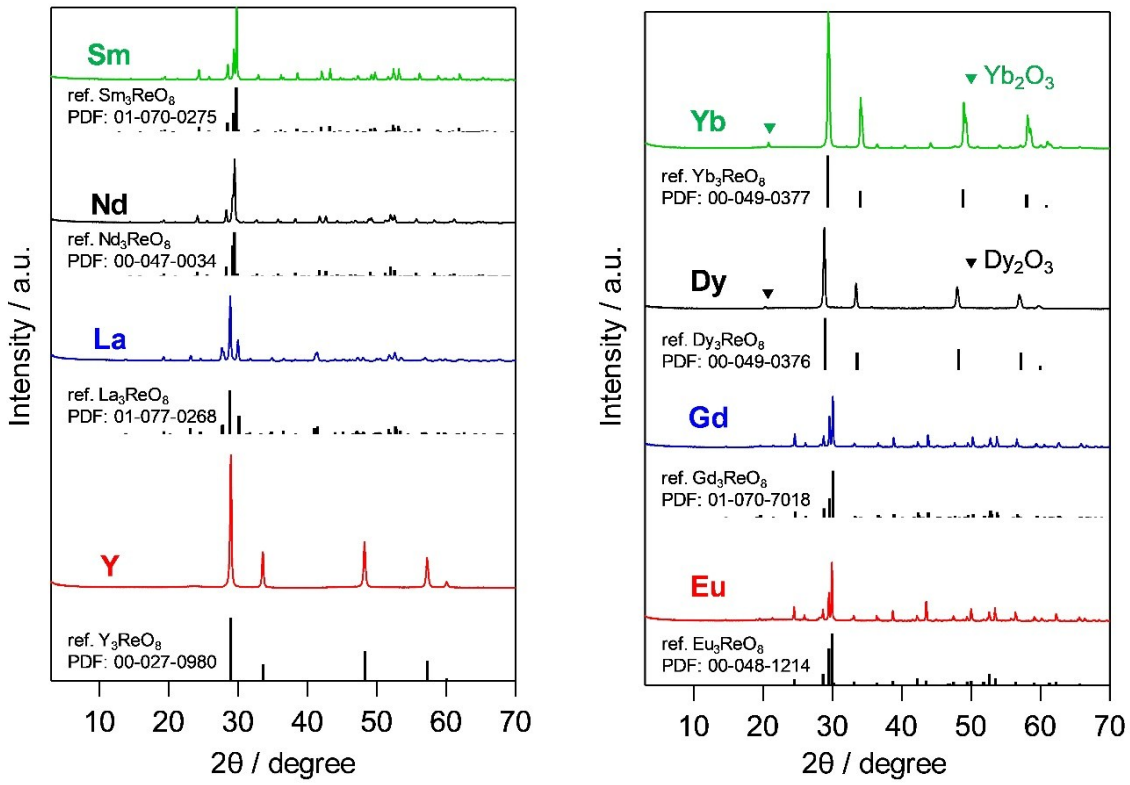

Figure S2. XRD patterns of M_3ReO_8 (M = Y, La, Pr, Nd, Sm, Eu, Gd, Dy, and Yb).

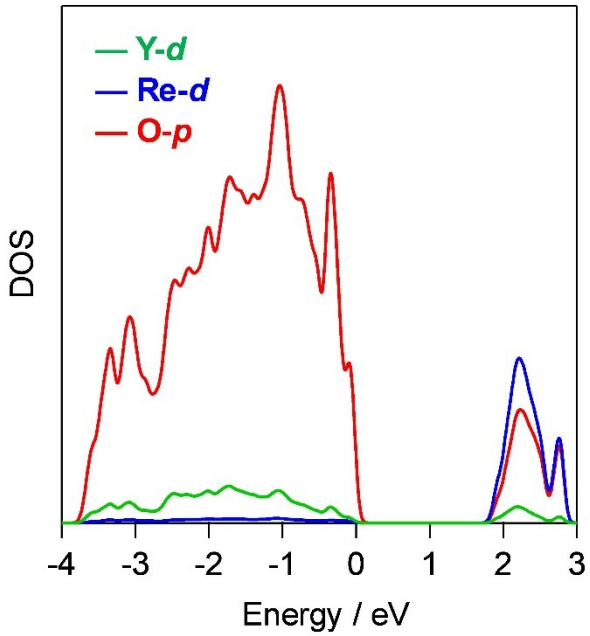

Figure S3. PDOS of Y-d, Re-d, and O-p orbitals in Y_3ReO_8.

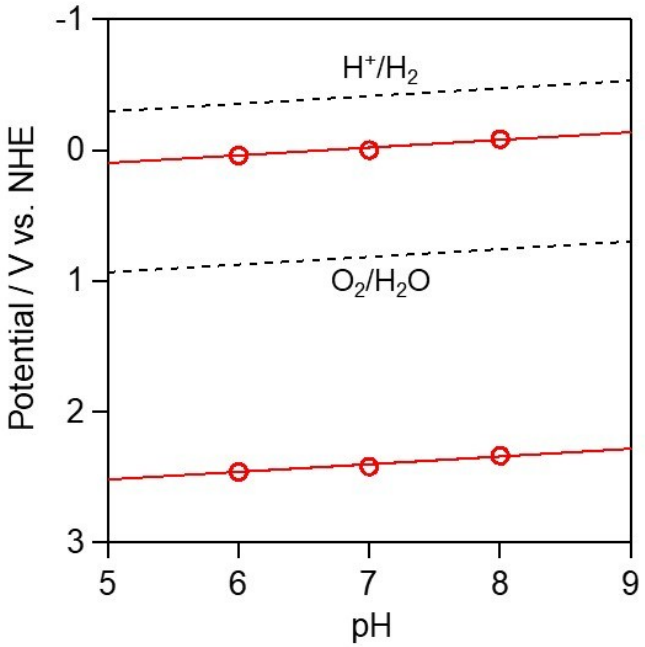

Figure S4. pH dependence of band edge potentials of Y_3ReO_8, determined by Mott–Schottky plots.

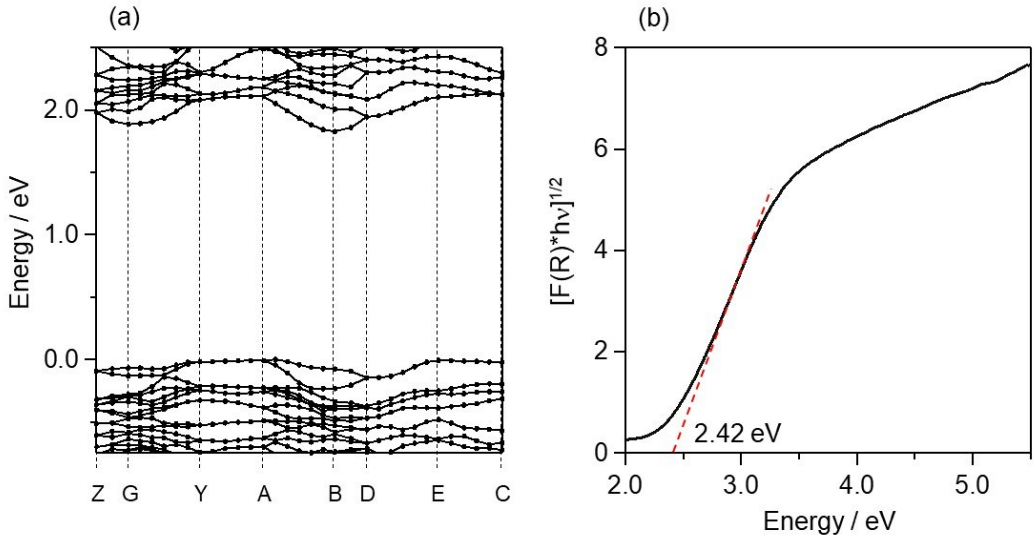

Figure S5. (a) Band structure of Y_3ReO_8, and (b) Tauc plot for Y_3ReO_8, where $(F(R)*h\nu)^{\alpha}$ against $h\nu$ is plotted. The DFT calculation suggests that Y_3ReO_8 is an indirect band gap semiconductor, and thus $\alpha = 1/2$ was used.

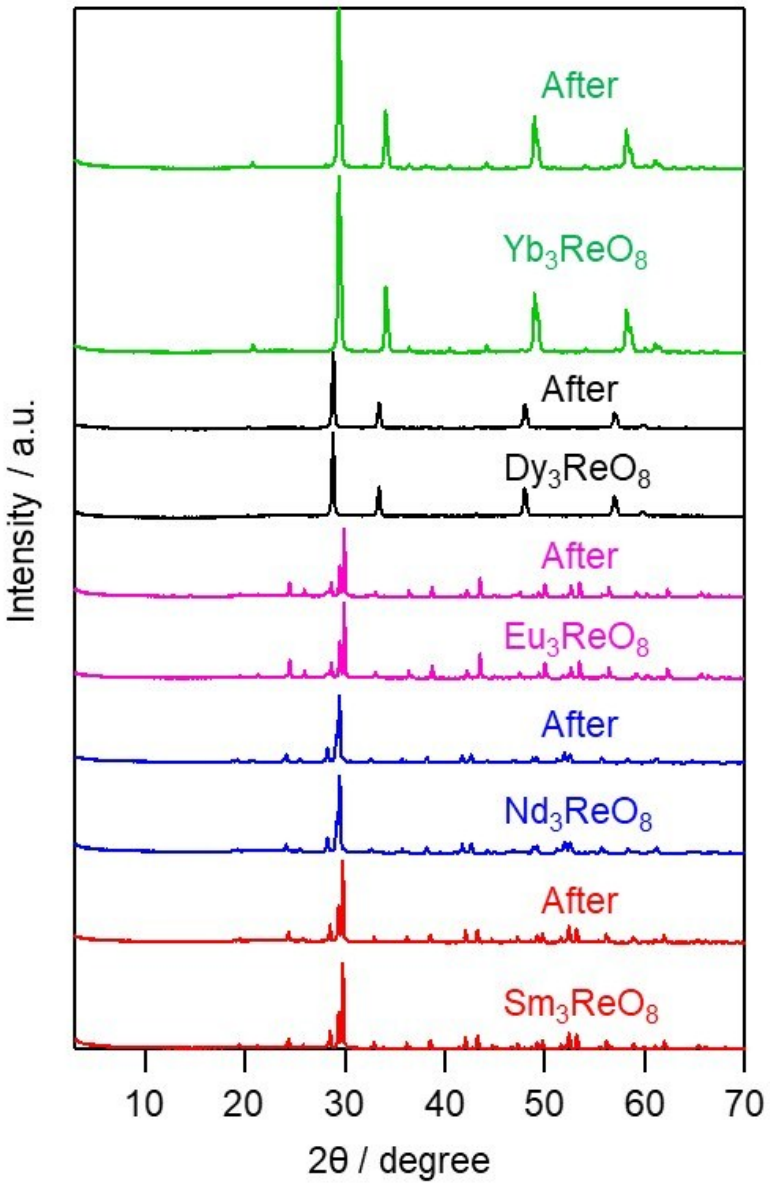

Figure S6. XRD patterns of M_3ReO_8 (M = Sm, Nd, Eu, Dy, and Yb) before and after O_2 evolution.

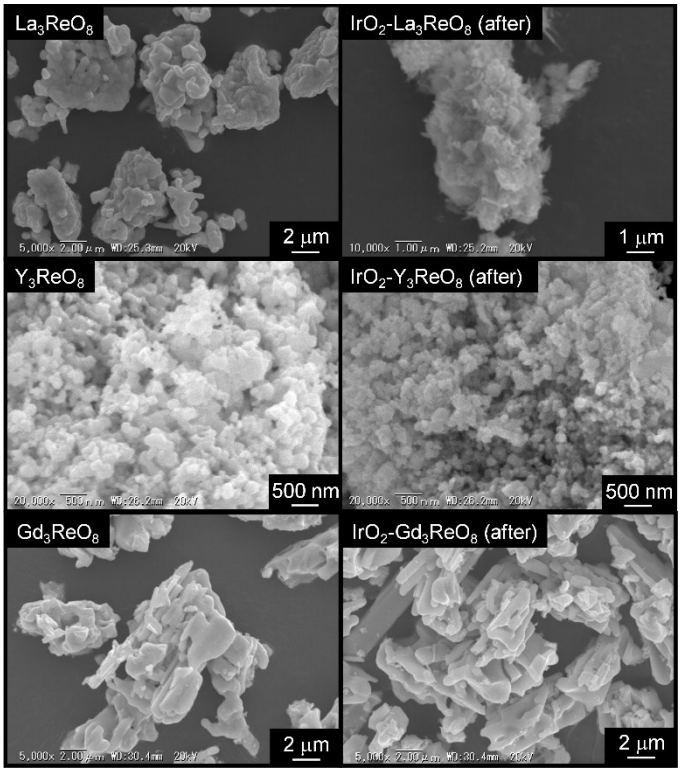

Figure S7. SEM images of M_3ReO_8 (M = Y, La, or Gd) and IrO_2-M_3ReO_8 (M = Y, La, or Gd) after light irradiation in aqueous $AgNO_3$ solution.

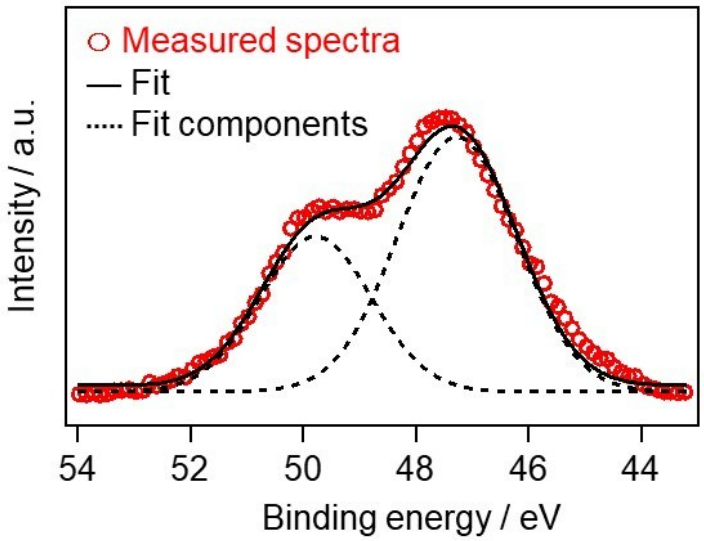

Figure S8. X-ray photoelectron spectroscopy result for IrO_2-Y_3ReO_8 after O_2 evolution from aqueous $AgNO_3$ solution under visible light irradiation ($\lambda > 400$ nm). The Re $4f_{7/2}$ peak position is close to that of Re_2O_7 (47.1 eV).[2, 3]

References

1. S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. J. Probert, K. Refson and M. C. Payne, *Z Kristallogr*, 2005, **220**, 567-570.
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3. A. Naor, N. Eliaz, L. Burstein and E. Gileadi, *Electrochem Solid St*, 2010, **13**, D91-D93.