## Solar-driven Z-scheme water splitting using tantalum/nitrogen co-doped rutile titania nanorod as an oxygen evolution photocatalyst

Akinobu Nakada,<sup>a</sup> Shunta Nishioka,<sup>a</sup> Junie Jhon M. Vequizo,<sup>b</sup> Kanemichi Muraoka,<sup>a</sup> Tomoki Kanazawa,<sup>a</sup> Akira Yamakata,<sup>b</sup> Shunsuke Nozawa,<sup>c</sup> Hiromu Kumagai,<sup>a</sup> Shin-ichi Adachi,<sup>c</sup> Osamu Ishitani,<sup>a</sup> and Kazuhiko Maeda<sup>a\*</sup>

<sup>a</sup>Department of Chemistry, School of Science, Tokyo Institute of Technology, 2-12-1-NE-2 Ookayama, Meguro-ku, Tokyo 152-8550, Japan.

<sup>b</sup>Graduate School of Engineering, Toyota Technological Institute, 2-12-1 Hisakata, Tempaku, Nagoya 468-8511, Japan.

<sup>c</sup>Photon Factory, Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK), 1-1 Oho, Tsukuba, Ibaraki 305-0801, Japan.

\*To whom corresponding author should be addressed.

TEL: +81-3-5734-2239, FAX: +81-3-5734-2284

Email: maedak@chem.titech.ac.jp

## **Electronic Supplementary Information**



Fig. S1. Ta 4f XPS spectra of TiO<sub>2</sub>:Ta, TiO<sub>2</sub>:Ta/N samples, along with  $Ta_2O_5$  and  $Ta_3N_5$  as references.



Fig. S2. DRS of TiO<sub>2</sub>:Ta samples (Ta/Ti = 0, 0.01, 0.05 and 0.10 by mole).



Fig. S3. SEM image of commercial TiO<sub>2</sub>.



Fig. S4. XRD patterns of TiO<sub>2</sub>:Ta/N samples at different nitridation temperatures.



Fig. S5. Ta  $L_3$ -edge XANES spectra for TiO<sub>2:</sub>Ta/N, TiO<sub>2</sub>:Ta and Ta<sub>2</sub>O<sub>5</sub>.



Fig. S6. Mott-Schottky plots for (A)  $TiO_2$ :Ta/N(773), (B)  $TiO_2$ :N(773) and (C)  $TiO_2$ :Ta electrodes at various pH values. Impedance frequency was 200 Hz.



Fig. S7. TEM image of RuO<sub>2</sub>/TiO<sub>2</sub>:Ta/N.



Fig. S8. Time-dependent photocatalytic  $O_2$  evolution over  $RuO_2/TiO_2$ :Ta,N(773) dispersed (50 mg) in an aqueous solution (100 mL) of NaIO<sub>3</sub> (1 mM) under irradiation at various wavelengths. Output current of the light source was 10 A (300 W, Xe lamp), which was one-half that used for other photocatalytic experiments in this study.



Fig. S9 (A) Current-voltage curves using a  $RuO_2/TiO_2$ :Ta/N(773) electrode after TiCl<sub>4</sub> necking treatment under intermittent visible-light irradiation in aqueous solution containing Na<sub>2</sub>SO<sub>4</sub> (0.1 M, pH 6.7). (B) Enlarged curves of (A) around the onset potential. Scan rate: 20 mV s<sup>-1</sup>.



Fig. S10. Time-dependent photocatalytic H<sub>2</sub> evolution over Ru/SrTiO<sub>3</sub>:Rh dispersed (50 mg) in an aqueous solution (100 mL) of NaI (1 mM, red) or FeCl<sub>2</sub> (1 mM, blue) under visible-light irradiation ( $\lambda > 420$  nm). Saturation of O<sub>2</sub> generation in the Fe<sup>2+</sup> solution was due to consumption of Fe<sup>2+</sup>.



Fig. S11. (A) XRD patterns and (B) DRS of as-prepared SrTiO<sub>3</sub>:Rh.