

*Electronic Supplementary Information (ESI)*

Enhanced water splitting through two-step photoexcitation  
by sunlight using tantalum/nitrogen-codoped rutile titania  
as a water oxidation photocatalyst

*Shunta Nishioka,<sup>a,b</sup> Kei-ichi Yanagisawa,<sup>c</sup> Daling Lu,<sup>d</sup> Junie Jhon M. Vequizo,<sup>e</sup> Akira Yamakata,<sup>e</sup>*

*Koji Kimoto,<sup>c</sup> Miki Inada,<sup>f</sup> 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> Japan Society for the Promotion of Science, Kojimachi Business Center Building, 5-3-1  
Kojimachi, Chiyoda-ku, Tokyo 102-0083, Japan

<sup>c</sup> Electron Microscopy Group, Research Center for Advanced Measurement and Characterization,  
National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

<sup>d</sup> Suzukakedai Materials Analysis Division, Technical Department, Tokyo Institute of Technology,  
4259-R1-34, Nagatsuta-cho, Midori-ku, Yokohama 226-850, Japan

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

<sup>f</sup> Center of Advanced Instrumental Analysis, Kyushu University, 6-1 Kasuga-koen, Kasuga,  
Fukuoka 816-8580, Japan

\*To whom corresponding author should be addressed.

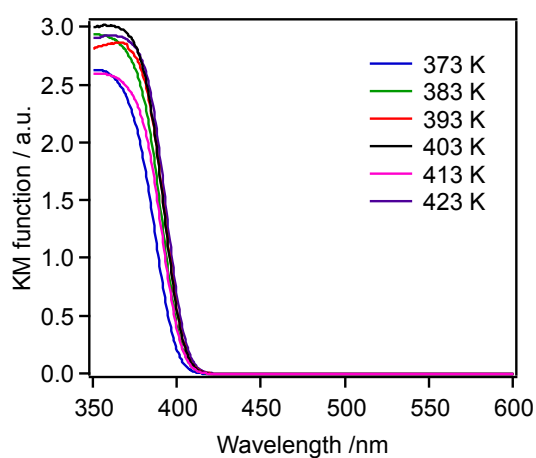
TEL: +81-3-5734-2239, FAX: +81-3-5734-2284

Email: [maedak@chem.titech.ac.jp](mailto:maedak@chem.titech.ac.jp)

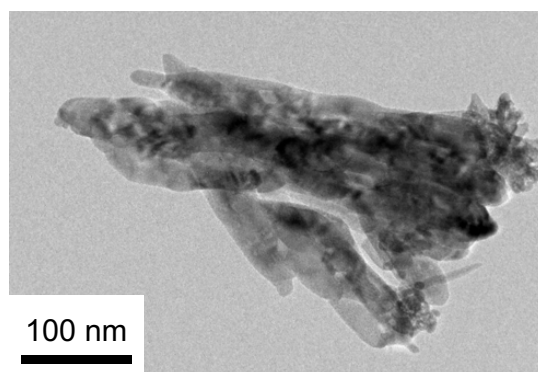
**Table S1.** Physicochemical properties of TiO<sub>2</sub>:Ta specimens prepared at different temperatures.

Entry	Amount of doped Ta / mol%	FWHM <sup>a</sup> / degree		Specific surface area <sup>b</sup> / m <sup>2</sup> g <sup>-1</sup>
		Before nitridation	After nitridation	
1	0	0.549	0.303	15
2	0.1	0.543	0.296	9
3	0.3	0.545	0.288	15
4	0.5	0.558	0.312	14
5	0.7	0.546	0.277	10
6	1.0	0.550	0.314	10
7	1.5	0.556	0.302	-

<sup>a</sup> Full width at half maximum for the (101) peak ( $2\theta = 36.0$  degree) in the XRD patterns. <sup>b</sup> The specific surface areas were measured by using after nitridation samples.



**Fig. S1.** DRS spectra of TiO<sub>2</sub>:Ta samples prepared at different temperatures.



**Fig. S2.** TEM image of TiO<sub>2</sub>:Ta,N (Ta 1.0 mol%).

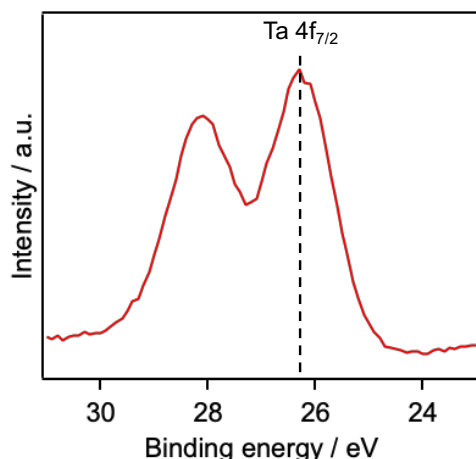


Fig. S3. Ta 4f XPS spectrum for TiO<sub>2</sub>:Ta,N powder (Ta 0.7 mol%).

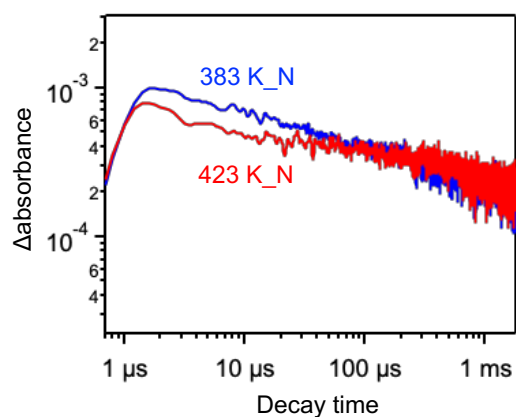


Fig. S4. Time profiles of differential absorbance at 2000 cm<sup>-1</sup> for TiO<sub>2</sub>:Ta,N prepared at two temperatures. Transmittance and reflectance were measured below and above 6000 cm<sup>-1</sup>, respectively, after visible light (450 nm) laser pulses under vacuum. The pump energy was 1 mJ per pulse with a repetition rate of 1 Hz.

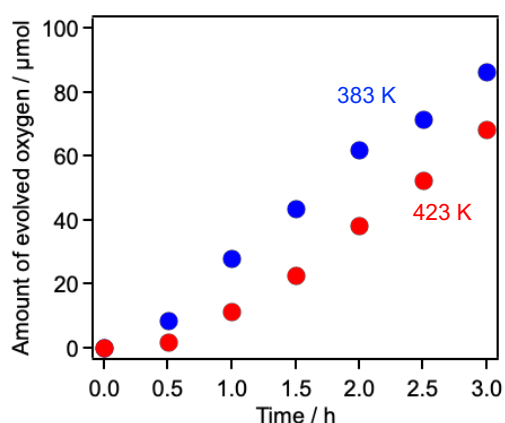
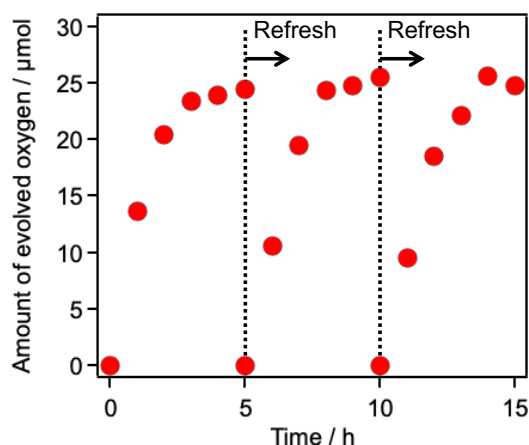
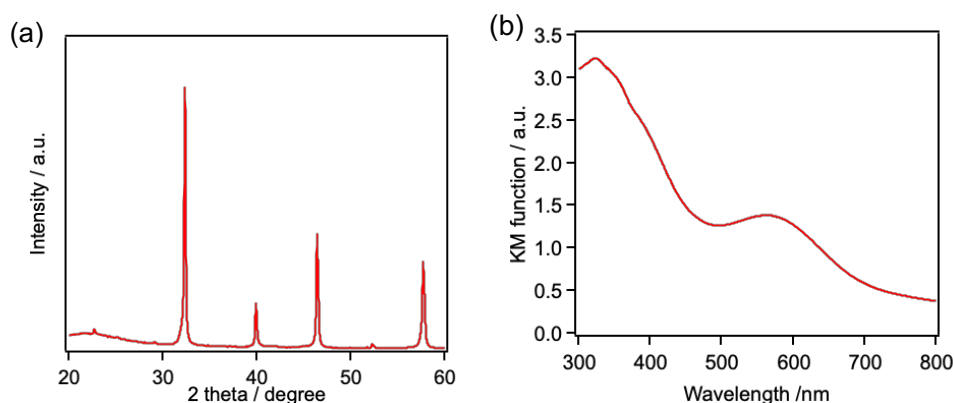


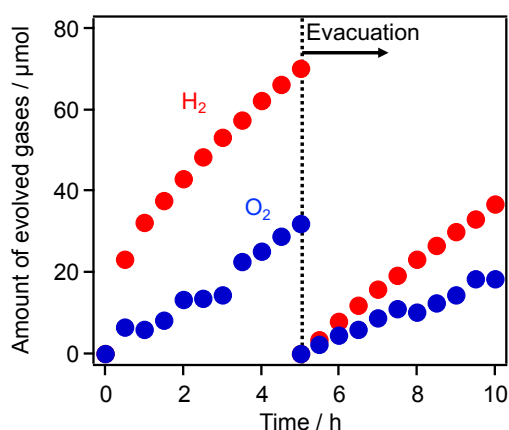
Fig. S5. Time course for O<sub>2</sub> evolution over RuO<sub>2</sub>/TiO<sub>2</sub>:Ta,N samples prepared at two temperatures under visible light irradiation ( $\lambda > 400$  nm). Reaction conditions: catalyst = 50 mg (cocatalyst = RuO<sub>2</sub> at 0.8 wt%); reactant solution = aqueous AgNO<sub>3</sub> (10 mM, 100 mL); light source = Xe lamp (300 W) with a cold mirror (CM-1) and a cutoff filter (L42).



**Fig. S6.** Time course for O<sub>2</sub> evolution over an IrO<sub>2</sub>/TiO<sub>2</sub>:Ta,N sample prepared at 423 K under visible light irradiation ( $\lambda > 400$  nm). Reaction conditions: catalyst = 50 mg (cocatalyst = IrO<sub>x</sub> at 1.0 wt%); reactant solution = aqueous FeCl<sub>3</sub> (1 mM, 100 mL); light source = Xe lamp (300 W) with a cold mirror (CM-1) and a cutoff filter (L42).



**Fig. S7.** (a) XRD pattern and (b) UV-visible DRS spectrum for SrTiO<sub>3</sub>:Rh.



**Fig. S8.** Time courses for water splitting reaction over IrO<sub>2</sub>/TiO<sub>2</sub>:Ta,N and Ru/SrTiO<sub>3</sub>:Rh under visible light irradiation ( $\lambda > 400$  nm). Reaction conditions: catalysts = IrO<sub>2</sub>/TiO<sub>2</sub>:Ta,N, 50 mg and Ru/SrTiO<sub>3</sub>:Rh, 25 mg; reactant solution = aqueous [Co(bpy)<sub>3</sub>]<sup>2+</sup> (0.5 mM, 100 mL); light source = Xe lamp (300 W) with a cold mirror (CM-1) and a cutoff filter (L42).