SUPPLEMENTARY INFORMATION

The Role of the Shell in Core-Shell-Structured La-Doped $NaTaO_3$ Photocatalysts

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■ CHARACTERIZATION

The crystallographic phase and bulk composition of the photocatalysts were checked with an X-ray diffractometer (Rigaku, SmartLab) and energy dispersive X-ray fluorescence spectrometer (Shimadzu, EDX-720), respectively. Light absorption spectra of the photocatalysts were observed with an ultraviolet-visible diffuse reflection spectrometer (Jasco, V-570) equipped with an integration sphere. Surface composition was quantified by an X-ray photoelectron spectrometer (ULVAC-PHI, PHI X-tool). The textural properties were examined using N_2 adsorption-desorption isotherms at liquid nitrogen temperature of 77 K by an adsorption instrument (Belsorp 28SA, Bel). The size and shape of the photocatalyst

particles were observed with a scanning electron microscope (Jeol, JSM-7100F). Raman scattering was observed in air using a Raman spectrometer (Jasco, NRS-7100). Energy dispersive X-ray mapping was done with a transmission electron microscope (FEI, TITAN^3 G2 60−300) equipped with a Si drift detector (FEI, super-X) and imaging software (Bruker, Esprit).

Light-induced infrared absorption spectra to evaluate the steady-state population of photoexcited electrons that had not yet recombined were recorded with a Fourier transform spectrometer (Jasco, FT/IR610). Details of the experimental setup are available elsewhere.[1]

Time-resolved microwave conductivity measurements were performed in a laboratory-made apparatus. The fourth harmonic (266 nm) of a Lotis TII LS-2137 Nd^{3+}:YAG laser was used for UV excitation at an intensity of 0.25 mJ cm^{-2}. Details of the experimental setup are available elsewhere.[2-3]

Reversed double-beam photoacoustic spectroscopy measurements were carried out in laboratory-made apparatuses. A stainless-steel sample holder was filled with a photocatalyst powder and set in a photoacoustic cell equipped with a MEMS (microelectromechanical system) microphone and a quartz window on the upper side. The cell was filled with methanol-saturated nitrogen. Using a UV quartz combiner light guide, the sample was simultaneously irradiated with two light beams, a continuous wavelength-scanned excitation beam and a modulated fixed wavelength detection beam. The recorded spectrum was differentiated from the lower-energy side to obtain an energy-resolved distribution of electron traps pattern. Details of the experimental setup are available elsewhere.[4-5]

X-ray absorption fine structure spectroscopy was employed to investigate the local environment around La cations. XAFS spectra were recorded at the La *K*-edge using the AR-NW10A beamline at the Photon Factory, Tsukuba, Japan in transmission mode with a Si(311) double crystal monochromator. The ATHENA and ARTEMIS package was used to process the recorded data. XAFS spectra were transformed using the Hanning window with k^3-weighting and a d*k* of 2 prior to single-shell curve fitting. Four parameters were refined: *L* (bond length), *N* (coordination number), d*E* (threshold energy difference), and DW (Debye−Waller factor).

■ OVERALL WATER SPLITTING ACTIVITY

Photocatalytic reactions for H_2 evolution were performed in a closed-gas circulation system. The photocatalyst powder (0.1 g) was dispersed in a reaction cell filled with distilled water (10 mL). The reaction cell was irradiated with a 300 W xenon lamp at an average intensity of 22 mW cm^{-2} at 254 ± 10 nm. The amounts of evolved gases were determined using gas

chromatography with a thermal conductivity detector (GC-8A, Shimadzu). Prior to the photocatalytic reaction, the photocatalyst powder was loaded with NiO as the cocatalyst using the impregnation method.[6] Briefly, an appropriate amount of $Ni(NO_3)_2 \cdot 6H_2O$ (98.0%, Wako) was mixed with photocatalyst powder (1 g) in a porcelain crucible containing a small amount of water (4 mL) to achieve a NiO loading amount of 2 wt%. The obtained suspension was stirred using a glass rod under heat treatment at approximately 80 °C to evaporate water. The dried powder was calcined at 270 °C for 1 h in an air atmosphere.

■ FIGURES AND TABLE

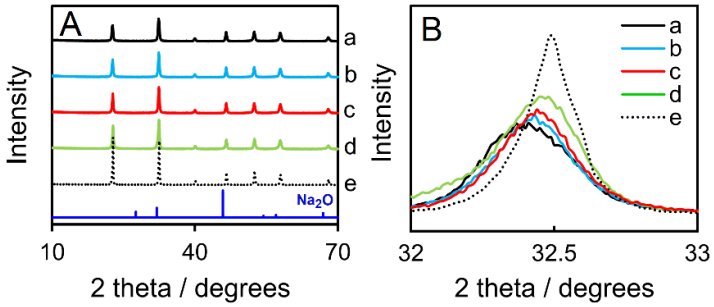

Figure S1. Diffraction patterns of La-NTO etched for (a) 0, (b) 30, (c) 60 and (d) 120 min, and (e) unetched NTO in the range of (A) 10-70° and (B) 32-33° around the main peak. The diffraction pattern of Na_2O (JCPDS 03-1074) is also shown in Panel A for reference.

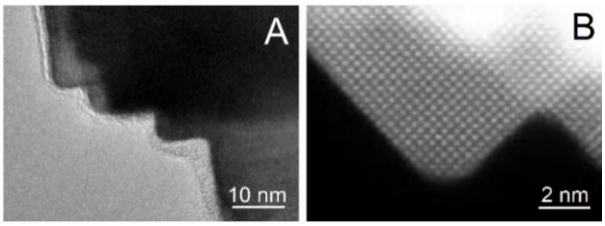

Figure S2. (A) TEM and (B) HAADF images of La-NTO etched for 30 min.

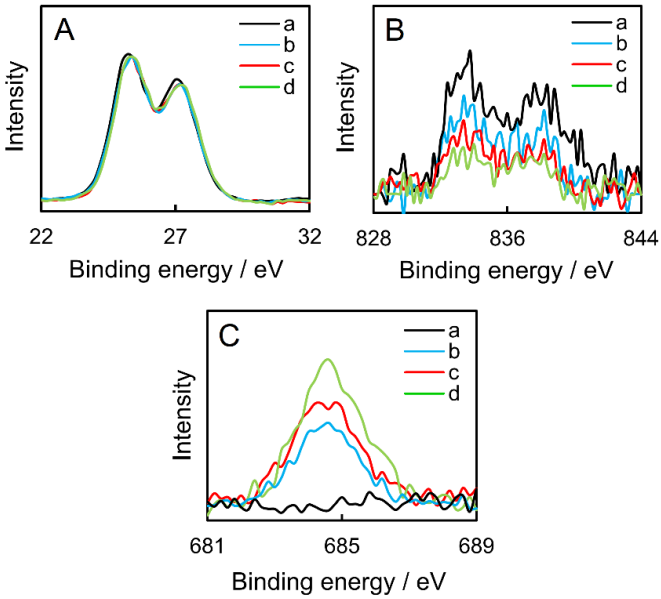

Figure S3. Photoelectron spectra of La-NTO etched for (a) 0, (b) 30, (c) 60, and (d) 120 min in the (A) Ta 4f, (B) La $3d_{5/2}$, and (C) F 1s regions.

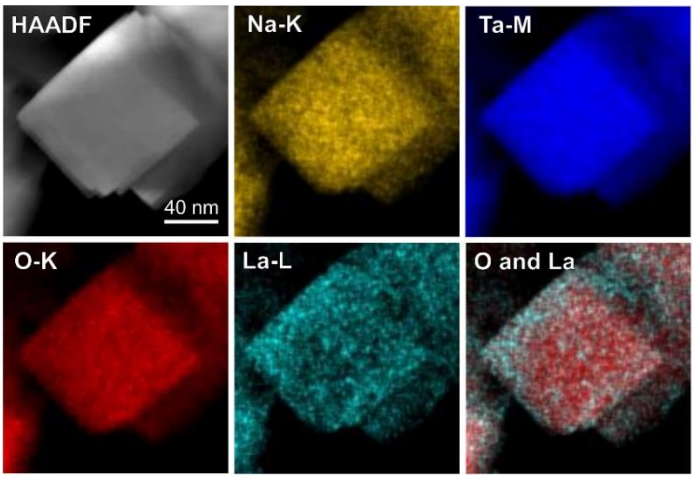

Figure S4. Low-magnification HAADF images of La-NTO etched for 30 min with element maps.

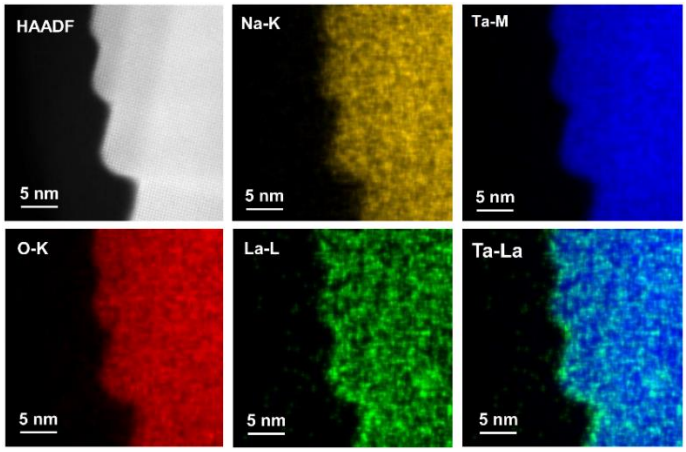

Figure S5. HAADF images of unetched La-NTO with element maps.

Table S1 XAFS curve fitting results.

Etching time / min	Shell	*L*/Å	*N*	d*E*/eV	DW/Å^2
0	La-O	2.52	9.4	-1.1	0.017
	La-Ta	3.46	8.1	0.8	0.006
30	La-O	2.56	9.1	-2.5	0.017
	La-Ta	3.48	8.2	-3.1	0.008
60	La-O	2.55	8.6	2.7	0.018
	La-Ta	3.47	7.7	-1.6	0.007
120	La-O	2.57	8.9	-1.5	0.019
	La-Ta	3.49	7.2	3.2	0.009

L is the bond length; *N* is the coordination number; d*E* is the threshold energy difference; and DW is the Debye−Waller factor.

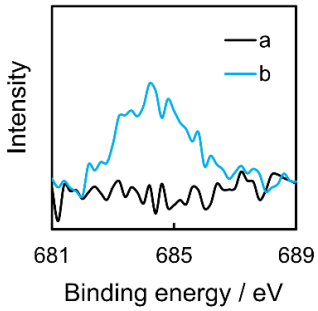

Figure S6. Photoelectron spectra of NTO etched for (a) 0 and (b) 120 min in the F 1s regions.

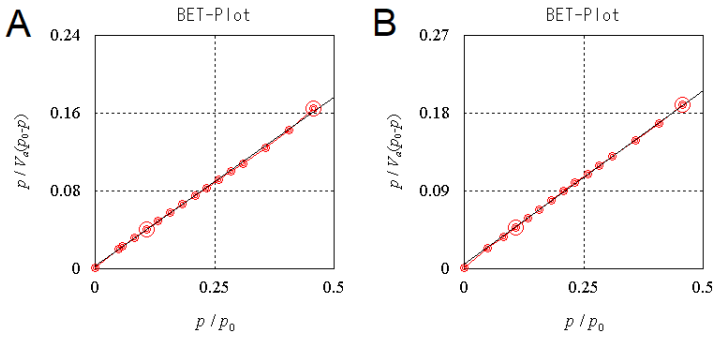

Figure S7. Brunauer-Emmett-Teller (BET) plots of La-NTO etched for (A) 0 and (B) 30 min. The specific surface area of sample A and sample B are 5.7 and 6.6 m^2/g, respectively.

References

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