

Supporting Information

Facet Engineering of LaNbON₂ Transformed from LaKNaNbO₅ for Enhanced Photocatalytic O₂ Evolution

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Results and Discussion

Crystal structure

Layered LaKNaNbO_5 possesses a tetragonal structure with the space group $P4/nmm$ and the corresponding unit cell parameters are $a=5.81350$, $b=5.81350$ and $c=8.28040$ Å. The perovskitetype LaNbON_2 possesses an orthorhombic structure with space group $Pnma$ and the corresponding unit cell parameters are $a=5.72210$, $b=8.06840$ and $c=5.74280$ Å.¹ Notably, the atomic arrangement of La and Nb ions in LaKNaNbO_5 along the $[001]$ direction is in very good agreement with that of LaNbON_2 along the $[010]$ direction. Therefore, the transformation of LaKNaNbO_5 to LaNbON_2 is viable.

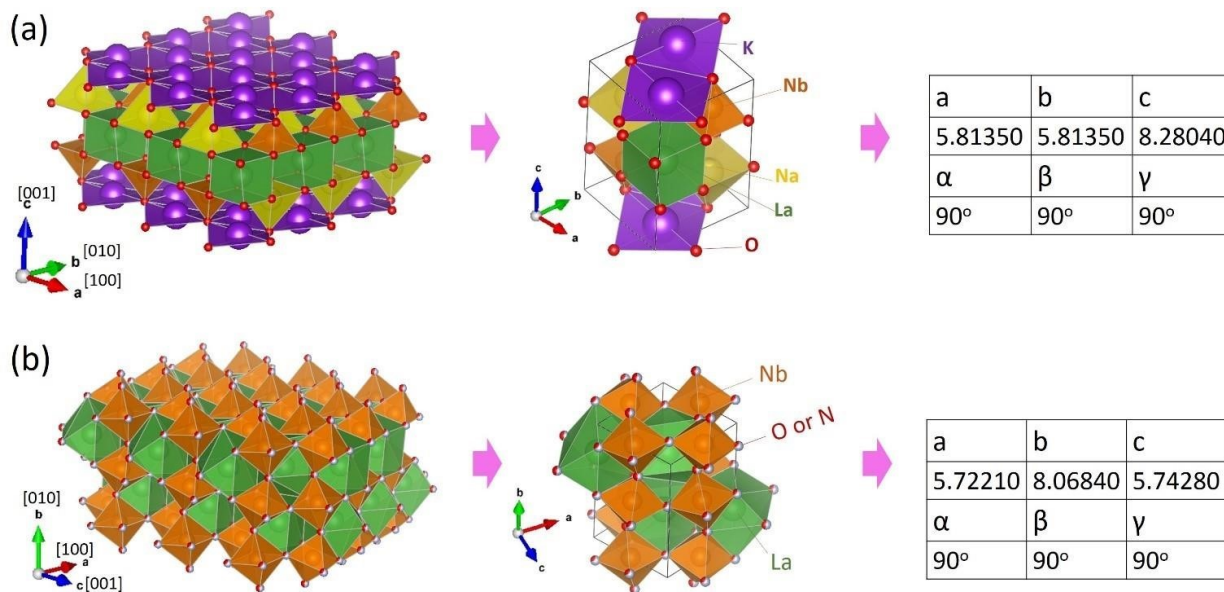


Fig. S1 Crystal structures and unit cell parameters of (a) LaKNaNbO_5 and (b) LaNbON_2 .

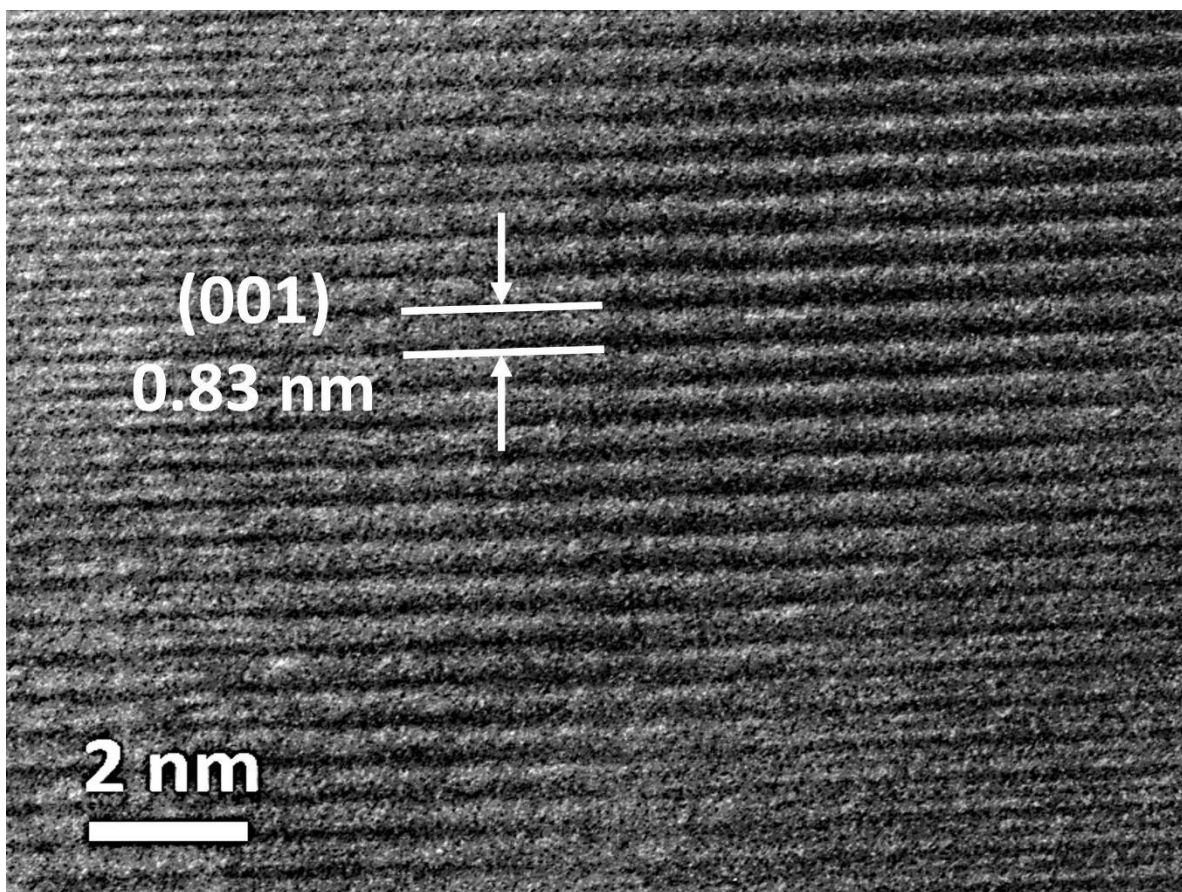


Fig. S2 HRTEM image of the plate-like LaKNbO₅ at a lateral face.

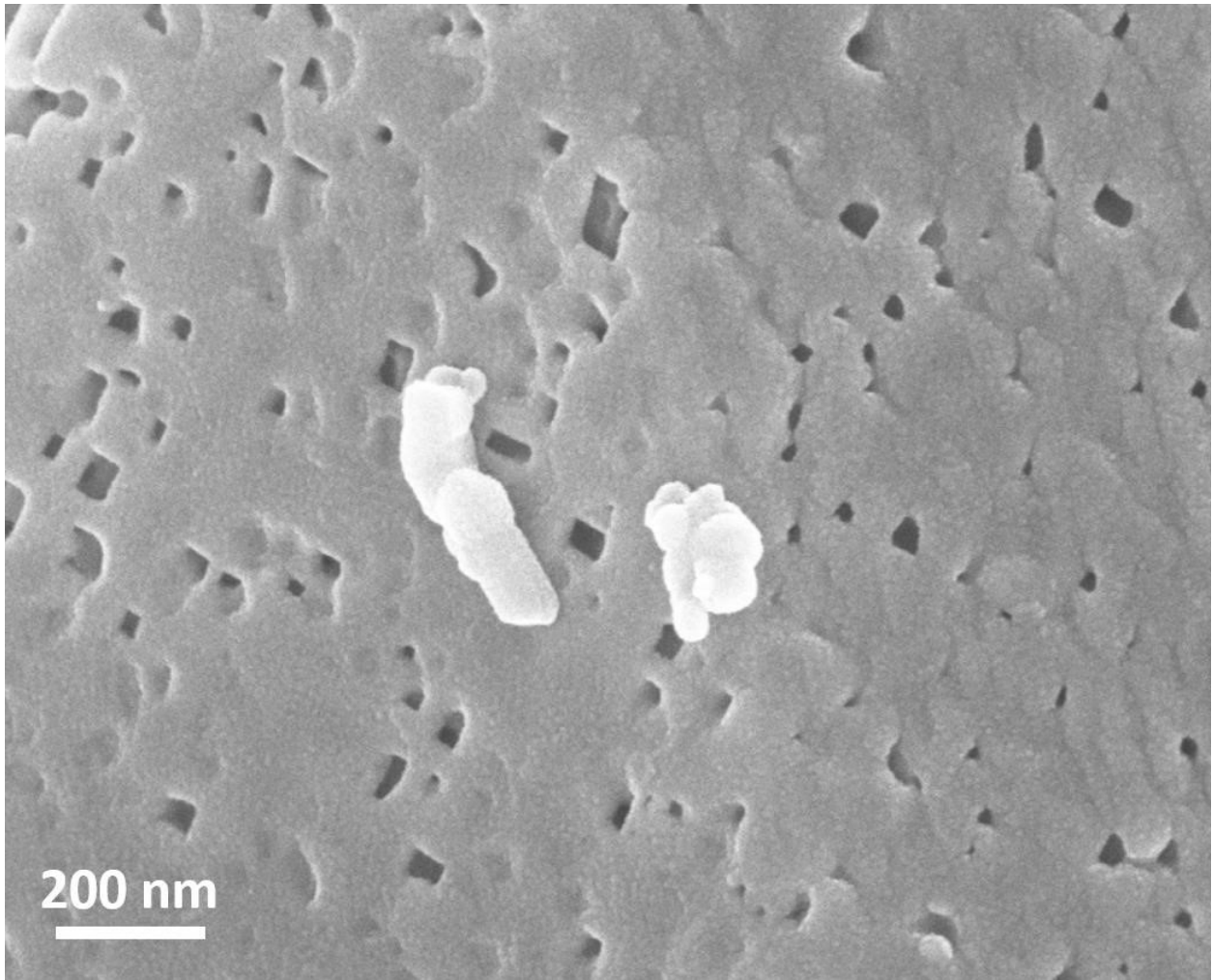


Fig. S3 SEM image of plate-like LaKNaNbO_5 nitrided at 1223 K for 4 h.

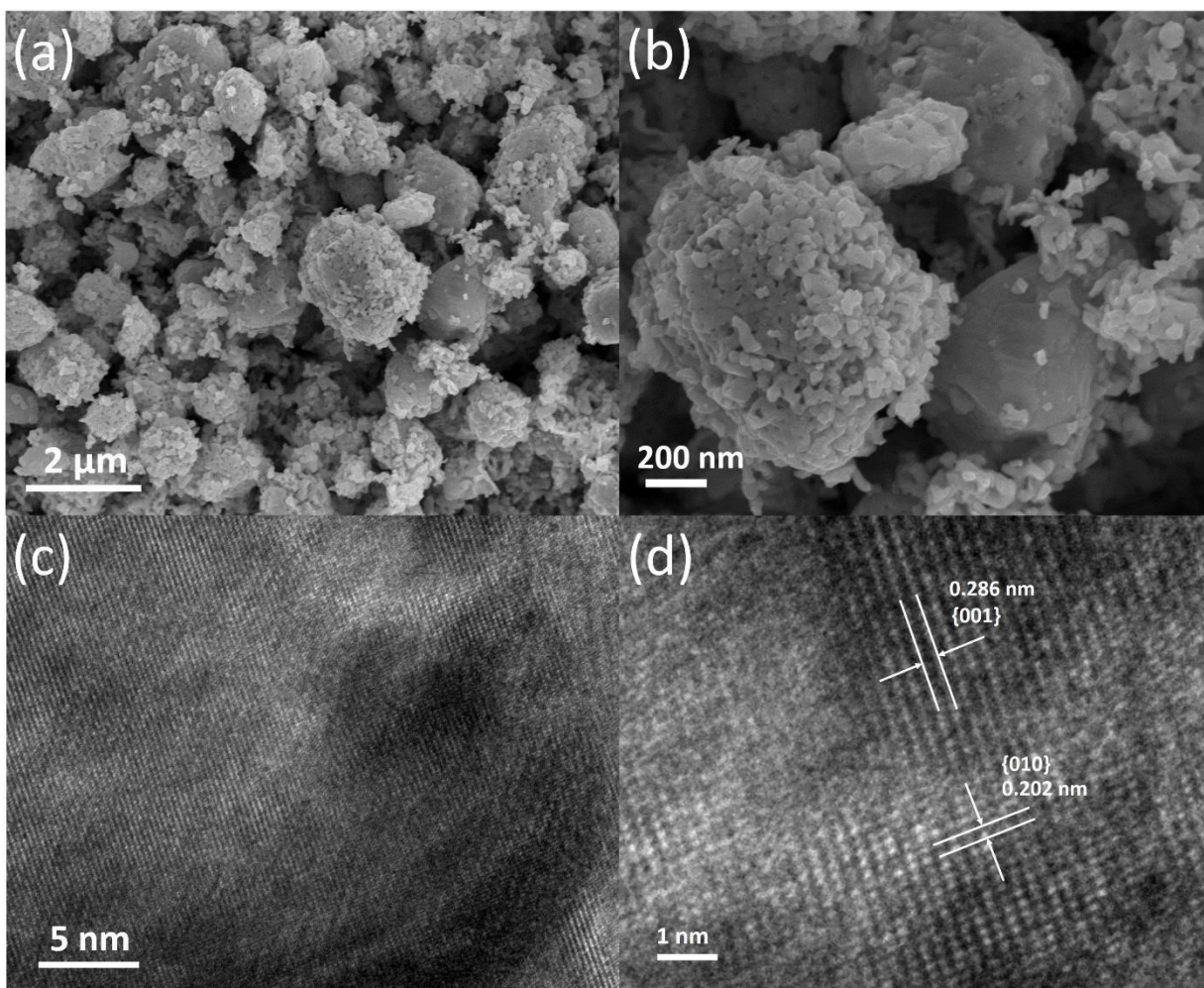


Fig. S4 (a,b) SEM image and (c,d) HRTEM image of conventional LaNbON_2 powder prepared by nitriding LaNbO_4 .

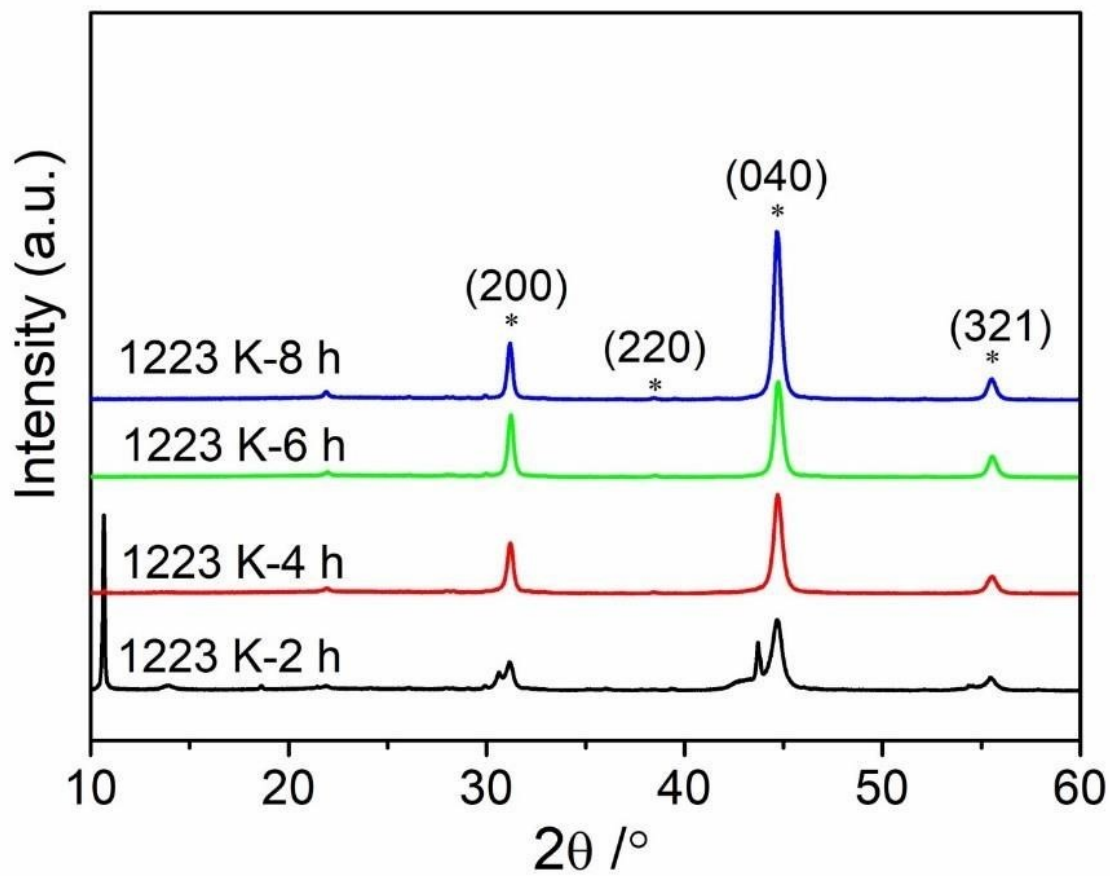


Fig. S5 XRD patterns obtained from LaKNaNbO₅ nitrided at 1223 for 2-8 h.

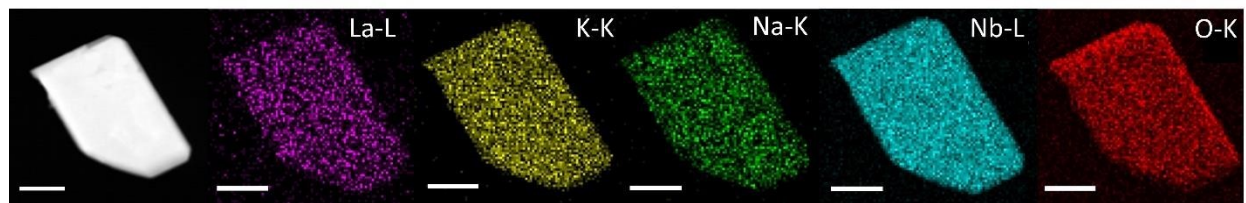


Fig. S6. EDS elemental maps of LaKNaNbO₅ precursor, the corresponding atomic ratios were about La/Nb=1.2; K/Nb=1.4; Na/Nb=0.9; O/Nb=6.5. Scale bars indicate 1 μm.

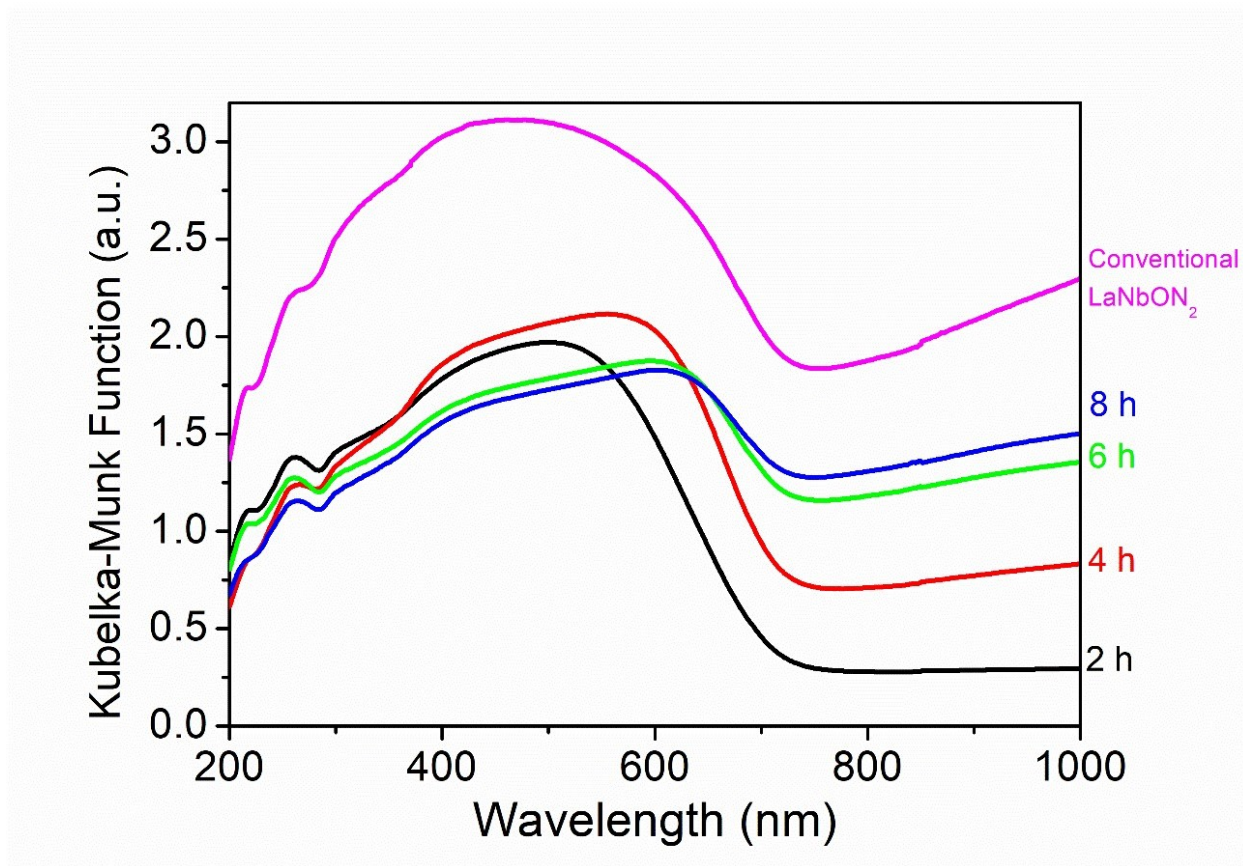


Fig. S7 UV-vis DRS data for LaKNaNbO₅ nitrided at 1223 K for 2–8 h and for conventional LaNbON₂ prepared from LaNbO₄.

Table S1. Fractions of surface Nb species for LaKNaNbO₅, LaKNaNbO₅ nitrated at 1223 K for 4 h, and conventional LaNbON₂ obtained from LaNbO₄, estimated based on the narrow-scan Nb 3d XPS spectra shown in Figure 2E.²⁻⁴

Samples	Fractions of surface Nb species			
	Nb ₅₊ /Nb _{total}	Nb ₄₊ /Nb _{total}	Nb ₃₊ /Nb _{total}	(Nb ⁴⁺ +Nb ³⁺)/Nb _{total}
LaKNaNbO ₅	1.00	0.00	0.00	0.00
LaKNaNbO ₅ nitrated at 1223 K for 4 h	0.28	0.61	0.11	0.72
The conventional LaNbON ₂	0.14	0.45	0.41	0.86

Table S2. Effective electron (m_e^*) and hole (m_h^*) masses along the [100], [010] and [001] directions, where m_0 is the free electron mass.

Direction	m_e^*/m_0	m_h^*/m_0
[100]($\Gamma \rightarrow Y$)	1.682	0.835
[010]($\Gamma \rightarrow X$)	0.838	10.238
[001]($\Gamma \rightarrow Z$)	1.642	0.947

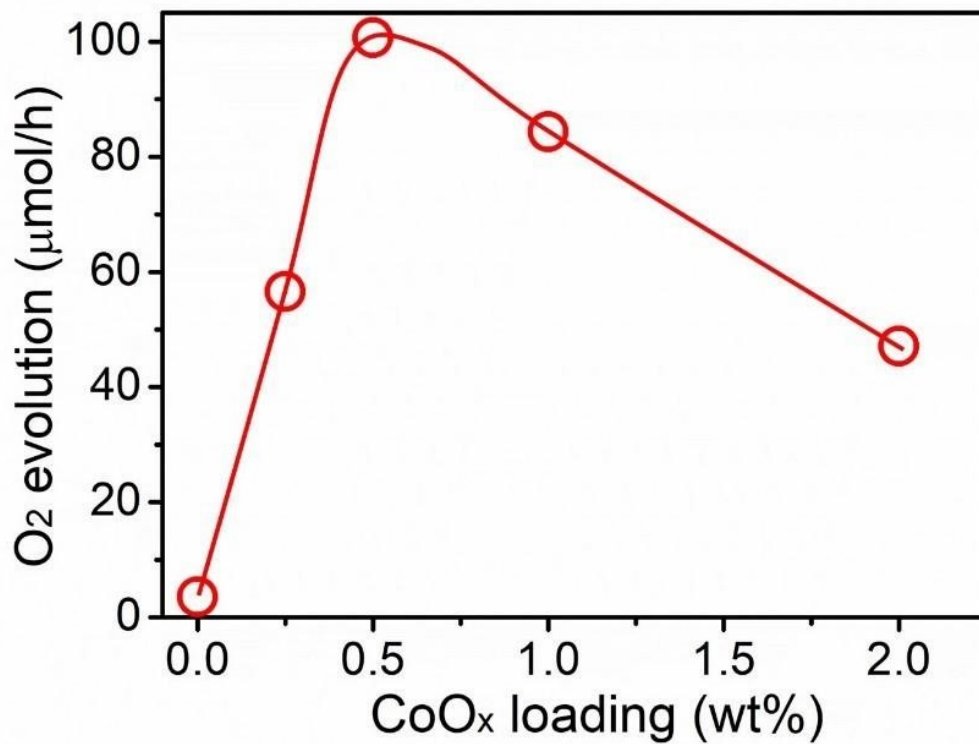


Fig. S8 The effect of the CoO_x loading amount on photocatalytic O₂ evolution activity using LaKNaNbO₅ nitrated at 1223 K for 4 h. Reaction conditions: in 150 mL of an aqueous 50 mM AgNO₃ solution containing 0.20 g of La₂O₃, photocatalyst: 300 mg, light source: 300 W xenon lamp ($\lambda \geq 420$ nm), reaction cell: top-irradiation cell with a Pyrex window.

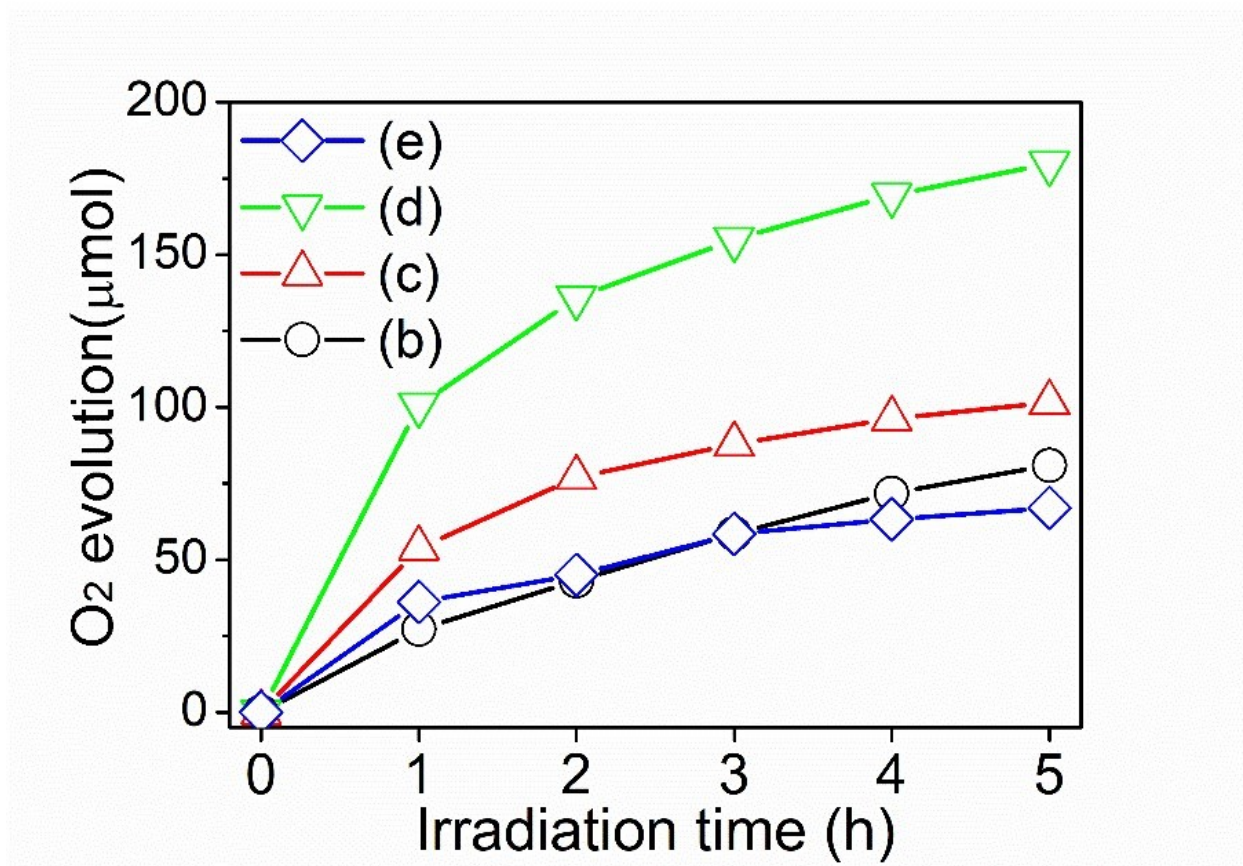


Fig. S9 Time courses of photocatalytic O₂ evolution over LaKNaNbO₅ nitrided at (b) 1123, (c) 1173, (d) 1223 and (e) 1273 K for 4 h. Reaction conditions: in 150 mL of an aqueous 50 mM AgNO₃ solution containing 0.20 g of La₂O₃, photocatalyst: 300 mg, co-catalyst: 0.5 wt% CoO_x, light source: 300 W xenon lamp ($\lambda \geq 420$ nm), reaction cell: top-irradiation cell with a Pyrex window.

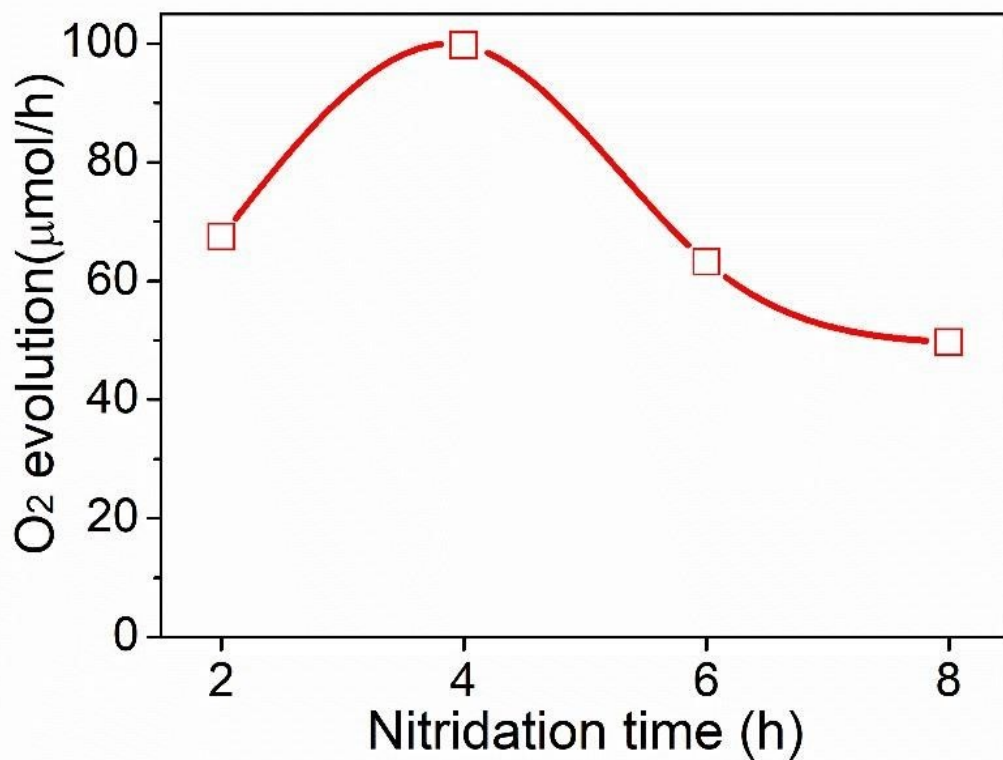


Fig. S10 Photocatalytic O₂ evolution rates for LaKNaNbO₅ nitrided at 1223 K for 2-8 h. Reaction conditions: in 150 mL of an aqueous 50 mM AgNO₃ solution containing 0.20 g of La₂O₃, photocatalyst: 300 mg, co-catalyst: 0.5 wt% CoO_x, light source: 300 W xenon lamp ($\lambda \geq 420$ nm), reaction cell: top-irradiation cell with a Pyrex window.

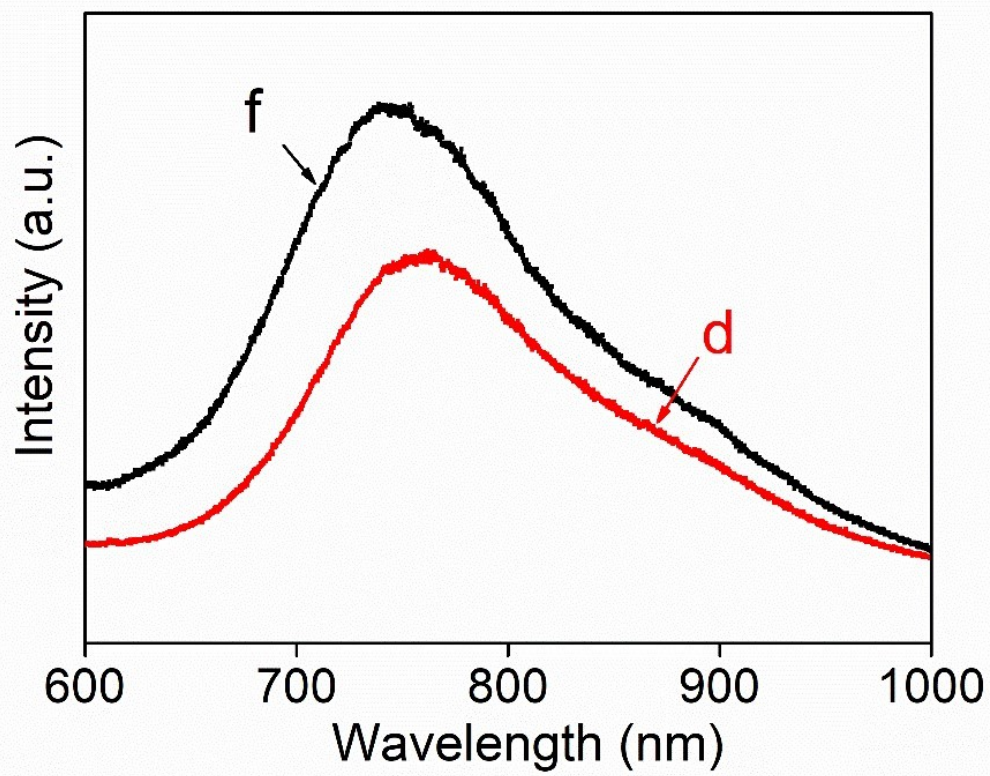


Fig. S11 Photoluminescence spectra of (d) LaKNaNbO_5 nitrided at 1223 K for 4 h and (f) conventional LaNbON_2 prepared from LaNbO_4 .

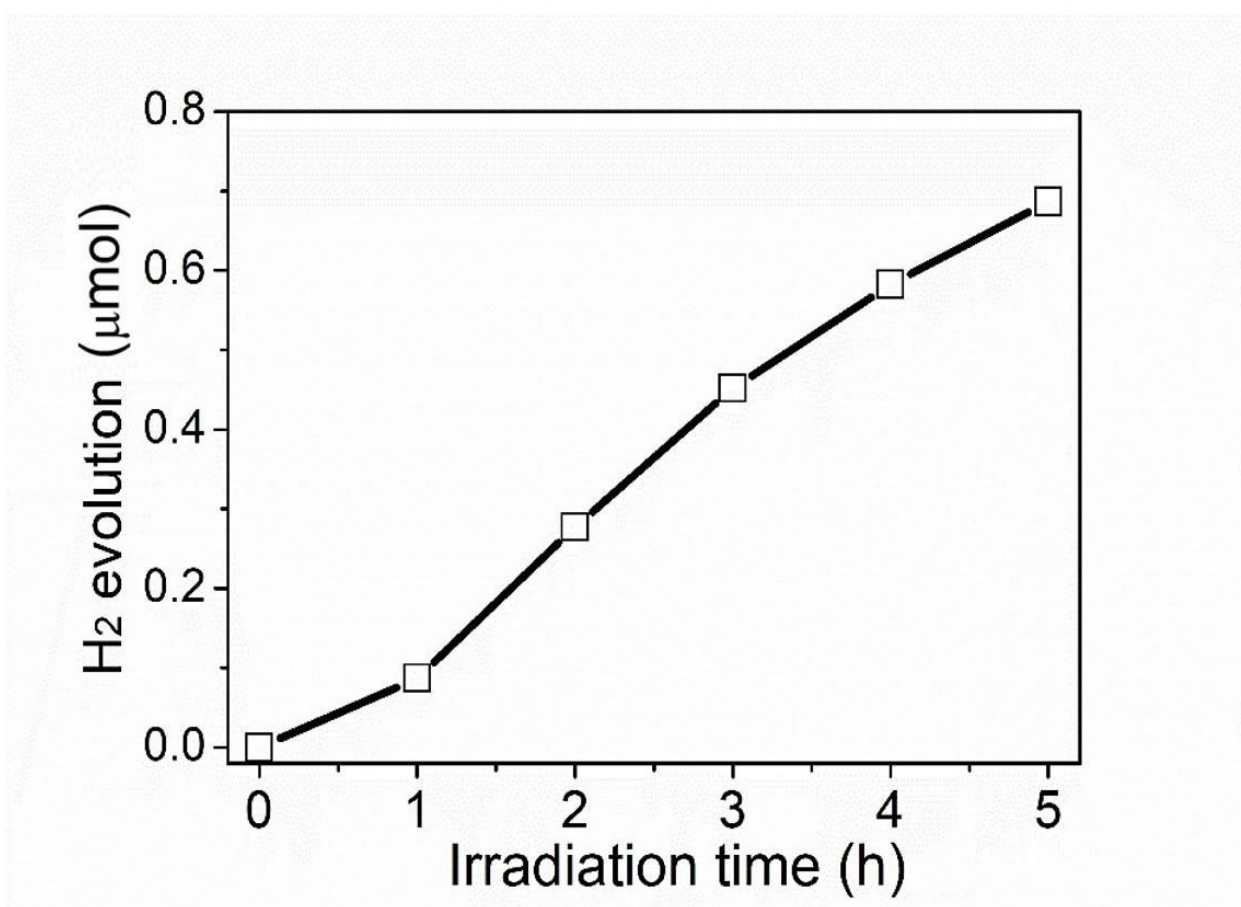


Fig. S12 Time courses of H₂ evolution over LaKNaNbO₅ nitrated at 1223 K for 4 h. Reaction conditions: in 150 mL aqueous methanol (20 vol%), photocatalyst: 300 mg, co-catalyst: 0.5 wt% Rh, loading method: impregnation with H₂ reduction, light source: 300 W xenon lamp ($\lambda \geq 420$ nm), reaction cell: top-irradiation cell with a Pyrex window.

References

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2. J. Seo, M. Nakabayashi, T. Hisatomi, N. Shibata, T. Minegishi, M. Katayama, K. Domen, *J. Mater. Chem. A*, 2019, **7**, 493.
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