Electronic supplementary information

Continuous solid solutions of Na_{0.5}La_{0.5}TiO₃–LaCrO₃ for

photocatalytic H₂ evolution under visible-light irradiation

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Calculation of quantum efficiency

The quantum efficiency (Φ) of photocatalytic H₂ evolution on NaLaTiCrO-0.3 should be ideally calculated according to Eq. S1 [S1-S4]:

 $\Phi = \frac{\text{Number of } H_2 \text{ evolved} \times 2}{\text{Number of photons absorbed}}$ (S1)

However, it is hard to determine the number of photons absorbed by a photocatalyst in a dispersed system due to non-negligible light scattering. As an alternative, the number of incident photons, which is easily determined by using a spectroradiometer, is generally employed to estimate the so-called apparent quantum efficiency (Φ_a) according to Eq. S2 [S4-S7]:

$$\Phi_{a} = \frac{\text{Number of } H_{2} \text{ evolved} \times 2}{\text{Number of incident photons}} = \frac{\text{Rate of } H_{2} \text{ evolved} \times 2}{\text{Photon flux of incident light}}$$
(S2)

It is obvious that the apparent quantum efficiency is the lower limit and a conservative estimate of the absolute value of quantum efficiency.

The rate of H₂ evolved on NaLaTiCrO–0.3 was 2.81 μ mol h⁻¹ under the irradiation of visible light by using a band-pass filter (λ = 425±10 nm). The photon flux of incident light was determined as described below.

The irradiance (*E*) of incident light by using a band-pass filter (λ = 425±10 nm) was measured by a spectroradiometer (AvaSpec-2048-USB2, Avantes, Netherlands) to obtain an average value of 5598 µW cm⁻². The photon irradiance (*E*_p) of incident light was calculated according to Eq. S3 to obtain a value of 71.60 µmol h⁻¹ cm⁻².

$$E_{\rm p} = \frac{E}{h\nu N_{\rm A}} = \frac{E\lambda}{hcN_{\rm A}}$$
(S3)

in which E_p , E, h, v, N_A , λ , and c represent the photon irradiance, irradiance, Planck's constant, light frequency, Avogadro constant, wavelength, and speed of light, respectively. The photon flux of incident light was calculated by multiplying the photon irradiance by irradiated area (13.85 cm²) to obtain a value of 991.7 μ mol h⁻¹.

Finally, the apparent quantum efficiency of photocatalytic H_2 evolution on NaLaTiCrO-0.3 was estimated to be 0.57% at 425 nm.

References

- [S1] Serpone, N.; Salinaro, A. Terminology, relative photonic efficiencies and quantum yields in heterogeneous photocatalysis. Part I: suggested protocol (technical report). *Pure Appl. Chem.* 1999, 71, 303–320.
- [S2] Salinaro, A.; Emeline, A. V.; Zhao, J. C.; Hidaka, H.; Ryabchuk, V. K.; Serpone, N. Terminology, relative photonic efficiencies and quantum yields in heterogeneous photocatalysis. Part II: experimental determination of quantum yields (technical report). *Pure Appl. Chem.* **1999**, *71*, 321–335.
- [S3] McNaught, A. D.; Wilkinson, A. IUPAC compendium of chemical terminology; Blackwell Science: Oxford, 1997.

- [S4] Shi, J. W.; Ye, J. H.; Ma, L. J.; Ouyang, S. X.; Jing, D. W.; Guo, L. J. Site-selected doping of upconversion luminescent Er³⁺ into SrTiO₃ for visible-light-driven photocatalytic H₂ or O₂ evolution. *Chem. Eur. J.* **2012**, *18*, 7543-7551.
- [S5] Hitoki, G.; Takata, T.; Kondo, J. N.; Hara, M.; Kobayashi, H.; Domen, K. An oxynitride, TaON, as an efficient water oxidation photocatalyst under visible light irradiation (ℤ <= 500 nm). *Chem. Commun.* **2002**, 1698-1699.
- [S6] Maeda, K.; Teramura, K.; Lu, D. L.; Takata, T.; Saito, N.; Inoue, Y.; Domen, K. Photocatalyst releasing hydrogen from water - enhancing catalytic performance holds promise for hydrogen production by water splitting in sunlight. *Nature* 2006, 440, 295-295.
- [S7] Kudo, A.; Miseki, Y. Heterogeneous photocatalyst materials for water splitting. *Chem. Soc. Rev.* **2009**, *38*, 253-278.



Fig. S1 Raman spectrum of as-prepared LaCrO₃.



Fig. S2 SEM images of NaLaTiCrO-*x* samples with *x* equal to (a) 0.0, (b) 0.1, (c) 0.2, (d) 0.3, (e) 0.4, (f) 0.5 and (g) 1.0.

Table S1 BET surface areas of NaLaTiCrO-x samples.

x value	0.0	0.1	0.2	0.3	0.4	0.5	1.0
BET surface area/m ² g ⁻¹	0.93	2.99	2.92	2.72	2.45	2.90	1.90