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Interlayer modification and single-layer exfoliation of the Ruddlesden-Popper perovskite oxynitride K₂LaTa₂O₆N to improve photocatalytic H₂ evolution activity

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Fig. S1. ¹³C CP/MAS NMR spectra of the EA/ $H_xK_{2-x}LaTa_2O_6N$ before and after the photocatalytic reaction. The samples from which these NMR spectra were obtained were the same ones used to generate the data in Fig. 6.



Fig. S2. TG curves obtained from the modified $K_2LaTa_2O_6N$ specimens under a 50 mL min⁻¹ flow of air at a heating rate of 5 K min⁻¹. The mass loss up to approximately 773 K exhibited by the $H_xK_{2-x}LaTa_2O_6N$ is attributed to the desorption of water molecules physisorbed on the external surfaces and in the interlayers.¹⁻³



Fig. S3. Results of the curve fitting of the layered $K_2LaTa_2O_6N$ XPS data. The original data are shown in Fig. 5 in the main manuscript. The peak positions of the Ta species having different oxidation states as determined in this work are close to those reported previously.⁴ Based on this curve fitting, the Ta^{4+}/Ta^{5+} ratio in the $K_2LaTa_2O_6N$ was determined to be 0.7. The Ta 4f XPS spectra acquired from the other $K_2LaTa_2O_6N$ derivatives could be fitted using a single component curve, indicating the predominance of the Ta^{5+} state in those samples.



Fig. S4. N 1s XPS spectra of the $H_xK_{2-x}LaTa_2O_6N$, $EA/H_xK_{2-x}LaTa_2O_6N$ and $R-K_2LaTa_2O_6N$.

Additional discussion on the N 1s XPS spectra. It has been reported that the N 1s peak of the ethyl ammonium cation intercalated into $K_2Ti_4O_9$ appeared at ~403 eV.⁵ As shown in Fig. S4, a very small shoulder can be seen at the lower binding energy side of the Ta 4p peak in the EA/H_xK_{2-x}LaTa₂O₆N, implying the presence of the intercalated EA species. However, quantifying the concentration based on this shoulder peak was not possible due to its broadened nature and significant overlapping with the Ta 4p peak.



Fig. S5. H₂ evolution over time under visible light ($\lambda > 400$ nm) using EA/H_xK_{2-x}LaTa₂O₆N specimens with different Pt loadings. Reaction conditions: catalyst, 50 mg (Pt photodeposited in situ); reactant solution, aqueous methanol (10 vol.%, 140 mL); light source, 300 W xenon lamp with a cutoff filter.



Fig. S6. H₂ evolution over time under visible light ($\lambda > 400$ nm) using R-K₂LaTa₂O₆N specimens with different Pt loadings. Reaction conditions: catalyst, 50 mg (Pt photodeposited in situ); reactant solution, aqueous methanol (10 vol.%, 140 mL); light source, 300 W xenon lamp with a cutoff filter.



Fig. S7. a) XRD patterns and b) UV-visible diffuse reflectance spectra of the EA/H_xK_{2-x}LaTa₂O₆N before and after the photocatalytic reaction. XRD data for $H_xK_{2-x}LaTa_2O_6N$ and $R-K_2LaTa_2O_6N$ are also shown for comparison. c) Time course of H₂ evolution with consecutive runs. The reaction was continued for 35 h, with solution-exchange at 10 and 20 h. The reaction condition was the same as in Fig. 6.

Additional discussion on the changes in the interlayer distance after photocatalytic reactions and in the H₂ evolution rate. The 001 peak position of the EA/H_xK_{2-x}LaTa₂O₆N reacted for 35 h was higher than that for 10 h, but lower than that of the H_xK_{2-x}LaTa₂O₆N (Fig. S7a). This indicates that the interlayer space was further narrowed by extended period of photocatalytic reaction. The rate of H₂ evolution was slightly decreased with consecutive runs (Fig. S7c). In H₂ evolution from aqueous methanol using Pt-loaded photocatalyst, carbon monoxide (CO), produced as one of the oxidation products of methanol, causes a poisoning of the Pt surface even when the CO concentration is very low, resulting in a gradual decrease of the H₂ evolution rate.^{6, 7} Therefore, it is likely that an irreversible deactivation, similar to that reported previously, occurred in the present Pt/EA/H_xK_{2-x}LaTa₂O₆N.



Fig. S8. XRD patterns obtained from the $R-K_2LaTa_2O_6N$ before and after the photocatalytic reaction. The original data are shown in Fig. 6.



2frig. Charge See distribution of Pt particles on the reacted R-K₂LaTa₂O₆N. The Pt particles were deposited in situ during the H₂ evolution reaction.



9 10

7 8

5 6

sition / nm







Fig. S11. Time courses of the H_2 – O_2 consumption reaction over the Pt/EA/ $H_xK_{2-x}LaTa_2O_6N$ and Pt/R- $K_2LaTa_2O_6N$. The reaction of H_2 and O_2 to form H_2O was assessed in pure water (140 mL) in which 10 mg of a photocatalyst sample was dispersed, working within a glass closed circulation system under degassed conditions. After introducing H_2 (200 µmol) and O_2 (100 µmol) into the reaction system, the amount of each gas in the gas phase of the reaction system was monitored by gas chromatography.



Fig. S12. a) HAADF/STEM image and b) the corresponding line mapping of the $Pt/EA/H_xK_{2-x}LaTa_2O_6N$.



Fig. S13. SEM images of EA/H_xK_{2-x}LaTa₂O₆N samples with different Pt loadings.

References

- 1. K. Toda, J. Watanabe and M. Sato, *Mater. Res. Bull.*, 1996, **31**, 1427-1435.
- 2. T. Mitsuyama, A. Tsutsumi, T. Hata, K. Ikeue and M. Machida, *Bull. Chem. Soc. Jpn.*, 2008, **81**, 401-406.
- T. Oshima, T. Ichibha, K. Oqmhula, K. Hibino, H. Mogi, S. Yamashita, K. Fujii, Y. Miseki, K. Hongo, D. Lu, R. Maezono, K. Sayama, M. Yashima, K. Kimoto, H. Kato, M. Kakihana, H. Kageyama and K. Maeda, *Angew. Chem. Int. Ed.*, 2020, **59**, 9736-9743.
- 4. R. V. Goncalves, R. Wojcieszak, P. M. Uberman, S. R. Teixeira and L. M. Rossi, *Phys. Chem. Chem. Phys.*, 2014, **16**, 5755-5762.
- 5. A. Jeffrey A, C. Nethravathi and M. Rajamathi, ACS Omega, 2019, 4, 1575-1580.
- 6. Z. Zou, J. Ye, R. Abe and H. Arakawa, *Catal. Lett.*, 2000, **68**, 235-239.
- 7. G. Wu, T. Chen, X. Zong, H. Yan, G. Ma, X. Wang, Q. Xu, D. Wang, Z. Lei and C. Li, *J. Catal.*, 2008, **253**, 225-227.