Supplementary Material (ESI) for Chemical Communications
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Nitrogen doping in ion-exchangeable layered tantalate towards visible-light induced water oxidation

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1. Experimental details

1.1 Preparation of photocatalysts

The ion-exchangeable layered tantalate $CsCa_2Ta_3O_{10}$ was prepared with a procedure reported in the literature.[1] Nitrogen doping in this layered tantalate was achieved by calcining $CsCa_2Ta_3O_{10}$ at temperatures from 923 to 1073 K in an ammonia atmosphere. Protonated layered compound of nitrogen-doped $CsCa_2Ta_3O_{10}$ was prepared by ion-exchange of the nitrogen-doped $CsCa_2Ta_3O_{10}$ compound in 4 M HNO_3 solution for 10 days.

1.2 Characterization of photocatalysts

The synthesized products were comprehensively characterized by X-ray diffraction (XRD, Rigaku D/max 2500PC), UV-Vis spectrometer (Shimadzu 2200), X-ray photoelectron spectroscopy (XPS, Thermo Escalab 250, a monochromatic Al KR x-ray source), and transmission electron microscopy (TEM, Philips Tecnei F20). The content of nitrogen dopant was analyzed using a flash elemental analyser (LECO TruSpec CHN analyser).

1.3 Photocatalytic reactions

The photocatalytic reactions were carried out in a quartz reaction cell connected to a closed gas circulation and evacuation system. 0.5 g of catalyst was suspended in 300 ml aqueous solution containing different sacrificial reagents. For photocatalytic O_2 evolution reactions, $AgNO_3$ (0.01 M) together with La_2O_3 (0.5 g) was used. For photocatalytic H_2 evolution reactions, methanol (20 V%) was used as the sacrificial reagent and Pt (0.5 wt%) loaded with photoreduction method was used as the cocatalyst. The suspension was then thoroughly degassed and irradiated by a 300 W Xe lamp (Beijing Trusttech Co. Ltd., PLS-SXE-300UV) equipped with an optical cut-off filter ($\lambda > 400$ nm) to eliminate ultraviolet light and a water filter to remove infrared light. The temperature of the reactant solution was maintained at 293±5 K by a flow of cooling water during the reaction. The amounts of O_2 and H_2 produced were analyzed using an on-line gas chromatography.

1.4 Computational details

In our calculation $CsCa_2Ta_3O_{10}$ is simulated by a 2×2×1 supercell (64 atoms, dimension size: 7.73Å ×7.73 Å ×15.25Å), as shown in Fig. S1 (a)**.** To investigate the N-doping effect, one oxygen (one-coordinated) is replaced by nitrogen, as shown in Fig. **S1 (b)**, with a doping concentration of 1/64 (atomic ratio). The electronic structures are obtained by spin-polarized density functional theory (DFT) calculations using the DMol3 code.[3, 4] The generalized gradient approximation (GGA) with the functional of Perdew–Burke–Ernzerhof functional (PBE)[5] was utilized, together with a double-numeric basis of effective core potentials for the description of core electrons. During our calculations, the convergence criteria for structure optimizations were set to (1) energy tolerance of 1.0×10^{-6} Ha per atom, (2) maximum force tolerance of 1.0×10^{-3} Ha/Å and (3) maximum displacement tolerance of 1.0×10^{-3} Å. The k-space is sampled only by gamma point due to the large size of the supercell. All local density of states (DOS) are expressed by the contribution of one atom for the comparison purpose. The above computation methods have been successfully employed in our recent doping studies of various catalysts (like graphitic C_3N_4[6], and TiO_2[7]).

References:

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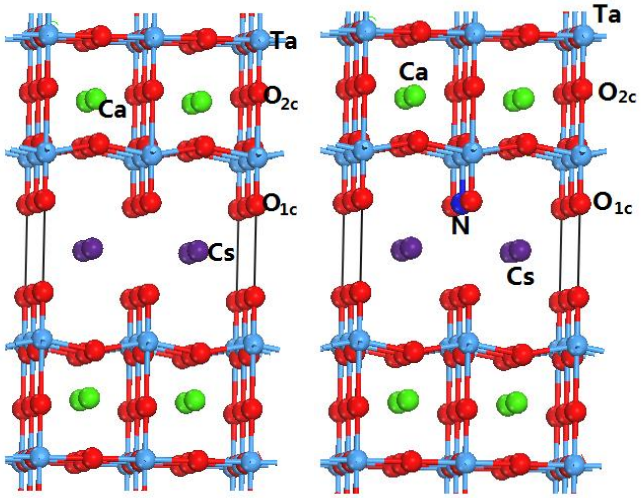
2. Results of Characterizations



(a) (b)

Fig. S1 Structure models of undoped and nitrogen-doped $CsCa_2Ta_3O_{10}$ for theoretical calculations. purple color, Cs; red, oxygen; green, calcium; blue, nitrogen; light blue, tantalum.

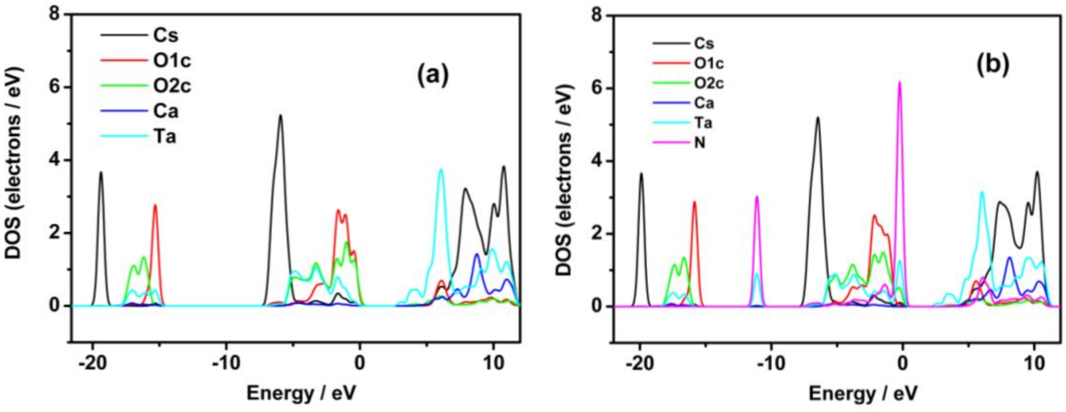


Fig. S2 Partial density of states of (a) undoped $CsCa_2Ta_3O_{10}$, and (b) nitrogen-doped $CsCa_2Ta_3O_{10}$.

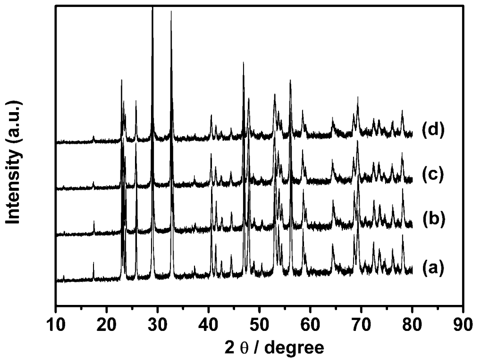


Fig. S3 X-ray diffraction patterns of (a) $CsCa_2Ta_3O_{10}$ and (b)-(d) nitrogen-doped $CsCa_2Ta_3O_{10}$ samples prepared by calcining $CsCa_2Ta_3O_{10}$ in ammonia gas flow at 973, 1023, and 1073 K, respectively.

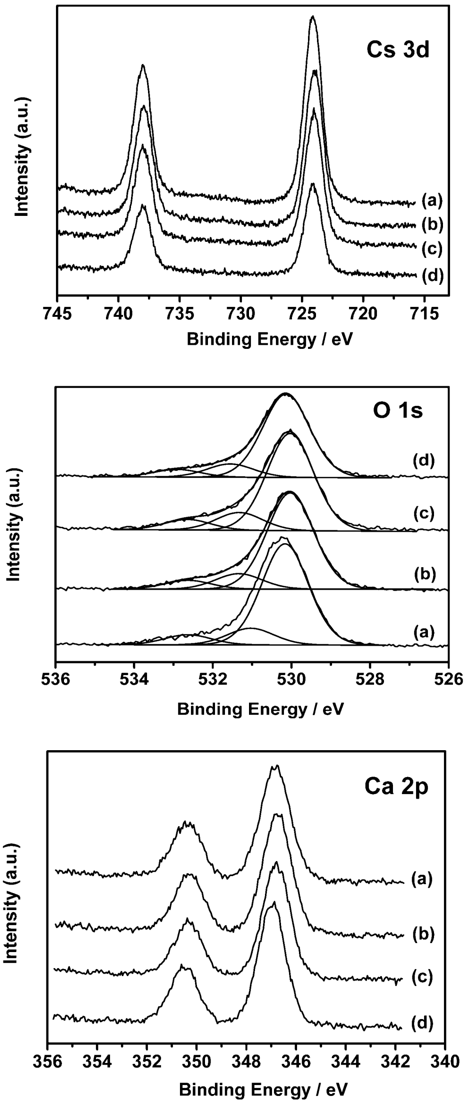


Fig. S4 High-resolution XPS spectra of O1s, Cs3d, and Ca 2p measured on (a) $CsCa_2Ta_3O_{10}$ and (b)-(d) nitrogen-doped $CsCa_2Ta_3O_{10}$ samples prepared by calcining $CsCa_2Ta_3O_{10}$ precursor in ammonia atmosphere at 973, 1023, and 1073 K.

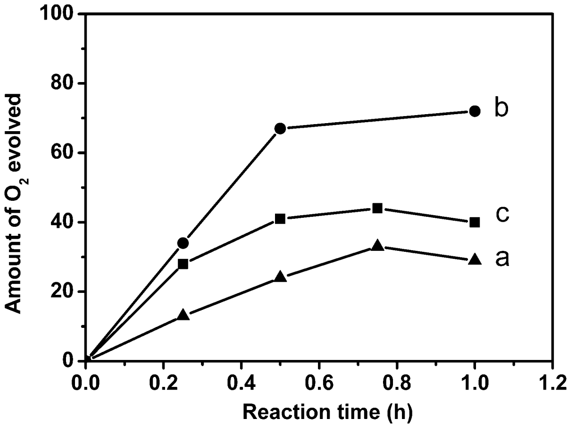


Fig. S5 Time courses of photocatalytic O_2 evolution on nitrogen-doped $CsCa_2Ta_3O_{10}$ photocatalysts prepared by calcining $CsCa_2Ta_3O_{10}$ precursor in ammonia atmosphere at (a) 1023 (15 h), (b) 1073 (15 h), and (c) 1023 (15 h) +1073 (15 h) K.

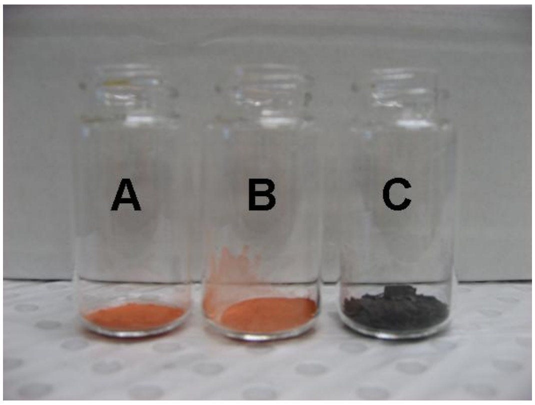


Fig. S6 Photos of (A) original nitrogen-doped $CsCa_2Ta_3O_{10}$ sample, (B) nitrogen-doped $CsCa_2Ta_3O_{10}$ sample collected after photocatalytic H_2 evolution reaction in the presence of methanol, and (C) nitrogen-doped $CsCa_2Ta_3O_{10}$ sample collected after photocatalytic O_2 evolution reaction in the presence of $AgNO_3$.