

Synthesis and photocatalytic activity of hydrated layered perovskite $K_{2-x}La_2Ti_{3-x}Nb_xO_{10}$ ($0 \leq x \leq 1$) and protonated derivatives

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A series of photocatalytic intercalated materials $K_{2-x}La_2Ti_{3-x}Nb_xO_{10}$ ($0 \leq x \leq 1$) and a series of its protonated derivatives $H_{2-x}La_2Ti_{3-x}Nb_xO_{10}$ were prepared by solid-state reaction and ion-exchange reaction. The photocatalytic activities of samples were evaluated using methanol as electron donor under UV irradiation. All $H_{2-x}La_2Ti_{3-x}Nb_xO_{10}$ samples possessed approximately two-fold higher photocatalytic activity than the corresponding $K_{2-x}La_2Ti_{3-x}Nb_xO_{10}$. This difference was most pronounced for the photocatalyst $H_{1.9}La_2Ti_{2.9}Nb_{0.1}O_{10}$ which showed the highest activity: 22 $\mu\text{mol H}_2/\text{catalyst (g)}$ for 5 h, more than three times the activity of $K_{1.9}La_2Ti_{2.9}Nb_{0.1}O_{10}$.

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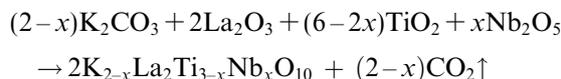
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Photocatalytic splitting of water into H_2 and O_2 by layered nanocomposite semiconductors has received special attention because this process may prove suitable for the conversion of solar energy into clean-energy H_2 fuel [1–5]. Due to the non-suitability of the band-edge positions, i.e. the position of the conduction and valence band edges, the quantum efficiency of these photocatalysts is moderate. Recently, the layered perovskites belonging to the Ruddlesden–Popper (RP) and the Dion–Jacobson (DJ) families, with general formula $A_2[A_{n-1}B_nO_{3n+1}]$ and $A'[A_{n-1}B_nO_{3n+1}]$, respectively, have attracted considerable attention due to their interesting optical and electrical transport properties, as well as their excellent photocatalytic activities [6–10]. These compounds contain two-dimensional perovskite slabs consisting of $[A_{n-1}B_nO_{3n+1}]$ as one of the units from which a layered structure can be built. A number (n) of corner-sharing BO_6 octahedral slabs and alkaline earth metal cations (A) stack along the (001) crystalline face and the alkali metal cations (A') are sandwiched between the layers.

The interlayer ions of these materials are easily exchanged with other cations or cationic structural units, e.g. H, K, Na, NH_4 , CuX_2 ($X = Cl, Br$), owing to the

lower interlayer charge density. The properties of these layered compounds can be controlled via this ion-exchange process [11–13]. Many series of layered oxides have been extensively studied [14,15]. Accordingly, to narrow the band-gap energy and improve the photocatalytic activity of such materials, we synthesized a novel series, $K_{2-x}La_2Ti_{3-x}Nb_xO_{10}$ ($0 \leq x \leq 1$), and their protonated derivatives, $H_{2-x}La_2Ti_{3-x}Nb_xO_{10}$, with layered perovskite structure from exchanging Nb^{5+} with Ti^{4+} in $La_2Ti_3O_{10}$. The end members, $K_2La_2Ti_3O_{10}$ ($x = 0$) and $KL_2Ti_2NbO_{10}$ ($x = 1$), are members of the RP and DJ phases, respectively. Their photocatalytic properties were evaluated.

$K_{2-x}La_2Ti_{3-x}Nb_xO_{10}$ were prepared by modifying the method in Ref. [16]. Starting materials of K_2CO_3 , La_2O_3 , Nb_2O_5 and TiO_2 powders were mixed in stoichiometric ratios according to the following equation and in the presence of excess amounts (20%) carbonate to compensate for its volatilization:



The mixture was calcined in platinum crucible at 1150 °C for 12 h in air followed by a grinding and recalcining at 1150 °C for another 40 h. The product was washed with distilled water to remove excess alkali, and then dried at 500 °C to obtain anhydrous

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compound. The exchange of potassium for hydrogen in $K_{2-x}La_2Ti_{3-x}Nb_xO_{10}$ was carried out by mixing the $K_{2-x}La_2Ti_{3-x}Nb_xO_{10}$ powder with 1 M HCl aqueous solution at room temperature for 96 h, with three intermediate replacements of the acid in 24 h. The exchange of potassium for hydrogen was determined by flame photometry to be $\sim 95\%$ after 24 h and nearly 100% after 96 h. The resultant solid product was centrifuged, washed with distilled water and air-dried at room temperature. The sample obtained was designated as $H_{2-x}La_2Ti_{3-x}Nb_xO_{10}$.

The structure of $K_2La_2Ti_3O_{10}$ has been confirmed as a layered perovskite-type compound [17–20] and is shown schematically in Figure 1a; the $0 \leq x \leq 0.75$ members are isostructural with the $x = 0$ member. The $K_2La_2Ti_3O_{10}$ is an n-type semiconductor layered compound consisting of negatively charge lanthanum titanate perovskite layers and interlayer K^+ ions. The crystal structure of $K_2La_2Ti_3O_{10}$ has tetragonal symmetry of space group $I4/mmm$ ($a = 0.387$ nm, $c = 2.98$ nm). The adjacent triple perovskite sheets, $La_2Ti_3O_{10}$, are stacked with a displacement of $1/2$ along the $[1\ 1\ 0]$ direction. A lanthanum ion occupies the 12-fold site in the center of the perovskite lattice. According to the X-ray diffraction data, the cell parameters $K_2La_2Ti_3O_{10}$ are $a = b = 0.387$ nm, $c = 2.98$ nm, face distance $(001) = 1.49$ nm, and $La_2Ti_3O_{10}^{2-}$ thickness 1.19 nm. The interlayers are bonded by static force. Due to the weaker combination between the interlayers, $K_2La_2Ti_3O_{10}$ can readily exchange its intercalation ion and expand. The $K_2La_2Ti_3O_{10}$ is hygroscopic, forming hydrates, $K_2La_2Ti_3O_{10} \cdot H_2O$, once exposed to air, as shown schematically in Figure 1b. The hydrated compound may have $P4/mmm$ symmetry.

The structure of $KL_aTi_2NbO_{10}$ is similar to that of $KCa_2Nb_3O_{10}$ [20], and is shown schematically in Figure 1c. It has tetragonal symmetry, space group $C222$ ($a = 0.385$ nm, $b = 0.385$ nm, $c = 3.007$ nm). The adjacent triple perovskite sheets, $La_2Ti_2NbO_{10}$, are stacked with a displacement of $a/2$ along the $[001]$ direction. The variation in displacement of the adjacent perovskite slabs in the layered perovskites $K_2La_2Ti_3O_{10}$ and KL_aTi_2-

Ti_2NbO_{10} occurs because of the differences in the size and the number of alkali-metal cations interleaved between the perovskite slabs.

$H_2La_2Ti_3O_{10}$ was formed when the interlayer K^+ ions of $K_2La_2Ti_3O_{10}$ were exchanged for H^+ ion. The structure of $H_2La_2Ti_3O_{10}$ is similar to its parent $K_2La_2Ti_3O_{10}$, except for a small decrease in the c -parameter ($c = 2.77$ nm); it is also a layered perovskite-type compound and is shown schematically in Figure 1d. The protons are arranged in the interlayers of the $La_2Ti_3O_{10}^{2-}$ unit layers. The interlayers are weakly combined by hydrogen bonding, so a “guest” can readily be incorporated, leading to the expansion of c -parameter on intercalation.

X-ray powder diffraction of the products was performed with a Bruker D8-advance X-ray diffractometer, using monochromatized Cu K_{α} ($\lambda = 0.154$ nm) radiation. The synthesized $K_{2-x}La_2Ti_{3-x}Nb_xO_{10}$ and $H_{2-x}La_2Ti_{3-x}Nb_xO_{10}$ were confirmed as single phase compositions and are shown in Figure 2a and b, respectively. All of the diffraction lines were matched well with the reported pattern [7]. The substitution of Nb for Ti did not produce a different diffraction pattern for $K_{2-x}La_2Ti_{3-x}Nb_xO_{10}$ and $K_2La_2Ti_3O_{10}$, which implies no significant $K_2La_2Ti_3O_{10}$ crystal structure change. As can be seen from Figure 2a, the $KL_aTi_2NbO_{10}$ phase showed a slight shift of diffraction peaks in accordance with the transformation from $I4/mmm$ to $C222$. The diffraction peaks of $KL_aTi_2NbO_{10}$ were sharpened significantly due to more niobium being incorporated into the lattice. It is possible that some structural distortion occurs due to the random distribution of the smaller Nb^{4+} cation into the TiO_6 lattice.

We have prepared the protonated phase, $H_{2-x}La_2Ti_{3-x}Nb_xO_{10}$, by ion exchange in 1 M HCl aqueous solution starting from the corresponding potassium compounds. More importantly, $K_{2-x}La_2Ti_{3-x}Nb_xO_{10}$ readily exchanges K^+ with H^+ on treatment with dilute

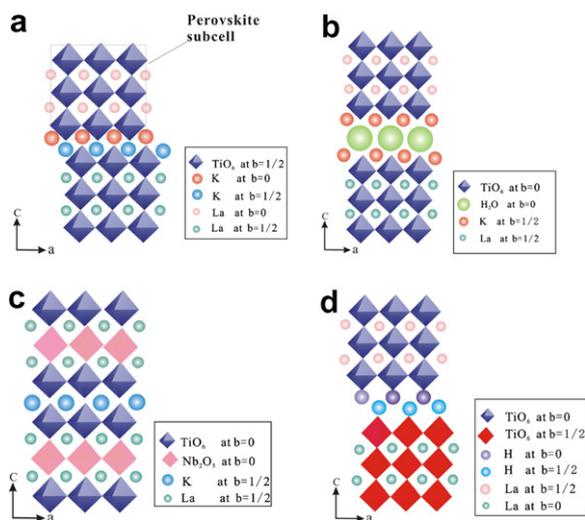


Figure 1. Schematic structure of (a) $K_2La_2Ti_3O_{10}$, (b) $K_2La_2Ti_3O_{10} \cdot H_2O$, (c) $KL_aTi_2NbO_{10}$ and (d) $HL_aTi_2NbO_{10}$.

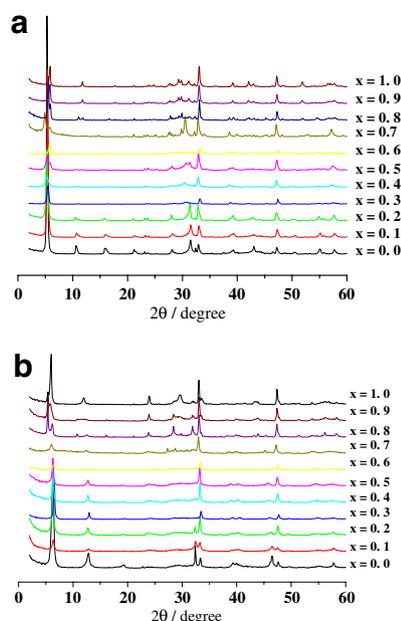


Figure 2. Powder X-ray diffraction patterns of (a) $K_{2-x}La_2Ti_{3-x}Nb_xO_{10}$ and (b) $H_{2-x}La_2Ti_{3-x}Nb_xO_{10}$.

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