

Efficient photocatalytic decomposition of water with the novel layered tantalate $\text{RbNdTa}_2\text{O}_7$

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Under UV irradiation, $\text{RbNdTa}_2\text{O}_7$, the first example of an active photocatalyst containing partially occupied 4f levels, demonstrated efficient evolution of stoichiometric H_2/O_2 mixtures from pure water even in the absence of loaded metal catalysts.

A variety of mixed metal oxides containing TiO_6 , NbO_6 or TaO_6 octahedral units have been extensively studied as photocatalysts. Representative catalysts reported so far include SrTiO_3 ,^{1,2} $\text{Na}_2\text{Ti}_6\text{O}_{13}$,³ BaTi_4O_9 ,⁴ $\text{K}_2\text{Ti}_4\text{O}_9$,⁵ $\text{K}_4\text{Nb}_6\text{O}_{17}$,⁶ $\text{K}_2\text{-La}_2\text{Ti}_3\text{O}_{10}$ ⁷ and $\text{K}_3\text{Ta}_3\text{Si}_2\text{O}_{13}$,⁸ which show potential activities for the decomposition of pure water. We have especially noted the use of layered materials because of the possibility of modifying the chemical composition as well as microstructure by means of ion-exchange or intercalation, which is useful for designing photocatalysts based on semiconducting metal oxide sheets.⁹ The present work has been directed towards the synthesis of novel layered perovskite tantalates $\text{RbLnTa}_2\text{O}_7$ (Ln = La, Pr, Nd or Sm), and evaluation of their photochemical activity for the decomposition of pure water. We report here the highly efficient evolution of stoichiometric H_2/O_2 mixtures over $\text{RbNdTa}_2\text{O}_7$ even in the absence of sacrificial agents and loaded metal catalysts.

The $\text{RbLnTa}_2\text{O}_7$ samples with various lanthanoids were prepared according to the procedure reported by Toda and Sato¹⁰ for $\text{RbLaTa}_2\text{O}_7$. Calculated amounts of powdered carbonates or oxides (Rb_2CO_3 , Ln_2O_3 , Pr_6O_{11} , CeO_2 and Ta_2O_5 , Rare Metallic Co. Ltd., Japan) were mixed together and calcined at 1100 °C for 10 h in air. The crystal structure of the products were identified by use of a powder X-ray diffractometer (XRD, Shimadzu XD-D1) equipped with Cu-K α radiation (30 kV, 20 mA). Diffuse reflectance spectra were recorded with a UV-VIS spectrometer (Jasco V-550). Photocatalytic H_2 evolution from water was conducted in an inner irradiation quartz cell, which was connected to a closed circulation system. The powder sample of the tantalate (0.2 g) was suspended in distilled water (200 cm³) in the cell by use of a magnetic stirrer. The reaction mixture was deaerated by evacuation and then flushed with Ar gas (20 kPa). The reaction was carried out by irradiating the mixture with light from a 400 W high-pressure Hg lamp. Gas evolved during irradiation was analyzed by an on-line gas chromatograph (Hitachi, TCD, Ar carrier, MS-5A and Porapak-Q columns). Evolution of H_2 and O_2 only was detected.

X-Ray diffraction patterns of the La sample (Ln = La) consisted of single phase of layered perovskite, $\text{RbLaTa}_2\text{O}_7$, and all the reflections were indexed based on a tetragonal lattice ($P4/mmm$, $a = 0.3885$ nm, $c = 1.112$ nm) as reported previously.¹⁰ Similar patterns were also obtained for Ln = Pr, Nd and Sm, and were free from reflections due to the starting materials or other impurities. By contrast, the systems containing Ln = Ce, Eu, or heavier lanthanoids consisted of mixtures of other lanthanoid tantalates, such as EuTaO_4 and TbTa_3O_9 , and unreacted oxides. For Ln = Ce, the reduction of Ce^{4+} to Ce^{3+} required to compensate the charge neutrality in $\text{RbCeTa}_2\text{O}_7$ did not take place during calcination in air, while the product in the other systems appear to be dependent on the ionic radius of Ln^{3+} . It is well known that the structural stability of

perovskite-type oxides (ABO_3) can be easily estimated by calculating the tolerance factor defined as $t = (r_A + r_O)/\sqrt{2}(r_B + r_O)$, where r_A , r_B and r_O are the radii of the respective ions, i.e., t would be unity for an ideal cubic structure.¹¹ In the present system, the value of t decreases from 0.920 for Ln = La with decreasing ionic radii of Ln^{3+} and no layered perovskite was produced at $t < 0.90$ (Ln = Ce, Eu and heavier lanthanoids). Therefore, the geometrical arrangement of the perovskite unit (Ln-Ta-O) governs the structural stability even in a layered structure.

Fig. 1 shows the UV-VIS diffuse reflectance spectrum of $\text{RbLnTa}_2\text{O}_7$. The La sample showed a clear absorption edge at ca. 300 nm and the corresponding band gap energy was ca. 3.8 eV, quite close to that of Ta_2O_5 . This can be explained by the reported band structure of the perovskite tantalate, where oxygen 2p and Ta s and p orbitals form the valence band and a high-lying antibonding band, respectively, whereas 5d states of the Ta occupy the wide intermediate gap.¹² Therefore, the band gap is likely to occur between the top of the oxygen 2p band and the bottom of the Ta 5d(t_{2g}) band. The position of the absorption edge was more or less red-shifted in the other three samples (Ln = Pr, Nd and Sm). Besides the band gap transition, these samples showed several sharp absorptions in the visible region (>350 nm). As indicated in Fig. 1, the positions of these absorptions are in accord with the internal 4f transitions observed in corresponding Ln(III) complexes, which give rise to narrow absorption bands quite unlike band gap transitions.¹³ The localized 4f levels in the present tantalate systems are

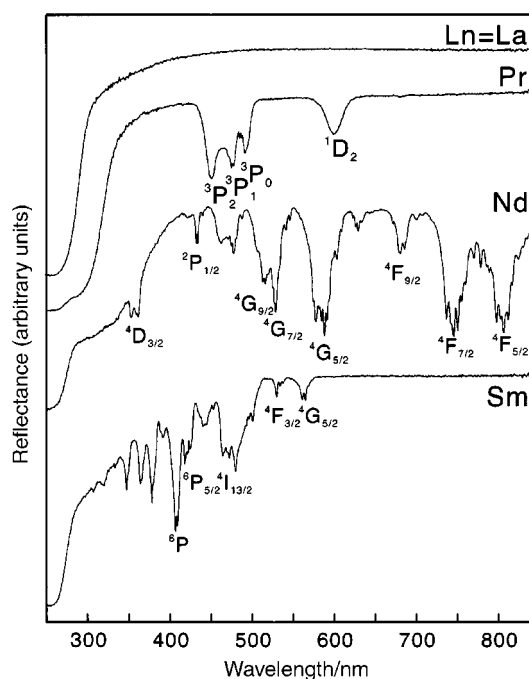


Fig. 1 UV-VIS diffuse reflectance spectra of $\text{RbLnTa}_2\text{O}_7$. Symbols for each absorptions show the excited states of isolated Ln 4f. The ground states are: La, $^1\text{S}_0$; Pr, $^3\text{H}_4$; Nd, $^4\text{I}_{9/2}$; Sm, $^6\text{H}_{5/2}$.

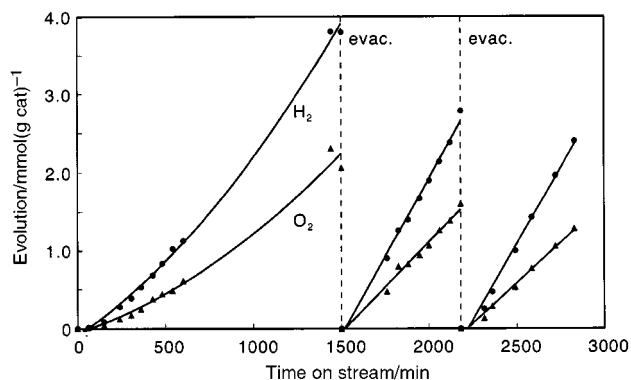


Fig. 2 Gas evolution from distilled water over RbNdTa₂O₇ under irradiation of UV light from 400 W high-pressure Hg lamp. Catalyst, 0.2 g, H₂O, 200 cm³. The rate of gas evolution over RbLnTa₂O₇ is summarized in Table 1.

Table 1 Rates of gas evolution over RbLnTa₂O₇

Catalyst	Evolution rate/ μmol h ⁻¹ (g cat) ⁻¹	
	H ₂	O ₂
RbLaTa ₂ O ₇	6.0	2.8
RbPrTa ₂ O ₇	4.2	Trace
RbNdTa ₂ O ₇	234.8	126.4
RbSmTa ₂ O ₇	53.2	28.7
0.1wt% Pt/P25	<3	0

considered to lie within the band gap. However, it should be noted that several absorptions overlapping the onset of the absorption edge in the Nd and Sm systems are not ascribable to internal transitions. In particular, a much broader absorption in the range 300–400 nm suggests possible charge-transfer transitions between Ln 4f and other bands.

The four as-prepared layered tantalates were applied to the photocatalytic decomposition of pure water in the absence of sacrificial agents. Fig. 2 shows the time course of gas evolution over RbNdTa₂O₇ while rate data of all the tantalate samples are given in Table 1. The RbLnTa₂O₇ samples, with the exception of the Ln = Pr case, gave stoichiometric evolution of H₂ and O₂. Interestingly, the rate of gas evolution was found to be strongly dependent on Ln³⁺ and was at a maximum for the Nd system. In this case, the rate of H₂ and O₂ evolution in the first run increased initially with progress of the reaction, but then became constant at 234.8 and 126.4 μmol h⁻¹ (g cat)⁻¹, respectively, after 10 h. A plausible reason for the upwardly deviating gas evolution in the initial stage is CO₂ adsorption onto the as-prepared samples, since structural change of the tantalate was unobservable by XRD. After evacuating the system, almost the same rate was reproduced in the second and third runs. The total amount of H₂ and O₂ evolved during these runs reached 6.32 and 3.25 mol (mol cat)⁻¹, respectively, suggesting that the reaction proceeded stoichiometrically and catalytically. A Degussa P25 catalyst loaded with 0.1wt% Pt as well as Ta₂O₅ were also applied to the reaction as reference samples; only H₂ was evolved over these catalysts at the rate of

< 3 μmol h⁻¹ (g cat)⁻¹, two orders of magnitude less than that for RbNdTa₂O₇. The prominent feature of the Nd system is the efficient formation of stoichiometric H₂/O₂ mixtures even without loading of metal catalysts such as Pt, Ni, and Cu. This is in complete contrast to conventional photocatalysts, such as TiO₂, which require the assistance of such metal catalysts to bring about water splitting. Reported photocatalysts that can decompose pure water in the absence of metal catalysts are K₄Nb₆O₁₇,⁶ K₂La₂Ti₃O₁₀,⁷ K₃T₃Si₂O₁₃⁸ and ZrO₂.¹⁴ However, the rate of H₂/O₂ evolution over RbNdTa₂O₇ is much higher compared to these reported catalysts. Furthermore, a most promising advantage of the present layered tantalates is the wide variety of possible structural modifications that can be made by means of ion exchange, intercalation and/or pillaring. In particular, the preparation of pillared layered structures capable of creating nanocomposites between different metal oxides in porous framework is expected to be a useful strategy for the development of excellent photocatalysts, which cannot be achieved for other semiconducting oxide systems.

The reason for the high photocatalytic activity for RbNdTa₂O₇ is not clear at this stage. To our knowledge, however, RbNdTa₂O₇ is the first example of a photocatalyst containing partially occupied 4f levels. It should be noted that the sequence of the activity, Nd > Sm ≫ La ≈ Pr (Fig. 2), is well reflected by the different shape of absorption edge (Fig. 1) which is possibly influenced by charge-transfer transitions. This is considered to largely be a consequence of the partially occupied Ln 4f levels, which form localized states within the band gap of the Ta–O sublattice. This may imply that excitation of Ln 4f electrons plays a key role in the photocatalysis of the present layered perovskite tantalates.

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