

Synthesis and Photocatalytic Properties of Ion-Exchangeable Perovskites

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RbLaNb₂O₇ was prepared by Pechini type polymerizable complex method. Its photocatalytic activity for pure water decomposition was improved by a series of ion-exchange and intercalation reactions as well as after the morphology modification by exfoliation and reassembling of the bulk material. It was also demonstrated that photocatalytic materials in principle can be applied directly for sea water decomposition to produce H₂ as a source of chemical energy without relying on the sources of fresh water.

Key words: Pechini method, photocatalyst, ion-exchange reaction, sea water, energy conversion

1. INTRODUCTION

Solar energy conversion into chemical energy by splitting of water has attracted considerable attention since the report of Honda-Fujishima effect [1]. Although the understanding of the photoelectrochemical reactions on the surface of a semiconductor has been significantly advanced in the past thirty years, industrial use of the heterogeneous photocatalysis for energy conversion still remains a dream and a challenge for chemists, materials scientists and engineers. Recent reports by Domen [2,3] and Kudo [4] groups on the outstanding activity of perovskite related layered titanium, niobium and tantalum based complex oxides bring us closer to the implementation of this dream and at the same time provide materials chemists with convenient pedestal photoactive compounds of rich and interesting chemistry, which can be easily modified and hopefully will yield even more efficient materials for light energy conversion. Relatively high hydrogen production by these materials is probably related to the ion-exchangeable nature of such phases and their ability to accommodate H⁺ and water molecules between perovskite blocks.

The aim of this work was to investigate photocatalytic properties of the phases derived from Dion-Jacobson phase of RbLaNb₂O₇ (and similar compounds) by systematic modification of chemical composition, band gap and sample morphology in a series of conversions of starting compound by carrying out ion-exchange reactions using the "toolbox of soft-chemical reactions" [5].

2. EXPERIMENTAL

Starting samples of RbLaNb₂O₇ and RbLaTa₂O₇ were

prepared by polymerizable complex method [6]. NbCl₅ (or TaCl₅) was dissolved in methanol with slow addition of approximately 1ml of H₂O₂ until formation of stable transparent solution. Stoichiometric amount of La₂O₃ (preliminary heat treated at 900°C) and 10%mol. excess of Rb₂CO₃ were dissolved in the solution of citric acid (CA) in ethylene glycol (EG). In all experiments the ratio of Cation/CA/EG was the same 1:4:16. After complete dissolution of metal precursors, both solutions were mixed and hot plate temperature was set to 120°C. After overnight stirring, polyesterification reaction results in the formation of viscous transparent gel. Subsequently the hotplate temperature was set to 200°C for several hours to ensure evaporation of excess EG. Formation of plastic-like resin was regarded as the end of gel formation. The obtained resin was heat treated in mantle heater at 350-450°C to oxidize the polymer, and it yielded a fine powder, which was slightly ground in the mortar and calcined at 700°C for 10h and 800°C for 12h in the flowing O₂.

CuClLaNb₂O₇ and Co_{1/2}LaNb₂O₇ were prepared by ion exchange reaction with anhydrous CuCl₂ and CoCl₂. The excess amount of CuCl₂ or CoCl₂ was mixed in the dry glovebox with RbLaNb₂O₇. The mixture was sealed in the evacuated quartz ampoule and heat treated at 300°C for 10 days. The obtained powders have been washed with water or methanol to eliminate chlorides until the mother liquor stopped giving AgCl precipitate with AgNO₃ solution. CuClPb₂Nb₃O₁₀ was prepared by the same synthetic procedure starting from RbPb₂Nb₃O₁₀ synthesized by polymerizable complex method.

HLaNb₂O₇ was prepared by treating RbLaNb₂O₇ with 40 times excess of 1.5M HNO₃ for 3-5 days at 60°C.

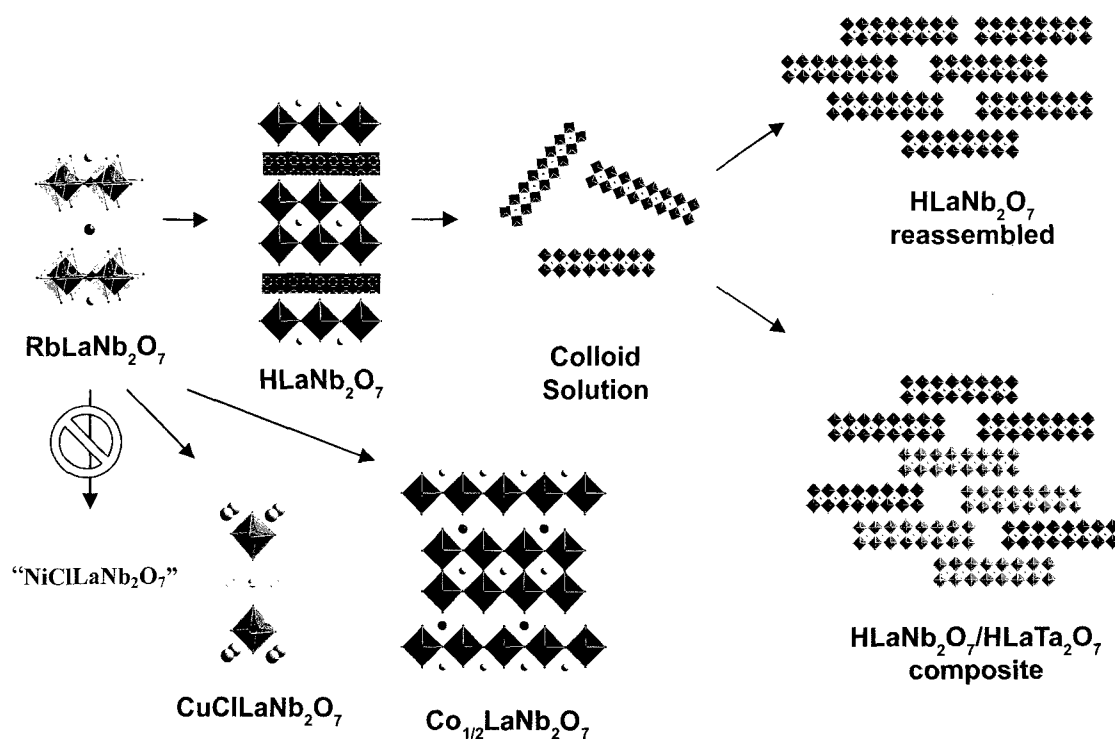


Fig. 1. Flowchart of ion-exchange and intercalation reactions applied to modify chemical composition, light absorbance and morphology of starting $\text{RbLaNb}_2\text{O}_7$ phase.

The nitric acid was replaced at least once. The powder was filtered out, washed with water till neutral pH and dried in the air. One of the samples was additionally activated by re-assembling of the exfoliated colloid. In this case hydrogen ions in HLaNb_2O_7 were replaced with tetrabutylammonium ions by treating the powder at room temperature by the 20 fold excess of TBA^+OH^- in the sealed flask for 3 weeks. After filtering out large particles, 1M HCl was added to the colloid solution. At $\text{pH}\sim 2$, the colloid solution became unstable and the obtained fluffy precipitate could be easily separated by filtration. The precipitate was washed with HCl solution several times and then 10-12 times with water until $\text{pH}\sim 7$. Thus obtained powder was dried in the oven. $\text{HLaNb}_2\text{O}_7/\text{HLa}_2\text{Ta}_2\text{O}_7$ composite was prepared in a similar way starting from the mechanical mixture of $\text{RbLaNb}_2\text{O}_7$ and $\text{RbLaTa}_2\text{O}_7$ in the molar ratio 1:1.

All powders were characterized by X-ray powder diffraction using MacScience X-ray diffractometer with $\text{CuK}\alpha$ radiation in the scanning mode with 1 deg/min. Several samples after ion-exchange reaction were additionally characterized by Hitachi field emission SEM MODEL S-4500 equipped with EDS detector and QUASAR-Kevex Software for quantitative micro-analysis. UV-VIS diffuse reflectance spectra of the samples were measured in the range of 200-1000 nm using a UV-VIS Spectrometer (Shimadzu UV-

3100PC).

Photocatalytic activities of the prepared powders for splitting of pure water were tested in the gas closed circulation system with the quartz cell using whole spectral range produced by Hg-lamp. Typically co-catalysts were not used. The mixture of the gases was analyzed by Shimadzu GC-14B gas chromatograph. The detector temperature was set to 50°C and Ar carrier gas pressure to 100kPa. The possible uptake of air was observed by monitoring the intensity of N_2 peak.

3. RESULTS AND DISCUSSIONS

Fig.1 presents the flowchart of ion-exchange and intercalation reactions carried out in this work.

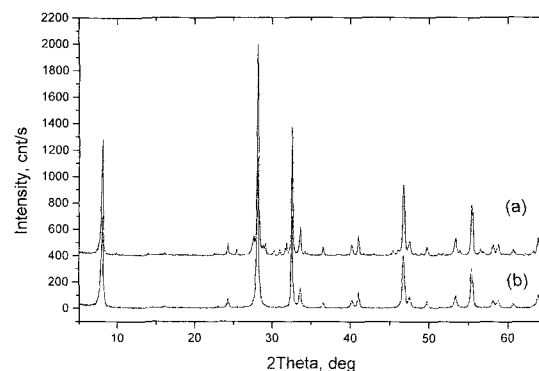


Fig. 2. XRD patterns of $\text{RbLaNb}_2\text{O}_7$ prepared by PC method at (a) 800°C and (b) 900°C .

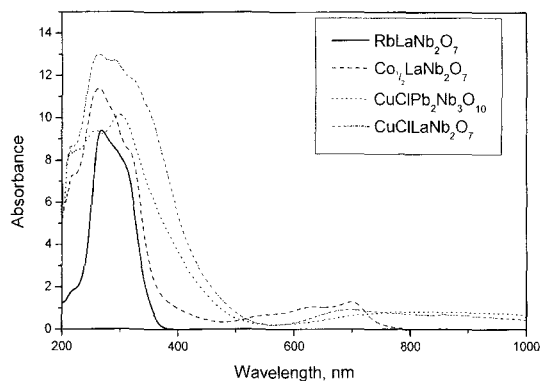


Fig. 3. Diffuse reflectance spectra of MLaNb_2O_7 ($M = \text{H}, \text{Rb}, \text{CuCl}, \text{Co}_{0.5}$) and $\text{CuClPb}_2\text{Nb}_3\text{O}_{10}$ materials

$\text{RbLaNb}_2\text{O}_7$ starts to form as a major phase at 700°C . The best samples can be obtained via polymerizable complex method after calcination at 900°C (Fig. 2b). However increase of unit cell volume by 3\AA^3 after the treatment at this temperature indicates possible loss of Rb. For this study we used samples prepared at 800°C , which contained approximately 5% LaNbO_4 as a secondary phase. Fig. 2a shows typical diffraction pattern of $\text{RbLaNb}_2\text{O}_7$ sample ($a=5.4858(6)\text{\AA}$, $b=5.4846(6)\text{\AA}$, $c=21.993(2)\text{\AA}$). The band gap estimated from absorption spectrum (Fig.3) is 3.5eV. This compound shows relatively low photocatalytic activity of $\sim 2.4 \mu\text{mol/g}\cdot\text{h}$ hydrogen evolution from pure water without any co-catalysts.

We intended to improve the efficiency of water splitting via increase of the absorbance in the visible light region by introducing layers containing transition metals instead of Rb. It is known that CuCl^+ and FeCl^+ layers may substitute for Rb in the simple ion-exchange reaction [7,8]. In the first case the compound has green color, in the second – light brown, which probably reflects possible limits for the choice of candidates for proper substitution to ensure light absorbance in the visible range. Therefore we chose Ni, Co and Cu for further investigations. Characterization of carefully washed samples by EDS revealed that Ni does not enter the crystal. In the case of reaction with CoCl_2 , both Rb and Cl were absent in the EDX spectra, while standardless analysis gave approximate composition of $\text{Co}:\text{La}:\text{Nb}=0.5:1:2$, which corresponds to $\text{Co}_{1/2}\text{LaNb}_2\text{O}_7$. The crystal structure of this phase is unknown; the structure in Fig.1 should be regarded only as a best guess considering that $\text{CN}=8$ is unlikely for Co and taking into account structural features of the similar reported compound $\text{CoLa}_2\text{Ti}_3\text{O}_{10}$ [9]. $\text{CuClLaNb}_2\text{O}_7$ samples contained less than 3 atomic% of Rb while metal and chloro-

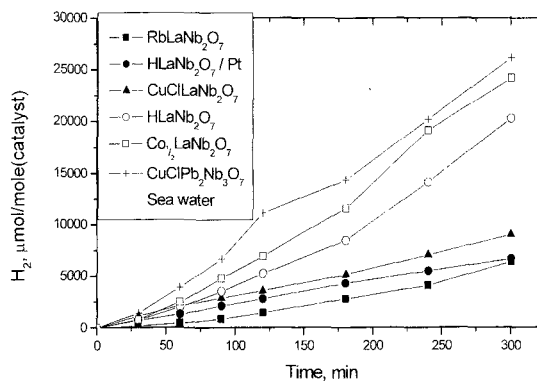


Fig. 4. Time dependence of H_2 evolution from water over MLaNb_2O_7 ($M = \text{H}, \text{Rb}, \text{CuCl}, \text{Co}_{0.5}$) and $\text{CuClPb}_2\text{Nb}_3\text{O}_{10}$ materials

rine ratio according to EDS analysis was $\text{Cu}:\text{Cl}:\text{La}:\text{Nb}=0.92:0.90:1.00:1.95$. Both $\text{Co}_{1/2}\text{LaNb}_2\text{O}_7$ and $\text{CuClLaNb}_2\text{O}_7$ samples start to absorb light already in the IR region (Fig.3) that corresponds to d-electrons transitions in Co and Cu. The energy gap between 3d states and the edge of the conduction band estimated from the slope of the main absorbance peak corresponded to 3.3 and 2.7 eV for $\text{Co}_{1/2}\text{LaNb}_2\text{O}_7$ and $\text{CuClLaNb}_2\text{O}_7$ phases respectively. Fig. 4 displays that both compounds demonstrated improved photocatalytic activity for water splitting. However, it turned out that $\text{CuClLaNb}_2\text{O}_7$ is unstable in water under illumination by UV light. The color of the sample changed from green to black, and chloride ions were found in the solution. $\text{CuClPb}_2\text{Nb}_3\text{O}_{10}$ demonstrated much better stability and was tested for photodecomposition of “sea water” – 3.5% solution of NaCl. Although the rate of hydrogen evolution in the photochemical reaction decreased, the main products still remained H_2 and O_2 (gas chromatograph did not resolve any peak which could be interpreted as Cl_2 or a chlorination product).

The high rate of H_2 evolution in the presence of HLaNb_2O_7 (Fig.4) made us attempt to improve this sample by Pt deposition via photochemical reaction. In contrast to our expectations the activity after Pt deposition decreased to the level of $\text{RbLaNb}_2\text{O}_7$. This fact helped us conclude that acidic treatment of starting $\text{RbLaNb}_2\text{O}_7$ may activate the powder, while photochemical deposition leads to the “poisoning” of catalyst since it is likely taking place on the same active sites as H^+ reduction. Therefore it was decided to activate the powder further by the exfoliation of obtained HLaNb_2O_7 and re-assembling of the nanosheets from colloid solution. The same technique was applied to assemble a composite $\text{HLaNb}_2\text{O}_7/\text{HLaTa}_2\text{O}_7$. In the

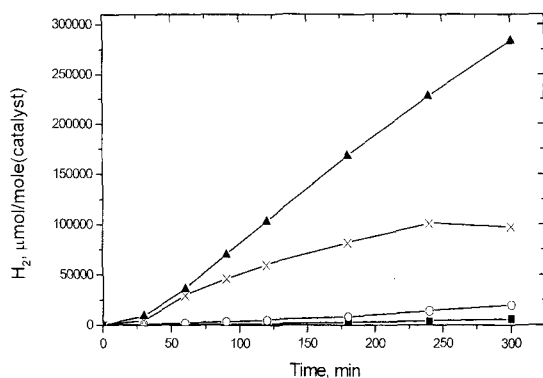


Fig. 5. Time dependence of H₂ evolution from water over (■) RbLaNb₂O₇, (○) HLaNb₂O₇, (x) reassembled HLaNb₂O₇, (▲) HLaNb₂O₇/HLaTa₂O₇ materials

latter case the differences of the valence band and conduction band energies of two compounds should favor the separation of the generated electron-hole pair, while chemical similarities of two phases must provide good lattice matching between assembled particles. Similar attempt has been reported by Kakihana group [10] for Sr₂Nb_xTa_{2-x}O₇ solid solutions. However solid solutions exhibited lower water decomposition rate than pure compounds probably due to the electron trapping by the foreign atoms in the lattice. Fig. 5 demonstrates that composite material provides higher rate of hydrogen evolution.

The data obtained in the current study are briefly summarized in the Table 1.

We have demonstrated that photocatalytic activity of the starting RbLaNb₂O₇ phase can be significantly increased by modifying light absorbance properties or sample morphology in a systematic way. It was also shown that photocatalytic materials in principle can be used for sea water decomposition to produce H₂ as a source of chemical energy.

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Table 1. Hydrogen evolution rate from pure water without co-catalysts.

Compound	Energy gap, eV	H ₂ evolution rate, μmol/g·h
RbLaNb ₂ O ₇	3.5	2.4
HLaNb ₂ O ₇	3.5	9.3
CuClLaNb ₂ O ₇	2.7	3.5
Co _{1/2} LaNb ₂ O ₇	3.3	10.2
CuClPb ₂ Nb ₃ O ₁₀	2.6	5.3
Reassembled HLaNb ₂ O ₇	3.6	56
HLaNb ₂ O ₇ /HLaTa ₂ O ₇		108

made it possible to participate in this work.

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