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Strategy for Modifying Layered Perovskites toward Efficient Solar Light-Driven Photocatalysts for Removal of Chlorinated Pollutants

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Abstract: We have explored an efficient strategy to enhance the overall photocatalytic performances of layered perovskites by increasing the density of hydroxyl group by protonation. The experimental procedure consisted of the slow replacement of interlayer Rb⁺ cation of RbLaTa₂O₇ Dion-Jacobson (DJ) perovskite by H⁺ via acid treatment. Two layered perovskites synthesized by mild (1200 °C for 18 h) and harsh (950 and 1200 °C, for 36 h) annealing treatment routes were used as starting materials. The successful intercalation of proton into D-J interlayer galleries was confirmed by FTIR spectroscopy, thermal analyses, ion chromatography and XPS results. In addition, the ion-exchange route was effective to enlarge the specific surface area, thus enhancing the supply of photocharges able to participate in redox processes involved in the degradation of organic pollutants. HLaTa_01 protonated layered perovskite is reported as a efficient photocatalyst for photomineralization of trichloroethylene (TCE) to Cl⁻ and CO₂ under simulated solar light. The enhanced activity is attributed to combined beneficial roles played by the increased specific surface area and high density of hydroxyl groups, leading to an efficiency of TCE mineralization of 68% moles after 5 h of irradiation.

Keywords: perovskite-type structure; ion-exchange; photocatalysis; TCE photodegradation; simulated solar light

1. Introduction

Solar energy represents one of the most attractive, easily available and accessible solutions for a variety of worldwide issues including water and air purification. The development of innovative functional materials for expanding the light-harvesting range and suppressing the quick recombination of photogenerated carriers is highly desirable for photocatalysis concerns.

Layered materials are promising candidates for light-related applications due to their numerous advantages which cannot be found in conventional materials: (i) possibility to increase the specific surface area; (ii) composition versatility due to doping choices with various elements; (iii) possibility of interlayer space tenability; (iv) good conductivity and superior electron mobility; (v) nanosized reaction interlayer spaces; (vi) extended light absorption capacity; (vii) improved photo-charge separation; (viii) cost-effectiveness and long-term stability. As an example, Dion–Jacobson (DJ)-type double-layered perovskites with the formula $M[A_{n-1}B_nO_{3n+1}]$ are among those materials which demonstrated interesting features, including optoelectronics [1] and heterogeneous photocatalysis [2,3].



One interesting feature of these lamellar structures refers to their photocatalytic performances which can be highly improved by partial substitution at A- and/or B-sites, while preserving the perovskite structure [4]. Introducing appropriate defects onto the surface of layered materials by substitution of parent cations has a positive effect on the electronic structure and optical absorption properties of the host materials [5]. Another interesting feature is using the perovskite interlayer space as reactions sites, retarding the recombination process by a better physical separation of the photogenerated carriers. Furthermore, their interlayer guests are ion-exchangeable with various

foreign species, being a facile method for the fabrication of layered assemblies [6,7].

Very recently, crystalline RbLaTa₂O₇ layered perovskites with predominant nanowire or platelet morphologies were developed and tested for trichloroethylene (TCE) photocatalytic degradation under simulated solar light [8]. The results suggest that the RbLaTa₂O₇ surface hydroxyl groups play an essential role in the photo mineralization of TCE, whereas the surface carbonate favors the formation of intermediate chlorinated product. The high-temperature solid-state route of layered perovskites is very easy to scale up, but it may have some limitations: (i) poor control over the properties of the final material; (ii) small specific surface area and (iii) low quantum efficiency because of inefficient visible-light harvesting. Consequently, the optimization of the synthesis protocol is crucial because it decides the crystallinity, defect concentration, morphology and physicochemical properties of the desired photocatalyst. In this scenario, cation-proton exchange route appears as an encouraging choice due to its simplicity and control over the product characteristics.

Generally, a DJ layered perovskite phase is converted to its protonated form (i.e., $H[A_{n-1}B_nO_{3n+1}]$) by acid treatment, where H is the proton, A is an alkali-metal, alkaline-earth, or rare-earth cation, *B* is a transition metal cation, and *n* is the thickness of the layers. Further on, the flexible structure of protonated layered perovskites makes them possible to be modified by intercalation with various organic bases [9], alcohols [10], phosphorous [11], grafting [12] or exfoliation in nanosheets [13,14]. The control of final properties of modified layered perovskites make them more interesting compared to the parent form due to their electronic properties [15–17] and increased photocatalytic activity [18,19]. Efficient layered perovskites for water splitting [20] or photodegradation of chlorinated compounds [21,22] are further developed, opening up new opportunities in the energy sector [23]. HLaNb₂O₇ prepared by proton exchange reaction of KLaNb₂O₇ with diluted acid exhibited high photocatalytic activity for decomposition of water under UV light [24]. The family of materials ALnTa₂O₇ (A = Cs, Rb, Na and H; Ln = La, Pr, Nd and Sm) were efficient catalysts for water splitting under UV irradiation, their activities depending markedly on lanthanide choice [25,26]. Protonated HTaO₃ tantalate was demonstrated to be encouraging photocatalyst for the degradation of rhodamine B [27]. Domen et al. [28] proved that the H⁺-exchanged form of RbPb₂Nb₃O₁₀ promotes H₂ formation under visible light exposure ($\lambda > 420$ nm). A strong gain in the photocatalytic decomposition rate of water under UV irradiation was observed after interlayer cations were replaced by protons in case of $ALaNb_2O_7$ and $ACa_2Nb_3O_{10}$ (A = Cs, Rb, K or H) layered niobates [29]. For instance, to the best of our knowledge, studies focusing on the photodegradation of harmful chlorinated compounds over HLaTa2O7 as protonated layered perovskite are limited. Therefore, replacing interlayer cations with H⁺ open new opportunities to design novel photocatalysts due to several positive effects: (i) it enables one to accommodate cationic species in the interlayer region that would provide absorption of visible light; (ii) photogenerated carriers are confined in a restricted area, limiting their migration and recombination.

Following our previous work on RbLaTa-based layered perovskites [8], the present study focuses on the photocatalytic degradation of trichloroethylene (TCE) over HLaTa₂O₇ layered perovskite obtained by protonation of RbLaTa₂O₇. For this purpose, two RbLaTa-based layered perovskites annealed in mild (i.e., 1200 °C for 18 h) or harsh (i.e., 950 and 1200 °C for 36 h) conditions were used as starting materials for the creation of protonated nanoarchitectures. The preparation, complex characterization and photocatalytic performances of two protonated perovskite, HLaTa_01(02), are presented in detail. Based on characterization and test data, the relationship between the density of O–H⁺ groups resulting from Rb⁺ replacement by H⁺ and TCE photomineralization activity is derived. The impact of perovskite protonation on charge recombination dynamics as well as on exposed reactive surface area is analyzed.

2. Results and Discussion

2.1. Phase Composition, Morphology and Structure of Ion Exchanged Layered Perovskites

The identification of crystalline phases of synthesized layered materials was carried out by X-ray diffraction. Figure 1A,B provides the XRD patterns of HLaTa_01(02) protonated products. For comparison, the diffractograms of parental RbLaTa_01 and RbLaTa_02 are given [8]. The unit cell parameters of the investigated samples are shown in Table 1. According to our previous paper [8], the diffraction lines of RbLaTa-based perovskites host structures were identified as RbLaTa $_{2}O_{7}$ (PDF card no. 01-089-0389) along with the existence of La_2O_3 and Rb_2CO_3 as minor phases. After Rb⁺ exchange with H⁺, the diffraction lines match the characteristic patterns of the HLaTa₂O₇ layered structure well. Besides the main component, both HLaTa_01(02) present weak reflections of the Ta₂O₅ crystalline phase. The protonated compound HLaTa₂O₇ (PDF card no. 01-081-1194) has a tetragonal cell indexed in a P4/m space group with lattice parameters of a = b = 0.3888(6) nm and c = 1.0548(3) nm [30]. The calculated lattice parameter values of our materials match the standard ones well. The impact of ion exchange treatment on the host layered perovskite can be seen by the significant intensity changes of (00*l*) reflections along with a slight shift of all diffraction lines towards higher angles due to lattice shrink. Moreover, the decrease in the c lattice parameter (Table 1) at 1.076 nm for HLaTa_01(02) protonated forms suggests that rubidium cation is replaced by a proton, in agreement with their ionic radii [$r(H = -0.38 \text{ Å and } r(Rb^+) = 1.61 \text{ Å}$] [31]. The *a* lattice parameter of protonated HLaTa₂O₇ was almost close to that of RbLaTa₂O₇ host, suggesting that the layered perovskite-type structure remained intact.



Figure 1. XRD patterns of (**A**) HLaTa_01 and (**B**) HLaTa_02 protonated perovskites. For comparison, both RbLaTa_01(02) hosts are represented. Reprinted with permission from reference [8]. Copyright (2019) Elsevier. Symbols: Δ —Ta₂O₅; *—Rb₂CO₃; #—La₂O₃, in brackets are given (*hkl*) Miller index of RbLaTa₂O₇ phase.

Sample Name	Reaction Temperature /Synthesis Time	D ₍₁₀₂₎ ¹ (nm)	Lattice Parameters (nm)	Interlayer Spacing ² (nm)	[Ref.]	
HLaTa_01	Protonation at <i>RT</i> */7 days	20.1	a = 0.388 c = 1.076	1.092	this work	
HLaTa_02	Protonation at <i>RT</i> */7 days	19.2	a = 0.388 c = 1.077	1.097	this work	
RbLaTa_01	RbLaTa_01 1200 °C/18 h		a = 0.387 c = 1.104	1.100	[8]	
RbLaTa_02	950 and 1200 °C/36 h	18.2	a = 0.388 c = 1.112	1.116	[8]	

Table 1. Synthesis conditions and lattice parameters of HLaTa_01(02) protonated products. For comparison, both RbLaTa_01(02) hosts [8] are given.

¹ Crystallite size calculated from (102) reflexion of RbLaTa₂O₇ and HLaTa₂O₇ phases, using the Debye–Scherrer equation. ² Interlayer spacing calculated from (001) reflexion of RbLaTa₂O₇ and HLaTa₂O₇ phases, using Bragg's law. * *RT* stands for room temperature.

The interlayer spacing between the perovskite layers (Table 1) of the synthesized samples before and after protonation was calculated using Bragg's law (Equation (1)):

$$n\lambda = 2d_{hkl} \cdot \sin\theta \tag{1}$$

where λ is the wavelength of incident X-ray (0.15406 nm), θ is the peak position (in radians) and *n* is the order of diffraction.

The layer distance decreases from 1.100 nm for unprotonated RbLaTa_01 to 1.092 nm for the HLaTa_01 protonated form. For the second sample, the *d*-spacing decreases from 1.116 nm for the RbLaTa_02 host to 1.097 nm for the HLaTa_02 protonated product (see Figure 2 and Table 1). Our observations are confirmed by study of Rodionov et al. [32], which observed a decrease in the interlayer distance of $H_2Nd_2Ti_3O_{10}$ after protonation in comparison to the initial alkaline parent form.



Figure 2. Schematic representation of the alkali cation-proton exchange process over RbLaTa_02 starting material yielding HLaTa_02 product.

The crystallite size (Table 1) calculated by Debye-Scherrer's equation from (102) reflexion of HLaTa₂O₇ phase, is around 20 nm for both HLaTa₂O1(02) protonated perovskites. These values are

higher compared to RbLaTa-based layered perovskite hosts, indicating an increased crystallinity after ion-exchange treatment.

The replacement of alkali cations in the interchannel positions of the perovskite framework by protons takes place without alteration of the crystalline structure [33]. It is expected that protons occupy the interlayer space of RbLaTa₂O₇ Dion–Jacobson perovskite, in agreement with their ionic radii. These observations are consistent with reports by Palacin and co-workers [30] for HLaNb₂O₇, who concluded that the space between the layers is occupied by protons and variable amounts of water. The authors found a general formula of H₃OLaNb₂O₇·xH₂O which, after drying at 100 °C, yielded the final product HLaNb₂O₇.

The SEM observations in Figure 3A,B show that HLaTa_01(02) products retain the lamellar structure of RbLaTa-based starting materials upon the acid treatment over a week. This observation is in agreement with other assemblies previously reported [34].



Figure 3. SEM images of (**A**) HLaTa_01 and (**B**) HLaTa_02 perovskites obtained by protonation of RbLaTa-based starting materials.

According to elemental mapping images of the HLaTa_01 material (Figure 4), Ta, La and O elements are homogeneously distributed in the material. The absence of a rubidium peak demonstrates that the cation exchange process was successful.

Ion chromatography (IC) is an appropriate technique to probe Rb⁺ cation release by replacement with H⁺, allowing the calculation of exchange degree. The amount of rubidium release at room temperature from a mixture of 50 mL of 1M HCl and 0.5 g of each RbLaTa_01 and RbLaTa_02 hosts was monitored for the time period of a week. The obtained results (Figure 5) reveal that 99.6% of Rb⁺ was replaced with H⁺ during the acid treatment of the host annealed in mild condition (i.e., RbLaTa_01). For the RbLaTa_02 parent perovskite, the leaching process is faster in the first day and slows down progressively, reaching a final value of 98.0%. The XRD patterns indicated that the RbLaTa_01 starting sample (thermal treatment at 1200 °C for 18 h) contains a larger amount of RbLaTa_07 crystalline phase compared to the RbLaTa_02 host, annealed in harsh conditions (i.e., 950 and 1200 °C for 36 h). We have observed a slightly faster ion exchange dynamic for the RbLaTa_01 sample compared with RbLaTa_02, but on the other hand there is no information on the precise location in the crystalline lattice of Rb⁺, which was replaced by H⁺.

As Colomban et al. [35] observed, in the beginning of the protonation reaction, the process takes place near the material surface. After the progressive filling of vacancies, the reaction could be slowed down because the protonation into the core/center of the materials requires a diffusion of protons, V_O (oxygen vacancy) and O^{2-} species. For our samples, it might be possible that HLaTa_01 solid contains more oxygen vacancies compared to HLaTa_02, facilitating the Rb⁺ exchanges with H⁺.



Figure 4. SEM-EDS elemental mapping images of HLaTa_01 protonated perovskite for La, Ta and O elements.



Figure 5. Time course of Rb⁺ leaching after acid treatment of RbLaTa_01(02) samples.

Thermogravimetric analyses carried out for HLaTa_01(02) catalysts (Figure 6) reveal four main mass loss steps in the 25–1000 °C temperature range (Table 2). The first two mass loss steps, with maximum at 104 and 329 °C for HLaTa_01 and 104 and 227 °C for HLaTa_02, can be assigned to the elimination of adsorbed water corresponding to values of 1 and 2 mol H₂O per unit formula of each protonated perovskite (Equations (2) and (3)):

$$HLaTa_2O_7 \cdot H_2O \rightarrow HLaTa_2O_7 + H_2O \text{ for } HLaTa_01 \text{ soild}$$
(2)

$$HLaTa_2O_7 \cdot 2H_2O \rightarrow HLaTa_2O_7 + 2H_2O \text{ for } HLaTa_02 \text{ solid}$$
(3)



Figure 6. Thermal analyses (TGA, DTG and DTA curves) of (**A**) HLaTa_01 and (**B**) HLaTa_02 protonated layered perovskites with a heating rate of 10 $^{\circ}$ C·min⁻¹ in air atmosphere.

Table 2. Mass loss at different steps of thermogravimetric (TG) curves, amount of water and exchange degree of HLaTa_01(02) protonated layered perovskites.

	Mass Loss (%)							Amount of H ₂ O	Protonation
Catalyst	Step I 25–250 °C	Step II 250–380 °C -	Steps I + II 25–380 °C		Step III 380–610 °C		Step IV	per Unit Formula (Moles)	Degree Calculated from
			th.	exp.	th.	exp.	610–1000 °C	Steps I + II	Step III (%)
HLaTa_01	1.61 (max. at 104 °C)	0.55 (max. at 329 °C)	2.80	2.16	1.46	1.07 (max. at 506 °C)	traces	1	73
HLaTa_02	4.11 (max. at 104 °C)	1.73 (max. at 227 °C)	4.90	5.84	1.46	0.67 (max. at 557 °C)	0.22 (max. at 749 °C)	2	46

th. and exp. denotes theoretical and experimental values.

The experimental values of the weight losses were 2.16% for HLaTa_01 and 5.84% for HLaTa_02, and are close to the theoretical values corresponding to elimination of one of two molecules of water, respectively. The third step with maximum at 506 °C for HLaTa_01 and 557 °C for HLaTa_02 assigned to the loss interlayer proton as water, takes place by consumption of lattice O²⁻ (Equation (4)). The experimentally observed mass losses for step III were 1.07% and 0.67% for HLaTa_01 and HLaTa_02, respectively. The fourth step on the thermogravimetric (TG) curve (Equation (5)) showing negligible mass loss is indicative that the deprotonation process was completed up to 610 °C [36]. The process can be described following Equations (4) and (5), in agreement with the literature [37,38].

$$HLaTa_2O_7 \rightarrow LaTa_2O_{6.5} + 1/2H_2O \text{ Step III}$$
(4)

$$LaTa_2O_{6.5} \rightarrow 1/2Ta_2O_5 + LaTaO_4 \text{ Step IV}$$
(5)

Step IV described in Equation (5) represents the endothermic lattice rearrangement process related to the segregation of the Ta_2O_5 phase. Silyukov et al. [39] witnessed four stages of weight loss for HNd Ta_2O_7 , the last step being associated to the phase transformation from the metastable Nd $Ta_2O_{6.5}$ to the thermodynamically stable LaNd O_4 compound. On the other hand, two weight losses owing to the elimination of intercalated water and deprotonation stage for $H_xNa_{1-x}LaTiO_4\cdot yH_2O$ compound were observed by Miyake and co-workers [40].

The analysis of step III thermogravimetric results, collected in the 380–610 °C temperature range, allows the calculation of perovskite protonation degree (Table 2). According to Equation (4), the theoretical weight loss in step III should be 1.46% if all Rb⁺ ions replaced by H⁺ are located in the interlayer positions. The experimental weight loss value of 1.07% obtained for HLaTa_01 leads to the idea that 73% of material is composed of HLaTa₂O₇ layered phase, in which H⁺ are located between

interlayer positions. For the second solid (i.e., HLaTa_02), a protonation degree of only 46% was obtained, resulting in that RbLaTa_02 starting material has a lesser RbLaTa₂O₇ phase in its composition compared to RbLaTa_01. Indeed, the XRD results prove that longer thermal treatment leads to Rb⁺ segregation as the Rb₂CO₃ phase on the surface of the RbLaTa_02 host [8], resulting in less of the layered RbLaTa₂O₇ phase being available for proton exchange. These observations are in agreement with XPS results (Table 3), certifying that larger amount of HLaTa₂O₇ phase was obtained on HLaTa_01 product (66%) compared to HLaTa_02 (61%). Moreover, monitoring by IC (Figure 5) of Rb⁺ cation leaching during the acid treatment of starting materials was slower for the sample calcined in harsh conditions (i.e., RbLaTa_02).

Table 3. Surface composition (in at. %), amount of hydroxyl groups and specific surface area of HLaTa_01(02) protonated layered perovskites.

Catalyst	0 (at. %)	La (at. %)	Ta (at. %)	La/Ta	Proportion of Phase Composition after Protonation (%) ¹		Amount of –OH Calculated from	SSA (m ² ·g ⁻¹)
					HLaTa ₂ O ₇	Ta_2O_5	⁻ FTIK (μmol·g ⁻¹) ⁻	
HLaTa_01	71.9	4.1	24.2	0.20	66	34	2876	8
HLaTa_02	73.7	3.8	22.5	0.20	61	39	2198	6

¹ Proportion of phase composition determined by XPS analysis from the inspection of Ta 4f emission line; ² determined by FTIR spectroscopy at the wavelength of 3407 cm^{-1} using La(OH)³ as standard.

The specific surface area (SSA) of HLaTa_01 catalyst is 25% larger (8 m²·g⁻¹) compared to HLaTa_02 (6 m²·g⁻¹) (see Table 3). According to XRD analysis (Figure 1), the RbLaTa_01 host annealed in milder conditions (i.e., 1200 °C and 18 h) contained higher concentration of layered RbLaTa₂O₇ crystalline phase compared to RbLaTa_02 host calcined in harsh conditions (i.e., 950 and 1200 °C, 36 h). This fact certifies the idea that the higher RbLaTa₂O₇ perovskite phase purity is, the larger the specific surface area of derived protonated material. Note that the SSAs of HLaTa_01(02) were enlarged by almost three times as compared to starting RbLaTa-based materials (see Table 4 from [8]). In essence, Rb⁺-proton exchange treatment was beneficial in terms of increasing the population of active sites responsible for photocatalytic activity as we will see in the next section. The XRD and BET analyses demonstrated the great influence of the modified proton-layered perovskites over the crystallinity and surface characteristics of the final products.

The optical properties of acid-treated layered perovskite catalysts were investigated through UV-Vis spectra (Figure 7). HLaTa_01(02) protonated products displays two absorption maxima at \approx 250 and 312 nm ascribed to the transition of the O 2p orbital from valence band to Ta 5d orbital from the conduction band. The optical band gaps of the protonated forms were calculated using the Tauc method (see insert of Figure 7) by representing $[F(R)h\nu]^{1/\eta}$ versus photon energy (hv), where F(R) is the Kubelka–Munk function and $\eta = 2$, the value specific for indirect transition. To calculate the band gap, it was firstly estimated a line segment to model the sub-gap absorption baseline for each of the linear decreases identified in the graph. The intersection of the linear parts/decreases of the Tauc relationship with these "baselines" gives the Eg values [41]. The calculated E_g were 3.22 eV for HLaTa_01 and 3.23 eV for HLaTa_02, respectively, and are in the range of values reported in the literature for protonated layered materials [32]. A second band gap could also be identified with results noted to 4.22 eV for both HLaTa_01(02). It was attributed to the minority Ta₂O₅ phase, which matches the experimental values previously reported in the literature for commercial Ta_2O_5 (4.0 eV) [42]. Indeed, XRD results (Figure 1) and XPS analysis (Table 3) confirms the presence of HLaTa₂O₇ and some amount of Ta₂O₅ phase existing in the obtained protonated perovskites. Similar additional band gaps were observed for binary (CuO)_{0.6}(CeO₂)_{0.4} system [43]. Due to wide band gap of Ta₂O₅ (\approx 4 eV), its light-absorption is limited to a very narrow part of the solar spectrum, thus strong UV light is necessary for performing photocatalysis. This indicates that HLaTa₂O₇ layered morphology is the active phase in our photocatalytic systems.



Figure 7. UV-Vis spectra of HLaTa_01(02) protonated products and their corresponding band gap energy values.

The FTIR spectra of HLaTa_01(02) protonated perovskites (Figure 8) show two broad bands around 3380 and 1647 cm⁻¹ assigned to stretching and bending vibration mode of O-H and/or H₃O⁺, respectively [44]. The new band appearing at 935 cm⁻¹ was allocated to the bending mode of hydroxyl groups [45]. We note that this absorption band was not evinced in the RbLaTa_01(02) parental layered oxides (see Figure S1, Supplementary Information). Sasaki and co-workers [46] pointed out that hydroxyl groups in layered protonated materials yield characteristic absorption band at 950–1000 cm⁻¹. On the other hand, the work of Yuan et al. [47] claimed that the band at 920 cm⁻¹ of protonated material can be assigned to hydroxyl groups. This last report agrees with our results, showing that the peak at 935 cm⁻¹ is indicative of the successful alkali-ion exchange by H⁺. The strong band at 654 cm⁻¹ increase significantly for HLaTa_01 and was attributable to the vibration of Ta-O bonds in TaO₆ octhaedral layers. The lower band absorption positioned at 463 cm⁻¹ corresponds to Ta-O-Ta vibrations [48].

The analysis of 1900–3700 cm⁻¹ domain (see the insert from Figure 8) corresponding to –OH group vibration reveals that HLaTa_01 possess higher concentration of interlayer hydroxyl groups compared to HLaTa_02 protonated material. The corresponding absorption band of hydroxyl groups of HLaTa_01(02) catalysts are observable at 3380 and 3275 cm⁻¹. The FTIR spectr results also confirm that the proton interlayer was successfully incorporated in the studied samples. This observation is well correlated with XPS results (see Figure 9A), evidencing the appearance of a new peak in the O 1s emission line, after the protonation process.



Figure 8. FTIR spectra of HLaTa_01(02) proton-exchanged layered perovskites. The insert represents the magnified region corresponding to hydroxyl group.



Figure 9. XPS spectra of HLaTa_01(02) protonated products for (**A**) O 1s and (**B**) Ta 4f emission lines. The O 1s spectrum of RbLaTa_01(02) starting materials (**C**) showing the presence of Rb-O species, is given. Reprinted with permission from reference [8]. Copyright (2019) Elsevier.

As has been reported in our previous work [8], we determined by FTIR spectroscopy the quantity of hydroxyl groups contained by HLaTa_01(02) protonated perovskites using the reference peak at 3407 cm⁻¹ of La(OH) standard. The obtained values (Table 3) demonstrated that concentration of hydroxyl groups increased twice for HLaTa_01 and tripled for HLaTa_02 after the ion-exchange reaction compared to the RbLaTa_01(02) starting materials (see also Table 4 from ref. [8]).

To provide more insight regarding the surface-decorated functional groups of the HLaTa_01(02) proton-containing layered perovskites, X-ray photoelectron spectroscopy (XPS) measurements were attained. The O 1s spectrum of HLaTa_01(02) (Figure 9A) is fitted with three peaks.

The peaks at binding energies 530.1 and 531.3 eV are ascribed to lattice oxygen (Ta-O and La-O bonds) [49] and surface hydroxyl groups (O/OH), respectively [50]. In this spectrum, a new peak, which is absent in unprotonated samples, appearing at 532.6 eV indicates the presence of protonated OH species (i.e., $H^+(O-H^+))$ [51] for both HLaTa_01(02) solids. It is noteworthy that the peak at 528.8 eV, characteristic of Rb-O bond stretching observed in RbLaTa-based perovskites starting materials (see Figure 9C), disappeared after the protonation procedure. This fact certifies that Rb⁺ cations were exchanged with H⁺, leading to HLaTa_01(02) products. The weight of O²⁻ (La-O, Ta-O), O (OH) and O (O-H⁺) oxygen species for HLaTa_01 catalyst was 53.8%, 28.1% and 18.1%, respectively. For the second investigated proton-containing catalyst (i.e., HLaTa_02), the relative concentration of O^{2-} (La-O, Ta-O), O (OH) and O (O-H⁺) species was 69.7%, 21.9% and 8.4%, respectively. The XPS results demonstrate that relative density of surface OH groups, with impact on surface-driven photocatalytic processes of HLaTa_01 sample is more than twice compared with HLaTa_02. Acknowledging that surface OH pool is essential for the supply of strongly oxidizing OH radical by reaction with photogenerated holes (h⁺) [52], we can predict that the higher the surface hydroxyl density is, the more active the photocatalyst will be to mineralize TCE to Cl⁻ and CO₂. As we shall see in what follows, the photocatalytic performances of HLaTa_01 greatly overpass those of HLaTa_02, and one pertinent explanation for this behavior resides in the creation of active photocatalytic sites by protonation.

The Ta 4f state of HLaTa_01(02) catalysts (Figure 9B) changes dramatically after alkali-proton exchange treatment. It is characterized by one broad peak composed of two sets of Ta 4f doublets, indicating the presence of two state of tantalum. The two peaks located at Ta $4f_{7/2} = 25.6$ eV and Ta $4f_{5/2} = 27.7$ eV are ascribed to Ta⁵⁺-dominant HLaTa₂O₇ phase (66% for HLaTa_01 and 61% for HLaTa_02). In this case, the spin orbit splitting is calculated at 2.1 eV. Another set of doublets observed at 26.9 and 28.8 eV, respectively, are attributed to Ta $4f_{7/2}$ and Ta $4f_{5/2}$ (energy separation of 1.9 eV) due to spin-orbital interactions belonging to Ta⁵⁺ species of the Ta₂O₅ phase (34% for HLaTa_01 and 39% for HLaTa_02) [53]. Indeed, the examination of the Ta 4f emission line corroborated with XRD patterns of protonated products (Figure 1), certifying the formation of Ta₂O₅ phase.

The deconvolution spectrum of La $3d_{5/2}$ recorded on HLaTa_01(02) (see Figure S2, Supplementary Information) indicates a peak at 835.0 eV which belongs to the La $3d_{5/2}$ component and its corresponding satellite at 838.7 eV [54]. For both investigated proton-containing perovskites, the binding energy difference between the main $3d_{5/2}$ peak and its characteristic satellite (ΔE_{sat}) is 3.73 eV. The ΔE_{sat} values reported in the literature for the La $3d_{5/2}$ peak are given as 4.6 eV for La₂O₃, 3.9 eV for La(OH)₃ and 3.5 eV in the case of La₂(CO)₃ [55]. The obtained ΔE_{sat} value of our protonated perovskites is attributed to HLaTa₂O₇ mixed oxide compound and corresponds to La³⁺ valence state.

The elemental compositions of HLaTa_01(02) protonated products (in at %) determined by XPS analysis of O, La and Ta are shown in Table 3.

The chemical formulas derived from the surface composition data for HLaTa_01 and HLaTa_02 are, in the limit of experimental determination errors, $H_{3.18}LaTa_{5.91}O_{17.67}$ and $H_{6.51}LaTa_{5.98}O_{19.39}$, respectively. The corresponding phase composition of HLaTa_01 can be approximated as HLaTa₂O₇, $(Ta_2O_5)_2 \cdot H_2O$ and of HLaTa_02 as HLaTa₂O₇, $(Ta_2O_5)_2 \cdot 2H_2O$. These data correlate with TG analysis results (Table 2), proving that the HLaTa_02 sample retains more water compared to HLaTa_01. The XPS analysis reveals also that some amount of Ta₂O₅ phase segregates at the material surface. This fact is certified by XRD weak reflection of Ta₂O₅ crystalline phase (see Figure 1). The La/Ta ratio

drastically decreases at a value of 0.2 after the proton exchange compared to the freshly RbLaTa_01(02) (i.e., La/Ta \approx 1). It indicates that beside the rubidium cation–proton exchange upon acid treatment, some of the Ta ions may be replaced with two protons (2H⁺) to form a hydrated tantalum pentoxide (Ta₂O₅·H₂O). Indeed, the Ta 4f core-level (Figure 9B) confirms the existence of Ta₂O₅ phase in both HLaTa_01(02) catalysts.

2.2. Photocatalytic Degradation of TCE over Rb⁺-Proton Exchanged Layered Perovskites

The photocatalytic performance of HLaTa_01(02) protonated perovskites was evaluated for photomineralization of trichloroethylene (TCE) under simulated solar light. TCE is a halogenated volatile organic compound (Cl-VOC) known for its excellent solvent properties, which become one of the most prevalent contaminants subsisted in environment media [56]. Figure 10 illustrates the time course of TCE and Cl⁻ concentrations over the HLaTa_01(02) photocatalysts in comparison with two commercial oxides supplied from Merck (i.e., La₂O₃, Ta₂O₅).



Figure 10. Time-evolution of trichloroethylene (TCE) and Cl⁻ concentrations over HLaTa_01(02) protonated photocatalysts and the commercial oxides. Closed symbols stand for TCE concentration, whereas the open symbols represent Cl⁻ concentration. Experimental conditions: initial concentration of TCE = 5 mg·L⁻¹; T = 18 °C; simulated solar irradiation, $m_{catalyst} = 0.05$ g; V water = 110 mL.

The TCE concentration decreases drastically over HLaTa_01 catalyst after 5 h of light irradiation (see close symbols in Figure 10). The less active HLaTa_02 photocatalyst show little improvement for TCE abatement compared to the unprotonated form (i.e., RbLaTa_01(02), ref. [8]). The amount of Cl⁻ released in time (see open symbols in Figure 10) during TCE degradation indicates that HLaTa_01 mineralize efficiently TCE to Cl⁻, which is an essential characteristic of a performant depollution photocatalyst. The order of activity based on the amount of Cl⁻ release in time is HLaTa_01 (1.026 mM) >> La₂O₃ (0.175 mM) > HLaTa_02 (0.084 mM) \approx Ta₂O₅ (0.078 mM).

Assuming pseudo-first order kinetics for TCE photodegradation, the apparent rate constant k (min⁻¹) was obtained from slope of ln (C/C_0) against time (t) and plotted in Figure 11. The C and C_0 designate TCE concentration at time 0 and time t, respectively. The order of rate constant values at

the end of reaction (see insert of Figure 11) is the following: HLaTa_01 (0.398 min⁻¹) > RbLaTa_02 (0.248 min⁻¹) > RbLaTa_01 (0.232 min⁻¹) > HLaTa_02 (0.197 min⁻¹) > La₂O₃ (0.123 min⁻¹) > Ta₂O₅ (0.078 min⁻¹). These results clearly demonstrate that the protonation route dramatically enhances the photodegradation of TCE over HLaTa_01 photocatalyst due to: (i) the increase in OH group density on photocatalyst surface and/or (ii) the increase in specific surface area.



Figure 11. Pseudo-first order representation for TCE photodegradation over HLaTa_01(02) protonated layered perovskites, RbLaTa_01(02) starting materials and the commercial oxides. Insert represents the rate constant k (min⁻¹).

Figure 12 displays the TCE conversion over HLaTa_01(02) catalysts, Ta₂O₅ and La₂O₃. Remarkably, the conversion of TCE over the most active protonated perovskite HLaTa_01 reached 89%. The HLaTa_02 sample exhibited significantly lower performance, showing only 63% conversion of TCE. It appears that the increase in surface area by protonation has a positive contribution by increasing the number of exposed photoactive sites and/or by improving TCE adsorption (retention). The obtained TCE conversion values are higher compared to commercial oxides.

Figure 13 shows the chlorine distribution (in mol. %) at the end of 5 h of simulated solar irradiation. The ionic chlorine (depicted in cyan color) is a crucial performance parameter because it reflects the photocatalyst mineralization activity. The organic chlorine (depicted in gray and yellow pale colors) represents the chlorine contained by unconverted TCE and that by the organic intermediate (dichloroacetyl chloride). The most efficient photomineralization catalyst, in terms of Cl⁻ extraction form TCE, is HLaTa_01 (\approx 68 mol. %) > La₂O₃ (\approx 12 mol. %) > HLaTa_02 (\approx 6 mol. %) > Ta₂O₅ (\approx 5 mol. %). Generally, replacement of interlayer Rb⁺ cations by protons in the galleries of HLaTa_01 perovskite drastically enhances photomineralization efficiency compared to RbLaTa_01 host, see ref. [8]. The obtained results reveal that the higher surface area of HLaTa_01 (i.e., 8 m²·g⁻¹) and its larger density of interlayer –OH (confirmed by IR spectra) favors the mineralization of the chlorinated pollutant.



Figure 12. TCE conversion of HLaTa_01(02) photocatalysts and the commercial oxides.



Figure 13. Chlorine distribution after 5 h of reaction time over HLaTa_01(02) protonated photocatalysts and the commercial oxides.

An important outcome of the obtained results is the identification of the parameters that govern the behavior of HLaTa_01(02) systems. The protonation process appears to be strongly dependent on the layered perovskite crystalline phase content of the RbLaTa-starting material. Indeed, the presence of a non-perovskitic impurifying phases leads to composition instability [34]. We claim that HLaTa_01 is close to the fully protonated form compared to HLaTa_02 catalyst. This fact implies higher activity for hydroxyl radical production and thus improved photocatalytic performance. Another aspect is related to the specific surface area of HLaTa_01 which was enlarged after Rb⁺/H⁺-exchange compared

to the HLaTa_02 photocatalyst. Also, the predominant sandwich nanoarchitecture of HLaTa_01 proved to be beneficial for enhanced charge transfer at the interface due to the reduction in photocharge and recombination. Figure 14 confirms the dependence of Rb⁺-H⁺ exchange degree measured by ion chromatography (see also Figure 5) with the amount of Cl⁻ obtained after the mineralization of TCE over HLaTa_01(02) catalysts. A performing photocatalyst for environmental remediation must be active to produce ·OH radicals which rapidly mineralize the organic pollutant to unharmful CO₂. The hydroxyl radicals are produced by the reaction between holes (h⁺) and the –OH groups of the photocatalyst [57].



Figure 14. Dependence of proton exchange degree measured by ion chromatography with the amount of Cl⁻ obtained after the mineralization of TCE over HLaTa_01(02) catalysts.

The photocatalytic degradation of TCE over the HLaTa_01(02) photocatalysts can be explained by two mechanism pathways: (1st step) the transformation of TCE to intermediate chlorinated compound and (2nd step) the mineralization of chlorinated intermediate to Cl⁻ and CO₂. The first step involves the redox process with participation of photogenerated electron/hole (h_{VB}^+ - e_{CB}^-) pairs. The increase in the photocatalytic efficiency is related to rate ·OH radicals photogeneration, principally by reaction between holes (h⁺) and surface hydroxyl groups (–OH). The formed OH radicals (·OH) are proposed to be strongly oxidizing agents and can mineralize the organic pollutant to unharmful products. Various possible mechanisms are postulated for TCE photodegradation. Pruden and Ollis [58] reported complete mineralization of TCE in water using TiO₂, suggesting that ·OH initiates the reaction and dichloroacetaldehyde is identified as by-product. In another study, hydroxyl radical or hydroperoxide radical were claimed to initialize the reaction which leads to the production of dichloroacetaldehyde as an intermediate [59]. The photo-oxidation of TCE on titanium dioxide has been investigated by Fan and Yates [60] using infrared spectroscopy, indicating dichloroacetyl chloride as intermediate species.

There are several factors influencing the rate of photocatalytic degradation of organic pollutants, such as initial concentration, pH value, wavelength, intensity of light, specific surface area and the morphology of the photocatalyst [61]. Apart from those listed above, reaction temperature is another parameter to be mentioned. In general, the temperature has little influence on photocatalyst performances because the rate determining step is the reactant diffusion to reactive sites. It is well

known that the diffusion coefficient dependence on temperature is $\alpha T^{1/2}$ [62]. Therefore, moderate variations in reaction temperature will have negligible effects on reaction rate.

Based on the obtained results, we have proved that there are some advantages induced by the protonation of layered perovskites, such as: (i) enlarging specific surface area; (ii) increasing of –OH group density; (iii) limiting poisoning of the catalyst surface with carbonate species which cannot be eliminated when strongly alkaline ions such as Rb⁺ are present. Replacing interlayer rubidium with protons in RbLaTa₂O₇ perovskite produces a better final product by limiting its degradation over time. Interlayer modification via ion-exchange of layered RbLaTa₂O₇ perovskite was found to serve as potential way to obtain novel photocatalysts with high activity for the abatement of harmful organochlorinated compounds under simulated solar light.

3. Materials and Methods

3.1. Synthesis of RbLaTa₂O₇ Starting Material

Two samples labeled as RbLaTa_01 and RbLaTa_02 prepared by a procedure reported elsewhere [8] were used as host compounds. Briefly, equimolecular amounts of Rb_2CO_3 , La_2O_3 and Ta_2O_5 with 50% molar excess of rubidium carbonate were mixed together and subjected to different thermal treatments as follows: the first sample was heated at 1200 °C for 18 h (i.e., RbLaTa_01) while the second was treated at 950 °C and 1200 °C for 36 h (i.e., RbLaTa_02).

3.2. Preparation of Protonated HLaTa₂O₇ Compound

Both RbLaTa_01(02) starting materials were ion exchanged with 1M HCl (37.5%, Alfa Aesar, Karlsruhe, Germany) at room temperature for one week with daily centrifugation and renewal of the acid solution to achieve complete exchange of Rb⁺ cation with H⁺ from the interlayer. The protonated products were recovered by centrifugation, washed with distilled water and finally dried in air atmosphere at 80 °C overnight. These samples were denoted as HLaTa_01, corresponding to the RbLaTa_01 starting material, and HLaTa_02, analogous to the RbLaTa_02 perovskite host.

3.3. Samples Characterization

The HLaTa_01(02) protonated perovskites were characterized by powder X-ray diffraction Rigaku Corporation, Tokyo, Japan, (XRD) collected on a diffractometer with monochromatic Cu Kα radiation $(\lambda = 1.5418 \text{ Å})$ in the $2\theta = 5^{\circ}-70^{\circ}$ range with 0.02° steps. The average crystallite size was calculated by the Scherrer equation. The morphology of the samples was analyzed with a high-resolution microscope, FEI Quanta3D FEG device, Brno, Czech Republic, operating at 5 kV, in high-vacuum mode with Everhart–Thornley secondary electron (SE) detector coupled with EDS analysis. The mapping measurements of the samples were determined at an ambient temperature by the EDAX-EDS system. The specific surface area measurements were determined by N₂ adsorption isotherm at 77 K using a Micrometrics ASAP 2020 apparatus, Norcross, GA, USA. Prior to measurements, the protonated materials were outgassed under vacuum at 200 °C for 4 h. the BET method was applied to only determine the specific surface area. The thermal behavior of the protonated compounds was measured by thermogravimetric/differential analysis, Mettler Toledo, Greifensee, Switzerland (TG/DTG/DTA) with Mettler Toledo TGA/SDTA 851^e apparatus in flowing air atmosphere using an alumina crucible. The maximum temperature was set at 1000 °C with a heating rate of 10 °C·min⁻¹. UV-Vis spectra were obtained using Perkin Elmer Lambda 35 spectrophotometer, Shelton, CT, USA equipped with integrating sphere. The reflectance was converted to absorption using the Kubelka–Munk function. Fourier transform infrared (FT-IR) spectra were recorded in transmission mode at room temperature from 4000 to 400 cm⁻¹ on a JASCO spectrophotometer, Tokyo, Japan. X-ray photoelectron spectroscopy (XPS) measurements were carried out using a SPECS spectrometer, Berlin, Germany with PHOIBOS 150 analyzer operating at a pass energy of 20 eV for the individual spectral lines and 50 eV for the extended spectra. A non-monochromatic radiation source (Al K α = 1486.7 eV) was used. The charge

compensation was realized by a flood gun of Specs FG15/40 type. The rubidium leaching during the acid treatment was verified by ion chromatography (Dionex ICS 900, Sunnyvale, CA, USA) through the dosing of Rb⁺ cations.

3.4. Photocatalytic Degradation of Trichloroethylene (TCE)

All photocatalytic experiments were carried out at 18 °C under simulated solar light irradiation using a 150 W short-arc Xe lamp (1000 W m⁻², Peccell-L01, Yokohama, Japan). The detailed procedure and the experimental set-up scheme were described elsewhere [8]. In brief, 0.05 g of photocatalyst was dispersed into the photoreactor containing 110 mL water and the desired concentration of TCE (50 mg·L⁻¹), and was kept under constant stirring to ensure adequate homogenization. Prior to irradiation, the suspension was stirred for 80 min in the dark to reach the adsorption–desorption equilibrium between the pollutant and the photocatalyst surface. The concentration of TCE in the head space was analyzed at regular time intervals (i.e., 30 min) by a gas chromatograph (Agilent 7890A) equipped with a flame ionization detector (FID) and an HP-PlotQ capillary column (30 m × 0.53 mm). The concentration of chloride ions (Cl⁻) was determined by ion chromatography (Dionex ICS 900) by extracting with syringe 2 mL liquid sample aliquots at 30 min time intervals and filtered through 0.45 µm Millipore filters to remove any nanoparticles before analysis.

4. Conclusions

We have explored an efficient strategy to increase the density of active sites of layered perovskites by protonation. Thereby, two RbLaTa-based stratified perovskite hosts have been successfully modified by replacing interlayer Rb cations with protons yielding HLaTa_01(02) protonated products. The predominant HLaTa₂O₇ crystalline phase was confirmed by XRD analysis in both samples. The quality of the obtained protonated products appeared to be dependent on the composition and structure of the parental layered perovskite. The O–H⁺ surface density as well as specific surface area of HLaTa_01 protonated solid exceeded that of the HLaTa_02 product. Hence, a dramatic increase in photomineralization of TCE was obtained for HLaTa_01 photocatalyst compared to HLaTa_02. We have demonstrated that layered perovskite modified by protonation leads to Cl⁻ enhancement due to multiple positive effects: (i) higher specific surface area; (ii) increasing of –OH group density and (iii) preventing poisoning with carbonate species coming from synthesis parameters. The proposed modification strategy opens up new opportunities for the design of successfully layered oxide photocatalysts with increased photocatalytic performance that cannot be obtained by common solid-state synthesis due to higher thermal treatment.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/10/6/637/s1, Figure S1: FTIR spectrum of HLaTa_01(02) protonated perovskites and RbLaTa_01(02) host materials in the region of interest < 1000 cm⁻¹, showing the modification of the bands absorption after Rb⁺/H⁺ exchange, Figure S2: XPS spectrum of La 3d emission line recorded for HLaTa_01(02) protonated products.

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