



# Photocatalytic Activity of *n*-Alkylamine and *n*-Alkoxy Derivatives of Layered Perovskite-like Titanates $H_2Ln_2Ti_3O_{10}$ (Ln = La, Nd) in the Reaction of Hydrogen Production from an Aqueous Solution of Methanol

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**Abstract:** Two series of hybrid inorganic-organic derivatives, obtained via the modification of protonated Ruddlesden–Popper phases  $H_2Ln_2Ti_3O_{10}$  (Ln = La, Nd) with intercalated *n*-alkylamines and grafted *n*-alkoxy groups, have been systematically investigated in relation to photocatalytic hydrogen production from a model of 1 mol % aqueous solution of methanol for the first time. Photocatalytic measurements were performed both for bare samples and for their composites with Pt nanoparticles as a cocatalyst using an advanced scheme, including dark stages, monitoring of the volume concentration of the sample in the reaction suspension during the experiment, shifts of its pH and possible exfoliation of layered compounds into nanolayers. It was found that the incorporation of organic components into the interlayer space of the titanates increases their photocatalytic activity up to 117 times compared with that of the initial compounds. Additional platinization of the hybrid samples' surface allowed for achieving apparent quantum efficiency of hydrogen evolution of more than 40%. It was established that the photocatalytic activity of the hybrid samples correlates with the hydration degree of their interlayer space, which is considered a separate reaction zone in photocatalysis, and that hydrogen indeed generates from the aqueous methanol solution rather than from organic components of the derivatives.

Keywords: photocatalysis; hydrogen; layered perovskite; titanate; intercalation; grafting

# 1. Introduction

The global environmental problems associated with the active industrial growth and the widespread use of fossil fuels over the last centuries are forcing humankind to develop waste-free technologies and alternative energy sources such as hydrogen fuel. Due to its undeniable eco-friendliness and high calorific value, hydrogen is a potential substitute for petroleum products and natural gas in various engines, which is of high significance in light of the impending energy crisis [1,2].

Heterogeneous photocatalysis is a promising method for hydrogen production from water and aqueous solutions of various organic compounds, including products of primary biomass processing [3]. Since water and solar energy are widely available free natural resources, their use for hydrogen generation appears to be efficient both in environmental and economic aspects [4,5]. However, photocatalytic water splitting with a high yield under solar radiation remains a difficult task due to thermodynamic and kinetic reasons [6,7];



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therefore, there is a need to search for other available substrates such as bioalcohols, carbohydrates and related biomass processing products. Their photocatalytic decomposition followed by the use of the hydrogen produced as fuel is expected to be much more energy efficient than direct biomass combustion due to a relatively low calorific value of the latter [8–16]. Furthermore, photocatalysis may also serve as a destructive method for aqueous media purification if the organic substances being decomposed are water contaminants [17–20].

Now most widely studied heterogeneous photocatalysts are simple wide-gap semiconductor oxides (TiO<sub>2</sub>, ZrO<sub>2</sub>, SnO<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub>, Ta<sub>2</sub>O<sub>5</sub>, WO<sub>3</sub>, etc.,) and materials on their basis [21]. However, their photocatalytic activity often proves to be insufficient due to the intensive electron-hole recombination, scarce specific surface area, and other reasons that justify the search for new, more efficient materials.

Among the promising heterogeneous photocatalysts for hydrogen generation, great attention is paid to ion-exchangeable layered perovskite-like oxides-solid crystalline compounds with a block-type structure, which can be represented as an alternation of negatively charged slabs with the thickness of the n corner-shared perovskite octahedra and interlayer spaces populated by alkali cations. According to structural features, ion-exchangeable layered perovskites may be classified into two groups: the Dion-Jacobson phases and the Ruddlesden–Popper phases, corresponding to general formulae  $A'[A_{n-1}B_nO_{3n+1}]$  and  $A'_{2}[A_{n-1}B_{n}O_{3n+1}]$ , respectively (A' = alkali cation, A = alkaline earth or transition cation, B = Nb, Ta, Ti, Zr, etc.,) [22–24]. Unique photocatalytic properties of these compounds are supposed to be associated with the propensity of their interlayer space for ion exchange and intercalation reactions [25-34], including potential intercalation of reactant species during a photocatalytic process [35,36]. A large number of studies are focused on the improvement of their photocatalytic activity via cationic and anionic substitution [37-41], introduction of metals and other inorganic particles [42–44], preparation of composite materials [45-49], creation of Z-schemes [50-54], sensitization with dyes [55], as well as exfoliation into nanolayers [56].

Protonated forms of ion-exchangeable layered perovskite-like oxides (A' = H), being solid acids, can also react with some organic substances, resulting in inorganic-organic derivatives, complex hybrid materials, consisting of chemically bonded layered perovskite matrix and interlayer organic components [57-59]. Introduction of organic modifiers into the interlayer space can proceed either as acid-base intercalation [60], which is typical of organic bases, or as esterification-like grafting [61], taking place in the case of reactions with alcohols [62], carbohydrates [63], alkoxysilanes [64], and organophosphorus acids [65]. A large number of recent studies in this field are devoted to the creation of hybrid inorganic-organic nanomaterials based on perovskite nanosheets that are suggested to be promising catalysts, chemical sensors, electrode components, and fillers for functional polymers. These hybrid materials may be prepared in a variety of ways, the main of which are the liquid exfoliation of organically modified hosts and covalent bonding of organic molecules with preliminarily obtained nanosheets. Having said so, a wide range of compounds can act as surface modifiers, such as simple *n*-alkoxy groups, unsaturated organic phosphates, polyacrylamides, cellulose diacetate, etc., [66–69]. In the last decade, special attention has also been focused on the use of microwave-assisted methods to speed up intercalation and grafting as well as post-synthetic surface modification of perovskite nanosheets with aliphatic and aromatic amines, diaminoalkanes, alcohols and other compounds [27,70,71]. Furthermore, the microwave approach allows for preparing those inorganic-organic derivatives that cannot be obtained directly via the conventional benchtop reactions [72]. Another actively developing area is the creation of inorganic-organic halide perovskites mainly for solar cells and related applications [73–77]. Nevertheless, the available literature poorly covers the use of the inorganic-organic oxides with regard to photocatalysis and, particularly, photocatalytic hydrogen production.

Since the interlayer space of layered perovskite-like oxides is should act as a separate reaction zone in photocatalysis [46], its modification with organic components may

strongly influence the photocatalytic activity. However, the number of reports on hybrid inorganic-organic photocatalysts remains low, which is probably connected with the doubts concerning their stability under the reaction conditions. For instance, the *n*hexylamine intercalated tantalate HCa2Ta3O10 [78] demonstrated increased photocatalytic activity towards water splitting under ultraviolet irradiation. Nevertheless, its activity was found to drastically decrease after a few hours of illumination, which was associated with the *n*-hexylamine oxidation and subsequent interlayer space contraction. Authors of another study [79] reported on the improved activity of the tantalate  $H_2CaTa_2O_7$ , modified by *n*-alkoxy groups, with regard to water purification from rhodamine and methyl orange as model pollutants. The photocatalytic performance of the *n*-alkoxy derivatives was established to increase with the raising hydrocarbon chain length. Our recent paper on photocatalytic properties of the *n*-butylamine intercalated titanate  $H_2Nd_2Ti_3O_{10}$  [80] demonstrated its high activity in the reactions of hydrogen evolution from aqueous nalcohols as well as pure water under ultraviolet light. Our other reports, devoted to the photocatalytic properties of the niobates  $HCa_2Nb_3O_{10}$  modified by *n*-alkylamines [81] and *n*-alkoxy groups [82], showed the correlation of the activity observed with the hydration degree of the interlayer space and the maximum interlayer water content corresponded to the most active sample. Thus, our recent investigations demonstrated the effectiveness of the interlayer organic modification as an approach to the enhancement of the photocatalytic performance of the Dion–Jacobson niobates. However, there are no other systematic studies in the literature that would show correlations between the photocatalytic properties and organic modifiers used. Particularly, this issue is not considered for the Ruddlesden-Popper phases being promising photocatalysts for hydrogen production [26].

Layered perovskite-like compounds  $H_2Ln_2Ti_3O_{10}$  are protonated forms of the Ruddlesden–Popper titanates  $A_2Ln_2Ti_3O_{10}$  (A = alkali cation, Ln = La or lanthanide) whose structure consists of alternating perovskite slabs with a thickness of n = 3 titanium-oxygen octahedra, separated by interlayer spaces containing single charged cations [83]. Their photocatalytic activity in the reaction of hydrogen production is known to rise in the series of interlayer cations  $A^+ = Li^+$ ,  $Na^+$ ,  $K^+$ ,  $Rb^+$  and to be lower in the case of completely protonated forms ( $A^+ = H^+$ ) [26]. The reports of the last decades are devoted to the modification of the aforementioned titanates with Ni, NiO, Au, Pt nanoparticles [84–86], doping by N, Fe, Sn, Ni, Zn, Cr, Nb, W and other elements [87–91], introduction of Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> into the interlayer space [92,93] as well as to influence of the preparation method on photocatalytic activity [94–96]. According to literature data, complex application of various modifications to the titanates  $A_2Ln_2Ti_3O_{10}$  allows for achieving the quantum efficiency of pure water splitting of more than 5% [26].

The present study is the first systematic investigation of the photocatalytic activity of hybrid inorganic-organic derivatives based on layered the perovskite-like titanates,  $H_2Ln_2Ti_3O_{10}$  (Ln = La, Nd), in relation to hydrogen generation from a model 1 mol % aqueous solution of methanol under near ultraviolet irradiation. This research uses relatively simple interlayer organic modifiers, *n*-alkylamines and *n*-alkoxy groups, to improve the photocatalytic performance of the inorganic hosts. Special attention is focused on structural features of the derivatives, feasible improvement of their activity via surface platinization as well as to their stability under photocatalytic conditions.

#### 2. Results and Discussion

#### 2.1. Identification of the Protonated Titanates

The initial protonated titanates,  $H_2La_2Ti_3O_{10}$  (HLT<sub>3</sub>) and  $H_2Nd_2Ti_3O_{10}$  (HNT<sub>3</sub>), used as precursors for the subsequent synthesis of inorganic-organic derivatives, were identified by means of XRD and TG. Their tetragonal lattice parameters were found to be a = 3.79 Å, c = 27.2 Å for HLT<sub>3</sub> and a = 3.78 Å, c = 27.2 Å for HNT<sub>3</sub>, which is consistent with the earlier reported values [83]. The *c* parameter in both cases is doubled towards the interlayer distance *d*, defined as the distance between the centers of adjacent perovskite slabs. Thus, the latter are stacked in a staggered conformation, characterized by a relative shift of the slabs on both lateral axes. The TG analysis of the titanates confirms the completeness of their interlayer space protonation as well as the presence of small amounts of intercalated water, which is typical of the compounds under consideration.

# 2.2. Analysis of the Inorganic-Organic Derivatives

Note: hereinafter, formulae  $HLT_3 \times RNH_2/HNT_3 \times RNH_2$  and  $HLT_3 \times ROH/HNT_3 \times ROH$  (R = methyl Me, ethyl Et, *n*-propyl Pr, *n*-butyl Bu, *n*-hexyl Hx, *n*-octyl Oc, and *n*-decyl Dc) are used only as conventions for corresponding inorganic-organic compounds, which do not reflect their true compositions.

The processing of XRD patterns of the hybrid inorganic-organic samples presented in Figure 1 proves the successful preparation of all of them in a single-phase state without noticeable amounts of impurities. All the reflections observed are amenable to indexing in the tetragonal system (only the indices necessary for discussion are signed in the figure). The modification of the interlayer space by *n*-alkylamines and *n*-alkoxy groups leads to its conspicuous expansion, confirmed by the characteristic low-angle offset of the (00x) reflections with an elongation of the organic chain length. At the same time, the *a* lattice parameter is practically unchanged indicating the preservation of titanium-oxygen octahedron sizes (Table 1). Unlike the case of the protonated titanates, XRD patterns of some inorganic-organic compounds, with the exception of methylamine, methoxy, ethoxy, *n*-propoxy and *n*-butoxy, can be fully indexed without the *c* parameter doubling, which points to the probable eclipsed conformation of their slabs. In addition, the (00x) reflections on the patterns of the hybrid samples are less intense and broader in comparison with those of the initial titanates, which may be due to the lowering of the lattice orderliness during the insertion of organic components as well as to smaller crystallite sizes.

Sample	a, Å	<i>c,</i> Å	d, Å	α, °	Sample	a, Å	c, Å	d, Å	
HLT <sub>3</sub>	3.79	27.2	13.6		HNT <sub>3</sub>	3.78	27.2	13.6	
$HLT_3 \times MeNH_2$	3.83	36.7	18.4		$HNT_3 \times MeNH_2$	3.81	35.4	17.7	
$HLT_3 \times EtNH_2$	3.82	20.2	20.2		$HNT_3 \times EtNH_2$	3.80	19.9	19.9	
$HLT_3 \times PrNH_2$	3.82	21.7	21.7	74	$HNT_3 \times PrNH_2$	3.78	21.5	21.5	71
$HLT_3 \times BuNH_2$	3.81	24.7	24.7	74	$HNT_3 \times BuNH_2$	3.78	24.4	24.4	/1
$HLT_3 \times HxNH_2$	3.87	29.4	29.4		$HNT_3 \times HxNH_2$	3.80	29.2	29.2	
$\text{HLT}_3 \times \text{OcNH}_2$	3.85	34.2	34.2		$HNT_3 \times OcNH_2$	3.80	33.4	33.4	
$HLT_3 \times MeOH$	3.81	35.1	17.6		$HNT_3 \times MeOH$	3.76	34.1	17.1	
$HLT_3 \times EtOH$	3.83	39.5	19.8		$HNT_3 \times EtOH$	3.77	40.9	20.5	
$HLT_3 \times PrOH$	3.83	44.2	22.1	79	$HNT_3 \times PrOH$	3.79	43.8	21.9	67
$HLT_3 \times BuOH$	3.82	48.5	24.3		$HNT_3 \times BuOH$	3.78	47.3	23.7	
$HLT_3 \times HxOH$	3.82	29.2	29.2		$HNT_3 \times HxOH$	3.81	28.3	28.3	
$\text{HLT}_3 \times \text{DcOH}$	3.82	31.3	31.3		$\text{HNT}_3 \times \text{DcOH}$	3.74	30.8	30.8	

**Table 1.** Structural parameters of the initial titanates and their inorganic-organic derivatives as well as tilt angles of organic chains.

The experimental dependences of the interlayer distance *d* on the number  $n_c$  of carbon atoms in the organic chain are shown in Figure 2 ( $n_c = 0$  relates to the unmodified protonated titanate). Assuming the all-trans-conformation of all interlayer organic components, their parallelism to each other and constant (or absent) chain overlapping, while taking into account the slope of the dependences (Figure 2) and hypothetical chain elongation with the insertion of the CH<sub>2</sub> group, we can estimate the average tilt angle  $\alpha$  between organic chains and perovskite slabs (Table 1). Thus, the inorganic-organic samples prepared are should have a paraffin-like bilayer with a slope of 67–79° (with the exception of R = Dc). The values obtained were found to be consistent with the literature ones calculated for related Ruddlesden–Popper titanates [32,62] and significantly exceed those determined for Dion– Jacobson niobates [61,65]. When going to the *n*-decoxy compounds, the graph slope vastly

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reduces, which may point to both the lower actual angle value and non-compliance with the aforementioned assumptions (for instance, other non-linear conformation of chains).

Figure 1. XRD patterns of the initial titanates and their inorganic-organic derivatives.



Figure 2. Dependences of the interlayer distance *d* on the organic chain length.

The Raman spectra of the inorganic-organic derivatives (Figure 3) consist of bands relating to the layered perovskite matrix  $(100-950 \text{ cm}^{-1})$  as well as to the inserted organic components. Particularly, latitudinal vibrations of H–C–O (1160–1170 cm<sup>-1</sup>), C–C–H  $(1340-1350 \text{ cm}^{-1})$ , CH<sub>2</sub>  $(1460-1470 \text{ cm}^{-1})$ , and NH<sub>2</sub>  $(1570-1580 \text{ cm}^{-1})$  fragments and the stretching of C–N (1030–1060 cm<sup>-1</sup>), C–O (1040–1060 cm<sup>-1</sup>) and C–H (2800–3050 cm<sup>-1</sup>) bonds are clearly seen. However, bands of the OH group stretching are not observed in the spectra of *n*-alkoxy derivatives, which is consistent with the presence in their structure of covalently bonded *n*-alkoxy groups, not intercalated molecular alcohols. Introduction of organic components into the interlayer space also leads to splitting of the band relating to the symmetric stretching mode of axial Ti–O bonds (820-830 cm<sup>-1</sup> for the initial titanates) into two new ones (720–780  $\text{cm}^{-1}$  and 870–910  $\text{cm}^{-1}$ ). Moreover, the position of the former depends on the *n*-alkylamine or *n*-alkoxy chain length, transferring to the lowfrequency region of Raman shifts with the chain elongation. The aforementioned splitting is, apparently, caused by the existence in the inorganic-organic derivatives of two types of external titanium-oxygen octahedra with different axial Ti-O distances, whose vertices are bonded to organic structures (Ti–O–RNH<sub>3</sub><sup>+</sup> or Ti–O–R, the low-frequency band) and protons (Ti– $O^-H^+$ , the high-frequency band). In the spectra of methoxy derivatives, the first band demonstrates much higher intensity and undergoes a greater low-frequency offset  $(670-680 \text{ cm}^{-1})$  whereas the second one becomes barely visible. However, the bands of the asymmetric stretching mode of axial Ti–O bonds (500–700 cm<sup>-1</sup>) and vibrations of central titanium-oxygen octahedra (470–490 cm<sup>-1</sup> and 680–700 cm<sup>-1</sup>) stay almost unchanged in the course of the organic modification of the interlayer space. During the collecting of Raman spectra, the distinctive propensity of *n*-alkoxy derivatives for fluorescence was also discovered. Specifically, visible lasers with a wavelength of 488-633 nm were found to be inapplicable for analysis of all the *n*-alkoxy compounds except the methoxy ones. The usage of these lasers resulted in the intense fluorescence in the Stokes bands' region, which completely overlapped Raman scattering regardless of a specific *n*-alkoxy group in the interlayer space ( $R \neq Me$ ). In view of these difficulties, the spectra of the corresponding derivatives were obtained using the 785 nm near-infrared diode laser. The location of the excitation wavelength near the absorption bands of the Nd-containing samples provided broad fluorescent stripes in the region of 1300–1800 cm<sup>-1</sup>, which can be seen in their spectra. Nonetheless, the data available do not provide a rigorous explanation to the fluorescence



under irradiation of the *n*-alkoxy derivatives by visible lasers since they, similar to the initial protonated titanates and *n*-alkylamine compounds, do not absorb light in this spectral range (Supporting Information S1 and S2).

Figure 3. Raman spectra of the initial titanates and their inorganic-organic derivatives.

The <sup>13</sup>C NMR spectra presented in Figure 4 clearly prove the successful obtainment of the inorganic-organic derivatives and confirm the absence of residual methyl and *n*butylamine in the interlayer space of those, which were synthesized using corresponding amine-containing compounds as precursors. In the spectra of the derivatives with longchain organic components (R = Hx, Oc, and Dc), some bands overlap because of close chemical shift values. Positions of the bands, referred to carbon atoms adjacent to the amine group, demonstrate a high field offset by an average of 2 ppm in comparison with those in the spectra of individual amines, which points to the existence of intercalated substances in the *n*-alkylammonium form. Carbon atoms adjacent to oxygen in the *n*alkoxy derivatives provide bands' offset by 16–19 ppm to the low field relative to the corresponding ones in the spectra of molecular alcohols, which serves as proof of the covalent bonding between the inorganic matrix and organic components. The *n*-decoxy derivative's spectrum also contains low intensity bands at approximately 21 and 41 ppm that can be assigned neither to the *n*-decoxy fragment nor to residual *n*-butylamine since the latter is absent in accordance with the elemental analysis data. These bands might be associated with the presence in the sample of small *n*-decanal amount formed via the partial oxidation of *n*-decanol by oxygen remaining in the reaction mixture. The first of the bands might also relate to residual *n*-heptane molecules, which was used as a solvent in the course of the synthesis.



Figure 4. <sup>13</sup>C NMR spectra of La-containing inorganic-organic derivatives.

The quantitative compositions of hybrid samples, established via the elemental CHNanalysis, are summarized in Table 2. The absence of nitrogen in *n*-alkoxy derivatives confirms the complete removal of the interlayer amines during the grafting of alcohols. Most compounds contain an average of 0.4–0.5 organic molecules or groups per proton of the initial protonated titanate as well as some amount of intercalated water. Participation of no more than half of the protons in the binding of the organic modifiers maintains with the literature's suggestion that already inserted organic components sterically block adjacent vertices of interlayer titanium-oxygen octahedra, making them unreactive [62], and clarifies the splitting of the bands, referred to the axial Ti–O bond symmetric stretching mode, in the Raman spectra (Figure 3). Most *n*-alkylamine derivatives, except those with long-chain amines (R = Hx, Oc), possess a higher degree of the interlayer space hydration compared with that of the initial titanates. Since the latter do not undergo direct water intercalation in the absence of amines, the hydration accompanying synthesis of the methylamine derivatives should be connected with the interlayer space broadening due to amine insertion as well as the formation of hydrogen bonds between amine and water molecules. Generally, the feasibility of quantitative hydration of the inorganic-organic derivatives is determined by the steric availability of their interlayer space and the intercalated amine's polarity compared with that of water. Moreover, the simultaneous influence of both factors may lead to non-monotonic correlations between the organic chain length and equilibrium amount of intercalated water. The inflow of the latter into the interlayer space of the *n*-alkylamine derivatives synthesized in aqueous solutions (R = Me, Et, Pr, and Bu) can occur from both these solutions and precursors, namely, protonated titanates and methylamine compounds. Those derivatives, which were prepared in anhydrous conditions, apparently preserve residual water from the methylamine precursors due to the thermodynamic unprofitability of its transition from the interlayer space into the less polar medium. In accordance with the synthesis methods, interlayer water in the *n*-alkoxy compounds may be both adopted from the amine-containing precursors and formed during the target grafting reaction. Among the *n*-alkoxy derivatives, greater degrees of the interlayer hydration are observed in the case of those with shorter organic chains (in particular, of the ethoxy compounds synthesized in the ethanol azeotropic solution).

**Table 2.** Quantitative composition of the initial titanates and their inorganic-organic derivatives written as  $H_2Ln_2Ti_3O_{10}$ ·xRNH<sub>2</sub>·yH<sub>2</sub>O (*n*-alkylamine samples) and  $H_{2-x}Ln_2Ti_3O_{10-x}$ ·xRO·yH<sub>2</sub>O (*n*-alkoxy samples).

Sample	x	у	Sample	x	у
HLT <sub>3</sub>	-	0.15	HNT <sub>3</sub>	-	0.15
$HLT_3 \times MeNH_2$	0.70	0.30	$HNT_3 \times MeNH_2$	0.70	0.30
$HLT_3 \times EtNH_2$	0.70	0.35	$HNT_3 \times EtNH_2$	0.70	0.35
$HLT_3 \times PrNH_2$	0.65	0.20	$HNT_3 \times PrNH_2$	0.70	0.20
$HLT_3 \times BuNH_2$	0.70	0.35	$HNT_3 \times BuNH_2$	0.75	0.35
$HLT_3 \times HxNH_2$	0.80	0.10	$HNT_3 \times HxNH_2$	0.90	0.10
$HLT_3 \times OcNH_2$	0.80	0.10	$HNT_3 \times OcNH_2$	0.85	0.15
$HLT_3 \times MeOH$	1.3	0.20	$HNT_3 \times MeOH$	0.95	0.25
$HLT_3 \times EtOH$	0.85	0.40	$HNT_3 \times EtOH$	0.85	0.35
$HLT_3 \times PrOH$	0.75	0.20	$HNT_3 \times PrOH$	0.75	0.30
$HLT_3 \times BuOH$	0.70	0.20	$HNT_3 \times BuOH$	1.1	0.25
$HLT_3 \times HxOH$	0.65	0.15	$HNT_3 \times HxOH$	0.80	0.10
$\text{HLT}_3 \times \text{DcOH}$	0.65	0.05	$\text{HNT}_3 \times \text{DcOH}$	0.65	0.05

The diffuse reflectance spectra of the samples under consideration as well as Tauc plots for the determination of optical bandgap energies  $E_g$ , are presented in Figure 5 as well as in Supporting Information S1 and S2. While light absorption by La-containing titanates in the absence of impurities is only due to interband transitions in the near-ultraviolet range, Nd-containing ones additionally have absorption bands in the visible region, which provides the purple color of their powders. The interlayer modification of the samples

by *n*-alkylamines and *n*-alkoxy groups does not affect the general spectrum appearance or provide new visible absorption bands. The change in the bandgap energy during the insertion of organic components does not exceed 0.16 eV and depends on the chain length non-monotonously (Table 3). All the hybrid samples possess lower  $E_g$  values compared with that of the unmodified titanates. Additionally, bandgap energies of most *n*-alkylamine derivatives are similar to those of *n*-alkoxy ones with the same chain length. According to the literature data, expansion of the interlayer space (for instance, by intercalated water molecules) is usually accompanied by a bandgap energy increase [97]. Since the formation of the inorganic-organic derivatives, despite the noticeable enlargement of the interlayer distance d, leads to  $E_{g}$  reduction, it appears reasonable to assume that the chosen organic components decrease its value, compensating for the opposite effect associated with drising. Unfortunately, the available data do not allow us to provide a rigorous explanation of the effect of organic components on the zone structure of the samples. This effect might be associated with a potential change in the energy level of photogenerated holes, localized on the interlayer oxygen atoms, under the action of organic structures bonded to them. However, this issue requires separate consideration. Generally, relatively weak influence of the organic modification on light absorption characteristics of the samples is quite expected since energy bands in titanium oxides are known to be formed by oxygen 2p-orbitals and titanium 3d-ones [98], which are not greatly affected by interlayer organic structures. Similar results were earlier observed for the inorganic-organic derivatives of the Dion-Jacobson niobate  $HCa_2Nb_3O_{10}$  [81,82]. Thus, the inorganic-organic samples in question should function as photocatalysts in the near-ultraviolet spectral range and the factor of available light cannot be the main reason for differences in their photocatalytic activity.



Figure 5. Tauc plots for the protonated titanates and some inorganic-organic derivatives.

The specific surface area of the samples is seen to slightly increase (1.2–1.7 times) upon the interlayer organic modification (Table 3). In the case of *n*-alkylamine derivatives, its value is proportional to the organic chain length. However, in the series of *n*-alkoxy compounds this trend is not observed. In general, the organically modified titanates in question demonstrate 2–3 times lower specific surfaces in comparison with the earlier reported inorganic-organic Dion–Jacobson niobates [81,82]. With that said, the factor of specific surface area should not be the key reason for differences in the photocatalytic activity of the samples.

An analysis of SEM images (Supporting Information S3 and S4) establishes that particles of both initial titanates and their inorganic-organic derivatives are predominantly plate-shaped, which is typical of layered perovskites [99]. Powders of the samples are clearly seen to be polydisperse. The lateral sizes of their particles are in the range of 0.5–4  $\mu$ m and the thickness of the particles is 200–600 nm. During the organic modification, the fraction of small particles no larger than 1  $\mu$ m increase, which apparently, is a result of their separation from bigger ones in the course of sonication of the precursors in the

methylamine solution and further chemical transformations. Some hybrid compounds also demonstrate partial lamination of polycrystals, resulting in the formation of visible slits, which may increase the specific surface area and make the derivatives in question potential precursors for the purposeful obtainment of perovskite nanosheets that are of great interest for many applications including photocatalysis.

Sample  $S, m^2/g$ Sample  $S, m^2/g$ Eg, eV  $\lambda_{max}$ , nm Eg, eV  $\lambda_{max}$ , nm HLT<sub>3</sub> 3.44 360 3.24 HNT<sub>3</sub> 3.47 357 3.08  $HLT_3 \times MeNH_2$ 3.34 371 3.88  $HNT_3 \times MeNH_2$ 3.40 365 3.72  $HLT_3 \times EtNH_2$ 3.39 366  $HNT_3 \times EtNH_2$ 3.32 373  $HLT_3 \times PrNH_2$ 3.40 365  $HNT_3 \times PrNH_2$ 3.33 372  $HLT_3 \times BuNH_2$ 3.42 363 4.09  $\text{HNT}_3 \times \text{BuNH}_2$ 3.33 372 3.89  $HLT_3 \times HxNH_2$ 3.41 364  $HNT_3 \times HxNH_2$ 3.35 370 4.39  $HLT_3 \times OcNH_2$ 3.40 365 4.38  $HNT_3 \times OcNH_2$ 3.36 369 5.73  $HLT_3 \times MeOH$ 3.33 3.33 372 4.51 372  $HNT_3 \times MeOH$  $\text{HLT}_3 \times \text{EtOH}$ 364 3.33 3.41  $HNT_3 \times EtOH$ 372 \_ \_  $\text{HLT}_3 \times \text{PrOH}$ 3.38 3.32 373 367  $HNT_3 \times PrOH$  $\text{HLT}_3 \times \text{BuOH}$  $\text{HNT}_3 \times \text{BuOH}$ 3.40 365 4.19 3.33 372 3.87  $HLT_3 \times HxOH$ 3.40 365  $HNT_3 \times HxOH$ 3.35 370  $HLT_3 \times DcOH$ 3.38 367 5.46  $HNT_3 \times DcOH$ 3.36 4.66 369

Table 3. Light absorption characteristics and specific surface area of the samples.

# 2.3. Thermal, Vacuum and Hydrolytic Stability of the Inorganic-Organic Derivatives

TG curves of the protonated precursors and hybrid compounds recorded in an oxidative atmosphere are shown in Supporting Information S5. The thermolysis of the former includes deintercalation of interlayer water (below 275 °C) and subsequent topochemical condensation of the anhydrous titanate (275–450 °C), providing products with gross formulae  $Ln_2Ti_3O_9$ . Thermal degradation of the *n*-alkylamine derivatives starts with the evolution of interlayer water and partially *n*-alkylamine molecules (50–250 °C). However, the amine deintercalation does not occur fully and its completeness declines with the growing of the amine chain length. As a result, the subsequent thermolysis stage (450–600  $^{\circ}$ C) demonstrates the mass gain due to partial oxidation of the carbon-containing interlayer component that later (600–900 °C) undergoes complete oxidation to carbon dioxide. In the case of the *n*-alkoxy derivatives, the initial thermolysis stage (50–250 °C) relates to interlayer water deintercalation. Heating up to 300–350 °C is accompanied by the partial degradation of *n*-alkoxy groups followed by surface oxidation of residual carbon (400–650  $^{\circ}$ C) and its complete burning out (650–900 °C). It is important to note that the liberation of molecular alcohols does not take place at any stage of thermolysis, which maintains with the covalent nature of the *n*-alkoxy derivatives.

Generally, total mass losses are proportional to molecular weights of interlayer organic components. Thermal stability of the *n*-alkylamine derivatives is relatively low because of the absence of covalent bonding between intercalated molecules and the layered perovskite matrix. Hence, work with these hybrid compounds should be performed at temperatures not exceeding the ambient room value. On the contrary, the covalent *n*-alkoxy derivatives demonstrate a much broader thermal stability range, which also allows their obtaining an anhydrous state via purposeful dehydration at temperatures up to 200 °C if necessary.

Some of the inorganic-organic derivatives obtained were tested for vacuum stability in connection with the use of BET and SEM methods, involving preliminary evacuation of the powders. The mass losses observed upon the vacuuming are summarized in Supporting Information S6. It was revealed that keeping of the hybrid samples under deep vacuum ( $\sim 1 \times 10^{-4}$  atm) for 5 d results in mass losses of 0–2.9% depending on the specific organic modifier. At the same time, further vacuuming (10 d) does not lead to any perceptible mass loss. Hypothetically, the mass losses observed may be associated with the liberation of both interlayer components (first, the intercalated *n*-alkylamines and water) as well as

surface adsorbed moisture or atmospheric gases. The evolution of organic components of the *n*-alkoxy samples appears to be unlikely because of their covalent bonding with the inorganic matrix. Generally, the vacuum mass losses decrease with an increase in the organic chain length and are seen to be significantly lower for the *n*-alkoxy derivatives than for *n*-alkylamine ones. Moreover, the mass loss value does not exceed the mass fraction of water in all the samples excluding the methylamine one. This fact indicates that intercalated water is probably the main component evolving upon deep evacuation. Furthermore, the Raman spectra of the inorganic-organic derivatives exposed to 10 d evacuation (Supporting Information S7) clearly show highly intense vibrational bands of the interlayer organic components, including those of methylamine. Thus, the organic modifiers mainly retain in the samples kept under reduced pressure.

Understanding of the potential processes, occurring when the inorganic-organic derivatives are exposed to water, is of high importance for the correct interpretation of their photocatalytic activity and the further practical use. In general, their contact with an aqueous medium may result in extra hydration of the interlayer space, changes in spatial arrangement of interlayer organic structures, and their washout into the solution. Although the study of these phenomena requires determination of not only the crystal structure, but also the quantitative composition of water-treated samples using the CHN and TG analysis. Primary investigation of the hydrolytic stability may be conducted through the means of XRD. The comparison of the diffraction patterns of the inorganic-organic derivatives, recorded before and after 10 d water treatment, allows for concluding that none of the compounds in question undergo hydrolytic decomposition to the protonated titanates (Supporting Information S8). Meanwhile, some of the samples definitely experience structural changes. So, water treatment of the ethylamine one leads to a pronounced broadening of the first (00x) reflection accompanied by its large-angle offset, which indicates the formation of by-phases and interlayer space constriction possibly caused by partial hydrolysis. Similar changes are also observed in the patterns of the *n*-alkoxy derivatives with an intermediate chain length, ethoxy, n-propoxy and n-butoxy samples. Water treatment of the *n*-hexoxy compound does not lead to the interlayer contraction but provides a new by-phase, possessing the enlarged interlayer distance, which may be connected with additional hydration of the initial phase without hydrolysis of the grafted *n*-hexoxy groups. In the case of other inorganic-organic derivatives, the (00x) reflections mainly preserve their positions, emphasizing hydrolytic stability under chosen conditions. The trends observed are in good consistency with the idea that the propensity of the derivatives to the reactions with water depends on steric accessibility of their interlayer space for water molecules as well as energetic profitability of their contact with the interlayer organic component and its movement into the aqueous medium. For instance, hydrolysis of methylamine samples may be bound by the steric factor whilst that of *n*-hexyl and *n*-octylamine ones may be suppressed by the strong difference in the water and long-chain amine polarity.

#### 2.4. Photocatalytic Activity of the Hybrid Inorganic-Organic Titanates

In the course of photocatalytic experiments, we collected an extensive data array on the kinetics of photocatalytic hydrogen generation from the model 1 mol % aqueous solution of methanol as well as the auxiliary information necessary for their correct interpretation. All the measurements were carried out for both bare samples and their composites with Pt nanoparticles serving as a cocatalyst, providing improved charge separation and forming active sites for hydrogen generation. Full kinetic curves including dark and, if necessary, argon flushing stages as well as factual concentration and pH values of the reaction suspensions are presented in Figure 6 and Supporting Information S9–S13. Consideration of the dark stages allows for concluding that the reactions of hydrogen production over all the inorganic-organic hybrids in question are indeed photocatalytic, not just photoinitiated, since turning off the irradiation source causes the curves to reach a plateau, corresponding to a zero reaction rate.



**Figure 6.** Kinetic curves of photocatalytic hydrogen generation over some bare and platinized inorganic-organic derivatives.

Photocatalytic activity of the protonated titanates (Table 4) in the absence of a cocatalyst is relatively low ( $\phi = 0.017\%$  for the La-containing titanate and  $\phi = 0.027$  for the Nd-containing one). Surface platinization is accompanied by its increase by several orders of magnitude, and the former becomes more active ( $\phi = 1.1\%$ ) than the latter ( $\phi = 0.92\%$ ). However, even after platinization the protonated titanates turn out to be less active than the platinized niobate HCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub> studied earlier under the same conditions ( $\phi = 8\%$ ) [81,82]. The probable reason is the existence of the niobate in a highly hydrated state (1.5 water molecules per formula unit), which is not typical of the titanates under consideration.

All the inorganic-organic compounds obtained demonstrate superior photocatalytic activity towards hydrogen generation compared with that of the initial unmodified samples and titanium dioxide TiO<sub>2</sub> P25 Degussa ( $\phi = 0.039\%$ ). When moving from the protonated samples to inorganic-organic ones, the difference in activity of La- and Nd-containing compounds proves to be weakly pronounced (Table 4). The most photocatalytically active sample in the series of bare *n*-alkylamine derivatives HLT<sub>3</sub> × RNH<sub>2</sub> is the *n*-octylamine compound ( $\phi = 2.0\%$ ) while other representatives show lower activity values slightly different from each other ( $\phi = 0.61-0.97\%$ ). In the series HNT<sub>3</sub> × RNH<sub>2</sub>, the *n*-butylamine sample displays the highest activity ( $\phi = 2.0\%$ ). Somewhat less active derivatives are methyl, ethyl and *n*-propylamine ones ( $\phi = 1.4-1.8\%$ ) and the least activity values relate to *n*-hexyl and *n*-octylamine compounds ( $\phi = 0.56-0.73\%$ ). After platinization, differences in the activity of the *n*-alkylamine derivatives HLT<sub>3</sub> × RNH<sub>2</sub>/Pt are largely eliminated. Ethyl ( $\phi = 32\%$ ) and *n*-butylamine ( $\phi = 29\%$ ) samples become the most active; photocatalytic activity of the

rest of the compounds falls in the range of  $\phi = 22-27\%$ . In the series HNT<sub>3</sub> × RNH<sub>2</sub>/Pt, the activity values correlate with those observed for the corresponding bare samples; the maximum falls on the *n*-butylamine titanate ( $\phi = 28\%$ ). Among bare *n*-alkoxy derivatives HLT<sub>3</sub> × ROH, the highest photocatalytic activity is discovered for the *n*-propoxy compound ( $\phi = 1.9\%$ ). The middle positions are occupied by methoxy, ethoxy, *n*-butoxy and *n*-hexoxy samples ( $\phi = 0.73-1.6\%$ ); the least activity is established for the *n*-decoxy one ( $\phi = 0.20\%$ ). In the series HNT<sub>3</sub> × ROH, the greatest activity values fall on methoxy and *n*-propoxy derivatives ( $\phi = 1.5\%$ ). Intermediate photocatalytic activity is observed for ethoxy, *n*-butoxy, and *n*-hexoxy samples ( $\phi = 1.0-1.4\%$ ); its least value relates to the *n*-decoxy compound ( $\phi = 0.56\%$ ). Among the platinized compounds HLT<sub>3</sub> × ROH/Pt, activity values of ethoxy, *n*-propoxy, *n*-butoxy and *n*-hexoxy representatives are significantly levelled ( $\phi = 36-41\%$ ) while methoxy ( $\phi = 16\%$ ) and *n*-decoxy ( $\phi = 29\%$ ) ones turn out to be less active. In the series HNT<sub>3</sub> × ROH/Pt, photocatalytic activity raises when moving from the methoxy to *n*-butoxy compound ( $\phi = 23-35\%$ ) and reduces when going to *n*-hexoxy ( $\phi = 31\%$ ) and *n*-decoxy ( $\phi = 27\%$ ) ones.

Table 4. Data on photocatalytic activity of the protonated titanates and their inorganic-organic derivatives.

Sample	ω, µmol/h	φ, %	k <sub>Pt</sub>	Sample	ω, µmol/h	φ, %	k <sub>Pt</sub>
HLT <sub>3</sub>	1.27	0.0170	(( )	HNT <sub>3</sub>	2.01	0.0268	04.4
HLT <sub>3</sub> /Pt	85.1	1.14	66.9	HNT <sub>3</sub> /Pt	69.0	0.922	34.4
$HLT_3 \times MeNH_2$	81.9	1.10	20.1	$HNT_3 \times MeNH_2$	130	1.74	11 4
$HLT_3 \times MeNH_2/Pt$	1647	22.0	20.1	$HNT_3 \times MeNH_2/Pt$	1476	19.7	11.4
$HLT_3 \times EtNH_2$	61.6	0.824	29.7	$HNT_3 \times EtNH_2$	106	1.42	14.0
$HLT_3 \times EtNH_2/Pt$	2385	31.9	38.7	$HNT_3 \times EtNH_2/Pt$	1482	19.8	14.0
$HLT_3 \times PrNH_2$	45.9	0.614	42.2	$HNT_3 \times PrNH_2$	128	1.71	11 5
$HLT_3 \times PrNH_2/Pt$	1989	26.6	43.3	$HNT_3 \times PrNH_2/Pt$	1474	19.7	11.5
$HLT_3 \times BuNH_2$	72.3	0.966	20.2	$HNT_3 \times BuNH_2$	147	1.97	141
$HLT_3 \times BuNH_2/Pt$	2181	29.2	30.2	$HNT_3 \times BuNH_2/Pt$	2078	27.8	14.1
$HLT_3 \times HxNH_2$	53.8	0.719	20.8	$HNT_3 \times HxNH_2$	42.0	0.562	22.0
$HLT_3 \times HxNH_2/Pt$	1655	22.1	30.8	$HNT_3 \times HxNH_2/Pt$	965	12.9	23.0
$HLT_3 \times OcNH_2$	149	1.99	10.2	$HNT_3 \times OcNH_2$	54.6	0.730	19.9
$HLT_3 \times OcNH_2/Pt$	1836	24.5	12.3	$HNT_3 \times OcNH_2/Pt$	1027	13.7	10.0
$HLT_3 \times MeOH$	92.8	1.24	120	$HNT_3 \times MeOH$	115	1.54	15 5
$HLT_3 \times MeOH/Pt$	1198	16.0	12.9	$HNT_3 \times MeOH/Pt$	1787	23.9	13.5
$HLT_3 \times EtOH$	78.5	1.05	28.2	$HNT_3 \times EtOH$	75.8	1.01	20.0
$HLT_3 \times EtOH/Pt$	2997	40.1	36.2	$HNT_3 \times EtOH/Pt$	2268	30.3	29.9
$HLT_3 \times PrOH$	138	1.85	20.1	$HNT_3 \times PrOH$	112	1.49	21.9
$HLT_3 \times PrOH/Pt$	2783	37.2	20.1	$HNT_3 \times PrOH/Pt$	2430	32.5	21.0
$HLT_3 \times BuOH$	114	1.52	24.1	$HNT_3 \times BuOH$	83.5	1.12	20.0
$HLT_3 \times BuOH/Pt$	2751	36.8	24.1	$HNT_3 \times BuOH/Pt$	2584	34.5	30.9
$HLT_3 \times HxOH$	55.1	0.737	51 7	$HNT_3 \times HxOH$	97.9	1.31	22.4
$HLT_3 \times HxOH/Pt$	2851	38.1	51.7	$HNT_3 \times HxOH/Pt$	2285	30.6	23.4
$HLT_3 \times DcOH$	14.9	0.199	145	$HNT_3 \times DcOH$	42.0	0.561	18.6
$\text{HLT}_3 \times \text{DcOH/Pt}$	2155	28.8	140	$HNT_3 \times DcOH/Pt$	2039	27.3	40.0

As follows from the above, the experimental dependence of photocatalytic activity on the specific interlayer organic component demonstrates complex behavior, which may be associated with the simultaneous influence of a large number of factors. Since the interlayer space of layered perovskites is supposed to function as a separate reaction zone in photocatalysis [46], the multiple increases in the activity going from the protonated titanates to the hybrid inorganic-organic derivatives can be due to greater accessibility of their interlayer space for reactants (methanol and water). Additionally, the organic modification might provide changes in the energies of reactants' adsorption and products' desorption as well as affect other surface properties of the particles, which requires further investigation. However, the data obtained clearly indicate that a specific surface in the course of the organic modification increases no more than 1.7 times (Table 3), so morphology is not the key factor explaining the superior activity of the derivatives.

In general, the greatest values of photocatalytic activity fall on the *n*-alkoxy derivatives with the intermediate organic chain length, which were found to experience structural changes during prolonged water treatment. This fact supports the hypothesis that the activity of layered perovskites in relation to hydrogen generation strongly depends on their ability to intercalate water molecules quantitatively. Moreover, the quantum efficiency and the starting hydration degree of the titanates in question in most cases change symbatically (Figure 7). The similar correlation was earlier observed for the *n*-alkylamine and *n*-alkoxy derivatives of the Dion–Jacobson niobate HCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub> [81,82].



**Figure 7.** Correlation between photocatalytic activity and hydration degree of the interlayer space. Horizontal dashed lines correspond to the activity of bare (blue) and platinized (red)  $TiO_2$  P25 Degussa under the same conditions.

Deviations of the kinetic curves from linearity are negligible, indicating that the activity of most inorganic-organic derivatives in question stably maintains throughout the whole measurement time. The exception is the bare *n*-butylamine sample  $HNT_3 \times BuNH_2$ whose activity gradually increases during the experiment. This fact was proven by repeated experiments and requires further study. In the case of multistage photocatalytic measurements including argon flushing, the hydrogen evolution rate is preserved at all the stages. Moreover, the hydrogen indeed generates from the methanol solution rather than from the hybrid material, which was confirmed by our calculations. For instance, the hydrogen amount evolved over the ethoxy derivative  $HLT_3 \times EtOH/Pt$  during the 160 min photocatalytic measurement (7.99 mmol H<sub>2</sub>) exceeds 92 times the amount that can be generated via the complete oxidation of the interlayer ethoxy groups, contained in 25 mg of the irradiated sample (0.0865 mmol H<sub>2</sub>). Having said so, the reaction rate stably maintains. Thus, the organic modification proved to be an efficient way to improve photocatalytic activity of the titanates and apparent quantum efficiency in the case of the most active Pt-loaded ethoxy derivative HLT<sub>3</sub> × EtOH/Pt, which exceeded 40%. The outstanding activity of this sample can be due to the highest amount of intercalated water, which may take part in the indirect oxidation of methanol via the formation of highly reactive hydroxyl radicals when interacting with holes, localized on perovskite oxygen atoms. The same reason may explain the greatest activity of the Pt-loaded ethylamine derivative HLT<sub>3</sub> × EtNH<sub>2</sub>/Pt ( $\phi$  = 31.9%) that is the most hydrated among *n*-alkylamine samples. It is curious to note that among inorganic-organic niobates studied earlier [82] the most active sample was a platinized ethoxy derivative too ( $\phi$  = 20.6%), although its activity proved to be twice as low.

Thus, in the absence of a cocatalyst, the insertion of organic components into the interlayer space provides an increase in the photocatalytic activity up to 117 times in comparison with the initial unmodified titanates. Having said so, the inorganic-organic samples are up to 51 times superior in the activity to titanium dioxide  $TiO_2$  P25 Degussa.

As can be seen from Table 4, the platinization increase factor  $k_{Pt}$  (the multiplicity of the increase in the reaction rate upon the Pt introduction) for various samples varies greatly  $(k_{Pt} = 11-145)$ . In this connection, the activity values for bare and Pt-loaded compounds do not always change symbatically when going from one to another. In view of this, trends in changing photocatalytic properties in series of platinized samples cannot be interpreted solely by differences in properties of the titanates and their derivatives themselves. In other words, various photocatalysts, despite the common chemical nature, have an unequal potential to increase their activity at the expense of the same cocatalyst. The different effect of platinization on the activity of the samples is, apparently, associated with the various efficiency of spatial charge separation, determining the severity of electron-hole recombination. The latter is known to be connected with completeness of Pt reduction, its particle sizes, their distribution over the surface as well as displacement of the boundaries of energy bands in the near-surface layer of a sample, depending on the energetics of its interaction with a reaction medium, which in turn, may be influenced by an interlayer organic component. The value of  $k_{Pt}$  is seen to be relatively high in the case of the protonated titanates and *n*-decoxy derivatives. Since a strong correlation between k<sub>Pt</sub> and activity of bare samples is not observed, potential incompleteness of surface Pt reduction cannot be explained by the insufficient rate of photogeneration of conduction electrons realizing the reduction. Most photocatalytically active representatives of each series of Pt-loaded inorganic-organic titanates are characterized by the values of  $k_{Pt} = 14-39$ , which are not the maximum (maximum value is  $k_{Pt} = 145$ ). Consequently, their enhanced activity is more predetermined by their own properties than by the cocatalyst influence.

The rate of photocatalytic hydrogen evolution from aqueous media depends on their pH since the target product generates via the reduction of protons. Consequently, ceteris paribus, the pH downgrade is usually accompanied by the rate increase [7]. However, the dependence of the hydrogen generation performance on pH in real systems is more complex because pH may also affect properties of the photocatalyst itself (primarily, of its surface). In accordance with the pH measurement results (Supporting Information S12 and S13), the suspensions of the protonated titanates and *n*-alkoxy derivatives demonstrate an acidic reaction of the medium. In the case of the derivatives, the corresponding pH value is due to the presence of the residual interlayer protons. The *n*-alkylamine samples show a slightly alkaline reaction, and pH of their suspensions reduces with the amine chain length increasing. This fact may be associated with a lesser propensity of low-polar amines to transition into the polar aqueous solution, despite greater basicity. Lower pH values of suspensions of the *n*-alkoxy samples may determine their higher activity. However, a comparison of the latter with that of most *n*-alkylamine derivatives leads to the conclusion that this factor is not the main one. Since the Pt source is a  $H_2PtCl_6$  acid, platinization of the samples is clearly accompanied by pH reduction. Hence, some contribution to the

activity gain may also be made by a higher concentration of protons in the system. The pH decreases during a photocatalytic experiment ( $pH_1 > pH_2$ ), and is more pronounced in the case of highly active samples, which is potentially caused by the partial oxidation of methanol, not to formaldehyde but to formic acid. A minor pH increase observed in the case of some *n*-alkylamine derivatives ( $pH_1 < pH_2$ ), apparently, should be explained by partial amine deintercalation into the reaction medium during photocatalysis.

In the course of the preparation of reaction suspensions, it was found that the dispersibility of the samples in aqueous methanol is strongly dependent on the interlayer organic component. Particularly, the samples modified by short-chain *n*-alkylamines and *n*-alkoxy groups (R = Me, Et, Pr, and Bu) which readily form suspensions while those containing long-chain interlayer structures (R = Hx, Oc, and Dc) perform it reluctantly, as well as produce films on the surface of the suspension and walls of the glass flask due to the poor hydratability of low-polar organic components. Sonication of the protonated titanates is not accompanied by the formation of films. Nevertheless, their suspensions demonstrate low sedimentation stability in the absence of continuous stirring, which may be connected with larger sizes of their particles.

Experimental dependences of the bare sample concentrations in the beginning  $(c_1)$ and in the ending  $(c_2)$  of the photocatalytic experiment on a specific interlayer organic component (Supporting Information S14) show that their greater values are typical of the samples with intermediate lengths of *n*-alkylamine chains. In the case of the *n*-alkoxy derivatives, actual concentrations of suspensions reduce with the chain elongation due to the corresponding reduction of dispersibility in the water-methanol solution. During platinizing, concentrations  $c_1$  and  $c_2$  as a rule decline, which may be associated with the electrical double layer contraction because of the medium acidification. Despite a noticeable decrease in volume sample concentration during some experiments, accordant reduction of the hydrogen evolution rate is usually not observed. This fact may be due to two main reasons: either working in the saturation concentration range, where the reaction rate does not depend on the sample concentration, or full participation of all its particles (including those settled on the cell walls) in hydrogen formation. The first reason appears to be less probable since one of our previous reports shows the falling of maximum efficiency on greater sample concentration in comparison with that used in this research [80]. The second reason, apparently, takes place as the photocatalytic cell walls along with the volume are under irradiation, which allows precipitated particles to take part in the photocatalytic process, although perhaps with lower efficiency.

In addition to the sedimentation stability of the reaction suspensions, the issue of the potential exfoliation of layered samples into nanosheets is of high importance. The nanosheets' appearance may result in a substantial activity growth since they possess low thickness and vast specific surface, providing efficient reactants' adsorption and weakened volume electron-hole recombination. However, according to the data obtained (Supporting Information S12 and S13), the fine fraction of the particles (including exfoliated ones) is practically absent in the reaction suspensions of the inorganic-organic derivatives in question ( $c_3 < 1.5 \text{ mg/L}$ ). As it was shown earlier, inorganic-organic derivatives of the Ruddlesden–Popper titanates are indeed stable towards lamination even under prolonged sonication unless the exfoliating agent (such as TBAOH) is added [30].

#### 2.5. Analysis of the Hybrid Inorganic-Organic Titanates after the Photocatalytic Experiment

Despite the stable photocatalytic activity of most of the hybrid samples obtained, it was important to analyze some of the derivatives separated from the suspensions after photocatalytic experiments (Supporting Information S15–S18). Particularly, the issue of stability under the photocatalytic conditions was investigated for the most active La-containing platinized representatives of the *n*-alkylamine and *n*-alkoxy samples (ethylamine and ethoxy ones) as well as for those with the shortest and the longest organic modifiers (methylamine, *n*-octylamine, methoxy, and *n*-decoxy ones).

Surprisingly, XRD patterns of all four short-chain derivatives separated after the photocatalytic experiment (methylamine, ethylamine, methoxy, and ethoxy) (Supporting Information S15) do not show any reflections corresponding to the initial inorganic-organic compounds and are generally similar to the pattern of the protonated titanate, differing from the latter only by a slightly larger interlayer distance d (13.9 Å for HLT<sub>3</sub> × MeNH<sub>2</sub>, 14.3 Å for HLT<sub>3</sub>  $\times$  EtNH<sub>2</sub>, 13.8 Å for HLT<sub>3</sub>  $\times$  MeOH and 13.9 Å for HLT<sub>3</sub>  $\times$  EtOH vs. 13.6 Å for initial HLT<sub>3</sub>). The interlayer space contraction observed indicates that a significant part (or even a vast majority) of the corresponding organic modifiers, apparently, undergoes degradation during photocatalysis, due to which the samples become structurally similar to the protonated precursors. The degradation can proceed as the deintercalation of *n*alkylamines, hydrolysis of n-alkoxy groups and as the photocatalytic oxidation of these modifiers by holes or hydroxyl radicals. The Raman spectra of the aforementioned samples (Supporting Information S16) clearly confirm the above statement: those of methylamine and methoxy derivatives taken after photocatalysis do not demonstrate any noticeable bands, corresponding to the interlayer organic components. In the case of the ethylamine and ethoxy samples, C–H stretching bands of the organic residues are barely seen. In accordance with the results of the CHN-analysis, the final samples, indeed, contain only small amounts of organic components per formula unit (0.15 for HLT<sub>3</sub>  $\times$  MeNH<sub>2</sub>, 0.25 for HLT<sub>3</sub>  $\times$  EtNH<sub>2</sub>, 0.05 for HLT<sub>3</sub>  $\times$  MeOH and 0.15 for HLT<sub>3</sub>  $\times$  EtOH) that are 5–35% of the initial organic content. As a consequence, TG curves of the final samples show lower mass losses than those of the initial derivatives (Supporting Information S17). Moreover, methoxy and ethoxy compounds taken after photocatalysis do not demonstrate any mass gain in the range of 400–600 °C.

Long-chain inorganic-organic titanates (n-octylamine and n-decoxy ones) turned out to be more stable under photocatalytic conditions, although they do not preserve their original state either. Their XRD patterns recorded after photocatalysis (Supporting Information S15) demonstrate strongly broadened (002) reflections, pointing to a lower degree of the orderliness in the relative arrangement of adjacent perovskite slabs. Assuming the preservation of (001) reflections ( $2\theta < 3^\circ$ , only right shoulder is visible), we can estimate the interlayer distances d of the final samples (approximately 29 Å for HLT<sub>3</sub>  $\times$  OcNH<sub>2</sub> and 31 Å for HLT<sub>3</sub>  $\times$  DcOH), which are seen to be slightly less than those of the initial derivatives. The Raman spectra (Supporting Information S16) confirm the preservation of organic components in the samples. However, the intensity of C-H stretching bands is somewhat lower than in the case of the initial compounds and the fingerprint region  $(1000-1600 \text{ cm}^{-1})$ experienced some changes in the course of the photocatalytic experiments. These facts indicate that even long-chain derivatives lose a part of the organic component and the latter do not preserve its native form. Indeed, the CHN-analysis revealed that the final samples contain no more than half of the organic modifier of its initial amount (0.40 for  $HLT_3 \times OcNH_2$  and 0.30 for  $HLT_3 \times DcOH$  per formula unit). In accordance with these data, the TG curve of the *n*-octylamine sample taken after photocatalysis (Supporting Information S17) demonstrates half the mass gain in the range of 400–600 °C. In the case of the final *n*-decoxy derivative, the mass gain is practically not pronounced, and the curve shows gradual mass loss along its entire length, which is not typical of the initial derivative. Apparently, the partially oxidized organic modifier proves to be less strongly bound to the perovskite matrix, which explains the TG curve's behavior.

SEM images of the derivatives obtained after photocatalytic measurements with the cocatalyst (Figure 8 and Supporting Information S18) confirm successful platinum photodeposition: its nanoparticles 5–7 nm in size are clearly seen on the samples' surface as bright light dots. At the same time, the lamellar morphology of the final samples in general practically does not differ from that of the initial compounds (Supporting Information S3 and S4).



Figure 8. SEM images of some derivatives before and after photocatalytic platinization.

# 2.6. Possible Explanations of Photocatalytic Properties of the Hybrid Inorganic-Organic Titanates

The hybrid titanates obtained demonstrate stably high activity throughout the whole measurement time, and hydrogen indeed generates from the methanol solution, which was confirmed by the aforementioned calculations.

However, despite the sustainable activity, the inorganic-organic derivatives proved to be chemically instable under the photocatalytic conditions. Particularly, the short-chain ones lost the vast majority of the organic modifier upon the photocatalysis and became similar to the protonated titanates in structure (but not in the activity). The long-chain interlayer organic components are more stable towards photocatalytic degradation, although they did not preserve the initial composition either. Thus, the superior photocatalytic activity, at least in the later measurement stages, corresponds not to as-prepared inorganicorganic derivatives but to the products of their partial degradation being formed under photocatalytic conditions. At the same time, different derivatives demonstrate unequal activity, so the nature of the organic modifier plays a significant role in the formation of the final photocatalyst. The organic modification may result in the increasing of accessibility of the interlayer space, considered a separate reaction zone, for reactants, methanol and water molecules. In other words, intercalated *n*-alkylamines and grafted *n*-alkoxy groups significantly enlarge the interlayer distance, creating channels for penetration of the reactants into the reaction zone, which are inactive in the case of the initial protonated titanates. These channels, apparently, continue functioning even after partial or even complete degradation of the organic components, which may explain the stable photocatalytic reaction rate. Another possible explanation is the selective platinum reduction in those areas of the samples where it does not take place in the absence of organic modifiers. Particularly, the in situ platinization of inorganic-organic derivatives thanks to their expanded interlayer space may provide composite nanostructured photocatalysts with platinum nanoparticles deposited on interlayer active sites. The samples formed in this way might demonstrate enhanced activity even after complete degradation of interlayer organic matter. Indeed, some of the SEM images allow one to see platinum nanoparticles (light dots of 5–7 nm), located in the region of the crystal lamination (Figure 8), which points to the possible platinum deposition also in the interlayer space far from the crystal boundaries. However, additional study is required to confirm these assumptions.

The positive correlation between the photocatalytic activity and interlayer hydration degree indicates that water molecules also participate in the photocatalytic process. The same trend was earlier observed for the organically modified Dion–Jacobson niobates: their most photocatalytically active derivatives were the most hydrated [81,82]. Apparently, water may perform the indirect oxidation of methanol via the formation of highly reactive hydroxyl radicals when interacting with holes, localized on perovskite oxygen atoms. Changes in the morphology of the particles accompanying the insertion of organic substances, namely, size reduction and slits' formation, provide a slight increase in the specific surface, which can also provide a beneficial effect on photocatalytic activity, although it appears not to be a critical factor. At the same time, the substantial activity rise from the protonated titanates to hybrid samples is not connected with the bandgap energy reduction, functioning of organic components as photosensitizers, enhancement of crystallinity of the samples, their exfoliation into nanosheets or noticeable change in the equilibrium pH value.

#### 3. Materials and Methods

#### 3.1. Synthesis of Initial Protonated Titanates

Alkaline layered perovskite-like titanates  $K_2Ln_2Ti_3O_{10}$  were prepared according to the standard ceramic method using preliminarily calcined TiO<sub>2</sub>,  $Ln_2O_3$ , and  $K_2CO_3$  as starting compounds. The oxides were taken in stoichiometric amounts, potassium carbonate, with a 30% excess to compensate for the loss during calcination. All the substances were placed into a grinding bowl with silicon nitride balls and ground under an *n*-heptane layer in a Fritsch Pulverisette 7 planetary micro mill at a rotation speed of 600 rpm, using a program of 10 repetitions of 10 min each with 5 min intervals. The mixture obtained was dried and pelletized into ~2 g tablets at a pressure of 50 bar using an Omec PI 88.00 hydraulic press. The tablets were placed into corundum crucibles with lids, kept at 1100 °C for 12 h in a Nabertherm L-011K2RN muffle furnace and, after cooling down, ground in an agate mortar.

To prepare the protonated titanates  $HLT_3$  and  $HNT_3$ , further used as precursors for the synthesis of inorganic-organic derivatives, powders of  $K_2Ln_2Ti_3O_{10}$  were kept in the atmosphere of humid air for 1 d. Hydrated alkaline titanates obtained in this way were treated with water at a ratio of 200 mL per 1 g of the titanate for 1 h and then with a 0.1 M hydrochloric acid solution taken in the same ratio for 1 d. Then solid phases were separated via centrifugation and dried in a desiccator over CaO for 2 d. Thereafter the protonated titanates obtained were additionally ground in a Fritsch Pulverisette 7 planetary micro mill in the aforementioned mode.

#### 3.2. Synthesis of Inorganic-Organic Derivatives

The methylamine derivatives  $HLT_3 \times MeNH_2$  and  $HNT_3 \times MeNH_2$  were directly prepared from the protonated titanates. For this, 3 g of each titanate was placed in a glass tube with 30 mL of 38% aqueous methylamine, whereupon the mixture was sonicated on an ultrasonic homogenizer Hielscher UP200St (200 W) at a half power for 5 min. Then the tube was sealed and the suspension was stirred at 60 °C for 10 d. Preparation of other amine derivatives  $HLT_3 \times RNH_2$  and  $HNT_3 \times RNH_2$  (R = Et, Pr, Bu, Hx, Oc) was carried out using the methylamine ones as precursors. In each case, 1 g of the methylamine derivative was placed in a sealed glass tube with 10 mL of a corresponding amine solution, after which the reaction mixture was stirred at the temperature T for the predetermined time D.

The preparation of alkoxy derivatives  $HLT_3 \times ROH$  and  $HNT_3 \times ROH$  was conducted on the basis of the amine ones under solvothermal conditions. In each case, 1 g of the amine derivative was placed into a sealed PTFE vessel of a steel laboratory autoclave containing 35 mL of the alcohol being grafted or in its solution. After thorough shaking, the autoclave was kept at the temperature T for the predetermined time D.

After cooling down, the target products were filtered and rinsed with an appropriate volatile solvent to remove residual surface adsorbed amines and alcohols. Detailed conditions of the inorganic-organic derivatives' synthesis are summarized in Table 5.

Synthesis of <i>n</i> -Alkylamine Derivatives								
Amine	Precursor	Amine Concentration, %	Т, °С	D, d	Solvent for Flushing			
MeNH <sub>2</sub>	HLT <sub>3</sub> (HNT <sub>3</sub> )	38 (in water)	60	10	acetone			
EtNH <sub>2</sub>	HLT3 (HNT3) $\times$ MeNH2	70 (in water)	25	1	_//_			
PrNH <sub>2</sub>	<u> </u>	90 (in water)	_//_	_//_	_//_			
BuNH <sub>2</sub>	—//—	_//_	_//_	_//_	_//_			
$HxNH_2$	<u> </u>	30 (in n-heptane)	60	7	n-hexane			
OcNH <sub>2</sub>	_//_	—//—	_//_	_//_	_//_			
Synthesis of <i>n</i> -Alkoxy Derivatives								
	Synthesis	of <i>n</i> -Alkoxy Derivation	ives					
Alcohol	Synthesis Precursor	of <i>n</i> -Alkoxy Derivati Alcohol Concentration, %	ives T, °C	D, d	Solvent for Flushing			
Alcohol MeOH	Synthesis Precursor HLT <sub>3</sub> (HNT <sub>3</sub> ) × MeNH <sub>2</sub>	of <i>n</i> -Alkoxy Derivation	<b>T,</b> ° <b>C</b> 100	D, d 7	Solvent for Flushing acetone			
Alcohol MeOH EtOH	Synthesis Precursor HLT <sub>3</sub> (HNT <sub>3</sub> ) × MeNH <sub>2</sub> HLT3 (HNT3) × BuNH2	of <i>n</i> -Alkoxy Derivation Alcohol Concentration, % 100 96 (in water)	<b>T,</b> ° <b>C</b> 100 180	D, d 7 _//	Solvent for Flushing acetone -//-			
Alcohol MeOH EtOH PrOH	SynthesisPrecursor $HLT_3$ (HNT_3) × MeNH2 $HLT3$ (HNT3) × BuNH2 $-//$	of <i>n</i> -Alkoxy Derivation	<b>T,</b> °C 100 180 _//_	D, d 7 _// _//	Solvent for Flushing acetone _//_ _//_			
Alcohol MeOH EtOH PrOH BuOH	SynthesisPrecursor $HLT_3$ (HNT_3) × MeNH2 $HLT3$ (HNT3) × BuNH2 $-// -//-$	of <i>n</i> -Alkoxy Derivation	<b>T,</b> °C 100 180 -// -//	D, d 7 _// _// _//	Solvent for Flushing acetone -//- -//- -//-			
Alcohol MeOH EtOH PrOH BuOH HxOH	Synthesis Precursor HLT <sub>3</sub> (HNT <sub>3</sub> ) × MeNH <sub>2</sub> HLT3 (HNT3) × BuNH2 -//- -//- -//-	of <i>n</i> -Alkoxy Derivation	T, °C 100 180 -// -// -//	D, d 7 -// -// -//	Solvent for Flushing acetone _//_ _//_ n-hexane			

**Table 5.** Conditions for synthesis of inorganic-organic derivatives.

#### 3.3. Investigation of Vacuum and Hydrolytic Stability

To study the stability of inorganic-organic derivatives obtained at reduced pressure, their preliminarily weighted hitches of ~0.5 g were placed in a desiccator equipped with an oil vacuum pump UED-Lab 115-SG and held under residual pressure of ~1 × 10<sup>-4</sup> atm. Sample weights were remeasured after 5 and 10 d of vacuuming and compared with initial values. The weighing was performed with an accuracy of  $1 \times 10^{-4}$  g using an Ohaus Pioneer PA214C balance. Some of the samples held in the vacuum for 10 d were additionally analyzed by means of Raman spectroscopy to establish the preservation of organic modifiers.

# 3.4. Investigation of Photocatalytic Activity

Photocatalytic activity was studied with regard to light-driven hydrogen generation from the model 1 mol % aqueous solution of methanol both for bare samples and for their composites with Pt nanoparticles as a cocatalyst. The same measurements were also carried out for the "classic" photocatalyst TiO<sub>2</sub> P25 Degussa as a reference. The hydrogen evolution rate  $\omega$ , apparent quantum efficiency  $\phi$  and multiplicity of increase in the rate after Pt loading (platinization increase factor k<sub>Pt</sub>) were used as quantitative indicators of photocatalytic activity.

Measurements were performed on the laboratory photocatalytic setting used in our previous reports [80–82], consisting of an illuminator, photocatalytic cell additionally providing light filtration and the reaction mixture cooling, gas chromatograph, and closed gas circulation system, connecting the last two components (Supporting Information S19). An arc mercury tube lamp DRT-125 (125 W) serves as an ultraviolet irradiation source with the irradiation intensity of 14.96 mE/h in the range of the photocatalysts' absorption. The self-made photocatalytic cell represents an external irradiation reactor, including two compartments equipped with branch pipes for the supply and removal of solutions and gases. The closest compartment to the lamp, used for light filtration, is filled with an aqueous solution of KCl and NaBr (6 g/L of each salt). The light filter allows the cutting

of hard ultraviolet irradiation ( $\lambda$  < 220 nm), which can promote the undesirable reaction of direct methanol photolysis. The light filter also provides the cooling of the cell, which is achieved by its continuous circulation through the thermostat, connected to the coldwater system and maintaining a temperature of 15 °C. The compartment farthest from the lamp is for the reaction suspension, intensively stirred during the experiment. Gaseous reaction products come from the cell into the gas circulation system. Their detection is conducted according to a specified program at fixed time intervals by a Shimadzu GC-2014 gas chromatograph, equipped with a 30 m long Rt-Msieve 5A capillary column as well as thermal conductivity detector using argon as a carrier gas.

To prepare the reaction suspension, in each case 0.03 g of the sample was placed in a round-bottom flask containing 60 mL of 1 mol % aqueous methanol. The flask was shaken, sealed and left for 10 min. Then the mixture was sonicated in an Elmasonic S10H bath (60 W) for 10 min. In the case of bare samples' investigation, after the light filter circulation and magnetic stirrer were turned on, 54 mL of the suspension obtained were pumped into the reaction compartment of the cell and irradiation and argon flushing were switched on. After 15 min, 4 mL of the suspension was taken from the cell to establish volume sample concentration and pH of the media before the measurement  $(c_1, pH_1)$ . After 15 min, argon flushing of the cell was switched off and the photocatalytic activity measurement, consisting in chromatographic analysis of the gaseous phase every 15 min, was conducted for 2 h. Afterwards, the dark stage was organized via the lamp turning off and monitoring the dark activity of the sample for 45 min. Thereafter, 4 mL of the suspension was sampled to determine volume sample concentration and pH of the media at the end of the measurement ( $c_2$ ,  $pH_2$ ). After this, 30 mL of the residual suspension was centrifuged at a separation factor F = 1000 for 1 h to precipitate bulk non-exfoliated particles and find the concentration of fine fraction (perovskite nanolayers) in the final colloidal solution as well as its pH value  $(c_3, pH_3)$ . In the case of platinized samples' investigation, the volume of the initial suspension for loading into the reaction compartment was 53 mL. After 15 min of the lamp and argon flushing being switched on, 1.1 mL of the 2.56 mM  $H_2$ PtCl<sub>6</sub> aqueous solution was injected into the reaction suspension to perform in situ photocatalytic platinization. The solution volume was calculated to provide mass fraction of Pt in the photocatalyst of 1% assuming its full reduction. The gaseous phase was analyzed every 5 min and the dark stage duration was 20 min. If the hydrogen evolution rate exceeded 500 µmol/h, the photocatalytic measurement program was divided into several sections of 20–30 min each one, separated by a 10 min argon flushing to reduce pressure in the system, and an additional dark stage after the first section. Other experimental conditions and procedures were the same.

# 3.5. Instrumentation

#### 3.5.1. XRD

A powder X-ray diffraction (XRD) analysis of the samples was performed on a Rigaku Miniflex II benchtop diffractometer (Tokyo, Japan) using  $CuK_{\alpha}$  radiation, an angle range of  $2\theta = 3-60^{\circ}$ , scanning rate of  $10^{\circ}$ /min, and step of  $0.02^{\circ}$ . The lattice parameters in the tetragonal system were calculated on the basis of all the reflections observed using the DiffracPlus Topas software.

# 3.5.2. Raman Spectroscopy

The Raman scattering spectra were collected on a Bruker Senterra spectrometer (Billerica, USA) in the Raman shifts range of  $100-3700 \text{ cm}^{-1}$ . For analysis of protonated titanates the amine and methoxy derivatives incident laser 488 nm was used (power, 0.1–4 mW; and accumulation time, 10-120 s depending on the intensity of the fluorescent background), and for other alkoxy derivatives, 785 nm was used (power, 50 mW; and accumulation time, 30-60 s). In the latter case, the high-frequency region in the figures was presented on an enlarged scale to make bands of the organic component more visible relative to high-intensity ones of the perovskite matrix.

# 3.5.3. NMR Spectroscopy

Carbon nuclear magnetic resonance (<sup>13</sup>C NMR) spectra of La-containing inorganicorganic derivatives were recorded on a Bruker Avance III 400 WB spectrometer (Billerica, USA) at an operating frequency of 100.64 MHz following the cross-polarization technique and using tetramethylsilane as an external reference. An NMR analysis of Nd-containing samples was not possible due to their paramagnetism.

# 3.5.4. DRS

The diffuse reflectance spectra (DRS) were obtained on a Shimadzu UV-2550 spectrophotometer (Kyoto, Japan) with an ISR-2200 integrating sphere attachment in the range of 220–800 nm, using barium sulphate as an external reference with reflection coefficient R = 1. Optical bandgap energies  $E_g$  were found via the transformation of reflectance spectra into coordinates  $(F \cdot h\nu)^{1/2} = f(h\nu)$ , where  $F = (1 - R)^2/2R$  is the Kubelka-Munk function, and further determination of abscissas of the intersection points of linear sections of the graphs.

#### 3.5.5. CHN-Analysis

Quantitative compositions of inorganic-organic samples were calculated on the basis of carbon, hydrogen and nitrogen content determined via the elemental CHN-analysis on a Euro EA3028-HT analyzer (Pavia, Italy).

# 3.5.6. TG

The thermogravimetric (TG) analysis was performed on a Netzsch TG 209 F1 Libra thermobalance (Selb, Germany) in a synthetic air atmosphere. The temperature program included heating each sample from room temperature to 950 °C at a rate of 10 °C/min followed by keeping at the maximum temperature for 20 min to achieve the establishing of the constant mass.

# 3.5.7. SEM

The morphology of the particles was investigated on a Zeiss Merlin scanning electron microscope (SEM) (Oberkochen, Germany) equipped with a field emission cathode, electron optics column Gemini II and oil-free vacuum system.

# 3.5.8. BET

All specific surface area measurements were performed on a Micromeritics ASAP 2020 (Norcross, USA) volumetric adsorption analyzer. Prior to analysis, a 150–200 mg portion of each sample was degassed for 12 h without heating (+25-30 °C). Adsorption isotherms were measured at a liquid nitrogen bath temperature (ca. -196 °C) with krypton Kr as an adsorptive. Specific surface areas were calculated via the conventional Brunauer–Emmett–Teller method (BET) using at least five points from the relative pressure range of 0.05–0.15. The krypton molecular cross-sectional area was assumed 0.210 nm<sup>2</sup>.

# 3.5.9. ICP-AES

Concentrations of the colloidal solutions of perovskite nanolayers, used for building spectrophotometric calibration plots, were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on a Shimadzu ICPE-9000 spectrometer (Kyoto, Japan) after preliminary acid digestion.

# 3.5.10. Spectrophotometry

Actual volume concentrations of the samples in reaction suspensions  $c_1$ ,  $c_2$ , and  $c_3$  were determined via their spectrophotometric analysis performed on a Thermo Scientific Genesys 10S UV-Vis spectrophotometer (Waltham, USA) using previously built calibration plots (Supporting Information S20). Measurements were conducted in the range of optical density A < 2. The 1 mol % aqueous methanol was used for dilution and baseline recording.

## 3.5.11. pH Measurement

The pH values of a reaction suspensions' medium were determined using a laboratory pH-meter Toledo SevenCompact S220 (Greifensee, Switzerland) equipped with an InLab Expert Pro-ISM electrode.

# 4. Conclusions

As the study showed, organic modification of layered perovskite-like titanates  $H_2Ln_2Ti_3O_{10}$  (Ln = La, Nd) can provide a great increase in their photocatalytic activity towards hydrogen generation from aqueous methanol under ultraviolet light. The hybrid derivatives prepared were found to be superior in the activity up to 117 times to the initial protonated titanates and 51 times to titanium dioxide  $TiO_2$  P25 Degussa. Additional platinization of the samples' surface allowed for achieving apparent quantum efficiency in the reaction of hydrogen formation of more than 40%, which is twice as much as was achieved in the case of the most active derivative of the Dion–Jacobson niobate  $HCa_2Nb_3O_{10}$  reported earlier [82]. The hybrid titanates obtained demonstrate stably high activity throughout the whole measurement time and hydrogen indeed generates from the methanol solution.

At the same time, despite the sustainable activity, the inorganic-organic derivatives are chemically instable under the photocatalytic conditions: their organic modifiers undergo partial or even almost complete degradation. Thus, the great photocatalytic activity, at least in the later measurement stages, corresponds not to as-prepared inorganic-organic samples but to the products of their decomposition being formed under photocatalytic conditions. Nevertheless, different samples exhibit unequal activity, so the specific organic modifier does play a significant role in the formation of the final photocatalyst. We can assume that the organic modification leads to the increase in the interlayer space's accessibility for reactants, methanol and water molecules. Particularly, *n*-alkylamines and *n*-alkoxy groups, significantly enlarging the interlayer distance, can create new channels for penetration of the reactants into the reaction zone, which are inactive in the case of the unmodified protonated titanates. Despite the degradation of organic components, these channels continue working, which explains the stable photocatalytic reaction rate. Moreover, the superior photocatalytic properties of the derivatives may be associated with the selective platinum reduction in the interlayer space and other areas of the samples where it does not occur in the absence of organic modifiers. However, this issue requires further investigation.

Thus, organic modification represents a highly effective approach to the preparation of new layered perovskite-based photocatalytically active materials. This approach is especially interesting since the final photocatalyst is not as-prepared but formed in situ under the conditions of the target photocatalytic reaction.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/ 10.3390/catal11111279/s1, S1: Diffuse reflectance spectra and Tauc plots for the initial protonated titanates, S2: Diffuse reflectance spectra and Tauc plots for inorganic-organic derivatives, S3: SEM images of HLT<sub>3</sub> and its inorganic-organic derivatives, S4: SEM images of HNT<sub>3</sub> and its inorganicorganic derivatives, S5: TG analysis of the initial protonated titanates and their inorganic-organic derivatives, S6: Data on vacuum stability of inorganic-organic derivatives, S7: Raman spectra of some inorganic-organic derivatives held under vacuum for 10 d in comparison with those of the initial derivatives, S8: XRD patterns of Nd-containing inorganic-organic derivatives before and after 10 d water treatment, S9: Full kinetic curves of photocatalytic hydrogen generation over initial protonated titanates and their composites with Pt as a cocatalyst, S10: Full kinetic curves of photocatalytic hydrogen generation over *n*-alkylamine derivatives and their composites with Pt as a cocatalyst, S11: Full kinetic curves of photocatalytic hydrogen generation over *n*-alkoxy derivatives and their composites with Pt as a cocatalyst, S12: Actual volume concentrations and pH values of reaction suspensions of La-containing samples, S13: Actual volume concentrations and pH values of reaction suspensions of Nd-containing samples, S14: Comparison of actual concentrations of samples in the reaction suspensions in the beginning and in the ending of the photocatalytic measurement, S15: XRD patterns of some inorganic-organic derivatives before and after photocatalytic (PC) experiments, S16: Raman spectra of some inorganic-organic derivatives before and after photocatalytic (PC) experiments, S17: TG curves of some inorganic-organic derivatives before and after photocatalytic (PC) experiments, S18: SEM images of some inorganic-organic derivatives before and after photocatalytic (PC) experiments, S19: Scheme of photocatalytic setting and reaction cell, S20: Spectrophotometric calibrations for express measurement of reaction suspensions' concentrations.

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