

# A Fluid Bioethanol Setup is Photocatalyzed to Produce Hydrogen

## Abstract

Using XRD, CHN, TG, <sup>13</sup>C NMR, BET, SEM, and GC-MS, the solidity of platinized n-butylamine-intercalated layered titanate H<sub>2</sub>La<sub>2</sub>Ti<sub>3</sub>O<sub>10</sub> was investigated during photocatalytic hydrogen production from fluid methanol under UV light. After three hours of reaction, the photocatalyst's particle morphology and specific surface area remained the same, and n-butylamine completely left the interlayer space to become n-butyraldehyde. Carbon is present in at least two distinct oxidation states in the final solid phase because the intermediate products of methanol oxidation are bound to the perovskite matrix. An approximate linear equation of 29.2 pH holds for the apparent quantum efficiency of producing hydrogen at a concentration of one mole between 220 and 340 nm. In contrast to the parent H<sub>2</sub>La<sub>2</sub>Ti<sub>3</sub>O<sub>10</sub> or TiO<sub>2</sub>, this photocatalyst's activity is stable over time and strongly influenced by the pH of the medium. methanol concentration. In the acidic medium, the investigated photocatalyst outperforms the platinized H<sub>2</sub>La<sub>2</sub>Ti<sub>3</sub>O<sub>10</sub> by more than one order of magnitude. At 10 mol. %, The highest quantum efficiency of hydrogen production was achieved by altering the methanol grouping. to be present there.

**Keywords:** Photocatalysis • Hydrogen • Layered perovskite • Titanate • Intercalation • Amine • Hybrid

## Introduction

The nursery effect, rising global temperatures, and pollution of soil, water, and air over the past few years are largely to blame for the global escalation of environmental issues like these. New environmental remediation strategies, waste-free technologies, and renewable energy sources like hydrogen are encouraged by the imminent energy and ecological crisis. Due to its unprecedentedly high calorific value and lack of secondary pollution in comparison to conventional fuels, the latter is regarded as a promising energy carrier [1].

Water photoelectrolysis, which was first described by Fujishima and Honda and led to the active development of photoelectrochemical cells and powder photocatalysts, is one of the most environmentally friendly methods for producing hydrogen. Even though significant progress has been made in this direction in recent years, it is still challenging to develop highly effective photocatalytic hydrogen generators due to the thermodynamic and kinetic limitations of the water splitting reaction [2]. In this regard, in addition to the previously mentioned water splitting method, another method for producing hydrogen is the focus of research at the moment: the primary byproducts of photocatalysis processing of plant biomass (methanol, other bioalcohols, carbohydrates, and so forth) which makes it possible to achieve much higher quantum yields [3].

Notwithstanding the "exemplary" photocatalyst TiO<sub>2</sub>, investigation into particle replaceable layered oxides with a perovskite structure and an assortment of sulfide-and nitride-based materials fundamentally progressed photocatalytic hydrogen creation. These oxides have promising photocatalytic properties due to the distinctive 3D crystal lattice of their perovskite layers. Using this lattice, photoexcited charge carriers and chemically active interlayer spaces can be effectively separated [4]. By ion substitution in the perovskite block with a variety of cocatalysts and photosensitizers, as well as exfoliation into perovskite nanosheets, these materials can also be transformed into new, efficient photocatalysts with a large light absorption region and high specific surface area. The possibility that the interlayer space of ion-exchangeable layered perovskites plays a role in the photocatalytic reaction by serving as an additional reaction zone

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for reactants from the solution is yet another intriguing feature of these materials. Layered perovskite-type oxides provide researchers with a lot of room to experiment with a variety of modifications through the topochemical reactions of intercalation.

By intercalating organic bases or grafting alcohols and other hydroxy compounds in a manner resembling esterification, layered perovskite-type oxides can be used to produce hybrid inorganic–organic materials after the interlayer cations are replaced with protons [5]. These inorganic–organic samples may also exhibit novel properties that are uncharacteristic of the parent substances in addition to combining practically significant characteristics of the parent substances into a single material. Due to the organic modifiers' potential photodegradation, hybrid materials of this kind were until recently practically ignored as hydrogen evolution photocatalysts, despite their numerous promising applications. At the same time, there were a few reports that the light-induced disintegration of natural colors as model water impurities increased the movement of layered oxides changed by polyaniline and alkoxy groups [6]. In addition, our most recent research demonstrates that in aqueous solutions of methanol, glucose, and xylose, the organically modified layered perovskite-type oxides  $\text{HCa}_2\text{Nb}_3\text{O}_{10}$  and  $\text{H}_2\text{Ln}_2\text{Ti}_3\text{O}_{10}$  ( $\text{Ln} = \text{La}, \text{Nd}$ ) exhibit excellent hydrogen evolution activity. The photocatalytic reaction rate, which was significantly higher than that of the unmodified oxides, remained constant over time. However, as our initial research also demonstrated, the photocatalytic reaction in some hybrid photocatalysts causes a significant contraction of the interlayer space, indicating either the escape or destruction of the inserted organic molecules. We decided to investigate the ongoing processes in greater depth due to the conflict between the apparent chemical instability of hybrid photocatalysts and their stable photocatalytic activity. Understanding the chemical nature of hybrid photocatalysts under operation conditions and the factors that account for their high and stable activity may, in our opinion, result in significant advancements in the design of new photocatalytic systems that are highly efficient in the future [7].

The primary goal of this study was to explain how the UV-light-induced reaction of hydrogen production from aqueous methanol changes the hybrid photocatalyst. As an exploration object, we chose one of the mixture photocatalysts

that we have found to be the most dynamic:  $\text{H}_2\text{La}_2\text{Ti}_3\text{O}_{10}$  is a layered titanate of the perovskite type that has been intercalated with n-butylamine and cocatalyzed by platinum nanoparticles. We examined the photocatalyst's structure, organization, molecule morphology, and surface region during the photocatalytic response. During the photocatalytic process, we also looked at the composition of the reaction solution. Additionally, we investigated the relationship between the pH of the medium and the amount of methanol present, as well as the correlation between the similarly altered isostructural titanate  $\text{H}_2\text{Nd}_2\text{Ti}_3\text{O}_{10}$  [8].

## Results and Discussion

### XRD Analysis

The methylamine and n-butylamine additions that resulted in the n-butylamine-intercalated titanate  $\text{H}_2\text{La}_2\text{Ti}_3\text{O}_{10}\text{BuNH}_2$  (further referred to as  $\text{HLT}_3\text{BuNH}_2$ ) were followed by protonation, which produced  $\text{H}_2\text{La}_2\text{Ti}_3\text{O}_{10}$  ( $\text{HLT}_3$ ). Each sample was found to be a single-phase product with no significant impurities by powder XRD analysis. The comparable neodymium-containing series  $\text{K}_2\text{Nd}_2\text{Ti}_3\text{O}_{10}$  ( $\text{HNT}_3$ ),  $\text{H}_2\text{Nd}_2\text{Ti}_3\text{O}_{10}$  ( $\text{HNT}_3$ ), and  $\text{H}_2\text{Nd}_2\text{Ti}_3\text{O}_{10}\text{BuNH}_2$  ( $\text{HNT}_3\text{BuNH}_2$ ) are not covered in this article. This series' XRD patterns and lattice parameters [9].

The initial alkaline form of the layered titanate  $\text{KLT}_3$  was found to be indexed in the  $I4/mmm$  space group, which is a staggered conformation of perovskite layers. This finding is in good agreement with the data in the literature. Additionally, its lattice parameters were slightly larger than those of the  $\text{KNT}_3$  analog. The interlayer distance  $d$  decreased from 14.87 to 13.71 following protonation as potassium cations replaced smaller protons. The interlayer space significantly expanded by 11.35 following the intercalation of n-butylamine and transitioned into the  $P4/mmm$  space group, which represents the eclipsed conformation of perovskite layers that are adjacent to one another [10].

The mixture contained 100 mg of  $\text{HLT}_3\text{BuNH}_2$  in 50 milliliters of 1%. to get the sample ready for "after photocatalysis" use. As is typical for our photocatalytic experiment, aqueous methanol with 5.1 mol  $\text{H}_2\text{PtCl}_6$  as a platinization agent was irradiated with ultraviolet light for 150 minutes in the photocatalytic reactor. The solid sample that was obtained by centrifugation and drying in this manner is known as  $\text{HLT}_3\text{BuNH}_2/$

Pt\_PC [11].

The XRD analysis of the HLT3BuNH<sub>2</sub>/Pt\_PC sample showed that the interlayer distance was close to the pre-butylamine intercalation value (HLT3). This strongly suggests that the intercalated butylamine was at least partially removed from the interlayer space through photocatalytic degradation or deintercalation. This could be due to the stacking issue of the perovskite layers caused by extreme responses in the space between the layers and the break of butylamine particles. It was impossible to even approximate the distance between the layers due to the much stronger anisotropic broadening effect of the neodymium-containing analog, HNT3BuNH<sub>2</sub>/Pt\_PC. In comparison to HLT3, the XRD pattern of HLT3BuNH<sub>2</sub>/Pt\_PC displayed significant anisotropy, particularly in the low-angle peaks whose positions are solely determined by the layer distance [12].

#### CHN Analysis

The XRD data are supported by the results of the elemental CHN analysis. As can be seen, the expected values of one molecule of methylamine and n-butylamine per formula unit were met by the measured amounts of carbon and nitrogen in the layered oxide. However, the amounts of the interlayer amine molecules in samples containing neodymium and lanthanum were comparable. However, despite the fact that the photocatalytic reaction decreased the amount of carbon present by a factor of four, neither of the samples contained any nitrogen. Although the chemical nature of the remaining carbon is still unknown, its presence accounts for the slightly longer interlayer distance than the protonated form [13].

#### TG Analysis

The thermogravimetric analysis's findings are supported by the data. As is typical, the TG curve of the protonated sample HLT3 reveals two stages of mass loss: The first occurs when T 200 °C deintercalates only a small amount of water. The second occurs when the layered oxide H<sub>x</sub>K<sub>2x</sub>La<sub>2</sub>Ti<sub>3</sub>O<sub>10</sub> undergoes complete thermolysis at T 600 °C. Water leaks out as a result, and residual K<sub>2x</sub>La<sub>2</sub>Ti<sub>3</sub>O<sub>10x/2</sub> forms as a result. In light of the mass misfortunes at these two stages, we determined the degree of protonation ( $x/2 = 0.83$ ) and the quantity of intercalated water per equation unit ( $y = 0.22$ ) [14].

It is challenging to break down the 12.99% total

mass loss into steps that follow one another on the HLT3-BuNH<sub>2</sub> TG curve. Each formula unit contained 0.99 molecules of butylamine, according to the CHN analysis. Deducting the mass loss of 2.27 percent that must have been caused by the protonated form's thermolysis and assuming that the remaining 10.72 percent only consists of butylamine (although there may also be a small amount of water and/or methylamine) yields 0.99 molecules of butylamine per formula unit. The fractional oxidation that results in the mass increase that is typical of these mixture materials between 450 °C and 650 °C is caused by natural particles that do not break free at low temperatures but remain bound to the perovskite framework. These particles are the source of the fractional oxidation. The sample's mass again decreases as these species oxidize to gaseous CO<sub>2</sub> at sufficiently high temperatures.

The sample's TG curve (HLT3BuNH<sub>2</sub>/Pt\_PC) clearly demonstrates that the photocatalytic reaction cleared the interlayer space of at least a significant amount of n-butylamine. However, it is abundantly clear that this sample is in no way comparable to HLT3, the initial protonated form. Even though the stage of mass increase that is typical of oxidizable organic-containing samples moved to lower temperatures by roughly the same amount, it is still being observed. 80 degrees Celsius versus HLT3-BuNH<sub>2</sub>. In addition, the total mass loss was nearly 2 percent greater than that of HLT3. Because we do not know the specific nature of the organic species that are still present in the sample, we are unable to make any additional quantitative inferences from these results. The only thing that can be said at this time is that neither the sample HLT3BuNH<sub>2</sub> with butylamine intercalated nor any of its hydrated derivatives returned to their protonated states during the photocatalytic reaction; However, it contained organic compounds that, when exposed to high temperatures, could oxidize in the air [15].

## Materials and Methods

### Titanates with n-Butylamine intercalated synthesis

We will only provide a brief explanation of the synthesis of the layered oxides under investigation here because it has already been extensively covered in our previous publications. The initial alkaline forms of the layered titanates K<sub>2</sub>La<sub>2</sub>Ti<sub>3</sub>O<sub>10</sub> (KLT3) and K<sub>2</sub>Nd<sub>2</sub>Ti<sub>3</sub>O<sub>10</sub> (KNT3) were produced through solid-state

synthesis using  $K_2CO_3$ ,  $TiO_2$ , and  $La_2O_3$  (or  $Nd_2O_3$ ) as starting reagents (Vekton, Saint Petersburg, Russia, 99.9%). Stoichiometric amounts of  $TiO_2$  and  $La_2O_3$  (or  $Nd_2O_3$ ) were combined with a 50% excess of  $K_2CO$  in a planetary micro mill with a silicon nitride bowl, ground under an n-heptane layer, dried, pressed into pallets, and calcined for 10 hours at 1000 °C in corundum crucibles.

Over the course of seven days at room temperature, the protonated forms  $H_2La_2Ti_3O_{10}$  (HLT3) and  $H_2Nd_2Ti_3O_{10}$  (HNT3) were produced through ion exchange reactions with an excess of 0.1 M hydrochloric acid. Prior to the reaction, KLT3 and KNT3 underwent overnight exposure to humid air with a relative humidity of 75% to achieve preliminary water intercalation. The solids were separated from the solution by centrifugation at 3000 RCF, and after being separated from the solution, they were dried over CaO. There were two steps involved in the intercalation of n-butylamine ( $BuNH_2$ ) into the protonated forms, the intermediate step being the intercalation of methylamine ( $MeNH_2$ ). In the first step, 120 milliliters of the 38% aqueous  $MeNH_2$  solution and 12 grams of HLT3 (or HNT3) were combined and stirred for ten days at 60 degrees Celsius in a closed flask. Photocatalytic experiments with the solid samples referred to as HLT3- $BuNH_2$  and HNT3- $BuNH_2$  were carried out as the primary focus of this work. In the second step, the separated and dried solid referred to as HLT3  $MeNH_2$  (or HNT3  $MeNH_2$ ) was mixed with 80 milliliters of n-butylamine and 10 milliliters of water, and the mixture was stirred for four days at room temperature.

#### Identifying hybrid photocatalysts

At each phase of the union, powder X-beam diffraction (XRD) was performed using  $CuK$  radiation on a Rigaku Miniflex II diffractometer in Tokyo, Japan, with a  $2\theta$  scope of 3–60° and a sweep speed of 10°/min. Bruker's DiffraPlus Topas 4.2 software was used to index the XRD patterns that were obtained and determine the unit cell parameters.

On a Euro EA3028-HT analyzer located in Pavia, Italy, elemental CHN analysis was used to determine the amounts of carbon, hydrogen, and nitrogen present in the inorganic–organic hybrids.

Thermogravimetric (TG) analysis was carried out with a Netzsch TG 209 F1 Libra microbalance

from Selb, Germany, and a synthetic dry air atmosphere. Following a 20-minute isotherm stage, the temperature program involved heating the samples from room temperature to 880–950 °C at a rate of 10 °C/min.

#### Conclusions

The platinized n-butylamine-intercalated layered titanate  $H_2La_2Ti_3O_{10}BuNH_2/Pt$ , which had previously been described as a highly effective photocatalyst for the production of hydrogen from aqueous methanol under UV irradiation, was found to be unstable under operating conditions. In particular, the molecules of intercalated butylamine leave the interlayer space and are oxidized to butyraldehyde, which goes through additional transformations. In spite of this, when compared to the initial protonated titanate  $H_2La_2Ti_3O_{10}$ , the remaining solid phase exhibits photocatalytic activity for hydrogen evolution that is unprecedentedly high and stable. The intermediate products of methanol oxidation that are bound to the perovskite matrix in the interlayer space explain why the solid phase formed by photocatalysis contains significant amounts of carbon in at least two distinct oxidation states.  $H_2La_2Ti_3O_{10}BuNH_2/Pt$ 's photocatalytic activity was found to be strongly influenced by pH, peaking in an acidic medium (pH 3) and monotonically decreasing about 10 times when the reaction medium changed to an alkaline one (pH > 12). Such way of behaving isn't commonplace of either the underlying  $H_2La_2Ti_3O_{10}$  or mass  $TiO_2$  and, hence, demonstrates a unique response component, presumably including the interlayer space as an extraordinary response zone.

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