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FULL PAPER



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Solvothermal fusion of Ag- and N-doped LiTaO₃ perovskite nanospheres for improved photocatalytic hydrogen production

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T.S. Senthil, Department of Physics, Erode Sengunthar Engineering College, Perundurai 638057 Tamil Nadu, India. Email: tssenthi@esec.ac.in Tantalate semiconductor photocatalyst has received significant attention as an alternative promising material to mitigate the globally increasing energy demand with the course of action of the produced hydrogen. In this report, an efficient enhancement in the hydrogen production under ultraviolet (UV) light by Ag- and N-doped LiTaO₃ via solvothermal strategy is proposed. The structural appearance and the spherical morphology are affirmed from the X-ray diffraction and field emission scanning electron microscopy (FESEM) analysis. The bandgap of the prepared photocatalysts is calculated as 5.12, 4.92, and 4.82 eV for undoped LiTaO₃, Ag, and N-doped LiTaO₃ nanoparticles using Tauc's plot. Moreover, the band position of the synthesized LiTaO₃ and also with its dopants is calculated by the Mulliken electro negativity method. The elemental composition of the synthesized photocatalyst is confirmed from the energy dispersive analysis (EDS). Photocatalytic water splitting results over Ag- and N-doped LiTaO₃ photocatalyst showed that the rate of H₂ evolution from formic acid aqueous solution was 240 and 123 µmolh⁻¹ with an apparent quantum yield of 3.11% and 1.59%, whereas for undoped LiTaO₃, the rate is quite lower to be 71 µmolh⁻¹. The reason behind the high catalytic activity of Ag-doped LiTaO₃ is explained by the fact that the higher electronegativity of Ag (1.93) as compared with Ta (1.5) resulted in quite transfer of photoexcited electrons from the conduction band of LiTaO₃ to the Ag species. Interestingly, up to the best of our knowledge, this is the first study regarding the photocatalytic hydrogen evolution for Ag- and N-doped LiTaO₃.

KEYWORDS

hydrogen production, perovskite, photocatalysis, spherical morphology

1 | INTRODUCTION

The energy crisis has become one of the major concerns in the 21st century owing to the fast development of the global economy and population. Hydrogen, a most prominent energy carrier, has laid for environment friendly solution by photocatalytic water splitting because the combustion reaction of it produces only water. Moreover, it is the cheapest water splitting system and suitable to have for large scale applications for H_2 evolution.^[1] Hence, hydrogen production by the way of photocatalytic water splitting is the best choice. In this perspective, an effort has been made for search in materials that are eco-friendly and stable, and also it should afford for energy

insight in the future. In the family of lead-free perovskite oxides such as titanates, tantalates, niobates, vanadates, and ferrites, tantalates and niobates are being explored as a captivating material with versatile properties for various applications such as dielectrics, ferroelectrics, and electro-optic waveguides and photocatalyst for water splitting to produce H₂ or treatment of effluents in water.^[2,3] Moreover, inorganic semiconductors are found to be a substitute because it had feasibility in the synthesis process, and also the production cost is low.^[4] Alkali tantalate perovskites like LiTaO₃, NaTaO₃, and KTaO₃ have accepted significant consideration as they can disintegrate water as H₂ and O₂ without the need of any cocatalyst, whereas the water splitting process in TiO2 usually needs a cocatalyst such as Pt.^[5] In the titanates group, for example, in the case of ZnTiO₃ doped with Ag, nanoparticles played its dual aspect in the photocatalytic dye degradation and also investigated for its antibacterial activity.^[6]

Among photocatalytically active semiconductors, tantalate perovskites have been widely explored because their electronic band structure fulfills the requirements for water splitting, as it consists of three dimensional framework consisting of TaO₆ octahedra with their bottom level of conduction bands consisting of Ta 5d located at a more negative state of redox potential of H^+/H_2 than TiO_2 (Ti 3d), the most prevalent material in this field.^[7] Despite its significant advantage for water splitting without cocatalyst, their main demerit is with its high bandgap as 4.7 eV for LiTaO₃, 4.0 eV for NaTaO₃, and 3.6 eV for KTaO₃, which reduces their photocatalytic activity.^[8] Therefore, the bandgap can be effectively reduced with the addition of suitable dopants. Furthermore, the hydrogen generated by this process can be directly used as a fuel in hydrogen fuel cells.

Among alkali tantalates, lithium tantalate (LiTaO₃) is one of the most admirable photocatalyst materials owing to its impressive physical properties such as its piezoelectric, pyroelectric, electro-optic, and photo-refractive properties.^[9] It also spreads its wings for extensive applications as an ultra-fast switchers, multiplexors and demultiplexors, optical amplifiers, or waveguide lasers.^[10] It is also being investigated as an effective photocatalyst involved in the reaction process of photocatalytic hydrogen evolution. Kato and Kudo^[11] described the photocatalytic water splitting ability into H_2 and O_2 over the alkali tantalates (LiTaO₃, NaTaO₃, and KTaO₃) processed by the conventional solid-state method and also investigated the various factors affecting the photocatalytic activities of various tantalates based on their crystal and energy structure. Photocatalytic H₂ production of La-doped alkali tantalate was studied by Fu et al.,^[12] and they reported that NaTaO₃ exhibited higher

activity for H₂ evolution than LiTaO₃. Edalati et al.^[13] measured the enhanced hydrogen evolution on CsTaO₃ and LiTaO₃ when they are subjected to severe plastic strain using the high-pressure torsion (HPT) method. Zhou et al.^[14] reported that LiTaO₃ possessed the highest photocatalytic ability on tree trunk derived alkali tantalates. The authors also affirmed that the high photocatalytic performance of LiTaO₃ is due to its higher reduction potential, which is more favorable for CO₂ photoreduction despite its larger bandgap. A comparative analysis is made with nobel metal free 1-D CdS coreshell structure-based photocatalyst with its distinct properties such as narrow bandgap, suitable band edge position, and having admirable charge transfer finds its application in photocatalytic hydrogen production with the rate of evolution of 7.6 μ molh⁻¹ with lactic acid as a sacrificial agent.^[15-18]

Tantalate photocatalysts are synthesized by numerous methods such as a solid state reaction, sol-gel, and hydrothermal method. Of all the methods, hydrothermal synthesis is considered as a promising wet chemical process as it generates output in a highly crystalline nature with high purity and low aggregation. Moreover, it regulates the morphology and crystalline structure of the final products by adjusting the hydrothermal reaction conditions.^[19] Hence, in the present work, we address the simple solvothermal route for the synthesis of LiTaO₃ perovskite for photocatalytic hydrogen evolution. Moreover, to enrich further, the discussion is being made on the doping of Ag cations and N anions in to and also its photocatalytic water splitting for the hydrogen production was evaluated. This is the first report regarding the addition of dopants to LiTaO₃ perovskite for the hydrogen evolution.

2 | EXPERIMENTAL DETAILS

2.1 | Preparation of LiTaO₃ nanoparticles

High analytical grade tantalum pentoxide and lithium carbonate are used as a precursor for synthesizing lithium tantalate perovskite (LiTaO₃). In this process, 0.13 M of Ta_2O_5 is dispersed in 30-ml double distilled water and 30-ml ethylene glycol under magnetic stirring. Then 1.62 M of Li₂CO₃ is added into the Ta_2O_5 suspension and again stirred well to attain a homogeneous solution. The desired solution is then transferred into a Teflon-lined stainless steel autoclave that is filled with the mixture to nearly 80% of the total volume. The autoclave is kept at 200°C for a designed period of 15 h. The obtained precipitate is centrifuged and washed three times with double

distilled water and once with ethanol thoroughly in order to remove impurities. Subsequently, the products are dried at 120° C. Then it is grounded well to obtain a perovskite structured LiTaO₃ photocatalyst. The schematic representation of the preparation of LiTaO₃ is presented in Figure S1.

The above same procedure has to be followed with the addition of 0.43 wt% of silver nitrate and 0.025 wt% urea as a nitrogen source for anion doping into the solution containing Ta_2O_5 and Li_2CO_3 such that we have the incorporation of Ag and N into $LiTaO_3$ nanoparticle. Then the synthesized perovskite photocatalysts are undergone for various characterization techniques and also for photocatalytic H_2 evolution measurements.

The structural property of the photocatalyst is analyzed with X-ray diffractometer (XPERT-PRO PW3050) adopting a Cu K α radiation. The surface morphology is learned through field emission scanning electron microscope (FESEM, Zeiss supra 55Ve),s and the composition of elements present in the sample is done by energy dispersive X-ray analysis (EDS). The optical properties of the prepared photocatalyst are examined from the ultraviolet (UV)-visible absorbance spectra recorded using a spectrophotometer (JASCO V-570) in the range of 200–800 nm. Photocatalytic hydrogen evolution measurements are carried out using Shimadzu (GC-2014) gas chromatograph equipped with a thermal conductivity detector (TCD).

3 | RESULTS AND DISCUSSION

The crystalline structure of the LiTaO₃ photocatalysts is identified by X-ray diffraction (XRD) pattern as shown in the Figure 1. It is confirmed that for our sample, the rhombohedral phase of LiTaO₃ nanoparticle is attained, which is in good agreement with the standard data (JCPDS Card No: 29-0836), and the lattice constants are found to be $a = 5.153 \text{ A}^{\circ}$ and $c = 13.755 \text{ A}^{\circ}$.^[20] The characteristic reflection peaks found at 20 are 23.4°, 32.03° , 34.31° , 37.25° , 40.13° , 44.54° , 46.50° , 46.68° , 50.15°, 55.54°, 63.58°, and 71.02°, which are indexed as (012), (104), (110), (006), (113), (330), (024), (002), (082),(122), (300), and (010), correspond to LiTaO₃ planes whereas some additional peaks noted at 2θ are 21.27° , 26.75°, 28.69°, and 30.69°, which are inscribed as (170), (061), (200), and (240) planes that inferred some unreacted Ta₂O₅ species exist in the crystal structure of LiTaO₃ that are verified with JCPDS card No: 71-0639. Moreover, one more peak recorded at 59.96° referred to the plane (116) related to the formation of Ta_2N_5 as confirmed from the standard data (JCPDS card No: 89-5200).



FIGURE 1 Powder X-ray diffraction (PXRD) pattern for (a) undoped LiTaO₃, (b) Ag-doped LiTaO₃, and (c) N-doped LiTaO₃ nanoparticles

From the XRD pattern, it is inferred that only the intensity of the peak slightly varies with the addition of Ag and N dopants.

The crystallite size (*D*) of the particle is calculated using Debye–Scherrer relation $D = k\lambda/\beta \cos\theta$, where λ is the X-ray wavelength (1.54 A°), θ is the diffraction angle, β is the full width at half maximum (FWHM), and *k* is a constant equal to 0.94. The average crystallite size is found to be 8.18, 7.92, and 6.2 nm for undoped LiTaO₃, Ag-, and N-doped LiTaO₃ nanoparticles, respectively. Hence, we inferred that Ag- and N-doped LiTaO₃ nanoparticles exhibited a smaller grain size than the undoped LiTaO₃, which accounts for high photocatalytic activity.

The morphology of the synthesized $LiTaO_3$ and also with its dopants is examined by FESEM as shown in the Figure 2a–c. It is examined that the undoped $LiTaO_3$ nanoparticles exhibited a spherical morphology, and no significant change in the morphology is noted in the case of Ag- and N-doped $LiTaO_3$, whereas the particle gets agglomerated for the addition of dopants. The particle size that lies in the range of 100–300 nm is noted whereas the average crystallite size estimated as below 10 nm has been confirmed from XRD analysis.

EDS reveals the composition of elements present in the synthesized photocatalyst. It is recorded in the range



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FIGURE 2 (a) Field emission scanning electron microscopy (FESEM) image of undoped LiTaO₃, (b) Ag-, and (c) N-doped LiTaO₃ nanoparticles

dispersive analysis (EDS) image of undoped LiTaO₃, (b) Ag-, and (c) N-doped LiTaO₃ nanoparticles

FIGURE 3 (a) Energy

from 0- to 20-keV binding energy region. Figure 3a clearly shows the presence of elements such as Ta and O for pure samples, and from Figure 3b,c, additionally, the presence of Ag and N as doped materials is confirmed. There is no signal regarding the presence of lithium been noted since it has very low energy of characteristic radiation not easy to detect. Table 1 showed the quantitative analysis of elements present in the synthesized photocatalyst. Further, it is confirmed that the addition of dopants affects the composition of the material.

UV-visible absorbance spectroscopy is used to characterize the bandgap of the prepared photocatalyst. Next to crystallinity and morphology, the bandgap of the semiconductor is the primary concept in determining the efficiency of the photocatalyst.^[21] Figure 4a showed the optical absorption spectra for LiTaO₃ with its dopants. The high bandgap of LiTaO₃ is reported due to an increase in deviation from 180° of Ta–O–Ta bond angle due to decreased conduction bandwidth. Figure 4b showed the absorbance spectrum of LiTaO₃ with its dopants, and from that absorbance value, Tauc's relation is used to probe the optical bandgap of the synthesized photocatalyst as represented in the Equation 1.

$$(\alpha h\gamma)^n = K(h\gamma - E_g) \qquad \cdots \qquad (1)$$

TABLE 1Elemental composition of LiTaO3 with its dopants

	Atomic ratio (%)				
Element composition	Li	Та	0	Ag	N
Undoped LiTaO ₃	-	3.11	96.89	-	-
Ag-LiTaO ₃	-	7.36	91.37	1.26	-
N-LiTaO ₃	-	4.87	94.52	-	0.61

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where α refers to the absorption coefficient ($\alpha = 2.303$ A/I), $h\gamma$ denotes the photon energy, $E_{\rm g}$ denotes the optical bandgap value, *K* represents the energy independent constant, and *n* for the occurence of nature of transition. Using the above relation, the energy bandgap value is found to be 5.12, 4.92, and 4.82 eV for undoped LiTaO₃, Ag-, and N-doped LiTaO₃ nanoparticles as appeared in the Figure 5b. Moreover, it is inferred from the analysis that the bandgap value decreases with the addition of dopants.







FIGURE 5 (a) Amount of H_2 generated for various photocatalystand and (b) H_2 production with the time of irradiation for LiTaO₃ photocatalyst with its dopants

Another significant parameter that determines the water splitting capability of the photocatalyst is the location of the bandgap. More precisely, the conduction-band minimum (CBM) and valence-band maximum (VBM) must straddle the redox potentials of H^+/H_2 and O_2/H_2O . While the semiconductor surface is exhibited to the reaction solution in the photocatalytic reaction system, the flat-band potential favors to shift along with the potential of redox species in the solution.^[22] Thus, there is a need to study the position of the band edge potential of the used photocatalyst (LiTaO₃) by Mulliken electro negativity method. Mulliken's definition of the electronegativity of a neutral atom is the arithmetic mean of the atomic electron affinity (A_f) and the first ionization energy (I_1) . The absolute electronegativity (X) is calculated for LiTaO₃ and found to be 6.03.^[23] As the photocatalytic H₂ generation reaction can be split into two portions: (i) oxidation for the evolution of O_2 by the equation $H_2O \rightarrow 4H^+ + 4e^- + O_2$ and (ii) water reduction to produce H_2 by the equation $4H^++4e^- \rightarrow 2H_2$, it is desirable to know the edge of valence and conduction band for the fruitful activity of the photocatalyst. The conduction and valence band position is calculated from the formula $E_{CB} = X - E_c - 1/2E_g$ and $E_{VB} = E_g + E_{CB}$, where E_c is the energy of the free electrons of hydrogen scale (1.23 eV) and E_{CB} and E_{VB} are the energy of conduction and valence band. The edges of the valence band (E_{VB}) and conduction band (E_{CB}) of LiTaO₃ are determined to be 2.58 and -2.54 eV (vs. normal hydrogen electrode, NHE). The valence band is more positive than the oxidation potential of O₂ whereas the conduction band is more negative than the reduction potential of H₂.^[24] This hampers the catalytic active sites to have surface interface reactions.

The photocatalytic hydrogen production is carried out in an air free closed gas system with a quartz reactor provided with the sealant at the top using rubber septum. and a light source of 450-W Xe-Hg UV lamp is used for irradiation. The gas evolved in this process is detected by online analysis with a multichannel analyzer equipped with TCD for the determination of the concentration of hydrogen.^[25] In the present examination, the prepared photocatalyst powder with 10 mg is dispersed in 38-ml distilled water, and 12-ml formic acid serves as a sacrificial agent altogether taken in the quartz reactor.^[26] Then it is subjected to sonication and followed by stirring for 20 min in order to attain a homogeneous solution. Finally, the quartz reactor is tightly closed with a rubber septum and carried out for degassing in such a way to evacuate the undesired gases inside the reactor, eventually purged with ultra-pure N2 gas to have an inert atmosphere setup. Photocatalytic experiments are functioned with revealed to UV light radiation along with the continuous stirring of the quartz reactor. The rate of H₂ gas evolved is computed using a gas chromatograph equipped with TCD detector.

The photocatalytic hydrogen production measurements were evaluated for undoped LiTaO₃ and also for Ag- and N-doped LiTaO₃ in formic acid and water mixture under UV light. Figure 5a exhibits the comparison of H₂ evolution for undoped LiTaO₃ and also with its Ag and N dopants. The rate of H₂ production for Ag-doped LiTaO₃ is found to be 240 μ molh⁻¹, whereas for undoped and N-doped LiTaO₃, the rate of H₂ production is only 71 and 123 μ molh⁻¹. The apparent quantum yield (A.Q.Y) for Ag-doped LiTaO₃ is 3.11%, which is higher than that for undoped and N-doped LiTaO3 as 0.92% and 1.59%. When comparing the obtained A.Q.Y value with other alkali tantalates such as NaTaO₃ and KTaO₃, the value is quite lower than 7.22% and 4.87%. Figure 5b showed the production rate at which H₂ evolution increases linearly for the time interval up to 4 h as 269 μ mol for undoped LiTaO₃, whereas for Ag and Ndoped LiTaO₃, the rate is 956 and 505 μ mol. There should be noted that no addition of cocatalyst to avoid any disturbance caused by the addition of cocatalyst. The lowest photocatalytic activity observed may be due to the fact that the bond angle of Ta–O–Ta is 143° which is too small been responsible for the migration of UV light excited charge carriers. Moreover from the structural point of view, though the crystallite and particle size is low, the spherical surface attributes to have an exposure to the low surface area might be one of the reasons for the low production output in hydrogen evolution.

The observed photocatalytic activity is compared with the previous reported values that are presented in Table 2.

4 | PROBABLE MECHANISM OF LITAO₃ FOR H₂ EVOLUTION

As viewed from the photocatalytic hydrogen evolution measurements that Ag doped showed its improvement in the photocatalytic performance whereas in the case of N doping the catalytic activity is decreased due to the fact it acts as a electron-hole recombination centers resulted in low hydrogen production. The reason behind this is explained by the fact that it showed higher electronegativity of Ag (1.93) as compared with Ta (1.5), which resulted in quite transfer of photoexcited electrons from the conduction band of LiTaO₃ to the Ag species. This hampers the rapid recombination of electron-hole pairs leading to the high catalytic activity. Moreover, it is possible for the Ag-doped LiTaO₃ serves as active sites for proton reduction.^[29] A possible mechanism is proposed based on the obtained results in the form of an equation from 2 to 7.

$$Ag-LiTaO_3 + h\gamma \rightarrow e^- + h^+ \qquad \cdots \qquad (2)$$

$$H_2O + h^+ \to H^+ + OH \qquad \cdots \qquad (3)$$

$$OH + OH \rightarrow H_2O + \frac{1}{2}O_2 \qquad \cdots \qquad (4)$$

TABLE 2 Comparison of the rate of photocatalytic H₂ evolution for LiTaO₃ with its various dopants

Photocatalyst	Cocatalyst	Evolution of H_2 (µmolh ⁻¹)	Light source	Reference	
LiTaO ₃	NiO (0.10 wt%)	98	400-W Hg lamp	Kato and Kudo ^[27]	
	-	430			
La-LiTaO ₃	Pt (0.2 wt%)	20	125-W Hg lamp	Fu et al. ^[12]	
LiTaO ₃	Pt (0.2 wt%)	4.3	500-W Xe lamp	Hagiwara et al. ^[28]	
LiTaO ₃	Before processed by HPT method	10	300-W Xe lamp	Edalati et al. ^[13]	
	After processed by HPT method	27			
LiTaO ₃	-	`71	450-W	Present work	
Ag-NaTaO ₃	-	240	Xe-Hg		
N-NaTaO ₃	-	143	UV lamp		

Abbreviations: HPT, high-pressure torsion; UV, ultraviolet.



FIGURE 6 Photocatalysis mechanism involved in Ag-doped LiTaO₃ for H₂ production

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 $HCOOH \rightarrow HCOO^- + H^+ \qquad \cdots \qquad (5)$

 $HCOO^- + 2h^+ \rightarrow H^+ + CO_2 \uparrow \qquad \cdots \qquad (6)$

$$2H^+ + 2e^- \to H_2 \uparrow \qquad \cdots \qquad (7)$$

UV light is absorbed by the Ag-doped LiTaO₃ photocatalyst and thereby electron-hole pairs created (Equation 2). The molecules of water present in the formic acid solution split into H⁺ ions and hydroxyl radicals ('OH) by oxidation reaction (Equation 3). The generated hydroxyl radicals produce molecular hydrogen and oxygen (Equation 4). Formic acid dissociates in to HCOO⁻ and H⁺ ions as seen from the equation (Equation 5). The photogenerated holes then attack the generated HCOO⁻, which, in turn, form H⁺ and CO_2 (Equation 6). The produced H^+ ions in the entire process transferred to the doped Ag species where the reduction process occurs with the generation of H₂ in the last step of the entire process (Equation 7). Figure 6 signifies the mechanism involved in the process of generation of hydrogen in Ag-doped LiTaO₃.

5 | CONCLUSION

In summary, Ag- and N-doped LiTaO₃ photocatalysts have been synthesized by solvothermal strategy. The resultant Ag-doped LiTaO₃ showed its enhancement in the rate of H₂ evolution of 240 μ molh⁻¹ with formic acid as a sacrificial agent with an A.Q.Y to be 3.11%, which is quite higher than N-doped LiTaO₃. Compared with nonmetal (N) doping, noble metal (Ag) provides a favorable route for the transfer of photoexcited electrons between semiconductor and Ag nanoparticle. Further, this study perhaps provided an effective path in designing LiTaO₃ photocatalyst with other suitable dopants towards boosted H₂ evolution.

DATA AVAILABILITY STATEMENT

Data are available on request from the authors.

AUTHOR CONTRIBUTIONS

C.R. Kalaiselvi: Conceptualization; formal analysis; investigation; methodology; validation; visualization. **T.S. SENTHIL:** Conceptualization; investigation; supervision. **M.V. SHANKAR:** Methodology; project administration; validation. **V. SASIREKHA:** Data curation; resources.

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