SOLID STATE SYNTHESIS OF La-DOPED NaTaO$_3$ UNDER TIME-REDUCED CONDITIONS AND ITS PHOTOCATALYTIC PROPERTIES

#RIGOBERTO LÓPEZ-JUÁREZ*, FEDERICO GONZÁLEZ**, SANDRA CIPAGAUTA***,
SIMÓN Y. REYES-LÓPEZ****, RICARDO GÓMEZ***

*Unidad Morelia del Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México,
Antigua Carretera a Pátzcuaro No. 8701, Col. Ex Hacienda de San José de la Huerta, C.P. 58190, Morelia, Michoacán, México
**Departamento de Ingeniería de Procesos e Hidráulica, Universidad Autónoma Metropolitana-Iztapalapa,
A.P. 55-534, 09340 México D.F., México
***Departamento de Química, Universidad Autónoma Metropolitana-Iztapalapa,
Av. San Rafael Atlixco No 186, Col. Vicentina, México 09340, D.F. México
****Departamento. de Ciencias Químico Biológicas, Instituto de Ciencias Biomédicas,
Universidad Autónoma de Ciudad Juárez. Anillo Envolvente del PRONAF y Estocolmo s/n,
C.P. 32300,Cd. Juárez Chih, México

#E-mail: rlopez@iim.unam.mx

Lanthanum-doped sodium tantalate was synthesized by solid state method at low temperature and short calcination time. Pure phase powders were obtained after calcination at 950°C and 1000°C for 1h with average crystal size below 150 nm. The photocatalytic performance was increased with La concentration, reaching a maximum at 2 mol. % La. Good activity was observed even without any loading cocatalyst. After further calcination, there was no evidence of improvement of the photocatalytic performance.

INTRODUCTION

Sodium tantalate (NaTaO$_3$, abbreviated NT) has been extensively studied because is a material with suitable band gap for water splitting under ultraviolet radiation [1-2]. This material has been synthesized using several chemical wet methods, including sol-gel [3-6], conventional hydrothermal [7-8], solvothermal [9] microwave hydrothermal route [10] and some others [11-13]. The aim of using chemical wet methods is to avoid high temperature and long thermal treatment for crystallization. Also, to reduce the volatization of sodium during processing, and thus, to minimize the amount of vacancies (defects in general) which serve as electron-hole recombination centers [1, 14].

Some of these methods require expensive reagents and too much care is needed. For example, in the sol-gel method the tantalum alkoxide needs to be handled into a glovebox because its high reactivity. The hydrothermal and microwave hydrothermal routes require long synthesis time and expensive equipment, respectively. So, the solid state method is the cheapest and easier way to synthesize NT powders.

The methodology used for preparing sodium tantalate strongly influence defect concentration (crystallinity) and crystal structure [1-2, 14]. As described above, it is stated that crystallinity of NT powders is a crucial issue to overcome the recombination of electron-hole pairs. Sometimes, the term "crystallinity" is related with well-defined edges. Most of the reports associate crystallinity with crystal size, because they underline the intensity and peak width in X-Ray analysis. Others, said that well-defined edges are necessary for high photacalytic activity [1, 3]. In addition, it can be related to the minimization of defect concentration in materials [2]. But it is difficult to control and quantify defect concentration on NT.

Then, in this work, La doped NaTaO$_3$ powders were synthesized by solid state method with reduced heat treatment and their properties evaluated.

EXPERIMENTAL

Synthesis of powders

Synthesis of pure and La-doped NaTaO$_3$ powders was performed using Na$_2$CO$_3$ (99.9 % Fermont), Ta$_2$O$_5$ (99.99 % Sigma-Aldrich) and La$_2$O$_3$ (99.9 % Sigma-Aldrich). Before weighting, the reagents were dried for 2 h at 200°C in order to eliminate absorbed moisture. They were mixed using an agate mortar and pestle with acetone. Then, the mixture was calcined at 950°C for 1 h. After that, the powders were ball milled for 12 h in a plastic jar with zirconia grinding media using ethanol, dried at 120°C for 3 h and calcined at 1000°C for 1 h.

Half of each sample was further calcined at 950°C for 4h without further milling step for evaluating the influence of thermal treatment on crystal size and photocatalytic performance. Before this calcination, 2 mol. % of sodium was added as Na_2CO_3 to compensate its losses at high temperature.

Structural and microstructural characterization

The structural and microstructural characterization of powders was done with X-Ray diffraction analysis (Bruker D8 with Cu Ka radiation) and Scanning Electron Microscopy (JEOL JSM IT300 with Oxford EDS detector). Rietveld refinement was performed for calculating the mean crystal size. The orthorhombic space group *Pcmn* (No. 62) was used for fitting the experimental results with the Topas academic software. The thermal parameters and atomic positions were taken from Ref. [15].

Optical absorption and band gap calculation

The absorption spectra were obtained by using the diffuse reflectance technique. The measurements were performed in a Cary 5 spectrophotometer equipped with a Praying Mantis (Harrick Scientific Products, Inc.) accessory for diffuse reflection spectroscopy. The spectra were recorded in the wavelength range between 250 and 700 nm. The band gaps were estimated from absorption spectra following the procedure described in elsewhere [16].

Measurements of specific surface area

In order to obtain the specific surface area, physical nitrogen adsorption was carried out using a Quantachrome 3B instrument. Prior to the analysis, the catalyst was degassed at 200°C for 6 h to remove the adsorbed impurities. BET equation was applied for obtaining the specific surface area.

Photocatalytic performance

The photocatalysis performance was measured by quantifying the evolution of H_2. For a typical experiment, 25 milligrams of powders were loaded in a water-methanol solution (2:1 ratio). This solution was maintained under magnetic stirring at room temperature. The water splitting reaction was done in a quartz closed reactor cell coupled with a gas chromatograph (Shimadzu G-08) equipped with a thermal conductivity detector (TCD) and a Shincarbon packed column (2 m length, 1 mm ID and 25 mm OD), using N_2 as carrier gas. The amount of evolved H_2 was measured at intervals of 1 h. To assure the adsorption/desorption

equilibrium, the system was stirred in the dark for 30 min and degassed by bubbling nitrogen prior to the photochemical reaction. The experiments were performed with UV radiation (254 nm) produced by a high pressure mercury lamp (Pen-Ray Mercury Lamp with I_0= 2 mW·cm^{-2}) and without any cocatalyst loaded.

RESULTS AND DISCUSSION

From the X-ray analysis shown in Figure 1, it is clear that pure phase was obtained for undoped and La-doped sodium tantalate powders. The common secondary phases that appear during synthesis depends upon the method used. When the solid-state method is used for the synthesis of NT, the unreacted phases commonly found are Ta_2O_5 or sodium related phases [14]. For hydrothermal and microwave hydrothermal, tantalum oxide is the most frequently secondary phase encountered [7, 10, 17].
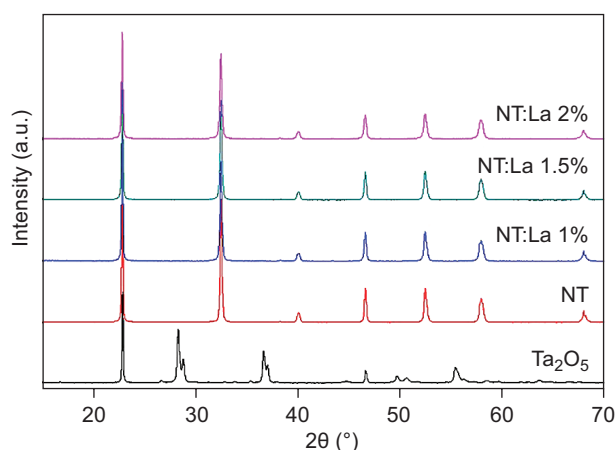

Figure 1. XRD patterns of Ta_2O_5, $NaTaO_3$ and La-doped $NaTaO_3$, calcined at 950° C for 1 h plus 1 h at 1000° C.

When the solid state is used, high temperature and time is required for producing crystalline sodium tantalate, because the high melting point of tantalum oxide. In our case, the heat treatment has been reduced to 2 h, 1 h at 950°C and another at 1000°C. Then, it is possible to synthesize La-doped $NaTaO_3$ powders lowering calcination time, without secondary phases. Comparing these crystallization conditions by solid state method with previous reports [1, 3, 15], the conditions used in this work are less stringent, which is beneficial for energy saving as well as for reducing crystal size.

Chemical analysis was carried out on some samples by EDS, and the results for the undoped and the 2 mol. % La doped samples are shown on Table 1. The measured atomic compositions are close to the theoretical values, and considering the experimental error included due to the technique, the results match pretty well.

In the solid state method, two main issues need to be overcome, crystal growth and sodium volatilization at high temperature. Then, is common practice to regrind and add near 5 mol. % sodium in excess [3, 15]. The powders obtained by this methodology have large crystals, low surface area, and less reaction sites.

Table 1. Chemical analysis by EDS of undoped and 2 mol. % La doped powders.

Composition	NT		NT:La 2 %	
Element	Atomic %	Atomic % (theoretical)	Atomic %	Atomic % (theoretical)
O	62.71	60	61.99	60
Na	18.22	20	17.47	19.6
Ta	19.06	20	20.18	20
La	0	0	0.36	0.4
Total:	100.00	100.00	100.00	100.00

Volatilization of sodium produce defects, so, it is possible to diminish calcination time for reducing crystal size and sodium volatilization. This would somehow increase photocatalytic performance of pure and La-doped sodium tantalate comparing with those powders synthesized under more stringent conditions by the solid state method.

For comparison, we performed calcination to half of each sample at 950°C for 4 h, in order to identify if there is considerably further crystal growth and its influence on the photocatalytic properties. The X-Ray results after the second calcination are shown in Figure 2. No evident broadening is observed in the X-Ray analysis. The XRD results are similar to those of samples calcined at 950° and 1000°C for 1 h, which are pure perovskite phase. The XRD are similar because there are no considerable difference in crystal size between calcinations for 2 h and 4 h. This will be evidenced below with SEM images.
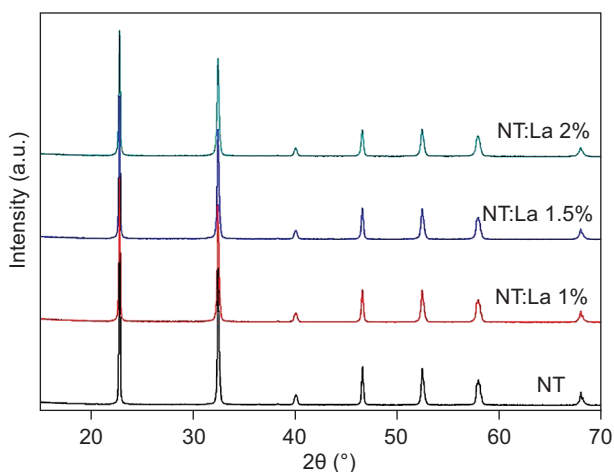

Figure 2. XRD of tantalate powders after second calcination at 950° C for 4 h.

The mean crystal size and other crystallographic data were obtained by Rietveld refinement technique. The calculated crystal size diminish from ~127 nm for undoped NT to ~82 nm for 2 mol. % of lanthanum content. After further calcination at 950°C for 4 h, the crystal size increased slightly to ~143 nm for NT and ~87 nm for 2 mol. % La. Data for the other compositions fall between these values and have almost linear behavior i.e. the crystal size decreases with lanthanum content. As an example, the Rietveld refinement fitting for NT is shown in Figure 3.
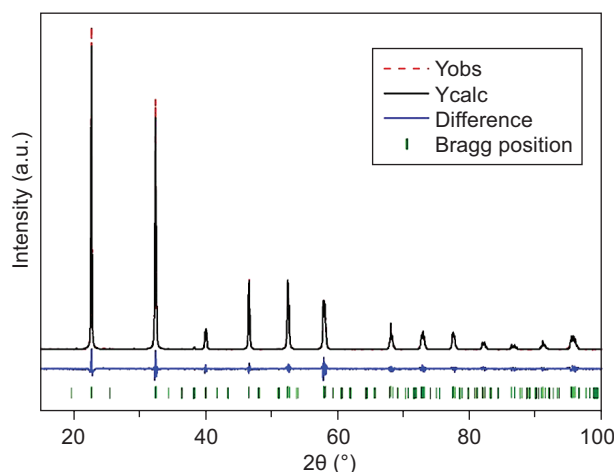

Figure 3. Rietveld refinement for undoped NT calcined at 950°C for 1 h plus 1 h at 1000°C.

In Figure 4, the SEM images of sodium tantalate powders are shown. It is worth to note the submicrometric crystal size for all compositions. This is hard to achieve under conventional solid state synthesis conditions [15]. So that, low surface area is obtained, commonly below 0.44 - 5 m$^2 \cdot$g^{-1} [1,14].

The high surface area means that more active sites are available for the photocatalytic reactions. Then, it would be plausible that the submicrometric powders synthesized would have higher reactivity compared to powders obtained by solid state method but under more severe conditions.

The SEM images of samples further calcined at 950°C for 4 h are shown in Figure 5. The mean crystal size has not increased considerably (as stated above); then, the results of SEM corroborate those ones of the XRD analysis for these samples, where no evidence of severe crystal growth was observed. The reason why there is not a noticeable crystal size increment could be due to the relatively short (4 h) calcination time, and to the relatively low calcination temperature (950°C). In the synthesis of NT powders by the conventional solid state method, usually, precalcination at 1170 K for 1 h (~900°C) and calcination at 1420 K (~1150°C) for 10 h is performed twice or three times for synthesis of NT [1, 3, 15, 18]. These synthesis conditions promote considerable crystal growth.

a) NT

b) 1 % La doped NT

c) 1.5 % La doped NT
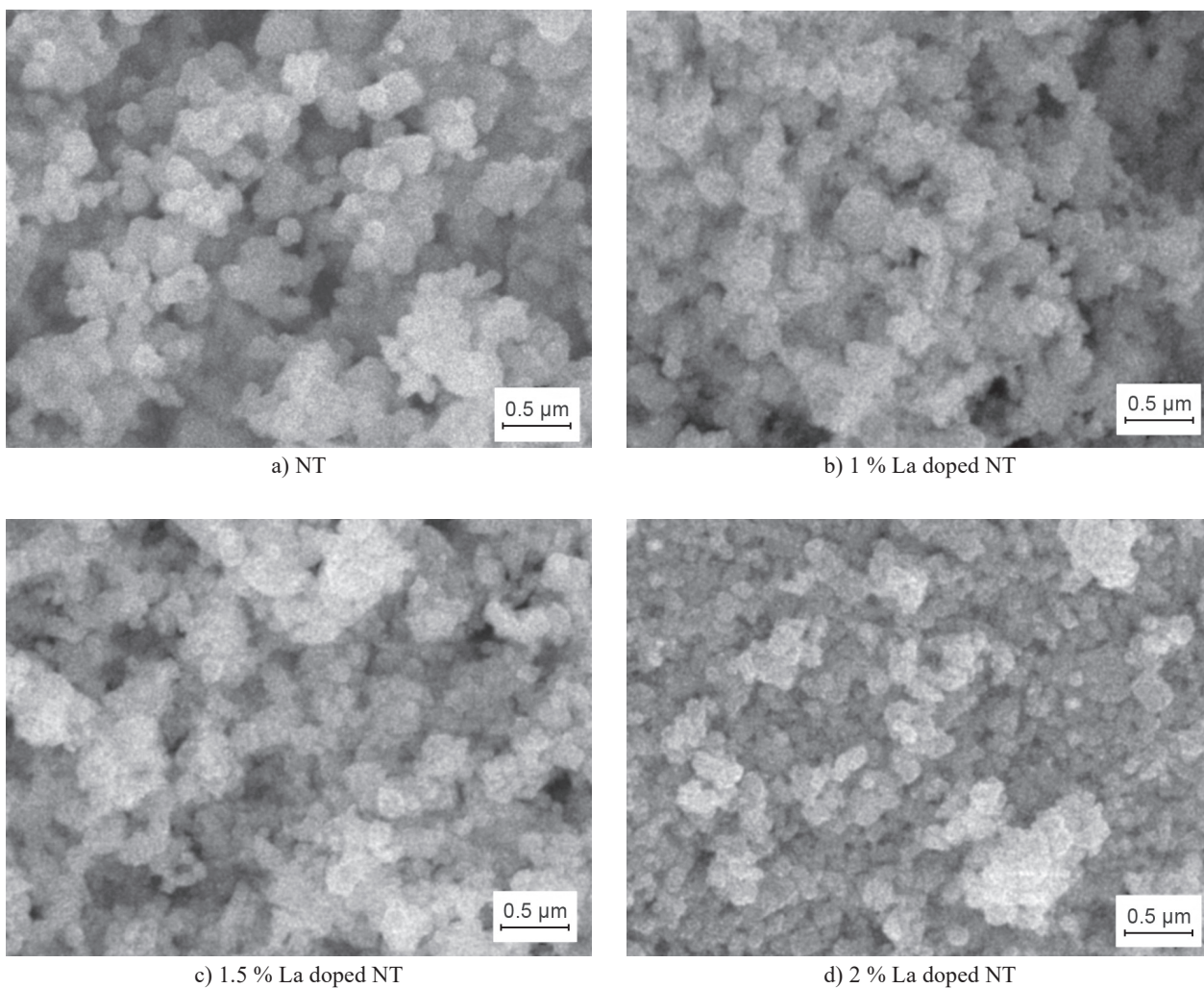

d) 2 % La doped NT

Figure 4. SEM images of a) NT, b) 1 % La doped NT, c) 1.5 % La doped NT and d) 2 % La doped NT calcined at 950°C for 1 h, ball milled for 12 h and calcined at 1000°C for 1 h.
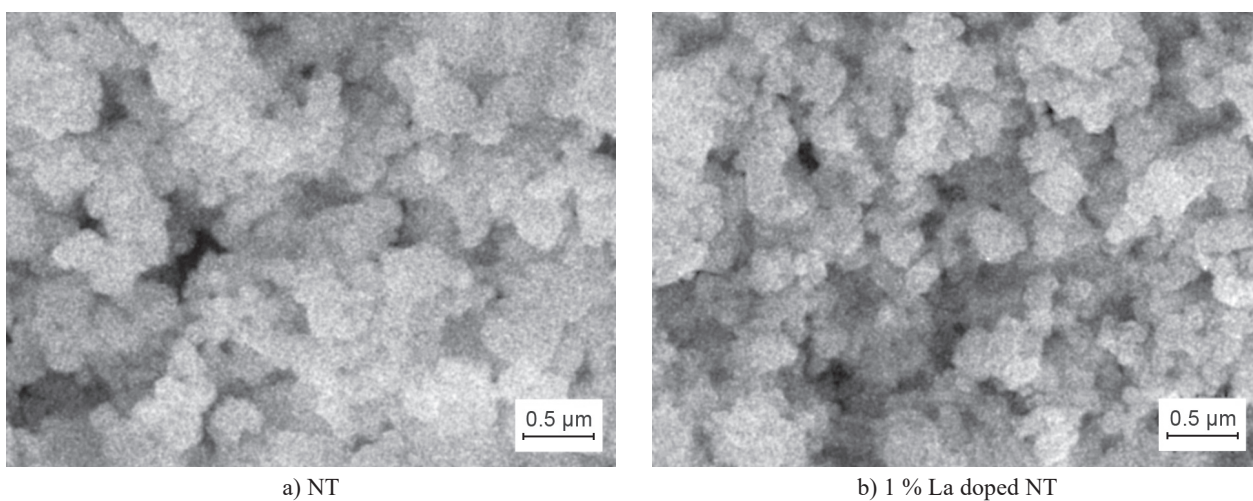

a) NT

b) 1 % La doped NT

Figure 5. SEM images of a) NT, b) 1 % La doped NT, c) 1.5 % La doped NT and d) 2 % La doped NT, calcined as reported in Figure 3 and additional treatment at 950°C for 4 h. *(Continue on next page)*
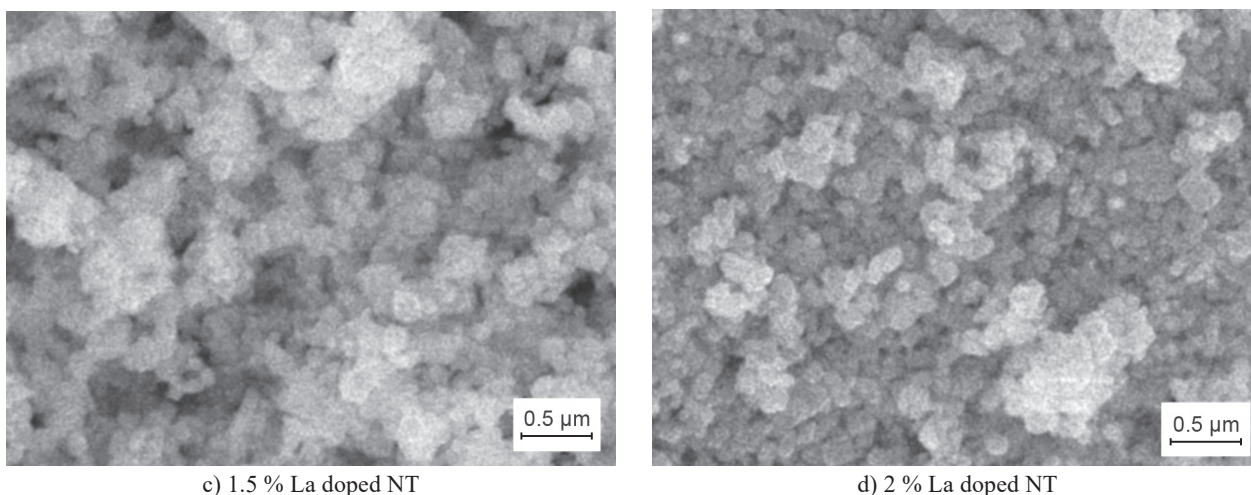
c) 1.5 % La doped NT

d) 2 % La doped NT

Figure 5. SEM images of a) NT, b) 1 % La doped NT, c) 1.5 % La doped NT and d) 2 % La doped NT, calcined as reported in Figure 3 and additional treatment at 950°C for 4 h.

The results of hydrogen production are shown in Figure 6. As it can be seen, the amount of evolved H_2 increases almost linearly with the amount of La content as expected from previous results [1,3] for samples calcined at 950°C for 1 h plus 1 h at 1000°C (Figure 6a).
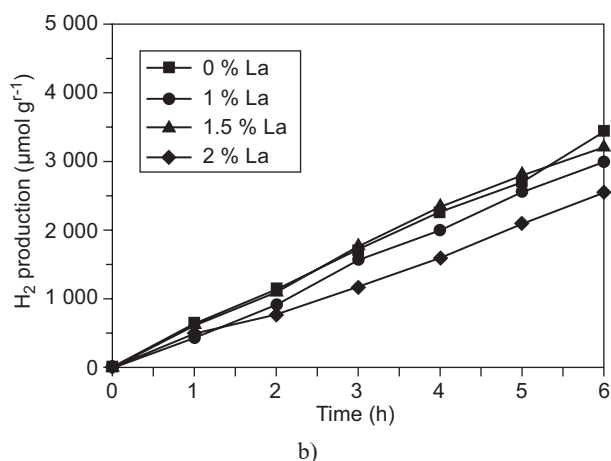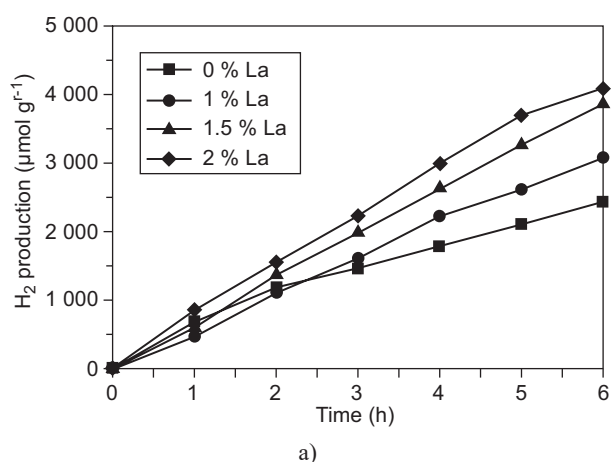

a)

b)

Figure 6. H_2 production with La-doped NT powders.

In Figure 6b, the results for hydrogen production on samples further calcined are shown. As observed the photocatalytic performance has dropped, two issues are considered for explaining this behavior. First, the lower surface area due to crystal growth, and to the agglomeration promoted in the second calcination step, both are evident in the SEM images (Figure 5).

The H_2 rate production are similar to those reported for $NaTaO_3$ synthesized by microwave-hydrothermal method [9], hydrothermal method [17], flux method [19], and superior to other results for solid state method [15,20], and confined space synthesis [12]. Our results are promising considering that in most of the mentioned studies, the NT powders have been coated with cocatalyst (NiO, NiOx or Pt derived compounds) which increase the performance.

The band gap of prepared powders are shown in Table 2. Looking at the results, it seems that the additional thermal treatment has not affected the electronic structure, i.e., the La-doped did not transform to other crystalline structure. Furthermore, the band gap is similar for all compositions. So, the only difference between the powders is the crystal size due to La-doping. These results are similar to others studies that reports band gap values in the order of 3.6 - 4.0 eV [3,14] for undoped NT, depending upon synthesis method. While for La-doped the range is spanned over 4.09 - 4.17 eV [1, 19]. It is well-known that band gap and specific surface are sensitive to the synthesis conditions i.e. the chemical route and calcination temperature. When a soft chemical method is used for preparing NT powders, nanometric crystal size is obtained (high surface area) and there is a phase transition due to size effect [3]. This phase transition also affects the band gap, so the photocatalytic properties are affected as well.

As seen from Table 2, in general the specific surface area decreases comparing samples with additional ther-

Table 2. Band gap and specific surface of synthesized powders.

Composition/Thermal treatment	Band gap (eV)	Specific surface area ($m^2 \cdot g^{-1}$)
NT / 950°C 1 h – 1000°C 1 h	4.16	4.9
NT:La 1 % / 950°C 1 h – 1000°C 1 h	4.17	6.4
NT:La 1.5 % / 950°C 1 h – 1000°C 1 h	4.18	6.8
NT:La 2 % / 950°C 1 h – 1000°C 1 h	4.16	7.6
NT / 950°C 1 h – 1000°C 1 h – 950°C 4 h	4.16	4.0
NT:La 1 % / 950°C 1 h – 1000°C 1 h – 950°C 4 h	4.16	5.5
NT:La 1.5 % / 950°C 1 h – 1000°C 1 h – 950°C 4 h	4.17	5.7
NT:La 2 % / 950°C 1 h – 1000°C 1 h – 950°C 4 h	4.18	7.2

mal treatment because the crystal growth and further agglomeration is induced. That is why the photocatalytic performance is deteriorated.

So, it is been demonstrated that high purity NT and La-doped NT powders can be obtained by solid state method. The produced powders having high photocatalytic activity.

CONCLUSIONS

Pure and La-doped sodium tantalate powders were synthesized using solid state method under moderated synthesis conditions of time and temperature. Pure perovskite crystalline phase was achieved for all compositions. Submicrometric average crystal size was obtained even after a second calcination stage at 950°C for 4 h. This crystal size was possible because of the low temperature and calcination time. This allowed to increase photocatalytic performance of prepared powders. The higher photocatalytic activity was observed in the 2 mol. % doped NT powders.

Aknowledgements

REFERENCES

1. Kato H., Asakura K., Kudo A. (2003): Highly efficient water splitting into H₂ and O₂ over lanthanum-doped NaTaO₃ photocatalysts with high crystallinity and surface nanostructure. *Journal of the American Chemical Society*, *125*(10), 3082-3089. doi:10.1021/ja027751g
2. Kudo A., Miseki Y. (2009): Heterogeneous photocatalyst materials for water splitting. *Chemical Society Reviews*, *38*(1), 253-278. doi:10.1039/B800489G
3. Hu C.C., Teng H. (2007): Influence of structural features on the photocatalytic activity of NaTaO₃ powders from different synthesis methods. *Applied Catalysis A: General*, *331*, 44-50. doi:10.1016/j.apcata.2007.07.024
4. Husin H., Mahidin M., Zuhra Z., Hafita F. (2014): H₂ evolution on Lanthanum and Carbon co-doped NaTaO₃ Photocatalyst. *Bulletin of Chemical Reaction Engineering & Catalysis*, *9*(2), 81-86. doi:10.9767/bcrec.9.2.5530.81-86
5. Husin H., Pontas K., Sy Y., Syawaliah S., Saisa S. (2014): Synthesis of Nanocrystalline of Lanthanum Doped NaTaO₃ and Photocatalytic Activity for Hydrogen Production. *Journal of Engineering and Technological Sciences*, *46*(3), 318-327. doi:10.5614/j.eng.technol.sci.2014.46.3.1
6. Husin H., Chen H.M., Su W.N., Pan C.J., Chuang W.T., Sheu H.S., Hwang B.J. (2011): Green fabrication of La-doped NaTaO 3 via H 2 O 2 assisted sol-gel route for photocatalytic hydrogen production. *Applied Catalysis B: Environmental*, *102*(1), 343-351. doi:10.1016/j.apcatb.2010.12.024
7. Li X., Zang J. (2009): Facile hydrothermal synthesis of sodium tantalate (NaTaO₃) nanocubes and high photocatalytic properties. *The Journal of Physical Chemistry C*, *113*(45), 19411-19418. doi:10.1021/jp907334z
8. Liu J.W., Chen G., Li Z.H., Zhang Z.G. (2007): Hydrothermal synthesis and photocatalytic properties of ATaO₃ and ANbO₃ (A= Na and K). *International Journal of Hydrogen Energy*, *32*(13), 2269-2272. doi:10.1016/j.ijhydene.2006.10.005
9. He Y., Zhu Y. (2004): Solvothermal synthesis of sodium and potassium tantalate perovskite nanocubes. *Chemistry Letters*, *33*(7), 900-901. doi:10.1246/cl.2004.900
10. Shi J., Liu G., Wang N., Li C. (2012): Microwave-assisted hydrothermal synthesis of perovskite NaTaO₃ nanocrystals and their photocatalytic properties. *Journal of Materials Chemistry*, *22*(36), 18808-18813. doi:10.1039/C2JM33470D
11. Nelson J.A., Wagner M.J. (2003): Synthesis of sodium tantalate nanorods by alkalide reduction. *Journal of the American Chemical Society*, *125*(2), 332-333. doi:10.1021/ja028125m
12. Yokoi T., Sakuma J., Maeda K., Domen K., Tatsumi T., Kondo J.N. (2011): Preparation of a colloidal array of NaTaO₃ nanoparticles via a confined space synthesis route and its photocatalytic application. *Physical Chemistry Chemical Physics*, *13*(7), 2563-2570. doi:10.1039/C0CP02141E
13. Tüysüz H., Chan C.K. (2013): Preparation of amorphous and nanocrystalline sodium tantalum oxide photocatalysts with porous matrix structure for overall water splitting. *Nano Energy*, *2*(1), 116-123. doi:10.1016/j.nanoen.2012.08. 003
14. Torres-Martínez L.M., Cruz-López A., Juárez-Ramírez I., Meza-de la Rosa M.E. (2009): Methylene blue degradation by NaTaO 3 sol–gel doped with Sm and La. *Journal of hazardous materials*, *165*(1), 774-779. doi:10.1016/j.

jhazmat.2008.10.060

15. Hu C.C., Tsai C.C., Teng H. (2009): Structure Characterization and Tuning of Perovskite-Like NaTaO₃ for Applications in Photoluminescence and Photocatalysis. *Journal of the American Ceramic Society*, *92*(2), 460-466. doi:10.1111/j.1551-2916.2008.02869.x

16. Chakrabarti S., Das D., Ganguli D., Chaudhuri S. (2003): Tailoring of room temperature excitonic luminescence in sol-gel zinc oxide–silica nanocomposite films. *Thin Solid Films*, *441*(1), 228-237. doi:10.1016/S0040-6090(03)00862-9

17. Zhao Y., Xiang T., Han P. (2014): Hydrothermal synthesis and investigation of photocatalytic properties of Fe–N co-doped NaTaO₃. A*pplied Mechanics and Materials*, *457-458*, 202-205. doi:10.4028/www.scientific.net/AMM.457-458.202

18. Zhou X., Shi J., Li C. (2011): Effect of metal doping on electronic structure and visible light absorption of SrTiO₃ and NaTaO₃ (Metal= Mn, Fe, and Co). *The Journal of Physical Chemistry C*, *115*(16), 8305-8311. doi:10.1021/jp200022x

19. Porob D.G., Maggard P.A. (2006): Flux syntheses of La-doped NaTaO₃ and its photocatalytic activity. *Journal of Solid State Chemistry*, *179*(6), 1727-1732. doi:10.1016/j.jssc.2006.03.008

20. Noda Y., Lee B., Domen K., Kondo J.N. (2008): Synthesis of crystallized mesoporous tantalum oxide and its photocatalytic activity for overall water splitting under ultraviolet light irradiation. *Chemistry of Materials*, *20*(16), 5361-5367. doi:10.1021/cm703202n