

**9th International Symposium on New Materials and Nano-Materials for
Electrochemical Systems
XII International Congress of the Mexican Hydrogen Society
Merida, Mexico, 2012**

Synthesis of NaTaO₃ by a New Solvo-Combustion Method and its Hydrogen Production Photoactivity

C. Gómez-Solís^{1,2,*}, I. Juárez-Ramírez¹, L. M. Torres-Martínez¹, M. Z. Figueroa-Torres¹, M. A. Ruiz-Gómez¹, D. Sánchez-Martínez¹, E. Zarazúa-Morín¹

¹Universidad Autónoma de Nuevo León, UANL, Facultad de Ingeniería Civil, Departamento de Ecomateriales y Energía, Av. Universidad S/N Ciudad Universitaria San Nicolás de los Garza Nuevo León, C.P. 66451 México

²Facultad de Ciencias Químicas, Universidad Autónoma de San Luis Potosí, Av. Manuel Nava #6, San Luis Potosí, S.L.P. 78290, México

*Tel: (81)83521984 ext. 222, fax (81)83760477, mail: lienquidremo@hotmail.com

ABSTRACT

Significant attention has been paid on the photocatalytic production of hydrogen from water by using semiconductors. The NaTaO₃ has been regarded as one of the most promising material for water splitting, since it has shown remarkable water splitting activity due to its high potential to generate charge carriers by absorbing the photons energy. This work reports for the first time the NaTaO₃ synthesized through a new solvo-combustion method, in this case the acetylacetone was used as template and fuel for the combustion reaction. The DRX analysis results showed that NaTaO₃ phase could be obtained from the as-grown material. The SEM micrographs revealed that NaTaO₃ has hierarchical cubic morphology in the nanometer level. The materials possess a high specific surface area around 50-90 m².g⁻¹, which is one of the highest reached when compared to other synthesis methods. The UV-visible analysis show a band gap value (*E_g*) close to 3.9 eV. The material exhibited attractive photocatalytic activity for water splitting reaction to produce hydrogen. An enhanced of the hydrogen production was obtained by annealing the material at 600 °C from 418 to 644 μmol, because of the higher crystallinity degree.

1. Introduction

Several researches have been conducted in order to produce alternative clean energy sources. In this way, hydrogen production is one of the most important technologies studied hardly during the last decade. Particularly hydrogen produced from water splitting reaction by photocatalysis has been attracted considerable attention because of the possibility to develop new or better catalyst materials using metal transition oxides, which are active under UV and visible light irradiation [1,2,4,5]. Some oxides like tantalates, titanates, niobates and tungstanates have been showed important activity for water splitting in comparison with TiO₂, commonly used as photocatalyst [3-9]. Additionally the modifications of electronic structure, crystal structure or physicochemical properties could be enhancing the activity of catalytic materials for water splitting reaction [4-10]. Therefore, it is important to produce catalyst materials with strict control of the composition, homogeneity, size and particle shape, as well as at low temperature. In recent years, several chemical methods such as hydrothermal, solution combustion, sol-gel and co-precipitation have been employed to synthesize new and better materials. Perovskite-type sodium tantalite NaTaO₃ has attracted



**9th International Symposium on New Materials and Nano-Materials for
Electrochemical Systems
XII International Congress of the Mexican Hydrogen Society
Merida, Mexico, 2012**

much attention from researchers due to its highly efficient photocatalytic activity for overall water splitting under ultraviolet (UV) irradiation [15].

This work focuses on the synthesis of NaTaO_3 material by a new solvo-combustion method with high surface area. NaTaO_3 will be tested as catalyst material for water splitting reaction in order to produce hydrogen under UV-light irradiation.

2. Experimental

2.1 Synthesis of NaTaO_3 by solvo-combustion method

NaTaO_3 powder was prepared by a new solvo-combustion method. Acetylacetone (Aldrich 99.5 %), was mixed with ethanol (DEQ 95 %) in a 1:1 Vol. ratio, the solution was kept in a reflux system by 10 minutes at 75°C. Then, etoxide (V) tantalum (99.98% Aldrich) and sodium acetate (DEQ) was added in 1:1 molar ratio (Na:Ta) and kept the system with vigorous stirring during 5 minutes. After that, it was added 1 mL of nitric acid as oxidant agent. Finally, the solution was heated at 180°C to provoke the solvo-combustion reaction where a polycondensation reaction occurs between acetylacetone and nitric acid. The fresh powder was thermally heated by 2 hours at 400°C and 600°C.

2.2 Characterization

The crystal structure and phase transformation of the obtained powder were characterized by X-ray powder diffraction (XRD) using a Bruker D8 Advance diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The morphology and particle size of the synthesized NaTaO_3 were determined by Scanning Electron Microscope (SEM) in a JEOL 6490 LV. The energy band gap (E_g) was determined by the Kubelka-Munk function using a UV-vis spectrophotometer (Lambda 35 Perkin Elmer Corporation) coupled with an integrating sphere. Specific surface area (S_{BET}) was measured by N_2 physisorption through the BET method using Quantachrome NOVA 2000e equipment.

2.3 water splitting test

The water splitting was carried out at low pressure in a batch-type reactor using an inner irradiation cell and argon as carrier. Firstly, 300 mL of distilled water were bubbled with argon for 15 min. Then, 300 mg of material was dispersed into water under vigorous stirring. The system was kept at 100 Torr and the water temperature was maintained at 25°C during the test using a cooling system. Afterwards, the batch-reactor was irradiated with a UV source, Hg lamp with intensity of 400 W, and heterochromatic irradiation ($\lambda = 200$ to 800 nm). The evolved hydrogen was analyzed using a gas chromatograph with a TCD detector and a packed column Haysep D 100/120. The analysis was carried out in intervals of 30 minutes for 4 h.

3. Results and discussion



**9th International Symposium on New Materials and Nano-Materials for
Electrochemical Systems
XII International Congress of the Mexican Hydrogen Society
Merida, Mexico, 2012**

Figure 1 shows the XRD patterns of NaTaO_3 , fresh and thermal treated samples at 400°C and 600°C . It is evident the presence of NaTaO_3 phase from the fresh sample and it becomes more crystalline as the temperature increases. Accordingly to the JCPDS file, NaTaO_3 phase detected in the fresh sample and the thermal treated at 400°C correspond to a monoclinic structure. While sample thermal treated at 600°C corresponds to an orthorhombic symmetry. In addition, this sample shows the presence of some peaks corresponding to the secondary phase, $\text{Na}_2\text{Ta}_4\text{O}_{11}$; however its intensity is very low. The presence of the monoclinic symmetry is due to the low temperature of synthesis where the crystal structure is mainly formed by TaO_6 octahedral slightly distorted; however when temperature increases TaO_6 octahedral tends to be highly disordered provoking an orthorhombic arrangement.

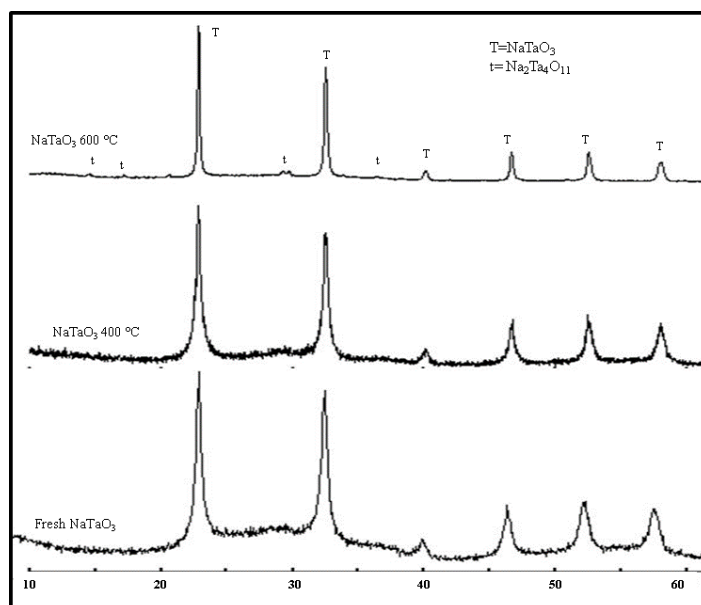


Figure 1. XRD patters of NaTaO_3 powders prepared by solvo-combustion method.

Through SEM micrographs it was possible to determine that NaTaO_3 particles presented micro-cavities formed by the union of NaTaO_3 particles with size lower than 1 micron; it is assumed that NaTaO_3 has hierarchical cubic morphology in the nanometer level. The morphology observed is due to the synthesis method; NaTaO_3 particles are formed from the fresh sample and its particle size increases as the temperature increase. As it is observed, cavities still remains present after thermal treatment indicating an interesting morphology of NaTaO_3 for certain applications.

9th International Symposium on New Materials and Nano-Materials for
Electrochemical Systems
XII International Congress of the Mexican Hydrogen Society
Merida, Mexico, 2012

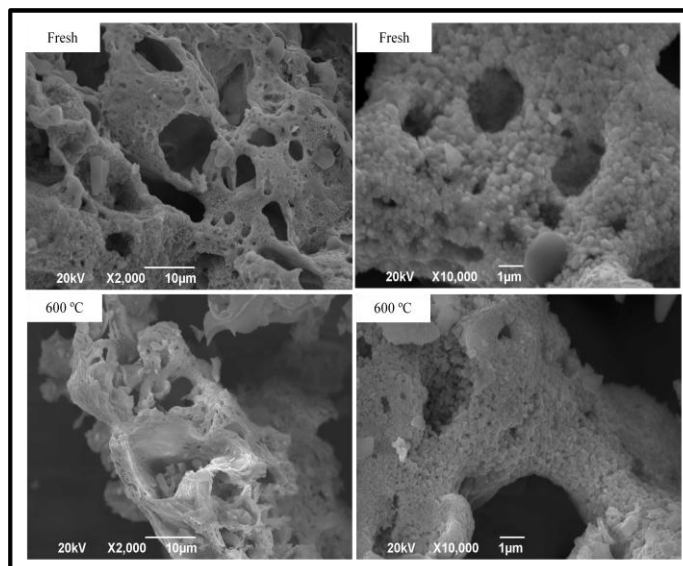


Figure 2. SEM micrographs of NaTaO₃ powders prepared by solvo-combustion method.

On the other hand, results about energy band gap (E_g) and specific surface area (S_{BET}) indicate that NaTaO₃ synthesized in this work shows similar E_g values that expected for NaTaO₃ material, see table 1. It means NaTaO₃ could be absorbing energy efficiently below 400 nm in order to be activated for photocatalytic processes which could be enhanced also due to the S_{BET} values obtained for this material.

Table 1. Energy band gap (E_g) and specific surface area values (S_{BET}) for NaTaO₃ samples.

Sample	E_g /eV	S_{BET} / m ² .g ⁻¹
Fresh-NaTaO ₃	3.94	118
NaTaO ₃ -400	3.98	75
NaTaO ₃ -600	4.01	41

The S_{BET} values here obtained are higher than those reported commonly for NaTaO₃ prepared by other synthesis methods, see table 2. Therefore NaTaO₃ synthesized in this work could be used in several applications where surface area is important such as absorbents, catalysts, substrate, and so on.

**9th International Symposium on New Materials and Nano-Materials for
Electrochemical Systems
XII International Congress of the Mexican Hydrogen Society
Merida, Mexico, 2012**

Table 2. Comparison of specific surface area values (S_{BET}) for NaTaO_3 samples synthesized by several methods.

Synthesis Method	Temperature/ $^{\circ}\text{C}$	$S_{BET} / \text{m}^2 \cdot \text{g}^{-1}$	Ref.
Solid State	1200	0.6	[11]2006
Sol-Gel	600	23	[12]2007
Sol-Gel	600	14	[13]2010
Electrolysis and Hydrothermal	180	58	[14]2010
Confined Space synthesis route	500	46	[15]2011
Solvo-combustion	fresh	118	This work
	400	75	
	600	41	

Figure 3 shows the hydrogen evolution during the water splitting reaction. The material exhibited attractive photocatalytic activity for water splitting reaction to produce hydrogen under UV-light irradiation. Results here obtained are very similar to the commonly reported for NaTaO_3 synthesized by other methods, mainly sample thermal treated at 600°C .

According to these results, it seems that crystal structure is more important than specific surface area. In this case, the fresh- NaTaO_3 and NaTaO_3 -400 produce hydrogen in similar amount, and both samples are monoclinic while NaTaO_3 -600 is orthorhombic. Recombination process is favored in the monoclinic structure due to the slight distorted TaO_6 octahedral because distance is shorter than distance presented in the orthorhombic structure where TaO_6 octahedral are more distorted.

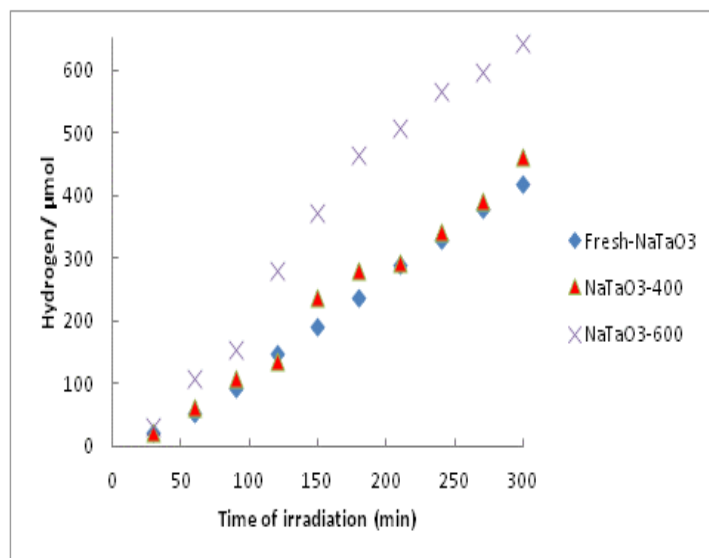


Figure 3. Hydrogen production from water splitting using NaTaO₃ semiconductor synthesized by solvo-combustion

Finally, another important aspect of this work in comparison with other reports is that due to the new solvo-combustion method used in this work, NaTaO₃ can be obtained in a few minutes at low temperature of synthesis. NaTaO₃ synthesized in this work showed high specific surface area and the phase appears from the fresh sample.

4. Conclusions

NaTaO₃ was obtained by the first time from the as-grown material using a new solvo-combustion method. NaTaO₃ particles have hierarchical cubic morphology in the nanometer level and possess high specific surface area, which is one of the highest values reached when compared to other synthesis methods. This material exhibited attractive photocatalytic activity for water splitting reaction where the crystal structure plays an important role because the fresh-NaTaO₃ and NaTaO₃-400 produce hydrogen in similar amount, and both samples are monoclinic while NaTaO₃-600 is orthorhombic and therefore enhances the hydrogen production.

5. Acknowledgements

Thanks to CONACYT for the financial support through the projects CB-98740, CB-84809 and INFR-2011-3-173625 and PAICYT-UANL2009 through the project IT171-09. Dr Isaias Juarez Ramirez wants to thank to the Nanoscience and Nanotechnology Network to support this project. Also authors want to thank CONACYT for the scholarship for PhD. Student Christian Gomez Solis, No. 201958, Miguel A. Ruiz Gomez, No. 239336 and Elvira Zarazua Morin, No. 87101.

**9th International Symposium on New Materials and Nano-Materials for
Electrochemical Systems
XII International Congress of the Mexican Hydrogen Society
Merida, Mexico, 2012**

6. References

- [1] K. Maeda and K. Domen, J. Phys Chem Lett, 1, 2655 (2010).
- [2] X. Hu, G. Li and J.C. Yu, langmuir, 26, 3031 (2010).
- [3] M.N. Chong, B. Jin, W.K. Chow, c. Sain , Water Research, 44, 2997 (2010).
- [4] J. Kim, D.W. Hwang, H. G. Kim, S. W Bae, J. S. Lee, W. Lib and S. H. Oh, Topics in Catalysis, 35. 295 (2005)
- [5] A.L. Stroyuk, A. I. Kryukov, S. Y. Kuchmii, V. D. Pokhodenko, Theoretical and Experimental Chemistry, 45 209 (2009).
- [6] D.W. Hwang, H.G. Kim, J. Kim, K.Y. Cha, Y.G. Kim and J.S. Lee, Journal of catalysis, 193, 40 (2000).
- [7] J. Kim, D.W. Hwang, H. Kim, S. W. Bae, S. M. Ji and J. S. Lee, Chemical Communications, 21, 2488 (2002)
- [8] Y. Inoue, Energy & environmental Science, 2, 364 (2009).
- [9] A. Iwase, H. Kato and A. Kudo, Catalysis Letters, 108, 7 (2006).
- [10] M. Tabata, K. Maeda, T. Ishihara, T. Minegishi, T. Takata, K. Domen, The journal of physical Chemistry C, 114, 11215 (2010).
- [11] W. Lin, C. Cheng, C. Hu and H. Teng, Applied Physics Letters, 89, 211904 (2006).
- [12] C. Hu, H. Teng, Applied Catalysis A: General, 331, 44 (2007).
- [13] L.M. Torres-Martinez, R. Gomez, O. Vazquez-Cuchillo, I. Juarez-Ramirez, A. Cruz-Lopez, F.J. Alejandro-Sandoval, Catalysis Communications, 12, 268 (2010).
- [14] Y. Cui, L. Liu, Y. Chen, D. Yu, X. Zhou, N. Xu, W. Ding, Solid State Science, 12, 232 (2010)
- [15] T. Yokoi, J. Sakuma, K. Maeda, K. Domen, T. Tatsumi and J. N. Kondo, Phys. Chem. Chem. Phys, 13, 2563 (2001).