

Synthesis of La/N Co-Doped SrTiO₃ Using Polymerized Complex Method for Visible Light Photocatalysis

Uyi Sulaeman¹, Shu Yin², Tsugio Sato²

¹Department of Chemistry, Jenderal Soedirman University, Purwokerto, Indonesia

²Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Japan

Email: uyi_sulaeman@yahoo.com

Received December 16, 2012; revised January 15, 2013; accepted January 25, 2013

ABSTRACT

Lanthanum and nitrogen co-doped SrTiO₃ was synthesized using polymerized complex method with Ti(OC₃H₇)₄, SrCl₂·6H₂O and La(NO₃)₃·6H₂O as starting materials followed by calcinations in NH₃. Ethylene glycol and anhydrous citric acid were used as the precursors of synthesis. The samples were characterized using XRD, TEM, DRS, BET, EDX and XPS. The cubic-perovskite type of La/N co-doped SrTiO₃ nanoparticle could be successfully synthesized. The photocatalytic activity of SrTiO₃ for DeNO_x ability in visible light region ($\lambda > 510$ nm) could be improved by co-doping of La³⁺ and N³⁻. The high visible light photocatalytic activity of this substance was caused by a narrow band gap energy that enables to absorb visible light.

Keywords: Photocatalysis; Visible Light; SrTiO₃; Polymerized Complex; La-Doping; N-Doping

1. Introduction

Recently, synthesis of strontium titanate based photocatalyst for converting visible light energy to photoreaction has been a great attention [1-6]. Among the modifying of SrTiO₃, doping with nitrogen is the most effective to enhance photoreaction in visible light. The mixing of N 2p with O 2p states narrows the band gap energy and enhances the photocatalytic ability in visible light. However, substituting O²⁻ by N³⁻ will generate residual anionic vacancies which suppress the photocatalytic activity of SrTiO₃. To solve this problem, co-doping of lanthanum and nitrogen into SrTiO₃, can decrease the band gap energy without forming lattice defect and lattice strain, and consequently lead to generate high visible light photocatalytic activity. The La³⁺ can substitute Sr²⁺ without large lattice strain because of the similar ionic radius.

Many researchers had developed the synthesis of La/N co-doped SrTiO₃ catalysts. Miyauchi *et al.* [7] reported that the synthesis of La/N co-doped SrTiO₃ catalysts using sol-gel method decreased the ionic vacancy and then increased the photocatalytic activity in a visible light. Wang *et al.* [8] found that the synthesis of La/N co-doped SrTiO₃ catalysts using mechanochemical reaction enhanced the photocatalytic activity in a visible light. However, they had a large particle and low specific surface area which limited the catalytic ability. To improve the photocatalytic ability, synthesis of fine particle which has a large specific surface area should be realized.

Polymerized complex method using citric acid and ethylene glycol as polymeric precursors has been widely used for metal oxide synthesis [9,10]. The polymerized complex process has great advantages over other synthesis techniques due to mixing of several components in atomic scale, good stoichiometry control, high purity, low cost and relatively low processing temperature [11]. The metallic ions are dispersed in the polymeric network at the atomic scale without precipitation and phase segregation [12]. Based on this consideration, the fine particles of La-doped SrTiO₃ could be synthesized by the polymerized complex process and then followed by calcinations in ammonia to obtain the La/N co-doped SrTiO₃ nanoparticles.

In the present paper, we report the synthesis of La/N co-doped SrTiO₃ using polymerized complex method. The lanthanum and nitrogen co-doping effectively narrowed the band-gap energy of SrTiO₃. The photocatalytic activity of SrTiO₃ for NO decomposition in visible light region ($\lambda > 510$ nm) could be enhanced. The high visible light photocatalytic activity of this substance might be caused by the low band gap energy and high specific surface area.

2. Experiment

2.1. Preparation of Catalyst

The La/N co-doped SrTiO₃ with variation of lanthanum doping was prepared by the polymerized complex method

[9]. The $\text{Ti}(\text{OC}_3\text{H}_7)_4$ and $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were dissolved in ethylene glycol. As amount of 38.2 gram of anhydrous citric acid and 100 mL of methanol were added to the solution and the mixture was stirred at 130°C until a transparent gel was formed. The polymer was carbonized at 350°C and calcined in air at 620°C for 2 h to remove carbon, and the product ($\text{Sr}_{1-x}\text{La}_x\text{TiO}_3$) was grinded. The products of $\text{Sr}_{1-x}\text{La}_x\text{TiO}_3$ were then nitrogenized by heating at 700°C for 5 h under NH_3 (flow rate 400 ml/L). The as-prepared sample of $\text{Sr}_{1-x}\text{La}_x\text{TiO}_3$ with $x = 0, 0.25, 0.5, 0.7$ and 1 are named as STN, STN-0.25, STN-0.5, STN-0.7 and LTN, respectively.

2.2. Characterization

The powder product was characterized by XRD (Shimadzu XD-D1) using graphite-monochromized $\text{CuK}\alpha$ radiation. The mean crystallite size of the powders was determined by the XRD-Scherrer equation [13]. Microstructure examinations were obtained by transmission electron microscopy (TEM, JEOL JEM-2010). The band gap energies of the products were determined using DRS (Shimadzu UV-2000). The chemical compositions were analyzed by EDX (Shimadzu, EDX-800HS). The specific surface area was determined by the nitrogen adsorption at 77 K (BET, Quantachrome NOVA 4200e). Binding energies of element were analyzed at room temperature by XPS (Perkin-Elmer PHI5600).

2.3. Photocatalytic Activity

The photocatalytic activities were evaluated using NO_x analyzer (Yanaco, ECL-88) [5]. A 450 W high-pressure mercury arc was used as the light source. The wavelength of the irradiation light was controlled by selecting filters, *i.e.*, Pyrex glass for $\lambda > 290$ nm, Kenko L41 Super Pro (W) filter $\lambda > 400$ nm and Fuji, tri-acetyl cellulose filter $\lambda > 510$ nm. The photocatalyst sample was placed in a hollow of 20 mm length \times 15 mm width \times 0.5 mm depth on a glass holder plate and set in the bottom center of the reactor. The concentration of NO gas at the outlet of the reactor during the photoirradiation was monitored for 10 minutes for every filter.

3. Result and Discussion

3.1. XRD Analysis

The XRD profiles of La/N co-doped SrTiO_3 are shown in **Figure 1**. The single phase of cubic-perovskite could be observed at samples of STN, STN-0.25 and STN-0.5, while the sample of LTN contains an impurity. The intensity of diffraction decreased with increasing La doping, indicating that the crystalline properties was strongly affected by La doping. The particle sizes of La/N co-

doped SrTiO_3 calculated by Scherrer equation are listed in **Table 1**. The particle of 52 nm could be obtained in the sample of STN, and decreased with increasing La doping to 39 nm, 17 nm, 23 nm and 18 nm for STN-0.25, STN-0.5, STN-0.7 and LTN, respectively. The smallest of particle size could be found on the sample of STN-0.5.

3.2. Morphology

Figure 2 shows the morphology of STN and STN-0.5. The particle size of 40 - 60 nm in diameter could be observed in STN and 15 - 20 nm in STN-0.5. The particle size observed by TEM agreed with that measured by Scherrer equation (see **Table 1**). The particle size of STN-0.5 is smaller than that of STN, indicating that the La doping affected the process of crystallization.

3.3. Uv-Vis Diffusion Reflectance Spectroscopy

Figure 3 shows the absorbance spectra of La/N co-doped SrTiO_3 . The absorption edge shifted to higher of wavelength, indicating the narrow band gap was generated by La/N co-doping. The band-gap energies of La/N co-doped

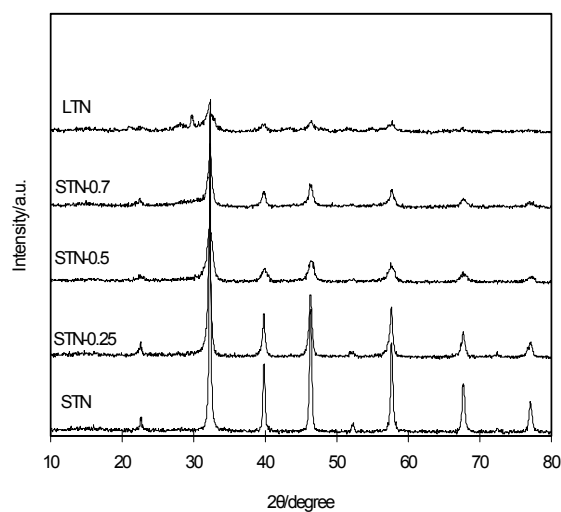


Figure 1. XRD patterns of La/N co-doped SrTiO_3 samples synthesized by the polymerized complex method.

Table 1. The crystallite sizes, specific surface areas, Sr/Ti and La/Ti atomic ratios from EDX of La/N co-doped SrTiO_3 synthesized by the polymerized complex method.

Sample	Crystallite Size (nm)	Specific Surface Area (m^2/g)	Atomic Ratio Sr/Ti	Atomic Ratio La/Ti
STN	52	17.30	1.076	-
STN-0.25	39	25.75	0.757	0.218
STN-0.5	17	65.43	0.467	0.443
STN-0.7	23	30.36	0.280	0.653
LTN	18	58.25	-	-

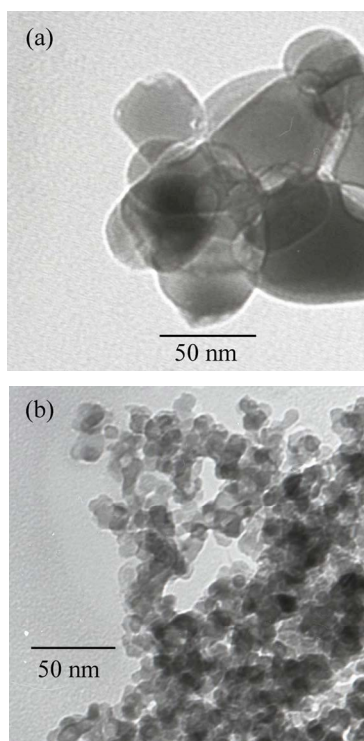


Figure 2. TEM images of STN (a) and STN-0.5 (b) synthesized by polymerized complex method.

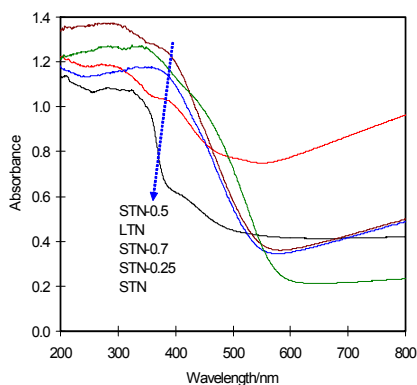


Figure 3. DRS of La/N co-doped SrTiO₃ synthesized using polymer complex method.

SrTiO₃ were calculated according to the equation of $E_g = 1240/\lambda$ [14]. The results were 2.95, 1.87, 2.13, 2.16 and 2.08 eV for STN, STN-0.25, STN-0.5, STN-0.7 and LTN, respectively. The variations of color could be observed in the samples, they are grey, blue, greenish-yellow and yellow, for STN, STN-0.25, STN-0.5, STN-0.7, respectively. The highest band gap energy of 2.95 eV could be observed for STN, indicating that the doping of nitrogen without lanthanum did not effectively narrow the band gap energy.

The broad absorption above 500 nm could be found in the spectra of STN and STN-0.25. The sample of STN-0.25 showed high broad absorption which was assigned

to the oxygen vacancy states. They were located between 0.75 and 1.18 eV below the minimum level of the conduction band [15]. The similar results were also found in the samples prepared with different methods [7]. The strontium titanate with oxygen vacancies can absorb a broad range of visible light above 500 nm. The lower broad absorption above 500 nm could be found in the sample of STN-0.5, STN-0.7 and LTN, indicating that the samples have lower oxygen vacancy.

3.4. XPS Analysis

Figure 4 shows XPS profiles of the STN-0.5 after sputtering at 3 kV for 3 minutes. The peak N1s could be observed at 396.0 eV shown in **Figure 4(a)**, indicating the formation of nitrogen doped SrTiO₃ [7]. This result proves that nitrogen was incorporated in the lattice. The lanthanum ion could be identified at 833.7 eV and 850.5 eV (**Figure 4(b)**), which correspond to La 3d_{5/2} and La 3d_{3/2}, respectively [16]. The spectrum for titanium exhibits two different signals corresponding to the Ti 2p_{3/2} and 2p_{1/2} with binding energies of 457.5 and 463.2 eV, respectively. The peak position of Ti 2p_{3/2} agreed with that of the Ti⁴⁺ [17-19]. The peak of O1s was observed at 529.1 eV which is the characteristic of metal oxides [20].

3.5. Photocatalytic Activity

Figure 5 shows the photocatalytic activity of La/N co-doped SrTiO₃ for the NO elimination under visible light irradiation ($\lambda > 510$ nm, $\lambda > 400$ nm), and UV light irradiation ($\lambda > 290$ nm). It took about 10 min to reach the steady state after light irradiation. There is no significant activity in visible light ($\lambda > 510$) for STN, presumably due to higher band gap energy of 2.95 eV. The sample of STN-0.25 exhibits low photocatalytic activity both in visible light and UV light. It showed the highest broad absorption above 500 nm which is assigned to the oxygen vacancy states. The existences of oxygen vacancy increase recombination of hole-electron pairs and then decrease the photocatalytic ability [7]. The sample of STN-0.5 showed the highest activity under the visible light irradiation ($\lambda > 510$ nm), *i.e.*, 28.8% NO could be destructed. Moreover, the photocatalytic ability of STN-0.5 was also higher than TiO₂ (P-25) in the ultraviolet light, *i.e.*, 42.3% of NO could be destructed. The excellent photocatalytic was attributed to both narrow band gap energy and high specific surface area (see **Table 1**). The photocatalytic activity decreased with increasing lanthanum doping (STN-0.7 and LTN). It may be attributed to low crystallinity of the sample.

4. Conclusion

Cubic perovskite of La/N co-doped SrTiO₃ nanoparticles, Sr_{1-x}La_xTiO_{3-y}N_y ($x = 0, 0.25, 0.5, 0.7$ and 1), could be

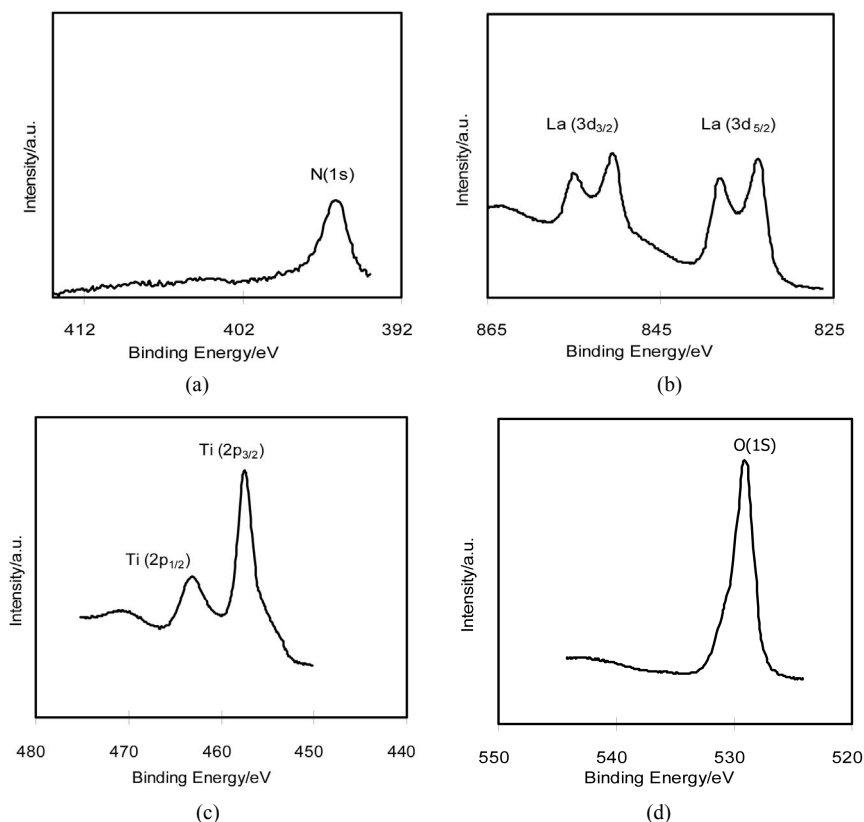


Figure 4. XPS profiles of La/N co-doped SrTiO₃ (STN-0.5) synthesized using the polymerized complex method.

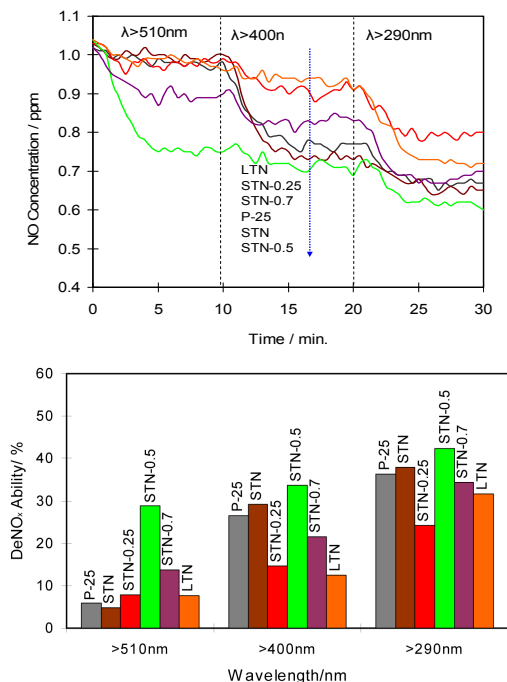


Figure 5. The photocatalytic NO destruction activities of La/N co-doped SrTiO₃.

synthesized by the polymer complex (PC) method using Ti(OC₃H₇)₄, SrCl₂·6H₂O, and La(NO₃)₂·6H₂O as starting

materials followed by calcinations in ammonia. Ethylene glycol and anhydrous citric acid could be used as the precursors of synthesis. The catalytic degradation of NO over La/N co-doped SrTiO₃ is significantly improved in the presence of visible-light irradiation. The sample with $x = 0.5$ is the highest photocatalytic activity for NO degradation under visible light irradiation ($\lambda > 510$ nm).

5. Acknowledgements

This research was partly supported by the Management Expenses Grants for National Universities Corporations from the Ministry of Education, Culture, Sports, Science for Technology of Japan (MEXT).

REFERENCES

- [1] Y. Sun, J. Liu and Z. Li, "Design of Highly Ordered Ag-SrTiO₃ Nanotube Arrays for Photocatalytic Degradation of Methyl Orange," *Journal Solid State Chemistry*, Vol. 184, No. 8, 2011, pp. 1924-1930. doi:10.1016/j.jssc.2011.05.037
- [2] G. Wang, Y. Qin, J. Cheng and Y. Wang, "Influence of Zn Doping on the Photocatalytic Property of SrTiO₃," *Journal of Fuel Chemistry and Technology*, Vol. 38, No. 4, 2010, pp. 502-507. doi:10.1016/S1872-5813(10)60042-4
- [3] J. Wang, S. Yin, M. Komatsu, Q. Zhang, F. Saito and T.

- Sato, "Preparation and Characterization of Nitrogen Doped SrTiO₃ Photocatalyst," *Journal of Photochemistry and Photobiology A: Chemistry*, Vol. 165, No. 1-3, 2004, pp. 149-156. [doi:10.1016/j.jphotochem.2004.02.022](https://doi.org/10.1016/j.jphotochem.2004.02.022)
- [4] A. Jia, Z. Su, L. Lou and S. Liu, "Synthesis and Characterization of Highly-Active Nickel and Lanthanum Co-Doped SrTiO₃," *Solid State Science*, Vol. 12, No. 7, 2010, pp. 1140-1145. [doi:10.1016/j.solidstatesciences.2010.04.005](https://doi.org/10.1016/j.solidstatesciences.2010.04.005)
- [5] J. Wang, H. Li, H. Li, S. Yin and T. Sato, "Preparation and Photocatalytic Activity of Visible Light-Active Sulfur and Nitrogen Co-Doped SrTiO₃," *Solid State Science*, Vol. 11, No. 1, 2009, pp. 182-188. [doi:10.1016/j.solidstatesciences.2008.04.010](https://doi.org/10.1016/j.solidstatesciences.2008.04.010)
- [6] T. Ohno, T. Tsubota, Y. Nakamura and K. Sayama, "Preparation of S, C Cation-Codoped SrTiO₃ and Its Photocatalytic Activity under Visible Light," *Applied Catalysis A: General*, Vol. 288, No. 1-2, 2005, pp. 74-79. [doi:10.1016/j.apcata.2005.04.035](https://doi.org/10.1016/j.apcata.2005.04.035)
- [7] M. Miyauchi, M. Takashio and H. Tobimatsu, "Photocatalytic Activity of SrTiO₃ Codoped with Nitrogen and Lanthanum under Visible Light Illumination," *Langmuir*, Vol. 20, No. 1, 2004, pp. 232-236. [doi:10.1021/la0353125](https://doi.org/10.1021/la0353125)
- [8] J. Wang, S. Yin, M. Komatsu and T. Sato, "Lanthanum and Nitrogen Co-Doped SrTiO₃ Powders as Visible Light Sensitive Photocatalyst," *Journal of the European Ceramic Society*, Vol. 25, No. 13, 2005, pp. 3207-3212. [doi:10.1016/j.jeurceramsoc.2004.07.027](https://doi.org/10.1016/j.jeurceramsoc.2004.07.027)
- [9] A. Kasahara, K. Nukumizu, G. Hitoki, T. Takata, J.N. Kondo, M. Hara, H. Kobayashi and K. Domen, "Photo-reactions on LaTiO₂N under Visible Light Irradiation," *The Journal of Physical Chemistry A*, Vol. 106, No. 29, 2002, pp. 6750-6753. [doi:10.1021/jp025961+](https://doi.org/10.1021/jp025961+)
- [10] S. Farhikhteh, A. Maghsoudipour and B. Raissi, "Synthesis of Nanocrystalline YSZ (ZrO₂-8Y₂O₃) Powder by Polymerized Complex Method," *Journal of Alloys and Compounds*, Vol. 491, No. 1-2, 2010, pp. 402-405. [doi:10.1016/j.jallcom.2009.10.196](https://doi.org/10.1016/j.jallcom.2009.10.196)
- [11] J. P. Zhao, M. H. Quan and L. Zhang, "Preparation of Potassium Lithium Niobate Powders with Low Li Content via the Pechini Method," *Ceramics International*, Vol. 32, No. 7, 2006, pp. 843-846. [doi:10.1016/j.ceramint.2005.05.010](https://doi.org/10.1016/j.ceramint.2005.05.010)
- [12] S. Qiu, H. Fan and X. Zheng, "Pb(Zr_{0.95}Ti_{0.05})O₃ Powders Synthesized by Pechini Method: Effect of Molecular Weight of Polyester on the Phase and Morphology," *Journal of Sol-Gel Science and Technology*, Vol. 42, No.1, 2007, pp. 21-26. [doi:10.1007/s10971-006-1509-3](https://doi.org/10.1007/s10971-006-1509-3)
- [13] B. Dcullity, "Elements of X-Ray Diffraction," 3rd Edition, Addison-Wesley Publishing Co., Boston, 1976.
- [14] S. X. Liu, X. Y. Chen and X. Chen, "Preparation of N-Doped Visible Light Response Nanosize TiO₂ Photocatalyst Using the Acid-Catalyzed Hydrolysis Method," *Chinese Journal of Catalysis*, Vol. 27, No. 8, 2006, pp. 697-702. [doi:10.1016/S1872-2067\(06\)60037-5](https://doi.org/10.1016/S1872-2067(06)60037-5)
- [15] D. C. Cronemeyer, "Infrared Absorption of Reduced Rutile TiO₂ Single Crystals," *Physical Review*, Vol. 113, No. 5, 1959, pp. 1222-1226. [doi:10.1103/PhysRev.113.1222](https://doi.org/10.1103/PhysRev.113.1222)
- [16] A. J. Nelson, T. Buuren, T. M. Willey, C. Bostedt, J. J. Adams, K. I. Schaffers, L. Terminello and T. A. Callcott, "Electronic Structure of Lanthanum Calcium Oxoborate LaCa₄O(BO₃)₃," *Journal of Electron Spectroscopy and Related Phenomena*, Vol. 137-140, No. 2004, pp. 541-546.
- [17] S. Martinez-Mendez, Y. Henriquez, O. Dominguez, L. D'Ornelas and H. Krentzien, "Catalytic Properties of Silica Supported Titanium, Vanadium and Niobium Oxide Nanoparticles towards the Oxidation of Saturated and Unsaturated Hydrocarbons," *Journal of Molecular Catalysis A: Chemical*, Vol. 252, No. 1-2, 2006, pp. 226-234. [doi:10.1016/j.molcata.2006.02.041](https://doi.org/10.1016/j.molcata.2006.02.041)
- [18] M. Ziolk and I. Nowak, "Characterization Techniques Employed in the Study of Niobium and Tantalum-Containing Materials," *Catalysis Today*, Vol. 78, No. 1-4, 2003, pp. 543-553. [doi:10.1016/S0920-5861\(02\)00353-X](https://doi.org/10.1016/S0920-5861(02)00353-X)
- [19] R. E. Tanner, Y. Liang and E. I. Altman, "Structure and Chemical Reactivity of Adsorbed Carboxylic Acids on Anatase TiO₂(0 0 1)," *Surface Science*, Vol. 506, No. 3, 2002, pp. 251-271. [doi:10.1016/S0039-6028\(02\)01388-2](https://doi.org/10.1016/S0039-6028(02)01388-2)
- [20] M. Z. Atashbar, H. T. Sun, B. Gong, W. Wlodarski and R. Lam, "XPS Study of Nb-Doped Oxygen Sensing TiO₂ Thin Films Prepared by Sol-Gel Method," *Thin Solid Films*, Vol. 326, No. 1-2, 1998, pp. 238-244. [doi:10.1016/S0040-6090\(98\)00534-3](https://doi.org/10.1016/S0040-6090(98)00534-3)