Available online at http://www.journalcra.com

International Journal of Current Research
Vol. 7, Issue, 11, pp.23162-23166, November, 2015

INTERNATIONAL JOURNAL OF CURRENT RESEARCH

ISSN: 0975-833X

RESEARCH ARTICLE

SYNTHESIS AND CHARACTERIZATION OF SnO_2 NANOPARTICLES BY MICROWAVE - ASSISTED SOLUTION METHOD

[1]Thenmozhi, C., [2]Manivannan, V., [3*]Kumar, E. and [4]Veera Rethina Murugan, S.

[1]PRIST University, Thanjavur, Tamilnadu, India
[2]Director (R & D) Retd, PRIST University, Thanjavur, Tamilnadu, India
[3]Department of Physics, School of Science, Tamil Nadu Open University, Chennai, Tamilnadu, India
[4]Department of Physics, R.S.Govt. College, Thanjavur, Tamilnadu, India

ARTICLE INFO

Article History:
Received 09th August, 2015
Received in revised form
15th September, 2015
Accepted 07th October, 2015
Published online 30th November, 2015

Key words:

Microwave, nanoparticles,
XRD, FT-IR, SEM and TEM.

ABSTRACT

SnO_2 nanoparticles were synthesized by microwave assisted hydrothermal method using $SnCl_2 \cdot 2H_2O$ as a precursor. The synthesized SnO_2 nanoparticles were characterized by X-ray diffraction (XRD), Fourier Transform Infra-Red spectroscopy (FT-IR), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), to find their structure and crystal size, functional group, particle morphology, surface morphology respectively. The broad peaks in the X-ray diffraction spectra indicate that the obtained powder is SnO_2 and are in crystalline nature. The size of the crystalline SnO_2 nanoparticles was found to be in the range of 10-21nm as calculated from the Debye - Scherrer formula.

Citation: Thenmozhi, C., Manivannan, V., Kumar, E. and Veera Rethina Murugan, S. 2015. "Synthesis and characterization of SnO_2 nanoparticles by microwave - Assisted solution method", *International Journal of Current Research*, 7, (11), 23162-23166.

INTRODUCTION

SnO_2 is a remarkable n-type semiconducting material having large band gap (3.6 eV) (Batzill, 2005) and is known for variety of applications. It has been used as a solid state sensor mainly due to its sensitivity towards different gaseous species (Deshpande *et al*., 2009; Krivetskiy *et al*., 2010), photovoltaic energy conversion (Snaith and Ducati, 2010), etc. Recently, the use of nanomaterials for solar energy conversion (Li and Liu, 2010) has been one of the most active research areas in photo catalysis (Hao *et al*., 2010; Wang *et al*., 2009; Zhang *et al*., 2008). Due to its unique electrical properties, tin oxide has been used for various electrochemical applications, such as gas sensors for environmental monitoring (Moseley, 1997) and catalysts (Arico *et al*., 2001). For these applications, the small particle size or large surface area of SnO_2 is essential for high performance. Tin oxide semiconductor has tetragonal rutile structure, its unit cell parameters and space group are a = 4.738 Å, c = 3.187 Å and $P4_2/mnm$ (Sanjay *et al*., 2004) respectively. The techniques reported for obtaining semiconducting oxide nanoparticles includes chemical vapour condensation (Liu *et al*., 2005), colloidal growth, microwave technique (Krishnakumar *et al*., 2009), sol–gel method (Niesz *et al*., 2005), surfactant assisted synthesis (Wang *et al*., 1999), precipitation technique (Park *et al*., 2008), spray pyrolysis (Paraguay-Delgado *et al*., 2005; Ashok *et al*., 2013; Fang and Ying, 2012; Ho *et al*., 2009), hydrothermal synthesis (Fujihara *et al*., 2004) and laser ablation in liquids and gases (Comini, 2006; Shankar and Raychaudhuri, 2005; Chen and Gao, 2004; Komarneni *et al*., 1992). Among the various techniques, microwave assisted synthesis is preferred due to its controlled grain size, morphology and crystal structure by changing the experimental procedure. Microwave assisted hydrothermal synthesis has smaller processing time and provides uniform nucleation of the powders (Komarneni *et al*., 1992; Komarneni *et al*., 1996).

Since, microwave assisted synthesis is a rapid technique and also cost effective compared to other conventional methods, this method is chosen for producing high purity SnO_2 nanoparticles. This method also provides precise temperature control, high reaction rate and quality product (Krishnakumar *et al*., 2009). Microwave heating not only enhances the rate of formation, but also enhances the size distribution and material quality. In addition to that, the method provides uniform

****Corresponding author: Kumar, E.,***
Department of Physics, School of Science, Tamil Nadu Open University, Chennai, Tamilnadu, India.

heating of the reaction mixture, small particle size, more yield and materials with high purity (Perreux and Loupy, 2001).

Experimental

Microwave Synthesis

All the chemicals involved in this microwave assisted method were used as received from the chemical suppliers without any further purification and processing. For the synthesis of SnO_2 nanoparticles, 0.03 M solution of stannous chloride dihydrate ($SnCl_2 \cdot 2H_2O$ - AR grade) was prepared and 5ml ammonia solution was added with it, drop by drop, till its pH value raises upto10. Then the mixture was kept in a magnetic stirrer for 30 minutes, at 80°C. This solution is sealed and kept in a microwave oven and heated for 6 minutes at 800 Watts (300 Hz), till the volume becomes one fourth of its initial value. The colloidal solution obtained was filtered with whattsman filter paper. In order to remove the impurities, the solution was washed with deionized water. In order to remove the moisture content, the wet nanoparticles were dried in air for 3 days. The dried powder was ground using pestle and mortar.

Characterization Techniques

The crystal structure of the SnO_2 nanoparticles was investigated by X-ray diffraction (XRD) technique and the data were recorded using a X-ray diffractometer (Model Bruker D8) with Nickel filtered Cu - Kα radiation. Data were collected in the range of 2θ from 10° to 80° using step scan mode with step size of 0.0170° and step time of 1.0000s. SEM images of SnO_2 nanoparticles were recorded using the Model Hitachi SEM S 2400 device at SAIF-STIC, CUSAT, Cochin. Microstructural analysis were made by Transmission Electron Microscopy (TEM - MODEL – JEM100 CX II) and HRTEM (MODEL - JOEL - J2000), operating at 200KV at SAIF-NEHU, Shillong. FT-IR spectra of the sample were recorded in the range of 400 – 4000cm^{-1}, using a Shimadzu 8400S FT-IR Spectrometer.

RESULTS AND DISCUSSION

X-Ray Diffraction (XRD) pattern of synthesized SnO_2 nanoparticles

The X-ray diffraction pattern of SnO_2 nanoparticles is shown in Figure 1. The XRD result shows that the sharp diffraction peaks formed at 26.6^0, 34^0 and 51.9^0 confirms the formation of SnO_2 nanoparticles. All the peaks were indexed as the tetragonal rutile SnO_2 structure (JCPDS Card No 41-1445) (Baohua Zhang *et al.* ; Cullity, 2005). The crystallite size of SnO_2 nanoparticles was calculated using the value of FWHM from the most intense XRD peaks using Debye-Scherrer formula (1)

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (nm) \ldots..(1)$$

where D is the crystallite size, K is the shape factor (0.94), λ is the wavelength of X-rays (λ = 1.54059A^0), β is the full width at half maximum (FWHM) of the diffraction peaks and θ is the angle of diffraction. The sharpness of the peaks shows that SnO_2 nanoparticles are highly crystalline. Crystallite size for SnO_2 nanoparticles synthesized in this method was found to be 10 - 21nm. The peaks formed at 26.6^0, 34^0 and 51.9^0 can be indexed to (1 1 0), (1 0 1), (2 1 1) planes of SnO_2 crystal which matches well with JCPDS card # 41–1445 and the structure of the SnO_2 crystal was found to be Cassiterite type tetragonal. The lattice parameters for the tetragonal phase structure were calculated using the relation (2) (Kasar *et al*., 2008)

$$\frac{1}{d^2} = \left(\frac{h^2 + k^2}{a^2}\right) + \frac{l^2}{c^2} \quad \ldots..(2)$$

The lattice parameters of the SnO_2 nanocrystals were calculated as a = 4.7615Å and c = 3.9639Å which matches well with the standard values (a = 4.738 A°, c = 3.187 A°) (Cirera *et al*., 2001).

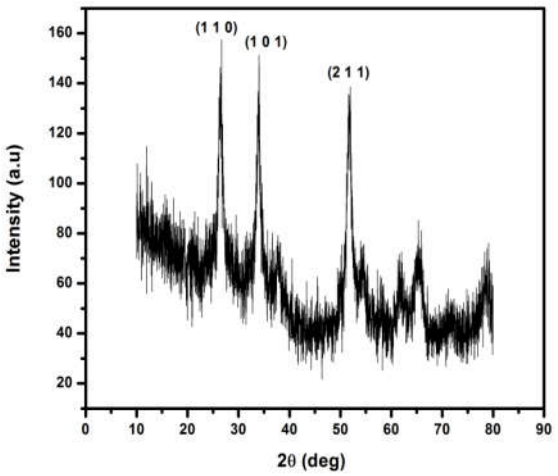

Figure 1. XRD pattern of the synthesized SnO_2 nanoparticles

The unit cell volume of the tetragonal lattice is given by the equation (3):

$v = a^2 . c \quad \ldots.. (3)$

$= 89.869 \times 10^{-30} m^3$

The calculated value of unit cell volume of SnO_2 nanoparticles matches well with the standard value.

The lattice distortion can be calculated by the following relation (4)

$$U = \frac{a}{c} \quad \ldots. (4)$$

i.e, U = 1.2012

The specific surface area of the crystal can be calculated by the following relation (5)

$$S = \frac{6}{\rho D} (m^2/g) \ldots.. (5)$$

The specific surface area of as-prepared SnO_2 powdered particle is 81.24 m^2/g

SEM Analysis

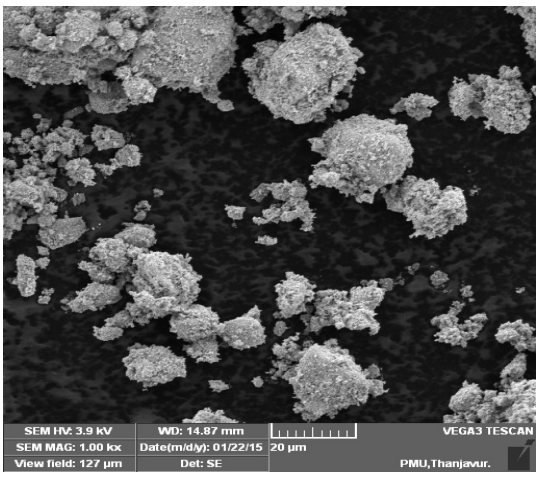

Figure 2. SEM image of the prepared SnO_2 nanoparticles

Figure 2 shows the SEM micrograph of the pure SnO_2 nanoparticles synthesized by microwave assisted hydrothermal synthesis. It can be observed that nanosized SnO_2 particles are interconnected, which shows strong agglomeration with lot of small spherically shaped particles. This agglomerate actually consists of much smaller grains of about 10–21 nm in diameter.

Microstructural properties by TEM and SAED pattern

The morphology and particle size of tin oxide nanoparticles were observed using TEM micrograph (Fig. 3a). The presence of spherical shaped particles with particles size ranging from 10 to 21nm was observed. The calculated particle size from XRD investigation matches well with the particles size observed from TEM micrograph. These results suggest the formation of crystalline tin oxide nanoparticles. The corresponding SAED pattern of SnO_2 nanoparticles is shown in Figure 3b. SAED pattern provides rings made up of discrete spots, denotes the crystalline nature of the prepared SnO_2 particles with nanosize. The bright image in the SAED pattern confirms the spherical shape of SnO_2 nanoparticles and the narrow distribution of particle size.

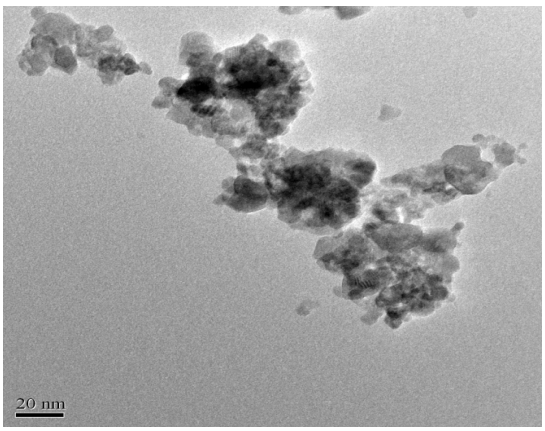

Figure 3(a).TEM micrograph of the prepared SnO_2 nanoparticles

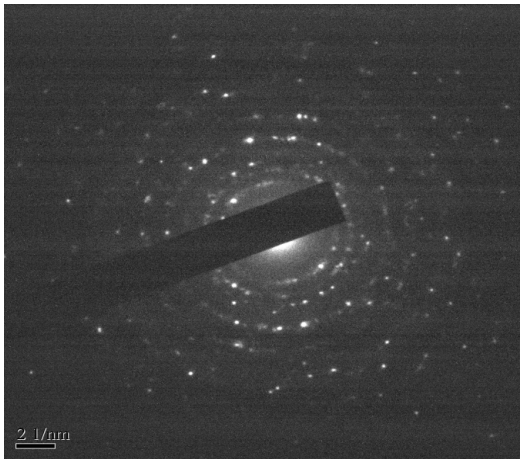

Figure 3(b). SAED pattern of SnO_2 nanoparticles

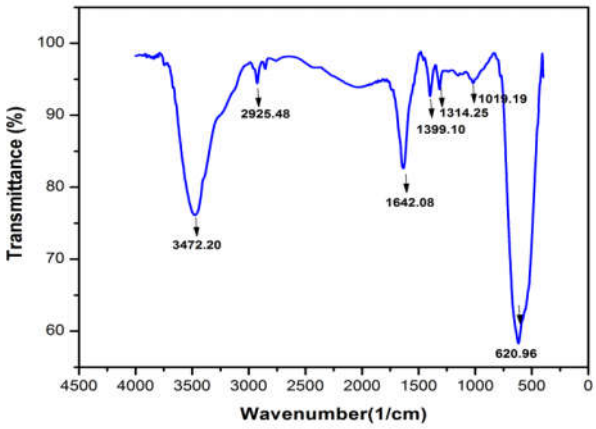

Figure 4. FT IR spectra of the prepared SnO_2 nanoparticles

The FT-IR spectra of SnO_2 nanoparticles synthesized by microwave assisted hydrothermal method are shown in Figure.4. It supports the presence of tin hydroxyl and tin dioxide functional group available in SnO_2 nanoparticles. The sharp peak at low wave number region of 620cm^{-1} is due to the anti-symmetric vibration of O-Sn-O (Liu *et al*., 2006; Punnoose *et al*., 2005) and also attributed to oxide-bridge functional group (OSnO) (Lin Yung-Jen and Wu Ching-Jiunn, 1996). The peak around 1019cm-1 is due to Sn(OH) vibrations (Abello *et al*., 1998). Thus the FT IR spectrum confirms the presence of Sn-O bonds and O-H groups. The band appears at 1642 cm^{-1} may be attributed to the bending mode of O-H bond. The broad band appearing in the region 3000-3700 cm^{-1} may be due to the vibration of adsorbed water. The assignments match very well with those reported in the literature (Jun-Jie Zhu *et al*., 2002; Harrison and Guest, 1987; Srinivas *et al*., 2009).

Conclusion

High purity SnO_2 nanoparticles were rapidly synthesized in a successful manner by microwave assisted hydrothermal method using $SnCl_2 \cdot 2H_2O$ as precursor. The structural and morphological properties of SnO_2 nanoparticles were investigated. The XRD result shows that the obtained SnO_2 nanoparticles were found to be with tetragonal crystalline structure and the calculated particle size was in the range of 10-21nm, which were in good agreement with TEM results. TEM

micrograph shows that SnO_2 nanoparticles were spherical in shape. SnO_2 nanoparticles with uniform size were achieved using microwave synthesis which is considered to be a green, efficient and cost effective method having potential for large scale synthesis of nanoparticles.

REFERENCES

(a) Arico, A.S, P.Creti, P.L. Antonucci, V.Antonucci, Elecrochem. Solid State Lett. 1998, 1, 66. (b) Lamy.C, E.M. Belgsir, J.M. Leger, Appl. Electrochem. 2001, 31, 799. (c) Zhou, W. J.; Zhou, Z. (3) H.; Song, S. Q.; Li, W. Z.; Sun, G. Q.; Tsiakaras, P.; Xin, Q. Appl. Catal.B 2003, 46, 273. (d) Jiang, L. H.; Sun, G. Q.; Zhou, Z. H.; Zhou, W. J.; Xin, Q. Catal. Today 2004, 93-95, 665

(a) Moseley, P. T. Solid State Gas Sensors (Review Article). Meas Sci. Technol. 1997, 8, 223-237.

(b) Liu, C. C. Nano-Crystalline Tin Oxide Film for Chemical Sensor Development. Abstracts from the 2nd International Symposium on Electrochemical Microsystem Technologies, Sept 9-11, 1998, Tokyo, Japan; 1998; p 32.

(c) Moseley, P. T, J. Norris, D.E.Williams, Techniques and Mechanisms in Gas Sensing; Adam Hilger: Bristol, U.K., 1991.

Abello, L, B. Bouchu, A. Gaskov, S. Koudryavtseva, G. Lucazeau, M. Roumyantseva, *J.Solid State Chem*., 135(1998) 78.

Ashok K.Singh, Umash T.Nakate, Microwave synthesis, Characterization and photo catalytic properties of SnO_2 nanoparticles. *Adv.in. Nano*., (2013),2,66-70

Baohua Zhang,†, ‡ Xiaoyuan Yu,†Chunyu Ge,† Xianming Dong,† Yueping Fang,*,† Zesheng Li *,‡ and Hongqiang Wang‡ Novel 3-D superstructures of SnO_2@C core-shell nano chain for energy storage application

Batzill.M, U. Diebold, The surface and materials science of tin oxide, *Prog. Surf. Sci*., 79, 47 (2005)

Chen. D, L.Gao, Facile synthesis of single-crystal tin oxide nanorods with tunable dimensions via hydrothermal process, *Chem. Phys. Lett*., 398 (2004) 201.

Cirera. A, Vila. A, Cornet. A, Morante. Microwave-assisted synthesis and investigation of SnO2 nanoparticles, J.R, Mater Sci Eng C 2001;15:203–5

Comini. E, *Anal. Chim. Acta*., Metal oxide nano-crystals for gas sensing, 568 (2006) 28.

Cullity. B. D, "Elements of X-Ray Diffraction," Addison - Wesley, Reading, 2005.

Deshpande.N. G, Y. G. Gudage, R. Sharma, J. C. Vyas, J. B. Kim and Y. P. Lee, "Studies on Tin Oxide-intercalated Polyaniline Nanocomposite for Ammonia Gas Sensing Applications," Sensors and Actuators B: Chemical, Vol. 138, No. 1, 2009, pp. 76-84. doi:10.1016/j.snb.2009.02.012.

Fang.L.I, ZHU Ying – Chun Synthesis and electro chemical properties of porous SnO_2 *J.I norg. Mat*., (2012) 27, 2.

Fujihara.S, T. Maeda, H. Ohgi, E. Hosono, H. Imai, S.H. Kim, Langmuir, Hydrothermal routes to prepare nanocrystalline mesoporous SnO_2 having high thermal stability, 20 (2004) 6476.

Hao.Y, W. Wu and L. L. Xie, "Preparation and Photo-catalytic Properties of Nanometer SnO_2," 2*nd International conference on Chemical, Biological and Environmental Engineering* (*ICBEE*), Cairo, 2-4 November 2010, pp. 96-100.

Harrison. P.G, A. Guest, Tin oxide surfaces. Part 17.—An infrared and thermogravimetric analysis of the thermal dehydration of tin(IV) oxide gel, *J. Chem. Soc, Faraday Trans*., 1 83 (1987) 3383.

Ho S.Y, A.S.W.Wong and G.W.Ho Controlled porosity of monodispersed Tin Oxide nanospheres. *Cryst.growth.Des*., (2009) 9(2) 732 – 736

Jun-Jie Zhu, Jian-Min Zhu, X. Liao, J. Fang, M. Zhou, H. *Chen, Mat. Lett*., Rapid synthesis of nanocrystalline SnO powders by microwave heating method, 53 (2002) 12. 15 7.

Kasar, R.R, N.G. Deshpande, Y.G. Gudage, J.C. Vyas, R. Sharma, "Studies and correlation among the structural, optical and electrical parameters of spray deposited tin oxide (SnO< sub> 2</sub>) thin films with different substrate", 403, pp. 3724-3729, Physica B 2008

Komarneni S, R. Roy, Q.H. Li, *Mater. Res. Bull*., Nanophase materials by hydrothermal, microwave hydrothermal and microwave-solvothermal method, 27 (1992) 1393.

Komarneni.S, Q.H. Li, R. Roy, *J. Mater. Res*. Microwave-hydrothermal processing of layered anion exchangers,11 (1996) 1866.

Krishnakumar. T, R. Jayaprakash, Pinna Nicola, Singh VN, Mehta BR, AR. *Phani Mater Lett*, Microwave-assisted synthesis and characterization of flower shaped zinc oxide nanostructures, 2009;63:242–5.

Krishnakumar.T, R.Jayaprakash, M.Parthibavarman, A.R.Phani, V.N. Singh, B.R. Mehta, *Mater. Lett*., Microwave-assisted synthesis and investigation of SnO_2 nanoparticles, 63, 896 (2009)

Krivetskiy.V, A. Ponzoni, E. Comini, S. Badalyan, M. Rumyantseva and A. Gaskov, "Selectivity Modification of SnO_2-Based Materials for Gas Sensor Arrays," Electro analysis, Vol. 22, No. 23, 2010, pp. 2809-2816. doi:10.1002/elan.201000277.

Li, L., C. Liu, J. Phys. Chem. Mesoporous Titania (A) Nanoparticles Prepared by a Solvothermally Treated Organic Small Molecule System: Formation Mechanism and Behavior in Photocatalysis and Dye-Sensitized Solar Cells, C 114, 1444 (2010)

Lin Yung-Jen, Wu Ching-Jiunn. *Surf Coat Technol*., 1996;88 : 239–47.

Liu.CM, XT Zu, WL Zhou, *J. Phys.: Condens. Matter,* 2006, 18, 6001.

Liu.Y, E. Koep, M. Liu, *Chem. Mater*, highly sensitive and fast-responding Sn02 sensor fabricated by combustion chemical vapor deposition, 17 (2005) 3997.

Niesz.K, P.Yang, G.A.Somorjai, *Chem. Comm*. Chemistry on Modified Oxide and Phosphate Surfaces: Fundamentals and applications , 2005, 1986 (2005)

Paraguay-Delgado F, W.Antúnez-Flores, M.Miki-Yoshida, A.Aguilar-Elguezabal, P. Santiago, R. Diaz, J.A. Ascencio, *Nanotechnology*, 16 (2005) 688

Park.J.W, D.S.Jung, M.E.Seo, S.Y. Kim, W.J. Moon, C.H. Shin, G.Seo, *Microporous Mesoporous Mater*., 112, 458 (2008)

Perreux.L and A. Loupy, "A Tentative Rationalization of Microwave Effects in organic synthesis according to the reaction medium and mechanistic considerations," *Tetrahedron*, Vol. 57, No. 45, 2001, pp. 9199-9223. doi:10.1016/S0040-4020(01)00905-X

Punnoose. A, J. Hays, A. Thuber, M.H. Engelhard, R.K. Kukkadapu, C. Wang, V. Shutthanandan, S. Thevuthasan. *Phys. Rev.,* 2005, B 72, 54402.

Sanjay R Dharge, SP. Gaikwad, Violet Samuel, V. Ravi, Synthesis of nanocrystalline SnO_2 powder at 100° C, *Bull. Mater. Scie*., 27 (2004) 221-222.doi:10.1007/BF02708509

Shankar. K.S, A.K. Raychaudhuri, Mater. Sci. Eng., C, *Bionim. Mater., Senss. Syst*., 25 (2005) 738.

Snaith.H. J and C. Ducati, "SnO_2-Based Dye-Sensitized Hybrid Solar Cells Exhibiting Near Unity Absorbed Photon-to-Electron Conversion Efficiency," *Nano Letters*, Vol. 10, No. 4, 2010, pp 1259-1265. doi:10.1021/nl903809r.

Srinivas.K, M.Vithal, B. Sreedhar, M.M. Raja, and P.V. Reddy, "Structural, optical, and magnetic properties of nanocrystalline Co doped SnO2 based diluted magnetic semiconductors", *J. Phys. Chem*., C 113 (2009) 3543.

Wang. L, Z.Wang, J.Zhao, Z.Yuan, H.Yang, M.Zhao, *Mater. Chem. Phys*., 59, 171 (1999)

Wang. Q.Q, B.Z. Lin, B.H. Xu, X.L. Li, Z.J. Chen and X.T. Pian, "Preparation and Photo catalytic Properties of Mesoporous SnO_2 Hexaniobate Layered Nano-composite," *Microporous and Mesoporous Materials*, Vol. 130, No. 1-3, 2010, pp. 344-351. doi:10.1016/j.micromeso.2009.11.033

Zhang. L. H, P. J. Li, Z.Q. Gong and X. M. Li, "Photo-catalytic Degradation of Polycyclic Aromatic Hydrocarbons on Soil Surfaces Using TiO_2 Under UV Light," *Journal of Hazardous Materials*, Vol. 158, No. 2-3, 2008, pp. 478-484. doi:10.1016/j.jhazmat.2008.01.119

****