

Comparative analysis and characterization of TiO₂ nanotubes produced by microwave assisted hydrothermal method and normal hydrothermal

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Nanotubes, Nanorod and Nanosheet of TiO₂ were synthesized by the normal hydrothermal method and the microwave hydrothermal method by constant temperature and aqueous NaOH concentration, each using TiO₂ powder (Degussa, P25) as precursor material. These products were elucidated phases, morphologies and optical characteristics by X-ray diffraction pattern (XRD) analysis, Transmission Electron Microscopy (TEM) and Diffuse Reflectance Spectroscopy (DRS), respectively. It was found that a nanostructure varied according to a generation method. In comparison with the normal hydrothermal method found that the microwave hydrothermal method produces the nanotubes mainly. Photocatalytic activity was evaluated by the degradation of methylene blue (MB) dye under simulated solar light condition. The photocatalytic efficiency of particle structure was found to be higher as compared to other nanostructures such as sheets, rods or tubes. Morphology-dependent optical and catalytic activities of the synthesized TiO₂ nanostructures were evaluated. The decrease in concentration of MB depended on adsorption mainly.

Key words: Hydrothermal synthesis, Microwave hydrothermal synthesis, TiO₂ nanotubes, Nanotube, Nanorod, Nanosheet.

Introduction

Hydrothermally synthesized nanostructures have been shown strong potentiality for a variety of applications due to their inherent ion-exchange capabilities and the unique morphologies. The term hydrothermal was first used by the prominent British geologist, Sir Roderick Murchison [1]. Since the 1900s, hydrothermal processing has become an increasingly popular procedure to synthesize materials of a specific phase, composition and morphology [2, 3]. Hydrothermal processing has also been used for the reclamation and leaching of organic and inorganic materials [4, 5], growth of inorganic single crystals [6, 7] and for the development of materials designed for specific applications [8]. For many years, it was believed that pressures greater than 1 atm and temperatures greater than 100 °C were required to classify a reaction as hydrothermal [1]. However, recently it has been established that hydrothermal reactions can occur under milder conditions [9, 10]. In 1986, Gedye and Giure used the microwave, at first time, to study esterification reaction [11]. Since then, interest in organic reaction studies by using microwaves has increased tremendously in esterification, Williamson ether synthesis, Diels-Alder reaction [12, 13], sigmatropic rearrangements, oxidation,

hydrolysis, substitutions, de-protection and a wide variety of organic reactions [12]. The microwave is a form of energy with a lower frequency of the electromagnetic wave, revealed the fact that the material can be heated up. It began to find application on heating of the dielectric materials [13, 14]. To a common heating method for heating the material by using the heat source, i.e. conductive heating, external heat is to be transferred into the inside. In order to deliver heat to the material which is present in reaction container, at first, heat is to be passed through sample container and then via sample and solvent. This method of heating is affected by the thermal conductivity of the various substances and is very slow and inefficient process in terms of energy transfer. In addition, until the mixture of the sample container has reached thermal equilibrium, the temperature of the sample container is higher than the temperature of the mixture. Furthermore, conductive heat is difficult to control the reaction. The heat source must be removed physically and cooled to lower the internal temperature. In contrast, a heating by using a microwave as an internal heating method has a given energy, it is converted to heat by the interaction between the medium dipole rotation and ionic conduction. In general, the heating effect is known to be much higher due to dipole rotation in relation to the ionic conduction. This heating method is fast enough to raise the temperature as it is not affected by the thermal conductivity of the sample vessel or materials. As a result of dipole rotation and the ionic conduction, it quickly

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heats up substances as super heating. In addition, it is possible to heat the object having an arbitrary shape. And the stability of power fluctuation to changes in load condition is higher. Furthermore, there is the advantage of being easy to adjust the atmosphere surrounding the object [16, 17].

In this study, we have explored the effect of synthesis parameters on the formation of TiO₂ nanostructures, principally focusing on the nanostructures formed through the microwave assisted hydrothermal method and normal hydrothermal method.

Experimental Procedure

TiO₂ nanostructures were prepared by using precursors titanium dioxide (99.9% purity, P25, Degussa), sodium hydroxide (98.0% purity, Duksan chemical), and Hydrogen chloride (Extra pure grade, Duksan chemical). All of the chemical reagents used in the experiments were of analytical grades and were used without further purification. Distilled water was used in all aqueous solution preparations and washing processes. The centrifugation was used in 50 ml Oak Ridge PPCO and washed with distilled water until the absence of residual Cl⁻ ions (tested by precipitation reaction with AgNO₃ aqueous solution). The synthesis of titania based nanostructures has been performed by the Microwave assisted hydrothermal method (products were named MWTNT) and normal hydrothermal method (products were named NHTNT). Calculated amount of P25 TiO₂ powder 2 g was added in 100 mL of a 10 M NaOH aqueous solution in a 500 mL beaker. The suspension was agitated by a magnetic stirrer at 250 rpm for 15 min. And then, it was treated for 5 min with ultrasound to eliminate any agglomeration of TiO₂. The mixture was put in a Teflon vessel reactor of 130 ml. The mouth of a reactor vessel was closed perfectly to assure hermetic conditions during microwave assisted hydrothermal reaction. Microwave conditions for the synthesis of titania nanotubes were set to 150 °C temperature, 195 W microwave power, with stirring rate of 400 rpm for 4 h. After the microwave irradiation, it was cooled down inside the microwave vessel under 35 °C. The reaction product was transferred into the glass beaker and washed with 5N HCl solution to achieve pH 7. The precipitated product was washed with distilled water until pH 7 was achieved. It was frozen and lowered the temperature to -83 °C. Then it was dried by freeze dryer for 24 hours. Thus, the samples synthesized in method of normal hydrothermal process and method of microwave assisted hydrothermal reaction process, both are listed in each, Table 1. After centrifugation and drying, the samples were subjected to the characterizations.

The specific surface areas of all samples were determined by the Brunauer-Emmett-Teller (BET, ASAP2010, Micromeritics Instrument Corporation) method. The crystal phase composition of the samples

Table 1. Sample list and results of binding energies, BET and DRS

Sample name	Synthesized* conditions	Binding energy (eV)		BET surface area (m ² /g)	Band gap energy (eV)
		Ti2p	O1s		
MWTNT	Microwave assisted, 195 W	457.8	529.3	214	3.55
NHTNT	Normal hydrothermal	457.9	529.5	175	3.68

*Common condition: 150 °C, 4 h and 10 M aq. NaOH solution.

was analyzed by X-ray diffraction patterns (XRD), using Rigaku RINT-2200 X-ray diffractometer operated at 40 kV and 40 mA using Cu-Kα¹ radiation $\lambda = 1.54 \text{ \AA}$. The morphological characterization was achieved through transmission electron microscopy (TEM) by JEOL (Japan) JEM-2010. The synthesized powders were ultrasonically dispersed in ethyl alcohol and supported on the ultra thin carbon film on holey carbon support copper grids (400mesh, Cu, TED Pella, INC) for TEM observation. Raman spectroscopy was performed on a Horiba LABRAM HR800 Raman microscope coupled to a Olympus BX41 microscope using a Nd:YAG laser to produce 532 nm excitation radiation. The samples were analyzed from 50-1200 cm⁻¹ at a resolution of ca. 2 cm⁻¹ with Rayleigh rejection achieved through a 532 nm Lasers sf notch filter. The laser power was 200 mW. The determination of chemical composition of the synthesized powder was performed by X-ray photoelectron spectroscopy (XPS, Ulvac- PHI 5000 VersaProbe). Optical properties and band gap energy were measured by UV-Vis diffuse reflectance spectroscopy (UV-VIS, V-500, Jasco).

Results and Discussion

It is known that the titanium oxide forms some crystal phases. Fig. 1 shows the XRD patterns of the samples, MWTNT and NHTNT, were produced by the microwave assisted hydrothermal method and normal hydrothermal method, respectively. It revealed that samples composed of hydrogen trititanate (H₂Ti₃O₇, JCPDS card No. 41-1092), anatase (TiO₂ anatase JCPDS card No. 21-1272) and rutile (TiO₂ rutile JCPDS No. 75-1755) with detailed phase analysis. We can also observe that NHTNT possesses a mixture of hydrogen trititanate and rutile. In many literatures, they argued that TiO₂-derived nanotubes and nanorods are composed of sodium trititanate (Na₂Ti₃O₇) and hydrogen trititanate (H₂Ti₃O₇) [18, 19 and 20]. It is worth pointing out that the nanorod structures of sodium tetratitanate (Na₂Ti₄O₉) and hydrogen pentatitanate (H₂Ti₅O₁₁) are also produced during hydrothermal reaction of TiO₂ in NaOH solution which has not been described much in the state-of-the-art literature. Several possible crystal structures of nanotubular products from the alkaline hydrothermal treatment of TiO₂ have been proposed, including hydrogen

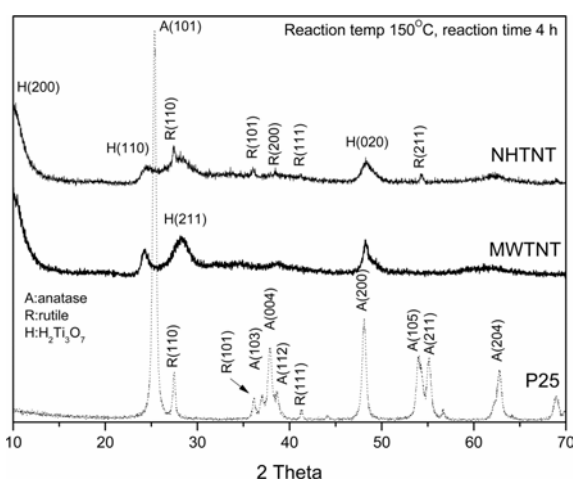


Fig. 1. XRD pattern of P25, MWTNT and NHTNT.

tritanate $\text{H}_2\text{Ti}_3\text{O}_7$ [21, 22], $\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7$ ($x \leq 7$) [22], Naposed, including titanates $\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$ [23] and tetratitanates $\text{H}_2\text{Ti}_4\text{O}_9$ [24]. Nanobelts, nanowires and nanorods structures tend to have good crystallinity.

In order to investigate the changes in a state of nanostructures, TEM observation was performed. Fig. 2(a) shows the TEM images of NHTNT which was prepared by normal hydrothermal method in a solution of 10 M NaOH for 4 hours at 150 °C as optimized condition. It expresses nanosheet and nanotubular nanostructures. Fig. 2(b) shows the TEM image of MWTNT which was prepared by microwave assisted hydrothermal in a solution of 10 M NaOH for 4 hours at 150 °C as optimized condition. This micrograph shows the nanostructures which mainly express nanotube structures with the diameter of about 8 ~ 10 nm and the tube length of about 200 nm. As the microwave treatment, the size of the nanotubes and the number of the nanostructures are also increased. Nanostructures in NHTNT have the length of about 100 nm and diameter of about 20 nm. In a TEM image of MWTNT, it was confirmed that MWTNT has the larger nanostructures (nanotubes) in comparison with NHTNT. Fig. 2(c) shows the TEM images of precursor sample (P 25) which has a particulate structure.

Usually the relation between the lengths of the edges corresponding to each crystallographic axis is arranged in the order (001), (100) and (010). The length of the nanowires (001) becomes several tens of micrometers, while the width [(100) or (010)] is typically in the range of 10 nanowires. Fig. 3 presents the Raman spectra for the samples of MWTNT, NHTNT and the precursor P25, which were prepared at 150 °C in 10 M NaOH solution as optimized condition. The appearance of nanotube structure is confirmed by the peaks of the range from 78 to 82 cm^{-1} . In the case of MWTNT, the peaks of nanotube phase were observed. No any powder phase is observed at microwave assisted hydrothermal treatment condition.

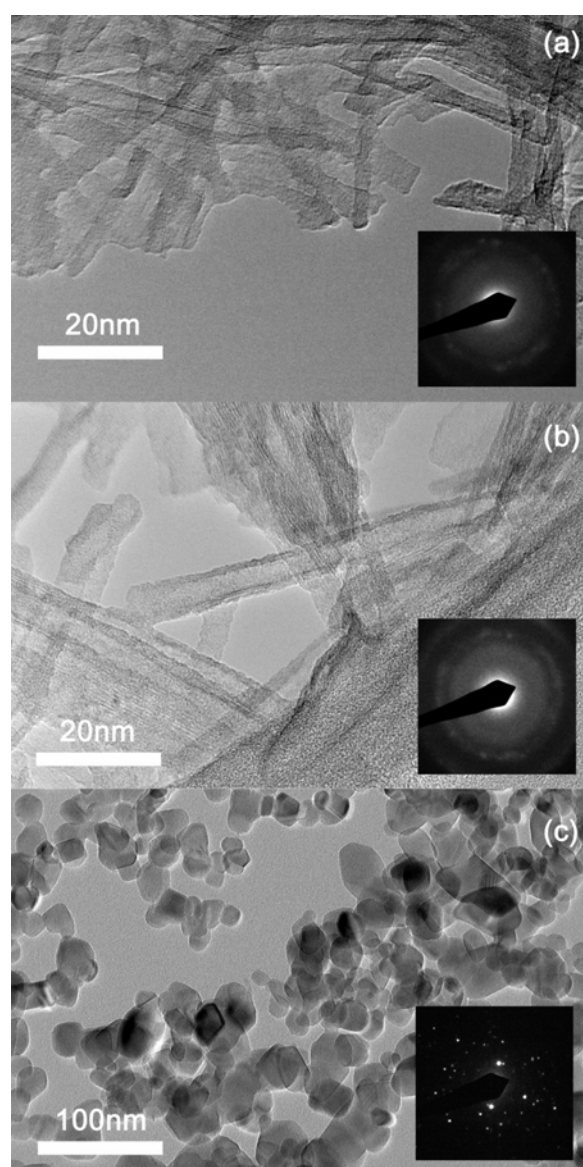


Fig. 2. TEM image of samples. (a) NHTNT sample, (b) MWTNT sample and (c) TiO₂ P25.

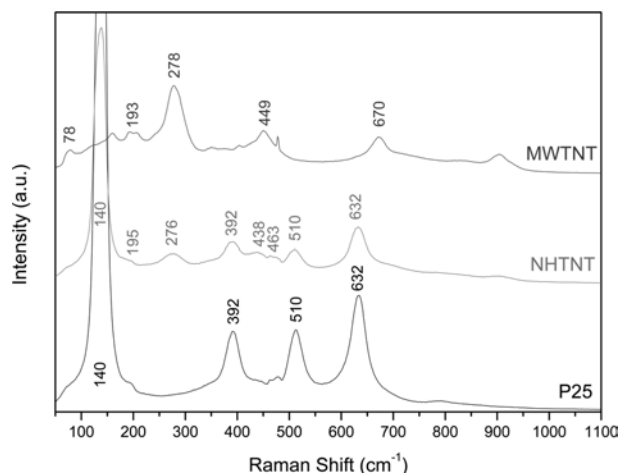


Fig. 3. Raman spectra collected from MWTNT, NHTNT and P25 TiO₂ in 10 M NaOH solution at 150 °C by different hydrothermal synthesis.

According to Group theory, there are eight sets of zone center optical phonons, where A1 and E1 modes are polar which split into transverse optical (A1TO and E1TO) and longitudinal-optical (A1 Low and E1 Low) phonons, while the E2 mode consists of two modes of low- and high-frequency phonons (E2 Low and E2 High) which are Raman-active [25, 26]. It is observed that the spectrum of the TiO₂-P25 shows four peaks at 142, 197, 398 and 445 cm⁻¹ (of very small intensity). According to the literature [27], anatase phase of TiO₂ has six Raman active modes ($A1g + 2B1g + 3Eg$) at 147, 198, 398, 515, 640 and 796 cm⁻¹, while rutile has four active modes ($A1g + B1g + B2g + Eg$) situated at 144, 448, 612 and 827 cm⁻¹, respectively. TiO₂-P25, as a mixture of anatase (80%) and rutile (20%), has five Raman peaks (at 143, 197, 396, 516 and 639 cm⁻¹) corresponding to anatase, but just one peak, at 445 cm⁻¹, corresponding to rutile [27]. Raman peak sets for NHTNT are quite similar to P25. In addition, NHTNT exhibited relatively weak Raman modes in comparison with P25 particulate structure. This observation can be explained by poor crystallinity of the obtained nanotubes (MWTNT). In the case of MWTNT, bands at approximately 78, 158, 193, 278, 373, 449, 670 and 903 cm⁻¹ are observed. The Raman modes, the around at 158, 193 cm⁻¹ and 278 cm⁻¹ were assigned to the stretching modes of Ti split peaks the around the 449 cm⁻¹ region and the peak of 670 cm⁻¹ which corresponds to the bending and stretching vibration of Ti. The Raman peaks observed for the nanotubes is also attributed to the stretching modes of Ti-O [28, 29, 30]. Based on the results from XRD, TEM and Raman analysis, nanostructures can be classified systematically. Additionally, the expected band at 670 cm⁻¹ is due to the Ti to the stretching modes of Ti-O results are consistent with XPS data. It is well known that the resolution of the Ti 2p spectrum into three spin orbit components of different binding energy corresponds to TiO, Ti₂O₃ and TiO₂ [31, 32]. The calibration of binding energy (460 eV) was in close agreement with TiO₂ (458.5 eV). The peaks observed close to the 1000 eV binding energies are derived from Na 3p1/2 and revealed the formation of Na on TiO₂. The observed peak at 539.8 eV corresponds to O 1s, and the binding energies were calibrated by taking the carbon C 1s peak (284.6 eV) as reference.

The photocatalytic activity of samples was evaluated by the degradation of Methylene Blue (MB) aqueous solution (30 mg/L) with 0.02 g photocatalyst under visible light (solar simulator AM 1.5) irradiation. The solar simulator (Portable solar simulator PEC-L01, Pecell) of 200 W was used as a simulated solar light source. The photocatalytic activities of all samples were evaluated by monitoring the photocatalytic decolorization of MB. The kinetics of photocatalytic degradation of MB dye in terms of C/C_0 plot are shown in Fig. 4. The kinetic plot shows that the decolorization profiles of MB dyes in

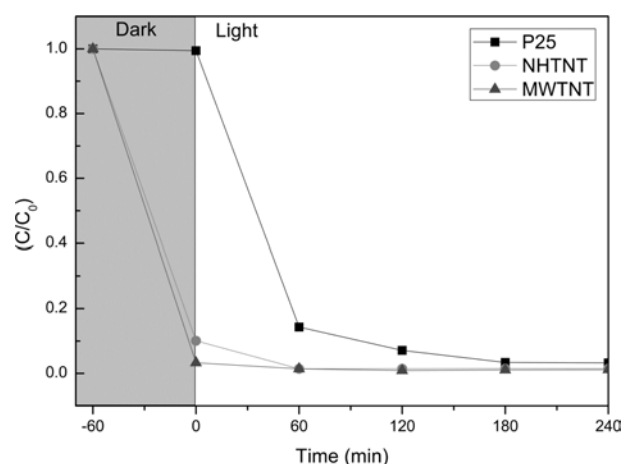


Fig. 4. Kinetics (C/C_0) of photocatalytic decolorization of MB under simulated solar light irradiation (P25, MWTNT and NHTNT).

a dark condition for 1 hour and in the presence of light until 4 hours. It was observed that there is no significant decolorization observed for P25 during initial 1 hour dark condition. In contrast, MWTNT and NHTNT samples have shown more than 90% decolorization in dark condition for 1 hour. This is resulted due to heavy adsorption of dyes on the surface of nanostructures. On the other hand, in the presence of light, precursor TiO₂ P25 has shown about 90% of MB decolorization during first 1 hour, NHTNT and MWTNT samples have shown only a small degree of decolorization (i.e. 8.6 ~ 4.5%). These can be explained on the basis of differences in nanostructures as discussed above. As presented above, NHTNT sample was only partially changed into the nanostructures morphologies such as a sheet or rod structures, and there was still remaining a particulate structure of starting precursor. Hence, the apparent changes in the concentration of MB are mainly accompanied due to the adsorption of dyes by these structures such as sheet/rod. It has already been shown that photocatalytic efficiencies of nanostructured titania (sheet, rod or tube) are very poor though these have high specific surface area (Table 1). The band gap energies of all investigated samples were determined by using modified Kubelka-Munk method. It is noteworthy that the band gap energy of MWTNT sample is smaller than that of NHTNT sample and the dye adsorption rate is high enough.

Conclusions

In this study, characterization and analysis of TiO₂ nanostructures synthesized via normal hydrothermal process and microwave hydrothermal process were performed. Furthermore, in comparison to other conventional methods, this microwave assisted hydrothermal process was effective and has the potentiality to form different TiO₂ nanostructures

within 4 hours as these experimental results revealed. The photocatalytic efficiency of particle structure was found to be higher as compared to other nanostructures such as sheet, rod or tubes. On the other hand, apparent decolorization of organic dyes was caused by adsorption for nanorod, nanosheet or nanotube structures mainly. Finally, the microwave hydrothermal process is found to be more efficient means for the formation of TiO₂ nanostructures. And these showed that there is possibility of application in several areas such as adsorptions, sensitive catalysis and Dye Sensitized Solar Cells (DSSCs).

Acknowledgments

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References

1. Byrappa, K. Yoshimura, M. Handbook of Hydrothermal Technology: A Technology for Crystal Growth and Materials Processing; Noyes Publications: Norwich, NY. (2001).
2. Feng, S. Xu, K, New Materials in Hydrothermal Synthesis, Acc. Chem. Res. 34 (2001) 239-247.
3. K.Y. Kang, J. H. Lim, Y-H, Korean J. Chem. Eng. 23 (2006) 81-84.
4. Brebu. M, Bhaskar. T. Muto, A. Sakata, Chemosphere. 64 (2006) 1021-1025.
5. Ellis, A. J, Acta 32 (1968) 1356-1363.
6. Bams. R. L. Kolb, E. D, Laudise. R. A, Simpson. E. E, Kroupa. K. M, J Cryst. Growth 34 (1976) 189-197.
7. Xing. Q, Xing. X, Yu. R., Du. L. Meng, J. Luo. Wang, D. Liu. G J Cryst. Growth 283 (2005) 208-214.
8. Bamey. G, Campbell, M. H., Ed. American Chemical Society, Washington, DC, 153 (1976) 108-125.
9. Chien. A, T. Speck, J. S. Lange, F. F. Daykm, A. C. Levi, C. G, J Mater. Res. 10 (1995) 1784-1789.
10. Greene, L. E. Law, M. Goldberger, J. Kim, F. Johnson, J. Zhang, Y. Saykally, R; Yang. P, Angew. Chem., Int. Ed. 42 (2003) 3031-3034.
11. Gedye. R. N, Smith. F. E, Westaway. K. Ali. H, Baldisera. L, Laberge. L, Rousell, J. Tetrahedron Lett, 27 (1986) 279.
12. Derreux. L, Loupy. A, Tetrahedron 57 (2001) 9199.
13. Loupy. A, Perreus. L, Liagre. M, Burle. K, Moneus. M, Pure Appl. Chem, 73 (2001) 161.
14. Loupy. A, Spectra Anal, 22 (1993) 175.
15. Jun. C. H, Chung. J. H, Lee. D. Y, Loupy. A, Chatti. S, Tetrahedron Lett, 42 (2001) 4803.
16. Mingos. D. M. P, Baghurst. D. R, Chem. Soc. Rev, 20 (1991) 1.
17. Loupy. A, Petit. A, Hamelin. J, Texier-Boullet. F, Kacqaualt. P, Mathe, D. Synthesis 9 (1998) 1213.
18. Ma. Y, Lin. Y, Xiao. X, Zhou. X, Li. X, Mater. Res. Bull, 41 (2006) 237.
19. Wei. M, Konishi. Y, Zhou. H, Sugihara. H, Arakawa. H, Solid. State Commun, 133 (2005) 493.
20. Yu. L, Zhang. X, Mater. Chem. Phys, 87 (2004) 168.
21. Q. Chen, W. Zhou, G. Du, L. M. Peng, Adv. Mater, 14 (2002) 1208-1211.
22. Q. Chen, G. H. Du, S. Zhang, L. M. Peng, Sect. B: Struct. Sci, 58 (2002) 587-593.
23. J. Yang, Z. Jin, X. Wang, W. Li, J. Zhang, S. Zhang, X. Guo, J. Zhang, Dalton Trans, (2003) 3898-3901.
24. A. Nakahira, W. Kato, M. Tamai, T. Isshiki, K. Nishio, Aritani, J. Mater. Sci, 39 (2004) 4239-4245.
25. Khan. A, Kordesch. ME, Mater Lett, 62 (2008) 230.
26. Umar. A, Karunagaran. B, Suh. E. K, Hahn. Y. B, Nanotechnology, 17 (2006) 4072.
27. Papp. S, Korosil. L, Meynen. V, Cool. P, Vansant. E.F, Dekany. I, J. Solid State Chem, 178 (2005) 1614.
28. Bavykin. D. V, Cressey. B. A, Walsh. F. C, Aust J Chem, 60 (2007) 95-98.
29. Lei. L. Shuming. Y, Feng. Han, Liangjun. W, Xiaotong. Z, Zhuangde. J. Sensors, 14 (4) (2014) 7332-7341.
30. Wei. M, Konishi. Y, Zhou. H, Sugihara. H, Arakawa. H, Solid. State Commun, 133 (2005) 493.
31. Q. Chen, W. Zhou, G. Du, L. M. Peng, Adv. Mater, 14 (2002) 1208-1211.
32. Q. Chen, G. H. Du, S. Zhang, L. M. Peng, Acta Crystallogr., Sect. B: Struct. Sci, 58 (2002) 587-593.