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Synthesis of ZnO Nano Rods through Mechano-Chemical Route: A Solvent Free Approach

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ABSTRACT: An efficient and inexpensive route for the synthesis of zinc oxide nano rods *via* a two step process is reported. In this study, zinc acetate dihydrate and sodium hydroxide were used as precursors and cetyl trimethylammonium bromide (CTAB) was employed as a capping agent. Mechano-chemically synthesized ZnO nanoparticles were characterized by X-ray diffraction (XRD), FT-IR spectroscopy, thermogravimetric analysis (TGA), dynamic light scattering measurements (DLS) and transmission electron microscopy (TEM). The highly crystalline nature of synthesized ZnO was confirmed from XRD analysis. The average particle size of ZnO nano rods obtained through the present solid-state method was 35 nm in size.

Keywords: ZnO nanoparticles, CTAB, Mechanical grinding, XRD, HRTEM

I. INTRODUCTION

In the domain of nano technology, oxide nano particles can exhibit unique chemical properties owing to their small size and high density of corner or edge surface sites [1]. Nano-ZnO as one of the multifunctional inorganic nano particle attract researchers due to its physical and chemical properties such as chemical stability, high luminous transmittance, higher catalytic activity, effective antibacterial property, intensive UV and IR absorption etc [2]. ZnO having a wide band gap of 3.37eV, large bond strength, large excitation binding energy (Eb=60meV) and higher melting temperature (2248K) [3] has been widely used in many applications such as transparent conductive films, varistors [4,5] and efficient photocatalysts [6]. The diverse applications exhibited by ZnO nano systems is because it can exist in different morphologies such as belts, wires, ribbons, tubes, rods, tetrapods, rings and needles [7-9]. Several methods for the synthesis of nano-ZnO are reported such as hydrothermal synthesis [10-12], micro emulsion hydrothermal process [13], chemical vapour deposition (CVD) [14] and sol-gel synthesis [15,16].

Mechano-chemical reactions are suitable for large scale production of nano particles with good yield. Because such method doesn't involves the use of organic solvents for controlling the nano particle growth. Hence they are attractive and less expensive. Pillai *et al* reported a mechano-chemical procedure for making nano-ZnO for varistor applications [4]. They have employed an annealing temperature of 500^0C and no ZnO was formed before this. In the current procedure a much lower temperature (i.e. 300^0C) was used to crystallize the zinc precursors to form ZnO.

In this article, a simple method for the preparation of hexagonal ZnO nano particles with the assistance of the surfactant cetyl trimethylammonium bromide (CTAB) is reported. The used preparation procedure was described by Sun et al. [20] but with the introduction of few modifications. This method is found to be cost effective, efficient and eco-friendly.

II. EXPERIMENTAL

A. Materials

Zinc acetate dihydrate and sodium hydroxide used were of analytical grade supplied by MERCK. Cetyl trimethylammonium bromide (CTAB) was obtained from CDH (New Delhi), Distilled water used was of HPLC grade (Spectrochem-Mumbai).

B. Preparation of nano-ZnO

In a typical synthesis 1M $Zn(OAc)_2$ $2H_2O$ and 0.3M CTAB were ground in an agate mortar for about 20min. 6g of NaOH was added to the above mixture and further ground for 45min at room temperature. The resulting pasty mass was washed with 100ml DW for 2-3 times and sonicated. It is then centrifuged at 600 rpm. The resulting supernatant solution was decanted off. The precipitate is filtered, dried and calcined at 300^0C for 2h.

C. Characterization

FT-IR spectra were recorded on a FT-IR spectrometer (Varian 660-IR model) (USA) in the wavelength range 400-4000cm^{-1}. TG-DTA studies of nano ZnO were carried out on a Perkin Elmer TGA 4000 model machine under N_2 atmosphere at a heating rate of 10^0C/min in the temperature range 30-900^0C. For dynamic light scattering (DLS) studies, Malvern- Zetasizer (Nano S-UK) was used. TEM images were taken on HRTEM machine (Model tecnai 30 G^2, Netherlands) operating at an accelerating voltage of 300kV. The X-ray diffraction (XRD) of ZnO nano particles were recorded on PANalytical X'pert machine with Cu-Kα radiation (λ=1.54056Aº). The mean grain size (D) of particles determined from XRD line broadening measurement from Scherrer equation [17].

III. RESULTS AND DISCUSSION

A solvent free, mechano-chemical reaction between zinc acetate and sodium hydroxide in presence of cetyl trimethylammonium bromide produced a pasty mass. This material was further washed and annealed and were subjected to various characterization methods.

TG-DTA curve of synthesized nano ZnO powder is shown in Fig. 1. TGA curve showed 11.21% weight loss at 241.1^0C and the corresponding DTA curve also showed an endothermic peak at this temperature. This might be due to the escape of remaining CH_3COOH and bonded water. Since the boiling point of CH_3COOH is 118.1^0C, remaining CH_3COOH can be totally removed only when temperature is higher than its boiling point. Weight loss at 241.1^0C implies the complete removal of CH_3COOH unreacted if any present and loss of water molecules and other volatile impurities from the system and thereafter no significant weight loss happened. Hence it is found that the purity of synthesized ZnO nano particles are high and temperature needed for the preparation is low compared with other methods. Using TG-DTA data, the zinc hydroxide obtained was decomposed at 300^0C and used for further study.

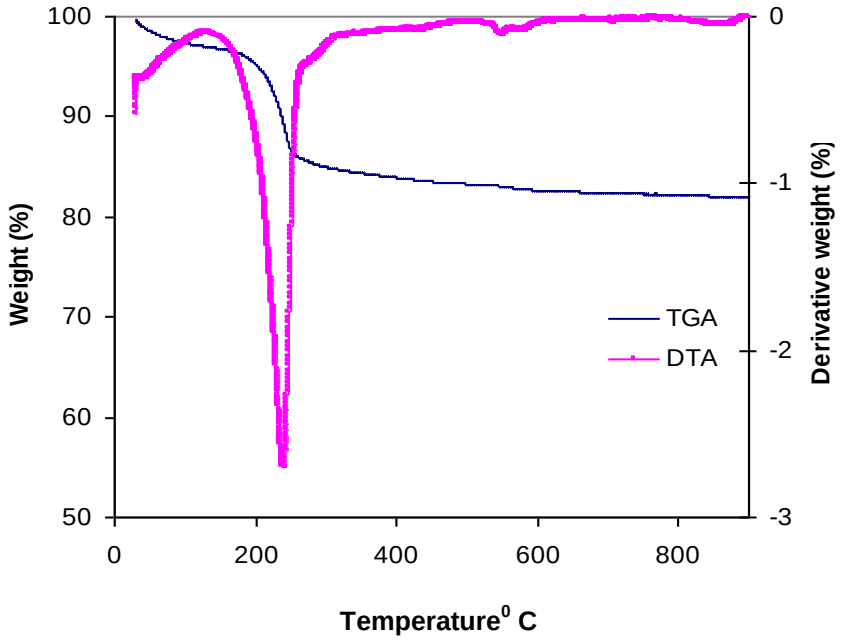

Fig. 1. TG-DTA curve of nanocrystalline ZnO powder precursor at a heating rate of 10^0C/min.

Fig. 2 shows the XRD pattern of synthesized nano ZnO particles. The diffraction peaks from various planes and d- values are matching well with the reported JCPDS data of nano-ZnO [18]. All the peak positions and relative peak intensities of ZnO product agrees well with standard JCPDS and no impurities such as Zn, $Zn(OH)_2$ or CTAB are observed. This indicates that the nano ZnO prepared through the present low temperature, mechano-chemical method are of high purity. The phase structure of nano ZnO belongs to wurtzite structure (hexagonal phase). Moreover the diffraction peaks of the product shows strong peak intensities indicating that the prepared ZnO nano particles have high crystallinity. They have an average grain size of 33.5$\pm$0.5 nm calculated from Scherrer equation.

The formation of hexagonal phase ZnO in the prepared samples were supported by FT-IR spectra shown in Fig. 3. There is a broad band at 3380cm^{-1} correspond to vibrational mode of OH group of water indicating some water adsorbed on ZnO crystal surface. Band near 1650cm^{-1} due to asymmetric stretching of zinc acetates or oxalates [19]. Band at 1533cm^{-1} corresponds to C=O stretching vibration of small fractions of unreacted COO-Zn. The intense band around 500cm^{-1} confirms the Zn-O vibration of ZnO.

Fig. 4 shows the DLS measurements of ZnO nano particles dispersed in 0.1% sodium lauryl sulphate (SLS). From the intensity statistics report it has been found that 16% of particles having size below 100nm. About 37% particles showed size in between 100-200nm. 48% particles having size varies from 200-800nm. Aggregation of particles also happened and their size ranged from 4-5 µm. However, particles having size above 4 µm are less compared to the bulk. Particle aggregation occurs because of the water absorption and the nano particles may not effectively protected by this lower surfactant concentration. The size and morphology of ZnO nano particles are analysed by HR-TEM technique, which is shown in Fig. 5. The image reveals that the product containing rod shaped particles with an average size range of 35-60 nm and is in good agreement with that estimated by Scherrer formula based on XRD pattern and DLS measurements.

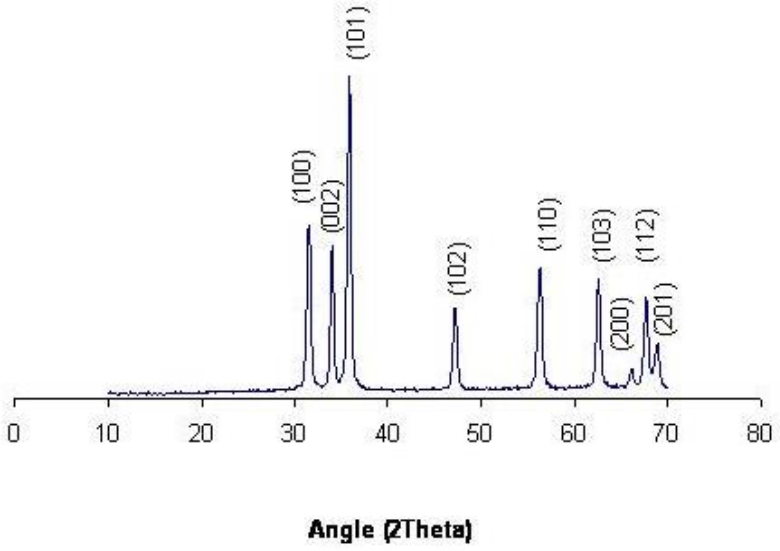

Fig. 2. XRD pattern of synthesized nano ZnO powder after calcination at 300^{0}C.

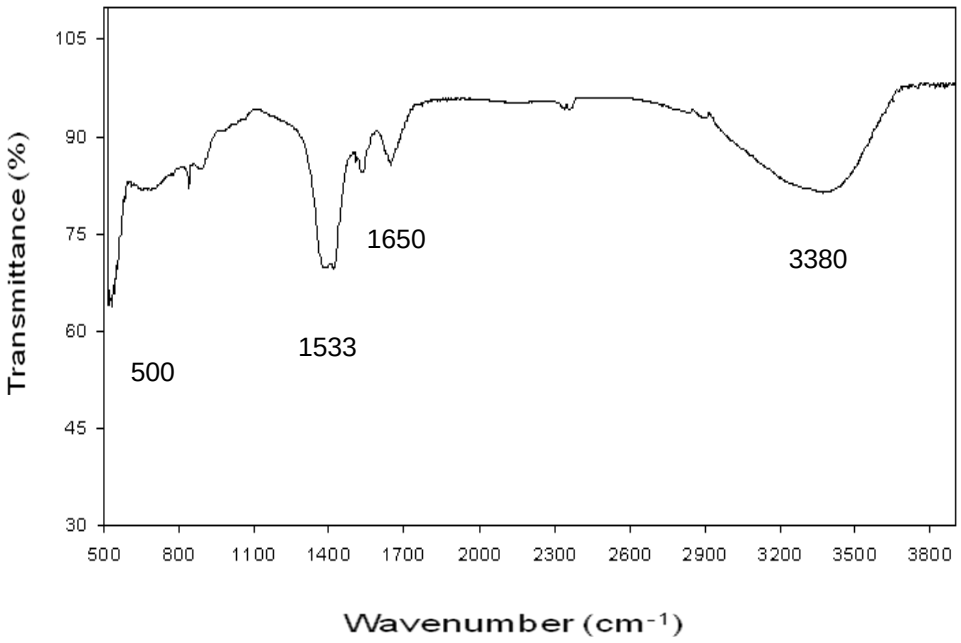

Fig. 3. FT-IR spectra of synthesized nano ZnO

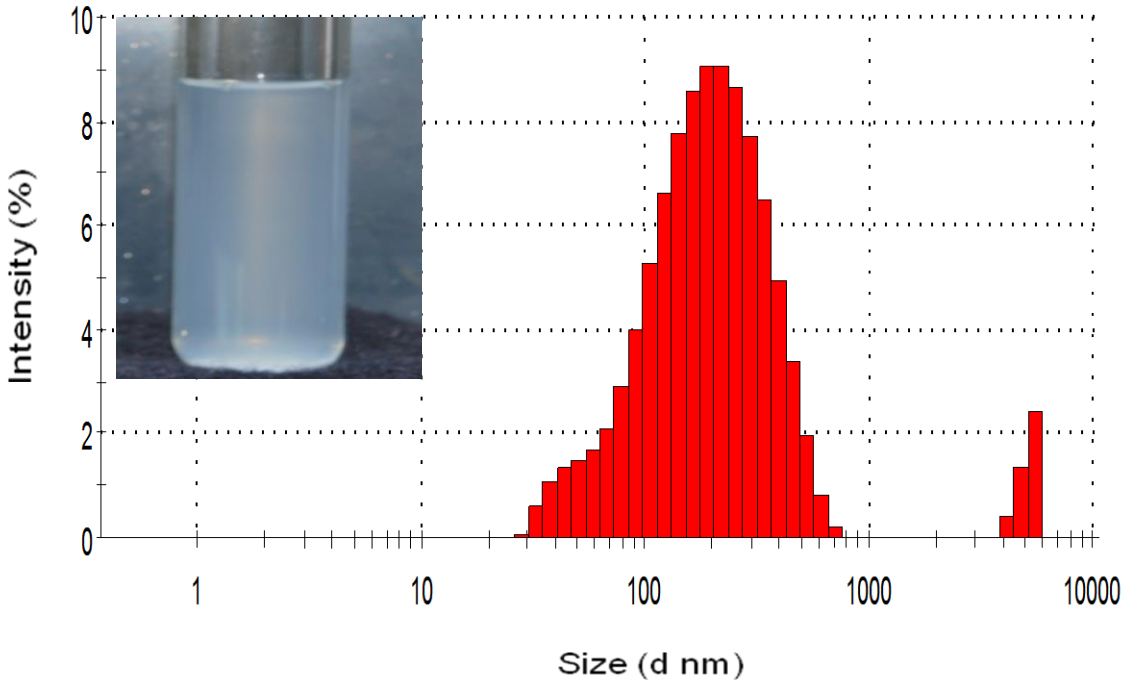

Fig. 4. Intensity distribution for synthesized ZnO nano particles dispersed in 0.1% sodium lauryl sulphate (SLS). The inset shows the stable ZnO nano dispersions.

A. Mechanism of ZnO nano particle formation

In this typical process metal oxides are obtained by grounding metallic salts with sodium hydroxide, which is different from results obtained by hydroxides in solution [20]. It is being expected that the mechanism of formation of nano ZnO under mechano-chemical method is as follows.

Previous research indicated that $[Zn(OH)_4]^{2-}$ nano particles are primarily produced by an exothermic reaction from Zn salt and NaOH as a result of the mechanical grinding (reaction 1 and 2) [21].

$$Zn(CH_3COO)_2\ 2H_2O + 2NaOH \longrightarrow Zn(OH)_2 + 2CH_3COONa + 2H_2O \quad \ldots(1)$$

$$Zn(OH)_2 + 2H_2O \longrightarrow [Zn(OH)_4]^{2-} + 2H^+ \quad \ldots(2)$$

Freshly produced $[Zn(OH)_4]^{2-}$ decomposes to produce ZnO nano particles at a low temperature within a short reaction time (reaction 3) [21].

$$[Zn(OH)_4]^{2-} \longrightarrow ZnO + H_2O + 2OH^- \quad \ldots(3)$$

The scheme of growth mechanism of ZnO nano rods are as shown in Fig. 6.

B. Role of CTAB in morphology of ZnO nano particles

The choice of surfactant decides the morphology of products. Reported works show that spherical ZnO nano particles can be prepared by using various alkyl amines [22-23]. In the current study it is being expected that CTAB provides a long chain reaction interface and allows the particles to grow in one direction and as a result particles assumes a rod like morphology (Fig. 6). It will not react with reactants and can be finally removed by washing the product with distilled water.

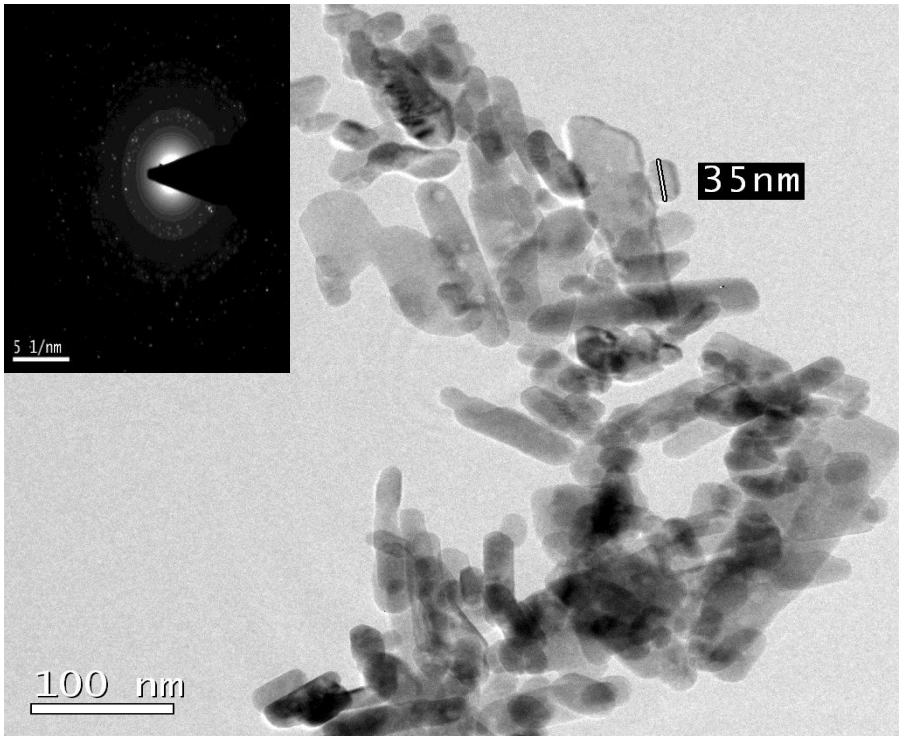

Fig. 5. HRTEM image of synthesized nano ZnO. Inset shows electron diffraction (SAED) pattern.

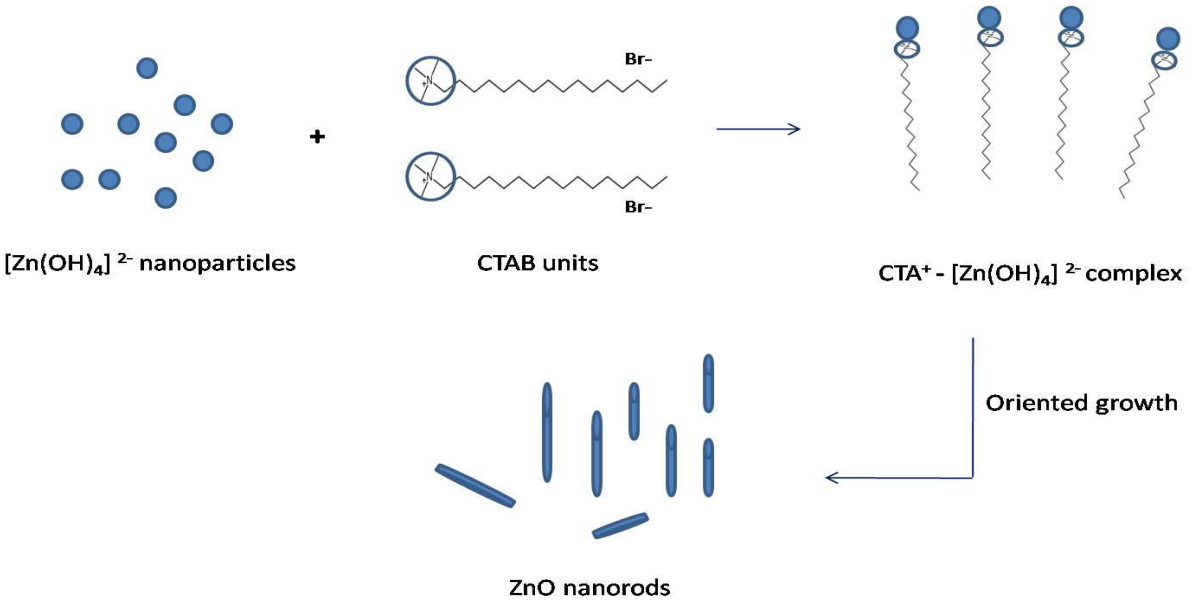

Fig. 6. Schematic diagram showing the growth mechanism of ZnO.

The sodium acetate formed in the initial stage of reaction can also be removed during the washing. Hence bi-products if any formed during the process and formation of any other un-wanted impurities can be completely eliminated during washing. Thus the ZnO nanoparticles synthesized by this route is free from impurities, which is confirmed by XRD and TEM techniques.

IV. CONCLUSIONS

Present study envisages the formation of ZnO nano rods from zinc acetate dihydrate, sodium hydroxide and CTAB through a mechano-chemical process. The average size of particles obtained through this technique is in the range 35-60 nm. This method is convenient, effective and inexpensive method for synthesizing ZnO nano particles. It should also be noted that the reaction yield was about 98%. Thermal studies revealed that the complete conversion of zinc hydroxide to zinc oxide happens at 241^0C. TEM images showed that aggregation of the synthesized nanoparticles is minimum and the purity of synthesized nano particles are good. FT-IR and XRD technique also support this comment. A suitable relationship between choices of substrates, concentration of substrates, type and dosage of capping agents on particle size as well as morphology of ZnO nanoparticles is still under debate.

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REFERENCES

[1]. Bhattacharjee C.R, Purkayastha D.D, Bhattacharjee S and Nath A. *Assam Univ. J. of Sci. and Tech: Phys. Sci. and Technol.,* **7**(II): 122-7 (2011).

[2]. Sawai J. *J Microbiol. Methods*. **54**(2): 177-82 (2003).

[3]. Azam A, Ahmed F, Arshi N, Chaman M and Naqvi AH. *Inter. J of Theo. and App. Sci*, .**1**(2): 12-4 (2009).

[4]. Pillai S.C, Kelly J.M, McCormack D.E and Ramesh R. *Mater. Sci. Technol.* **20**: 964-8 (2004).

[5]. Pillai S.C, Kelly J.M, McCormack D.E and Ramesh R. *Adv. Appl. Ceram.***105**(3): 158-60(2006).

[6]. Georgekutty R, Seery M.K and Pillai S.C. *J Phys. Chem C*. **112**(35):13563-70 (2008).

[7]. Ledwith D, Pillai S.C, Watson G.W and Kelly J.M. *Chem. Commun*. 2294-5 (2004).

[8]. Padmanabhan S.C, Ledwith D, Pillai S.C, McCormack D.E and Kelly J.M. *J. Mater. Chem.***19**(48): 9250-9 (2009).

[9]. Pillai S.C, Kelly J.M, McCormack D.E and Ramesh R. *J. Mater. Chem*. **14**(10):1572-8 (2004).
[10]. Li W.J, Shi E.W, Zheng Y.Q and Yin Z.W. *J Mater. Sci. Lett.* **20**:1381-4 (2001).
[11]. Liu B and Zeng H.C. *J Am Chem Soc.* **125**: 4430-1 (2003).
[12]. Cheng B and Samulski E.T. *Chem Commun.* 986-7 (2004).
[13]. Jiang J, Huang Z, Tan S, Li Y, Wang G and Tan X. *Mater Chem Phys.* **132**(2-3): 735-9 (2012).
[14]. Li Y.J, Duan R, Shi P.B and Qin G.G. *J Cryst. Growth.* **260**: 309-15 (2004).
[15]. Alam M.J and Cameron D.C. *J Vac. Sci. Technol. A.* **19**(4): 1642-6 (2001).
[16]. Toyoda M, Watanabe J and Matsumiya T. *J Sol-Gel Sci. Technol.***16**(1/2): 93-9 (1999).
[17]. Shen L, Bao N, Yanagisawa K, Domen K, Gupta A and Grimes C.A. *Nanotechnology* **17**: 5117-23 (2006).
[18]. JCPDS Card No. 36-1451.
[19]. Nolan N.T, Seery M.K and Pillai S.C. *Chem Mater.* **23**(6):1496-04 (2011).
[20]. Zhi-Peng Sun, Lang Liu, Li Zhang and Dian Zeng Jia. *Nanotechnology*. **17**: 2266-70 (2006).
[21]. Mamady N.C, Khalid D, Hafid Z, Karima A, Larbi L, Mohammed B and Boujemaâ J. *J of Mater Sci and Engg A*. **1**: 985-90 (2011).
[22]. Shim M and Guyot- Sionnest P. *J Am. Chem. Soc.* **123**: 11651-4 (2001).
[23]. Cozzoli P.D, Curri M.L, Agostiano A, Leo G and Lomascolo M. *J Phys. Chem. B.* **107**: 4756-62 (2003).