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Growth of Significantly Low Dimensional Zinc Orthotitanate (Zn_2TiO_4) Nanoparticles by Solid State Reaction Method

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Abstract:

In this work, the ZnO-TiO_2 mixed phase nanoparticles were prepared by solid state reaction method by using ZnO and TiO_2 powder as precursors. The X-ray diffraction pattern shows a dominant phase of Zinc Orthotitanate (Zn_2TiO_4). The average particle size (58±18 nm) calculated by the analysing FESEM data closely matches with the particle size calculated by Scherrer's equation. The calculated average particle size is significantly smaller than the previously published results of nanoparticles, prepared by same method. In the Brunauer–Emmett–Teller (BET) study the specific surface area of the nanoparticles was found as 8.78 m^2/g which is similar to the surface area reported in this material prepared by mechanochemical method. The method which we report is simpler and cost effective unlike the previous reported.

***Keywords*:** *Zinc Orthotitanate; Solid state reaction.*

1. Introduction

Nanostructures of TiO_2 and ZnO are widely used materials for various photonic applications. It has been observed that their titanate compound Zinc Orthotitanate (Zn_2TiO_4) nanostructures show superior behaviour in these applications due to enhance charge separation capability [1]. In doped and un-doped form, this material has been mostly used for hydrogen generation through photocatalytic decomposition of H_2S, water etc. [2, 3]. Zn_2TiO_4 has also been tested for efficient organic dye decomposition [4-6]. These nanoparticles have been investigated for dye sensitized solar cell and as a good dielectric material for microwave devices in area of mobile telephones, satellite communication and detection of ethanol vapour applications [7-12]. In the present work, we have demonstrated the growth of extremely low dimensional Zn_2TiO_4 nanoparticles by solid state reaction method and compared with previously published results [5].

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2. Experimental Details

Solid state reaction method was used for growth of ZnO-TiO_2 nanoparticles.TiO_2 (Product No. 28375, Fisher Scientific, purity: 98.99 %) and ZnO (Product No.28975, Fisher Scientific, purity: 98.99 %) powders were taken as the precursors for this growth. A multi step grinding/mixing process is adopted in our case. The ZnO and TiO_2 precursors were grinded individually for 1 hour each followed by their mixing in 2:1 molar ratio and further grinding in aceton medium for 1 hour.

The final powder mixture was calcined in a furnace (Lenton) at 1000 ^oC for 2 hours.

The X-ray diffraction (XRD) pattern of material was carried out to identify the phases of the nanoparticles. The field emission scanning electron microscopy (FESEM) was done to find the morphology of the nanoparticles using a Carl Zeiss Sigma system. The size distribution of the nanoparticles was estimated by analysing FESEM images by using commercial software ImageJ and Origin.

For the further analysis the BET studies of the titanate compound were also performed by using a conventional BET multi-point N_2 physisorption apparatus (Quantachrome ChemBET analyzer).

3. Results and Discussion

The XRD analysis result is shown in Fig. 1a.

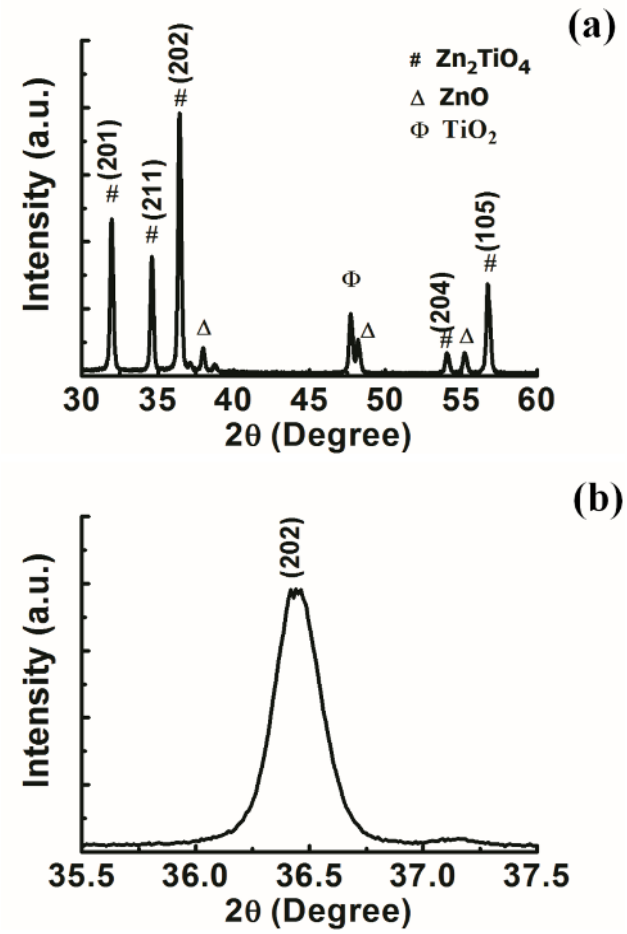

Fig. 1. (a) XRD pattern of Zn_2TiO_4, (b) XRD pattern of (200) plane in more specific angle.

Very predominant peaks of mixed phase material Zinc Orthotitanate (Zn_2TiO_4) were found at angle 2θ = 31.97, 34.62, 36.46, 53.98 and 56.81 degree. From The PCPDF database, peaks corresponding to these angles were identified as (201), (211), (202), (204) and (105) planes respectively. The results are also found to be in good agreement with the result published by Nikam et al. and Santhaveesuk et al. [6, 12]. Some minor peaks were also found originating from residual ZnO and TiO_2.

The Scherer's equation shown in equation (1) was used to calculate the average crystallite size (d) of the sample considering full width at half maximum (FWHM) for the (202) diffraction peak of Zn_2TiO_4 (Fig. 1b).

$$d = 0.9\lambda/\beta \cos\theta \quad (1)$$

Where 0.9 is Scherer constant, λ is wavelength of the X-ray (0.154 nm for Cu Kα radiation), θ is Bragg's diffraction angle and β is broadening of the diffraction peak measured at half of its maximum intensity (FWHM in radians). For (202) peak (Fig. 1b) the value for θ and β are found to be 36.44° and 0.18° respectively. With these values the size of the nanoparticles was found to be 55 nm.

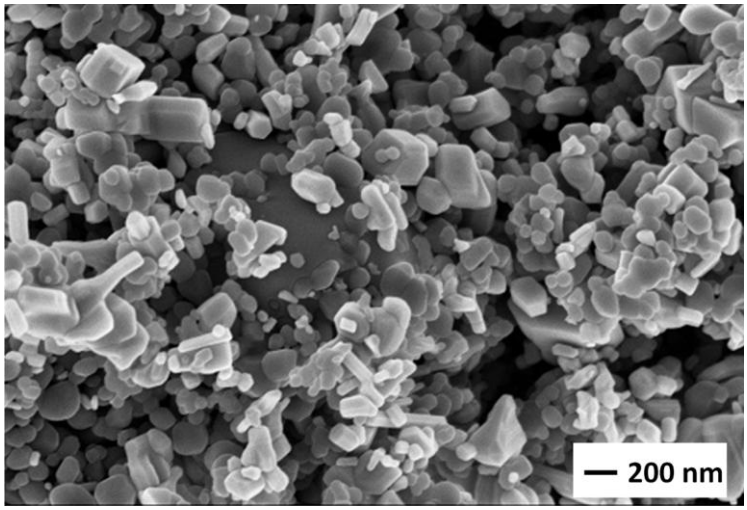

Fig. 2. Field Emission scanning electron microscope image of the nanoparticles.

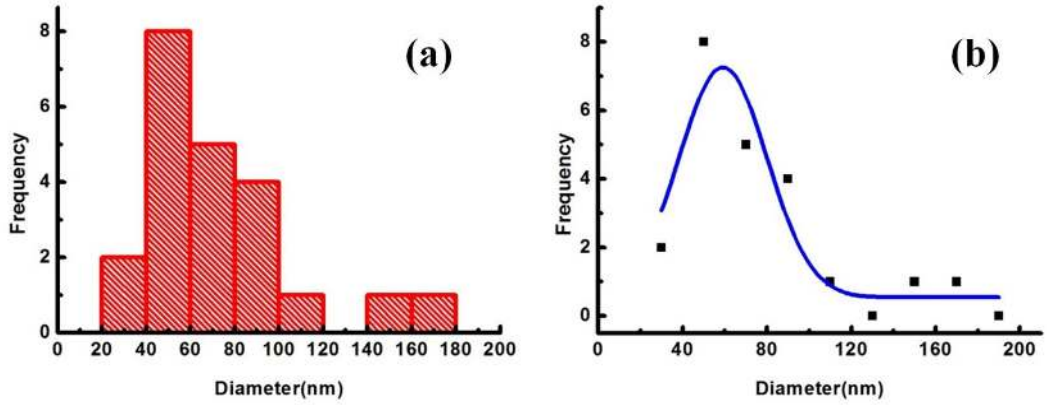

Fig. 3. (a) Statistical distribution of the particle size in terms of histogram, (b) Statistical distribution of the particle size in terms of Gaussian fit curve.

The FESEM image of the nanoparticles is shown in Fig. 2. The results of particle size analysis from this FESEM image are shown in form of histogram and its corresponding scatter plot in Fig. 3 (a) and Fig. 3 (b) respectively. From the histogram (Fig. 3a) the size of the particles were found within the range of 20-180 nm. The maximum numbers of particles (frequency) were found to have diameter of 58 ± 18 nm (Fig. 3b). This value is in consistence with the value estimated by Scherrer's equation.

The BET isotherm of our nanoparticles is shown in Fig. 4. From this, the estimated specific surface area of the nanoparticles is 8.78 m^2/g. Generally the particle size and specific surface area related to each other inversely. Therefore, one can calculate the average particle diameter from the BET specific surface area [13-16]. If the particles are of uniform dimension, their average diameter (d in nm) can be given by [13-15]:

$$d = 6 \text{ X } 10^3/s\,\rho \quad (2)$$

Where s is the specific surface area in m^2/g and ρ is the density of the nanoparticles in g/cm^3. The reported value of density of Zn_2TiO_4 is 5.28 g/cm^3 [16, 17]. Putting these values in Eq. 2 the average particle diameter is estimated as 129 nm. The particles of this study were not of same size, therefore this average particle diameter (129 nm) is not found be equal to the diameter (58±18 nm) in which maximum numbers of particles are there. Nonetheless it is worth to be noted here, that Habib et al. used the solid state reaction method to grow Zn_2TiO_4 nanoparticles and the dimension of particles reported by them was ~500 nm [5]. So our Zn_2TiO_4 nanoparticles are of significantly smaller dimension compared to the earlier reported nanoparticles of this material prepared with the same method. Habib et al., used a single step grinding/mixing process whereas we used the multi-step grinding/mixing process. So we assume that this multi-step grinding/mixing process may be the cause for reduced dimension.

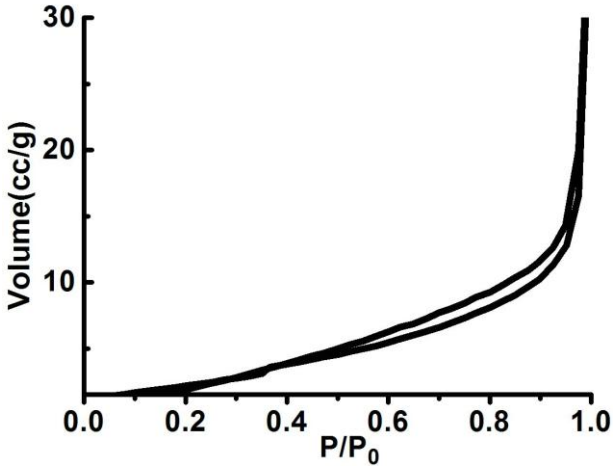

Fig. 4. BET isotherm of the nanoparticles.

Further it is to be note that previously Obradovic et al. have demonstrated the growth of Zn_2TiO_4 of BET surface area 6.4-14.4 m^2/g by the mechanochemical method with ball milling time 90-300 min [11]. Our material shows similar surface area. However unlike the ball milling our growth method is simpler and requires low capital investment.

4. Conclusion

In this work ZnO-TiO_2 mixed phase nanoparticles were prepared by solid state reaction method by taking ZnO and TiO_2 powders as precursors. The dominant phase was

found to be Zinc Orthotitanate. In the statistical analysis of their FESEM images the size of the particles were found within 20-180 nm with maximum numbers at 58±18 nm. This size is significantly smaller than previously published result on nanoparticles, prepared with the similar method. The estimated BET surface area (8.78 m^2/g) of the nanoparticles was found to be similar to the specific surface area reported in this material prepared by mechnanochemical method. However in comparison to that method, our growth method is simpler and cost effective. These nanoparticles may be found to be useful for applications like photocatalysis and dye sensitized solar cells etc.

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5. References

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Садржај: *У овом раду, ZnO-TiO_2 је припремљен реакцијом у чврстој фази полазећи од прахова ZnO и TiO_2 као прекурсора. Рендгенска дифракција указује на цинк-ортотитанат као доминантна фаза (Zn_2TiO_4). Просечна величина кристалита (58±18*

nm) рачуната FESEM-ом је у корелацији са резултатима добијеним Шереровом формулом. Израчуната просечна величина честица је мања од претходно објављених резултата, припремљеног материјала истом методом. Специфична површина је 8,78 m^2/g рачуната БЕТ методом, што је сличан резултат за материјал припремљен механичком активацијом. Метод који смо ми користили је једноставнији и јефтинији у поређењу са претходно објављеним резултатима.
Кључне речи: *цинк ортотитанат, реакције у чврстој фази.*