

# Synthesis and Characterization of TiO<sub>2</sub> Nanoparticles for Solar Cell Applications

Anuradha Gupta, Kamal K. Kushwah, Sujeet K. Mahobia, Payal Soni, V.V.S. Murty

**Abstract:** Titanium dioxide (TiO<sub>2</sub>) nanoparticles were synthesized using three different approaches successfully. These approaches were adopted as per different applications of TiO<sub>2</sub> nanoparticles. These samples were characterized using X-ray diffraction (XRD) technique. XRD revealed nanocrystalline regime of TiO<sub>2</sub> nanoparticles in each approach. The calculated size of nanoparticle was less than 11 nm in the used chemical approaches. Prominent and broad peaks were observed in XRD pattern for all samples, which showed all samples were in nanocrystalline form. The particle size was calculated for first three most intense prominent XRD peaks. By adopting sol gel method using Titanium tetra isopropoxide (TTIP) as precursor, the synthesized Titania particles were pure anatase and of size 7 to 11nm and using co-precipitation method using TiCl<sub>3</sub> as precursor synthesized Titania were pure rutile and of size 3 to 7 nm. The co-precipitation method has been best suited for getting smaller nanoparticles. It was also observed that Solid state mechanical reduction root can be used to reduce the size of Titania micro-particles up to about 60 nm but phase of nanoparticles remains same as starting microparticles. It has been seen that the material properties of TiO<sub>2</sub> can be tuned by proper method of synthesis. The work may play important role to choose particular synthesis method for specific application. These nano synthesized TiO<sub>2</sub> materials may be used in a wide range of applications such as dye sensitized solar cell, photocatalysis, antibacterial, environment pollutant removal and photoactivated self cleaning properties etc.

**Index Terms:** Ball milling, Co-precipitation method, Sol-gel method, Titanium dioxide (TiO<sub>2</sub>), X-ray Diffraction.

## I. INTRODUCTION

In recent years, TiO<sub>2</sub> has been renowned as a semiconductor with photocatalytic activities and incorporates a nice potential for applications like dye sensitized solar cell [1][2], environmental purification [3][4] and nanofluid applications [5][6]. Titania has been extensively studied because of its chemical and physical properties in photo-catalytic applications for environmental remediation [7]. It is mostly used in the form of nanoparticles in suspension for high catalytic surface area and activity [8]. Being a photo-catalyst material, TiO<sub>2</sub> has been important for various serious environmental and pollution challenges [9]. It is photo-catalyst and also relatively cheaper, high chemical stable and non toxic material therefore, widely used for

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Anuradha Gupta, Physics Department, Govt. Auto. Holkar Science College, Indore (Madhya Pradesh), India.

Kamal K. Kushwah, Department of Applied Physics, Jabalpur Engineering College, Jabalpur (Madhya Pradesh), India.

Sujeet K. Mahobia, Department of Applied Physics, Jabalpur Engineering College, Jabalpur (Madhya Pradesh), India.

Payal Soni, Physics Department, Govt. Auto. Holkar Science College, Indore (Madhya Pradesh), India.

V.V.S. Murty, Physics Department, Govt. Auto. Holkar Science College, Indore (Madhya Pradesh), India.

related applications. Umale S. et al. reported fabrication of dye sensitized solar cell (DSSC) using combustion synthesized and commercial TiO<sub>2</sub> exhibited a power conversion efficiency of 6.11% and 6.62 %, respectively [10]. Dhonde M. et al. report, Cu/N doped TiO<sub>2</sub> nanoparticle based DSSC showed best power conversion efficiency 11.7% for 0.3 mol % of Cu/N doped TiO<sub>2</sub> photoanode [11]. In most of these cases, the size of the TiO<sub>2</sub> particles is an important factor affecting the performance of the materials. Much effort has been devoted to the preparation of TiO<sub>2</sub> nanoparticles, including sol-gel route, homogeneous precipitation, hydrothermal methods, flame synthesis and relatively new molten salts method [12]. They were usually found that different routes often produce different results. Even for the same route, using different amount of the starting materials, the obtained powder size is different [13]. Consequently, phase and particle size are the important parameters that influence physical properties of material. XRD methods allow not only to measure the particle size, but also to identify crystalline phases. In the present study, we attempted to synthesize tetragonal pure anatase phase, pure rutile phase and mixed phase TiO<sub>2</sub> nanoparticles, in simple way and successfully prepared them. Besides, the present methods are economical, fast, free of pollution, environmentally safe, reproductive and can be used for larger production. The particle size of the samples was estimated through Debye-Scherrer formula.

## II. EXPERIMENTAL SECTION

### A. Synthesis of TiO<sub>2</sub> nanoparticles by sol gel method

All the chemical reagents used in this method were analytical grade. The chemicals required were titanium tetra isopropoxide (TTIP) (Sigma-Aldrich), ethanol (Merck), Hydrochloric acid (Merck). In this novel method pure anatase TiO<sub>2</sub> nanoparticles were prepared using TTIP as precursor. In first step 40 ml ethanol was taken in a large beaker and then 1.2 ml concentrated HCl was added dropwise to it under magnetic stirring. This solution was magnetic stirred slowly for half an hour. Then 5 ml TTIP was added drop wise to this solution under magnetic stirring and after that the solution was magnetic stirred slowly for 2 hrs. At last solution was kept in hot air oven for drying at 100°C for 10 hrs. Obtained TiO<sub>2</sub> powder were grounded well using agate mortar for 30 min and then kept in muffle furnace at 450°C for 1hrs for calcinations.



## B. Synthesis of TiO<sub>2</sub> nanoparticles by Co-precipitation method

This facile and simple room temperature method was used to prepare pure rutile TiO<sub>2</sub> nanoparticles. All chemical reagents used in this method were analytical grade. Titanium trichloride (15 wt% TiCl<sub>3</sub>, 10 wt% HCl) were used as titanium precursor and NH<sub>4</sub>OH (1.0 M) was used to carried out hydrolysis of TiCl<sub>3</sub>. 10 ml of titanium trichloride was added drop by drop to 60 ml NH<sub>4</sub>OH solution under vigorous stirring. Then the solution was kept stirred for 10 hrs and aged for 24 hrs. The white precipitates formed was filtered and washed thoroughly with distilled water. The TiO<sub>2</sub> precipitate so obtained were dried in hot air oven at 100°C for 12 hrs and further calcined in a muffle furnace at 450°C for 2 hrs.

## C. Synthesis of TiO<sub>2</sub> nanoparticles by ball milling method

In this method physical grinding process was adopted to reduce the size of TiO<sub>2</sub> powder. Nano-sized TiO<sub>2</sub> powders were prepared by a Mechanical dry ball milling method. Micron sized TiO<sub>2</sub> powder (99% pure) was purchased from Loba Chemic. Pvt. Ltd., Mumbai.

In a planetary ball mill, the dry milling of TiO<sub>2</sub> powder was performed. The weight ratio of the powder to the ball was maintained at 1:10 during the milling process. Nano sized TiO<sub>2</sub> powder was prepared by dry milling with Zirconia balls without using any liquid milling medium. The rotating speed for milling was maintained at 350 rpm and milling was done for 8 hrs. The finely grinded powder was drawn out at the end and stored at room temperature in plastic pouches until use.

## D. Characterizations

All the TiO<sub>2</sub> nanopowders prepared by different methods were characterized by X-ray diffraction technique in order to determine their crystalline phase and particle size. The X-rd analysis was performed by Bruker D8 Advance X-ray diffractometer with Cu-K $\alpha$  source of wavelength 0.154 nm.

## III. RESULTS AND DISCUSSIONS

The X-Ray diffraction (XRD) spectrum of TiO<sub>2</sub> nanoparticles, made by three different methods are shown in Fig. 1. The average particle size of all TiO<sub>2</sub> nanoparticles samples is calculated by using Scherrer's formula:

$$t = \frac{0.9\lambda}{\beta \cos\theta}$$

Where  $\beta$  is full width of half maximum (FWHM),  $\lambda$  is the wavelength of X-ray used and  $\theta$  is the diffraction angle. Fig. 1(a) shows XRD spectrum of TiO<sub>2</sub> nanoparticles, made by sol-gel method and it reveals that the pattern is tetragonal and pure anatas crystalline phase and analogous with the standards result. The XRD results are in good agreement with the JCPDS card No. 84-1286. Fig. 1(b) shows XRD spectrum of TiO<sub>2</sub> nanoparticles, made by co-precipitation method and it reveals that the pattern is tetragonal and pure rutile crystalline phase and analogous with the standards result. The XRD results are in good agreement with the JCPDS card No. 76-1941. In both the cases peaks are broad indicating the size of particle in the nanometer range and no impurity peaks are found in XRD results, indicates the formation of pure anatas or rutile phase. Fig. 1(c) shows XRD spectrum of TiO<sub>2</sub> nanoparticles, made by ball-milling method and it reveals that the pattern is tetragonal and mixture of anatas and rutile crystalline phase. This is confirmed with the JCPDS card No. 84-1286 and 76-194. In this case only particle size is reduced from micro to nano but phase did not change, it is same as the commercial micro powder used as precursor. It is also observed that particle size of TiO<sub>2</sub> depends on FWHM of XRD peaks, as the peak becomes more broaden the size of TiO<sub>2</sub> becomes less with more FWHM. The particle size of all three TiO<sub>2</sub> nanoparticles are calculated using Scherrer's relation for three most intense prominent peaks and are tabulated in Table 1. The particle size of as prepared TiO<sub>2</sub> nanoparticles using sol-gel method with TTIP as precursor lies between 7 to 11 nm (Table-1) and are pure

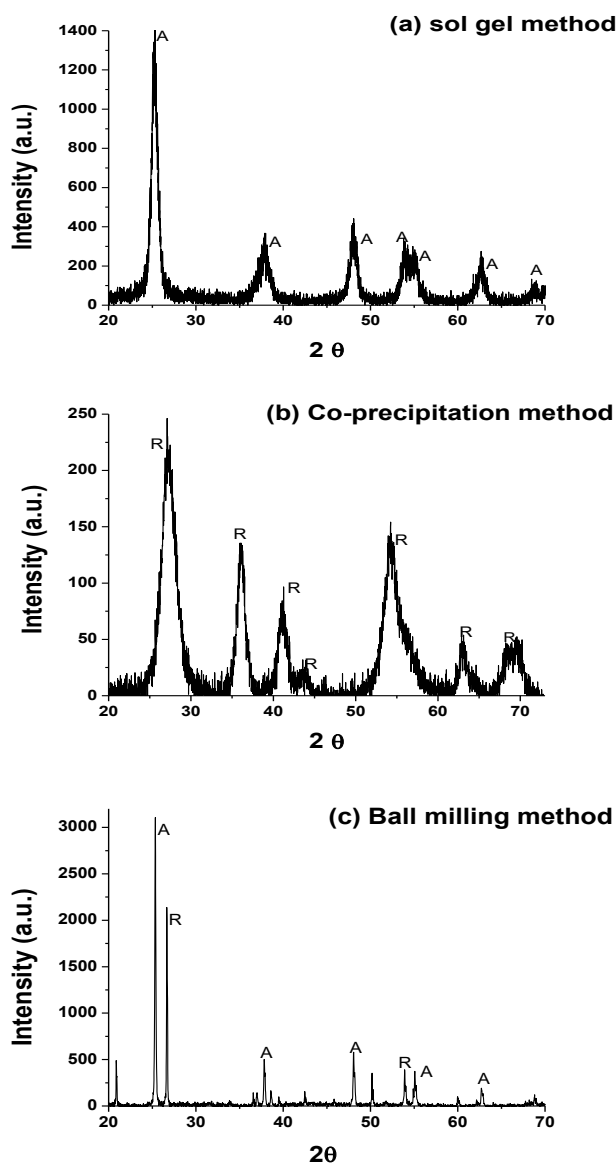


Fig. 1 XRD pattern of TiO<sub>2</sub> nanoparticles. A-anatas phase, R-rutile phase.

**Table 1: Peak position, FWHM & particle size for TiO<sub>2</sub> nanoparticles prepared by three different methods.**

Methods	2θ (in degree)	FWHM ( in radian)	Particle size (in nm)
I. Sol-gel	25.32	0.0136067	10.4397
	37.83	0.0211077	6.9407
	48.07	0.01765378	8.5955
II. Co-precipitation	27.29	0.0356976	3.9952
	35.89	0.0202465	7.1953
	53.98	0.0418286	3.7181
III. Ball-milling	25.35	0.0025744	55.1801
	27.11	0.0020818	68.4819
	37.85	0.0033078	44.2926

having pure anatase crystalline phase. The results match with the previous researchers results [14][15]. One of the important application of the anatase phase TiO<sub>2</sub> nanoparticles is in DSSC; being used as one of the photoanode [15][16]. As the band gap of pure anatase TiO<sub>2</sub> nanoparticle fall in ultra violet region so to utilize whole solar spectrum effectively and to improve efficiency of DSSC people try to engineering the band gap of TiO<sub>2</sub>. The TiO<sub>2</sub> nanoparticles prepared by co-precipitation method having their size range from 3 to 7 nm (Table -1) and are having pure rutile crystalline phase. The results are analogous to other researcher's results [17]. The rutile phase TiO<sub>2</sub> nanoparticles have potential for many photocatalytic applications such as degradation of pollutant [18][19]. The mixture of anatase and rutile phase showed synergistic effect in many photocatalytic applications including DSSC also [20][21]. The ball milling process has reduced the size of the particles in present study; the size range is from 44 to 69 nm. Ball milling process may be used to enhance the photocatalytic activity of TiO<sub>2</sub> nanoparticles [22]. TiO<sub>2</sub> nanoparticles based nanofluids and nanolubricants are also reflects significantly improved performance in many heat transfer applications [23][24].

#### IV. CONCLUSIONS

In the present work the TiO<sub>2</sub> nanoparticles were successfully synthesized using three different low cost novel methods; two belong to chemical route - sol-gel and co-precipitation methods and one belongs to physical route- ball milling. By XRD results, it was established that sol-gel method is useful for synthesis of anatase phase TiO<sub>2</sub> nanoparticles (7 to 11 nm) and Co-precipitation method is useful for synthesis of rutile phase TiO<sub>2</sub> nanoparticles (3 to 7 nm). The various applications of TiO<sub>2</sub> such as nanofluid, DSSC etc. depend on crystalline phase and particle size of samples, also sometimes optimized ratio of anatase and rutile phase showed synergistic effect such as in DSSC. The present paper described methods to produce both the phases- anatase phase and rutile phase TiO<sub>2</sub> nanoparticles. It may help in synthesis line of TiO<sub>2</sub> nanoparticles for many applications. The ball milling method is a powerful and green method to reduce the size of the TiO<sub>2</sub> nanoparticles and for large scale production. The size of TiO<sub>2</sub> commercial micro powder was reduced by ball milling method and ranged between 44 to 69 nm without changing the crystalline phase of commercial TiO<sub>2</sub> micro powder. The ball milling process may be used for improving the efficiencies of TiO<sub>2</sub> nanoparticles such as photo catalytic activity, mechanical strength and reducing the properties like particle

size, band gap and recombination rate of electron-hole pair. These parameters play important role in improving efficiency of DSSC. By optimizing the rotating speed, grinding time and ball to grinding material ratio the desired properties of grinding material may be tuned.

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National/ international journals. He has 12 years teaching experience.

**Dr. Sujeet Kumar Mahobia** Dr. Sujeet Kumar Mahobia has completed his Ph.D. from Rani Durgavati Vishwavidyalya, Jabalpur, Madhya Pradesh (MP) India. Presently he is working as Asst. Professor in Department of Applied Physics, Jabalpur Engineering College, Jabalpur, M P. He is doing research in material science and has published 15 research papers in reputed



**Mrs. Payal Soni** is pursuing her Ph. D. in Govt. Auto. Holkar Science College, Indore (M.P.). Her area of research is dye sensitized solar cells and material development for solar thermal energy storage systems. She has published good number of papers in national and international conferences and four papers in various reputed journals.



**Dr. V.V.S. Murty** is currently working as a Professor of Physics in Government College of Madhya Pradesh, India. He has guided six Ph. D. students and presently working on Plasmonic dye sensitized solar cells and material development for solar thermal energy storage systems. He has published good number of papers in various reputed journals and conferences.

## AUTHORS PROFILE



**Mrs. Anuradha Gupta** is pursuing her Ph. D. in Govt. Auto. Holkar Science College, Indore (M.P.). Her area of research is dye sensitized solar cells and material development for solar thermal energy storage systems. She has published good number of papers in national and international conferences and three papers in various reputed journals.



**Dr. Kamal Kumar Kushwah** Presently working as an Assistant Professor in Department of Applied Physics, Jabalpur Engineering College, Jabalpur, Madhya Pradesh, India He was selected through MP PSC. He has published 25 research papers in National and International journals. He was conferred upon with "Best Faculty" and "Rajya Gaurav Samman 2018". He has authored two Book chapters on Luminescence and Photovoltaic technology. He holds a high place in the field of Nanoscience and Nanotechnology internationally and nationally. He is also involved with the popularization of science through Indian Association of Physics Teachers (IAPT) and Anveshika Vigyan Prasar Yojna running by IIT Kanpur.

