Synthesis and Characterization of TiO_2 Nanoparticles for Solar Cell Applications

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

Abstract: Titanium dioxide (TiO_2) nanoparticles were synthesized using three different approaches successfully. These approaches were adopted as per different applications of TiO_2 nanoparticles. These samples were characterized using X- ray diffraction (XRD) technique. XRD revealed nanocrystalline regime of TiO_2 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 nanocrytalline 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 anatas and of size 7 to 11nm and using co-precipitation method using $TiCl_3$ 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_2 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_2 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_2), X-ray Diffraction.

I. INTRODUCTION

In recent years, TiO_2 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_2 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 related applications. Umale S. et al. reported fabrication of dye sensitized solar cell (DSSC) using combustion synthesized and commercial TiO_2 exhibited a power conversion efficiency of 6.11% and 6.62 %, respectively [10]. Dhonde M. et al. report, Cu/N doped TiO_2 nanoparticle based DSSC showed best power conversion efficiency 11.7% for 0.3 mol % of Cu/N doped TiO_2 photoanode [11]. In most of these cases, the size of the TiO_2 particles is an important factor affecting the performance of the materials. Much effort has been devoted to the preparation of TiO_2 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_2 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–Scherer formula.

II. EXPERIMENTAL SECTION

A. Synthesis of TiO_2 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 anatas TiO_2 nanoparticls 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_2 powder were grounded well using agate mortar for 30 min and then kept in muffle furnace at 450°C for 1hrs for calcinations.

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B. Synthesis of TiO_2 nanoparticles by Co-precipitation method

This facile and simple room temperature method was used to prepare pure rutile TiO_2 nanoparticles. All chemical reagents used in this method were analytical grade. Titanium trichloride (15 wt% $TiCl_3$, 10 wt% HCl) were used as titanium precursor and NH_4OH (1.0 M) was used to carried out hydrolysis of $TiCl_3$. 10 ml of titanium trichloride was added drop by drop to 60 ml NH_4OH 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_2 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_2 nanoparticles by ball milling method

In this method physical grinding process was adopted to reduce the size of TiO_2 powder. Nano-sized TiO_2 powders were prepared by a Mechanical dry ball milling method. Micron sized TiO_2 powder (99% pure) was purchased from Loba Chemic. Pvt. Ltd., Mumbai.

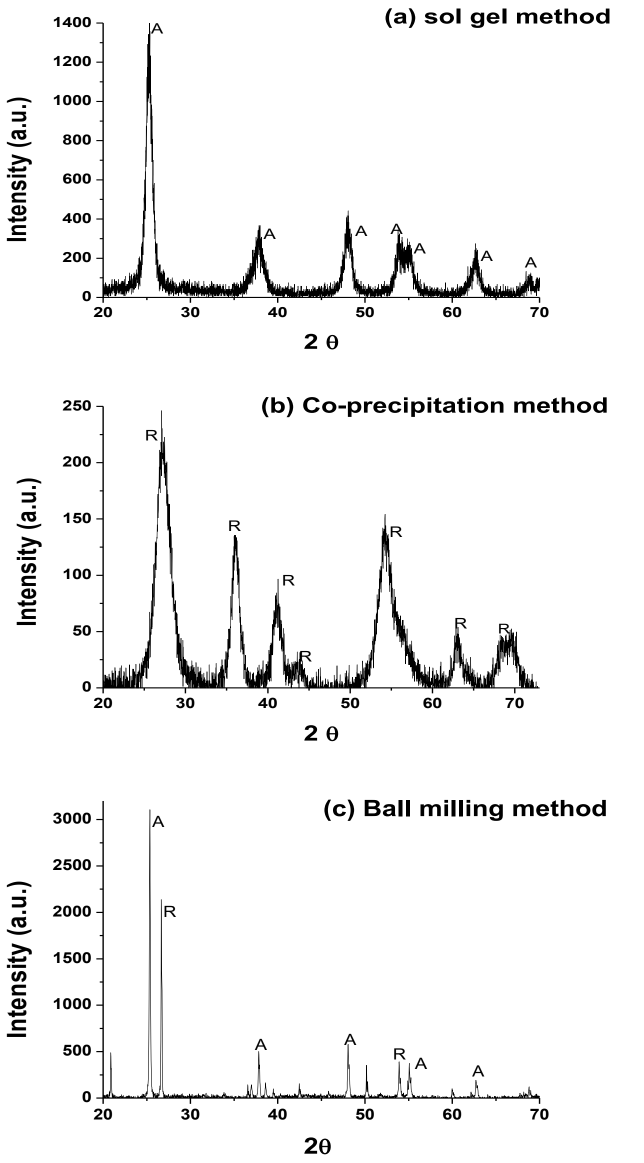

Fig. 1 XRD pattern of TiO_2 nanoparticles. A-anatas phase, R-rutile phase.

In a planetary ball mill, the dry milling of TiO_2 powder was performed. The weight ratio of the powder to the ball was maintained at 1:10 during the milling process. Nano sized TiO_2 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_2 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-Kα source of wavelength 0.154 nm.

III. RESULTS AND DISCUSSIONS

The X-Ray diffraction (XRD) spectrum of TiO_2 nanoparticles, made by three different methods are shown in Fig. 1. The average particle size of all TiO_2 nanoparticles samples is calculated by using Scherrer's formula:

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

Where β is full width of half maximum (FWHM), λ is the wavelength of X-ray used and θ is the diffraction angle. Fig. 1(a) shows XRD spectrum of TiO_2 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_2 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_2 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_2 depends on FWHM of XRD peaks, as the peak becomes more broaden the size of TiO_2 becomes less with more FWHM. The particle size of all three TiO_2 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_2 nanoparticles using sol-gel method with TTIP as precursor lies between 7 to 11 nm (Table-1) and are pure

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Table 1: Peak position, FWHM & particle size for TiO_2 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 anatas crystalline phase. The results match with the previous researchers results [14][15]. One of the important application of the anatas phaseTiO_2 nanoparticles is in DSSC; being used as one of the photoanode [15][16]. As the band gap of pure anatas TiO_2 nanoparticle fall in ultra violate region so to utilize whole solar spectrum effectively and to improve efficiency of DSSC people try to engineering the band gap of TiO_2. The TiO_2 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_2 nanoparticles have potential for many photocatalytic applications such as degradation of pollutant [18][19]. The mixture of anatas 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_2 nanoparticles [22]. TiO_2 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_2 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 root- ball milling. By XRD results, it was established that sol-gel method is useful for synthesis of anatas phase TiO_2 nanoparticles (7 to 11 nm) and Co-precipitation method is useful for synthesis of rutile phase TiO_2 nanoparticles (3 to 7 nm). The various applications of TiO_2 such as nanofluid, DSSC etc. depend on crystalline phase and particle size of samples, also sometimes optimized ratio of anatas and rutile phase showed synergistic effect such as in DSSC. The present paper described methods to produce both the phases- anatas phase and rutile phase TiO_2 nanoparticles. It may help in synthesis line of TiO_2 nanoparticles for many applications. The ball milling method is a powerful and green method to reduce the size of the TiO_2 nanoparticles and for large scale production. The size of TiO_2 commercial micro powder was reduced by ball milling method and ranged between 44 to 69 nm without changing the crystalline phase of commercial TiO_2 micro powder. The ball milling process may be used for improving the efficiencies of TiO_2 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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