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TECHNICAL NOTE

Effects of the pH of Initial Solution on Hydrothermally Synthesized TiO_2 Nanoparticles

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ABSTRACT

In this paper, we focused on the effects of the pH of initial solution on the chemical composition, size and morphology of hydrothermally synthesized titanium dioxide nanoparticles. $TiCl_4$ and NaOH were used as titanium source and precipitant, respectively. Chemical phase and structure of samples were determined by X-Ray Diffraction (XRD) analysis. Scanning Electron Microscopy (SEM) images were used for size and morphology evaluation of the resulting particles. Also, Simultaneous Thermal Analysis (STA) was used for evaluation of phase transformations during calcination process. Results indicated that increase in the initial pH of the solution leads to increase in crystallite size of hydrothermally obtained nanopowder, which is because of enhanced growth condition resulting from the increasing concentration of hydroxide groups in the solution. Particle sizes of the synthesized nanopowders were smaller than 100 nm and the average particle sizes decreased from 60 to 25 nm by increasing initial pH from 3 to 7. The results also showed that at initial pH=>9 the resulting synthesized nanopowders were in amorphous state and calcination at 700˚C led to sodium titanate.

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1. INTRODUCTION

Nanocrystalline metal oxides have gained a lot of attention because of their unique properties. Titanium dioxide is an important wide band gap n-type semiconductor because of its nontoxicity, chemical and optical stability, high strength, simple and relatively low cost production routes [1-3]. Titanium dioxide has various crystalline structures which are used in solar cells, air purifier catalysts, photovoltaic materials, gas and humidity sensors and antireflection coatings [4-6].
Titanium dioxide has 6 polymorphs of anatase, rutile, brookite, TiO_2-B, TiO_2-H and TiO_2-II [7]. Among these polymorphs, rutile with tetragonal structure (space group p42/mmm), anatase with tetragonal structure (space group I41/amd) and brookite with orthorhombic structure (space group Pcab) are more important because of their higher stability and useful properties. Rutile, the only thermodynamically stable phase at normal pressure and room temperature, have lower band gap energy (3 eV) in comparison with brookite and anatase phases (3.2 eV) which are metastable and can be transformed into rutile phase by calcination processing at 600-800˚C [8,9]. Particle size is one of the important factors in phase stability of nano TiO_2 particles.

Zhang and Banfield reported that anatase is the most stable phase when crystallites size are smaller than 11nm, brookite is the most stable phase when the crystalline size is between 11 and 35 nm and rutile is stable for crystallite bigger than 35 nm [10].

Photocatalytic properties of TiO_2 nanoparticles are highly dependent on morphology, chemical composition, pore structures, crystallinity, surface area of particles as well as the phase. It has been reported that anatase phase has a higher photocatalytic activity in comparison with rutile phase because of its lower electron-hole recombination rate [11, 12].

There are several methods for producing titanium dioxide nanoparticles such as: hydrolysis [13], sol-gel [14], liquid phase deposition [15], reverse micelle [16], microemulsion [17], ultrasonic chemical synthesis [18] and hydrothermal methods [19]. Among these methods, hydrothermal method is a relatively low temperature method for production of nano materials. This low temperature inhibits the undesired phase transformations and excessive growth of particles. This method also have some other advantages like high reactivity of the reactants, high controllability of the process, low energy consumption and ease of process. Hydrothermal reactions occur in closed environments. Therefore, by changing process parameters like pressure, temperature, duration, concentration of

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reactants, solvent type and pH, powders with various crystalline structure, morphology and chemical composition can be produced [1,2,15,16].

One of the most important variables that influence the crystallite size, surface area, phase structure and photocatalytic properties of hydrothermally synthesized TiO_2 nano particles is initial pH of the hydrothermal solution [10, 11]. In this paper, we discuss the effect of initial pH of hydrothermal solution on structure, morphology and size of the resulting powders.

2. EXPERIMENTAL

2.1. Raw Materials To synthesize titanium dioxide nanoparticles, titanium chloride ($TiCl_4$) and sodium hydroxide (NaOH) were purchased from Merck and used without further purification.

2.2. Equipments An X-ray diffractometer (Phillips – PW3710) with diffraction source of Cukα λ=0.154178 nm was utilized for conducting phase analysis. The morphology of the titanium dioxides nanoparticles was investigated by an Scanning Electron Microscope (Phillips – XL30). Also, for phase transformation evaluation at high temperature, an STA analyzer (STA 1640, Plymer Laboratories, England) was used.

2.3. Synthesis First, 12 ml of $TiCl_4$ was added to 100 ml distilled water placed in water and ice bath and stirred to obtain a transparent solution. After that, NaOH solution (4 M) was added drop by drop to the solution, meanwhile the pH of the solution was measured carefully and several samples collected at different pHs (3, 5, 7 and 9). Then, the samples were moved into 35ml Teflon lined autoclaves and filled up to %70 of their volume. The autoclaves were placed in an oven kept at 110˚C for 7 hours. After that, the autoclaves were cooled to room temperature. Finally, the samples were filtered and washed for several times with distilled water and ethanol to remove impurities and then dried in an oven at 50˚C for 24 hours.

3. RESULTS AND DISCUSSION

XRD patterns of the hydrothermally prepared samples are shown in Fig. 1. The results indicate the presence of anatase titanium dioxide. There is no evidence of any other crystalline phase in these patterns.
The mean crystallite size variations with initial pH of the samples are estimated from full width at half maximum of (101) planes sets' peaks by using Deby-Scherrer equation:

$$D = k\lambda / \beta \cos\theta \quad (1)$$

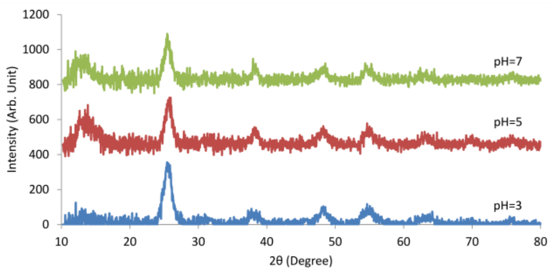

Figure 1. X-ray diffraction patterns of obtained samples synthesized at pH of 3, 5 and 7.

where, D is mean crystallite size, k is shape factor which is about 0.9 for spherical particles. λ is the wave length of the X-ray, -which in our experiment was equal to 0.154178 nm- and β is the full width at half maximum of (101) plane sets' peak [20]. The results are shown in Fig. 2. As can be seen, by increasing pH from 3 to 7, the mean crystallite size increases form 5.92 nm to 8.35 nm. This indicates faster growth rate for anatase crystals at higher pHs.

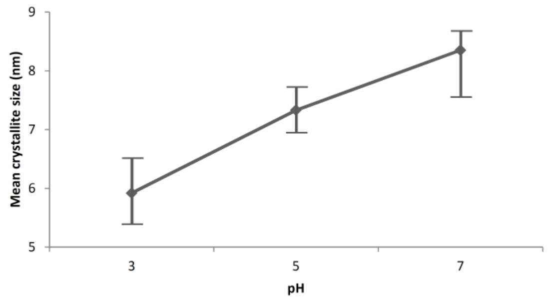

Figure 2. Mean crystallite size change by change in initial pH of hydrothermal solution.

This phenomenon can be described by mechanism of formation of this oxide. There are various theories for formation and growth mechanism of titanium dioxide crystals. One of the theories, which can describe formation and growth mechanism of crystalline ZnO from solution, is growth unit theory. The growth unit theory is based on formation and connection of growth units with $Ti(OH)_6^{2-}$ composition. In this theory formation of different crystalline structures of TiO_2 are described by different methods of connecting these growth units to each other. For example, to form an anatase structure, the growth units should connect to each other from their edges. To connect these units to each other, two hydroxide ions from two adjacent units should react with each other causing units to connect by Ti-O-Ti bonds. These reactions are called dehydration reactions because of releasing H_2O molecules [21]. It has been seen that by changing ions or their concentrations in the system , some growth units are replaced by other ions, so it can be expected that by reducing pH, which would result in lower concentration of hydroxide ion in the system, fewer hydroxide ions would be able to connect to titanium atoms [21]. Under these conditions, by decreasing pH of the solution, connection of these growth units to each other and crystal growth would be less probable. So, the growth rate would be lower in this condition which is in agreement with the results obtained in our experiments as shown in Fig. 2.

SEM images of the resulting samples and their particle size distribution plots are shown in Fig. 3. As can be seen, the morphology of the samples is semispherical. Also, agglomeration of particles decreases by increasing initial pH of the solutions.

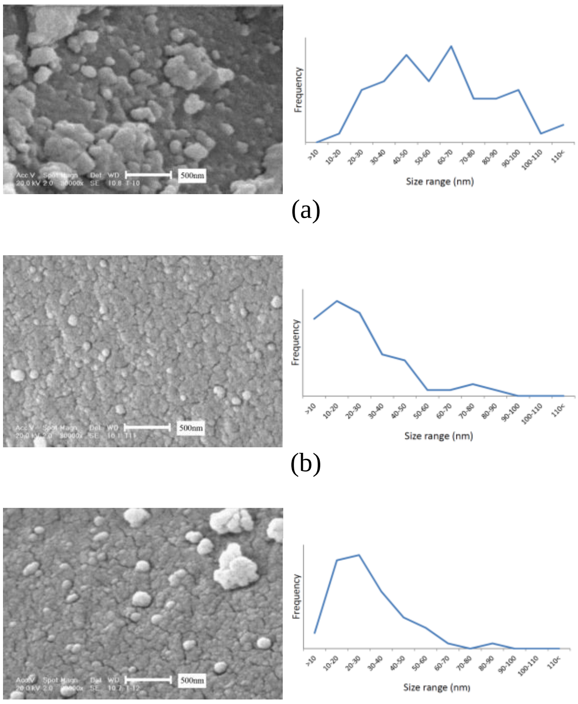

Figure 3. SEM images of the hydrothermally synthesized samples at pH of 3 (a), 5 (b) and 7 (c), their average particle sizes and particle size distributions.

X-ray diffraction pattern of the sample produced at pH=9 without calcination is shown in Fig. 4 (I). No crystalline phase could be identified at this pH.

The STA analysis result for this sample is shown in Fig. 5. Calcination of this sample was done at 700˚C for 2 hours based on the results obtained from STA analysis. The XRD result of calcinated sample is shown in Fig. 4 (II). It shows that sodium titanate crystalline phase with composition of $Na_2Ti_3O_7$ was formed during calcination processing at 700˚C. Researchers have reported that sodium titanate phase is formed as a result of some breaks in Ti-O bonds of the initial phase, and insertion of sodium ions into the crystal structure [21].

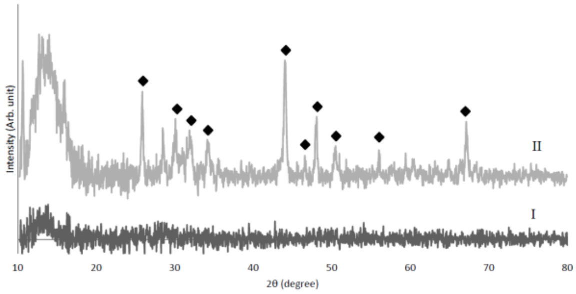

Figure 4. X-ray diffraction patterns of hydrothermally synthesized sample at pH=9 (I) before, and (II) after calcination at 700ºC for 2 hours. All $Na_2Ti_3O_7$ crystalline peaks are marked by ♦.

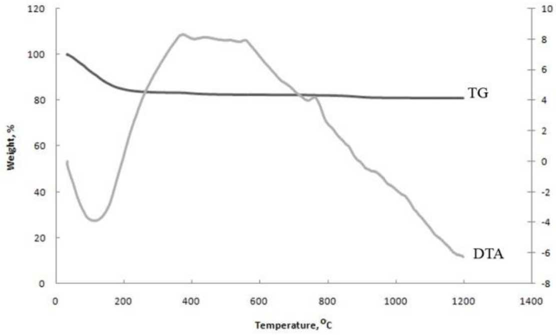

Figure 5. STA (TG-DTA) analysis result for the hydrothermally obtained sample at initial pH of 9.

Anatase structure is formed by connection of TiO_6 octahedrals which have two different Ti-O bond lengths of 0.1980nm (for two of the bonds) and 0.1934 nm (for other four bonds) Therefore, during the process involving high concentration of sodium ions, the bonds with higher length break and sodium ions enter into the titanate structure and form sodium titanate phase [7].

4. CONCLUSION

In this paper, the effects of initial pH of hydrothermal solution on crystalline structure, composition, and morphology and particle size of titanium oxide nanoparticles was evaluated. The results showed that at low pHs (3-7), the hydrothermal process leads to anatase phase, and by increasing the pH, its stability decreases, and finally at pH of 9 the resulted phase was amorphous titanate. The estimation of crystallite size showed that increasing the initial pH of hydrothermal solution before formation of the titanate phase from 3 to 7 increases the crystallite size from 6 to about 8.5nm. Also, the SEM images indicated that all the obtained samples had semispherical morphology and all samples average particle sizes were bellow 100nm. Also average particle sizes of samples decreased from 60 to 25 nm by pH values of 3-7.

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چکیده

در این مقاله تاثیر pH اولیه بر روی ترکیب، ساختار و مورفولوژی نانوذرات سنتز شده به روش هیدروترمال بررسی شده است. $TiCl_4$ به عنوان ماده اولیه تیتانیم و NaOH به عنوان منبع اصلی رسوب زا استفاده شده است. فاز و ساختار مواد بدست آمده در این روش توسط آنالیز پراش اشعه ایکس(XRD) تحلیل شده است. از تصاویر میکروسکوپ الکترونی روبشی(SEM) برای بررسی اندازه و مورفولوژی ذرات بدست آمده استفاده شده است. همچنین از آنالیز حرارتی همزمان(STA) برای بررسی تغییرات فازی در اثر حرارت دهی در مرحله کلسیناسیون استفاده شده است. نتایج بدست آمده موید آن است که pH اولیه محلول می تواند منجر به افزایش اندازه کریستالیت ذرات در هیدروترمال به علت افزایش غلظت گروههای هیدروکسیدی در محلول شود. همه ذرات تولید شده دارای اندازه ذره کمتر از ۱۰۰ نانومتر بودند و با تغییر pH از ۳ تا ۷ متوسط اندازه ذرات از ٦٠ به ۲۵ نانومتر کاهش یافت. همچنین با توجه به نتایج حاصل از این بررسی در pHهای اولیه برابر با ۹ و بالاتر پودر حاصل آمورف بوده و با کلسیناسیون در دمای ۷۰۰ درجه سانتیگراد تبدیل به فاز تیتانات سدیم می شود.

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