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Novel Solvothermal Route for the Synthesis of Pure Ultrafine Anatase Nanoparticles

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Abstract

Titanium oxide nanoparticles were synthesized via a solvothermal treatment of titanium isopropoxide in the presence of L-lysine (lysine). The prepared nanostructures characterized by atomic force microscopy (AFM), X-ray diffraction (XRD), thermogravimetric analysis (TGA), diffraction scanning calorimetry (DSC), scanning electronic microscopy (SEM), transmission electron microscopy (TEM) and photoluminescence (PL) spectroscopy. Results exhibited that peptization in the absence of the additive led to the non-uniform (from nano to micro size) anatase particles, while well-dispersed anatase nanoparticles were obtained in the small range from titania-lysine precursor. Well-organizing the growth of anatase particles during the calcinations can be attributed to initial amorphous phase of the as-synthesized lysine sample.
Keywords: *Solvothermal, Nanoparticles, L-lysine, Thermal analysis, Sol-gel, Anatase.*

Introduction

Titanium oxide (TiO_2) nanostructures [1] due to their unique optical [2], dielectric [3] and catalytic characterers [4], attracted attentions toward industrial applications such as pigments [5], cosmetics [6], catalyst supports [7], solar cells [8] and sensors [9]. Shape, size and monodispersity of the particles affect the mentioned above properties. Therefore, many synthetic approaches have been developed over the last decade. These methods can be classified as sol–gel [10], solvothermal [11], hydrothermal [12], chemical vapor deposition (CVD) [13] and RF thermal plasma [14]. From the experimental viewpoint, different titanium precursor such as titaniumalkoxides [15], $TiCl_4$ [16] and a variety of additives [17] have been used. The degree of aggregation to form

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different sizes, stabilization of the dispersed state, morphology and phase composition of TiO_2 nanoparticles depended upon many factors. Varying the temperature, solvent, reaction time and pH of the medium lead to the formation of different phase compositions of rutile, anatase and brookite with different size and shape.

Therefore, the size controlling with narrow distribution can be obtained by the optimization of the reaction conditions. Polyethylene glycol, vinyl-type polymers cellulose polymers, poly (methylacrylate-acrylic acid) copolymer and poly (acrylic acid) (PAA) are organic additives which have important role in stability and size of the particles [1]. Although octane-L-lysine-water system can be used in the synthesis of the porous titanium oxide without any further calcination [18], this report introduces novel route with lysine lonely as an effective additive to promote the synthesis of well-dispersed ultrafine TiO_2 nanoparticles through a solvothermal condition. Synthesis of anatase TiO_2 nanostructures is important. Purity, uniformity and the smaller size of the particles are the final interest in the synthesis. Our new formulation (obtained after many experiments) led to the pure, small and uniform anatase nanoparticles and is comparable with other methods or formulations.

Experimental

Lysine, Ti $(OiPr)_4$ and ethanol were pro analysis grade and purchased from the Merck Chemical Company. The physic-chemical characteristic were established by XRD (Brucker D8 Advance), TGA (Netzsch TG 209 F1), DSC (Netzsch DSC 204 F1 Phoenix), SEM (Leo 1455 VP), TEM (Philips CM 120 120kV), PL (JASCO FP-6500) and AFM (DME 95-50E). To find the optimum condition, the following reactions carried out (Table 1).

Table 1. Reaction condition for the synthesis of anatase phase.

Run	Reaction condition	mol of lysine : mol of Ti source	Phase (XRD)	Calcination Temperature (°C)
1	Reflux 70 °C	1 : 5.8	anatase	550
2	Autoclave 150 °C	0 : 5.8	anatase	550
3	Autoclave 150 °C	0.4 : 5.8	anatase	550
4	Autoclave 150 °C	1 : 6.8	anatase	550
5	Autoclave 150 °C	1 : 5.8	anatase	550
6	Autoclave 150 °C	1 : 5.8	amorphous	350
7	Autoclave 150 °C	1 : 5.8	anatase	650
8	Autoclave 150 °C	1 : 5.8	anatase & rutile	800

From the quality of the XRD pattern, Run 5 was selected as the best condition.

For achieving the optimum results in the synthesis of TiO_2 nanoparticles, different factors such as the ratio of titanium source, additive, amount of the solvent and the reaction conditions were surveyed. Finally, in the best conditions a mixture of lysine, Ti(OiPr)4, ethanol and water with the molar composition of 1:5.8:233.5:302.2 stirred for an hour. Then it was aged in a stainless steel PTFE-lined autoclave at 150 ^{o}C for 24 h. Then the solid product was filtered, washed with ethanol and dried at room temperature. Finally the white powder was calcined at 550 ^{o}C for 1 h with a heating rate of 1^{o}C/min to obtain the anatase phase.

Results and discussion

Before analyzing the samples, it is worth to explain that how the best optimum of the reaction conditions were investigated. As was shown in Table 1, lysine to Ti source was 1:5.8 as the best ratio. Table 2 shows the thermal treating assays for the selection of the best calcinations temperature to produce anatase phase for the mentioned ratio of synthesis. By considering the relative quality of XRD patterns and also the particle size (calculated from strongest reflection), 550 ^{o}C in run 5 was selected as the calcinations temperature. This point has the advantage of using lower temperature leading to smaller particles compare to the run 3, 4 and 6.

Table 2. Calcination temperatures effect on the phase of titanium oxide gels.

Run	Calcination Temperature (^{o}C)	Phase (XRD)	Size (from XRD) (nm)
1	as-made	amorphous	_
2	350	amorphous	_
3	425	anatase	11
4	500	anatase	13.6
5	550	anatase	18
6	650	anatase	27
7	800	anatase & rutile	37
8	900	rutile	41

To obtain the best aging temperature reaction, 70 and 150 ^{o}C was selected. XRD showed that at 150 ^{o}C more intense patterns are present at this temperature.

Figure 1 represents TG and DSC analysis of the as-made samples. TG curve of lysine assisted sample indicates a continuous weight loss up to 530 °C with the total weight loss of 34.6%. The TGA spectrum showed three steps weight loss. The first one is 9.6 % which is below 160 °C. Two other peaks with 10.7 and 14.3% weight loss are attributed mainly to the decomposition of organics and emphasize the presence of lysine inside the gels despite washing with alcohols. DSC measurements clearly demonstrate four peaks. The first endothermic one in the region of the first TGA weight loss is related to the physically adsorbed water. The exothermic peaks at about 230 and 460 °C assigned to lysine combustion [19, 20]. We can propose that the last peak at 430 °C corresponds to phase transfer to anatase because of negligible weight change.

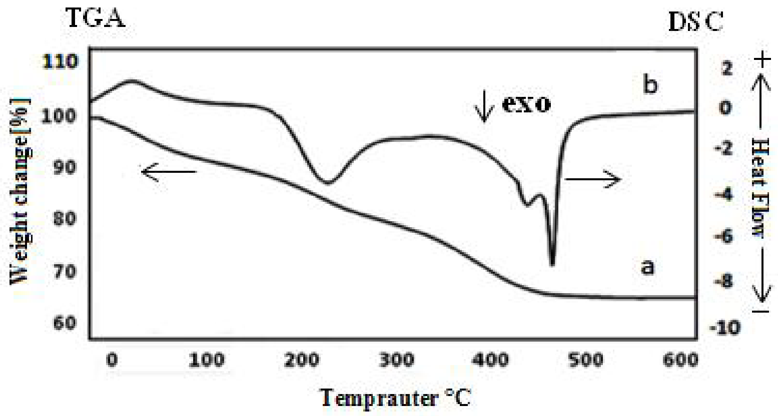

Figure 1. TGA and DSC spectrum of as prepared TiO_2 gel assisted by lysine.

The X-ray diffraction of TiO_2 samples prepared in the presence and absence of lysine is depicted in Figure 2. Brookite, anatase and rutile are three phases of titanium oxide [21]. XRD pattern of as prepared TiO_2-lysine gel and its calcinations at 350 ^oC imply amorphous phase (Figures 2a and 2b) while as synthesized TiO_2 gel prepared without using lysine additive indicates anatase phase (Figure 2c).

It can prove that the lysine is present inside the gel and prevent the aggregation of TiO_2 before calcinations in contrast to the pure gel. Calcinations of the both as-synthesized titanium dioxides at 550 ^oC show the pure anatase phase after peptization with no characteristic peaks of impurities with JPDS card No. of 21-1272 and no rutile phase was observed indicating the presence of only one crystalline phase. However, TiO_2-lysine sample has slightly more sharper pattern compare to the pure TiO_2 gel calcined at 550 ^oC. The intensity of the anatase peaks of TiO_2-lysine species enhanced by increasing the calcinations temperature up to 650 ^oC (Figure 2f). Finally, partial phase transformation to rutile was observed at 800 oC for TiO_2-lysine sample (Figure 2g).

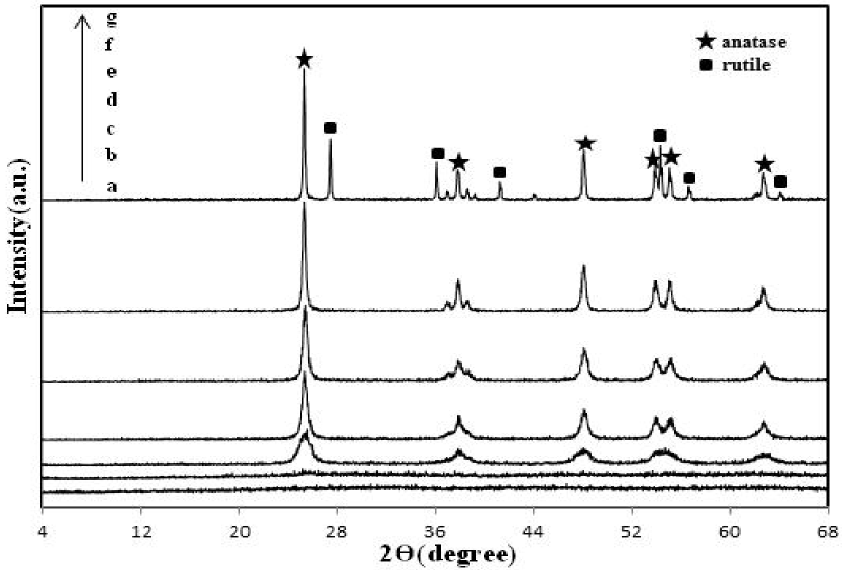

Figure 2. X-ray diffraction of: a) as-prepared TiO_2-lysine gel, b) TiO_2-lysine gel calcined at 350ºC, c) as-prepared TiO_2 gel, d) TiO_2 gel calcined at 550ºC, e) TiO_2-lysine gel calcined at 550 ºC, f) TiO_2-lysine gel calcined at 650 ºC, g) TiO_2-lysine gel calcined at 800 ºC.

Figure 3 provides schematic morphology evolution of anatase nanoparticles and shows the effect of lysine on dispersity of the product. To show the role of the additive, the synthesis carried out in its best conditions in the presence and the absence of the additive. Interestingly, by using lysine as a promoter, uniform anatase nanoparticls were formed with the size less than 30 nm. In contrast, by omitting the lysine additive from the reaction media, a non-uniform and almost micro size particles appears in the product. This observation reveals that lysine plays an important role in size and shape forming of the product by preventing the agglomeration of the nanoparticles. To propose a mechanism, initial pH of the lysisne solution changes from its isoelectric point (9.8) to 7.0 after the addition of the alkoxide solution. The change of the pH, converts $^+H_3N\ (CH_2)_4CHNH_2COO$- to $^+H_3N\ (CH_2)_4CHNH_3^+COO^-$. So, the carboxylate function can interact with the primary TiOx $(OH)_y$ gel and finally disperse the particles and form an amorphous phase. These reasons can be easily proved by comparing the XRD of the as-prepared TiO_2 without lysine and TiO_2-lysine gel (Figures 2a and 2c). Figure 2c shows crystalline phase because there is no lysine to prevent the aggregation of TiOx $(OH)_y$. In other hand, calcination of the crystalline primary gel leads to the un-uniform pure anatase while the calcinations of the amorphous primary TiO_2-lysine gel leads to ultrafine uniform anatase nanoparticles.

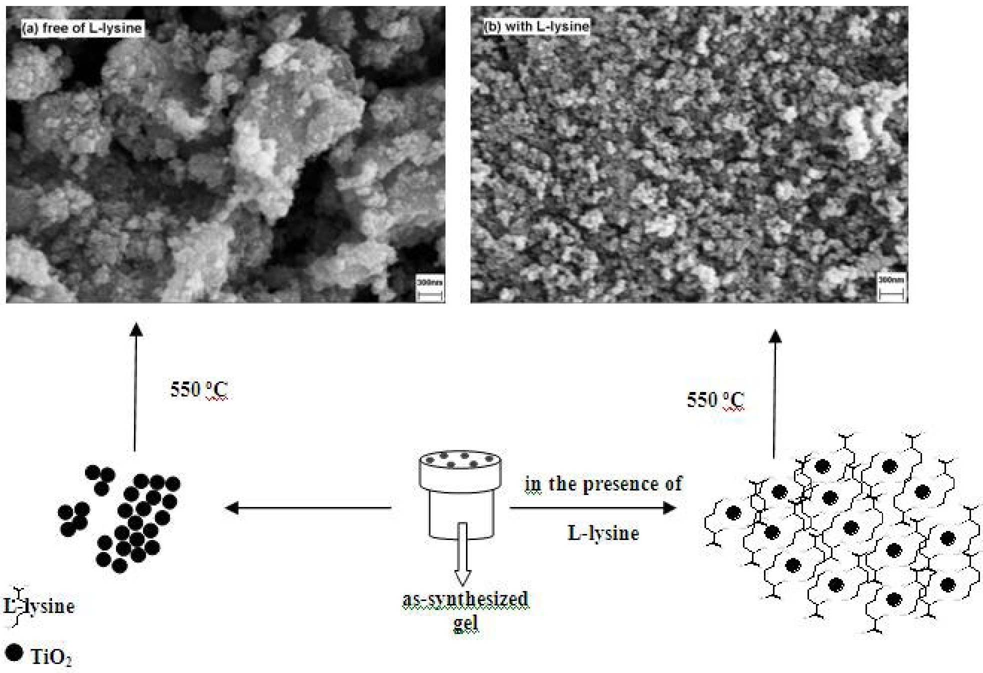

Figure 3. Schematic representation for the preparation of anatase.

Particle-size determinations carried out utilizing (101) reflection as the strongest line of anatase phase and the Scherrer equation:

$$L = \frac{K\lambda}{\beta \cos\theta}$$

Where θ is the Bragg's angle of the intense peak, λ is the full width at half-maximum (FWHM) measured in radians, λ is the x-ray wavelength, K is the shape factor which has a typical value of 0.9 and L is the average particle size in the direction of the d spacing. The average crystallite size of TiO_2 nanoparticles at 550 °C was estimated18 nm. As can be seen, anatase nanoparticles are in small ranges and are comparable with those obtained by other methods [22, 23]. The feature of the anatase nanoparticle synthesized assisted by lysine was observed by TEM micrograph study (Fig. 4). As it can be seen clearly from TEM, the particle sizes are uniform and in small ranges. Also the average size of the particles is comparable from the results obtained from FWHM [24].

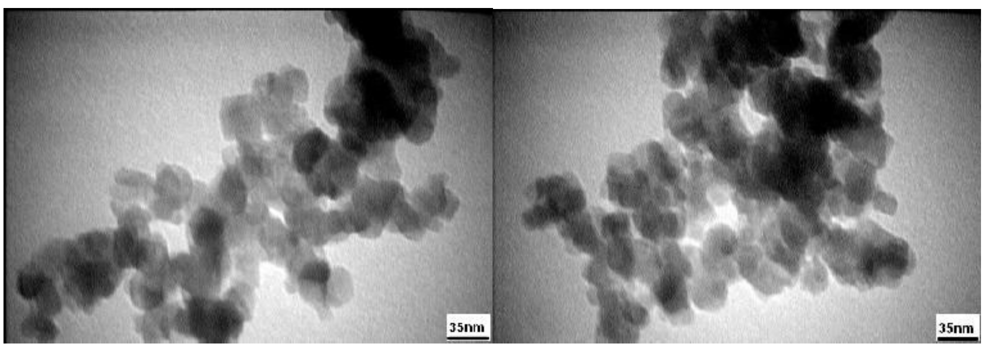

Figure 4. TEM photograph of TiO_2-L-lysine gel calcined at 550 °C.

Photoluminescence of the TiO_2-lysine gel calcined at 550 °C showed a good potential for commercial power generation because an excitation appeared near 600 nm in visible region (Figure 5). The peak near 600 nm was not a noise and did not result from interference phenomena because the excitation wavelength was 397.0 nm. Such a peak was appeared by a Fe-doped TiO_2 sample [25] while in our solvothermal method it was appeared without doping any elements [26]. The AFM picture represents well-dispersed particles with a few tens of nm in size.

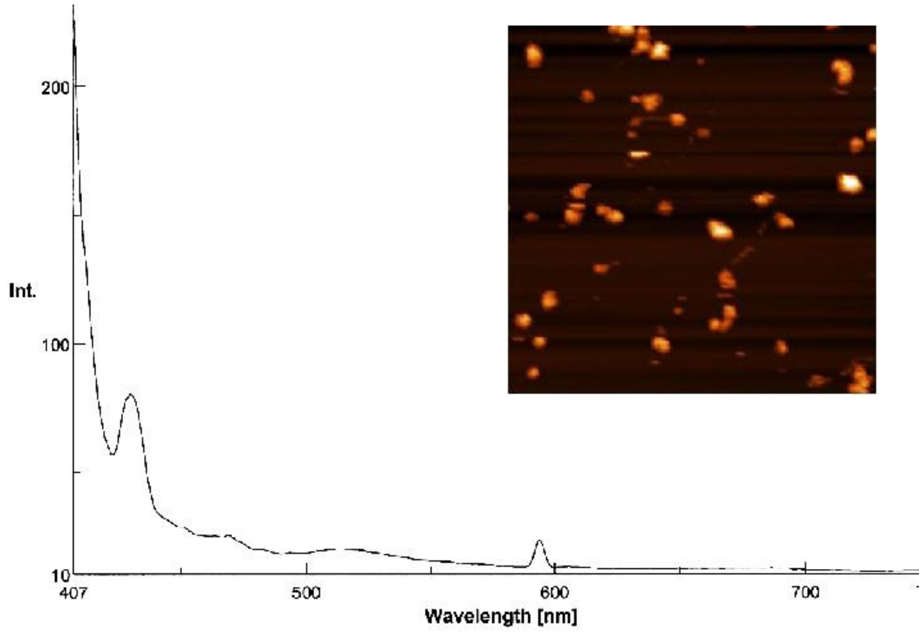

Figure 5. PL and AFM of TiO_2-lysine gel calcined at 550 °C.

Conclusions

By using the lysine as an additive, the tendency toward monodisperse titanium oxide nanoparticles significantly increases. XRD pattern of TiO_2 nano particles match the anatase phase with no rutile characteristic peaks of impurities. TEM image demonstrated small and well-dispersed size of the anatase phase synthesized in the presence of the lysine.

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