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Effect of pH on the surface morphology and structural properties of TiO_2 nanocrystals prepared by simple sol-gel method

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Abstract

Titanium dioxide nanocrystals were synthesized by sol-gel method at room temperature. Titanium isoprophoxide and absolute ethanol were used as precursors to prepare the sol. The pH of the solution was adjusted by adding nitric acid and sodium hydroxide solution. The prepared TiO_2 nanocrystals were annealed at 325°C, 425°C and 525°C respectively. The effect of pH on the surface morphology and structural properties of TiO_2 nanocrystals were studied.

Keywords: Citric acid; HPLC, partial recovery; optimization; physical and nutritional parameters

1. Introduction

Nowadays several techniques are used for waste water treatment among them photo catalysis has become very popular. Compared with all other wide band gap semiconducting materials TiO_2 nanocrystals alone have gained attention in various applications like photovoltaic, electro-optical, micro mechanical, photo catalytic and sensor devices. Among these, the most important application is dechloridization of organic pollutants present in water. TiO_2 nanocrystals can also be used for decomposition and mineralization of some persistent organic pollutants such as phenols, chlorophenols, pesticides, herbicides, benzenes, humic acids and others (Lin et al., 2009; Senthilnathan et al., 2009; Perchet et al., 2009; Vilar et al., 2012; You et al., 2012), as well as for water and air purification (Antoniadou et al., 2009; Han et al., 2009; Zhang et al., 2010; Liang et al., 2012). Due to their high chemical stability, non-toxicity and good heat resistance TiO_2 nanocrystals are being used in electronic, anti bacterial (Oh et al., 2009; Fu et al., 2005) and self cleaning applications (Kamegawa et al., 2012; Lai et al., 2012; Wang et al., 2006). TiO_2 has three crystalline structures: anatase, rutile and brookite (Park et al., 2009; Zheng et al., 2000). The anatase TiO_2 nanocrystal shows greater photo catalytic activity than rutile and brookite structures (Diebold 2002). Many researchers have agreed that anatase TiO_2 nanocrystal possesses the best photocatalytic properties for pollutant removal with high activity, high stability, low price and nontoxicity (Tian et al., 2012). The TiO_2 nanocrystal was prepared by various techniques such as chemical bath deposition method (Maleki et al., 2007), hydrothermal method (Ovenstone et al., 1999) and sol- gel method (Vilar et al., 2012; Liang et al., 2012; Pucher et al., 2007). Out of these methods, the sol–gel method is a simple, inexpensive, non-vacuum and low temperature technique for synthesizing nanocrystals. This process offers many advantages like, excellent control of the stoichiometry of precursor solutions, ease of compositional modifications, customizable micro structure, ease of introducing various functional groups and requires relatively low annealing temperatures. In recent years the ways to improve the photocatalytic properties of TiO_2 have been widely implemented. The surface morphology of TiO_2 and pH condition which is used during the preparation plays a major role in photocatlysis. Senthil et al., 2010, have prepared and reported anatase TiO_2 nanocrystalline films using sol–gel spin coating method for different concentrations of ethanol and acetic acid. Zhang et al., 1998, have prepared pure and doped nanocrystalline TiO_2 for photocatalysts using versatile wet-chemical process and they reported the role of particle size for the photocatalytic application. Pettibone et al., 2008; synthesized TiO_2 nanoparticles with different size using various pH values and reported the importance of these factors for adsorption of organic acids. To the best of our

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knowledge, however, there is no systematic study focusing on the effect of annealing and pH values on the surface morphology and structural properties of sol–gel derived TiO_2 nanocrystals. So the aim of the present work is to investigate the effect of different pH values and annealing temperatures on the surface morphology and structural properties of TiO_2 nanocrystals. Since the surface morphology of the nanocrystals plays an important role in the adsorption of dye molecules for photocatalytic applications.

2. Experimental

Titanium isopropoxide (Alfa Aaser 99.9%) is used as titanium precursor; the matrix sol was prepared by mixing titanium isopropoxide (2 ml) with 10 ml absolute ethanol (Hayman 99.9%) and dilute nitric acid at room temperature. Nitric acid and sodium hydroxide are used to change the pH of the solution. The molar ratio of the titanium isopropoxide and ethanol is 1:5 respectively. The solution was stirred for 3 hours at room temperature. After 3 hours, the suspension was centrifuged and washed with water and ethanol several times to remove the impurities present in the sample. After centrifugation, the samples were dried at room temperature. The TiO_2 nanocrystals were synthesized using different pH conditions (2.6, 7 and 10.6). The prepared samples were annealed at 325°C, 425°C and 525°C for 1 hr using a heating rate of 2°C/min.

The structural properties of the prepared TiO_2 nanocrystals have been studied by using x-ray diffractometer (PANalytical) with a copper Kα (λ =1.5406Å) radiation. The surface morphology and features of the nanocrystal are examined by scanning electron microscopy (Hitachi S-500). Optical characterization of the prepared nanocrystals has been carried out by using UV–VIS–NIR spectrophotometer (JascoV-570).

3. Results and discussion

X-ray diffraction pattern has been applied to investigate the phase of the prepared TiO_2 nanocrystals. The X-ray diffraction patterns of TiO_2 nanocrystals prepared using different pH values and annealed at different temperatures are shown in Fig. 1.

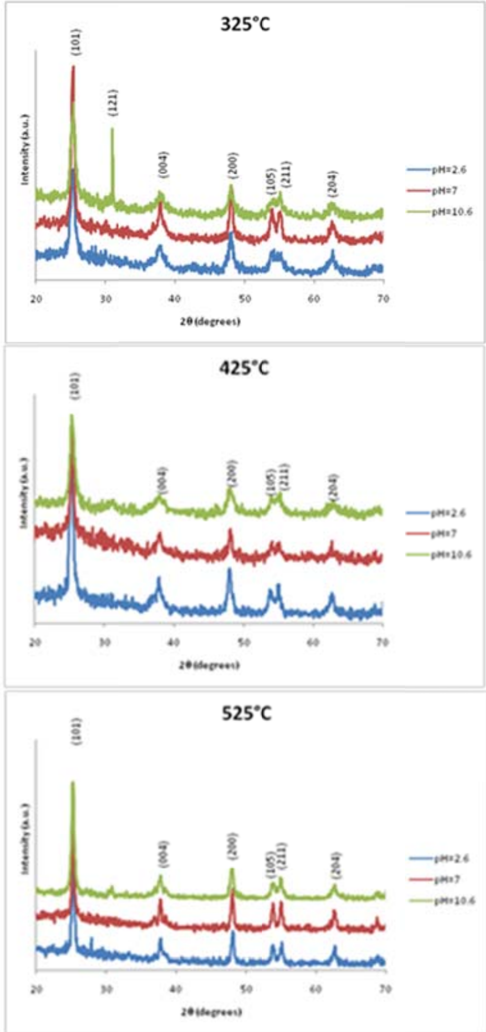

Fig. 1. X-ray diffraction patterns of TiO_2 nanocrystals prepared using different pH values and annealed at different temperatures

Typical peaks in XRD pattern are observed at 2θ values of 25.28°, 30.86°, 37.90°, 47.97°, 53.89°, 55.29°, and 62.61° which are assigned to (101), (121), (004), (200), (105), (211) and (204) planes of anatase TiO_2, and are in agreement with JCPDS data (84-1285, 1286). It should be noted that for all three pH values the formation of nanocrystals appeared when the annealing temperature was increased above 325°C. The intensity of the diffraction peaks has been observed to increase with increase of the heat treatment temperature. This is due to the improvement in the crystalline nature of the prepared TiO_2 nanocrystals with increase of annealing temperature. TiO_2 nanocrystals synthesized at pH =10.6 and annealed at 325°C shows an additional peak at 2θ=30.9°. This peak belongs to brookite phase and corresponds to (121) reflection. It is in good agreement with JCPDS data (00-003-0380). This may be due to addition of NaOH in the precursor sol to increase the pH (Kobayashi et al., 2011). The brookite phase (121) has disappeared at higher annealing temperatures. From Fig. 1, it is clearly seen that the intensity of (101) reflection increases with increase of pH value of the precursor solution. This shows the grain growth. The particle size is calculated using Scherer's formula (Que et al., 2006) and the derived values are tabulated in Table 1. It is clear from the data in the tabular column that the particle size increases in proportion with annealing temperature, and pH condition of the precursor solution. This is due to the agglomeration of TiO_2 particles at higher pH values. At higher temperatures the availability of OH^- ions are more.

Table1. Particle size of the TiO_2 nanocrystals prepared using different pH values and annealed at different temperatures.

pH	Particle size (nm)		
	325°C	425°C	525°C
2.6	6.80	6.98	18.18
7.0	8.53	10.17	20.70
10.6	11.60	14.30	22.00

When the TiO_2 nanocrystals react with the OH^-, dissolution occurs in the TiO_2 nanocrystals and this affects the grain growth (Alias et al., 2010).

Figure 2 (a-i) shows the SEM image of TiO_2 nanocrystals prepared using different pH values and annealed at different temperatures.

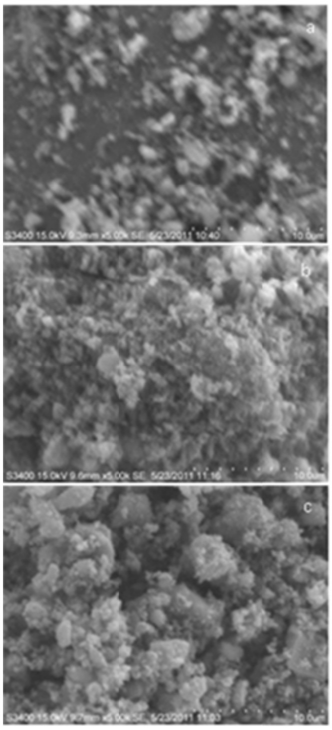

Fig. 2. (a, b, c) SEM images of TiO_2 nanocrystals prepared using pH=2.6 and annealed at 325°C, 425°C and 525°C respectively

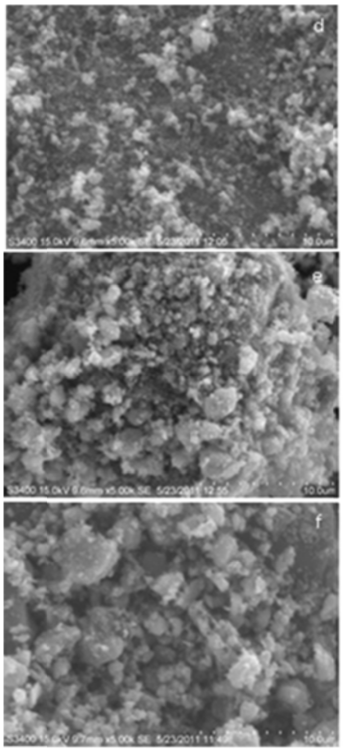

Fig. 2. (d, e, f) SEM images of TiO_2 nanocrystals prepared using pH=7 and annealed at 325°C,425°C and 525°C respectively

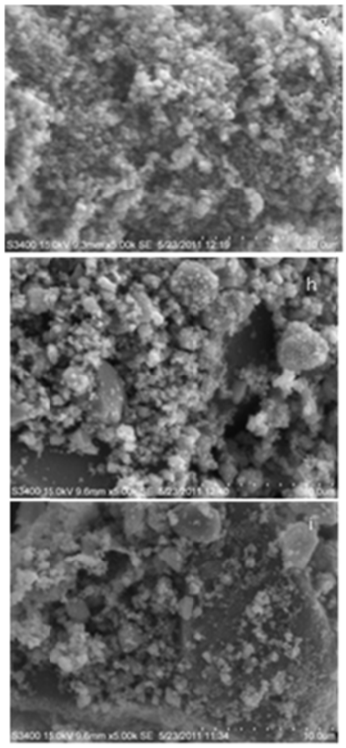

Fig. 2. (g, h, i) SEM images of TiO_2 nanocrystals prepared using pH=10.6 and annealed at 325°C, 425°C and 525°C respectively

The SEM images clearly shows that the grain size of the TiO_2 nanocrystals increases with increase of pH values and is in good agreement with the XRD results. The crystallization growth also increases with increase of annealing temperature. The particle size seems to be greater than XRD data. This is because some aggregation has occurred during synthesis process. In a particular temperature (example 425°C), the increase of pH value has been found to affect the surface morphology of the nanocrystals and it also increases the agglomeration of particles. For all the pH values nanocrystals annealed at higher temperature are found to exhibit a more clear surface morphology. The nanocrystals annealed at 325°C contain grains of smaller size. When the annealing temperature is raised to 425°C and 525°C, the grain size is found to increase.

Figure 3(a-c) shows the absorption spectra of the TiO_2 nanocrystals prepared using different pH values and annealed at different temperatures. For a particular annealing temperature (consider 525°C), the absorption edge of the UV–Vis absorption spectra is found to be red shifted (towards longer wavelength) with increase of pH values. This is due to the fact that increase of pH values varies with the grain size and the amount of light absorbed on the surface.

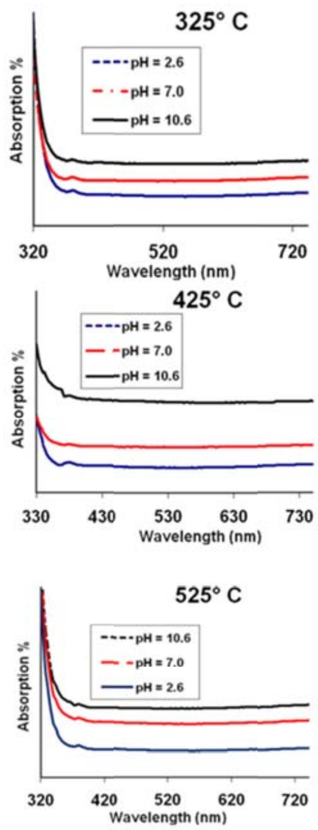

Fig. 3. Absorption spectra of TiO_2 nanocrystals prepared using different pH values and annealed at different temperatures

The changes in their surface morphology and particle size are confirmed by XRD and SEM analysis. It is also observed that for a particular pH value (consider 2.6), the absorption of the nanocrystals decreases with increase of annealing temperature. This can be ascribed to the formation of larger particles, which causes the scattering of light. By the extrapolation of the absorption edge onto the x-axis the band gap of the samples has been calculated and is tabulated in Table 2.

Table 2. Band gap value of the TiO_2 nanocrystals prepared using different pH values and annealed at different temperatures

pH	Band gap for different temperatures (eV)		
	325°C	425°C	525°C
2.6	3.722	3.702	3.698
7.0	3.703	3.702	3.680
10.6	3.670	3.645	3.630

The estimated values are in agreement with the reported values (Senthil et al., 2013). It is clearly observed that the band gap value decreased with the increase of annealing temperature. This is due to the formation of larger particles at higher temperature, these larger particles scatters more light.

4. Conclusion

TiO_2 nanocrystals were synthesized from sol-gel method at three different pH values. The prepared TiO_2 nanocrystals are annealed at three different temperatures. The x-ray diffraction results show that the pH of the precursor solution and annealing temperature affect the particle size of the TiO_2 nanocrystals. There is no appreciable phase change that takes place in the TiO_2 nanocrystals prepared at pH=7 of the precursor solution. TiO_2 nanocrystals prepared at pH= 10.6 and annealed at 525°C show what the minimum band gap value would be, such as 3.630 eV.

References

Alias, S. S., Ismail, A. B., & Mohamad, A. A. (2010). Effect of pH on ZnO nanoparticle properties synthesized by sol–gel centrifugation. *J. Alloy. Compd*., 499, 231–237.

Antoniadou, M., & Lianos, P. (2009). Photoelectrochemical oxidation of organic substances over nanocrystalline titania: Optimization of the photoelectrochemical cell. Catal. Today, 144, 166–171.

Diebold, U. (2002). Structure and properties of TiO_2 surfaces: a brief review. Appl. Phys. A, 76, 1–7.

Fu, G., Vary, P. S., & Lin, C. T. (2005). Anatase TiO_2 Nanocomposites for Antimicrobial Coatings. *J. Phys. Chem. B*, 109, 8889–8898.

Han, F., Kambala, V. S. R., Srinivasan, M., Rajarathnam, D., & Naidu, R. (2009). Tailored titanium dioxide photocatalysts for the degradation of organic dyes in wastewater treatment: A review. *Appl. Catal. A-Gen*, 359, 25–40.

Kamegawa, T., Shimizu, Y., & Yamashita, H. (2012). Superhydrophobic Surfaces with Photocatalytic Self-Cleaning Properties by Nanocomposite Coating of TiO_2 and Polytetrafluoroethylene. *Adv. Mater*, 24, 3697–3700.

Kobayashi, M., Petrykin, V., Tomita, K., & Kakihana. M. (2011). Hydrothermal synthesis of brookite-type titanium dioxide with snow flake-like nanostructures using a water-soluble citratoperoxotitanate complex. *J. Cryst. Growth*, 337, 30–37.

Lai, Y., Tang, Y., Gong, J., Gong, D., Chi, L., & Chen, Z. (2012). Transparent superhydrophobic/superhydrophilic TiO_2-based coatings for self-cleaning and anti-fogging. *Mater. Chem*., 22, 7420–7426.

Liang, W., Li, J., & Jin, Y. (2012). Photo-catalytic degradation of gaseous formaldehyde by TiO_2/UV, Ag/TiO_2/UV and Ce/TiO_2/UV. *Build. Environ*, 51, 345–350.

Lin, H., Ji, X., Chen, Q., Zhou, Y., Banks, C. E., & Wu, K. (2009). Mesoporous-TiO_2 nanoparticles based carbon paste electrodes exhibit enhanced electrochemical sensitivity for phenols. *Electrochem. Commun*, 11, 1990–1995.

Maleki, M., Ghamsari, M. S., & Ghasemzadeh, R., Sh. M. (2007). A facile route for preparation of CdS nanoparticles. Semiconductor Physics, Quantum Electronics & Optoelectronics, 10(1). 30–32.

Oh, W. C., Jung, A. R., & Ko, W. B. (2009). Characterization and relative photonic efficiencies of a new nanocarbon/TiO_2 composite photocatalyst designed for organic dye decomposition and bactericidal activity. *Mater. Sci. Eng. C-Mater*, 29, 1338–1347.

Ovenstone, J., & Yanagisawa, K. (1999). Effect of Hydrothermal Treatment of Amorphous Titania on the Phase Change from Anatase to Rutile during Calcination. *Chem. Mater*, 11, 2770–2774.

Park, J. Y., Lee, C., Jung, K. W., & Jung, D. (2009). Structure Related Photocatalytic *Properties of TiO_2. Bull. Korean Chem. Soc*, 30, 402–404.

Perchet, G., Merlina, G., Revel, J. C., Hafidi, M., Richard, C., & Pinelli, E. (2009). Evaluation of a TiO_2 photocatalysis treatment on nitrophenols and nitramines contaminated plant wastewaters by solid-phase extraction coupled with ESI HPLC–MS. *J. Hazard. Mater*, 166, 284–290.

Pettibone, J. M., Cwiertny, D. M., Scherer, M., Grassian, V. H. (2008). Adsorption of Organic Acids on TiO2 Nanoparticles: Effects of pH, Nanoparticle Size, and Nanoparticle Aggregation. *Langmuir*, 24, 6659–6667.

Pucher, P., Benmami, M., Azouani, R., Krammer, G., Chhor, K., Bocquet, J. F., & Kanaev, A. V. (2007). Nano-TiO_2 sols immobilized on porous silica as new efficient photocatalyst. *Appl. Catal. A-Gen*, 332, 297–303.

Que, W., Uddin, A., & Hu, X. (2006). Thin film TiO_2 electrodes derived by sol–gel process for photovoltaic applications. *J. Power Sources*, 159, 353–356.

Senthil, T. S., & Kang, M. (2013). Transparent Thin Film Dye Sensitized Solar Cells Prepared by Sol-Gel Method. Bull. *Korean Chem. Soc*, 34, 1188–1194.

Senthil, T. S., Muthukumarasamy, N., Agilan, S., Thambidurai, M., & Balasundaraprabhu, R. (2010). Preparation and characterization of nanocrystalline TiO_2 thin films. *Mater. Sci. Eng. B-Adv*. 174, 102–104.

Senthilnathan, J., & Philip, L. (2009). Removal of mixed pesticides from drinking water system by photodegradation using suspended and immobilized TiO_2. *J. Environ. Sci. Health. B*, 44, 262–270.

Tian, G., Fu, H., Jing, L., & Tian, C. (2009). Synthesis and photocatalytic activity of stable nanocrystalline TiO_2 with high crystallinity and large surface area. *J. Hazard. Mater*, 161, 1122–1130.

Vilar, V. J. P., Moreira, F. C., Ferreira, A. C. C., Sousa, M. A., Goncalves, C., Alpendurada, M. F., & Boaventura, R. A. R. (2012). Biodegradability enhancement of a pesticide -containing bio-treated wastewater using a solar photo-Fenton treatment step followed by a biological oxidation process. *Water Res*., 46, 4599–4613.

Wang, D. Y., Lin, H. C., & Yen, C. C. (2006). Influence of metal plasma ion implantation on photo-sensitivity of anatase TiO_2 thin films. *Thin Solid Films*, 515, 1047–1052.

You, Y., Wan, L., Zhang, S., & Xu, D. (2010). Effect of different doping methods on microstructure and photo-catalytic activity of Ag_2O–TiO_2 nanofibers. *Mater. Res. Bull*, 45, 1850–1854.

Zhang, Y., Wan, J., & Ke, Y. (2010). A novel approach of preparing TiO_2 films at low temperature and its application in photocatalytic degradation of methyl orange. *J. Hazard. Mater*, 177, 750–754.

Zhang, Z., Wang, C. C., Zakaria, R., & Ying, J. Y. (1998). Role of Particle Size in Nanocrystalline TiO_2-Based Photocatalysts. *J. Phys. Chem. B*, 102, 10871–10878.

Zheng, Y., Shi, E., Cui, S., Li, W., & Hu, X., (2000). Hydrothermal Preparation of Nanosized Brookite Powders. *J. Am. Ceram. Soc*, 83, 2634–2439.