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Bhim Charan Meikap *Editors*

Materials, Energy and Environment Engineering

Select Proceedings of ICACE 2015

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ISBN 978-981-10-2674-4 ISBN 978-981-10-2675-1 (eBook)
DOI 10.1007/978-981-10-2675-1

Library of Congress Control Number: 2016955788

Printed on acid-free paper

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The registered company is Springer Nature Singapore Pte Ltd.
The registered company address is: 152 Beach Road, #22-06/08 Gateway East, Singapore 189721, Singapore

Impact of Hydrochloric Acid on Phase Formation of Titanium Dioxide Nanoparticles

Swati Aggarwal, R.R. Ezhil Venuswaran and P. Balasubramanian

1 Introduction

Titanium dioxide (TiO_2) is a transition metal oxide ceramic material that acquires a prominent position in the wide range of applications (Yin et al. 2013). The field of nanotechnology had pioneered remarkable developments in the physical, mechanical, optical, biological and electronic properties of nanostructured TiO_2 in recent years. TiO_2 is predominantly preferred by most of the researchers in general due to its high refractive index, the capability of higher energy conversion, ease of handling and low toxic nature (Shi et al. 2013). Since titanium metal is the ninth prevalent element in the earth's crust, the preferable focus had been shifted towards the preparation of titanium dioxide nanoparticles in large quantities. Titanium dioxide exists in three different polymorphs—namely anatase, rutile, and brookite. A stable crystalline structure had been observed only with rutile TiO_2. However, the anatase and brookite phases exhibit a metastable crystalline structure (Hanaor and Sorrell 2011). Anatase TiO_2 can be formed under room temperature itself whereas rutile demands for high-temperature treatments for a complete phase formation.

The brookite form of TiO_2 is an extremely complex polymorph that can be synthesized only under specific temperature and optimum pressure conditions. Various investigations had revealed that the properties and efficiency of TiO_2 on a particular application purely depends on the morphology, crystalline phase, grain size and surface area. Thus, the controlled rate of handling the processing parameters

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R. Mohan B. et al. (eds.), *Materials, Energy and Environment Engineering*,
DOI 10.1007/978-981-10-2675-1_18

of a synthesis route is highly important (Li et al. 2008). Various methods can synthesize titanium dioxide nanoparticles—Sol-gel method, chemical vapor deposition method, hydrolysis method, sonochemical method and microwave assisted techniques (Zhou et al. 2012; Su et al. 2006). Each synthesis route underwent different modification in the properties of nanostructured TiO_2 particles. Furthermore, these synthesis methods made a continuous breakthrough in the recent years which gave various forms of TiO_2 as nanotubes, nanowires, nanosheets, etc. (Wu et al. 2002). Among these methods, hydrolysis method was prominently focused by the researchers due to its single step crystallization of TiO_2 nanoparticles.

The hydrolysis method is a simple method that can be carried out easily at room temperature. Under an acid medium, $TiCl_4$ - liquid precursor is hydrolyzed and crystallized for the formation of TiO_2 nanoparticles. The acid used in the synthesis performs a dual role—acts as a catalyst for hydrolysis reaction and solubilizes the liquid precursor. Homogeneity, short range of particle size and purity are the major advantages of this hydrolysis method. The concentration of the acid, volume of $TiCl_4$ and volume of the entire solvent plays a crucial role in influencing the morphology, crystalline phases and surface area of the nanoparticles (Chen and Mao 2007). In this paper, different volumes of solvent had been considered for investigating the significance of the processing parameters on the synthesis of Titanium dioxide nanoparticles.

2 Materials and Methods

Titanium dioxide nanoparticles had been synthesized by simple hydrolysis method in the presence of hydrochloric acid (HCl), 35 % purity ACS Reagent (Zheng et al. 2008). Titanium tetrachloride, 9 %, trace metal basis, Sigma-Aldrich, had been used as a liquid precursor. 1 ml of Titanium tetrachloride had been added to 50, 100, 150 and 200 ml of 1 M HCl and stirred for 12 h at room temperature. The liquid precursor had been hydrolyzed and the prepared solutions were aged by keeping it in a dry air oven for 12–18 h at 100 °C. Then the obtained product had been centrifuged at 7000 rpm and washed with deionized water followed by series of increasing concentrations of ethanol. The obtained phases on titanium dioxide nanoparticles on different volumes of HCl had been investigated by using Philips X-Ray Diffractometer with Ni filter Cu-Kα (λ = 1.5418 Å) with a scanning range of 5°–90°. Based on the following equation, the relative phase percentages of TiO_2 could be expressed as a function of XRD peak areas of different crystallographic forms.

$$\mathbf{W_A = K_A I_A (K_A I_A + I_R)} \tag{1}$$

$$\mathbf{W_R = I_R / (K_A I_A + I_R)} \tag{2}$$

Where, W_R and W_A are the weight fraction of rutile and anatase respectively; I_R and I_A are obtained from characteristic peaks areas of rutile and anatase respectively with $K_A = 0.886$ as constant (Zhang and Banfield 2000). Thermogravimetric analysis of titanium nanoparticles had been carried out by using NetzschSTA/409C, by firing till 650 °C under Argon atmosphere. The particle size and the particle morphology had been determined by using Nova Nanosem 450 FESEM.

3 Results and Discussion

1 ml of $TiCl_4$ had been hydrolyzed against 50, 100, 150 and 200 ml of 1 M HCl solution. After washing with series of concentrations of ethanol and water, the yield of Titanium dioxide nanoparticles had been weighed and reported in Table 1. It had been observed that the yield of Titanium dioxide nanoparticles had been decreasing

Table 1 Yield of titanium dioxide nanoparticles by hydrolysis method

Sample	Volume of HCl solution (mL)	TiO_2 powder yields before washing (g)	TiO_2 powder yields after washing (g)
S1	50	0.775	0.734
S2	100	0.720	0.604
S3	150	0.540	0.490
S4	200	0.310	0.231

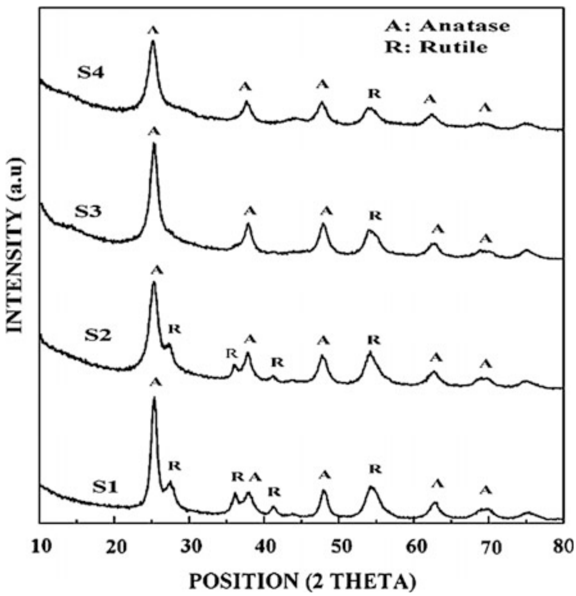

Fig. 1 Phase analysis of titanium dioxide nanoparticles

Table 2 Phase evaluation results of synthesized titanium dioxide nanoparticles

Sample	Volume of HCl solution (ml)	Crystallite size (nm)	JCPDS rutile file	JCPDS anatase file	Anatase (%)	Rutile (%)
S1	50	10.37	01–1292	01–0562	59.1	40.9
S2	100	5.09	01–1292	01–0562	68.6	31.3
S3	150	10.91	02–0494	01–0562	71.9	28.1
S4	200	5.70	02–0494	02–0387	71.9	28.1

gradually with higher volumes of 1 M HCl. Since the nucleation rate will be vigorous, and particle interaction is high in lower volumes of the aqueous solutions, the yield of titanium nanoparticles had been obtained with a higher amount. The crystalline phases obtained from the above mentioned samples S1, S2, S3 and S4 had been determined by XRD technique. The obtained phases on the synthesized Titanium dioxide nanoparticles had been shown in the Fig. 1.

The formation of brookite phase demands for optimum conditions, it had not been observed in these samples. The synthesized titanium dioxide nanoparticles attain neither a pure anatase phase nor a pure rutile phase. The obtained phases are a combination of rutile and anatase phases. When the volume of 1 M HCl increases from 50 ml to 200 ml, the crystallinity of rutile polymorph is reduced. Since the synthesized titanium nanoparticles featured with binary phase of anatase and rutile, the weight fractions of the individual had been evaluated by using Eq. 1 and Eq. 2, which had been reported in the Table 2.

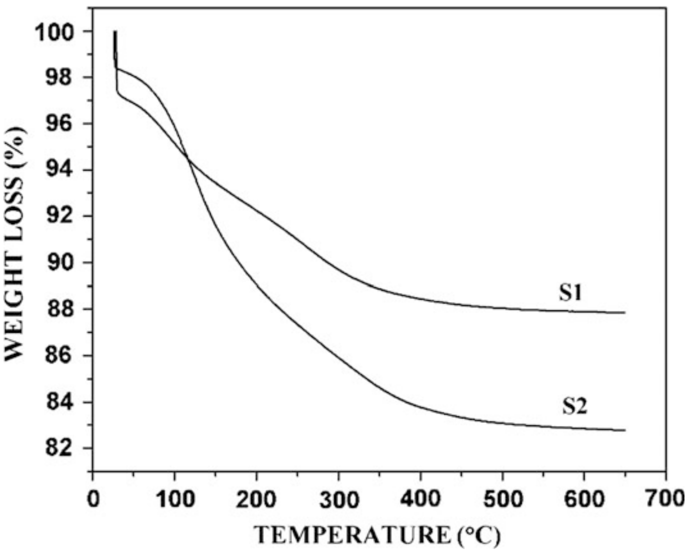

Fig. 2 TGA analysis of titanium dioxide nanoparticles

The thermogravimetric analysis of the samples S1 and S2 had been illustrated in the Fig. 2. For the sample S1, weight loss of around 12 % was noticed when the temperature reaches to 400 °C. Similarly for S2, weight loss of around 18 % had been observed when the temperature reaches to 500 °C. These weight loss might be due to the evaporation of water, HCl and decomposition of unreacted Ti–OH molecules. On further heat treatment, the unreacted Ti–OH molecules decompose to form TiO_2. Thus, if the samples had been heat treated, the weight fractions of anatase and rutile might change due to phase transformation and simultaneous crystallization.

The microstructures of titanium dioxide nanoparticles had been illustrated in the Fig. 3. All the samples acquired particle size in the range of 20–90 nm. It clearly

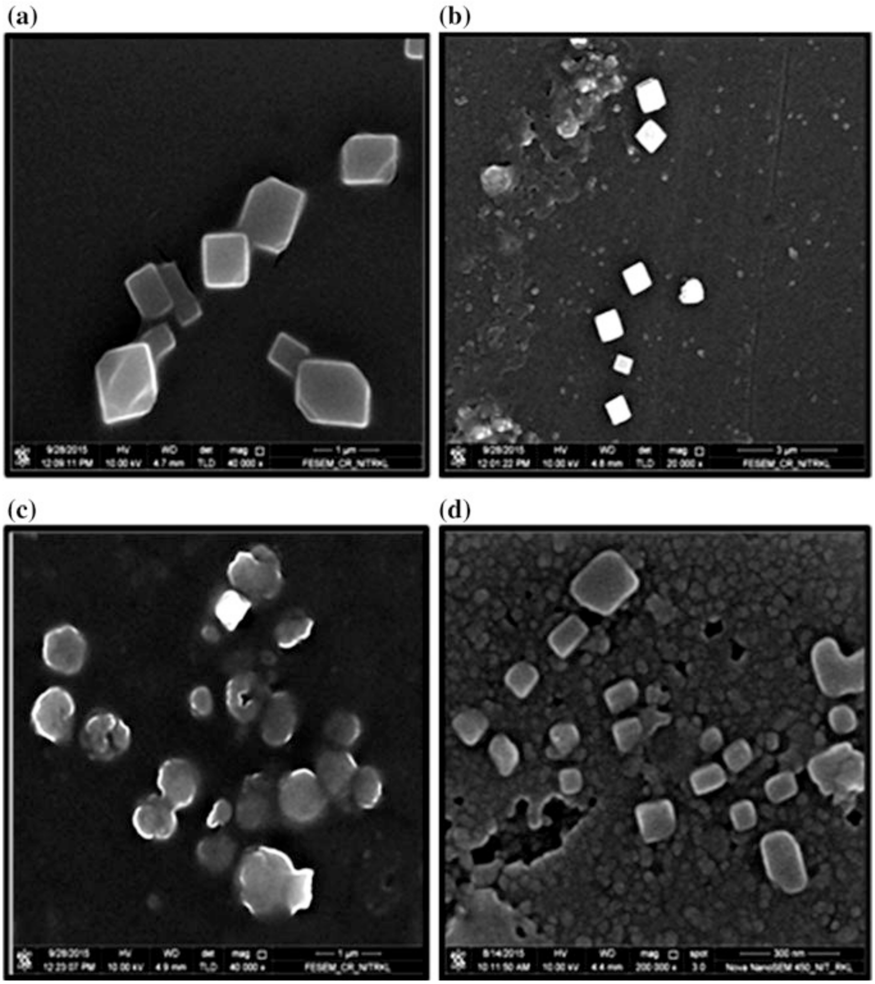

Fig. 3 FESEM images of titanium dioxide nanoparticles **a** S1 **b** S2 **c** S3 **d** S4

shows that the samples S1, S2 and S4 attained a cubical morphology. But the morphology of S3 was partly spherical and partly cubical. This clearly shows an unstable structure that had been attained due to the phase transformation from rutile to anatase. Similar kind of profile had been clearly illustrated in the results of phase analysis.

4 Conclusions

Titanium dioxide nanoparticles had been successfully prepared by hydrolysis method. Instead of pure anatase or pure rutile TiO_2 nanoparticles, anatase-rutile composite nanoparticles had been synthesized. On increasing the volume of HCl, the probability of rutile phase formation is reduced. No drastic change in morphology had been observed due to the changes in the volume of HCl. Hence by varying the processing parameters varieties of titanium dioxides nano-composites could be developed. The knowledge on the impact of processing parameters during synthesis on phase formation of TiO_2 nanoparticles could be implied further on its various environmental applications such as photocatalytic conversion of carbon dioxide to methanol and photodegradation of organic and inorganic compounds.

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