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Synthesis of anatase nanoparticles in a spiral microreactor

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ABSTRACT

Herein, we report on an efficient strategy to synthesize anatase nanoparticles in a spiral microreactor. The synthesized nanopowders were characterized by X-ray diffraction and high resolution transmission electron microscopy. $L_{25}(5^6)$ orthogonal experiments were performed in order to assess the effect of each factor on the particle size of anatase nanopowders. Finally, the residence time R value was 50.734, which was much larger than R values for other factors, highlighting residence time as the key factor determining anatase nanoparticle size.

1. Introduction

Due to its excellent chemical and physical properties, TiO_2 is commonly used in a variety of applications [1], particularly as a nanostructured material, such as in white pigment, industrial wastewater dye removal [2], and hydrogen production through solar energy [3,4]. Furthermore, a variety of organic pollutants can be degraded into CO_2 via photocatalytic reactions using TiO_2 particles with a large specific surface area [2,4]. There are three crystal phases of TiO_2, namely rutile, anatase, and brookite, of which anatase is considered as the most active phase [5]. A number of methods have been developed to prepare anatase TiO_2 nanoparticles, including sol-gel [6], co-precipitation [7], hydrolysis, and microemulsion [8]. All these processes require calcination of the intermediate products for conversion into crystalline materials, which can lead to particle agglomeration, and their mass transfer efficiency is considerably low [9]. Therefore, achieving greater control of particle agglomeration in the synthesis of nanostructured TiO_2 as well as improving the mass transfer efficiency would be highly beneficial [5]. In 2011, Priest et al. [10] proposed microfluidic devices, composed of micro-fabricated components like micromixers, microchannels, microtubes, and microreactors to improve the properties of nanostructured materials [11,12]. These techniques are now commonly used in chemical engineering processes. The significantly higher surface to volume ratio in microreactors leads to an improvement in heat and mass transfer rates in comparison with conventional reactors such as continuous stirred tank, plug flow, or batch reactors [11,12]. The present study describes the efficient synthesis of anatase nanoparticles in a spiral microreactor without the need for further calcination, thus overcoming issues with particle agglomeration and the low efficiency of mass transfer.

2. Experimental

2.1. Materials

$TiCl_4$ and deionized water were used as the starting materials to synthesize anatase nanoparticles. NaOH were used as the agent to adjust the pH of the solution in the microreactor. All the above-mentioned chemical reagents were purchased from Sinopharm Chemical Reagent Co, Ltd., China, and were used as received without any further purification. $TiCl_4$ used in this work was an analytical reagent (99.8 wt%; Cl and Na in $TiCl_4$ 0.05 wt%).

2.2. Synthesis of anatase TiO₂ nanoparticles

Fig. 1 shows the schematic diagram of the synthesis process. A Y-junction spiral microreactor was employed to perform the microfluidic synthesis of anatase nanoparticles. The microreactor was composed of two stainless steel chips, with a microchannel embedded inside each chip. The temperature of the solution was measured and controlled using a thermocouple. An oil bath was used in order to easily control the synthesis temperatures. The rectangular cross section of the microreactor channel had a length to width ratio of 4:3. For a typical synthesis process, prior to the synthesis experiments, the pH of the water was adjusted to 10 using NaOH solution (concentration 0.1 mol L^{-1}) and the channel width was set at 300 μm. $TiCl_4$ and deionized water were then injected into the Y-junction spiral microreactor at injection rates of 0.1 and 0.3 mL min^{-1}, respectively. The temperature was set at 75 °C. The retrieved mixture was then centrifuged at 18,000 rad

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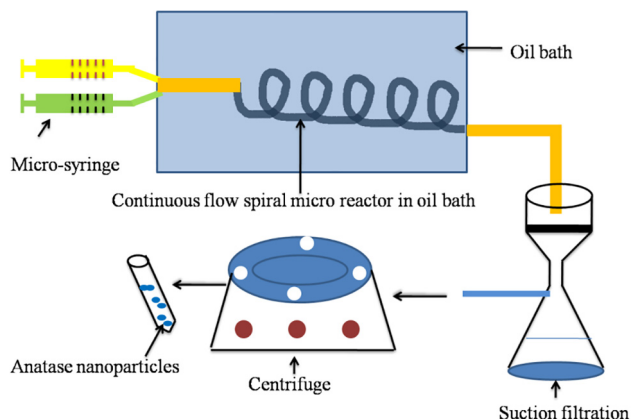*E-mail address:* neusmmzhangwu@163.com (W. Zhang).

Fig. 1. Schematic diagram of the synthesis process.

min^{-1} to separate the nanoparticles from the obtained suspension. The production capacity of the setup was of 0.3 g h^{-1}.

The residence time of the mixture in the channel was calculated by the formula [12]:

$$t = \frac{V_{channel}}{Q_a} \tag{1}$$

where t represents the residence time in the channel (in s), $V_{channel}$ is the volume of the channel (m^3), and Q_a is the aqueous phase volume flow rate (m^3 s^{-1}).

2.3. Sample characterization

High resolution transmission electron microscopy (HRTEM; KEM-ARM200F, JEOL Ltd. Tokyo, Japan), operated at 200 kV, was used to observe the morphology of the as-prepared nanoparticles. Prior to observation, a 2.5 wt% suspension of the prepared samples was dispersed in methanol using 3 min of ultrasound (FS-450, Shenxi Ultrasound Instruments, Shanghai, China). The suspension was deposited on a carbon-coated copper grid (Zhongjing Scientific Instrument, Beijing, China) and dried in an oven at 323 K for 20 min before loading into a single tilt holder.

The nanoparticle sizes were determined by laser particle analyzer (Zetasizer Nano S90, Malvern Instruments Ltd., UK). The particles were dispersed by ultrasonic dispersion in order to avoid particle aggregation prior to determination.

Further, samples were characterized using X-ray diffraction (XRD; MPDDY2094, Netherlands) with copper Kα irradiation (λ = 1.5406 nm), at an operating voltage of 30 kV, and a scanning angle of between 10° and 90°. Phases in the XRD patterns were analyzed by X pert high score plus software. The crystallite sizes of the prepared TiO$_2$ particles were calculated using the formula [13]:

$$D = \frac{K \times \lambda}{\beta \times COS\theta} \tag{2}$$

where K is the Scherrer constant, β is the width of the half height of the diffraction peak, λ is the wavelength of incident light, θ is the Bragg angle, and D is the grain size of TiO$_2$ particles.

2.4. Design of orthogonal experiments

L$_{25}$(5^6) orthogonal experiments were designed to assess the effect of each factor, namely the operating parameters, including pH (factor A), residence time (factor B), channel width (factor C), temperature (factor D), and injection rate of TiCl$_4$ (factor E), on the particle size of anatase nanoparticles.

The variance of orthogonal experiments was calculated by the following formula [14]:

$$S = \frac{(x_1 - \bar{x})^2 + (x_2 - \bar{x})^2 + \cdots + (x_n - \bar{x})^2}{n} \tag{3}$$

where S is the variance, x_n is the particle size, and $\bar{x}$ is the average size of the particles.

3. Results and discussion

3.1. Sample characterization

Fig. 2 shows the XRD patterns of the samples under different experimental conditions. All the obtained samples showed a clear anatase phase. The crystallite sizes of the samples were calculated using the Debye-Scherrer equation (Eq. (1)) to be 12, 26, and 27 nm at 75 °C (sample a), 95 °C (sample b), and 105 °C (sample c), respectively. A diffraction peak at 69° was observed in samples a and b, indicating that this peak is not the diffraction peak for anatase. In addition, the (1 0 1) lattice plane of anatase for sample a, b and c are 523, 598, 635, indicating that sample c had a better crystallinity than a orb. Moreover, the presence of amorphous phases in all samples was also confirmed.

The crystallite size of anatase particles increased with increasing temperature (Fig. 2), attributed to the faster reaction (TiCl$_4$ + 2H$_2$O → TiO$_2$ + 4HCl) rate at higher temperatures and crystallization of small TiO$_2$ crystals into larger ones. It is interesting that no rutile or brookite phases were found in the samples. In the present work, the experimental temperatures were much lower than the heating process often required to obtain crystalline TiO$_2$, which makes the crystallization of TiO$_2$ quite slowly.

To retrieve more information of the as-synthesized samples, we characterized the samples using HRTEM and laser particle analyzer (Fig. 3). Particle clusters of 2–3 nm in size were observed in the sample synthesized at 75 °C (Fig. 3a), while these clusters were not seen at 95 °C and 105 °C (Fig. 3b and c). Wang et al. [15] reported that nanoparticle growth occurs in two stages, namely the nucleation stage, where all nuclei are generated and crystallized into large crystals, and the growth stage, where small particles combine and grow into larger ones. Ge et al. [16] discussed the formation and growth mechanism of anatase via a hydrothermal method, and observed similar phenomena as described herein.
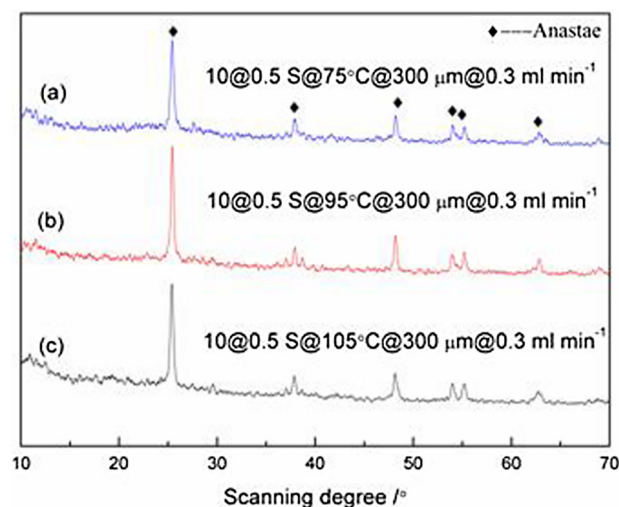

Fig. 2. XRD patterns of the prepared samples under the different experimental conditions (*Note*: pH@residencetime@temperature@channel width@TiCl$_4$ injection rate).