Comparative Study of Synthesis Parameters of Nanoporous Titania Particles to Improve Structural Properties and Photocatalytic Activity

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Abstract

Nanoporous materials have been widely used in many fields. However, their synthesis with uniform particle shapes, pore sizes, pore volumes, and surface areas remains a considerable challenge. Thus, choosing a suitable controllable method for synthesizing nanoporous materials is crucial to obtain appropriate properties. Herein, nanoporous titania particles (NPTPs) were prepared via the hydrothermal. This study investigated how the synthesis parameters such as the type of chelating agent, the hydrolysis method, and the drying technique affected the properties of NPTPs. The synthesis NPTPs were characterized by XRD, FESEM, and BET. The results demonstrated that when acetylacetone (ACAC) (as the chelating agent), the spray-hydrolysis (SH) method, and the freeze-drying (FD) technique were used, NPTPs achieved a more uniform particle shape, a smaller particle size, a larger pore size, a larger pore volume, and a higher surface area. Ultimately, the photocatalytic degradation (PCD) of methylene blue (MB) was examined using improved NPTPs.

1 Introduction

Nanotechnology has received international attention and various governments and agencies have made huge investments in it [1]. Nowadays, nanomaterials (notably metal oxides) which have unique properties are predominantly employed in most sciences and industries [1, 2]. Among metal oxides, titania (titanium dioxide, TiO_2) has received special attention in many applications such as pharmaceutical and food additives [3], medical components [4, 5], air purification [6], water disinfection [7, 8], etc. due to its specific properties [9, 10]. Furthermore, titania is used as photocatalysts for various environmental remediation [8, 11–13].

Generally, due to the development of industry and the expansion of production, a considerable volume of industrial waste is produced annually, which needs additional expenses for pollution treatment. Various industries make use of dyes (methylene blue, congo red, Eriochrome Black T, etc.) in the production process [14]. Among these dyes, methylene blue (MB) is highly carcinogenic and hazardous to human health and the environment [15]. Studies have shown that this cationic dye can be degraded by titania and converted to harmless substances [14].

Titania exists in three crystalline forms, namely anatase (with the highest activity), rutile, and brookite [16–21]. It is a non-toxic [22], non-hygroscopic, non-volatile, insoluble, inflammable [23], and biocompatible material [24] which has been extensively investigated owing to its high chemical [25, 26] and thermal stability [24, 27]. Moreover, the functional properties of titania are highly dependent on its morphology [28, 29]. Hence, employing an appropriate method is crucial to synthesize each of the abovementioned crystalline forms selectively [30, 31].

Nanoporous materials are typically obtained via different methods including sol-gel, hydrothermal, solvothermal, physical vapor deposition (PVD), chemical vapor deposition (CVD), electrochemical, and sonochemical methods [27, 31–33]. Among these techniques, the hydrothermal technique has more

advantages [34]. The precipitation prepared by this method is not agglomerated. In addition, it is fine-grained and highly pure and has a controlled particle morphology and a narrow size distribution. Besides, the hydrothermal technique does not require expensive and advanced equipment [32]. Furthermore, it is a method that is widely used for preparing nanostructures in the industry because it has an environmentally friendly and low-cost process [34–36]. The hydrothermal method is performed in a sealed steel autoclave with or without a Teflon liner via a reaction in aqueous solutions at a high temperature ($T \leq 200^{\circ}\text{C}$) and a high vapor pressure ($P < 100 \text{ atm}$). When a Teflon liner is used, pure and homogeneous titania particles are obtained [16, 36]. The hydrothermal temperature and the quantity of the solution introduced into the autoclave exert a powerful influence on the internal pressure. These parameters play a vital role in determining the morphology and crystalline structure of nanostructures [37, 38]. It is worth mentioning that the hydrothermal process involves the three main steps of hydrolysis, polymerization, and precipitation [39, 40]. Water may be fed to the reaction medium in different forms such as pouring all at once (immediately), pouring dropwise, and spraying which can affect the quality of the ultimate product differently. In the presence of water, a nucleophilic substitution reaction can occur between the metal center of the precursor and water called the hydrolysis process. The metal hydroxide groups link and form a network called polymerization. Then, the metal oxide is precipitated under a high temperature and pressure [41]. Moreover, the hydrolysis speed is a crucial factor in modifying the particle size, the phase morphology, and the precipitation properties. To decrease the hydrolysis rate of a metal compound, various compounds such as beta-diketones, beta-keto esters, diesters, carboxylic acids, amines, aminopolycarboxylic acids, etc. could be employed as chelating or capping agents [16, 42, 43].

The drying process is an indispensable part of the production of nanomaterials in removing the solvent and obtaining the desired qualities [44]. Oven-drying (OD), spray-drying (SD), freeze-drying (FD), and microwave-drying (MD) are some of the more common drying methods [45, 46]. Among these, OD and FD are drying processes which are used in various industries to produce nanoparticles [47–49]. An FD cycle includes two main steps of freezing and drying [48]. For the most part, the sample is either directly put in a freezer or immersed in liquid nitrogen (-196°C) before being placed into a freeze-dryer [44, 48, 49]. It is worth mentioning that a rapid freezing rate is desirable to prevent the agglomeration and recombination of the nanoparticles [44]. Therefore, rapid freezing with liquid nitrogen forms smaller crystals which have larger specific surface areas (SSA). Consequently, using liquid nitrogen is an appropriate method to produce nanoparticles [48]. After the ice crystals of pure water are formed, the sample is kept at a sub-zero temperature (less than -50°C) for several hours in a freeze-dryer. Several vacuum pumps are joined to the condenser chamber so that pressures ranging from 4 to 40 Pa can be obtained during the process. The primary drying step includes the sublimation of ice crystals from the frozen product and the second step is to remove the water which has not sublimated [48, 49]. After the removal of ice crystals, the voids left behind lead to the formation of nanoporous materials [49].

As was mentioned above, given the vital importance of nanoparticles for advanced technologies, the synthesis of nanoparticles with a uniform shape, a small particle size, and a high surface area has received a lot of attention because this characteristic provides some advantages. Furthermore, using nanoporous titania particles (NPTs) in advanced technologies is of tremendous importance owing to

their unique properties. Therefore, the first objective of this paper was to synthesize NPTPs with a uniform shape, a small particle size, and a high surface area, leading to desirable functional properties. The second goal of the current paper was to study the effects of different chelating agents on the properties of the ultimate product. The third aim was to evaluate the impacts of various hydrolysis methods to produce NPTPs through the hydrothermal process. The fourth purpose was to examine the effects of different drying techniques on the morphology of the synthesized NPTPs. The fifth aim was to study the photocatalytic property of improved NPTPs on the MB as a cationic organic pollutant. The sixth goal was to investigate different effective parameters on the photocatalytic degradation (PCD) of MB. Thus, for the first time, to improve the functional properties of pure titania, all the parameters affecting the production of titania particles were investigated simultaneously in both stages of hydrothermal synthesis and the performance of the photocatalytic activity.

2 Experimental Procedures

2.1 Materials

For the synthesis of NPTPs, the following materials were purchased in pure grade from Merck: Tetrabutyl orthotitanate (TBOT, $\text{Ti}(\text{OC}_4\text{H}_9)_4$, $M = 340.32 \text{ g.mol}^{-1}$), acetylacetone (ACAC, $\text{CH}_3\text{COCH}_2\text{COCH}_3$, $M = 100.11 \text{ g.mol}^{-1}$), ethyl acetate (ETAC, $\text{CH}_3\text{COOC}_2\text{H}_5$, $M = 88.11 \text{ g.mol}^{-1}$), ethyl acetoacetate (ETAA, $\text{CH}_3\text{COCH}_2\text{COOC}_2\text{H}_5$, $M = 130.14 \text{ g.mol}^{-1}$), glacial acetic acid (GLAA, CH_3COOH , $M = 60.05 \text{ g.mol}^{-1}$), methylene blue (MB, $\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$, $M = 319.85 \text{ g.mol}^{-1}$), hydrochloric acid (HCl, $M = 36.458 \text{ g.mol}^{-1}$), sodium hydroxide (NaOH, $M = 39.997 \text{ g.mol}^{-1}$), and 2-propanol (2-PrOH, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$, $M = 60.10 \text{ g.mol}^{-1}$). In addition, deionized water (DIWA, H_2O , $M = 18.02 \text{ g.mol}^{-1}$) was used in all the experiments.

2.2 The sample characterizations

To investigate and compare the structure and morphology of NPTPs produced through the hydrothermal technique in different conditions, some techniques such as X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), and Brunauer-Emmett-Teller (BET) were used.

The XRD was employed to identify the crystallinity and phase structure of the products. To collect the diffraction data, a Philips PW-3170 diffractometer was employed which had a Cu K α ($\lambda = 0.15418 \text{ nm}$) radiation source over the 2θ angle from 5° to 80° , a scan step size of 0.04, and a step time of 0.5 s. The accelerating voltage and the applied current were 35 kV and 30 mA, respectively. The results of the XRD pattern were extracted and analyzed by the X'pert High Score Plus software (version: 2.2b). The crystalline phases of the samples were determined by comparing the XRD patterns with the reference data from the files of the International Center for Diffraction Data (ICDD). The average crystal sizes were determined by the Scherrer formula (Eq. (1)):

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

where L is the crystallite size (nm), k is the Scherrer constant (0.89 in this study), λ is the X-ray radiation wavelength (0.15418 nm for Cu K α), β is the full-width at half-maximum (FWHM) for the diffraction peak under consideration (radian), and θ is the diffraction angle or Bragg angle (degree). The morphologies and the shapes of the synthesized NPTs were observed using FESEM by a MIRA3 TESCAN instrument with an accelerating voltage of 15 kV. The nitrogen adsorption-desorption isotherms and BET specific surface area of the synthesized NPTs were obtained by a Micromeritics ASAP 2020 instrument (version: 3.03 E). All the samples were degassed using flowing dry N₂ before analysis at 150°C/6 h. Then, the test was performed at -196°C. Then, the nitrogen adsorption-desorption experiment was conducted at -196°C. The UV-Vis spectrophotometer (Ocean Optics HR4000 High-Resolution Spectrometer) was used to record the optical absorption spectra of MB.

2.3 The synthesis method

In this study, NPTs were prepared using the hydrothermal technique via the hydrolysis of the alkoxide precursor. To investigate the effect of the synthesis parameters on the properties of the product, several experiments were performed.

(1) To study the effects of the chelating agents, different chelating agents such as ACAC, ETAC, ETAA, and GLAA were separately mixed with the same mole of TBOT as a precursor of titanium. Furthermore, another experiment was performed with TBOT and without a chelating agent.

(2) To investigate the effects of the hydrolysis methods, three different hydrolysis methods (namely immediate-hydrolysis (IH), droplet-hydrolysis (DH), and spray-hydrolysis (SH)) were used to add water to the autoclave (the reaction container) (Fig. 1).

To ensure a complete reaction, an excess amount of DIWA was added to the autoclave. At the end of the different hydrolysis processes, the autoclave door was sealed and the content was then heated at 130 °C for 12 h and stirred in an oil bath. Afterward, the content was spontaneously cooled down to ambient temperature. The obtained precipitation was then centrifuged at 15000 rpm and washed thoroughly several times with a mixture of 2-PrOH and DIWA (1:1).

(3) To examine the effects of the drying methods, the washed samples were either dried in an oven at 100°C for 12 h or were immediately frozen in liquid nitrogen (-196°C) and then freeze-dried via a vacuum freeze-dryer at -55 °C for 24 h. Finally, to produce NPTs, the dried precipitates were ground using an agate mortar and subsequently calcined at 450°C for 2 h (ramping rate of 5°C.min⁻¹). Figure 2 shows the schematic representation of the synthesis process of NPTs.

2.4 The photocatalytic degradation method

The PCD of MB was examined at ambient temperature under UV-light irradiation to evaluate the photocatalytic property of improved NPTPs. For this purpose, improved NPTPs were dispersed in an aqueous MB solution, stirred in the dark medium for 10 min at room temperature and allowed to obtain the equilibrium adsorption of MB molecules on the surface of the photocatalyst. Then, the mixture was irradiated under a UV-A lamp (364 nm/9 W). The sampling process was performed to evaluate degradation efficiency during the experiment (2 ml at 0.5 h intervals). Afterward, improved NPTPs were separated with a centrifuge. The concentration of the residual MB solution was monitored with a UV-Vis spectrophotometer ($\lambda_{\text{max}} = 638 \text{ nm}$). It should be noted that the effects of the UV-light irradiation time, MB concentration, catalyst amount, and pH value were investigated as crucial parameters affecting the degradation efficiency.

3 Results And Discussion

3.1 The characterization results

3.1.1 X-ray diffraction (XRD)

The XRD patterns of all the synthesized NPTPs are shown in Fig. 3. The main peaks at 2θ were 25.21, 37.91, 47.81, 53.81, 55.1, and 63.32 which indicate the planes indices of (101), (004), (200), (105), (211), and (204), respectively, conform to the crystalline structure of the anatase phase for all the samples. The peaks are rather sharp which shows that all the synthesized titania particles have relatively high crystallinity. This can be ascribed to the anatase phase without any secondary phases such as rutile or brookite [9, 27].

The phase identification as well as the approximate crystallite size of all the synthesized NPTPs from the XRD analysis are obtained in Table 1. The crystallinity of all the samples was quantitatively estimated via the relative intensity of the (101) diffraction peak [9, 27]. It can be observed that the crystallite sizes of the synthesized NPTPs obtained from different methods were not the same. The results revealed that the FWHM of the (101) main peak significantly increased and the average crystallite sizes decreased in the SH and FD methods. The sequence of the crystallite sizes for the studied parameters were as follows: (1) For the chelating agent, it was ACAC < ETAA < ETAC < GLAA < without a chelating agent; (2) For the hydrolysis method, it was SH < DH < IH; (3) For the drying method, it was FD < OD. Therefore, the smallest crystallite size was obtained for the synthesized sample when ACAC, the SH method, and the FD technique were used.

Table 1
Summary of the XRD analysis of the synthesized NPTs

Sample	Chelating Agent	Hydrolysis Method ^a	Drying Method ^b	Phase	FWHM ^c of (101)	Crystallite Size ^d (nm)
Sample 1	No Chelating Agent	IH	OD	Anatase	0.4800	16.9937
Sample 2	No Chelating Agent	DH	OD	Anatase	0.5567	14.6467
Sample 3	No Chelating Agent	SH	OD	Anatase	0.5989	13.6156
Sample 4	No Chelating Agent	SH	FD	Anatase	0.7202	11.3225
Sample 5	GLAA	IH	OD	Anatase	0.5280	15.4457
Sample 6	GLAA	DH	OD	Anatase	0.5760	14.1542
Sample 7	GLAA	SH	OD	Anatase	0.6337	12.5564
Sample 8	GLAA	SH	FD	Anatase	0.8160	9.9942
Sample 9	ETAC	IH	OD	Anatase	0.5280	15.4393
Sample 10	ETAC	DH	OD	Anatase	0.5833	13.6407
Sample 11	ETAC	SH	OD	Anatase	0.7200	11.3303
Sample 12	ETAC	SH	FD	Anatase	0.8640	9.4439
Sample 13	ETAA	IH	OD	Anatase	0.5760	14.1542
Sample 14	ETAA	DH	OD	Anatase	0.6720	12.1384
Sample 15	ETAA	SH	OD	Anatase	0.8640	9.4429
Sample 16	ETAA	SH	FD	Anatase	0.9120	8.9450
Sample 17	ACAC	IH	OD	Anatase	0.6011	13.2358
Sample 18	ACAC	DH	OD	Anatase	0.7201	11.3257

Sample	Chelating Agent	Hydrolysis Method ^a	Drying Method ^b	Phase	FWHM ^c of (101)	Crystallite Size ^d (nm)
Sample 19	ACAC	SH	OD	Anatase	0.9120	8.9450
Sample 20	ACAC	SH	FD	Anatase	1.1520	7.0800

^a IH: Immediate-Hydrolysis, DH: Droplet-Hydrolysis, and SH: Spray-Hydrolysis

^b OD: Oven-Drying and FD: Freeze-Drying

^c Full-width at the half-maximum

^d Approximation by using Scherrer formula

3.1.2 Field emission scanning electron microscopy (FESEM)

As shown in Fig. 4, when the chelating agent was used to synthesize NPTs, the particle size was smaller and more uniform compared to when no chelating agent was used. Moreover, when no chelating agent was used, agglomeration was observed in the particles. Besides, when the SH method was used, the particle shape was close to spherical and not agglomerated. When the IH method was employed, the particle shape became coarse and non-uniform and aggregation was observed. It should be noted that a higher aggregation of particles was evident when the OD process was employed compared with the FD method. Therefore, according to the results obtained from the FESEM images, it can be seen that using chelating agents, the type of the hydrolysis method, and the type of the drying process affected the morphologies of the obtained NPTs. The most uniform spherical morphology and the smallest particle size with no aggregation were observed for the sample synthesized using ACAC, the SH method, and the FD technique.

^a IH/OD: Immediate-Hydrolysis/Oven-Drying ^b DH/OD: Droplet-Hydrolysis/Oven-Drying

^c SH/OD: Spray-Hydrolysis/Oven-Drying ^d SH/FD: Spray-Hydrolysis/Freeze-Drying

^e GLAA: Glacial acetic acid ^f ETAC: Ethyl acetate

^g ETAA: Ethyl acetoacetate ^h ACAC: Acetylacetone

Figure 4 The FESEM images of NPTs (500 nm magnification)

3.1.3 Nitrogen adsorption-desorption isotherms analysis

The SSA, TPV, and APS were obtained by the NAD technique. The SSA and TPV were calculated using the adsorption of the BET plot. The APS was defined from the desorption isotherm by using the Barrett-Joyner-Halenda (BJH) model [21, 35, 50, 51]. The effects of the parameters on the SSA, TPV, and APS for all the synthesized NPTPs are summarized in Table 2. The results demonstrated that the synthesis of NPTPs using a chelating agent, the SH method, and the FD technique led to the production of mesoporous particles with a high SSA. The SSA of all the synthesized NPTPs was higher in the FD method than in the OD method. As can be obviously seen, the SSA significantly decreased for the synthesized NPTPs when no chelating agent was used. This decrease in SSA can be attributed to the increased particle size which is in turn due to aggregation. As expected, enhancing the particle size caused an increase in the APS and TPV of all the samples [21, 35].

Table 2
Structural parameters of all the synthesized NPTPs

Sample	Chelating Agent	Hydrolysis Method ^a	Drying Method ^b	SSA ^c (m ² /g)	TPV ^d (cm ³ /g)	APS ^e (nm)
Sample 1	No Chelating Agent	IH	OD	135.1926	0.359962	8.6072
Sample 2	No Chelating Agent	DH	OD	138.3129	0.308562	7.5423
Sample 3	No Chelating Agent	SH	OD	144.9078	0.300548	6.6072
Sample 4	No Chelating Agent	SH	FD	166.5842	0.298738	5.6812
Sample 5	GLAA	IH	OD	146.9325	0.435002	6.7261
Sample 6	GLAA	DH	OD	147.4228	0.334426	6.6968
Sample 7	GLAA	SH	OD	163.6455	0.311015	7.9833
Sample 8	GLAA	SH	FD	182.1658	0.302568	5.5225
Sample 9	ETAC	IH	OD	162.4532	0.426367	7.9452
Sample 10	ETAC	DH	OD	165.8115	0.414456	7.8944
Sample 11	ETAC	SH	OD	175.8719	0.409862	7.7015
Sample 12	ETAC	SH	FD	194.4256	0.300275	5.5721
Sample 13	ETAA	IH	OD	161.3813	0.421653	7.8961
Sample 14	ETAA	DH	OD	166.6659	0.370432	5.6893
Sample 15	ETAA	SH	OD	181.5537	0.334238	5.5795
Sample 16	ETAA	SH	FD	203.9013	0.301398	5.5563
Sample 17	ACAC	IH	OD	166.1592	0.410340	7.8525

Sample	Chelating Agent	Hydrolysis Method ^a	Drying Method ^b	SSA ^c (m ² /g)	TPV ^d (cm ³ /g)	APS ^e (nm)
Sample 18	ACAC	DH	OD	169.2604	0.403925	7.6121
Sample 19	ACAC	SH	OD	183.8827	0.368310	5.5662
Sample 20	ACAC	SH	FD	207.3367	0.320167	5.5472

^a IH: Immediate-Hydrolysis, DH: Droplet-Hydrolysis, and SH: Spray-Hydrolysis

^b OD: Oven-Drying and FD: Freeze-Drying

^c The BET surface area was determined by multipoint BET method using the adsorption data in $P/P_0 = 0.05-0.3$.

^d The TPV and APS were determined by nitrogen adsorption volume at $P/P_0 = 0.95-0.99$.

^e Average crystalline size of all the samples was determined by XRD using Scherrer formula.

3.2 The effective parameters on the characterization of the synthesized NPTs

3.2.1 The effect of chelating agent

A chelating agent is used to reduce the reactivity of the precursor and obtain a stable solution [52]. In other words, a chelating agent is added to slow down the rate of the hydrolysis process [53]. Diketones are well known among different complexing agents as good chelating agents. ACAC is a representative diketone usually employed to produce transition metal complexes. In general, 76% of ACAC is in the enol form and the rest is in the keto form [53]. Meanwhile, it should be noted that the most stable ring structures in chelation are five- or six-membered rings. If the result of complexation is a conjugated double bond system, the stability of the complex will be further enhanced through the resonance effect. Therefore, a six-member ring complex between Ti^{2+} and the carbonyls of ACAC is formed which is stabilized by resonance structures. The complexation is facilitated by the tautomerization of the compound from the keto to the enol form [54]. Since it has two $C=O$ bonds, ACAC is employed as a chelating agent in many studies because it has a stronger chelating power than the other chelating agents. Because TBOT is very sensitive to water, it quickly forms a three-dimensional network structure. Therefore, ACAC blocks the hydrolysis of TBOT. This can impede the progress of the polycondensation reaction. It is expected that ACAC ligands decrease the reactivity of the residual butoxy groups (BuO^-) as a result of steric hindrance [55]. During the process of adding water, the water molecules replace ACAC groups via SN_2 nucleophilic substitution reaction because ACAC is an excellent leaving group [56]. Therefore, fine-grained NPTs with a narrow size distribution are formed and ACAC is released. In

contrast, 8% of ETAA is in the enol form and the remnant is in the keto form. The enol contents of ETAC and GLAA are even smaller than that of ETAA because their keto isomers are stabilized by releasing electrons from OCH_3 and OH to C=O , respectively [57]. Hence, the titania particles synthesized using ACAC had smaller sizes. This is because complexation is stronger than the other chelating agents and slows down the hydrolysis rate. The enolization equilibria constant and the tautomeric forms of the chelating agents are presented in Table 3 [57].

Table 3

The enolization equilibria and tautomeric form of the chelating agents

Chelating Agent	Type	Enolization Equilibria Constant	Tautomeric Form
ACAC	Beta-diketone	$2 \cdot 10^{-1}$	

3.2.2 The effect of hydrolysis method

The SH technique is a technology that utilizes a spray instrument to generate millions of tiny droplets which are efficiently introduced to the reaction medium. The purpose of this procedure is to reduce water concentration in the hydrolysis step so that the hydrolysis process occurs more slowly. Furthermore, the hydrolysis reaction occurs only at the surface of the sprayed droplet. In this way, the hydrolysis rate is significantly slowed down and minimizes the particle size [58]. Because a slow hydrolysis does not provide an opportunity for particle growth, it produces fine-grained nanoparticles. Besides, the mole ratio of DIWA-to-TBOT is a significant parameter that affects both the phase type of the products and the average particle sizes during the hydrolysis reaction [59]. There are two methods to synthesize NPTPs from TBOT: synthesis with a low DIWA-to-TBOT mole ratio and synthesis with a high DIWA-to-TBOT mole ratio. At a low mole ratio, spherical and relatively monodisperse aggregates of nanocrystallites are obtained. In contrast, at a high mole ratio, the hydrolysis of TBOT is very quick and nucleation and growth occur in seconds. The formed titania particles are unstable and a white suspension is instantly produced because large aggregates are precipitated. In aggregation, the particles grow while the smaller particles are lost (known as Ostwald ripening) [60]. In other words, when DIWA has a high concentration, macromolecular networks form rapidly through hydrolysis and condensation. In contrast, when DIWA has a low concentration, networks form slowly [59]. Therefore, the synthesized titania particles are not aggregated via spray hydrolysis because water concentration is low in each injection.

3.2.3 The effect of drying process

NPTPs can be obtained from different drying methods. OD and FD are two most commonly used drying techniques to form nanoparticle powders. Unfortunately, the high temperature involved in OD leads to severe aggregation of the nanoparticles. FD (known as the ice-templating) is widely used to produce various porous materials and nanostructures. In this method, since ice crystals leave the frozen sample and form ice-templated structures, particles with small sizes are formed [49]. Therefore, compared with the traditional OD method, the powder prepared by FD has a smaller size, a more regular shape, a more

uniform distribution, a higher surface area, and a less agglomerated particle [61]. Figure 5 shows the schematic representation of the FD process.

3.3 The mechanism of the hydrothermal synthesis process

A typical hydrothermal method for preparing titania is to use a solution consisting of a titanium compound as the precursor, a chelating agent as the capping agent, and water as the hydrolysis agent [43]. Titanium compounds can be titanium alkoxides (including isopropoxide and butoxide) or non-alkoxides (including inorganic salts such as chloride, acetate, nitrate) [43, 59]. It is well known that titanium alkoxides (Ti(OR)_4) are more appropriate precursors than the other compounds [62]. Since titanium alkoxides have a Lewis center (Ti IV), which makes them very susceptible to the nucleophilic attack of water, hydrolysis occurs to form a product [10, 40]. In other words, the significant difference in the electronegativity values of Ti and O causes Ti to have a more partial positive charge. This makes Ti sensitive to the nucleophilic attack of water forming a saturated octahedral coordination [40]. Moreover, the alkoxide type is also very important since larger alkyl groups drastically reduce the hydrolysis rate. Indeed, the steric strain of a larger alkyl group dramatically impedes the substitution of a hydroxo ligand (OH^-) with an alkoxy ligand (OR^-). In fact, the larger alkyl groups decrease the diffusion of the species from the solution. This decreases the hydrolysis rate [16, 62, 63]. Therefore, TBOT ($\text{Ti(OC}_4\text{H}_9)_4$) is the most widely used precursor (notably in the hydrothermal method) for forming titania [10].

On the other hand, it should be noted that the slower the hydrolysis rate, the smaller the size of the titania particles. As was mentioned earlier, to decrease the hydrolysis rate of a titanium compound, various compounds such as beta-diketones, beta-keto esters, diesters, carboxylic acids, amines, aminopolycarboxylic acids, etc. could be employed as chelating agents [16, 42, 43]. Accordingly, the chelating agents are coordinated to the Ti atoms and donate their oxygen lone pairs to the empty d orbital of Ti. This leads to the formation of a complex. Therefore, the strain steric of the complex effectively impedes the attack of the hydroxo ligand (OH^-) of water towards the alkoxy ligand (OR^-) [40]. It should be noted that an equimolar mixture of titanium alkoxide and the chelating agent leads to the formation of titania nanoparticles. However, two equivalents of the chelating agent and one equivalent of titanium alkoxide are appropriate for the formation of a nanofiber structure [63].

In this study, the equimolar mixture of TBOT and the chelating agent was employed to produce titania nanoparticles. Therefore, the primary particles were formed after hydrolysis and nucleation. When the hydrolysis rate was decreased, there was no opportunity for the growth of the particles. Hence, nanoparticles were produced [64]. Therefore, both the precursor (TBOT) and the chelating agent were dissolved and formed a complex [59]. It is worth mentioning precursor is in dimeric form [56, 65, 66]. After adding the hydrolysis agent (DIWA) to the studied methods, hydrolysis was performed to obtain discrete nanoparticles and to release the chelating agent. Subsequently, the drying methods were performed. Finally, the dried precipitates were calcined to form the final phase porous structure (anatase) [59]. The scheme of the synthesis mechanism of NPTPs is shown in Fig. 6.

3.4 The effective parameters on the PCD of MB

In the current work, sample 20 (synthesized using ACAC, the SH method, and the FD technique) was selected as the improved NPTPs. The photocatalytic property of this sample was evaluated using the degradation of MB. Thus, the effects of the UV-light irradiation time, MB concentration, catalyst amount, and pH value were investigated as critical parameters affecting the degradation efficiency. For this reason, to achieve optimum conditions, the role of each parameter was evaluated by studying various experiments.

3.4.1 The effect of the UV-light irradiation time

The effect of the UV-light irradiation time on the PCD of MB was investigated using 1 g improved NPTPs and 20 mg.L⁻¹ MB at the pH of 7. In this step, the solution adsorption was measured from 1 to 3 h. Figure 7(a) shows that the adsorption peak of MB decreased when the UV-light irradiation time was enhanced which indicates an increase in degradation efficiency (Fig. 7(b)). Furthermore, the solution color changed from blue to colorless when the UV-light irradiation time was enhanced from 1 to 3 h.

3.4.2 The effect of the concentration of MB

To evaluate the effect of concentration of MB on the PCD, the concentration was altered from 5 to 20 mg.L⁻¹. The amount of 1 g modified NPTPs and the pH of 7 was used in these trials. Figure 7(c) shows that the relative concentration, C/C₀ (C is the MB concentration at the sampling time and C₀ is the initial MB concentration), was decreased when the UV-light irradiation time was increased. This behavior was more evident for the lower concentration studies, implying that the degradation occurred more. Furthermore, the degradation efficiency, R, was determined using Eq. (2):

$$R = \frac{C_0 - C}{C_0} \times 100$$

2

As shown in Fig. 7(d), the higher degradation efficiency was achieved using the lower concentration of MB. This is due to the fact that when there is a high concentration of MB in the medium, fewer photons pass through the solution and reach the surface of the catalyst. Hence, fewer OH radicals are generated as active sites. Furthermore, when the MB concentration is high, there are more MB and intermediate product molecules on the surface of the catalyst, which reduces the degradation efficiency [14].

Therefore, the MB concentration of 5 mg.L⁻¹ was chosen as the optimum MB concentration.

3.4.3 The effect of the amount of catalyst

The effect of various amounts of improved NPTPs (namely 0.25, 0.5, 0.75, and 1 g) on the PCD of MB was studied. The MB concentration of 5 mg.L⁻¹ and the pH of 7 were employed in these experiments. Figure 7(e) demonstrates that by increasing the amount of catalyst, the relative concentration of MB decreased. This is due to increasing adsorption sites and producing of free electrons on the surface of the catalyst. However, a higher catalyst amount increases the turbidity of the medium leads to lower photon adsorption. This is due to reducing light penetration and increasing its scattering [67, 68].

Figure 7(f) shows that the degradation efficiency increased when the amount of catalyst was enhanced. Hence, the catalyst amount of 1 g was selected as the optimum condition.

3.4.4 The effect of pH value

To study the effect of pH value on PCD of MB, experiments were examined in different pH (3, 5, 7, 9, and 11). These experiments were performed on 1 g improved NPTs and 5 mg.L⁻¹ MB solution. The pH adjustment was done by HCl and NaOH. Figure 7(g) demonstrates that C/C0 was decreased when the pH value was enhanced from 3 to 11. Therefore, the degradation process is strongly pH-dependent. This tendency is due to the increasing negative charge on the photocatalyst surface. Since MB is a cationic dye, it adsorbs on the surface of the catalyst due to the electrostatic interactions of the different charges [15, 69]. Figure 7(h) shows that the degradation efficiency increased by elevated the pH value from 3 to 11. Hence, the pH value of 11 was selected for the degradation process.

3.5 The mechanism of the PCD of MB

Interaction of NPTs (as a semiconductor) with photons (as light irradiation with energy in the near UV range: $\lambda < 390$ nm) causes excitation of electrons (e^-_{CB}) from the valance band (VB) into the conduction band (CB) which leading to the formation of holes in the VB (h^+_{VB}). This process is known as electron-hole pair generation (Eq. (3)).

The performed reactions on the surface of TiO₂ are described in Eqs. (4) to (7):

The hydroxyl radical ($-\text{OH}$, as a strong oxidizing agent) attack MB (as an electron donor species) at the surface of TiO₂, which capable to degrade into harmless species such as CO₂ and H₂O (Eqs. (8) to (10)) [14, 70]:

4 Conclusion

This study demonstrated that the type of chelating agent, the hydrolysis method, and the drying technique had considerable effects on the structural properties of the titania particles synthesized via the hydrothermal method. Therefore, the significant findings were as follows. (1) The titania particles synthesized by the aid of ACAC as the chelating agent formed ultrafine and more uniform particles with a high SSA, a large TPV, and a small APS. (2) The titania particles prepared via the SH method formed ultrafine and more uniform particles than those prepared by the DH and IH methods. (3) The titania particles which were dried via the FD technique were non-agglomerated. These findings demonstrated that the SH and FD methods had a vital role in forming NPTPs with ultrafine, uniform, and non-agglomerated particles with a high SSA, a large TPV, and a small APS. Furthermore, the PCD of MB which was carried out using improved NPTPs showed that the degradation efficiency depended on some crucial parameters. Therefore, the UV-light irradiation time of 2 h, MB concentration of 5 mg.L^{-1} , catalyst amount of 1 g, and pH value of 11 were obtained as the optimum conditions. Furthermore, the degradation efficiency of MB using the improved NPTPs during 2 h was > 93% at optimum conditions. Therefore, it is recommended that the hydrothermal synthesis method, ACAC (as a chelating agent), and the SH and FD techniques be employed so that NPTPs have appropriate properties.

Declarations

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Conflicts of interest/Competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Availability of data and material

All data generated or analyzed during this study are included in this paper.

Code availability

Not applicable for this paper.

Authors' contributions

All authors contributed to study, design, material preparation, experimentation, data collection, and analysis. All authors read and approved the final manuscript.

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Figures

Figure 1

(a) IH, (b) DH, and (c) SH methods

Figure 2

The scheme of the synthesis process of NPTs

Figure 3

The XRD pattern of all the synthesized NPTs (Sample 1: No Chelating Agent/IH/OD, Sample 2: No Chelating Agent/DH/OD, Sample 3: No Chelating Agent/SH/OD, Sample 4: No Chelating Agent/SH/FD, Sample 5: GLAA/IH/OD, Sample 6: GLAA/DH/OD, Sample 7: GLAA/SH/OD, Sample 8: GLAA/SH/FD, Sample 9: ETAC/IH/OD, Sample 10: ETAC/DH/OD, Sample 11: ETAC/SH/OD, Sample 12: ETAC/SH/FD, Sample 13: ETAA/IH/OD, Sample 14: ETAA/DH/OD, Sample 15: ETAA/SH/OD, Sample 16: ETAA/SH/FD, Sample 17: ACAC/IH/OD, Sample 18: ACAC/DH/OD, Sample 19: ACAC/SH/OD, and Sample 20: ACAC/SH/FD)

^a IH/OD: Immediate-Hydrolysis/Oven-Drying

^c SH/OD: Spray-Hydrolysis/Oven-Drying

^e GLAA: Glacial acetic acid

^b DH/OD: Droplet-Hydrolysis/Oven-Drying

^d SH/FD: Spray-Hydrolysis/Freeze-Drying

^f ETAC: Ethyl acetate

^g ETAA: Ethyl acetoacetate

^h ACAC: Acetylacetone

Figure 4

The FESEM images of NPTPs (500 nm magnification)

Figure 5

The scheme of the FD process

Figure 6

The scheme of the synthesis mechanism of NPTPs

Figure 7

The PCD behaviour of MB using improved NPTs (a) UV-Light irradiation time effect, (b) Degradation efficiency based on UV-light irradiation time, (c) MB concentration effect, (d) Degradation efficiency based on MB concentration, (e) Catalyst amount effect, (f) Degradation efficiency based on catalyst amount, (g) pH value effect, and (h) Degradation efficiency based on pH value