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Novel synthesis of nanophase anatase under conventional- and microwave-hydrothermal conditions: DeNOx properties

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Abstract

Nanophase anatase was synthesized by a novel simplified one-pot method using Ti alkoxides and hydrogen peroxide under conventional- and microwave-hydrothermal conditions. The specific surface areas (SSAs) of anatase ranged from 147 to 298 m^2/g under different hydrothermal conditions but higher SSAs were obtained under microwave-hydrothermal conditions. The novel method developed here results in nanophase anatase with superior $DeNO_x$ properties.

Keywords: Anatase; $DeNO_x$ property; Photocatalysis; Ti alkoxides; Microwave-hydrothermal

1. Introduction

Titanium dioxide (TiO_2) is a versatile material because it has been used for many years in a variety of industrial products such as pigments [1], sunscreens [2], paints [3], toothpastes [4], etc. In addition to these conventional applications much attention has been given to TiO_2 in the past several decades after the first report on photocatalytic spitting of water on a TiO_2 electrode under ultraviolet light [5]. This photocatalysis discovery led to intensive studies of TiO_2 due to its applications related with energy and environment [6], sensors [7], photovoltaic solar cells [6] and photocatalysts [8], the latter for environmental cleanup. The physiochemical properties leading to the efficiency of these applications are affected by titania's electronic structure, phase composition, particle morphology and size, aggregation, defects, and surface properties [9,10] which can be controlled by different methods of synthesis [11,12].

Various techniques have been used for the synthesis of TiO_2 such as sol–gel [13,14], hydrothermal [15–17], combustion syntheses [18], and gas phase methods [19]. The combustion synthesis is a single process producing pure phases. Hydrothermal methods are a good approach for synthesis of TiO_2 because crystalline TiO_2 can be prepared at relatively low temperatures as well as its phase, morphology, size, composition, etc., can be easily controlled by adjusting their synthesis conditions like temperature, pH, precursors, and heating time [20]. This tuning is significant in synthesizing TiO_2 because different applications require different characteristics of TiO_2 like particle size, morphology, or nature of crystalline phase [21]. For example, as the particle size of TiO_2 decreases, the sensing and photocatalytic activity increases [22]. The photocatalysis of crystalline anatase is generally superior to that of rutile [23]. Especially, the particle size is an important parameter to affect the efficiency and application of TiO_2 because many reactions occur on the surface. Hence, there have been numerous studies to synthesize TiO_2 with different particle sizes and shapes using the hydrothermal methods.

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Anatase nanoparticles with different particle size and shape were synthesized using titanium alkoxide and tetramethylammonium hydroxide [14]. Also, titanium isopropoxide was used with hydrothermal reaction in an acidic ethanol–water solution to synthesize TiO_2 nanoparticles [15]. However, the sol prepared by these methods was often unstable and acidic [24]. Due to this problem, Liu et al. [25] synthesized nanocrystalline titanium dioxide from peroxo titanic acid (PTA) approach by addition of titanium isopropoxide and then H_2O_2 to water, but the PTA solution was prepared through several cooling steps using an ice bath, which may limit the production on an industrial scale. The hydrothermal treatment was used to crystallize amorphous or semicrystalline TiO_2 into crystalline TiO_2 [12]. To increase kinetics of crystallization, Komarneni et al., [26,27] developed a novel microwave-hydrothermal method in a closed system controlling temperature and/or pressure to synthesize TiO_2 from $TiCl_4$. This microwave-hydrothermal method has several advantages such as (a) leading to rapid kinetics, (b) formation of new phases, (c) elimination of metastable phases, and (d) rapid heating to temperature of treatment [28,29].

Herein, we developed a simplified hydrothermal synthesis method for nanophase anatase using various titanium alkoxides (titanium ethoxide, titanium butoxide, and titanium isopropoxide) and H_2O_2 and compared the conventional-hydrothermal synthesis method with the microwave-hydrothermal method with respect to anatase syntheses and their $DeNO_x$ properties. This new simplified method of anatase synthesis was based on our pioneering paper on a new method of making titania gels [30]. Ribiero et al., [31] recently reported the synthesis of titanium oxide nanocrystals, especially the rutile TiO_2 phase by a method based on peroxotitanium complex decomposition. A new synthetic method for TiO_2 nanocrystals starting from metallic Ti and hydrogen peroxide was developed by Ribiero et al., [32,33]. The results reported here are for nanophase anatase synthesis using a highly simplified one-pot method by conventional- and microwave-hydrothermal methods.

2. Experimental

2.1. Materials

TiO_2 was synthesized using the conventional-hydrothermal (C-H) method or microwave-hydrothermal (M-H) method. Titanium ethoxide (99%, Alfa Aesar), titanium isopropoxide (99%, Acros Organics), titanium butoxide (99%, Alfa Aesar) and hydrogen peroxide (35%, Alfa Aesar), were used as precursors.

2.2. Synthesis of TiO_2

In a typical synthesis of TiO_2 from metal alkoxides, hydrogen peroxide was added to appropriate amount of titanium alkoxide in a Teflon vessel with a molar ratio of 0.05:0.12 ($Ti:H_2O_2$). All resulting mixtures were heated hydrothermally at different conditions (see Tables 1 and 2). The conventional-hydrothermal experiments were carried out in Parr reactors (Moline, Illinois, USA), while microwave-hydrothermal treatments were conducted using a multimode MARS-5 microwave digestion system (CEM corp. Mattews, NC), which was operated at a frequency of 2.45 GHz with a power of 300 W. Temperature or pressure can be controlled in

Table 1

Synthesis conditions, phase, and crystallite size of TiO_2 prepared from different titanium alkoxides using a $Ti:H_2O_2$ molar ratio of 0.05:0.12 under conventional-hydrothermal (C-H) and microwave-hydrothermal (M-H) conditions as a function of temperature.

	Run no.	Ti source	Crystallization		Phase	Crystallite size (nm)		Surface area (m^2/g)
			T (°C)	t (h)		XRD[a]	TEM	
C-H	1	Ti ethoxide	100	24	Anatase	6.9	4–10	212
	2	Ti ethoxide	125	24	Anatase	9	8–12	177
	3	Ti ethoxide	150	24	Anatase	9.3	10–15	174
	4	Ti ethoxide	175	24	Anatase	10	10–20	157
	5	Ti isopropoxide	100	24	Anatase	7.3	4–8	193
	6	Ti isopropoxide	125	24	Anatase	7.7	8–15	174
	7	Ti isopropoxide	150	24	Anatase	8.9		155
	8	Ti isopropoxide	175	24	Anatase	9.5		156
	9	Ti butoxide	100	24	Anatase	7.7	4–8	181
	10	Ti butoxide	125	24	Anatase	8.2	10–15	166
	11	Ti butoxide	150	24	Anatase	8.9		163
	12	Ti butoxide	175	24	Anatase	10.1		147
M-H	Ex. 15	Ti ethoxide	100	1	Anatase	6.1	5–8	232
	Ex. 17	Ti ethoxide	125	1	Anatase	6.3		215
	Ex. 19	Ti ethoxide	150	1	Anatase	6.9	8–15	201
	Ex. 23	Ti ethoxide	175	1	Anatase	7.5		187
	Ex. 14	Ti isopoproxide	100	1	Anatase	5.5	3–8	298
	Ex. 16	Ti isopoproxide	125	1	Anatase	6.6		212
	Ex. 18	Ti isopoproxide	150	1	Anatase	6.7	5–12	209
	Ex. 22	Ti isopoproxide	175	1	Anatase	7.6		194

[a] Calculated using $d_{(311)}$ peak based on Scherrer's equation.

Table 2
Synthesis conditions, phase, and crystallite size of TiO_2 prepared from different titanium alkoxides using a $Ti:H_2O_2$ molar ratio of 0.05:0.12 under conventional-hydrothermal (C-H) conditions as a function of time.

C-H Run no.	Ti source	Crystallization		Phase	Crystallite size (nm)[a]
		T (°C)	t (h)		
53	Ti ethoxide	175	4	Anatase	7.7
54	Ti ethoxide	175	8	Anatase	8.1
55	Ti ethoxide	175	16	Anatase	8.4
56	Ti isopropoxide	175	4	Anatase	7.7
57	Ti isopropoxide	175	8	Anatase	8.5
58	Ti isopropoxide	175	16	Anatase	9.5
59	Ti butoxide	175	4	Anatase	6.7
60	Ti butoxide	175	8	Anatase	7.0
61	Ti butoxide	175	16	Anatase	8.6
35	Ti ethoxide	200	24	Anatase	10.1
62	Ti ethoxide	200	48	Anatase	10.3
36	Ti isopropoxide	200	24	Anatase	10.3
63	Ti isopropoxide	200	48	Anatase	10.5
37	Ti butoxide	200	24	Anatase	10.6
64	Ti butoxide	200	48	Anatase	10.9

[a] Calculated using $d_{(311)}$ peak based on Scherrer's equation.

the MARS-5 system using an optical temperature probe situated in a sapphire tube or a pressure transducer, respectively. After heating, the solids were washed with water and ethanol several times and then dried at 60 °C prior to characterization by different techniques.

2.3. *Characterization of TiO_2*

Powder X-ray diffraction (XRD) patterns were collected using a Scintag or PANalytical X'Pert MPD X-ray diffratometer operated at 45 kV voltage and 40 mA current with CuKα radiation in order to identify phases and to calculate crystallite sizes of TiO_2 using the Scherrer's equation. N_2-sorption measurements were performed at 77 K on an Autosorb-1 (Quantachrome corp.) to determine Brunauer–Emmett–Teller (BET) specific surface areas. Prior to the measurement, the samples were degassed under vacuum for 3 h at 150 °C.

2.4. *Photocatalytic activity determination for nitrogen monoxide destruction*

The destruction of nitrogen monoxide by photocatalytic activity was determined by measuring the concentration of NO gas at the outlet of the reactor (373 cm^3 of internal volume) during the photo-irradiation of a constant flow (200 $cm^3\ min^{-1}$) of a gas mixture containing 1 ppm NO in 50 vol% air and 50 vol% N_2). The nanophase anatase photocatalyst was placed in a hollow tube of 20 mm length × 16 mm width × 0.5 mm depth of a glass holder plate and set in a bottle at the bottom center of the reactor. The anatase photocatalyst under test was first equilibrated with the flowing NO gas before turning on the light. A 450 W high-pressure mercury arc was used as the light source. The wavelength was controlled by selecting filters, i.e., Pyrex glass for >290 nm, Kenko L41 Super Pro (W) filter for >400 nm and Fuji triacetyl cellulose filter for >510 nm. The concentration of NO was determined using a NO_x analyzer (Yanaco, ECL-88A). Previous studies suggested that about 20% of NO is directly reduced to N_2 and the other 80% is oxidized to NO_3^- species during the photocatalytic destruction. For comparison with the anatase synthesized here, the photocatalytic reaction was also carried out using the standard commercial titania, Degussa P25.

3. Results and discussion

Table. 1 shows the temperature and time synthesis conditions, phase, and crystallite size of titania prepared from different titanium alkoxides using a $Ti:H_2O_2$ molar ratio of 0.05:0.12 under both conventional-hydrothermal (C-H) and microwave-hydrothermal (M-H) conditions. A perusal of all the results showed that nanophase anatase was obtained in all synthesis conditions (Table. 1) used here as determined by powder X-ray diffraction (Figs. 1 and 2). The XRD patterns of titania showed broad peaks of anatase polymorph at all temperatures under both C-H and M-H conditions (Figs. 1 and 2) suggesting extremely small crystal size for anatase, which is confirmed by crystal size calculations by Scherrer's equation (Table 1).

That the conventional-hydrothermally synthesized anatase is of nanophase was also confirmed by specific surface area measurements and TEM analyses (Table 1 and Fig. 3). Fig. 1 shows the powder X-ray diffraction (XRD) patterns of TiO_2 prepared from titanium ethoxide at 100 °C, 125 °C, 150 °C and 175 °C after heating for 1 day under conventional hydrothermal (C-H) conditions. As expected, crystallinity of anatase increased with increasing hydrothermal treatment temperature (Fig. 1) while surface areas decreased and crystal size as determined by TEM and XRD increased (Table 1). Fig. 2 shows the powder XRD patterns of TiO_2 prepared from titanium ethoxide at 100 °C, 125 °C, 150 °C and 175 °C after heating for 1 h under microwave-hydrothermal (M-H) conditions. The XRD patterns revealed broad peaks of

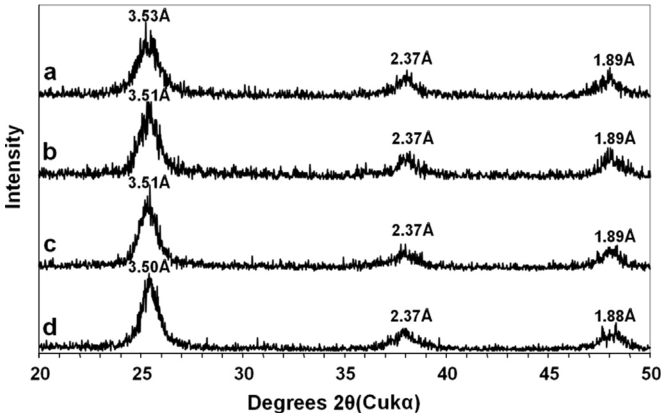

Fig. 1. X-ray diffraction patterns of TiO_2 (anatase) prepared with titanium ethoxide under conventional-hydrothermal conditions at (a) 100 °C (b) 125 °C (c) 150 °C and (d) 175 °C for 1 d heating.

anatase at all temperatures under M-H conditions (Fig. 2) suggesting nanocrystal size for anatase which is also deduced by crystal size calculations using Scherrer's equation (Table 1). That the microwave-hydrothermally synthesized anatase is of nanophase was also confirmed by specific surface area measurements and TEM analyses (Table 1 and Fig. 3).

Table 2 shows the results of titania syntheses as a function of time from different Ti alkoxides at two different temperatures. Crystal size as determined by Scherrer's equation increased only slightly with duration of treatment (Table 2). This suggests that there is not much growth of anatase after the initial nucleation because of the low solubility of anatase under the present conditions. Fig. 4 presents the XRD results of anatase synthesized at 175 °C for 4, 8 and 16 h under C-H conditions. The XRD patterns are similar for all durations and the slight improvement in crystallinity with time is detectable. Thus this new method of titania synthesis leads to nanophase anatase at all temperatures and durations of hydrothermal treatment with slight increases in crystallinity with temperature (Table 1; Figs. 1 and 2) and time of treatment (Table 2 and Fig. 4). Anatase synthesized by both C-H and M-H methods was tested for NO_x decomposition (Fig. 5) and anatase synthesized by both methods resulted in similar NO_x

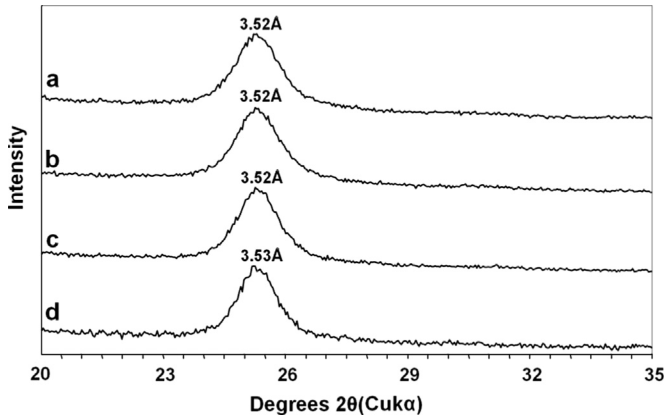

Fig. 2. X-ray diffraction patterns of TiO_2 (anatase) prepared with titanium ethoxide under microwave-hydrothermal conditions at (a) 100 °C (b) 125 °C (c) 150 °C and (d) 175 °C for 1 h heating.

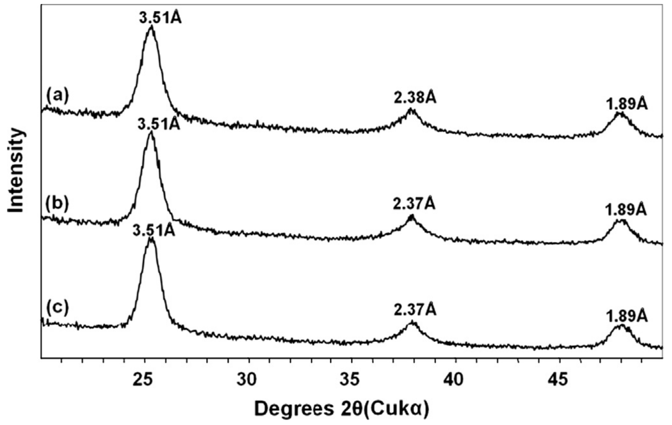

Fig. 4. X-ray diffraction patterns of TiO_2 (anatase) prepared with titanium ethoxide under conventional-hydrothermal conditions at 175 °C for (a) 4 h (b) 8 h and (c) 16 h heating.

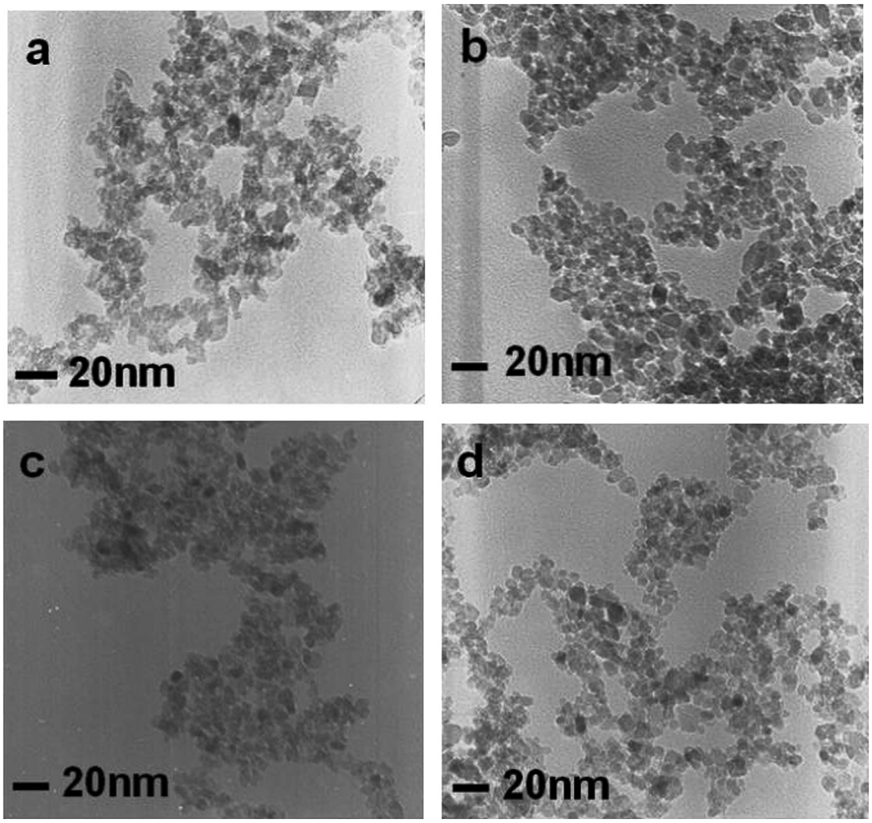

Fig. 3. Transmission electron micrographs of TiO_2 (anatase) prepared by using titanium ethoxide at 100 °C/24 h (a) and 150 °C/24 h (b) under conventional-hydrothermal conditions and at 100 °C/1 h (c) and 150 °C/1 h (d) under microwave-hydrothermal conditions.

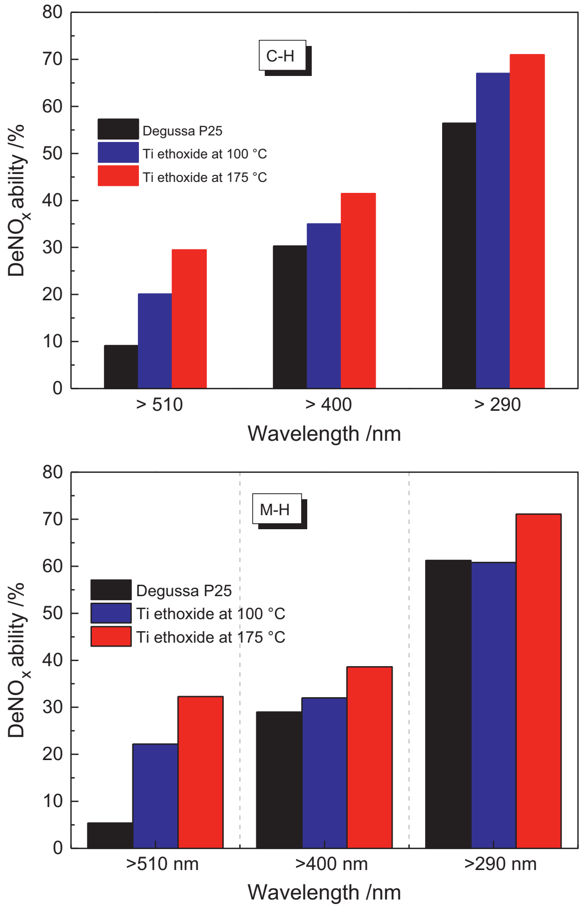

Fig. 5. NO_x decomposition by anatase prepared by conventional-hydrothermal (C-H) and microwave-hydrothermal (M-H) processes in comparison with standard commercial titania, P25.

destruction at all wavelengths. However, the nanophase anatase synthesized here is superior to commonly used standard commercial titania, P25 at all wavelengths but vastly superior at wavelengths greater than 510 nm for NO_x decomposition (Fig. 5) because of very high specific surface area of the former (Table 1). It is notable that the anatase titania samples prepared by the novel method here showed excellent photocatalytic activity under irradiation of not only UV light but also visible light ($\lambda > 510$ nm), the latter because of carbon doping from the alkoxide precursors. In addition, anatase prepared at 175 °C showed slightly better $\mathrm{NO}x$ decomposition than the one prepared at 100 °C (Fig. 5) at all wavelengths because clearly defined crystal faces apparently also play a role in NO_x decomposition. Thus the novel method developed here results in anatase with superior DeNO$_x$ properties.

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