

The effect of fuel-to-oxidizer ratio on the structure and photo-catalytic activity of TiO₂ nanosheets prepared by a microwave-assisted combustion method

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TiO₂ nanosheets were synthesized by a combustion method using a metal nitrate solution combustion and urea fuel. Microwave irradiation was used as the heating source. X-ray diffraction, scanning and transmission electron microscopy as well as specific surface area analysis and Fourier transform infrared spectroscopy were performed to characterize the samples obtained. X-ray diffraction patterns revealed that the ratio of rutile/anatase phases varied from 25/75 to 69/31 as the fuel-to-oxidizer (*i.e.* urea/titanyl nitrate) ratio changed from lean to rich. The crystallite size of the as-synthesized samples calculated by the Scherrer formula was 6.5–63 nm. From scanning and transmission microscopy images flaky particles with loose packed agglomerates in the form of nanosheets were detected. Due to the smaller crystallite size and higher content of the anatase phase, the fuel lean sample seemed to be a better candidate for photo-catalytic functions.

Key words: Nanosheets TiO₂, Combustion, Fuel effect, Photo-catalytic activity.

Introduction

Titanium dioxide (TiO₂) has been widely used as a pigment in paints [1] with the rutile phase, and as a photo-catalyst [2] with the anatase phase. However, for photo-catalytic oxidation of organic pollutants, a small amount of the rutile phase can result in a better performance [3].

Many chemical approaches have been used for the preparation of nano-sized TiO₂ including sol-gel method [4] and hydrothermal processing [5].

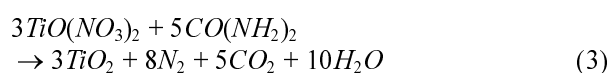
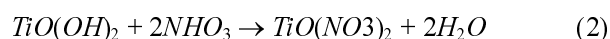
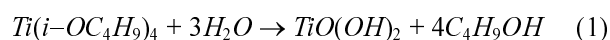
Solution combustion synthesis (SCS) has emerged as an important technique for the synthesis and processing of advanced ceramics (structural and functional), catalysts, composites, alloys, intermetallics and nanomaterials [6]. In SCS, the exothermicity of the redox (reduction-oxidation or electron transfer) chemical reaction is used to produce useful materials [7]. In this technique, a furnace is conventionally used as the heating source [8, 9]. Recently a novel technique called ‘microwave-assisted combustion synthesis’ has been used to synthesize oxide materials [10]. Microwave heating can be more advantageous than conventional heating because of the short processing time and volumetric heating. Microwaves are electromagnetic waves that have a frequency range of 0.3 to 300 GHz and corresponding wavelengths ranging from 1 m to 1 mm. A typical frequency for materials processing is 2.45 GHz. It has long been established that dielectric materials, such as many types of ceramics can be heated with energy in the form of microwaves [11]. Jia *et al.* reported the

synthesis of pure anatase nanorods with meso-pores by a microwave-assisted method when a tri-block copolymer was used as a structural stabilizer and TiCl₄ as a metal precursor [12].

In this paper, the combustion synthesis of TiO₂ nanoparticles is reported. Microwave irradiation was used as the heating source and urea as the fuel. The effects of the amount of fuel on the structure and photo-catalytic activity of the samples were also investigated. X-ray diffraction (XRD), scanning and transmission electron microscopy (SEM and TEM), specific surface area analysis (Brunauer-Emmett-Teller (BET)) and Fourier transform infrared spectroscopy (FT-IR) were applied to characterize the samples obtained.

Materials and Methods

Nano-sized TiO₂ was prepared by a solution combustion method using a precursor titanyl nitrate [TiO(NO₃)₂] and urea (2HN-CO-NH₂) as fuel (all from Merck, Germany). The titanyl nitrate was synthesized by the reaction of titanyl hydroxide [TiO(OH)₂] obtained by the hydrolysis of tetra-n-butylorthotitanat (TBT) [Ti(i-OC₄H₉)₄] with nitric acid. Assuming that the titanyl nitrate and urea undergo a complete reaction, the formation of TiO₂ can be described by equations 1-3:



In a typical combustion synthesis, a Pyrex dish (400 cm³)

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containing an aqueous redox mixture of stoichiometric amounts of titanium nitrate and urea in 20 ml of water was heated to 50 °C with continuous magnetic agitation. Under a constant temperature and agitation water was evaporated to obtain gel. Then, the gel was exposed to microwave irradiation (900 w) for 30 s. In order to study the effect of the ratio of fuel-to-oxidizer (*i.e.* urea/titanium nitrate, U/TN, being the molar ratio in equation 3) on powder properties and photo-catalytic activity, different U/TN ratios (1.16 (fuel lean), 1.6 (stoichiometric) and 2 (fuel rich)) were investigated.

A D-500 (Siemens, Karlsruhe, Germany) diffractometer was used for the XRD analysis. Morphology and size analysis was performed using a LEO 1455 VP (Oxford, UK) scanning electron microscope (SEM) and a Zeiss EM900 transmission electron microscope (TEM). The IR spectra of the powder prepared were determined by FT-IR (Spectrum one, FT-IR spectrometer, Perkin Elmer).

The photocatalytic performance was examined using a self-designed apparatus made from a 40 W/220 V UV lamp (365 nm) as the luminous source and methyl orange (MO) as the reactant.

Results and Discussions

An x-ray diffraction pattern of the as-synthesized TiO₂ sample is shown in Fig. 1 which demonstrates that a polycrystalline TiO₂ powder was obtained during the combustion process without a further calcination step. Both anatase and rutile phases, according to JCPDS 01-071-1167 and 01-076-0319 cards respectively, are observed in the XRD patterns. The percentage of the phases can be calculated by equation 4 [13, 14]:

$$x = \frac{1}{1 + 0.8 \left[\frac{I_A}{I_R} \right]} \quad (4)$$

where x is the weight percentage of the rutile phase, I_A and I_R are the peak intensities of the (101) and (110) planes for the anatase and rutile, respectively. From equation 4 and Fig. 1, there are 65% and 35% of anatase and

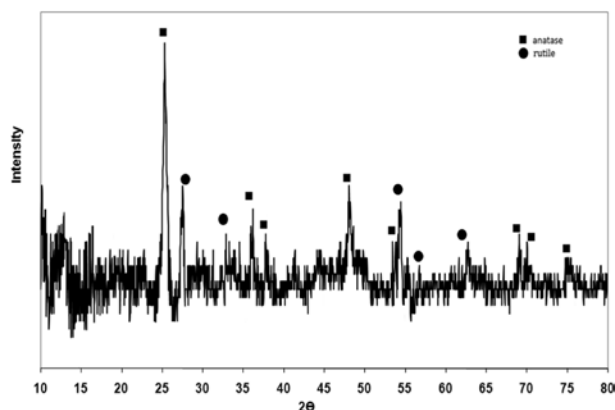


Fig. 1. XRD pattern of the as-synthesized TiO₂ powder.

rutile phases, respectively.

The morphology of the powder obtained was characterized by electron microscopy and Fig. 2 shows the result. From Fig. 2 the s-synthesized sample consists of thin and thick flakes. The morphology of primary particles in the loose packed agglomerates was evaluated by TEM. Figs. 3(a-b) show that the as-synthesized powder consists of TiO₂ nanosheets. Observation of the carbon grid on the backside of the sheets illustrated in Fig. 3(b) reveals that the thickness of the sheets is on a nanometric scale. The BET surface area of the as-synthesized TiO₂ nanosheets was about 22 m²/g.

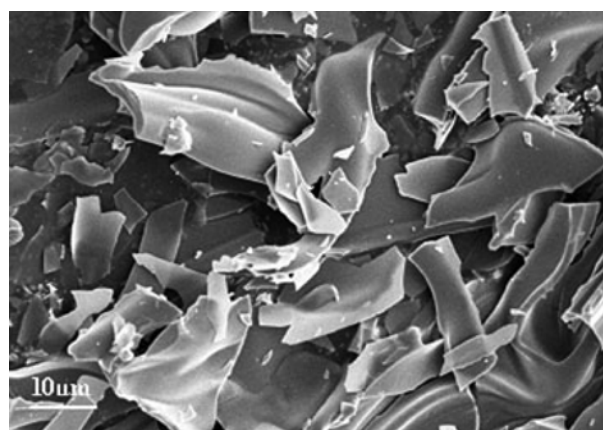


Fig. 2. SEM image of the TiO₂ sample.

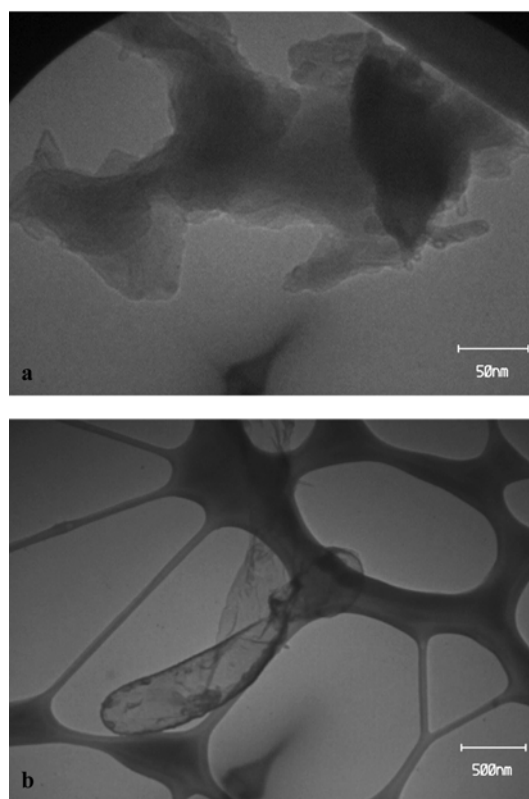


Fig. 3. TEM image of the as-synthesized TiO₂ powder at two magnifications.

In order to verify the chemical structure of the powder obtained FT-IR spectral analysis was performed. Fig. 4 shows the bands at 3493 and 1633 cm⁻¹, corresponding to the vibration mode of the water OH group indicating the presence of an amount of water adsorbed on the TiO₂ surface. The regions from 400 to 800 cm⁻¹ in Fig. 4 are dominated with weak and broad peaks identified to have the frequencies corresponding to the bulk titania skeletal [15].

The effect of the U/TN ratio (fuel richness and leanness) on the structure and crystallite size of the synthesized powders was also investigated. Fig. 5 demonstrates a comparison between X-ray results for the three U/TN ratios: 1.16, 1.6 and 2. Rutile/anatase ratios, crystallite sizes (calculated by the Scherrer formula, based on the full width half maxima of the X-ray diffraction pattern) and BET results are summarized in Table 1. From Fig. 5 and Table 1 it can be seen that the rutile/anatase ratio increases with the U/TN ratio which can be related to the increase of fuel content and hence, the energy of the system. Furthermore, the formation of the anatase phase can be related to the surface energy and surface area of the samples. The BET investigation showed a higher specific

Table 1. The effect of the U/TN ratio on the rutile/anatase content, crystallite size and the BET surface area of the TiO₂ powders

	rutile/anatase	Crystallite size (nm)	BET surface area (m ² /g)
U/TN = 1.16 (fuel lean)	25/75	6.5	28
U/TN = 1.6 (stoichiometric)	35/65	23.8	22
U/TN = 2 (fuel rich)	69/31	63	17

surface area for the fuel-lean sample. The average surface energies for anatase and rutile are ~1.3 and 1.9 J m⁻², respectively [14, 16]. Consequently, the surface contribution to the total free energy is a more rapid function of surface area for rutile relative to anatase. Anatase becomes the stable phase when the TiO₂ crystal size is below a certain value (~14 nm). Gilbert *et al.* [17] reported such observations for ZnS and TiO₂ nanocrystals synthesized by a sol-gel method.

According to Table 1 in which the crystallite size of the samples increases from 6.5 to 63 nm, the higher energy of the system led to a growth of the crystal size. The morphology of the powder obtained was investigated and Fig. 6 shows the SEM images. From Fig. 6 for all U/TN value, the flaky-like morphology was obtained. However, the fuel lean sample shows thick and small flakes. For the fuel rich sample the flakes became big and relatively porous which can be related to the large amount of gases produced by the fuel.

The photo-catalytic analysis was performed by a self-designed equipment. Fig. 7(a) provides the UV-Vis absorption spectra of the methyl oranges (MO) solution over various samples, after irradiation with a UV lamp. Interestingly, a larger amount of methyl orange adsorption was observed in the fuel lean sample than in the stoichiometric and fuel rich samples in our photo-catalysis experiment. Fig. 7(b) shows photodegradation of the MO dye on the synthesized TiO₂. A decrease in the concentration occurred after the samples were dispersed into the MO aqueous solution and subsequently stirred in darkness, revealing that parts of the MO molecules were adsorbed on the surface of the samples.

The results showed that the sample prepared with U/TN = 1.16 exhibits the highest photodegradation efficiency with a MO conversion of 80% after 10 h of irradiation. This result can be related to a well-crystallized mixed crystalline structure (75% anatase and 25% rutile) and also to the smaller crystallite size of the sample. Previous studies demonstrated that the catalytic activity of TiO₂ depends on the size and crystal structure. They showed that the anatase structure is suitable for photo-catalytic purposes with a few percent of the rutile structure [3]. The main reason for this phenomenon is the existence of a band gap equal to 3.2 eV. Therefore, it can be concluded that the fuel lean sample would be a better candidate

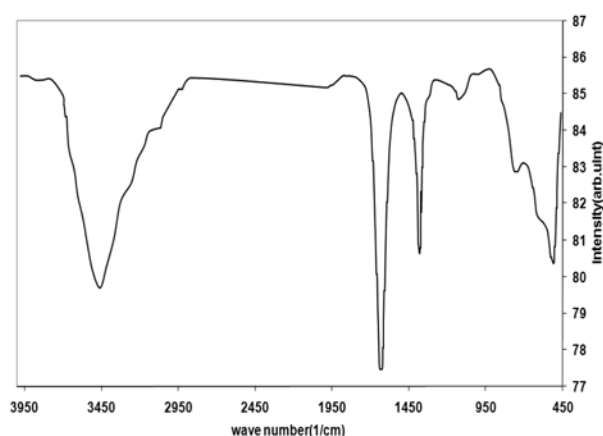


Fig. 4. FT-IR spectra of the prepared sample by a stoichiometric amount of fuel.

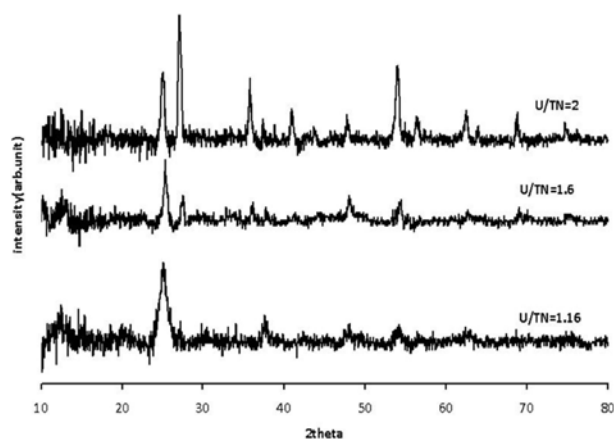


Fig. 5. The effect of the U/TN ratio (fuel richness and leanness) on the XRD patterns of the TiO₂ powders.

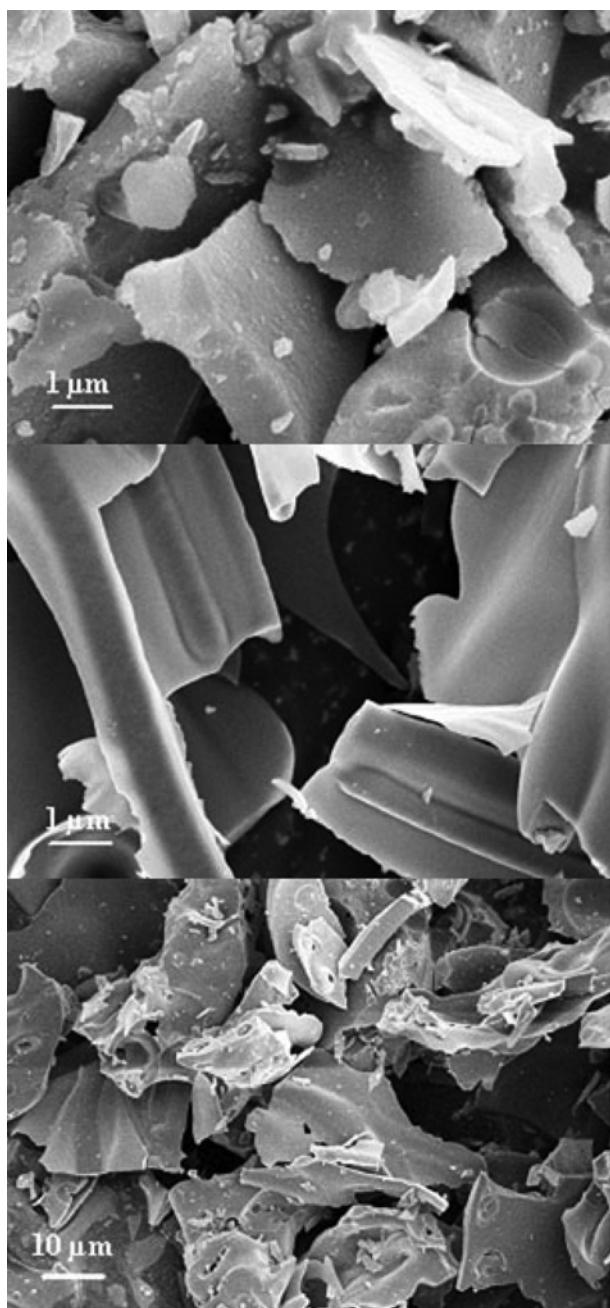


Fig. 6. SEM images of TiO_2 samples (a) fuel lean (b) stoichiometric and (c) fuel rich.

for photo-catalytic applications. Another reason for such an observation is the larger specific area of this sample in comparison with stoichiometric and fuel rich ones.

Conclusions

Microwave-assisted solution combustion is an efficient and rapid method to prepare TiO_2 nanosheets with a 6.5-63 nm crystallite size. Results showed that a mixture of rutile/anatase phases was obtained during the process and no calcination step was needed. The percentage of anatase phase depends to the U/TN ratio, which was varied

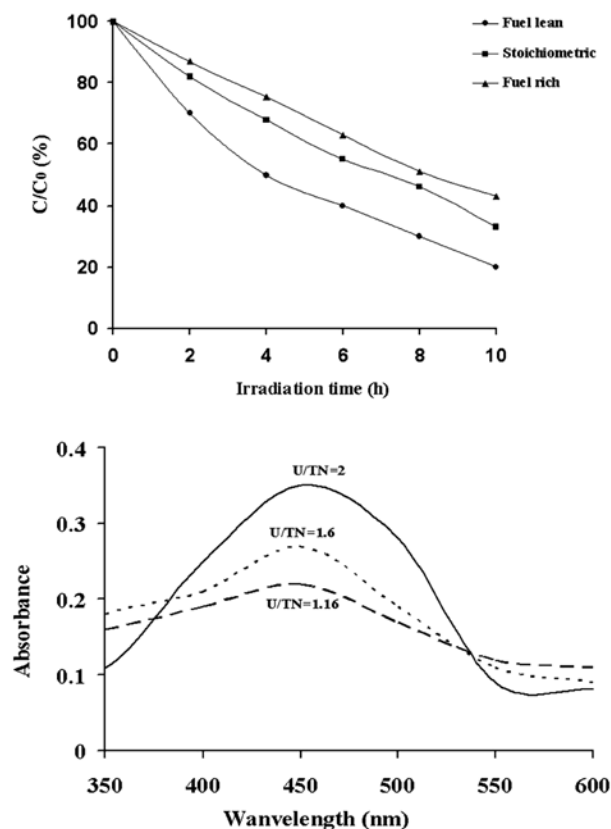


Fig. 7. (a) Absorption spectra of the MO solution after irradiation, (b) Photodegradation of MO solutions over TiO_2 samples.

from lean to rich. Furthermore, the photo-catalytic activity of the samples depends to the U/TN ratio. Due to the smaller crystallite size and higher content of the anatase phase, the fuel lean sample seemed to be a better candidate for photo-catalytic functions.

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