AN ULTRASOUND-ASSISTED SOL–GEL METHOD FOR THE SYNTHESIS OF NANO TITANIUM DIOXIDE

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Abstract

An ultrasound-assisted sol–gel method is used to prepare titanium dioxide (TiO_2) nanoparticles. The resulting nanoparticles are characterized by scanning electron microscopy (SEM) and FTIR spectroscopy. The applicability of the method is verified; the morphology of the nanoparticles is compared with that of the particles prepared by a sol–gel method that was not assisted by ultrasound. The main advantage of the ultrasonically assisted sol–gel method is the possibility of avoiding the use of ethanol, which is crucial for the industry in terms of process upscaling possibilities and ecological requirements.

1. Introduction

Recently, sol–gel technologies for preparing ultrafine powders have found wide application due to the possibility of obtaining high-purity products with a predetermined particle size distribution and various combinations of components [1–2]. Sol–gel technology is based on transformations in the following sequence: hydrolysis → polymerization → nucleation → particle growth → sol formation → gel. Therefore, hydrolysis is the most important step of the sol–gel process. The material's quality is affected by hydrolysis catalysts, pH, the amount of water used, the type of solvents used, and temperature. It has been experimentally proven that homogenous condensation, phase formation and particle growth in different steps of hydrolysis lead to the formation of a sol and a gel. In this case, growth temperature and pH are factors that increase the particle growth rate in different steps of hydrolysis and control the dimension and crystallinity of the particles [1–2].

Titanium is a crucial material for a variety of applications. For example, colloidal solutions of TiO_2 nanoparticles, which exhibit antibacterial and antistatic properties, are increasingly often used in textile processing [3, 4]. The sol–gel method has high potential in the case of TiO_2 nanoparticle synthesis because the morphology and structure of the particles are crucial for the functional properties of the particles. In the case of sol–gel synthesis, titanium alkoxides, such as tetraisopropoxide, titanium tetrabutoxide, or titanium tetrachloride, can be used as titanium-containing precursors [5]. Alcohols and ketones are suitable organic solvents for sol–gel methods in the case of TiO_2 synthesis.

It has been proven in several researches that the use of ultrasound can contribute to the formation of nanoparticles with a predetermined size in various processes [6, 7]. The use of ultrasound typically leads to the formation of smaller particles with a narrower particle size distribution [7]. In the case of Ti, it has been shown hat the use of ultrasound may also be of advantage for sol–gel synthesis [5]. The effect of ultrasound might also be important for the production of functionalized materials based on TiO_2, because it may be used for process triggering and particle size reduction in the case of hydrolysis at a low ethanol concentration. In the case of industrial processes, a reduction in the use of ethanolysis is very important for environmental and safety reasons.

In previous research, we prepared colloidal solutions and powders of zinc oxide nanoparticles using a combination of a sol–gel method and ultrasonic treatment [8].However, in recent years, few researches have been conducted to study nanoparticles obtained by a sol–gel method combined with ultrasonic treatment and the particle morphology. As mentioned above, the formation of titanium dioxide nanoparticles at low temperatures using inorganic solvents is relevant for industrial applications; it is especially important for the textile industry. Thus, the goal of this research is to study the particles prepared at a low ethanol concentration using an ultrasonically assisted sol–gel method and compare the morphology of the particles with that of the particles synthesized at a higher ethanol concentration in the absence of ultrasound.

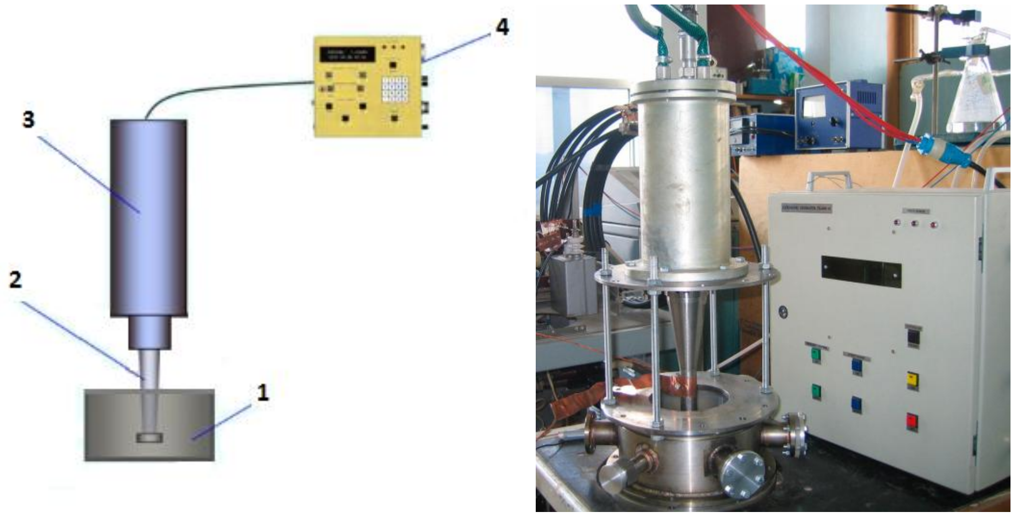
2. Experimental

2.1. Materials and equipment

Titanium sulfate $Ti(SO_4)_2$ (≥99.7%), urea $(NH_2)_2CO$ (≥99.0%), ethanol (≥98.5 %), and sodium hydroxide (≥99.9%) were purchased from Sigma-Aldrich. Distilled water was used in the experiment. All chemicals were used as received without further purification.

The setup for ultrasonic treatment of the solution included a reactor (*1*) with the working volume of 1 L. The emitter of the oscillations contained a waveguide (*2*) and an ultrasonic transducer (*3*). The waveguide system was fixed in a position to provide the generation of ultrasonic oscillations in the liquid volume in the reactor. The setup power and the liquid volume were chosen to provide the generation of oscillations in the entire volume of the fluid. The transducer was powered by an ultrasonic generator (*4*).

The output of the acoustical power of the system was 2.0 kW, the working frequency of the transducer and waveguide was 25 kHz. The parameters of acoustical equipment made it possible to reach an intensity of ultrasonic radiation into the liquid of 10 W/cm^2. To maintain the operating temperature at 60ºC, a heat exchanger was used. A scheme and a photograph of the ultrasonic setup are shown in Fig. 1.



(a) (b)

Fig. 1. Scheme (a) and photograph (b) of the ultrasonic setup

Two samples of nano TiO_2 were synthesized for comparison and morphological analysis.

2.2. Synthesis of nanoTiO_2 (sample 1)

TiO_2 nanoparticles were synthesized by hydrolyzing titanium sulfate $Ti(SO_4)_2$. A certain amount of titanium sulfate with a weight of 0.96 g was completely dissolved in 80 mL of distilled water and 10 mL of ethanol. The designated amounts of urea (2.4 g) and surfactant were subsequently added to the above solution. Synthesis was conducted at 60˚C under stirring for 1 h. The resulting gel was dried at 80°C for 4 h.

2.3. Synthesis of nanoTiO_2 (sample 2)

TiO_2 nanoparticles were synthesized by hydrolyzing titanium sulfate $Ti(SO_4)_2$. A certain amount of titanium sulfate with a weight of 0.96 g was completely dissolved into 80 mL of distilled water. The designated amounts of urea (2.4 g) and surfactant were subsequently added to the above solution. The prepared mixture was placed into the ultrasonic setup and heated to 60˚C under continuous ultrasonic impact for 1 h; the best results analyzed herein were obtained after a 4-h treatment. The operating frequency of the ultrasonic oscillations was 25 kHz (standard frequency for industrial applications). The resulting gel was dried at 80°C for 4 h.

2.4. Methods

The resulting material was studied by FTIR spectroscopy using a PerkinElmer Spectrum 100 FTIR spectrometer in a spectral range of 650–4000 cm^{-1}. Scanning electron microscope (SEM) images were recorded with a Quanta 200 electronic microscope operating at 30 kV with secondary and backscattered electrons in a high vacuum mode.

3. Results and discussion

The morphology and sizes of the titanium dioxide nanoparticles are shown in Figs. 2 (sample 1) and 3 (sample 2). Apparently, in the presence of water, hydrolysis results in the formation of hydrocomplexes, which can be represented as linear weakly crosslinked 'polymers' [9]. Further gelation can lead to the rearrangement of the atoms and the adhesion of intersecting linear chains of the polymer; these processes also have an effect on the grain growth during heat treatment. .An important role in the formation of a gel matrix is played by water molecules, which contribute to the formation of a continuous bound system owing to hydrogen bonding.

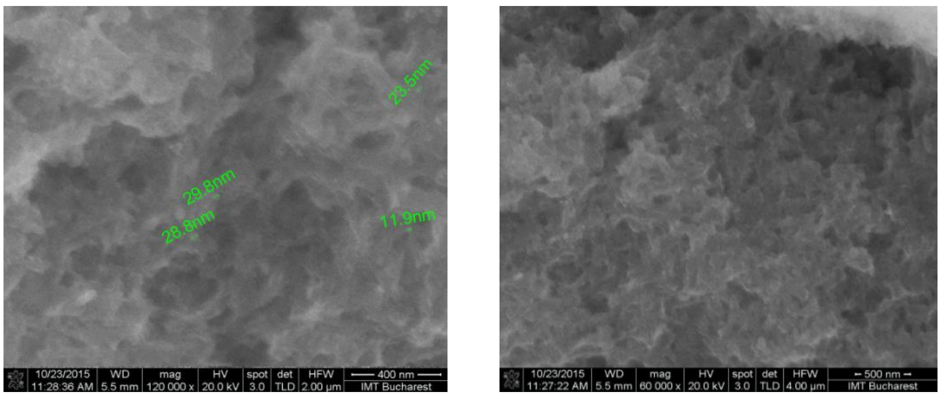


Fig. 2. SEM images of titanium dioxide nanoparticles (sample 1).

The micrographs in Fig. 2 show titanium oxide nanoparticles with sizes in a range of 10–30 nm in a gel matrix. The micrograph in Fig. 3 shows the nanoparticles synthesized using the ultrasonic setup. It was observed that these nanoparticles have a homogenous structure, which consists of well-formed spherical nanoparticles with sizes of about 50 nm.

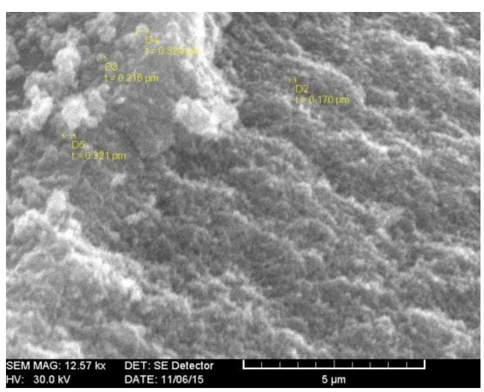


Fig. 3. SEM images of titanium dioxide (sample 2).

The FTIR spectra of TiO_2 nanoparticles of both samples lie in a range of 3600–550 cm^{-1}. No significant differences in the spectra of the two different samples were observed. A broad band was observed in a region of 3600–1650 cm^{-1}; it is assigned to stretching vibrations of hydroxyl (O–H), representing the water as moisture. An absorption band around 2054–2302 cm^{-1}

was observed; it is attributed to the existence of CO_2 molecules in the air. In both cases, we observed a peak between 800 and 450 cm^{-1}; this peak was assigned to the Ti–O stretching bands [10]. Strong absorption between 800 and 450 cm^{-1} has confirmed that the synthesized particles were TiO_2 nanoparticles.

4. Conclusions

In the present study, we have investigated the conditions of synthesis of nanosized titanium dioxide particles using a sol–gel method. We have studied the effect of ultrasound on the resulting nanoparticles and analyzed the possibility of using ultrasound during synthesis to avoid or reduce the use of ethanol. The morphology of the resulting nanoparticles has been studied. The research has confirmed that ultrasound contributes to the formation of nanoparticles with a homogeneous shape and a narrow size distribution. The research has shown a great potential for the application of ultrasound in new environmentally friendly industrial processes for the formation of TiO_2 nanoparticles with predefined characteristics owing to the substantiated possibility of reducing the ethanol consumption.

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