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ORIGINAL PAPER

Preparation of Sn doped nanometric TiO_2 powders by reflux and hydrothermal syntheses and their characterization

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Abstract Hydrothermal and reflux synthesis methods were utilized for the preparation of 5% Sn doped TiO_2 nanopowders. Obtained powders were subjected to particle size and specific surface area measurements, flame atomic absorption spectroscopy, X-ray diffraction analyses and transmission electron microscopy examination. TiO_2 powder prepared by hydrothermal synthesis presented a bimodal particle size distribution with average particle sizes of about 3 and 10 nm, whereas TiO_2 powder synthesized by reflux method had an average particle size of 7 nm. Specific surface areas of hydrothermal and reflux synthesized TiO_2 were 130 and 115 m^2/g, respectively. Sn doping in TiO_2 was 95.8% in hydrothermal and 86.4% in reflux synthesis as measured by FAAS, respectively. Photocatalytic activities of the obtained TiO_2 powders were evaluated by decomposition of malachite green solution in a solar box. Photocatalytic activity of hydrothermally synthesized TiO_2 was fairly higher in visible light and slightly higher in UV light than the activity of reflux synthesized TiO_2.

Keywords Nano particle · TiO_2 · Photocatalysis · Hydrothermal synthesis · Reflux synthesis

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1 Introduction

TiO_2 powder in nanometric form has been widely utilized as a pigment, as an additive in paints and in ointments, and in photovoltaic and electrochromic applications. It has also been used in photocatalytic sterilization, self-cleaning (SC), organic contaminant treatment and air purification applications due to its well-known photocatalytic effect [1–5]. Photocatalysis is essentially the breakdown of organic pollutant compounds on the surface of TiO_2, with the aid of ultraviolet (UV) or visible (VIS) light [1–3, 6]. The SC property of TiO_2 in both powder and film form has been widely investigated [1, 2, 4, 5, 7, 8], however, these studies mostly dealt with TiO_2 powder [2, 7, 8]. The efficiency of photocatalysts in powder form is superior to films due to the much larger specific surface area of powders, which provides relatively shorter duration of photocatalytic cleaning reactions.

Removal of organic contaminants in wastewater is an important issue for preventing the pollution of environment and preserving the clean water sources. Dyes, arising especially from textile industry are toxic pollutants that are present in industrial wastewater. Their treatment via physical or biological means is difficult. Utilization of TiO_2 as a promising heterogeneous photocatalyst for removal of organic pollutants from industrial wastewater has emerged in the last decade.

Many oxides have suitable band gap for photocatalysis. Among them, TiO_2 has attracted attention since it encompasses better properties such as low cost, non-toxicity and chemically stability. One significant downside of TiO_2 for SC applications is its wide band gap (Eg = 3.2 eV), which bounds its service to UV irradiation only. Thus, most of the solar irradiation (~95%) cannot be benefited by the TiO_2 photocatalyst. Metal ion doping into TiO_2 has been investigated for providing absorbance also in the visible region. Another aid of doping TiO_2 with metal ions in proper amounts, was suggested to be suppressing of the hole–electron recombination. Electron- hole recombination is detrimental for photocatalytic activity and it decreases efficiency of photocatalyst [9, 10].

Photocatalytic activity of TiO_2, doped with metal ions such as Al^{3+}, V^{5+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Zn^{2+}, Sn^{4+}, and Ce^{4+}, has been investigated [5, 11–14]. Type and amount of doping is important in enhancing the photoactivity of TiO_2 under UV and visible light. Dopants, in specific ranges depending on the type of the dopant, were reported to be effective in augmenting the photocatalytic activity of TiO_2. On the other hand, ratios of dopants out of the proper range were harmful [11, 13, 15, 16]. It is difficult to compare the activities or ratios of dopants in TiO_2 reported in different studies in literature, since TiO_2 was prepared by various methods and doping contents were reported in various forms like mole %, wt. %, or wt. % of dopant compound for instance in the form of metal nitrate, etc. [17].

Photoactivity of Sn doped TiO_2 powder has been investigated [12–15, 18], and 5% Sn was reported to enhance the activity of TiO_2 [12, 13]. The positive effects of SnO_2 and also of other dopants was proposed to be introducing new electronic states into the band gap of TiO_2, decreasing the TiO_2 particle size and increasing the surface area thereby providing higher adsorption, and separation of the charge carriers [14, 15, 18].

TiO_2 powders, doped with different metal ions were prepared via various techniques such as sol–gel [11–14], hydrolysis of inorganic salts [19], ultrasonic technique [20] and hydrothermal method [13, 21–23]. The extent of doping depends on the type of the synthesis method. In most of the processes, a calcinations step is required in order to attain the crystal structure of TiO_2. Calcination results in growth of TiO_2 grains, leading to loss of surface area and loss of photocatalytic efficiency [21]. Hydrothermal process is a relatively low temperature technique, in which the reaction takes place in a closed autoclave under high vapor pressure. Good control of the composition of the products is achieved in hydrothermal process and calcination of the products is mostly not necessary. It is environmentally friendly since reactions proceed in a closed system [21, 22, 24]. The need for an expensive autoclave may be counted as the drawback of this process. Reflux synthesis is also a low temperature method. In this method the reaction takes place in a heated container, which is connected to a reflux condenser system open to atmosphere. The vaporized solvents are condensed back into the reaction medium and long lasting reactions can be accomplished.

Aim of this study is to prepare Sn doped TiO_2 nanopowders by two different techniques, namely reflux and hydrothermal methods, and to investigate the photocatalytic activity of the formed powders. These methods were selected due to their low process temperature and lack of necessity for calcination of the products. For this purpose, photocatalytic degradation of malachite green (MG), a dye that is commonly used in textile industry, was tested in the presence of prepared TiO_2 powders by two different methods.

2 Materials and methods

2.1 Chemicals and apparatus

The reagents employed were titanium (IV)-*n*-butoxide [$Ti(OBu^n)_4$, 97%, Fluka] as TiO_2 source, hydrochloric acid (Merck, 37%) as catalyst, tin (IV) chloride (Alfa Aesar, 98%) as dopant, deionized water as hydrolysis agent. Malachite Green (MG) was used as a model pollutant (analytical reagent grade).

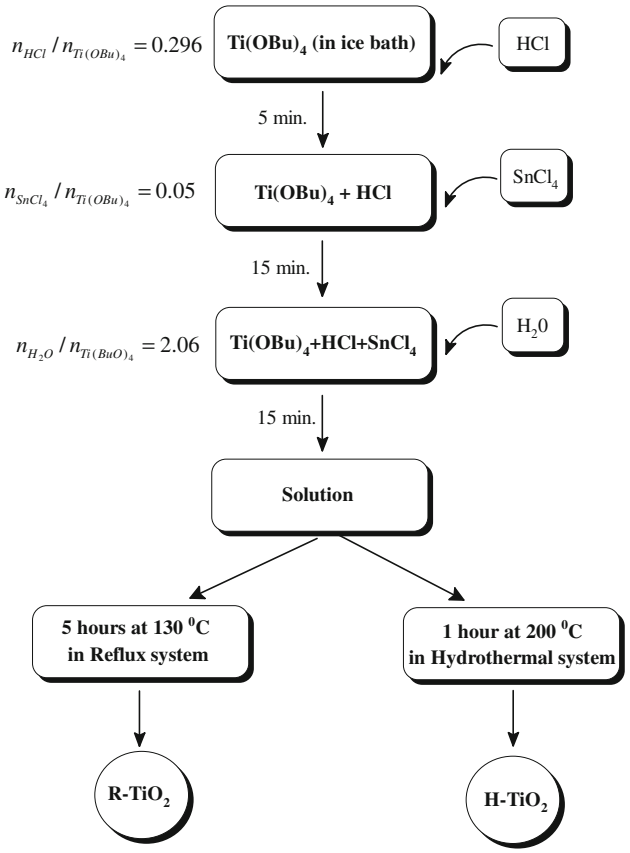
Nano-TiO_2 powders were synthesized by two different methods. In the first method, a Berghoff hydrothermal unit having time and temperature controllers was utilized. In the second method a condenser reflux system was used. A Rigaku Geigerflex D Max/B model X-ray diffractometer (XRD) with Cu Kα radiation ($\lambda = 0.15418$ nm) in the region $2\theta = 10°–70°$ with a step size of 0.04° was used for determining the crystalline phases.

Size of Sn doped TiO_2 particles was investigated by transmission electron microscopy (TEM, FEI Tecnai G2F30). Elemental composition of the particles was investigated by flame atomic absorption spectroscopy (FAAS).

Dye concentration in the aqueous solution was measured in predetermined durations after irradiation by a Varian Carry 5000 model UV–vis–NIR spectrophotometer. Sn doped TiO_2/dye solution was irradiated with/without 400 nm cut-off filter in a solar box (Erichsen, Model 1500) with an Xe lamp (690 W/m^2).

2.2 TiO_2 powder synthesis

Flowsheets for hydrothermal and reflux syntheses are presented in Scheme 1.



Scheme 1 Preparation steps and parameters of TiO_2 by hydrothermal and reflux methods

2.2.1 *Hydrothermal method*

$Ti(OBu^n)_4$ was cooled in an ice-bath, then HCl (37% w/w) was added within 15 min into the cooled $Ti(OBu^n)_4$ dropwise by a burette. After stirring for 5 min at ambient temperature, required amount of tin (IV) chloride was added. Final solution was stirred until a clear and homogeneous solution was formed. Then, required amount of water was added within 10 min into the solution dropwise by a burette. $HCl/Ti(OBu^n)_4$, $SnCl_4/Ti(OBu^n)_4$ and $H_2O/Ti(OBu^n)_4$ mol/mol ratios were 0.296, 0.05 and 2.06, respectively. Gelation occurred after water addition. Reaction was allowed for 2 h, and then a viscose solution was obtained. The solution was transferred into a 250 mL Teflon bomb which was then closed. The closed bomb was placed inside a preheated (200 °C) stainless steel autoclave. Reaction was conducted at 200 °C for 1 h. The Teflon bomb was removed from the hydrothermal unit and it was cooled to room temperature. Obtained powders were separated by centrifuging and they were dried in a vacuum sterilizer. Thus, nanosized TiO_2 particles having yellow color were obtained.

2.2.2 *Reflux method*

Nano-TiO_2 particles were synthesized with the same molar ratios as mentioned above. The reaction was carried out in a glass balloon which was heated in an oil bath at 130 °C for 5 h. The balloon was connected to a reflux condenser system open to atmosphere.

2.3 Preparation of TiO_2 sols

TiO_2 (0.625 g) sols were prepared by ultrasonically dispersing the synthesized TiO_2 powder in deionized water (for H-$SnTiO_2$), and in water: n-propanol (for R-$SnTiO_2$) (1:1, w/w) mixture without using a dispersant. The solvents and TiO_2 particles were treated in an ultrasonic bath for a few minutes. Finally, transparent TiO_2 sols were obtained.

2.4 Photocatalytic degradation of malachite green

For photocatalytic decomposition experiments, 62.5 μL of dye solution (from 2.5 ppm stock solution of MG) was added into TiO_2 sol (24.94 mL, 2.5% TiO_2 (w/w)). The light of the empty solar box was kept on for 15 min for stabilization before starting the test. Meanwhile, the nano-TiO_2/MG sol was poured into the transparent polysytrene reaction cell consisting of 12 separate compartments. The cell was placed into the Solar Box. The decomposition of MG was monitored by measuring the absorbance at 617 nm (λ_{max}) by UV–VIS spectrophotometer. Decomposition of MG was quantified by detecting the MG concentration after 20, 40 and 60 min during UV and VIS—irradiation.

3 Result and discussions

3.1 Structure of TiO_2 powders

XRD patterns of Sn doped TiO_2 powders prepared by hydrothermal and reflux methods are presented in Fig. 1. It was seen that TiO_2 powders synthesized by both methods had anatase crystal structure. All the peaks of anatase phase TiO_2 could be clearly determined on the XRD patterns of the synthesized powders. Peaks of rutile and brookite phases, which are known to have less photocatalytic effect, were not present. The peaks on the XRD patterns at 25.39°, 38.11°, 48.47° and 55.01° pertaining to (101), (004), (200) and (211) planes matched well with those of anatase TiO_2 reported in literature [25] (ICDD card no: 21-1272). The peaks were seen to be wide, which can be taken as an indication of the nanometric size of the TiO_2 crystallites.

Particle size distributions of the synthesized TiO_2 powders which were determined by a Malvern Zetasizer Z/S unit are presented in Fig. 2. TiO_2 powder which was

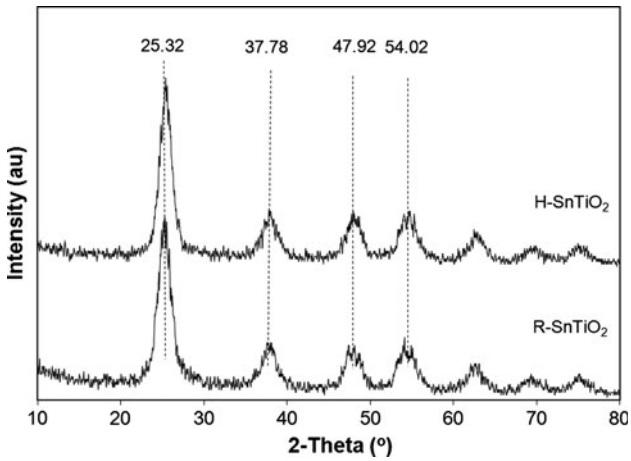


Fig. 1 XRD patterns of Sn doped TiO_2 powders synthesized by hydrothermal (H-$SnTiO_2$) and reflux (R-$SnTiO_2$) methods

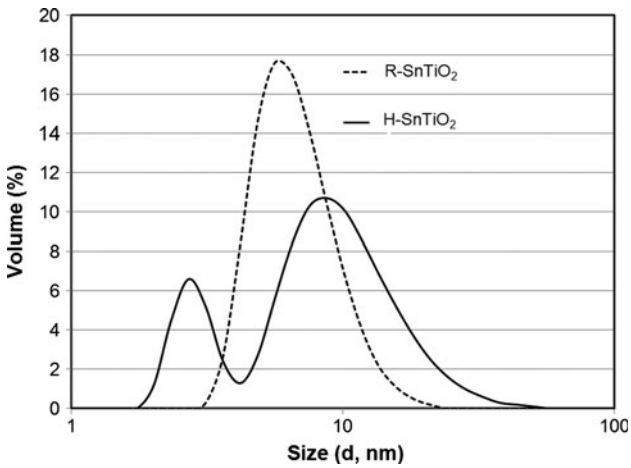


Fig. 2 Particle size distribution plots of Sn doped TiO_2 powders synthesized by hydrothermal (H-$SnTiO_2$) and reflux (R-$SnTiO_2$) methods

synthesized by reflux method had an average particle size of 7 nm. On the other hand, hydrothermally synthesized TiO_2 presented a bimodal particle size distribution with average particle sizes of about 3 and 10 nm. Formation of larger particles in hydrothermal synthesis as compared to reflux method may be due to higher temperature utilized in this process. Hydrothermal synthesis was conducted at 200 °C, whereas in reflux method temperature was kept at 130 °C. Surface areas of the Sn doped TiO_2 powders synthesized by hydrothermal and reflux methods were 130 and 115 m^2/g, respectively. Comparison of the particle size and specific surface area of TiO_2 powders is presented in Table 1. Photocatalytic activity of nano TiO_2 powder is strongly related to particle size and specific surface area. The lower is the particle size and the higher is the specific surface area, the higher is the photocatalytic effect. In the employed methods, crystalline anatase phase TiO_2 was obtained at low temperatures and as a result the calcination step was avoided. This helped preserving the nanostructure of the TiO_2 particles. Therefore, the obtained powders in both methods presented high specific surface areas.

TEM micrographs the TiO_2 powders which were obtained by hydrothermal and reflux methods are presented in Fig. 3a, b c, d respectively. In the presented TEM micrographs sizes of the individual particles can be visualized to be in nanometric scale. The particle sizes observed in the TEM micrographs are in accord with the particle sizes which were measured by Zetasizer Nano Z/S as presented in Fig. 2. TiO_2 particles are about 5 nm as shown in Fig. 3.

The molar ratio of Sn to Ti was kept at 5–95 as shown in Scheme 1. This amount of Sn corresponds to 4.71 mol % (or 6.83 wt%) in the total amount of synthesized Sn doped TiO_2 powders. The filtrate solutions after reflux synthesis and hydrothermal synthesis were analyzed by FAAS and it was determined that formed TiO_2 contained 5.9 wt% Sn and 6.54 wt% Sn, respectively. These results indicate that 86.38% of the Sn in reflux synthesis and 95.75% of Sn in hydrothermal synthesis were incorporated into the TiO_2 lattice structure. Higher doping amount of Sn into TiO_2 in hydrothermal synthesis may be due to higher temperature applied in this method and also may be due to high pressure provided in the autoclave.

3.2 Photocatalytic activity tests

Photocatalytic effects of Sn doped TiO_2 powders obtained by the two methods were investigated by keeping 2.5 ppm MG in 2.5% (w/w) TiO_2 sol for 20–60 min under UV and VIS light in a solar box and by measuring the absorbance of MG by spectrophotometer. Height of the MG peak at 617 nm corresponds to the concentration of MG in solution. Height of the peak of MG was measured and thus % decomposition of MG as a result of photocatalytic reaction

Table 1 Properties and photocatalytic activities of synthesized powders

	Average particle size (nm)	Specific surface area of powder (m^2/g)	Sn doping achieved (%)	Degradation % of MG in visible light in 60 min.	Degradation % of MG in UV light in 60 min.
H-TiO_2	3, 10	130	95.8	81	90
R-TiO_2	7	115	86.4	61	92

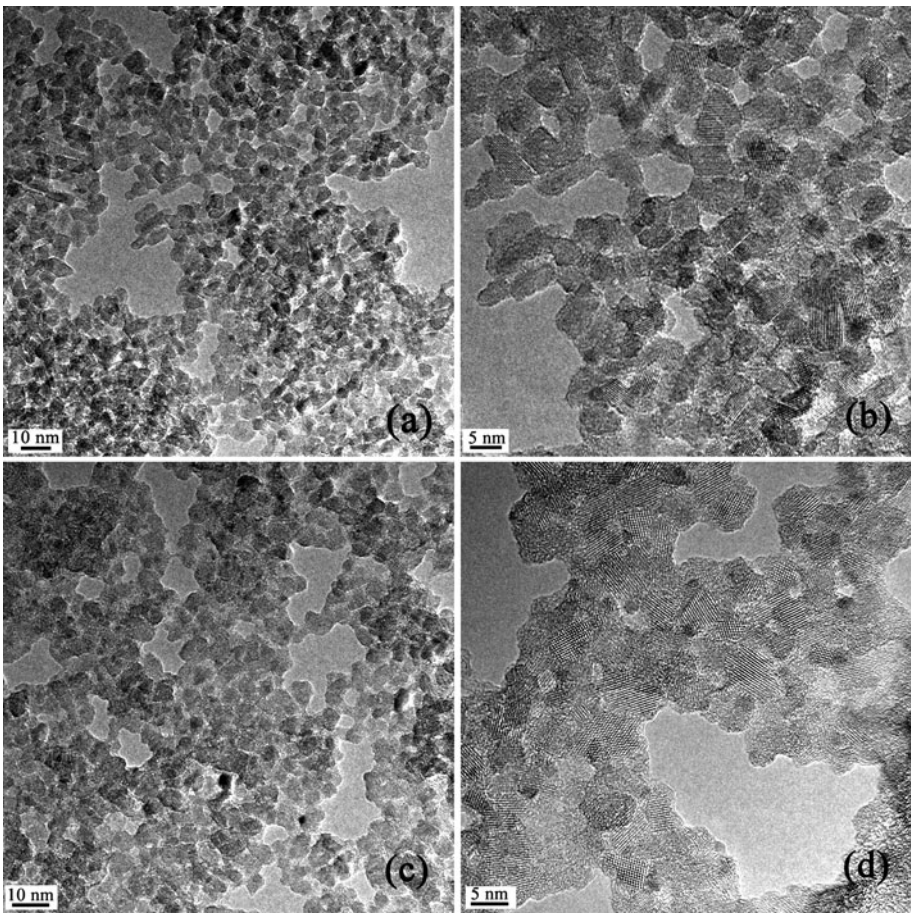


Fig. 3 TEM micrographs of TiO_2 powder agglomerates formed in **a**, **b** hydrothermal synthesis and **c**, **d** reflux synthesis

was determined by following the decrease of the peak height. The results are presented in Fig. 4. Photocatalytic activity of hydrothermally synthesized TiO_2 was seen to be considerably higher than that of reflux synthesized TiO_2. This was an expected result since Sn doping achieved in hydrothermally synthesized TiO_2 was higher than that in reflux synthesized TiO_2, as shown in Table 1 and Fig. 4. Sn doping causes a shift in the absorbance of the TiO_2 powders into visible region [22]. Higher Sn dopant amount leads to larger absorbance, which results in higher photocatalytic activity under visible light. In addition, specific surface area of H-$SnTiO_2$ was larger than that of R-$SnTiO_2$. This is another reason of higher photocatalytic activity of H-$SnTiO_2$. On the other hand in the UV illumination, photocatalytic activity of H-$SnTiO_2$ was slightly higher than or similar to that of R-$SnTiO_2$ as shown in Fig. 4. Slightly higher photocatalytic activity of H-$SnTiO_2$ may be a consequence of its larger surface area.

It is difficult to compare the obtained results with those of the previous studies since in the literature decomposition of different organic agents at different concentrations was investigated. In the study of Liqiang et al. [26], Sn doped TiO_2 nano powder was obtained through sol–gel route by mixing $Ti(OBu)_4$, ethanol, H_2O and HNO_3. Products were calcined at

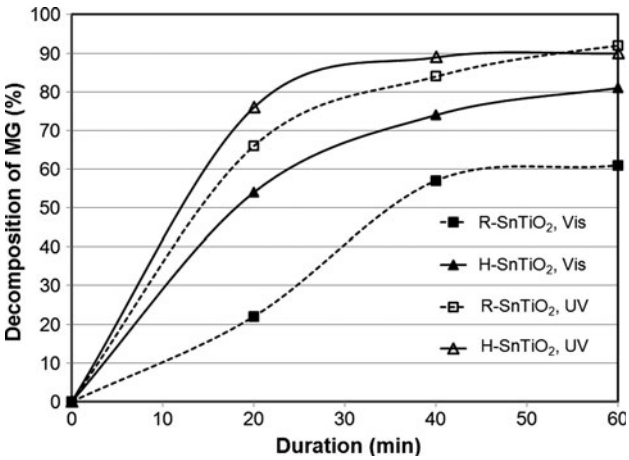


Fig. 4 Decomposition plots of MG via photocatalytic reaction of Sn doped TiO_2 powders synthesized by hydrothermal (H-$SnTiO_2$) and reflux (R-$SnTiO_2$) methods

500–700 °C. Photocatalytic degradation of phenol was the highest (20% degradation in 1 h) when the powder was calcined at 600 °C. In another study, Sn doped TiO_2 was utilized in the form of films on glass surfaces by Sayılkan et al. [27]. MG degradation of the obtained films were much lower when compared to that of the Sn doped TiO_2 powders in the present

study. In 1 h, degradation of MG was reported to be less than 50%. This is an expected result since the surface area of the film is lower than that of TiO_2 in powder form.

4 Conclusion

Synthesis of 5 mol % Sn doped TiO_2 (Sn to Ti molar ratio 5/95) nanopowders were accomplished through hydrothermal and reflux methods at 200 and 130 °C, respectively. Both methods produced anatase phase TiO_2 at low temperatures therefore calcination of obtained powders was not necessary. Hydrothermally synthesized TiO_2 powder presented higher photocatalytic activity than that of reflux synthesized TiO_2. This was attributed to higher Sn content as well as larger specific surface area of hydrothermal TiO_2. Reflux method is advantageous in terms of lower equipment cost and less labor over hydrothermal synthesis. Further adjustment of experimental parameters of reflux synthesis such as lower temperature and longer duration may result in formation of TiO_2 powders having higher Sn content and higher specific surface area. Hazardous effects of organic contaminants to the environment can be prevented by the use of photocatalytic TiO_2 powder prepared by hydrothermal or reflux synthesis.

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