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Effect of microwave heating on the structure, morphology and photocatalytic activity of hydrogen titanate nanotubes

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ABSTRACT

Microwave annealing was employed to prepare well defined titanate nanotubes after hydrothermal treatment of titania precursor at mild conditions. The microwave annealed samples were used for the enhancement of UV-light-driven photocatalysis capabilities of Rose Bengal from liquid phase. The structural and catalytic activity changes were studied as a function of microwave annealing temperature. Different characterization techniques such as thermal and spectroscopic techniques were employed to characterize the as-prepared and microwave annealed samples. Characterizations confirmed the formation of hollow layered titanate nanotubes with diameter of ≈11–13 nm and several millimeter in length in the as prepared samples. Titanate was the main structure of the prepared hollow nanotubes. These nanotubes undergo a partial collapse after elevating the microwave temperature to 450–550 °C. Moreover, all the nanotubes were converted to nanoparticles after 600 °C with particle size ranged between 9 and 16 nm. The prepared samples showed significant catalytic performance in the photo oxidation of Rose Bengal (probe reaction) under UV irradiation. Moreover, the sample heated at 300 °C presented the highest catalytic activity among the prepared samples.

Introduction

A revolution of nanotechnology and its research fields and applications was initiated in the past few years. Nanostructures (nanotubes, nanowires, and nanobelts) containing Ti such as titania (TiO_2) and titanate ($Na_xH_{1-x}Ti_3O$ and $H_2Ti_3O_7$) have attracted much attention due to its multiple applications in electronics, optics, catalysis, sensors, and energy conversion [1–4]. Large specific surface area is one of the most important characteristics of nanotubes compared to bulk materials. Titania nanotubes (TNTs) also provide channels for enhanced electron transfer. Thereby, they help to increase the efficiencies for solar cells, electrolysis, and photocatalysis [5]. Besides the larger specific surface area of TNTs, they have elongated shape that helps to exhibit improved photogenerated charge carrier separation than bulk TiO_2 nanoparticles [1,2].

Microwave annealing method has many advantages in preparation and application reactions. It offers an energy efficient, cost effective, clean, and eco-friendly method of heating. It also gives rise to higher yields, leads to enhanced structural and morphological properties of nanomaterials compared with classical thermal heating [6].

Because it is a low temperature technology, hydrothermal synthesis is used in the fabrication of titania nanotubes and it has been comprehensively investigated in previous reports [7,8]. Moreover, it is preferred because of the simple control of the aqueous solution. Also, it is environmentally friendly since water is used as a solvent in a closed system [9–12]. Nevertheless, this method needs more studies to discuss detailed information about the thermal stabilities mechanisms, crystalline structures, compositions and post-treatment functions which are still matters of debates [13,14]. Hydrothermal method was introduced by Kasuga et al. [7,8] who used it for the production of small diameter TNT and he concluded that the as-prepared nanotubes were mainly titania and were formed during the process of washing after the hydrothermal treatment. On the other hand, hydrogen titanate ($H_2Ti_3O_7$) nanotubes were observed by Du et al. [15], however, Suzuki et al. [16] proved that the composition of the as-prepared nanotubes was mainly hydrated hydrogen titanate, $H_2Ti_3O_7.nH_2O$ ($n < 3$).

It is noteworthy to mention that TNTs based materials combine the properties of TiO_2 nanoparticles (e.g. photocatalytic activity)

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with the properties of layered titanates (e.g. ion-exchange facility). Therefore, TNTs can be widely used in various applications such as photocatalysis [17], as substrates decorated with different active catalysts [18], dye-sensitized solar cells [19], transparent optical devices [20], and gas or humidity sensors [21]. To the best of our knowledge, there is a lake of studies on the effect of microwave heating treatment of hydrothermally prepared TNT derived from anatase precursor.

The release of industrial wastewater containing wide spectrum of organic hazardous pollutants in the environment has been widely known as a potential environmental threat. Therefore, environmental degradation has now become a global problem and maintaining the ecosystem is a serious issue [22]. Rose Bengal (RB) is a halogen-containing fluorescein water soluble dye which has wide medical applications. Neckers [23] reported that RB has an important role among dyes due to a number of reasons related to its photophysical and photochemical properties. It is used as a stain for identifying certain types of tissues while screening for diseases. Also, it is used in liver function testing, staining of necrotic tissue in the eyes, treatment of eczema and psoriasis, cancer treatment for certain types of melanoma and breast cancer, etc. [24]. Although, as above-mentioned, RB has several medical applications, it has severe toxic effects on the human corneal epithelium [25,26]. Moreover, it is extremely hazardous when it comes in contact with skin and creates itching, scaling, irritation, reddening and even blistering. Also, it causes redness, watering, inflammation and itching in eyes. On ingestion by inhalation, it damages mucous membranes, which leads to respiratory irritations in humans [24]. Additionally, RB is a xanthenes dye and is widely used in photochemical industries, textiles, dyeing and many other applications. The toxic effect of RB has been studied by Sako et al. [27,28] on *Paramecium caudatum* and cultured fetal rat hepatocytes. The authors observed that RB is toxic and also inhibits leucine aminopeptidase. Therefore, there is an urgent need to get rid of it from industrial wastewater.

Besides photocatalysis, there are some conventional methods used for the removal of RB such as ultra filtration, extraction, adsorption and oxidation with ozone and hydrogen peroxide. Photocatalytic reaction is favoured due to its simple reactor design. Generation of highly reactive hydroxyl radicals is considered as the base of the full degradation of dyes in general [29]. Photocatalysis in general and photo-catalytic detoxification of industrial wastewater samples had wide applications [30]. Over the last two decades, photocatalysis using TiO_2 nanoparticles has been shown to be potentially advantageous and useful for the degradation of wastewater pollutants because of its non-toxicity, biological and chemical inertness and high photoactivity [29].

Considering the above indicated facts in this context, the aim of the present work was to apply microwave heating and study its effect on the structure and morphology of titania nanotubes prepared by hydrothermal method. Different thermal and spectroscopic techniques will be used in the characterization of the prepared nanotubes. The photocatalytic degradation of the hazardous organic pollutant RB over TNT was used as a probe reaction to evaluate the catalytic activity of the prepared TNT samples and to test its efficiency to upgrade water quality.

Experimental

Preparation of titania nanotubes

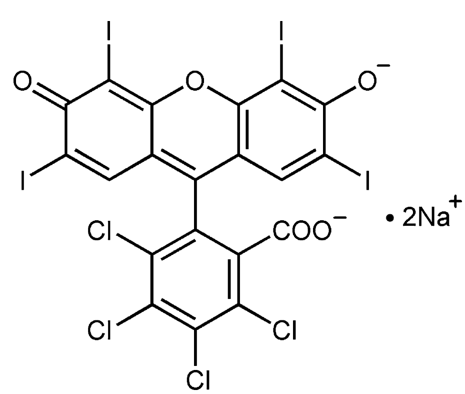
Titanate nanotubes (TNTs) were synthesized by hydrothermal method using TiO_2 (anatase) precursor as described before in literature [7,8]. Briefly, a sample weighing 2.0 g TiO_2 was added to 75 ml of 10 M NaOH solution under vigorous magnetic stirring for about 1 h to form a white suspension. This suspension was then transferred into 100 ml Teflon-lined stainless steel autoclave, which was allowed to react at 130 °C for 24 h. After being cooled to room temperature, the titanate powder was washed with dilute HNO_3 (pH 3) and then distilled water for several times till the residue solution was neutralized. This washed paste was dried in air overnight at 60 °C and then heated at different temperatures in the range of 100–600 °C for 30 min in Phoenix Microwave Muffle Furnace (CEM Corporation, Matthew, NC, USA).

Characterization of titania nanotubes

Thermogravimetric analysis and differential scanning calorimetry supply information about the thermal stability of the samples, their composition and possible phase transformations. Thermogravimetric (TG) and differential scanning colourimetric (DSC) analyses were performed on Netzsch STA 449F3 with system interface device. Experiments were performed using sample weight of 6.0 ± 0.3 mg. All the experiments were conducted under nitrogen as the purge gas with 50 ml/min flow rate in the temperature range of 30–1000 °C and ramp rate of 5 °C/min. The shape and particle size distribution were studied using transmission electron microscope (TEM) operated at 120 kV accelerating voltage (JTEM-1230, Japan, JEOL). X-ray diffraction (XRD) analysis was performed using an automated diffractometer (Philips type: PW1840) with Cu Kα radiation (λ = 1.54060 Å). Scans were performed in step of 0.02°, scanning rate of 2° in 2θ/min in the range of 4–80°. EDX analysis was accomplished to detect the presence of Na ions using an X-ray energy dispersive spectroscopy (JOEL, Model: JSM-5600, Japan) and all the samples were coated with gold. FTIR spectroscopic measurements were carried out using a spectrometer (FTIR, JASCO 470). The samples were mixed with KBr with a sample/KBr weight ratio of 1/100 and compressed to a desk for measurements. Raman laser spectra of samples were measured in the range of 100–1000 cm^{-1} using Bruker FT-Raman microscope with laser 50 mW.

Photocatalytic activity of titania nanotubes

The photocatalytic activity of TNT heated in microwave at different temperatures was evaluated using the photocatalytic degradation of Rose Bengal (RB) as a probe reaction in Pyrex made beaker over a magnetic stirrer. For irradiation experiments, 100 ml (1×10^{-5} M) solution RB ($C_{20}H_2C_{l4}I_4Na_2O_5$, MWt. 1017.65, LABA Chemie, CI # 45440), Structure 1 , was taken into the reactor. 2 ml H_2O_2 (35%) was added before addition of the required amount of the catalyst (0.1 g) to the dye solution. Before irradiation, the solution was magnetically stirred in the dark for 20 min to attain the adsorption equilibration of the system and therefore, the zero time reading (t_0) was obtained before irradiation using Varian Carry



Structure 1. Molecular structure of Rose Bengal salt: quinoid (q) form.