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Microwave Assisted Hydrothermal Synthesis of TiO_2 Nanorods for Photocatalytic Application

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Abstract- *In this work, TiO_2 nanorods were grown using microwave assisted hydrothermal technique. The samples were characterized in detail by XRD, FE-SEM, Raman, and UVvisible spectrometry techniques. Besides, photocatalytic characteristics were evaluated through measuring the degradation rate of methylene blue to establish a correlation between structure and photochemical properties. We were able to control morphology of the TiO_2 nanorods by changing the reaction time during synthesis. The samples possessed a rutile phase and the crystallinity of the samples was significantly enhanced when the reaction time increased. The FE-SEM images show that nanostructures consist of several nanorods coming out of a single core and have very sharp edges. It was observed that the length and diameter of nanorod can be modified by changing the reaction time. The as prepared sample (for reaction time of 45 min) shows good photocatalytic activity. We established photocatalytic characteristics of TiO_2 nanorods for technological application.*

Keywords: Titania, Hydrothermal, Photocatalysis, XRD, FE-SEM

Introduction

Recently, metal oxide based photo catalysts have been center of attention due to their potential photo degradation of pollutants [1-2]. As a kind of metal oxide, TiO_2 was recognized as the best photo catalyst to decompose the pollutants for the waste water treatment and air pollution due to its good performance, such as long-term stability, broad functionality, and non-toxicity [2]. Up to date, many research works have been published in respect to the synthesis and high photocatalytic efficiencies of TiO_2 nanostructures [1-3]. The hydrothermal method is widely used due to its small particle size, and low cost [4]. In this technique, surface morphology and crystal size can be easily controlled through various parameters, such as synthesis temperature, time, reactants concentration, etc [5]. Therefore, many studies have been focused on synthesis of TiO_2 by using hydrothermal method [4-5]. But these works are mainly in respect to TiO_2 prepared with longer than 12 h of reaction time. There are few works reported about the influence of a short reaction time [6].

In this paper, we report the synthesis of the TiO_2 nanostructure with a very short reaction time. The TiO_2 nanorods were synthesized by a microwave assisted hydrothermal method, and a photocatalytic property of the samples has been studied. The prepared TiO_2 nanorods have potentials to be used as photo catalysts.

Experimental Procedure

The reagents titanium butoxide (C16H36O4Ti; 99.9%), cetyltrimethylammonium bromide (CTAB) [(C16H33)N(CH3)3Br, 99.9%], and hydrochloric acid (HCl; 99.99%) used in the experiments were of analytical grade. The CTAB (1.5 g) was added into 30 ml of distilled water and fixed amount of titanium butoxide was dissolved in 15 ml of HCl, separately. Then the both solution was mixed and stirred for 1 h. Finally, the resultant solution was transferred into a 100 ml Teflon-lined digestion vessel and treated at a selected temperature (150 o C) for three different reaction time of 30, 45, and 60 min at a selected pressure of 150 psi in a microwave-hydrothermal (CEM; MARS-5). After microwave processing, the solution was cooled to room temperature. The resulting precipitate was separated by centrifugation, then washed with distilled water and absolute ethanol several times, and dried in an oven at 80 o C for 10 h. The crystal structure of the samples were analyzed by a Phillips X'pert (MPD-3040) Xray diffractometer with Cu Kα radiation (λ = 1.5406 Å). The morphologies were characterized by FE-SEM (MIRA II LMH microscope). The length and diameter of the nanorods was evaluated from the FE-SEM images by image processing software. The Raman spectra were recorded by a Raman spectrometer (Renishaw inVia) with 514.5 nm Ar laser. The UV-visible absorption measurements were performed on a UV-3600 system (Shi-madzu, Japan). The photocatalytic performance of the TiO_2 nanorods was evaluated by the degradation of methylene blue (MB) under UV-light irradiation.

Results and Discussion

The crystal structure and phase purity of the all TiO_2 nanorods samples were confirmed by XRD. As shown in Fig. 1a, they were well matched with pure tetragonal rutile phase (JCPDS. 21-1272) with no impurities. As the reaction time increased, the diffraction peaks became sharper and their intensities increased, indicating a sample with high crystallinity. It is also confirmed by the FWHM values of XRD (110) peak as shown in inset of Fig.1a. Raman spectra were employed to further investigate the crystallinity and microstructure. The Raman spectra of the as obtained TiO_2 nanorods are displayed in Fig. 1b. The bands centered at 442.5, 606.0, 144.4 cm-1 are assigned to Eg, A1g, and B1g modes, respectively, and attributed to Ti-O vibrations [7]. These are the characteristic peaks of a rutile TiO_2 crystal system. The broad Raman peak at 238 cm-1 is attributed either to the second order scattering or disorder effects [7]. Also, the sharpness of the Raman peaks was observed to increase with increasing reaction time show that the crystallinity of the nanorods increased for the higher reaction time. These results well agree with the characterization by XRD analysis.

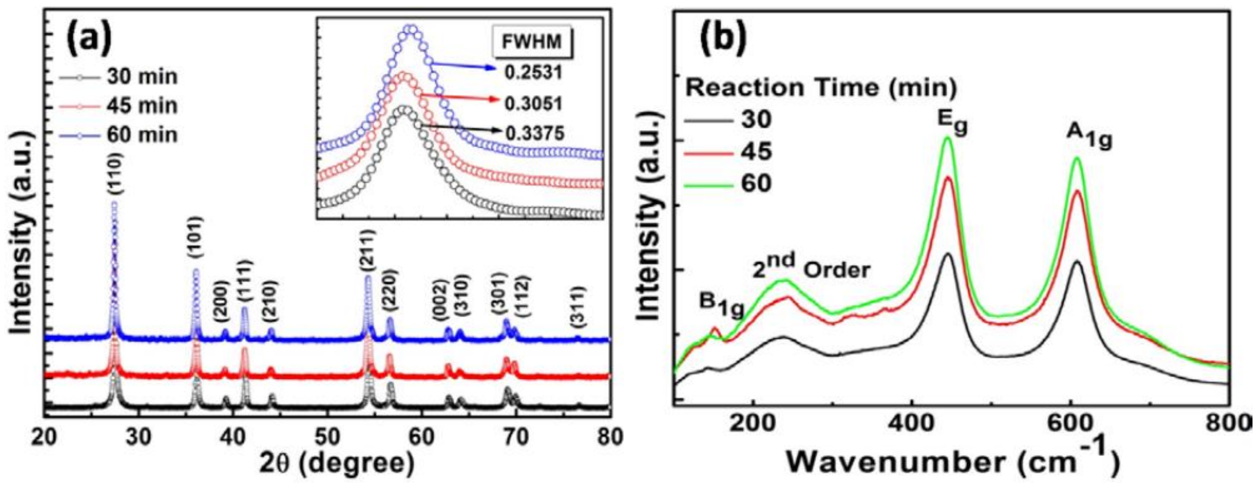

Fig. 1 (a) XRD and (b) Raman spectra of TiO_2 nanorods prepared for different reaction time.

The FE-SEM micrographs of the as prepared nanorods are shown in the Fig. 2(a-c). It can be seen from the obtained images that the nanostructures have three dimensional flowers like morphology. The nanostructures consist of several nanorods coming out of a single core and have very sharp edges. The diameter of the nanorods was calculated using image processing software by line intercept method. The obtained diameters are shown in the Fig 2e. From the XRD it was observed that upon increasing the reaction time the crystallinity increase, which holds true as we see the results of the FE-SEM, the overall length and the diameter of the nanorods increase as we go on increasing the reaction time. However, with increasing reaction time, the small primary particles eventually coarsen to form larger, more cohesive crystals with fewer visible defects, which is in agreement with the XRD peak narrowing (Fig. 1a).

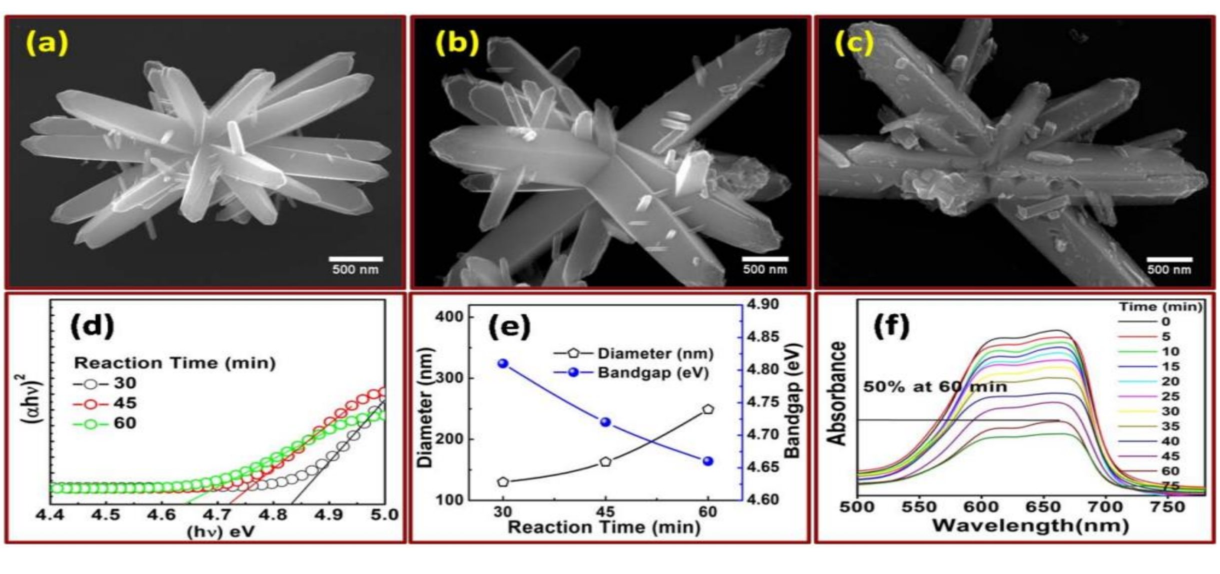

Fig. 2 FE-SEM images of the TiO_2 nanorods prepared for different reaction time: (a) 30 min, (b) 45 min, (c) 60 min; (d) Band gap, (e) Diameter, (f) Photocatalytic degradation of MB at different time intervals for the sample preapred with the 45 min of reaction time.

The optical band gap, Eg (see Fig. 2d) values of the TiO_2 nanorods were determined from the intercept of (αhν) 2 versus (hν) curves and found to be 4.83, 4.72, and 4.64 eV for the samples prepared with the reaction time of 30, 45, and 60 min, respectively. In contrast, the band gap obtained decreased monotonically from 4.83 to 4.64 eV (see Fig. 2e) as the reaction time of sample preparation increased from 30 to 60 min. This decrease is attributed to the shrinkage effect of the Eg because of the increase in nanorods dimension [8].

The photocatalytic activity of TiO_2 nanorods is examined by measuring the photodegradation of methylene blue (MB) under UV-light illumination, as shown in Fig. 2f. It is clearly observed from Fig. 2f that the intensity of the characteristic adsorption peak of MB decreased with the increase of irradiation time in the degradation process. Meanwhile, the color of the suspension faded away gradually with the increase of irradiation time in the experiment. It has been commonly accepted that a large surface area means high photo activity, because many substances can absorbed onto the active sites of the catalyst [9], and TiO_2 nanorods have high surface area as compared to their bulk counterpart. However, after 60 minutes of irradiation time the MB dye has been degraded to ~ 50% of its initial intensity. This is due to the efficient charge separation through the length of the nanorods and the high surface area enables the crystals to absorb more radiation for enhanced photocatalytic activity [9].

Conclusions

The TiO_2 nanorods with flower like morphology have been successfully prepared by microwave assisted hydrothermal method. The structural, morphological, and photocatalytic properties were analyzed. It was observed that the all the samples have pure tetragonal rutile structure. The crystallinity was found to increase with increasing the reaction time. The FESEM micrographs reveal that the TiO_2 nanostructures consist of several nanorods coming out of a single core and have very sharp edges. A good photocatalytic activity of the sample prepared for 45 min of reaction time was observed. This is due to the efficient charge separation through the length of the nanorods and the high surface area.

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