Preparation of TiO_2 nanorods by Sol–Gel template method and measured its photo- catalytic activity for degradation of methyl orange

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Abstract

Titanium dioxide nanorods have been prepared by sol-gel template method. The structural and surface morphology of the TiO_2 nanorods was investigated by X-ray diffraction (XRD) and atomic force microscopy (AFM), it was found that the nanorods produced were anatase TiO_2 phase. The photocatalytic activity of the TiO_2 nanorods was evaluated by the photo degradation of methyl orange (MO). The relatively higher degradation efficiency for MO (D%=78.2) was obtained after 6h of exposed to UV irradiation.

Key words

TiO_2 Nanorods, Photocatalytic activity, Methyl orange.

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تحضير قضبان نانوية من ثاني اوكسيد التيتانيوم بطريقة السول-جل وحساب فعالية التحفيز الضوئي لها من خلال تحلل المثيل البرتقالي

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الخلاصة

تم تحضير ثاني اوكسيد التيتانيوم قضبان نانوية بطريقة السول-جل. درس التركيب البلوري و طبيعة السطح لاوكسيد التيتانيوم نوع قضبان نانوية باستخدام حيود الاشعة السينية ومطياف القوة الذرية. لقد وجد ان ثاني اوكسيد التيتانيوم من نوع قضبان نانوية هو من طور الانتاس. كما تمت دراسة التحفيز الضوئي لثاني اوكسيد التيتانيوم من خلال التحلل الضوئي لصبغة المثيل البرتقالي، ان مقدار التحلل العالي لصبغة المثيل البرتقالي 78.2% حدث بعد مرور 6 ساعات من التعرض للاشعة فوق البنفسجية.

Introduction

Titanium dioxide (TiO_2) one-dimensional (1D) nanostructured materials (nanorods, nanowires, nanotubes, nanofibers) have attracted considerable attention because of their applications in various fields such as in dye-sensitized, solar cells, photo catalysis, photo-electrochemical applications, gas sensors and water splitting [1,2]. Various methods for the synthesis of TiO_2 one-dimensional (1D) nanostructures have been developed in recent years, including hydrothermal method, solvothermal method, sol-gel method, direct oxidation method, chemical vapor deposition (CVD), electro deposition, sonochemical method, and microwave method [3,4]. Among them template assisted synthesis is one of the most effective and promising method to synthesis nanoscale materials in nanotechnology because of its uniform pore size, relatively low cost and mode of preparation has been found as a productive way for the analysis of one dimensional structures of TiO_2. In the present work, TiO_2 nanorods are synthesized by direct sol gel filling and heating template method. The morphologies and crystal structures of the prepared TiO_2 nanorods were characterized using atomic force microscopy (AFM) and x-ray diffraction (XRD) and UV–vis spectrophotometry techniques. The photocatalytic efficiency of the nanorods was evaluated via photodegradation of methyl orange (MO) solution under UV irradiation.

Experimental

1. Preparation of TiO_2 samples

TiO_2 nanorods were prepared by using heating sol gel template method similar to that described previously [4, 5]. Briefly, the cleaned anodic alumina membranes (AAMs) with 60 μm thickness and80- 100 nm diameter pores (homemade) were used as template. The anodic alumina membranes were firstly boiled in ethanol at about 75-77 ºC for 10 min to enhance the hydrophilicity of alumina pore with TiO_2-sol, and then these anodic alumina templates were immersed into TiO_2-sol solutions at about 80 ºC for 10 min.

The TiO_2-sol is formed by mixing of titanium tetraisopropoxide (TTIP, Aldrich 97 %), acetylacetone (ACAC, HiMedia 99%), deionized water and ethyl alcohol (EtOH, Merck 99 %) at molar ratio of 1:1:3:20, TTIP is dissolved in a half amount of ethanol and then, a second solution is prepared by mixing ethanol with deionized water and ACAC. The EtOH/ACAC/H_2O solution was slowly added into the TTIP/EtOH solution to form the TiO_2 sol. The mixture was then stirred for approximately 2h at the room temperature. The resulting TiO_2 samples were drying in the air at room temperature for 24 h, then were put into a muffle furnace and heat-treated as the followed procedure. The samples were first held at 100°C for 4 h to remove the residual water. For the preparation of anatase TiO_2, the samples were heated up to (500) °C at a rate of 2.5±°C/min and held at this temperature for 2 h. The furnace was shut down and the samples were cooled back to room temperature naturally. Fig. 1 illustrates schematic flow chart of the procedure used in this study.

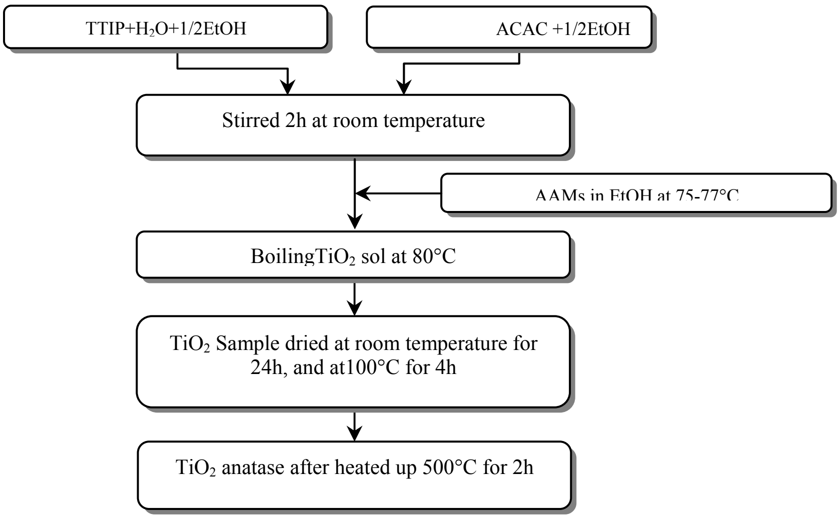


Fig.1: Flow chart showing preparation of TiO_2 nanorods through heating sol-gel template process.

2.Photocataiytic activity measurements

The photocatalytic activity of the samples was estimated by methyl orange (MO) ($C_{14}H_{14}N_3NaO_3S$) degradation performed in a 50-ml cylindrical glass photocatalytic reactor, and a 300W Xenon lamp was selected as the UV light source, then it was placed in photochemical box equipped with a fan with stirring in 30 cm distance from UV lamps, the concentration of MO solution was (5 ppm $=1.25\times10^{-5}$ M). The actual effect of photocatalytic activity by chemical reaction was studied by maintaining the solutions in the dark for 1 h before irradiation by UV. The MO solution (3 ml) was taken out every 2h and analyzed using UV–V is spectrophotometer. The degradation (D %) of MO can be calculated via the formula

$$D\% = (1 - A_i / A_o)\ \times 100 = (1 - C_i/C_o)\ \times 100 \qquad (1)$$

where A_o is the absorbance of the original MO solution before irradiation and A_i is the absorbance of MO solution measured every 2h.C_i and C_o are the corresponding dye concentrations, respectively. The photodegradation of MO follows pseudo-first-order kinetics. Its kinetics can be expressed as

$$\ln(C_o / C) = k\ t \qquad (2)$$

where k (min^{-1}) is the degradation rate constant. [6, 7]

Results and discussion

The X-ray diffraction patterns of the TiO_2 nanorods annealed at (500) °C for 2 h are shown in Fig. 2., All peaks are clearly assigned to the anatase of TiO_2 The sharp peaks at 2θ values of 25.392°, 37.661°and 47.134°, are a good match with the characteristic peaks of (101), (004), and (200), planes of the anatase phase of TiO_2 (JCPDS no. 21-1272).

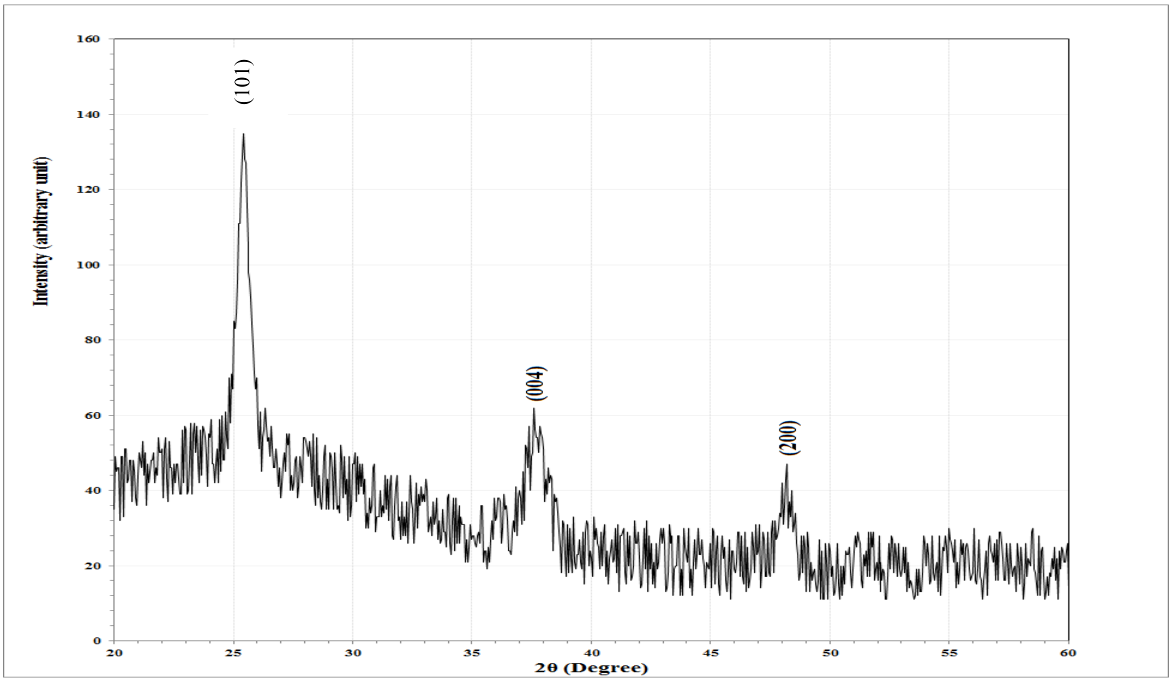
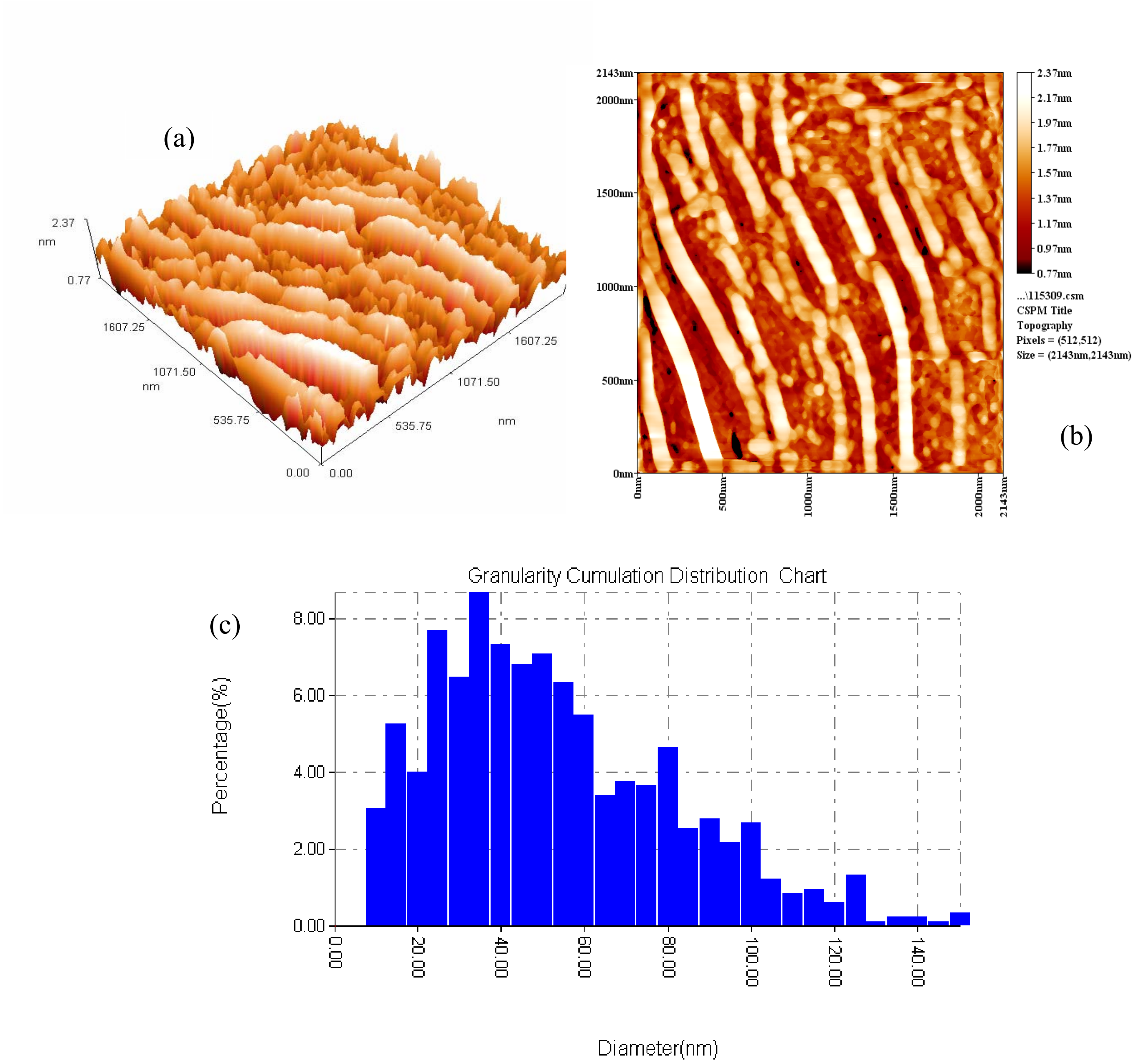


Fig.2: XRD pattern of TiO_2 nnorods prepared by sol gel template method and annealed at 500°C for 2h.

The surface morphologies and roughness of the TiO_2 nanorods are presented in Fig.3a and b, the histogram is shown in Fig.3c. The Avg. Diameter of TiO_2 nanorods is equal to 50.71 nm.



Roughness Average	Root Mean Square	Surface Seqewness	Surface Kurtosis
0.276 nm	0.325nm	0.132	2.16

Fig.3: AFM image of TiO_2 nanorods prepared by sol gel template method and annealed at (500) °C for 2h. (a) 3D image (b) 2D image (c) Histogram.

Fig.4 reveals absorption spectra of MO decomposed in the presence of TiO_2 nanorods photocatalyst under UV irradiation. The spectrum ranges from 200 to 800 nm with peak at the wavelength of 463 nm. It can be seen that the characteristic absorption peak intensity of MO decreases with increasing degradation time. After 360 min of UV irradiation, the degradation of MO is up to 78.2% and the absorption peak is totally removed.

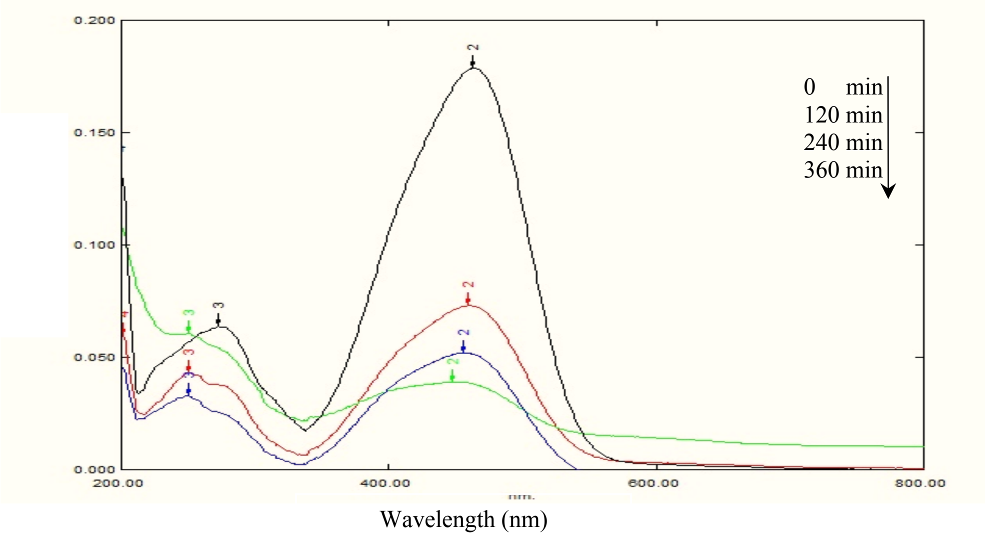


Fig. 4: Absorption spectra of MO degraded by TiO_2 nanorods under U.V. irradiation.

The mechanism of the photodegradation of MO by using TiO_2 is proposed as follows [8]

$TiO_2 + h\nu \rightarrow TiO_2\,(e^-, h^+)$

$h^+ + OH^- \rightarrow \cdot OH$

$e^- + O_2 \rightarrow O_2^-$

dye + O_2^- or $\cdot OH$ → peroxylated or hydroxylated intermediates → degraded products.

UV irradiation of TiO_2 excites electrons from a filled valence band to an empty conduction band, giving rise to electron–hole pairs. The valence band holes (h^+) can migrate to surfaces of TiO_2 and react with adsorbed OH^- to produce hydroxyl radicals ($\cdot OH$), whereas the conduction band electrons (e^-) migrate to the surfaces and react with adsorbed electron acceptors, such as O_2, involved in the oxidation of dye pollution as shown in Fig. 5.

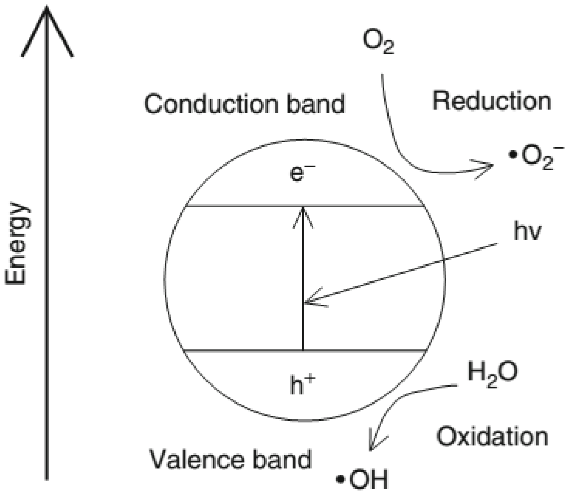


Fig.5: Photopromotion of an electron, reduction of oxygen and oxidation of water.

Fig.6 shows the degradation percentage of MO when treated with prepared TiO_2 nanorods after 6 h of U.V. irradiation, which were calculated by using Eq. (1). After 6 h exposure to U.V. light, the degradation of MO obtained of the TiO_2 nanorods as 78.2%, this degradation may due to their high specific surface area.

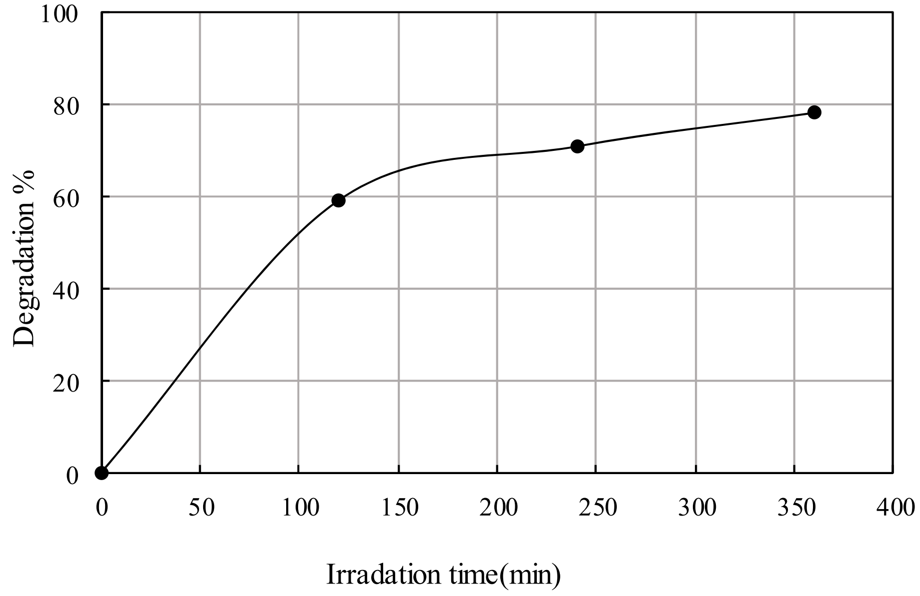


Fig.6. Degradation of MO(5ppm) verses irradation time

As shown in Fig.7, ln (A_o/A_i) is linear vs. irradiation time which is in accordance with Eq. (2), the degradation rate constant (k) of MO decomposition with TiO_2 nanorods is equal to the slope as evaluated in the Fig.7.

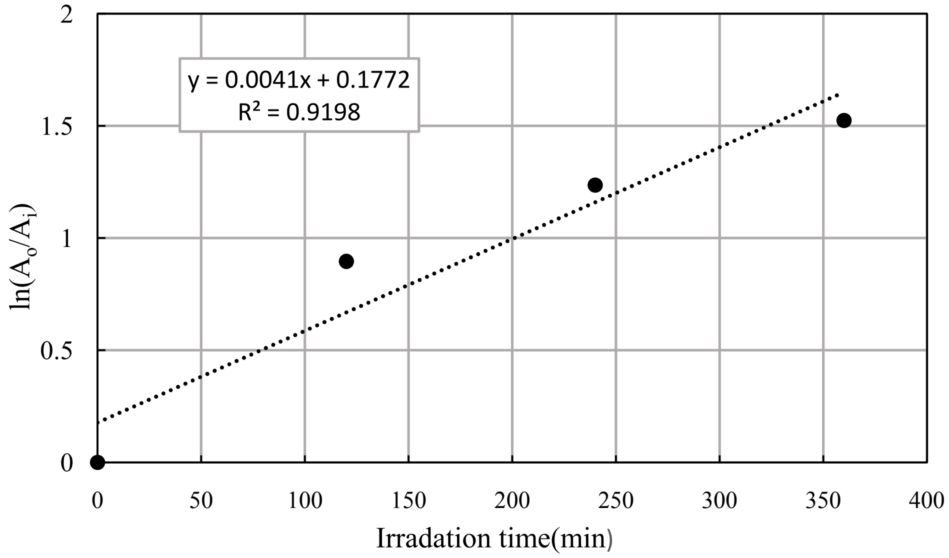


Fig.7: Pseudo-first order kinetics for MO(5ppm) photocatalyized degradation.

Conclusions

TiO_2 naorods with anatase structures have been prepared via sol-gel template method using titanium (IV) isopropoxide as a precursor. Uniformly sized TiO_2 nanorods of approximately 50 nm in average diameter, length of several micrometers. The photodegradation rate constant of TiO_2 is 0.041 min^{-1}, the rod-like photocatalyst can be easily separated and recycled, which could enhance the stability of the photocatalyst. The results provide useful insights for designing highly active photocataly.

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