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Controllable hydrothermal synthesis, optical and photocatalytic properties of TiO_2 nanostructures

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ABSTRACT

Different surface morphologies of TiO_2 thin films were prepared by hydrothermal synthesis method on Ti substrates through changing reaction time. The microstructure, composition, optical properties and photocatalytic properties of TiO_2 thin films were systematically investigated by x-ray diffraction, scanning electron microscopy, x-ray photoelectron spectrometer and ultraviolet-visible spectroscopy. As the reaction time increases, anatase structure and brookite structure of TiO_2 films respectively increases and decreases, corresponding to surface morphology changes from irregular structure to regular geometrical shape structure. These structural changes are accompanied by significant variations of optical properties and photocatalytic properties including a widening of the band gap from 2.86 to 3.19 eV, photocatalytic degradation efficiency from 92.5 to 98.1% and photocatalytic degradation rate from 0.032 to 0.048 min^{-1}. Among all samples, TiO_2-1 shows the best photocatalytic properties. Compositional analysis indicates that TiO_2 surface layer contains Ti and O elements, the ratio of Ti:O is 1:2.28 which is close to the atom ratio of TiO_2.

1. Introduction

TiO_2 has become the most widely used nanometer photocatalytic materials with higher oxidation activity, non-toxic, non-polluting, good chemical stability and low cost [1–10]. Strong light catalytic activity of TiO_2 on degrading organic pollutants depends on its microstructure. In various forms of TiO_2, anatase TiO_2 has high catalytic activity and been commercially used, the rutile and brookite TiO_2 also show photocatalytic properties but not so useful practically [11]. Since 1970, Carey applied photocatalyst to the degradation of polychlorobiphenyls [12]. Frank reported the photocatalytic properties of TiO_2 on cyanide and sulfite in aqueous solutions [13]. Macak studied the influence of different nanostructure TiO_2 on the electrocatalytic oxidation of methanol [14]. Zhang reported the importance of the relationship between surface phases and photocatalytic activity of TiO_2 [15].

Up to now, many works have been published in respect to the synthesis and high photocatalytic efficiencies of TiO_2 nanoparticles [16], powders [17] and colloids [18]. But for water treatment applications, TiO_2 thin films are preferred to avoid the separation of the catalyst after the degradation process [19]. Hydrothermal method is widely used due to its good dispersibility, small particle size, and low cost [20–22]. The surface morphologies, grain size and form can be easily controlled through various parameters, such as synthesis temperature, concentration of reactants, pH of reactants [23,24]. Therefore, many studies have been focused on TiO_2 were prepared hydrothermal method [25–29]. But these researches are mainly in respect to TiO_2 prepared with longer than 12 h reaction time. There are little researches about the influence of a shorter reaction time (shorter than 6 h).

In this context, TiO_2 thin films were prepared without any surfactants or templates by hydrothermal method. Different morphologies and properties were generated by changing the reaction time. The microstructure, composition, surface topography, optical properties and photocatalytic properties were investigated using x-ray diffractometer (XRD), x-ray photoelectron spectrometer (XPS), field-emission scanning electron microscope (SEM), and ultraviolet-visible spectroscope (UV–Vis).

2. Experimental

Titanium substrates (99.6% purity, 0.1 mm thickness, 10×40 mm^2 size) were first ultrasonically cleaned with acetone, ethanol

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and deionized water for 30 min, respectively. After drying, they were placed at an angle against the wall of Teflon-lined stainless steel autoclave. Inside, there was 25 mL of 10 M NaOH aqueous solution. The hydrothermal synthesis was carried out at 120 °C for 1 h in an electric oven. After reaction, the samples were dried in oven then immersed in 1 M HCl for 10 min, the Na of samples was exchanged with H. Then the samples were cleaned with ethanol and deionized water. At last they were calcinated at 500 °C for 30 min to convert to TiO_2. The reaction time of all experiments was 1, 2, 3 and 4 h respectively.

The microstructures of TiO_2 thin films were tested by XRD (MAC, M18XHF) employing CuKα radiation. The surface morphology of TiO_2 thin films was characterized by SEM (Hitachi, S4800) and an atomic force micros-copy (AFM, Veeco DI) operating in contact mode. XPS (Thermo, ESCALAB250) was employed to analyze the surface composition of the samples. The absorption spectra of samples were recorded by an UV–Vis spectrophotometer (Shimadzu, UV-2550) within the wavelength range of 300–900 nm. Besides, Methyl orange was used as a representative dye pollutant to evaluate the photocatalytic activity of TiO_2 thin films. The TiO_2 thin films (10 mm × 10 mm) were immersed in 10 mL 15 ppm methyl orange solutions and were irradiated with a 36 W high pressure mercury lamp, which emits visible light of 404.7, 435.8, 546.1, and 577.0–579.0 nm, and ultraviolet light of 365 nm. The distance between the sample and the high pressure mercury lamp was 3.0 cm. The transmittance of the methyl orange solution was measured every 10 minutes. Turn on the lamp in the 40th min and the irradiation time is 80 min.

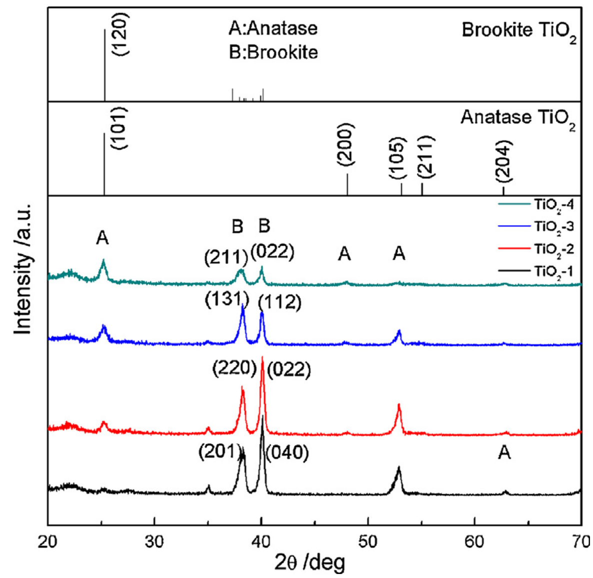

Fig. 1. XRD patterns of TiO_2 thin films.

3. Results and discussion

3.1. Microstructure analysis

Fig. 1 shows the XRD patterns of TiO_2 films, anatase TiO_2 (PDF# 21-1272) and brookite TiO_2 (PDF# 29-1360). The sharp

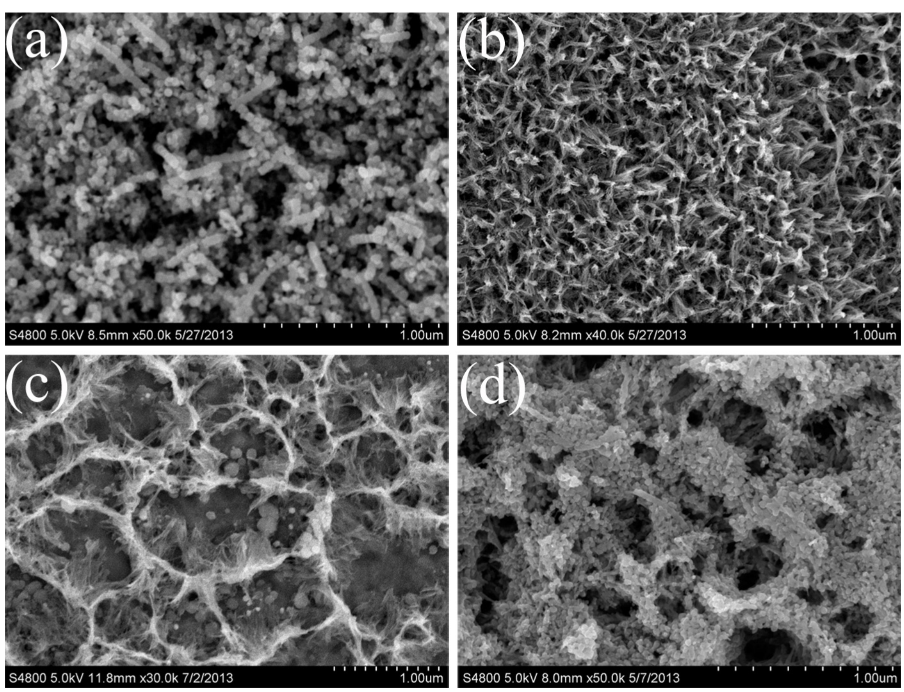

Fig. 2. SEM images of TiO_2 thin films: (a) TiO_2-1, (b) TiO_2-2, (c) TiO_2-3 and (d) TiO_2-4.

Table 1
Microstructure parameter, the average absorbance with 400-600 nm and band gap of TiO_2 thin films.

Samples	Reaction time/h	Average crystalline size/nm	RMS roughness/(nm)	Average absorbance/a.u.	Band gap/eV
TiO_2-1	1	18.5	3.0	1.097	2.86
TiO_2-2	2	20.2	20.7	0.770	2.91
TiO_2-3	3	20.0	43.8	0.735	3.11
TiO_2-4	4	16.5	58.2	0.516	3.19
Brookite TiO_2	–	–		–	2.36
Anatase TiO_2	–	–		–	3.20