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Photocatalytic degradation of formaldehyde using mesoporous TiO_2 prepared by evaporation-induced self-assembly

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Abstract: The mesoporous TiO_2 has been synthesized by evaporation induced self assembly (EISA) method. The thermo-gravimetric/differential scanning calorimetric (TG/DSC), X-ray diffraction (XRD), high-resolution transmission electron microscopy (HR-TEM) and N_2 adsorption desorption and adsorption are used to study the effects of the synthesized process condition on the microstructure of the as-synthesized mesoporous TiO_2. The photocatalytic performances of as-synthesized samples are evaluated by the degradation of the formaldehyde under ultraviolet light irradiations. The results demonstrate that the as-synthesized mesoporous TiO_2 are anatase with the uniform size about 20−40 nm. The sample is prepared using cetyltrimethyl ammonium bromide (CTAB) as the template with average pore size distribution of 8.12 nm, specific surface area of 68.47 m^2/g and pore volume of 0.213 mL/g. The samples show decomposition of formaldehyde 95.8% under ultraviolet light irradiations for 90 min. These results provide a basic experimental process for preparation mesoporous TiO_2, which will posses a broad prospect in terms of the applications in improving indoor air quality.

Key words: mesoporous TiO_2; photocatalysis; formaldehyde; evaporation induced self assembly (EISA)

1 Introduction

The indoor air quality is crucial for human health considering that people spend more than 80% of their time in houses, offices, and cars. Volatile organic compounds (VOCs) are among the most abundant indoor air pollutants. Formaldehyde (HCHO) is a major pollutant of VOCs. Long-term exposure to HCHO may cause health problems such as nasal tumors and skin irritation [1]. In recent years, the research on the photocatalytic degradation of formaldehyde for improving indoor air quality (IAQ) has become a hot topic [2]. Photocatalytic oxidation reaction can be carried out under room temperature and at atmospheric pressure. Photocatalytic oxidation under UV light to decompose formaldehyde has been recognized as one of the most effective strategies for the removal of indoor air contaminants.

It is an efficient photocatalyst for the detoxication of air and water pollutants and thus has attracted much research attention during the past two decades [3]. The properties of TiO_2 nanoparticles (NPs) depend on their crystal structure, size, and morphology. For practical applications, it is important to design an efficient TiO_2-based functional material as far as its photocatalytic properties are concerned. Since ANTONELLI [4] firstly synthesized mesoporous titanium dioxide (TiO_2) by a modified sol-gel method, there have been many reports using different template agents, such as dodecylamine [5], block polymer [6], ionic surfactants [7], and non-surfactant templates [8−9]. However, most of the above mentioned mesoporous TiO_2 with high surface area have an amorphous titania channel wall. Although the crystallization of mesoporous amorphous titania to anatase is achieved by calcination at a higher temperature, the mesoporous structure is collapsed in the process of calcination, which leads to the rapid decrease of specific surface area [10−12]. Therefore, new methods are still required for the synthesis of mesoporous TiO_2 with high photocatalytic activity.

In this work, the mesoporous TiO_2 is synthesized by the evaporation-induced self assembly using cetyltrimethyl ammonium bromide (CTAB) as template.

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X-ray diffraction (XRD), thermo-gravimetric/differential scanning calorimetric (TG/DSC), high-resolution transmission electron microscopy(HR-TEM) and N_2 adsorption desorption and adsorption are used to study the effects of the synthesized process condition on the microstructure of the as-synthesized mesoporous TiO_2. The possible formation mechanism of mesoporous TiO_2 is discussed, and its photocatalytic activity for degradation of formaldehyde under ultraviolet light irradiations is also investigated.

2 Experimental

2.1 Preparation of mesoporous TiO_2 by EISA

The mesoporous TiO_2 was synthesized by the evaporation-induced self assembly using titanium tetrabutyloxide ($Ti(OC_4H_9)_4$, TTBO), acetylacetone ($C_5H_8O_2$, AcAc), anhydrous alcohol (C_2H_5OH, EtOH), cetyltrimethyl ammonium bromide (CTAB) and hydrochloric acid (HCl, 6 mol/L, HCl) as starting materials. All reagents were analytical grade and used without further purification. In typical synthesis process, 17 mL TTBO was mixed with 5.0 mL AcAc and 5.0 mL EtOH was magneticly stirred for 30 min at room temperature and nominated as "solution A". Solution B was prepared by mixing 3.0 g CTAB, 0.9 mL deionized water and 2.4 mL HCl dissolving in 10 mL EtOH, add solution B to solution A drop by drop stirring vigorously for 120 min, during the stirring process, the TTBO was hydrolyzed with the H_2O. The AcAc and HCl serve as stabilizer to hinder the hydrolysis of TTBO. The fresh transparent solids were left in glass plates (1−2 mm thick liquid layers) at T=25−70 °C. Translucent glasslike xerogels were obtained upon solvent evaporation. As-synthesized samples were submitted to mild thermal treatment (100−150 °C overnight) to consolidate the inorganic network. The mesoporous TiO_2 was prepared after calcined at 500 °C for 2 h.

2.2 Characterization

Thermal gravity and differential scanning calorimetry (TG/DSC) test of the freeze dried sample were carried out on a NETZSCH STA449C thermal analyzer. 30 mg of the powder was filled into a corundum pot and the same mass of R-Al_2O_3-filled pot was used as a reference. Crystal structure of the synthesized mesoporous TiO_2 were identified by X-ray diffraction (XRD) using a Rigaku D/max 2550 diffractometer with graphite monochromatized Cu K_α radiation (λ=1.54056 Å). The accelerating voltage and the applied current were 40 kV and 300 mA, respectively. Phases were measured using the Search/Match capabilities of the JADE 5.0 program along with the ICDD (International Center for Diffraction Data) powder diffraction file (PDF) database. Mesoporous TiO_2 morphology was characterized by high-resolution transmission electron microscopy (HR-TEM, JEM-3010) at an operating accelerating voltage of 200 kV with spot resolution of 0.19 nm. The pore size distribution and Brunauer-Emmett-Teller (BET) surface area of the mesoporous TiO_2 particles were determined by nitrogen adsorption-desorption isotherm measurements at 77 K on a Quantachrome Autosorb-1 analyzer. All the measured samples were degassed at 180 °C for 3 h before the measurement. Pore size distribution and pore volume were calculated by the Barrett-Joyner-Halenda (BJH) method using the Halsey equation.

2.3 Photocatalytic property test

The photocatalytic properties for degrading formaldehyde were based on Chinese standard of HJ601 — 2011 (water quality-dertermination of formaldehyde–acetylacetone spectrophotometric method). The concentration of formaldehyde solutions was determined by UV-vis spectroscopy using UV-1601. 100 mL of formaldehyde solution (10×10^{-6}mol/L) was mixed with 0.05 g as-prepared catalysts in a quartz beaker under solar light irradiation with constant mechanical stirring. Before the irradiation, the solution was stirred for 20 min in dark to allow the system to reach adsorption equilibrium. The determined absorbance was converted to concentration through the standard curve method of formaldehyde. The degradation efficiency of formaldehyde was calculated by $R=(1-C/C_0)\times100\%$, where C_0 and C were the concentrations of formaldehyde when reaction time was 0 and t, respectively.

3 Results and discussion

Figure 1 shows the typical DSC and TG curves for the as-prepared precursor. It was found that there were three main stages during the mass loss process of TiO_2 gel from the TG curve. One was the mass loss of about 4.76% from room temperature to 200 °C, which was due to free adsorbed water and ethanol in the gel. The second stage was the obvious mass loss of 12.56% from 200 °C to 478 °C. According to the DSC curve, the endothermic peaks around 295 °C is probably due to the combustion decomposition of some organic matters. It was not evident after 400 °C, which possibly was a result of the desorption of the hydroxyl (OH) group on the suface of TiO_2 nanoparticles. It is known that there are two types of surface OH groups, terminal Ti–OH and bridge Ti(OH)Ti [13]. Dissociation temperatures of these surface OH groups differ from each other, and each temperature also is affected by the chemical surroundings. Thus, the decrease in the mass loss was not

obvious. In DSC curve, there is an exothermic peak around 450−470 °C resulted from the crystallization of TiO_2 from the amorphous phase to the anatase phase. The temperature of 500°C is selected for calcinations.

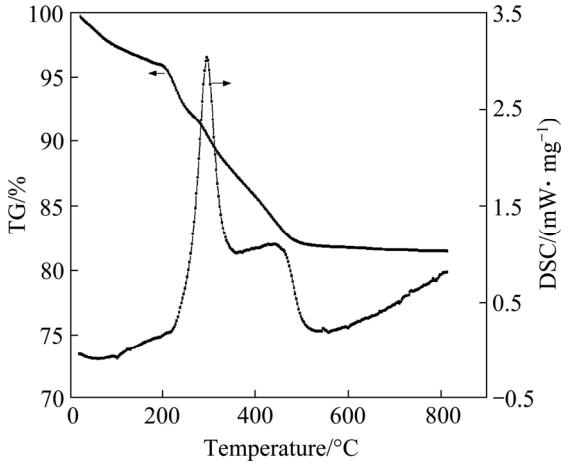

Fig. 1 TG-DSC curves for as-prepared precursor (TiO_2 gel)

Figure 2 shows wide-angle XRD and small-angle XRD (inset) patterns of the synthesized mesoporous TiO_2. As shown in Fig. 2, the presence of peaks can be readily indexed to diffraction peak of anatase phase TiO_2 (JCPDS 21-1272) for the samples. The wide-angle XRD pattern clearly shows the presence of nano-crystalline anatase. There are sharp diffraction peak at 2θ=1.0−1.5°. The small-XRD results demonstrate that the well-organized mesostructure has been formed, which can be confirmed by the results of HR-TEM and nitrogen adsorption-desorption isotherm measurements.

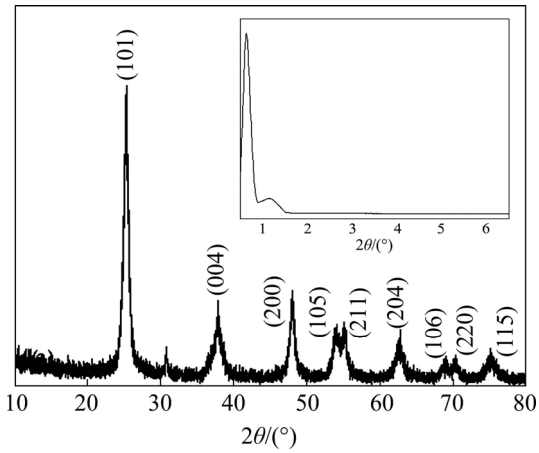

Fig. 2 Wide-angle and small–angle (inserted profile) XRD patterns of synthesized mesoporous TiO_2

HR-TEM examinations provide more information about the morphology and microstructure of the mesoporous TiO_2. Figure 3 shows a typical TEM image of the mesoporous TiO_2 calcined at 500 °C for 2 h, which indicates that the mesoporous TiO_2 particles are composed of nanoparticles with diameter in the range of 20−30 nm. The porous structure of the mesoporous TiO_2 can also be observed, which seems to be formed by the dense packing of nanoparticles. The grain boundary of sample is clearly observed, indicating that the nanoparticles are highly crystalline. The results of HR-TEM reveal that the mesostructure TiO_2 is as well-organized as in case of as-synthesised TiO_2.

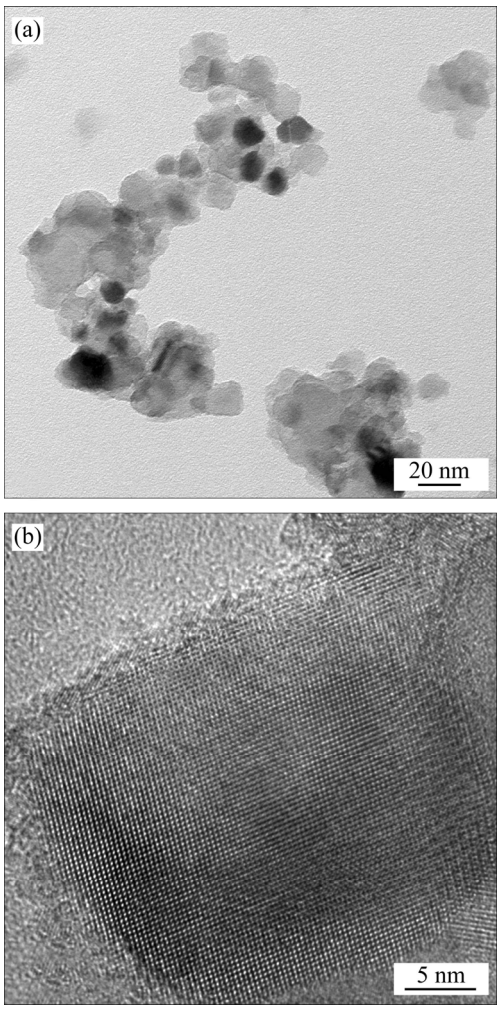

Fig. 3 HR-TEM images of synthesized mesoporous TiO_2

Figure 4 shows the nitrogen adsorption-desorption isotherms of the samples whereas the corresponding Barret-Joyner-Halenda (BJH) pore size distributions plots (calculated from the adsorption branch) are presented in Fig. 5.

According to IUPAC classification [14], the similar nitrogen adsorption-desorption isotherms of samples can be classified as a type IV isotherm, and hysteresis loop is type H2, typical of a mesoporous material. The sharp decline in the desorption curve and the hysteresis loop at high relative pressure are indicative of mesoporosity. During the process of adsorption, single molecular layer adsorption occurred at relatively low pressure and multimolecular layer adsorption occurred at higher pressure [15]. From Fig. 5, it can be seen that the average

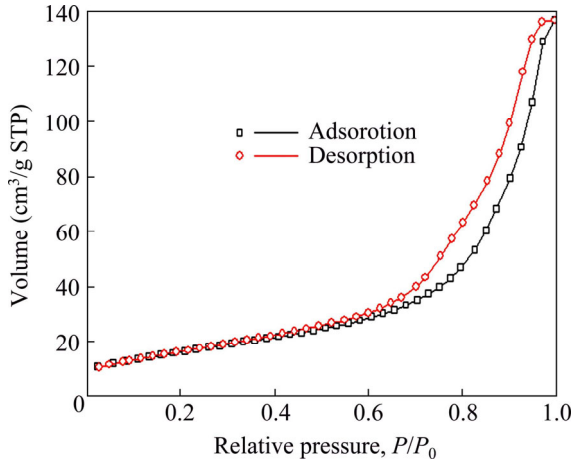

Fig. 4 Nitrogen adsorption-desorption isotherms of synthesized mesoporous TiO_2

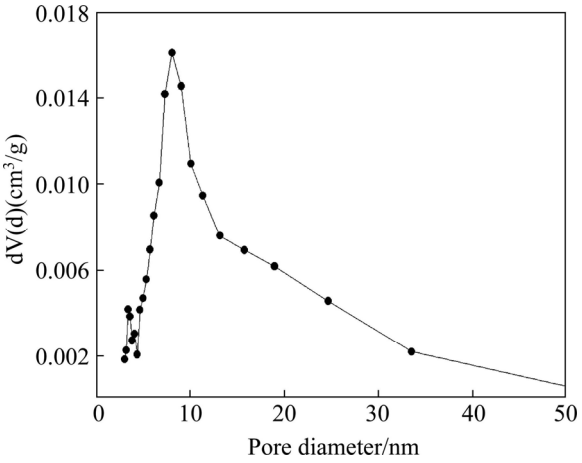

Fig. 5 Pore size distribution curves of synthesized mesoporous TiO_2

pore sizes of mesostructure TiO_2 is about 8.12 nm. The shape of the curve, in agreement with results from small-angle XRD and HR-TEM studies, indicates the absence of a narrow pore size distribution. The calculated BET specific surface area and pore volume are 68.47 m^2/g and 0.213 cm^3/g, respectively.

Photocatalytic activity of mesoporous TiO_2 is estimated by measuring decomposition rates of formaldehyde. Figure 6 shows the degradation rate of formaldehyde for the as-prepared samples and Degussa P-25 TiO_2 under UV light. It indicates that the photodegradation ratio of formaldehyde increases with the increase of photocatalytic time. The highest decomposition rate of formaldehyde for the mesoporous TiO_2 is about 95.8% at 90 min, while that for Degussa P-25 is only 66.4%. The results indicate that the photocatalytic activity of formaldehyde degradation is better improved for the mesoporous TiO_2 than that for the Degussa P-25. Researches on the reason and the mechanism for enhancing the photocatalytic activity are in progress.

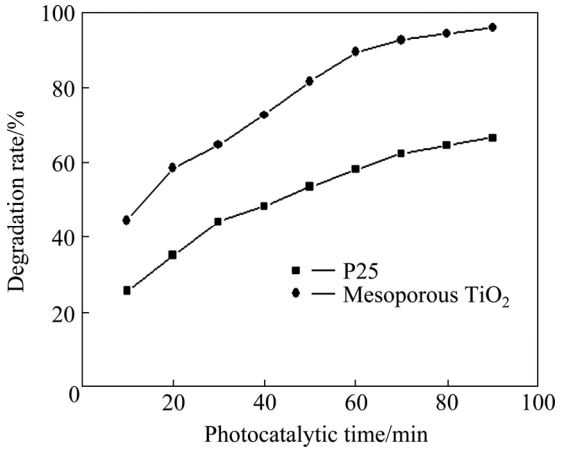

Fig. 6 Photocatalytic degradation rate of formaldehyde for as-prepared mesoporous TiO_2 and Degussa P-25 TiO_2, respectively

On the basis of the above results and discussion, the mechanism of photocatalytic oxidation of formaldehyde on the anatase TiO_2 surface under UV light is as follows: First, TiO_2 is irradiated by UV light, which have exceeding band gap photo energy, electrons are transferred from the VB to CB of TiO_2, meanwhile, leaving holes. Photo-generated holes that have the strong oxidizing oxidize OH^- or H_2O into ·OH and capture the electrons of organic pollutants absorbed on the surface of photocatalyst materials. On the other hand, the photohenerate electrons possess strong reducibility and reduce the adsorbed oxygen into $\cdot O_2^-$. After that, generated ·OH and $\cdot O_2^-$ on the surface of TiO_2 can degrade the absorbed HCHO [16]. The photocatalytic mechanism can be described as Eqs. (1)−(7) [13, 17−18]:

$$TiO_2+h\nu(>3.2eV)\longrightarrow TiO_2(e^-+h^+) \quad (1)$$

$$e^-+O_2\rightarrow \cdot O_2^- \quad (2)$$

$$h^++H_2O\rightarrow \cdot OH+H^+ \quad (3)$$

$$HCHO+\cdot OH\rightarrow \cdot CHO+H_2O \quad (4)$$

$$\cdot CHO+\cdot OH\rightarrow HCOOH \quad (5)$$

$$\cdot CHO+\cdot O_2^-\xrightarrow{+H^+}HCOOOH\xrightarrow{+HCHO}HCOOH \quad (6)$$

$$HCOOH\xrightarrow{\cdot OH\text{ or }\cdot O^{2-}}H_2O+CO_2 \quad (7)$$

4 Conclusions

1) The mesoporous TiO_2 are synthesized by evaporation induced self assembly (EISA) method.

2) The as-synthesized mesoporous TiO_2 are anatase with the uniform size about 20−40 nm, average pore size distribution of 8.12 nm, specific surface area of 68.47 m^2/g and pore volume of 0.213 mL/g, respectively.

3) Studies of the samples show decomposition of formaldehyde 95.8% under ultraviolet light irradiations for 90 min.

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