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Synthesis of nanosized $NaTaO_3$ in low temperature and its photocatalytic performance

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Abstract

A simple synthetic route in mild condition to obtain nanosized $NaTaO_3$ powder with cubic morphology is reported in which the compound was hydrothermally prepared at 120 °C for 12 h. The cubic crystalline structure of this nanosized $NaTaO_3$ product was ensured by using XRD and TEM. The band gap of the nanosized $NaTaO_3$ was 3.96 eV based on UV spectrum. The hydrothermal process probably follows the dissolution–precipitation mechanism. Also this $NaTaO_3$ powder showed high photoreactivity under UV light in gas phase and liquid phase photoreactions.

Keywords: $NaTaO_3$; Hydrothermal; Photocatalysis

1. Introduction

Many efforts have been devoted in developing heterogeneous photocatalysts with high activities in recent years, especially for the application in splitting water into hydrogen and oxygen and removing toxic organic and inorganic materials in air or solution [1,2]. Most of the photocatalysts have been studied, including TiO_2 [3], $SrTiO_3$ [4,5], $K_4Nb_6O_{17}$ [6], $Na_2Ti_6O_{13}$ [7], $BaTi_4O_9$ [8], $K_2La_2Ti_3O_{10}$ [9] and so on, are mainly TiO_2 and titanates. Kudo and Kato have recently studied a series of novel tantalate photocatalysts for overall water splitting [10–15]. The photocatalytic activities of tantalate photocatalysts for splitting water were better than those of TiO_2 photocatalysts [14]. Among the tantalates, $NiO/NaTaO_3$ showed the highest activity [13,14].

In the previous work [12], the tantalate photocatalysts were synthesized via solid state reaction in high temperature (1420 K) and the crystalline size and particle size were of large micrometer. So it is meaningful to develop a simple method to synthesize the nanosized tantalate photocatalysts for the smaller the photocatalyst is, the higher photoactivity it probably has [15]. Hydrothermal method is proved to be an effective way to synthesize $BaTiO_3$ [16,17], $LiNbO_3$ [18], $Ba_5Nb_4O_{15}$ [19], $KTaO_3$ [20,21]. In this paper, we report the hydrothermal synthesis of photocatalyst $NaTaO_3$ and study the decomposition of gaseous formaldehyde and rhodamine B (RB) solution under UV light irradiation. The performances of decomposition of organic pollutants of tantalates have not yet been reported before.

2. Experimental section

The starting materials for the synthesis of $NaTaO_3$ were Ta_2O_5 (AR) and NaOH (AR). In a typical synthesis procedure, 0.60 g NaOH and 0.442 g Ta_2O_5 were added into a Teflon-lined autoclave with capacity of 40 ml, and deionized water was added up to 30 ml.

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The autoclave was sealed and maintained at 120 °C for 12 h without shaking or stirring and allowed to air cooled to room temperature naturally. The crystalline powder product was filtered off, washed with deionized water and dried in air at 60 °C.

The product was characterized by powder X-ray diffraction (XRD) on a D8 Advance Bruker X-ray diffractometer with monochromatized CuK_α ($\lambda = 1.5418$ Å) incident radiation. XRD patterns were recorded from 10 to 70° (2θ) with a scanning step of 0.01°. The morphology and particle size of the product was analyzed by transmission electron microscopy (TEM) observation on a H-800 transmission electron microscope operated at 200 kV. UV-Vis diffused reflection spectrum was recorded in Shimazu S2600 UV spectroscopy.

The formaldehyde was used in the gas phase photocatalytic evaluation of the $NaTaO_3$ products in a 400 ml cylindrical quartz vessel, with a 8 W bactericidal lamp (254 nm) as the light source. The intensity of UV 254 at the surface of sample was about 2.5 mW/cm^2. 0.06 g sample was tested in the vessel under the light beam each time. The concentration of formaldehyde in the photoreactor, obtaining by a gastight syringe from the sample port, was measured by a SP-502 gas chromatograph (GC) equipped with a flame ionization detector and a 2 m stainless steel column (GDX-403) at 373 K. Rhodamine B was employed in the liquid phase photocatalytic evalution of the products. The water solution of RB (about 5 mg/L, 100 ml) was illuminated with near UV light (254 nm, 8 W). The change of concentration was detected with the UV spectrum.

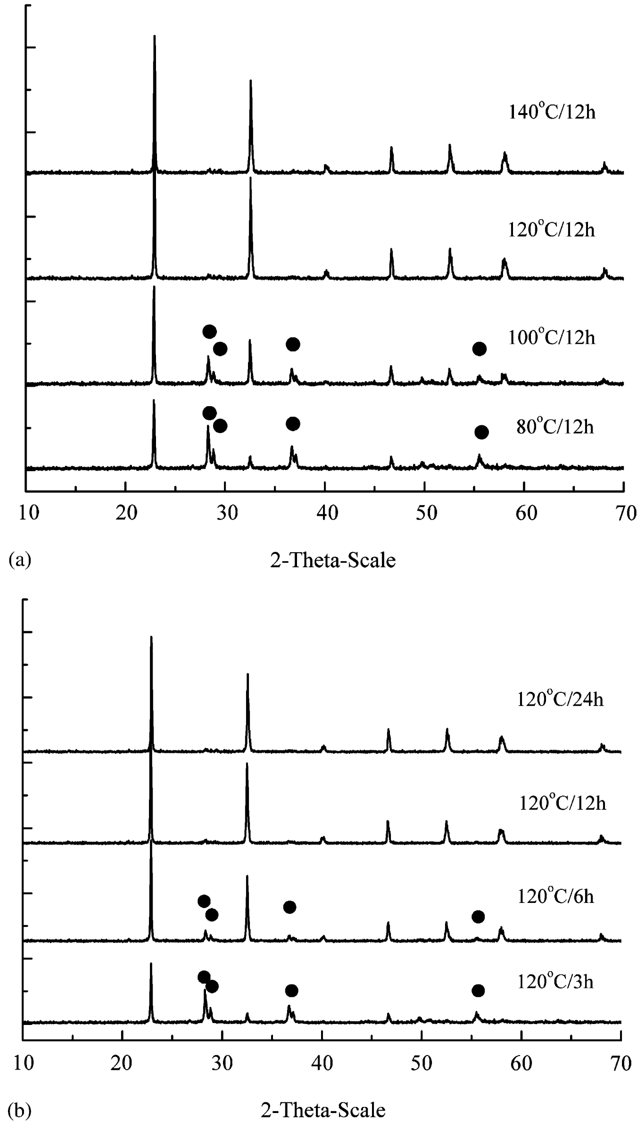

Fig. 1. XRD patterns of samples prepared at different temperatures for (a) 12 h: 80, 100, 120 and 140 °C. (b) At 240 °C for different times: 3, 6, 12 and 24 h. A dot represents unreacted Ta_2O_5.

3. Results and discussion

3.1. Formation of $NaTaO_3$ crystalline phase

In the synthesis of $NaTaO_3$, the NaOH concentration is a critical factor. When the NaOH concentration is lower than 0.1 mol/L, we can only obtain unreacted Ta_2O_5 in the products. This result is similar to the literature [19]. And if we want to obtain pure $NaTaO_3$ product with low NaOH concentration, the longer time or higher temperature should be used. It is obvious that maintaining a certain level of NaOH concentration is crucial to the reaction.

In our experiments, the NaOH concentration about 0.5 mol/L was chosen. Fig. 1 shows XRD patterns of the $NaTaO_3$ products synthesized in different conditions. All the reflections of the products can be readily indexed as a pure orthorhombic phase [space group: 62] of $NaTaO_3$, identical to the reported data in the JCPDS cards (70-0399). The XRD patterns show that the $NaTaO_3$ synthesized by hydrothermal method is well crystallized. Also there is nearly no Ta_2O_5 impurity existing in the products obtained at 120 °C for 12 h. Compared to the conventional high-temperature solid state reaction, it is obviously a low-cost, energy saving and easy way to obtain well-crystallized $NaTaO_3$ with nano-size.

Various crystallization temperatures (80–140 °C) were examined at a reaction time of 12 h. Fig. 1(a) shows the XRD patterns of some samples prepared at different temperatures. $NaTaO_3$ appears at 80 °C, together with some unreacted Ta_2O_5 impurity. With the increase of the temperature, the signals of unreacted Ta_2O_5 become weaker and weaker. Pure $NaTaO_3$ is, however, obtained at 120°C. It means that temperature exerts a great influence on the crystal phase of the products.

Fig. 1(b) shows the XRD patterns of some samples formed at 120 °C for different times. The $NaTaO_3$ phase first appeared at 120 °C after 3 h, together with a lot of unreacted Ta_2O_5 starting materials existing. Increase the time to 6 h, the XRD pattern shows that the unreacted Ta_2O_5 in the final product is no more than 5%. The completion of $NaTaO_3$ crystallization required about 12 h. This shows that the speed of the reaction is fairly low and also reaction time is one of the key factors which determine the final products.

3.2. Morphology characterization

TEM photographs (Fig. 2(a)) show the well crystallized cubic morphology and a particle size of about 200 nm. Increasing the reaction temperature or prolonging the reaction time brings little influence to the morphology of the products.

The size of the Ta_2O_5 starting material ranges from tens of nanometers to several micrometers while the $NaTaO_3$ products are all about 200 nm in size. So the hydrothermal process cannot agree with the in situ mechanism and probably follows the dissolution–precipitation mechanism [22,23]. During the hydrothermal process, Ta_2O_5 partially dissolves into the solution and then reacts with the NaOH, forming a lot of $NaTaO_3$ crystal nucleus. Then the nucleus increases with the time. Temperature and reaction time are both important to the dissolving process of the Ta_2O_5, also they have a strong influence on the final $NaTaO_3$ products as a result. Fig. 2(b) shows the morphology appears after the reaction under 100 °C for 12 h. The entirely crystalline $NaTaO_3$ and amorphous grains coexist in the final products. It also gives evidence that the hydrothermal process follows the dissolution–precipitation mechanism.

3.3. UV diffuse reflectance property

Fig. 3 shows that the UV diffuse reflection spectrum of the $NaTaO_3$ product. According to the formula: $E_g(\mathrm{eV}) = 1240/\lambda_g$ (nm), the E_g of the as-prepared $NaTaO_3$ is estimated to be about 3.96 eV, which is similar to that of the bulk $NaTaO_3$ (4.0 eV). This result

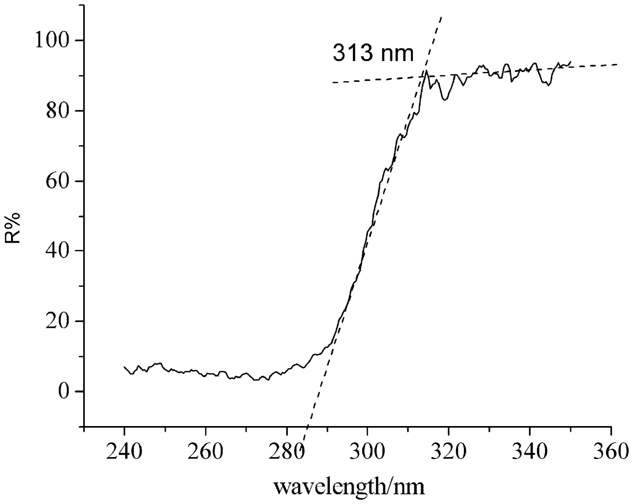

Fig. 3. UV diffuse reflection spectrum of as-prepared $NaTaO_3$.

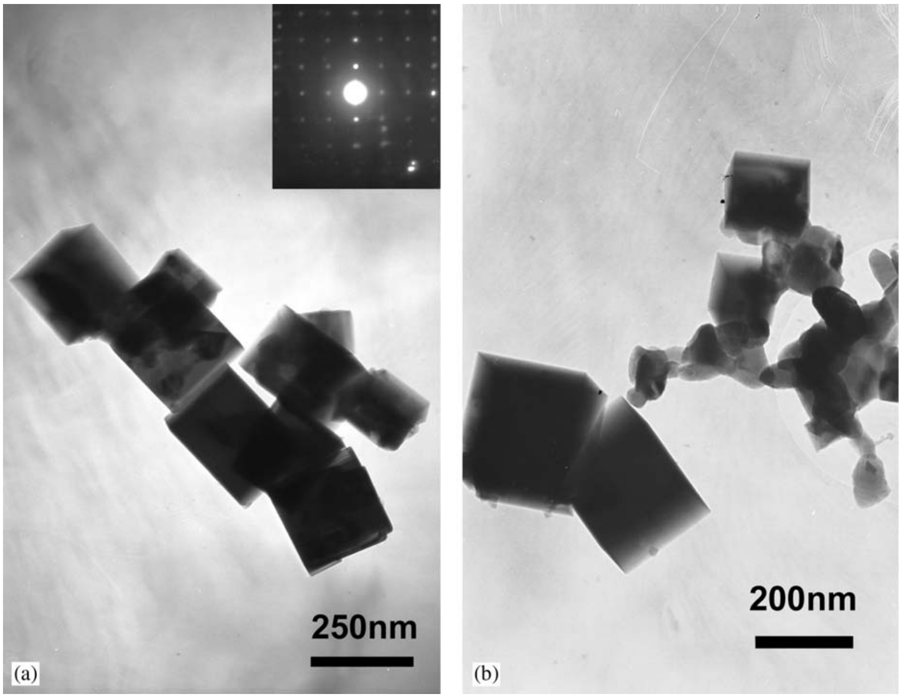

Fig. 2. TEM of $NaTaO_3$ hydrothermally synthesized at (a) 120 °C for 12 h (The insert is electron diffraction pattern) and (b) 100 °C for 12 h.

shows that quantum size effects did not appear in the as-prepared $NaTaO_3$ crystal which is several hundred nanometers in size.

3.4. Photoreactivity of as-prepared $NaTaO_3$

Fig. 4(a) shows gas phase photocatalytic activity of the as-prepared $NaTaO_3$ photocatalysts under ultraviolet (UV) light irradiation. In this airtight system, reaction could be nearly regarded as a zero order reaction in dynamics. Therefore, the slope of the decomposition curve was direct ratio to the reaction constant. The fitted equation of the reaction is $C = -43.27t + 1389.7$, in which C is the formaldehyde concentration and t is the reaction time (min). In the reaction when photocatalyst was free, the concentration of formaldehyde was almost unchanged under UV light irradiation.

Liquid phase photocatalytic activity was evaluated by measuring decomposition rate of RB solution. Fig. 4(b) shows the photo degradation curves of RB solution using as-prepared $NaTaO_3$ powder and photocatalyst free. As is shown, the reaction is a first-order one in which the nature logarithm of the formaldehyde concentration is linear to the reaction time. It is consistent with the photodegradation of RB solution with TiO_2 as the photocatalyst [24]. The as-prepared $NaTaO_3$ shows a relatively high activity in the reaction and the fitted equation is $\ln(C) = -0.5288t + 1.5714$.

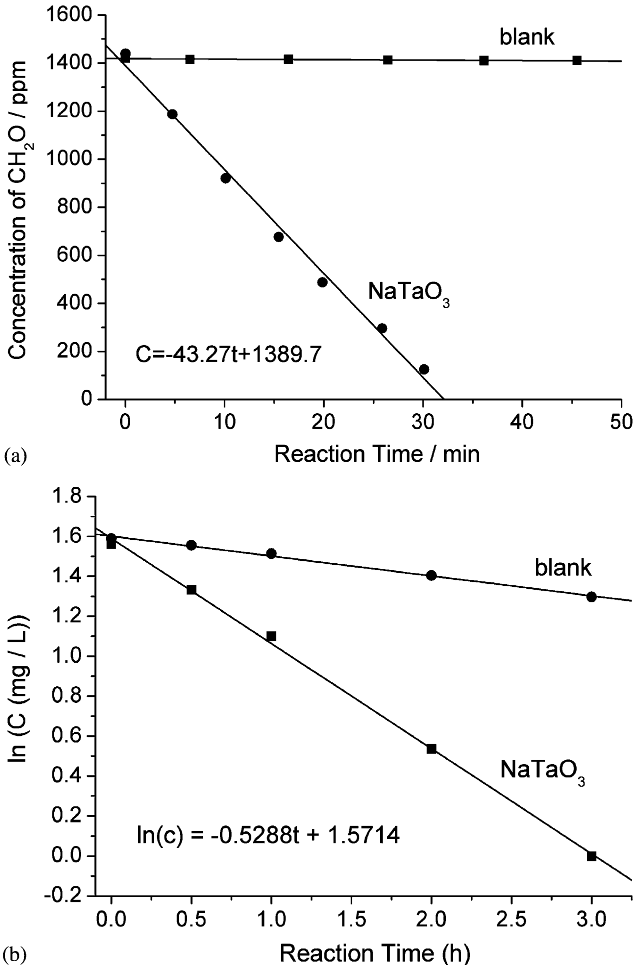

Fig. 4. The photo degradation curve of gaseous formaldehyde (a) and RB solution (b) using $NaTaO_3$ photocatalyst.

4. Conclusion

Well-crystallized $NaTaO_3$ powder about 200 nm in size can be successfully synthesized by hydrothermal reaction in rather low temperature. The as-prepared $NaTaO_3$ has cubic morphology and also shows rather high photoreactivity in the degradation of gaseous formaldehyde and rhodamine B solution. The hydrothermal method will greatly reduce the production cost and offer great opportunity for the synthesis of such novel tantalate photocatalyst.

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