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Hydrothermal synthesis and photocatalytic property of KNb_3O_8 with nanometer leaf-like network

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Abstract

The KNb_3O_8 photocatalyst with nanometer leaf-like network was obtained by the hydrothermal synthesis. Scanning electron microscope (SEM) and X-ray diffractometer (XRD) were used to characterize the morphologies and structure of the photocatalyst. The band gap of KNb_3O_8 crystals was estimated to be about 3.47 eV from the onset of UV–vis diffuse reflectance spectrum of the photocatalyst. The crystalline of KNb_3O_8 catalyst prepared becomes well with increasing the hydrothermal reaction time, which markedly increases the photocatalytic activity of the catalyst. The photocatalytic degradation reaction of acid red G on the catalyst KNb_3O_8 is a pseudo-first-order reaction. Although the surface areas of the photocatalyst prepared are much lower than that of P25-TiO_2, its photocatalytic activity of photodegrading acid red G is much higher than that of P25-TiO_2.

Keywords: Niobate; Potassium triniobate; Hydrothermal synthesis; P25; Photocatalytic degradation; Acid red G

1. Introduction

The textile industry produces large quantities dye pollutants, which are toxic and mostly nonbiodegradable and also resistant to destruction by physico-chemical treatment methods, and are readily reduced under anaerobic conditions to produce potentially more hazardous aromatic amines [1,2]. Conventional methods, such as chemical precipitation and separation of pollutants, coagulation, electrocoagulation, adsorption by activated carbon, etc, cannot eliminate the contamination thoroughly but only transfer it from one phase to another. Heterogeneous photocatalysis has been considered as a cost-effective alternative as pre-or post-treatment of biological treatment process for the purification of dye-containing wastewater [3–7].

Although titanium dioxide is the most widely used photocatalyst, many research efforts are focused on the discovery of new photocatalysts which are more efficient than TiO_2 in recent years [8–11]. A lot of layered niobate compounds, such as Ni–$K_4Nb_6O_{17}$ [12], Bi_2InNbO_7 [13], $Sr_2Nb_2O_7$ [14], $Sr_2Ta_{1-x}Nb_xO_7$ [15], $A_2SrTa_2O_7.nH_2O$(A = H, K, and Rb) [16], TiO_2 and Pt pillared $HCa_2Nb_3O_{10}$ [17], SiO_2-pillared $HCa_2Nb_{2.9}Cr_{0.1}O_{10}$ [18] etc., have attracted special attention from researchers because of their excellent photocatalytic activity property in the field of water splitting to H_2 and O_2 [19–23]. The photocatalytic property of niobate $K_6Nb_{10.8}O_{30}$ for the degradation of organic pollutant was studied recently [24].

Among the layered niobate compounds, the photocatalytic property of potassium triniobate (KNb_3O_8) for oxidizing organic contaminants in water is hardly reported. KNb_3O_8 contains corner-shared octahedral [NbO_6] units forming an anionic sheet disposed in a stacking arrangement and K^+ ions are located between the layers to compensate for the negative charges [25]. KNb_3O_8 was mainly obtained by high temperature solid-state reaction through the heating of a stoichiometic mixture of Nb_2O_5 and K_2CO_3 [14,26,27]. The fiber nanocrystalline KNb_3O_8 was synthesized by hydrothermal reaction through adjusting the alkalinity in the procedure by Liu et al. [28]. In an earlier study, most of research works on KNb_3O_8 were focused on its luminescence performance [29,30] and its ionic exchange intercalation and exfoliation reactions [26]. In the present article, a kind of

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KNb_3O_8 material with nanometer leaf-like network was synthesized by hydrothermal method, its property of photocatalytic degrading acid red G was studied and compared with the photocatalyst TiO_2 (P25).

2. Experimental

2.1. Preparation of samples

Tri-steps hydrothermal synthesis procedure was used [28]. 1–2 g of Nb_2O_5 (analytical grade) powder was added to 70 ml 2–3 mol/l KOH (analytical grade) solution, and stirred for 30 min. Then the white slurry was loaded into a 100 cm^{-3} Teflon-lined stainless autoclave. After the sealed autoclave was heated at 200 °C for 4 h, a clear solution was obtained. The pH of the solution was slowly and accurately adjusted with diluted HCl solution to 5.5 by pH meter (DELTA 320) and under stirring condition. After sealed autoclave was heated at 200 °C for 4–72 h in an oven, the final product was collected by filtration, washed with deionized water, and dried at 353 K under vacuum.

2.2. Characterization

The structures of the synthesized materials were confirmed by powder X-ray diffraction (XRD) using a Rigaku D/MAX-RB powder X-ray diffractometer with graphite monochromater and CuKα radiation.

The morphologies of as-prepared powder were observed using a scanning electron microscope (SEM) (JSM-5610).

Diffuse reflectance spectral analysis of the photocatalyst was determined by UV–vis spectrometer (UV-2100).

BET surface areas were determined using nitrogen as the sorbate at 77K in a static volumetric apparatus (Micromeritics ASAP 2010 sorptometer). The samples were previously outgassed at 180 °C for 16 h under a vacuum of 6.6×10^9 bar.

2.3. Evaluation of photocatalytic activity of the samples

The photocatalytic properties of photocatalyst were determined by the photodegradation of acid red G (industrial product), carried out in a 500 ml glass vessel with magnetic stirring. A commercial 20 W UV lamp (λ = 253.7 nm) was used as the light source. Reaction suspension was prepared by adding 150 mg prepared sample into a 150 ml of aqueous acid red G solution and stirred without UV irradiation for 5 min. The light intensity was about 0.745 mW/cm^2 measured by using an UV-B radiatometer and the distance between the liquid surface and the light source was about 8 cm. Sampling the solution 6 times in 2 h during the photocatalytic process, and the concentration of aqueous acid red G was determined by measuring the absorbance at 505 nm with an UV–vis spectrophotometer (UV-751GD) and a calibration curve. By this method, the conversion percent of acid red G can be obtained in different intervals. The photodegradation rate (X) is given by $X = (C_0–C)/C_0 \approx (A_0\text{-}A)/A_0$, where C_0 is initial concentration of acid red G, C is concentration at time t, A is the absorbance. The linear relationship between the absorbance at 505 nm (A) and the concentration of acid red G(C) (mg/l) can be represented empirically by the equation:

$$A = 0.01\mathrm{C} - 0.0003. \quad (1)$$

The activities of the catalysts obtained were evaluated by calculating the photodegradation rate of acid red G as a function of illumination time.

The photocatalytic property of P25-TiO_2 powder was determined and compared with the prepared sample.

3. Results and discussion

3.1. Physical characterization of the sample prepared at different conditions

The pH value was the critical factor during the synthesis process of KNb_3O_8 [28]. Fig. 1 shows the XRD pattern of the samples obtained in the same condition except the pH values were different, which indicate that when pH was lower than 5, most of the obtained product was the Nb_2O_5 with poor crystalline; when pH was higher than 6, it was very difficult to obtain

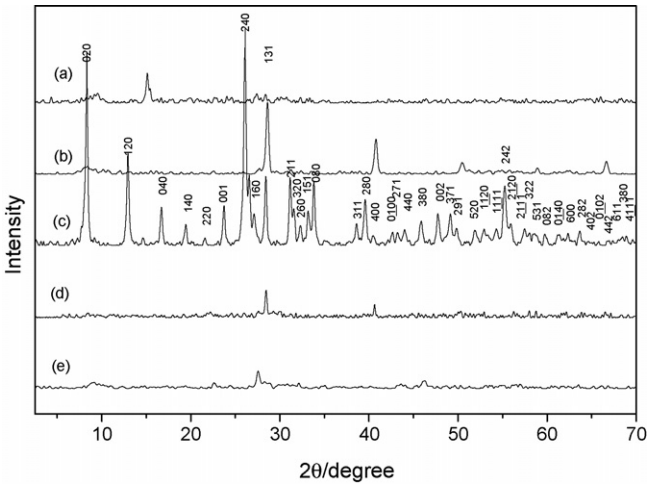

Fig. 1. X-ray powder diffraction patterns of samples obtained under (a) pH 9; (b) pH 6.5; (c) pH 5.5; (d) pH 4; (e) pH 2.

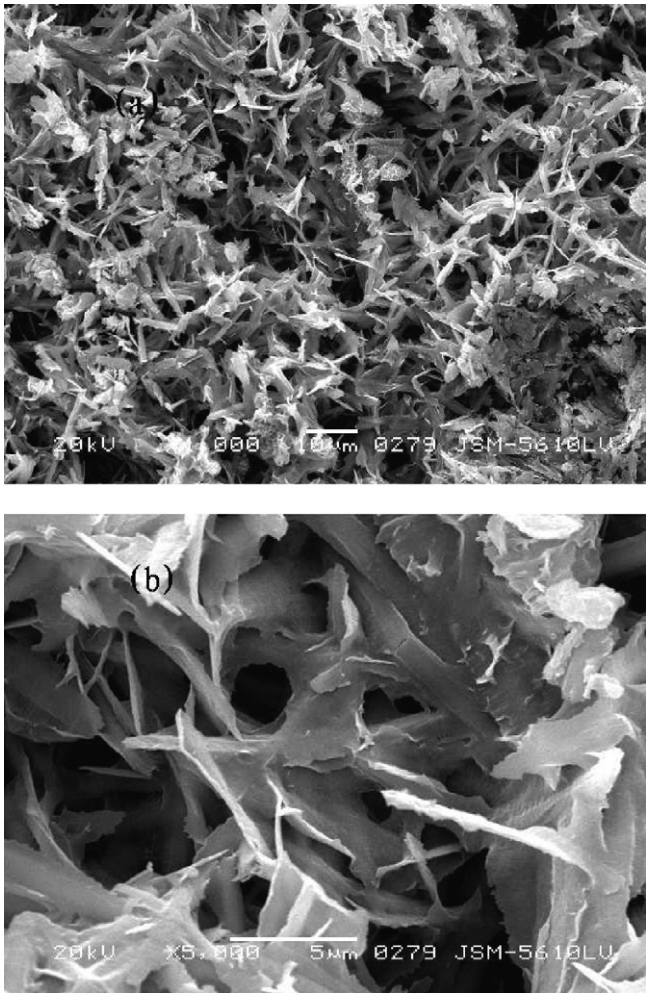

Fig. 2. SEM images of KNb_3O_8 obtained by hydrothermal method.