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Preparation and photocatalytic properties of mesoporous SnO_2–hexaniobate layered nanocomposite

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ABSTRACT

SnO_2–hexaniobate layered nanocomposite was prepared via an exfoliation–restacking route and characterized by powder X-ray diffraction, scanning electron microscope, thermogravimetric analysis, IR, UV–vis, X-ray photoelectron spectroscopy, specific surface area and porosity measurements. It was shown that the host layer structure remains unchanged after the exfoliation and restacking processes, and that the nanocomposite has an interlayer expansion of about 2.8 nm even after calcination at 250 °C for 2 h. The nanocomposite is mesoporous with a high specific surface area (more than 120 m^2/g). It was revealed the nanocomposite demonstrates a high photocatalytic activity in the degradation of acid red G under UV-light irradiation, which can be ascribed to its high surface area, mesoporosity and the synergistic effect of the two components.

1. Introduction

There has been extensive interest in photocatalysis of semiconductors for their potential application in decontamination of water using solar energy. Apart from bulky semiconductors like TiO_2, SnO_2 and ZnO, many efforts have been carried out to explore the photocatalytic properties of inorganic layered semiconductors. One of the promising methods is to fabricate layered nanocomposites through intercalating guest species into the host layered inorganic lattices [1–3]. Such nanocomposites are expected to exhibit properties synergistically derived from the two components, and possess porous textures with higher specific surface areas, which provide better accessibility of reactant molecules to the active sites on surface [4,5].

The potassium hexaniobate presents a lamellar structure built up by stacked negative charged layers, and its interlayer region is filled with potassium ions that maintain the charge neutrality [6]. $K_4Nb_6O_{17}$ is a photocatalytically active wide band-gap semiconductor [7,8] and was used as a photocatalyst for water splitting into O_2 and H_2 [9]. Domen et al. reported Ni-intercalated $K_4Nb_6O_{17}$ showed the marked photocatalytic activity in H_2 evolution [7]. Photoevolution of hydrogen on $TiO_2/K_4Nb_6O_{17}$ microporous nanocomposites was investigated by Tawkaew et al. [10]. However, the intercalation of most species into layered niobate matrices is not easy to achieve because of their high layer charge densities, compared to other layered materials like smectite clays. The exfoliation–restacking technique, which has been well developed in MoS_2 intercalation chemistry, is an attractive way to prepare layered nanocomposites [4,11]. When the layered host lattice can be readily exfoliated into single sheets in an appropriate solution to form a colloid, the resulting colloidal nanosheets in suspension can be restacked in the presence of proper pillaring agents in the solution [12]. In the recent decade, the exfoliation–restacking technique has been introduced to prepare titanate- [13], niobate- [14–16] and titanoniobate-based layered nanocomposites [17]. Incorporating ultrafine semiconductor particles in the interlayer region, the resulting nanocomposites create a mesoporous texture depending on the sizes of incorporated semiconductor particles. And the incorporated guest semiconductor particles are not necessary to be removed, which is helpful to couple with the host layers to form a heterojunction structure to suppress the recombination of photo-generated electrons and holes by electron transfer between the two semiconductor composites and therefore improve the photocatalytic activity [18]. In the present paper, the mesoporous SnO_2–hexaniobate layered nanocomposite with high surface area was synthesized by exfoliation–restacking method. Instead of water splitting for hydrogen generation, to which most of the studies on preparation of layered niobate materials have been devoted, the photocatalytic property of the as-prepared nanocomposite for photodegradation of organic pollutants was investigated using acid red G as a model substrate.

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2. Experimental

2.1. Reagents and materials

Nb_2O_5 (Wako Pure Chemical, 99.9%) and K_2CO_3 (Wako Pure Chemical, 99.9%) were used as received. Milli-Q water was used throughout in this study. The host potassium hexaniobate ($K_4Nb_6O_{17}$) was prepared by a conventional solid-state method. The mixture of Nb_2O_5 and K_2CO_3 was mixed in molar ratios of 2.1:3 and calcined at 1100 °C for 10 h in a corundum crucible, similar to the method described in Refs. [16,19]. The crystal structure of $K_4Nb_6O_{17}$ was confirmed by powder X-ray diffraction (XRD). The potassium hexaniobate was converted into its acid phase (designated as H^+-niobate) by refluxing a suspension of $K_4Nb_6O_{17}$ in a 6 M HNO_3 solution at 60 °C for 1 week [20]. During the proton exchange reaction, the acid solution was replaced with a fresh one each two days.

2.2. Niobate exfoliation

The exfoliation of niobate sheets was achieved by reacting the proton niobate with tetrabutylammonium hydroxide (TBAOH) with the butylamine/H^+-niobate molar ratio equal to 1:1. In a typical reaction, 0.5 g proton niobate was added to 250 ml TBAOH aqueous solution, and ultrasonicated at ambient temperature for 2 h. Exfoliation occurs as a result of the penetration of large TBA^+ molecules into the interlayer, opening up the interlayer to delaminate the powder into single nanosheets. After the exfoliation reaction, the flask was kept without stirring for 1 day to allow the separation of the non-delaminated particles (solid fraction deposited in the bottom of the flask) from the dispersion of the exfoliated particles. The obtained colloidal suspension of individual niobate nanosheets was centrifuged, washed three times with water to remove the excessive TBA^+, and then redispersed in water. The pH value of the colloidal suspension was about 10.

2.3. Preparation of SnO_2–hexaniobate layered nanocomposite

A dispersed SnO_2 nanosol was prepared by hydrolysis of $SnCl_4$ in a NaOH aqueous solution, according to the procedure reported previously [21]. The as-prepared SnO_2 sol was then dispersed into the obtained niobate colloidal suspension with a Sn/Nb molar ratio of 1:1 under vigorous stirring. Prior to the addition, the pH value of the exfoliation suspension was carefully adjusted to 8 with a 0.5 M HNO_3 solution. After stirring at room temperature for 12 h, an amount of 0.5 M HNO_3 was slowly dropped under vigorous stirring to adjust the pH value of the mixed suspension to less than 3, and flocculation was observed. Then, the mixture was continuously kept stirring for 5 h and aging for 2 days to ensure completion of the intercalation reaction. The floccule was separated by centrifugation at 4000 rpm, washed several times with ethanol/water mixed solvent (1:1 in v/v) and deionized water to remove other soluble products. The product was finally dried in a desiccator under vacuum at 100 °C for 24 h (designated as SnO_2/Nb_6O_{17} nanocomposite). For comparison, a sample flocculated without SnO_2 loading (designated as restacked niobate) was prepared as well, and the as-prepared SnO_2/Nb_6O_{17} nanocomposite was calcined at 250 °C in N_2 atmosphere for 2 h (designated as SnO_2/Nb_6O_{17}-250).

2.4. Characterization

Powder X-ray diffraction (XRD) measurements were performed at ambient temperature on a Bruker D8 Advance diffractometer using Ni-filtered Cu Kα radiation (λ = 1.5418 Å) under the accelerating voltage of 36 kV at a scanning rate of 2° at 2θ min^{-1} from 2° to 50°. Scanning electron microscope (SEM) images were examined with a Hitachi S-3500 N microscope. Infrared spectra were recorded at room temperature on a Nicolet 470 FT-IR spectrophotometer as KBr pellets in the 4000–400 cm^{-1} region. Simultaneous TG/DSC measurements were performed from ambient temperature to 1000 °C in flowing N_2 at a rate of 10 °C min^{-1} using a Shimadzu TGA-60H thermal analyzer. X-ray photoelectron spectroscopy (XPS) measurements were performed on a VG Escalab MK II spectrometer (Scientific Ltd., UK) with non-monochromatic Al Kα X-ray (1486.6 eV). The pressure in the chamber during the experiments was less than 10^{-6} Pa. The analyzer was operated at 20 eV pass energy with an energy step size of 0.1 eV. Specific surface area and porosity measurements were carried out on a Nova 1200e instrument at liquid-nitrogen temperature using ultrapure nitrogen gas as the adsorbate. The samples were degassed at 120 °C for 1 h under vacuum prior to the adsorption measurements. Diffuse reflectance UV–vis spectra were recorded on a Shimadzu UV-2550 spectrophotometer equipped with an integrating sphere 60 mm in diameter using $BaSO_4$ as a reference. The diffuse reflectance R was transformed to a magnitude proportional to the extinction coefficient by Kubelka–Munk function [22],

$$F(R) = (1 - R)^2/2R \tag{1}$$

The band gap energy was determined from the onset of the diffuse reflectance spectrum.

2.5. Photodegradation of acid red G

The photocatalytic activities of the as-prepared photocatalysts were evaluated by the photodegradation of acid red G aqueous solution in a quartz vessel in response to ultraviolet light at ambient temperature. 0.1 g of the samples was dispersed in 100 mL of 50 mg/L acid red G aqueous solution in a 150-mL vessel. Prior to illumination, the suspensions were magnetically stirred in the dark for 2 h to ensure the establishment of adsorption–desorption equilibrium of acid red G on the sample surfaces. The equilibrium adsorption degrees for all investigated samples were determined to be less than 2.5%. Subsequently, the photocatalytic reactivity tests were carried out in aerobic conditions and irradiated under a Philips TUV4 W/G4T5 lamp with a peak wavelength of 254 nm. At given intervals, 5 mL of the suspension was extracted and subsequently centrifuged at a rate of 5000 rpm for 10 min to remove the particles of catalyst. The concentration change of acid red G was then determined by measuring the maximum absorbance at 505 nm as a function of irradiation time using a Shimadzu UV-2550 UV–vis spectrophotometer. The photodegradation efficiency of acid red G was defined as $\eta = (C_0 - C_t)/C_0 \times 100\%$, where C_0 is the initial concentration of acid red G and C_t is the concentration at certain reaction time t (min). The activities of the as-prepared photocatalysts were evaluated by calculating the photodegradation efficiency of acid red G as a function of illumination time.

3. Results and discussion

3.1. Characterization of the photocatalysts

The synthetic technique for the preparation of the layered nanocomposite is represented in Scheme 1. The powder XRD patterns of the as-prepared $K_4Nb_6O_{17}$, H^+-niobate, restacked niobate, SnO_2, SnO_2/Nb_6O_{17} nanocomposite and its calcined derivative SnO_2/Nb_6O_{17}-250 are shown in Fig. 1. The strong and sharp (0 4 0) diffraction peak with d = 0.94 nm (2θ = 9.4°) of $K_4Nb_6O_{17}$ indicates that the well-ordered lamellar structure was formed. After acid treatment, the (0 2 0) and (0 4 0) diffraction peaks of $K_4Nb_6O_{17}$ were shifted toward higher angles (from 4.7° and 9.4° to 5.5° and