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Facile synthesis and characterization of low crystalline Nb_2O_5 ultrafine nanoparticles as a new efficient photocatalyst

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ABSTRACT

Low crystalline Nb_2O_5 ultrafine nanoparticles were successfully prepared via a facile solvothermal method using $NbCl_5$ as precursor in this investigation. The crystalline structure of the Nb_2O_5 ultrafine nanoparticles is characterized by the X-ray diffraction (XRD) and high resolution transmission electron microscopy (HRTEM). The Nb_2O_5 nanoparticles have large surface area and very fine particle size, which are favorable for increasing the active sites to take part in the catalytic reaction. The Nb_2O_5 nanoparticles exhibited high degradation rates for organic dye degradation under visible light irradiation and exhibited stable photocatalytic hydrogen evolution activity under simulated sunlight irradiation. The nanocrystals highly dispersed in the amorphous matrix are found to be responsible for the photocatalytic ability of the material.

1. Introduction

Semiconductor photocatalysis is believed to be one of the most promising technologies to solve the environmental problems related to greenhouse gas emissions and wastewater pollution [1]. The performance of the used photocatalyst is the most significant factor influencing catalytic efficiency. Pure or doped metal oxide semiconductors (e.g., TiO_2 and WO_3) are commonly employed as photocatalysts [2,3]. However, most of these photocatalysts are either UV-light responsive or low efficiency, which limit their long term and large scale applications. During the recent years, intensive research effort has been spent on searching for more suitable semiconductors for efficient photocatalytic applications.

High crystallinity is normally considered to be important in enabling the efficient separation and diffusion of photogenerated charge carriers, which is crucial for obtaining high photocatalytic efficiency. Numerous defects in amorphous semiconductors may act as the recombination center for the photogenerated electrons and holes and lower the photocatalytic activity. However, several reports demonstrated that amorphous photocatalysts, such as C_3N_4 [4], $Co_{1.28}Mn_{1.71}O_4$ [5] and $NaTaO_x$ [6], have shown a remarkable success in achieving high photocatalytic activity. The advantages of using amorphous semiconductors as photocatalysts include their much wider light absorption range, much higher specific surface area and much smaller particle size. Unfortunately, due to many reasons, the systematic study of amorphous photocatalysts is rarely reported. Most studies were focused on the crystalline semiconductors which are relatively easy to prepare and usually exhibit high photocatalytic activity. In this investigation, we found that Nb_2O_5 ultrafine nanoparticles with low crystallinity are visible light responsive and could be utilized as an efficient photocatalyst for hydrogen production and water decontamination.

Nb_2O_5 has attracted increasing attention in view of its potential utility for the fabrication of nanostructured materials with energy storage functions [7]. On the other hand, the photocatalytic properties of this semiconductor, especially its H_2 production [8] and photodegradation performance [9], have drawn much intention in the past ten years. Although Nb_2O_5 is reported to exist in many polymorphic forms [10], the hydrothermally prepared Nb_2O_5 is usually in an amorphous state, and it is usually annealed to form crystalline state since crystalline Nb_2O_5 is expected to have better photocatalytic activity [8–10]. However, thermal annealing inevitably causes an aggregation of the nanoparticles and a decrease of surface area, which probably lower the catalytic efficiency of the photocatalyst. Herein, we report the facile preparation method of Nb_2O_5 ultrafine nanoparticles via a solvothermal process using $NbCl_5$ as precursor. Though with low

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crystallinity, the resulting Nb_2O_5 possesses a large surface area and small particle size, which could offer numerous active sites for photocatalytic reactions. The Nb_2O_5 ultrafine nanoparticles showed stable photocatalytic activity under visible light or simulated sunlight irradiation.

2. Experimental details

2.1. Preparation of Nb_2O_5 nanoparticles

All the chemicals are analytical grade and used as received without further purification. Typically, 0.18 g $NbCl_5$ was dissolved in 40 mL of an ethanol/water mixture with a volume ratio of 1:1. After stirring for 2 h at room temperature, the transparent solution was sealed into a 50 mL Teflon-lined autoclave, and treated at a desired temperature for 48 h. The product is isolated and dried at 80 °C. The samples treated at 120 °C, 160 °C and 200 °C were accordingly identified as 120-Nb_2O_5, 160-Nb_2O_5 and 200-Nb_2O_5, respectively.

2.2. Material characterization

The crystal structure of samples was investigated using X-ray diffraction (XRD; Bruker D8 Advance diffractometer) with Cu Kα radiation at a scan rate of 1°min^{-1}. The chemical state of niobium and oxygen in the Nb_2O_5 nanoparticles was investigated by X-ray photoelectron spectroscopy (ESCALAB 250XI). The particle size and morphologies of the samples were investigated by scanning electron microscopy (SEM, Hitachi S4800) and transmission electron microscopy (HR-TEM, FEI Tecnai F20 G2 S-TWIN). High-resolution transmission electron microscopy (HRTEM) and selected-area electron diffraction (SAED) were performed on a system at 200 kV to further investigate the crystallographic structure of the Nb_2O_5 nanoparticles. UV–visible diffuse reflectance spectra of the samples were conducted on a UV/Vis NIR scanning spectrophotometer (Hitachi, UV-4100) equipped with an integrating-sphere accessory in the wavelength range of 200–800 nm. Nitrogen adsorption-desorption measurements were conducted at 77.35 K using a Micromeritics 3Flex analyzer (Micromeritics Instrument Corporation). The Brunauer-Emmett-Teller (BET) surface area was calculated from adsorption data.

2.3. Photocatalytic reactions

Photocatalytic degradation of Rhodamine B (RhB) was carried out in a PCX50A Discover (PerfectLight Co., Ltd.) multi-channel parallel photocatalytic reaction system equipped with a 5 W white LED light (400 nm ≤ λ ≤ 800 nm). In a typical process, 50 mL of an aqueous suspension of RhB (5 mg/L) and 50 mg of the prepared Nb_2O_5 powders were placed in a 50 mL bottle with a cap. The suspensions were magnetically stirred in the dark for 30 min before the light was turn on. The concentrations of the RhB were monitored using UV–vis spectrophotometer (Hitachi U-3010). The degradation efficiency could be calculated by the formula: $\eta\ (\%) = (C_0 - C)/C_0$ where C_0 refers to the initial concentration of the RhB and C the concentration of RhB at the specific testing time during the degradation.

The evaluation of hydrogen production by photocatalytic water splitting was performed under simulated sunlight irradiation using a 500 W Xe lamp (SQ-GXB500). 100 mg photocatalyst was placed into an aqueous methanol solution (100 mL, 10%) in a closed gas circulation system (Perfectlight labsolar-III). Methanol was used as a sacrificial reagent. The amount of generated H_2 was detected in every 3 h by a gas chromatograph (Shimadzu GC-2014) with TCD detector. In order to improve the photocatalytic activity of the samples, 1 mL 0.01 mol/L $HAuCl_4{\cdot}4H_2O$ solution as co-catalyst was added to the reactor.

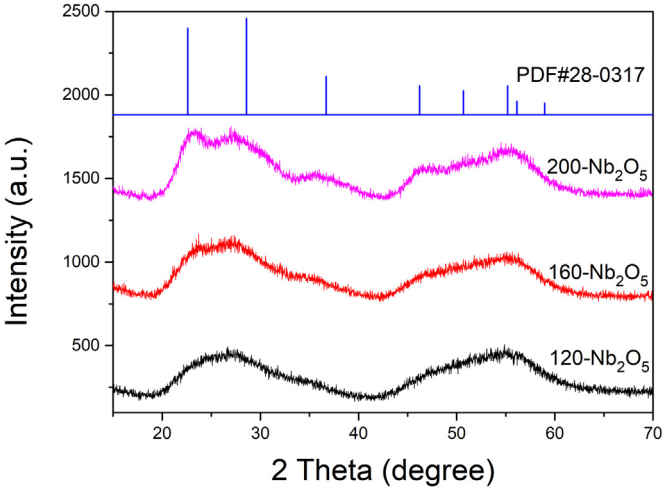

Fig. 1. XRD patterns of the Nb_2O_5 nanoparticles synthesized at different temperature.

3. Results and discussion

The XRD patterns of the as-prepared Nb_2O_5 ultrafine nanoparticles were shown in Fig.1. As can be seen, the XRD pattern of 120-Nb_2O_5 is characterized by two large and broad peaks centered at about 27°and 55°, which is consistent with those reported in the reference [8]. The comparison among the three samples suggests that the peak intensity of the Nb_2O_5 ultrafine nanoparticles was increased with increasing the solvothermal temperature, indicating the crystallinity was increased with an increase in the solvothermal temperature. Though the peak intensity was very low, it is true that all the three samples, especially 160-Nb_2O_5 and 200-Nb_2O_5, were not necessarily amorphous, because of their enhanced XRD peaks. These peaks are attributed to the formation of hexagonal Nb_2O_5 phase according to the standard ICDD PDF (Card No. 28-0317) even though a considerable amount of amorphous phase was simultaneously contained. However, the crystallinity is very low or the crystallite size is very small, and their identification by XRD then becomes very difficult.

Surface chemical states of the Nb_2O_5 nanoparticles were examined by the XPS technique. The survey spectrum of in Fig.2a indicated that the photocatalyst contain Nb, O and C elements. The C element is from the XPS instrument itself. The binding energies for Nb $3d_{3/2}$ levels in 120-Nb_2O_5, 160-Nb_2O_5 and 200-Nb_2O_5 were found to be 207.06 eV, 207.11 eV and 206.96 eV, respectively. It is known that samples with higher crystallinity sometimes exhibit shifts of the binding energies to higher values [11]. In this investigation, this feature did not occur, which is another evidence of the low crystallinity of the Nb_2O_5 nanoparticles. The peaks located at 530.01 eV, 530.11 eV and 530.01 eV for 120-Nb_2O_5, 160-Nb_2O_5 and 200-Nb_2O_5 were corresponds to O1s in Nb_2O_5 [12]. The XPS data revealed that there was only Nb_2O_5 species in the Nb_2O_5 nanoparticles.

As shown in Fig.3(a), the morphologies of the resulting 160-Nb_2O_5 were investigated by scanning electron microscopy (SEM). The micrographs show the presence of porous agglomerates composed of nanometre-sized ultrafine particles. These agglomerates exhibit an irregular morphology and a wide size distribution. To further observe the morphology of the ultrafine particles, the corresponding TEM image of 160-Nb_2O_5 is shown in Fig.3(b). It is clear that the size of the agglomerates is from a few tens to hundreds of nanometres, in good agreement with the SEM result. HRTEM analysis revealed the presence of nanocrystals with a size of about 3–4 nm embedding in an amorphous matrix, as indicated by the rectangles in Fig.3(c). The lattice fringe spacing of the nanocrystals was measured to be 0.3937 nm, which matches well with the d-spacing of the (001) plane of hexagonal Nb_2O_5 (JCPDS 28–0317).