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A kind of economical, environment-friendly and controllable synthesis of Nb_3O_7F nanowalls and their photocatalytic properties

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ABSTRACT

Niobium oxyfluoride (Nb_3O_7F) with excellent optoelectronic properties holds great promise for applications in photocatalysis, hydrogen production and solar cell. However, how to avoid volatile, pungent & corrosive hydrofluoric acid (HF) in Nb_3O_7F production is always an important issue. Here, we demonstrate a facile hydrothermal approach to prepare Nb_3O_7F nanowalls without adding HF. Different characterization tools have been used to analyze the phase, microstructure and photocatalytic properties. The calculated UV-vis and XPS spectra show that the bandgap (E_g) of Nb_3O_7F nanowalls is about 3.03 eV and valence-band maximum (VBM) is about 1.82 eV. The photocatalytic experiments show that Nb_3O_7F nanowalls with good stability and repeatability exhibit higher visible-light activity for degrading methylene blue (MB) than commercial P25.

1. Introduction

Over the past few decades, TiO_2 photocatalytic technology has attracted wide attention for water purification and environmental protection [1–4]. However, its application has been limited by its low spectrum absorption, high electron-hole recombination and weak carrier separation capacity [5]. Although great progress has been made after years of efforts, it is still a long way to realize the commercial applications [6,7]. Therefore, developing alternative or novel semiconductor photocatalysts has been one of research hotspots in recent years [8,9].

Therein, Nb_3O_7F (denoted as NOF) is emerging as a promising photocatalytic material due to its favorable optoelectronic properties, good crystallinity and excellent chemical stability [10,11]. However, traditional high-temperature solid-state synthesis results in low photocatalytic activity because of its small specific surface area, large particle size and nonuniform size distribution. To solve these problems, wet-chemical method has been developed recently [12,13]. But these approaches are unexceptionally evolved in volatile, pungent, poisonous & corrosive HF, resulting in security risk, high disposal cost and complicated process. On the other hand, it is hard for such methods to control the structure, morphology & particle size because the reaction rate is very fast in HF solutions. Finally, these methods, using high-purity Nb powder as niobium resource, are involved into high cost and disposal cost, rapid reaction rate and uncontrollable process. Therefore, it is very urgent to develop some new methods for the synthesis of NOF nanomaterials without adding HF.

In this work, NOF nanowalls with low cost have been successfully synthesized through a simple hydrothermal method, employing NbF_5 as the niobium source and fluorine source directly. The effects of preparation process on the phase and photocatalytic performance have been investigated in details.

2. Experimental

All chemicals were analytical grade and used without further purification. Typically, 3 mmol NbF_5 was dissolved into DI water and stirred vigorously at room temperature to achieve transparent solution. Subsequently, above solution was transferred to a Teflon-lined autoclave and heated to 180 °C for 24 h. After cooled down to room temperature naturally, the final products were collected, washed with deionized water & absolute ethanol for several times, and dried at 70 °C for 5 h.

3. Results and discussion

Fig. 1a shows the X-ray diffraction (XRD) patterns of final products prepared at different temperatures. When the temperatures

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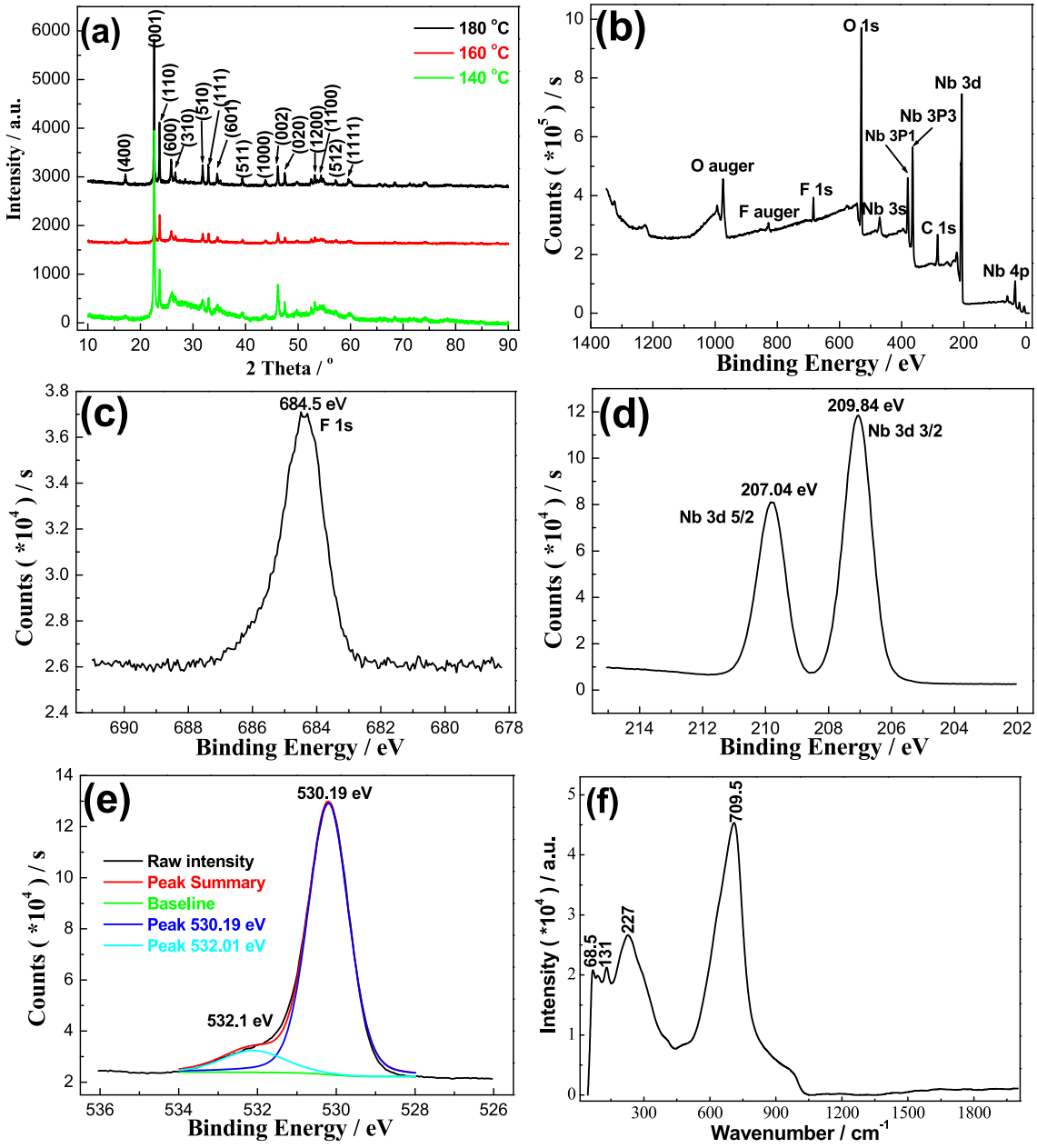

Fig. 1. Structural characterization. (a) XRD patterns; (b) wide-scanned XPS spectrum; (c–e) narrow-scanned XPS spectra of F 1s, Nb 3d and O 1s; (f) Raman spectrum.

are 180 °C and 160 °C, all peaks match well with orthorhombic NOF (JCPDS No. 74-2363). The main peaks can be indexed to (4 0 0), (0 0 1), (1 1 0), (6 0 0), (5 1 0), (1 1 1), (0 0 2), (0 2 0), (1200) and (1110) planes at 2 = 17.145°, 22.624°, 23.587°, 25.840°, 31.811°, 32.912°, 46.195°, 47.397°, 53.132° and 54.327°. However, the diffraction peaks at 2 = 22.62° and 47.40° deviate markedly and broaden clearly at 140 °C, indicating that the crystallinity decreases at low temperature. That is, low temperature is not in favor of the synthesis of pure NOF materials.

X-ray photoelectron spectrometer (XPS) spectra were used to further reveal the surface species and chemical states of final samples prepared at 160 °C. As shown in Fig. 1b, the survey spectrum proves the existence of Nb, O and F elements. The peak at 684.5 eV is typically attributed to F 1s (Fig. 1c). Nb $3d_{3/2}$ and Nb $3d_{5/2}$ peaks match the binding energies well at 209.84 and 207.04 eV (Fig. 1d), belonging to Nb^{5+} oxidation state [14]. Two peaks at 530.19 and 532.1 eV in the O 1s correspond to the lattice oxygen and surface adsorbed oxygen, respectively (Fig. 1e). Above results confirm the existence of Nb—F bond and Nb—O band [15–17]. Raman spectroscopy was applied to further understand the microstructure (Fig. 1f). Obviously, there are four main peaks at 68.5, 131, 227 and 709.5 cm^{-1}, corresponding to O=Nb—O—F vibration mode, Nb—F vibration mode, O=Nb=O twisting mode and Nb—O—Nb stretching vibration mode in NOF, respectively [11,18]. Based on these results, it can be confirmed that NOF has been successfully synthesized.

The morphological evolution was monitored by field-emission scanning electron microscopy (FESEM). As shown in Fig. 2a, the products are composed of nanosheets with a length of about 1 μm and a width of about 500 nm. The BET characterization shows that specific surface area is 77.748 cm^2/g, further indicating that the product is a kind of nanomaterials. With the increase of temperature, the average thickness of nanosheet also increases from 30 nm to 120 nm (Fig. 2b). Low-magnified FESEM images show that nanosheets are easy to gather together and form spherical nanowalls. Moreover, hydrothermal time has a great influence on