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Large-scale synthesis of single-crystalline KNb_3O_8 nanobelts via a simple molten salt method

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Abstract

Single-crystalline potassium triniobate (KNb_3O_8) nanobelts with widths of 50 to several hundreds nanometers and length up to tens of microns were synthesized in a large-scale by a facile molten salt synthesis method. The phase of the as-prepared nanobelts was determined by X-ray diffraction, and the morphology and structure were characterized by scanning electron microscopy, transmission electron microscopy, and selected area electron diffraction. The band gap of KNb_3O_8 nanobelts was estimated to be about 3.45 eV from the onset of UV–vis diffuse reflectance spectrum. The obtained KNb_3O_8 nanobelts exhibited high photocatalytic efficiency for the degradation of methyl orange under UV irradiation.

Keywords: Niobates; Nanomaterials; Molten salt synthesis; Photocatalytic property

1. Introduction

Complex oxides of niobium comprise a large group of compounds that are known to exhibit a variety of properties, including excellent nonlinear optical property, high dielectric constants, high photocatalytic activity, etc. [1–5]. Among these complex oxides, potassium triniobate (KNb_3O_8) with unique layered structures has excellent photochemical and semiconductor properties, which could have applications in photocatalyst and luminescence fields [6–8]. Conventionally, potassium niobates were prepared by solid state reaction through heating stoichoimetic mixture of Nb_2O_5 and potassium carbonates at high temperature [9]. Recently, with the rapid development of synthetic strategies of nanomaterials, several wet-chemical methods have been explored to prepare a wealth of potassium niobates nanostructures. Li and co-workers [10] developed a low temperature hydrothermal method for the synthesis of $KNbO_3$, KNb_3O_8 and $K_4Nb_6O_{17}$ nanocrystals with different morphologies by adjusting alkalinity of the reaction system. A successful preparation of $KNbO_3$ nanowires was reported by a hydrothermal route [11]. Zhang et al. [6,7] demonstrated a hydrothermal route to synthesize KNb_3O_8 nanoscaled leaf-like network, and investigated its photocatalytic degradation of acid red G. Despite the progress in niobate nanomaterials, no synthesis of KNb_3O_8 one-dimensional (1D) nanostructure has been reported yet. Herein, we report a facile one-step molten salt synthesis (MSS) method to prepare single-crystalline KNb_3O_8 nanobelts in a large-scale through simply calcining Nb_2O_5 in molten mixture salts of KCl and K_2SO_4. This method is promising for environment-friendly, large-scale, and low-cost synthesis of KNb_3O_8 nanobelts with high quality and uniform morphology since no harmful surfactants or templates are used.

2. Experimental

In a typical synthetic process, 0.2 g Nb_2O_5 powders were first mixed with 1 g KCl and 2 g K_2SO_4, and then ground thoroughly for about 20 min. The mixture was placed in an alumina boat and heated at 900 °C for 2 h, and then cooled naturally to room temperature. Finally, the pristine powders were washed in distilled water several times to remove the remnant salts, and then dried at 80 °C for several hours.

The phase of the obtained products was determined using X-ray diffractometer with Cu K_α radiation (Rigaku D/max-γB,

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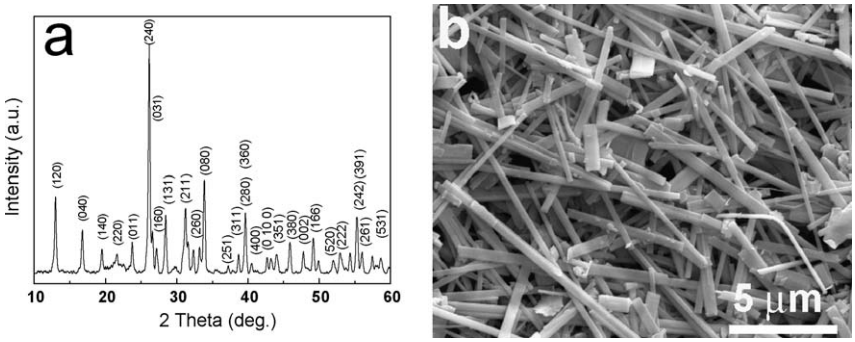

Fig. 1. (a) XRD pattern and (b) typical SEM image of the as-synthesized KNb_3O_8 nanobelts.

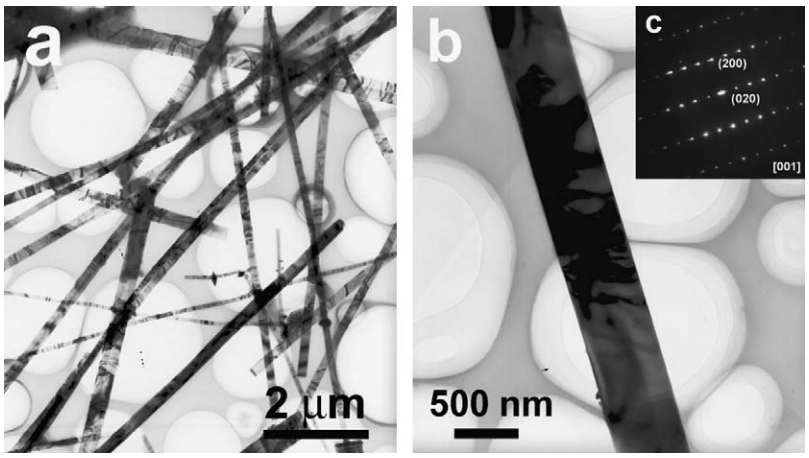

Fig. 2. (a) TEM image of the as-synthesized KNb_3O_8 nanobelts showing their general morphology, (b) TEM image of an individual nanobelt and (c) corresponding SAED pattern taken from the selected nanobelt.

λ = 1.5406 Å). The morphology of the sample was examined by scanning electron microscopy (SEM, FEI Sirion). Transmission electron microscopy (TEM) observation and selected area electron diffraction (SAED) were carried out on a Philips CM-12 microscope operated at 120 kV. The as-prepared nanobelts were dispersed in ethanol aided by ultrasonic treatment. One droplet of the suspension was added to a holey carbon film supported on a copper grid for TEM characterization.

Ultraviolet–visible (UV–vis) light diffuse reflectance spectrum of the synthesized nanobelts was obtained using a TU-1901 spectrometer. The photocatalytic activity of KNb_3O_8 nanobelts was evaluated by measuring the photodegradation of a solution of methyl orange (50 μL, 1 mmol/L) in the presence of KNb_3O_8 nanobelts (3 mL, 60 mg/L) under exposure to UV light (300 W). The characteristic absorption of methyl orange was chosen to monitor the online photocatalytic degradation process using Halogen Light Source HL-2000 (Ocean Optics Inc.).

3. Results and discussion

Fig. 1a shows XRD pattern of the as-synthesized KNb_3O_8 nanobelts. All the diffraction peaks could be readily indexed to orthorhombic phase of KNb_3O_8 (PDF No. 38-0296) with lattice parameters of a = 0.8903 nm, b = 2.116 nm, and c = 0.3799 nm, indicating that the obtained product is highly crystallized phase-pure KNb_3O_8 without any impurities. A typical SEM image of the as-prepared KNb_3O_8 nanobelts is shown in Fig. 1b. The belt-like characteristics of the obtained product are well depicted for

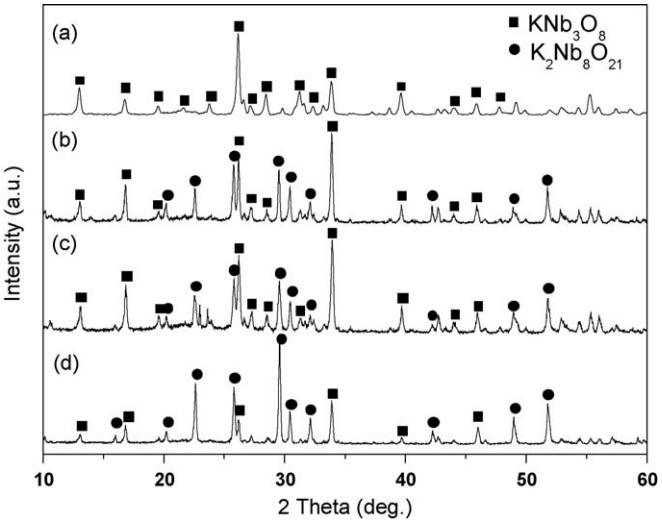

Fig. 3. XRD patterns of the obtained products with different weight ratios R of KCl to K_2SO_4. (a) R = 0.5; (b) R = 1; (c) R = 2; (d) R = 4.

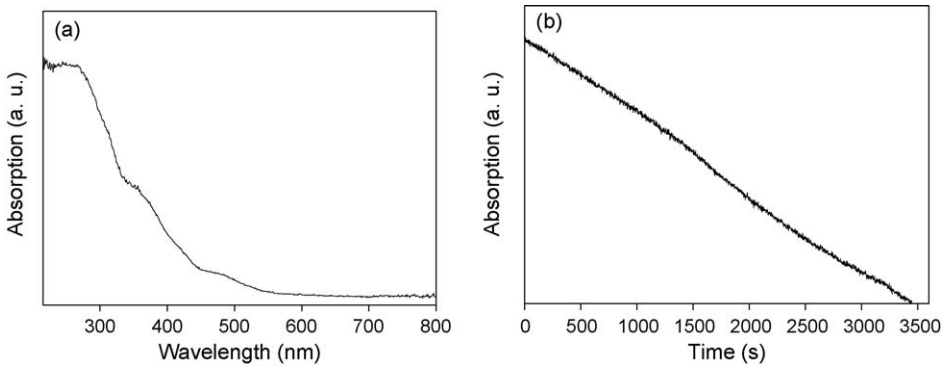

Fig. 4. (a) UV–vis diffuse reflectance spectrum of KNb_3O_8 nanobelts. (b) Time-dependent absorption of methyl orange solution in the presence of KNb_3O_8 nanobelts under exposure to UV light.

some wide belts, and most of the nanobelts have widths of several hundreds nanometers and lengths up to tens of microns. The SEM image demonstrates that high yield of the KNb_3O_8 nanobelts can be obtained by this facile MSS route.

TEM image in Fig. 2a shows the general morphology of the as-synthesized KNb_3O_8 nanobelts. It is obvious that almost all the nanobelts are very thin with uniform belt-like morphology. Some narrow nanobelts with widths of 50–100 nm could be also found from TEM observation. Fig. 2b displays TEM image of an individual KNb_3O_8 nanobelt. The surface of the selected nanobelt is rather smooth. Although the width of this nanobelt is as large as 600 nm, it is still transparent to electron beam since the copper grid pattern below the nanobelts could be clearly seen, which indicates that the obtained nanobelts are very thin. The strain-induced ripple-like contrast is due to the bending of the nanobelts, which substantiates the small thickness of the nanobelts. Fig. 2c gives the corresponding SAED pattern taken from the selected KNb_3O_8 nanobelt shown in Fig. 2b. The highly single-crystallized structure of the KNb_3O_8 nanobelts is depicted. The zone axis of the SAED pattern is indexed to be [0 0 1] axis. The streaks in the pattern further suggest the 1D characteristics of the nanobelts, and the growth direct of the nanobelt is determined to be [1 0 0] crystallography direction.

As for MSS, the molten salt is used as a reaction medium for reactant dissolution and precipitation. The features of this synthesis method are related to the surface and interface energies between the constituents and the salt, resulting in a tendency to minimize the energies by forming a specific morphology [12]. In the current work, the mixture salts of KCl and K_2SO_4 supplied not only molten salt environment but also K^+ source for the formation of KNb_3O_8 nanobelts. Using KCl as molten salt, single-phase $K_2Nb_8O_{21}$ nanoribbons or nanowires were obtained at calcining temperatures of 800 °C or 1000 °C, respectively [13–15]. The introducing of K_2SO_4 salt leads to rather different phase of the obtained product. In order to understand the effects of sulfate on the final product phase, several batches of experiments with different weight ratios (R) of KCl to K_2SO_4 were performed. XRD patterns of the obtained products were shown in Fig. 3. Single-phase of KNb_3O_8 was obtained with R of 0.5. With increasing KCl content in the mixture salts, the ratio of $K_2Nb_8O_{21}$ phase in the obtained product increased accordingly, as shown in panels b and c in Fig. 3. $K_2Nb_8O_{21}$ phase was dominant in the final product with R of 4 (see panel d in Fig. 3). When only KCl was used, single-phase of $K_2Nb_8O_{21}$ was obtained [13–15]. It is speculated that the solubility of Nb_2O_5 in K_2SO_4 should be much larger than that in KCl, and thus the reaction between Nb_2O_5 and K_2SO_4 would be preferable, resulting in the formation of KNb_3O_8 rather than $K_2Nb_8O_{21}$.

The UV–vis diffuse reflectance spectrum of KNb_3O_8 nanobelts is shown in Fig. 4a. The band gap of KNb_3O_8 nanobelts was estimated to be about 3.45 eV from the onset of spectrum. The photocatalytic degradation of methyl orange on KNb_3O_8 nanobelts was evaluated at room temperature, as shown in Fig. 4b. The absorption of methyl orange decreased almost linearly as the UV light exposure time increased, indicating that the photocatalytic degradation of methyl orange by KNb_3O_8 nanobelts with UV irradiation was a pseudo-first-order reaction. It was shown that the methyl orange was completely photodegraded after about 1 h, which suggested that KNb_3O_8 nanobelts could exhibit high photocatalytic efficiency for the degradation of methyl orange.

4. Conclusions

In summary, we have developed a simple one-step MSS method for the large-scale synthesis of single-crystalline KNb_3O_8 nanobelts. The introduction of certain amount of sulfate to molten chloride is vital for the formation of phase-pure KNb_3O_8 nanobelts, which is probably due to the solubility difference of Nb_2O_5 in these two kinds of salts. Since this method does not need any seed or surfactant, it is promising for environment-friendly, large-scale, and low-cost fabrication of 1D nanostructures with high quality. The obtained KNb_3O_8 nanobelts exhibit high photocatalytic efficiency for the degradation of methyl orange under UV irradiation.

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