

Synthesis and Characterization of KTiNbO_5 Nano-particles by Novel Polymerizable Complex Method

Ning-ning Wang, Yun-xiang Lan, Jie He,* Rui Dong,[†] and Jin-song Hu

School of Chemical Engineering, Anhui University of Science and Technology, Huainan 232001, P.R. China

*E-mail: jhe@aust.edu.cn

[†]Chemical and Biological Engineering College, Yancheng Institute of Technology, Yancheng 224051, P.R. China

Received May 3, 2013, Accepted June 25, 2013

The layered KTiNbO_5 was successfully synthesized with titanium(IV) isopropoxide and niobium oxalate by a novel polymerized complex (PC) method. The morphology and structure of the as-prepared sample was characterized by means of High-Resolution Transmission Electron Microscope, powder X-ray diffraction, and Laser Raman Spectroscopy. The spectral response characteristic was recorded by using UV-vis Diffuse Reflectance Spectroscopy. Results show that KTiNbO_5 as-prepared by PC method presents an uniform morphology of nano-particles, the mean particle sizes is *ca.* 28 nm corresponding to the (002), and the crystal structure can be well indexed to the orthorhombic phase. The sample as-prepared by PC method has higher band gap energy than that of the sample prepared by a solid-state reaction method due to the quantum size effect.

Key Words : Polymerizable complex, Niobium oxalate, Potassium titanoniobate, Structural characteristics

Introduction

Layered inorganic compounds have been interesting for many years because of their unique structures and chemical reactivity. They can be modified through ion-exchange,^{1,2} organic intercalation^{3,4} or exfoliation-assembly.⁵ Based on these modification, a lot of new materials can be constructed, such as photoluminescence material,⁶ fast proton conductivity,⁷ photocatalysts,^{8,9} solid acid catalyst,¹⁰ as well as functional composite material.¹¹

KTiNbO_5 is a well-known layered semiconductor material. Its structure is consisted of octahedral layers built up of structural units of 2×2 edge sharing octahedral to form

infinite ribbons, as shown in Figure 1.

As a photo-catalytic material, the properties of layered potassium titanoniobate depend on its structure and morphology, which was related to its synthetic method to some degree. KTiNbO_5 can commonly be prepared by a solid-state reaction (SSR),^{12,13} polymerizable complex (PC),¹⁴ or hydrothermal synthesis.² The SSR method is completed at a relative high temperature (> 1273 K), and can obtain a relatively stable product. However, the product has low specific surface area, non-uniform particle size and low reaction activity. The hydrothermal method is effective for synthesizing inorganic photocatalysts such as titanium oxide, niobium oxide and their composites KTiNbO_5 , and its condition is mild.^{2,15} The method has the ability to synthesis large crystals with high quality, but it is difficult to control the sample morphology. Polymerized complex method is a new method to prepare layered materials, which has also been used to prepare KTiNbO_5 .¹⁴ KTiNbO_5 obtained by PC method showed that the efficiency of photolysis of water was 10 times faster than that of the sample obtained by the SSR method. Unfortunately, the existing PC method requires expensive precursor such as niobium pentachloride or niobium ethoxide, and organic solvent such as methanol. Then, it is significant to use cheaper raw materials and an environment friendly process for PC method to prepare KTiNbO_5 .

In present study, KTiNbO_5 was synthesized by PC method used titanium(IV) isopropoxide and niobium oxalate as precursors. In order to explore the effect of PC method on the structure and morphology of the sample, the XRD, HRTEM, EDS, LRS and UV-vis DRS were used as the methods of characterization.

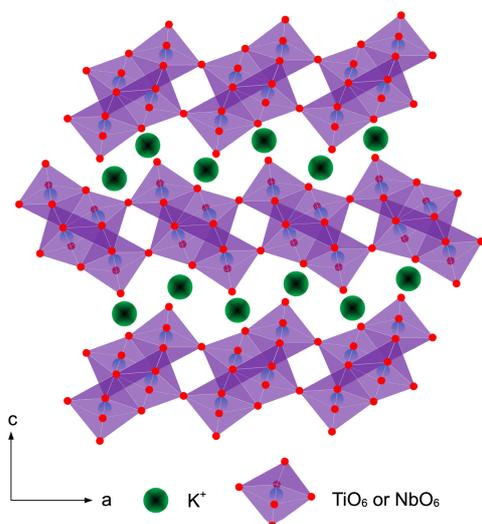


Figure 1. Structure diagram of KTiNbO_5 .

Experimental

Reagents and Materials. All chemicals used in this study were reagent grade, obtained from commercial sources and used without further purification.

Preparation of KTiNbO_5 . KTiNbO_5 was prepared by a polymerized complex (PC) method. The typical procedure is described as follows. Titanium (IV) isopropoxide (95%) was dissolved in ethylene glycol (EG, A.R.), the mixture was labeled solution A; a certain amount of citric acid (CA, A.R.) and potassium chloride (A.R.) were mixed with the solution A at room temperature, and a transparent solution (labeled solution B) was obtained. And then, the aqueous solution of Niobium oxalate was added into the solution B. The molar ratio of K:Ti:Nb:CA:EG is 1:1:1:15:60 in the last mixture. This mixture was pretreated at 353 K for 24 h, and then heated at 403 K for 24 h to obtain a polymeric gel. The gel was heated at 673 K for 4 h, and calcined at 973 K in air for 4 h. The powder was washed by deionized water and dried in air at 373 K for 10 h.

For the purpose of comparison, KTiNbO_5 was also prepared by the solid-state reaction method using K_2CO_3 (99.0%), Nb_2O_5 (99.5%) and TiO_2 (99.0%) as raw materials with a molar ratio of 1.15:1:2. The mixture was heated at 1373 K in air for 24 h.

Sample Characterization. The phase structure of the sample was determined by powder X-ray diffraction (XRD) performed on an XD-3 diffractometer (Beijing Purkinje General Instrument Co. Ltd.) by using $\text{Cu-K}\alpha$ radiation ($\lambda = 0.15406$ nm). The morphology and micro-structure observed by the high resolution transmission electron microscopy (HRTEM) by using a TECNAIF20S-TW2N (FEI Co. Ltd.) electron microscope, the composition of the powder was analyzed by energy dispersive X-ray spectroscopy (EDS) at operating voltage of 200 kV. The structure feature was characterized by Laser Raman spectra (LRS) with a resolution of 1 cm^{-1} by using a Confocal Raman Microscope (InVia Reflex Spectrometer System, Renishaw). The spectral response feature of the samples as-prepared was analyzed with a TU-1901 UV-visible diffuse reflectance spectrometer (Beijing Purkinje General Instrument Co. Ltd.) with an integrating sphere, and BaSO_4 was used as a reference sample.

Results and Discussion

Phase Structure and Morphology of KTiNbO_5 . The technology of powder X-ray diffraction was used to characterize the phase structures of the samples as-prepared, the results are presented in Figure 2.

It is proved that the sample as-prepared by PC method has an orthorhombic phase structure. All diffraction peaks can be well indexed to KTiNbO_5 , which agrees well with JCPDS 71-1747. The diffraction peaks at $2\theta = 9.56^\circ$, 19.21° , 23.95° and 27.66° are corresponded to (002), (004), (011) and (200) plane, respectively. Based on the Bragg angle of (002) plane, the d-spacing is 0.92 nm, which was calculated by Bragg equation $\lambda = 2d\sin\theta$. The mean size of the ordered (crystal-

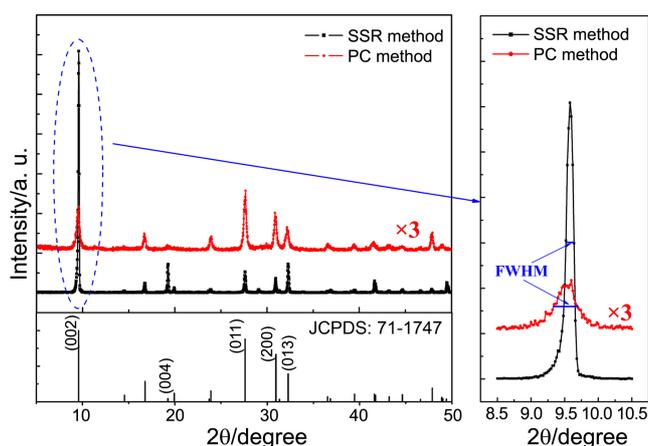


Figure 2. XRD patterns of the KTiNbO_5 samples.

line) domains τ_{hkl} was calculated according to the Scherrer's equation:

$$\tau_{hkl} = \frac{K\lambda}{\beta\cos\theta} \quad (1)$$

Where, K is the Scherrer's constant about 0.94, λ is the wavelength of the X-ray radiation used and β is the corrected full-width at half-maximum (FWHM) of corresponding peak in radians. According to the equation, the mean particle sizes τ_{002} is approximately 28 nm.

It can be observed in Figure 2 that the diffraction peak corresponding to (002) plane has a lower intensity and a wider FWHM for the sample prepared by the PC method than that of the sample prepared by SSR method. The phenomena are resulting from the smaller mean particle size, which is nanometer scale based on the Scherrer's equation and HRTEM results as follow shown.

HRTEM images of KTiNbO_5 prepared by PC method are shown in Figure 3. One can find that the sample has a well-ordered layer structure and a uniform particle size. The nano-particle in width and length is *ca.* 30 nm and 50 nm respectively. The width of the nano-particle is almost the same to the average dimensions of the elementary crystal-lites along the (002) plane, which is calculated based on Scherrer's equation. Figure 3(c) is the lattice fringe image of a KTiNbO_5 particle. The d-space of (002) plane is 0.94 nm in Figure 3(c), which is approach to 0.92 nm calculated based on the Bragg equation. The EDS data in Figure 3(d) and e shows that the molar ratio of K, Ti, Nb and O in the sample is approximately equal to 1:1:1:5, it is proved that the chemical composition of the titanoniobate as-prepared is KTiNbO_5 .

Microstructure and Spectral Response Characteristics of KTiNbO_5 . The vibration spectra related to specific polyhedral structures of the KTiNbO_5 as-prepared were determined by the Raman spectroscopy, and the results are showed in Figure 4. The bands located at 235, 268, 342 and 871 cm^{-1} are assigned to the stretching and bending vibrations of TiO_6 octahedral.¹⁶ And the bands at about 444 and 653 cm^{-1} originate from the framework Ti–O–Ti vibrations

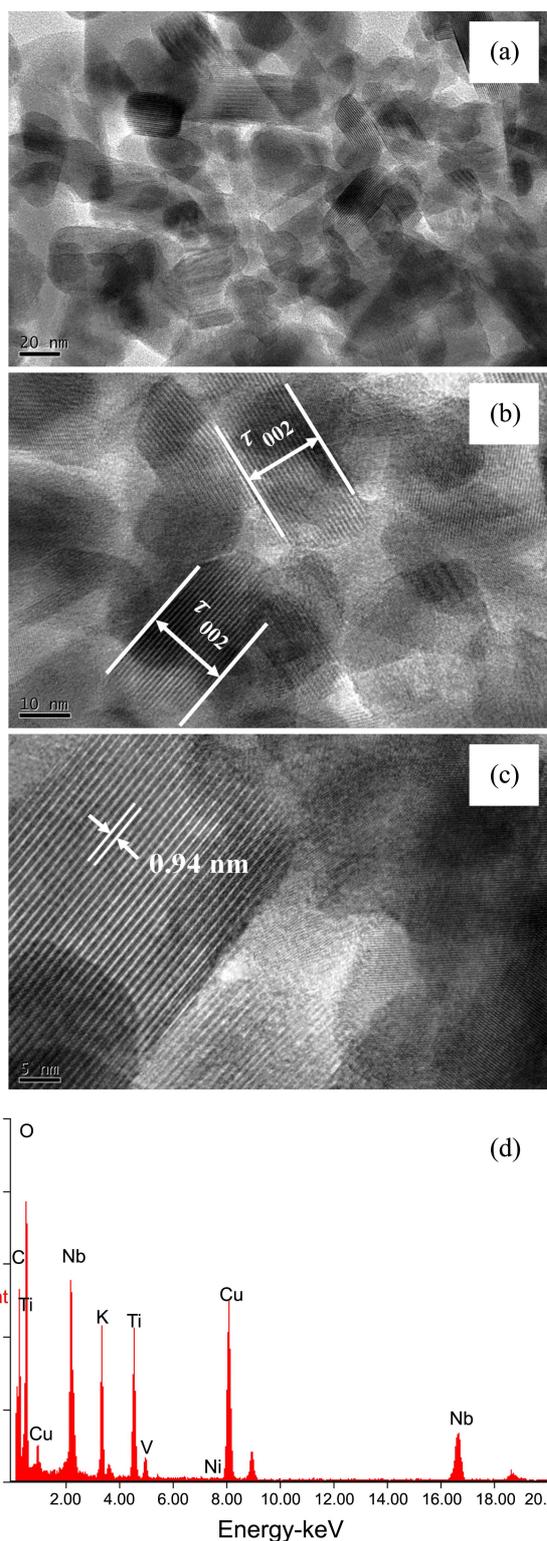


Figure 3. HRTEM images (a, b, c) and EDS (d) of the KTiNbO_5 sample prepared by PC method.

and Ti–O–Ti stretch in the edge-shared TiO_6 , respectively.¹⁷ The band located at 544 cm^{-1} is attributable to the Nb–O–Nb stretching mode, and the band located at 891 cm^{-1} for the sample, which should ascribe to the short Nb=O stretching mode.¹⁸

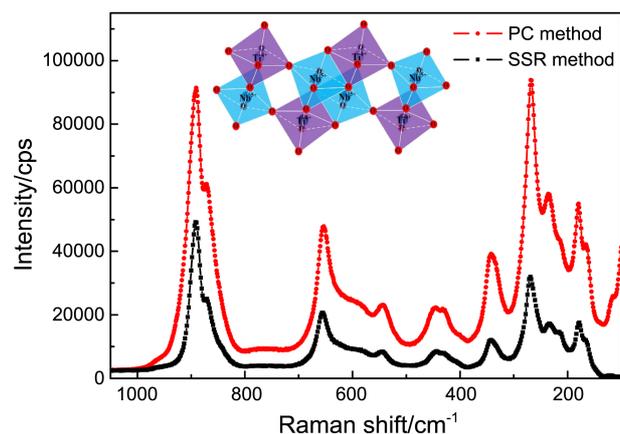


Figure 4. Raman spectra of the KTiNbO_5 samples.

The Raman shifts of the relevant functional groups are almost the same to the samples prepared by PC method (Fig. 4(a)) and SSR method (Fig. 4(b)). It can be inferred that the molecular environment such as the local stress in structure of the KTiNbO_5 crystal which was prepared by two methods is almost the same. However, the FWHMs and relative intensities of some peaks in Raman spectra have differences. The scattering behavior and peak intensity of Raman spectra are affected by the thin-layer structure compounds having different grain boundaries and curvature. For example, the FWHM of the bands located at about 871 cm^{-1} and 891 cm^{-1} are *ca.* 24 and 34 in Figure 4, respectively, while the values in Figure 4(b) are *ca.* 19 and 25. The sample prepared by SSR method has a smaller FWHM due to its higher crystallinity.¹⁹

As shown in Figure 5, the spectral response characteristics of the samples as-prepared were studied by UV-vis-DRS. The obtained reflectance spectra were transformed into the dependencies of the modified Kubelka–Munk function:²⁰

$$F(R) = \frac{(1-R)^2}{2R} \quad (2)$$

The band gap energy E_g was determined by the extrapolation of the linear portion of the $(F(R) \cdot hv)^{0.5}$ curve via the photon energy hv to $(F(R) \cdot hv)^{0.5} = 0$. According to Figure 5, the KTiNbO_5 prepared by PC method has an absorption band edge at about 355 nm (corresponding band gap energy E_g is 3.49 eV). The value E_g is higher than that of the sample prepared by SSR method ($E_g = 3.35\text{ eV}$). This higher band-gap energy may be caused by its quantum size effect.

Matsumoto has noted an empirical correlation²¹ of metal oxide semiconductors containing d^0 and d^{10} metal ions between the conduction band potential (E_{CB}) and the band gaps (E_g) as follows:

$$E_{CB} \approx 1.23 - \frac{1}{2} E_g \quad (3)$$

Thus, one can estimate that the conduction band potential are -0.515 eV and -0.445 eV for the sample as-prepared by the PC and SSR method, respectively. The result indicates that there is a larger driving force resulted from the electrons

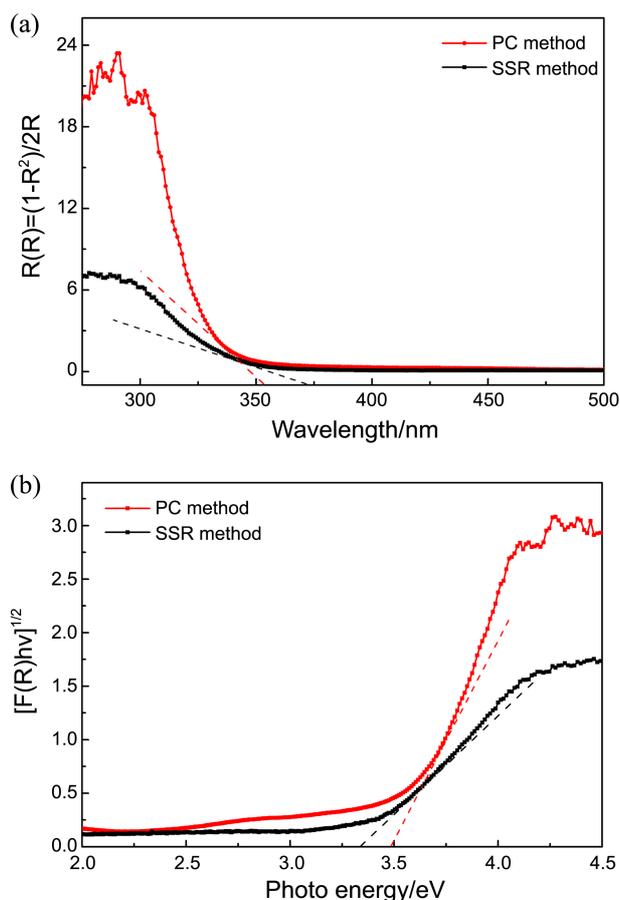


Figure 5. UV-vis DRS spectra of the KTiNbO_5 samples (a) and after transformed by Kubelka-Munk function (b).

in the conduction band of the KTiNbO_5 as-prepared by PC method.

Conclusion

In summary, the KTiNbO_5 nano-particles with apparently layered structure have been successfully prepared through the PC method using niobium oxalate and titanium(IV) isopropoxide as precursors. The KTiNbO_5 nano-particles have almost uniform size and well-ordered structure. Compared to the sample prepared by SSR method, the KTiNbO_5 nano-particles have obviously a quantum size effect. This novel polymerizable complex route provides an environment-

friendly process to prepare titanoniobates with niobium oxalate aqueous solution.

Acknowledgments. This work was supported by Natural Science Foundation of China (21271008), Natural Science Foundation of Anhui Province of China (11040606M38), and research fund of Key Laboratory for Advanced Technology in Environmental Protection of Jiangsu Province (AE201106). And the publication cost of this paper was supported by the Korean Chemical Society.

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