

# Exfoliation of layered hexaniobate in tetra(*n*-butyl)ammonium hydroxide aqueous solution

Ana Lucia Shiguihara, Marcos A. Bizeto, Vera R.L. Constantino\*

*Departamento de Química Fundamental, Instituto de Química, Universidade de São Paulo, C.P. 26077, CEP 05513-970, São Paulo, SP, Brazil*

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## Abstract

In this work, it is reported the influence of tetra(*n*-butyl)ammonium hydroxide (TBAOH) concentration on the  $\text{H}_2\text{K}_2\text{Nb}_6\text{O}_{17}$  exfoliation. A fixed amount of  $\text{H}_2\text{K}_2\text{Nb}_6\text{O}_{17}$  was reacted with solutions containing varied TBAOH concentrations (TBA<sup>+</sup>/H<sup>+</sup>-niobate molar ratios = 0.25, 0.50, 0.75 and 1.0). Two different niobate fractions are produced as the exfoliation reaction comes along: the first consists of a solid fraction that remains deposited at the bottom of reaction flask; the other is an opaque and stable suspension containing the exfoliated hexaniobate particles. The deposited solids have no organic species intercalated and the highest amount of exfoliated niobate particles was produced (ca. 65 wt%) when the TBA<sup>+</sup>/H<sup>+</sup>-niobate molar ratio was  $\geq 0.5$ . The delaminated particles were recovered by centrifuging the niobate dispersions and the isolated solids were characterized by X-ray diffractometry, surface area measurement, SEM and HRTEM microscopies. The solid isolated from colloidal dispersions with molar ratio 0.75 contains ca. of 10% of TBA<sup>+</sup> neutralizing the niobate layer charge, and the particles seems to be very thin and flexible under TEM observation. The decreasing of dispersion pH to 7 favors the particles coiling producing spiral nanotubes. Some particles consist of two tubes joint together in a parallel orientation, which suggests that these particles are formed by the opposite edges curling of one niobate sheet (like a parchment scroll with one roll to the left and one roll to the right). Further acidification to pH around 1 produces bent particles with specific area of  $139 \text{ m}^2 \text{ g}^{-1}$  (while  $\text{K}_4\text{Nb}_6\text{O}_{17}$  possesses only  $2 \text{ m}^2 \text{ g}^{-1}$ ) and the TEM micrographs suggest that scrolled particles are uncoiling at strong acid condition.

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## 1. Introduction

The preparation of colloidal dispersions of exfoliated nanosheets of layered compounds is a very interesting and important topic related to production of bulky pillared compounds, multilayers thin films, membranes or supports (for making proton conductors or coatings, for example), organic–inorganic nanocomposites, interstratified material and high surface area catalysts [1]. Layered exfoliated materials can also be used to form one-dimensional structures, such as nanotubes, nanorods and nanowires through soft chemistry routes [2,3].

The hexaniobate with formula  $\text{K}_4\text{Nb}_6\text{O}_{17}$  is a layered *n*-type semiconductor oxide constituted by negative layers built by distorted  $[\text{NbO}_6]$  octahedral units jointed by edges and corners.

Potassium cations sandwiched between these layers maintain electroneutrality [4]. The orthorhombic unit cell of  $\text{K}_4\text{Nb}_6\text{O}_{17}$  has four layers along the *b*-axis, oriented in such a way that it originates two different interlayer regions (designated I and II). Regions I and II are crystallographically distinct and also show different intercalation properties (intercalation and cation exchange are easier to occur in interlayer I) [5].

To promote exfoliation, it is necessary to decrease the electrostatic interaction between niobate layers and the cations in their vicinity, and also to promote water intercalation (osmotic swelling) [1]. This condition can be achieved by the correct combination of interlayer cation, exfoliation agent and swelling agent. Tetra(*n*-butyl)ammonium hydroxide (TBAOH) aqueous solution is an efficient medium to promote the separation of  $\text{H}_2\text{K}_2\text{Nb}_6\text{O}_{17}$  layers [6,7]. Further transformation of exfoliated layers into nanoscroll particles can be achieved by decreasing the pH or increasing the dispersion ionic strength [8,9]. The understanding of exfoliation process and also the possibility of controlling this process are crucial points for nanostructured

\* Corresponding author. Tel.: +55 11 30912151; fax: +55 11 38155579.  
E-mail address: [vrlconst@iq.usp.br](mailto:vrlconst@iq.usp.br) (V.R.L. Constantino).

materials development. Sazaki and Watanabe [10] have observed that the concentration of TBAOH is closely related to the delamination process of the layered titanate  $\text{H}_{0.7}\text{Ti}_{1.83}\square_{0.17}\text{O}_4$ . No similar studies are reported in the literature for layered niobates using this exfoliation agent.

Previous studies [11,12] had shown that it is also possible to use *n*-alkylamines instead of alkylammonium solutions to promote hexaniobate delamination. In recent paper [13], it is showed that *n*-butylamine is also an efficient exfoliation agent and delamination extension depends on amine/ $\text{H}^+$ -niobate molar ratio (where  $\text{H}^+$ -niobate represents the total amount of  $\text{H}^+$  in  $\text{H}_2\text{K}_2\text{Nb}_6\text{O}_{17}$ ). The best results were obtained using an amine to  $\text{H}^+$ -niobate ratio equal to 0.5. Low amine content in inter-layer region is an important condition to be guaranteed since the van der Waals forces between carbon chains preclude niobate layers separation and water intercalation when gallery region is saturated. Tubular particles with tunable diameters can also be isolated from alkylamines exfoliated hexaniobate dispersions [14]. These studies have shown that layered hexaniobate can be transformed directly into multi-walled nanoscrolls by means of easy soft chemical routes.

Recently it was demonstrated that tubular hexaniobate particles maintain the intercalation properties of pristine niobate [15]. The inclusion of a cationic porphyrin into hexaniobate nanoscrolls produced a nanocomposite with surface area of  $65\text{ m}^2/\text{g}$  while the same composite obtained from a dispersion of flat delaminated particles has only  $8\text{ m}^2/\text{g}$  [11]. Larger surface areas and tunable particles morphologies can expand the uses of layered niobates.

In this work, the influence of TBAOH concentration in hexaniobate exfoliation process was evaluated using  $\text{TBA}^+/\text{H}^+$ -niobate molar ratios 0.25, 0.50, 0.75 and 1.0. Solid samples were analyzed by powder X-ray diffractometry (XRD), thermal analysis (TGA), elemental analysis, infrared (IR) spectroscopy, scanning (SEM) and high-resolution transmission electron (HRTEM) microscopies. To our knowledge, this is the first time that a study about the appropriate conditions for hexaniobate exfoliation using TBAOH solution is performed.

## 2. Experimental

$\text{Nb}_2\text{O}_5$  was obtained from Companhia Brasileira de Metalurgia e Mineração (CBMM, Brazil). Reagents  $\text{K}_2\text{CO}_3$  and 20% TBAOH aqueous solution were obtained from Merck. All reagents were used as received.

### 2.1. Hexaniobate synthesis

$\text{K}_4\text{Nb}_6\text{O}_{17}$  was prepared by ceramic method heating a stoichiometric mixture of  $\text{Nb}_2\text{O}_5$  and  $\text{K}_2\text{CO}_3$  at  $1100^\circ\text{C}$  for 10 h, as previously described [11]. Hexaniobate crystal structure was confirmed by powder X-ray diffractometry (XRD). The  $\text{H}^+$ -exchanged form was prepared by ion exchange, refluxing a suspension of  $\text{K}_4\text{Nb}_6\text{O}_{17}$  in  $\text{HNO}_3$  6 mol/L solution for 3 days. Afterwards, the isolated material was characterized by XRD and thermogravimetric analyses (TGA) as previously

reported [16]. These data confirmed the isolation of the acidic hexaniobate of composition  $\text{H}_2\text{K}_2\text{Nb}_6\text{O}_{17}$ .

### 2.2. Hexaniobate exfoliation in TBAOH aqueous solution

The influence of tetra(*n*-butyl)ammonium hydroxide concentration in the exfoliation process was evaluated by using solutions with molar ratios  $\text{TBA}^+/\text{H}^+$ -niobate of 0.25, 0.50, 0.75 and 1.0. The  $\text{H}_2\text{K}_2\text{Nb}_6\text{O}_{17}$  mass and the suspensions volumes were kept constant at 0.50 g and 250 mL, respectively. Capped flasks containing fixed amounts of  $\text{H}_2\text{K}_2\text{Nb}_6\text{O}_{17}$  in TBAOH aqueous solution were maintained under constant stirring at room temperature for 2 weeks. Shaker was switched off during night. After this period, the flasks were kept without stirring for 1 day, and the opaque supernatants were separated from deposited solids (*i.e.* the sediment at bottom of the flasks) using Pasteur pipette. Afterwards, the deposited solids fraction were washed with water and dried under vacuum in a desiccator with silica gel. These solid samples are here abbreviated as TBAXX-dep where XX is  $\text{TBA}^+/\text{H}^+$ -niobate ratio used in the experiment.

Electronic absorption spectra of supernatant aliquots containing colloidal particles were recorded diluting 50-fold with deionized water.

### 2.3. Recovering of solids from TBAOH aqueous dispersion

Each colloidal dispersion was utilized as follow. Colloidal dispersion containing  $\text{TBA}^+/\text{H}^+$ -niobate molar ratio equal to 0.75 was dialysed against deionized water to remove the TBAOH excess. This process was over when water pH external to membrane reached 7.0. Afterward, niobate particles were isolated by submitting the aqueous dispersion to lyophilization (this solid sample is here abbreviated as TBA0.75-exf).

To niobate dispersions with  $\text{TBA}^+/\text{H}^+$ -niobate molar ratio equal to 1.0 and 0.50, an HCl (0.1 mol/L) solution was added until pH reached 7.0 and 1.0, respectively. After that, solids of both dispersions were recovered by centrifuging, washed with water and dried under vacuum in a desiccator with silica gel (these samples are here abbreviated as TBA1.0-exf(pH7) and TBA0.50-exf(pH1), respectively). Scheme 1 summarizes all experimental steps described in Sections 2.1–2.3.

### 2.4. Samples characterization

Elemental analyses (C, H, N) were carried out using a Perkin-Elmer model 2400 analyzer. Thermogravimetric analyses were carried out using a Shimadzu TGA-50 instrument under synthetic air (flow rate = 50 mL/min) and a heating rate of  $10^\circ\text{C}/\text{min}$  up to  $900^\circ\text{C}$ .

XRD patterns of samples were recorded on a Rigaku diffractometer mod. Miniflex using  $\text{Cu K}\alpha$  radiation ( $1.541\text{ \AA}$ , 30 kV and 15 mA) and a step of  $0.03^\circ$ . Specific area data (BET- $\text{N}_2$  method) were determined on Quantachrome model Quantasorb sorption system after heating samples at  $120^\circ\text{C}$  for 2 h under nitrogen gas flow.

FT-IR spectra of samples in KBr pellets were recorded on a Perkin-Elmer mod. 1750 spectrometer in the range

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