Lepidocrocite-like ferrititanate nanosheets and their full exfoliation with quaternary ammonium compounds

Bojan A. Marinkovic [a,*], Patricia I. Pontón [a], Juliana M. Resende [a], Sonia Letichevsky [a], Margarita Habran [a], Juliana Bento Viol [a], Omar Pandoli [b], Lidija Mancic [a,c]

[a] Department of Chemical and Materials Engineering, Pontifical Catholic University of Rio de Janeiro, CEP 22451-900 Rio de Janeiro, RJ, Brazil
[b] Department of Chemistry, Pontifical Catholic University of Rio de Janeiro, CEP 22451-900 Rio de Janeiro, RJ, Brazil
[c] Institute of Technical Sciences of SASA, Knez Mihailova 35/IV, Belgrade, Serbia

A B S T R A C T

Efficient methods for the synthesis of layered structure nanomaterials (nanosheets), their complete exfoliation (delamination) into the layers of atomic thickness and design of organic–inorganic nanohybrids present important stages toward development of improved polymer-based nanocomposites and pillared heterostructures with potential application in purification technologies such as photocatalysis. A rapid and efficient exfoliation process of protonated layered ferrititanates with lepidocrocite-like structure and formation of organic–inorganic nanohybrids is performed starting from the nanosheets composed of only a few host layers and nanometric lateral dimensions using quaternary ammonium compounds. These nanosheets are initially synthesized from a highly abundant precursor through an alkaline hydrothermal route. We demonstrated that dimethyldioctadecylammonium cations strongly interact with the exfoliated single host layers (0.75 nm thick) providing thermal stability (~500 °C) to the as-prepared organic–inorganic nanohybrid over the temperature range commonly applied for the processing of thermoplastic nanocomposites.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Layered titanates with lepidocrocite-like structure (hereafter LTs) and general formula $A_xTi_{2-y}M_yO_4$ (A = alkaline cation; M = $M^{3+}/2+/1+$ cation or vacancy; $0.8 \geq x \geq 0.7$) have been reported for the first time by Reid et al. [1]. This crystal structure (Fig. S1, Supplementary file) is built from dense, negatively charged, puckered layers consisted of edge shared distorted $Ti_{1-x}M_xO_2$ octahedra, whereas the charge neutrality is maintained by alkaline cations situated inside the off-centered rectangular prism sites within open spaces (galleries) formed between dense layers [1–4]. The occupancy of these sites by alkaline cations is maintained at about 70%. Like in some other layered structures, water molecules can swell the galleries, increasing, therefore, the interlayer spacing [5], reaching in some cases extraordinary 100-fold increase [6], while ion exchange reactions are readily performed through aqueous or molten exchangers [7].

It is worth noting that LTs present one of the lowest charge density of the host layers (~1/32 $Å^{-2}$) among layered materials, with the exemption of smectite clays [8,9]. Yamanaka et al. [10], reported, taking

as an example $Rb_{0.75}Ti_{1.25}Mn_{0.75}O_4$, that it is possible to tune and additionally reduce the charge density in LTs compounds by partial oxidation of Mn^{3+} to Mn^{4+} (reducing Rb^+ content in more than 60%), causing simultaneously an increase of interlayer distance due to a decrease of electrostatic interactions between Rb^+ and negatively charged manganese titanate layers. The exfoliation of LTs nanosheets into individual host layers is carried out through intercalation–swelling–agitation process, also known as ion exchange mechanism, mainly with the use of some tetraalkylammonium cations [11,12]. It is suggested that protonated LTs generally present the largest interlayer spacing in LTs family (~9.4 Å) [9], capable to accommodate bulky molecules. In accordance to that, it was demonstrated that fully protonated LTs, with Brønsted solid acidity, were suitable for exfoliation into individual host layers in aqueous solution of tetraalkylammonium compounds, being tetrabutylammonium hydroxide (TBAOH) the archetypal one [13,14], although ethylamine aqueous solution was recently reported to be capable of exfoliation as well [15]. It was suggested an optimal $TBA^+/H^+ = 5$ for the total exfoliation of LTs synthesized by solid state route, while the ratios ≥ 10 would predominantly lead to water swelling; on the other hand, the ratios ≤ 0.5 should cause only the intercalation of TBA^+ inside the galleries without exfoliation [16,17]. However, Yuan et al. [18] suggested that there was no lower TBA^+/H^+ threshold for the exfoliation with TBA^+. The same authors showed that the as-exfoliated individual

* Corresponding author.
  E-mail address: bojan@puc-rio.br (B.A. Marinkovic).

host layers could be further transformed into films by Langmuir–Blodgett deposition technique. It is worth noting, however, that layered phases without interlayer counterions, such as graphene, BN or transition metal dichalcogenides, are exfoliated differently, either by low yield mechanical exfoliation approach or more efficiently by sonication in an adequate solvent [12].

Intercalation of organic functionalities inside LTs galleries is also reported [19–21]. Octadecylsilyl and phenylsilyl groups were successfully intercalated inside $K_{0.80}Ti_{1.73}Li_{0.27}O_4$ through a stepwise procedure in which intermediate dodecyltrimethylammonium-exchanged $K_{0.80}Ti_{1.73}Li_{0.27}O_4$ had been formed first. This new material presented an excellent selectivity for 4-nonylphenol absorption from water, serving, therefore, for water purification. Dodecyltrimethylammonium-exchanged LTs intercalated with glycidyl and octadecyl functionalities were used for preparation of epoxy based nanocomposites with improved UV-light durability [21].

LTs are commonly synthesized through solid state reaction between alkali metal carbonates, metal oxides and TiO_2 at high temperatures between 800 and 1300 °C [20,22–24], resulting in crystals with submicronic sizes along *b* crystallographic direction (perpendicular to the host layers) and lateral dimensions reaching several or even tens of microns. A newly proposed approach for synthesis of titanate nanotubes with corrugated, stepped, layered structure [25] and LTs nanosheets [26–28] through alkaline hydrothermal treatment of an abundant precursor such as raw mineral sand provides a straightforward route for preparation of LTs nanosheets consisting of only a few stacked layers and with lateral (planar) lengths not larger than a few tens to several hundreds of nanometers. Although Maluangnont et al. [29] demonstrated recently that it is possible to control the lateral size of LTs originally synthesized by solid state route, through an additional step including the correct choice of tetraalkylammonium cation, tetraalkylammonium-to-proton ratio and the mode of the ion-exchange reaction, the lateral dimension of LTs is generally predefined by the size of the precursor crystals [23]. Therefore, it is advantageous to control dimensions of LTs crystals already in the synthesis stage. The LTs nanosheets currently synthesized through alkaline hydrothermal treatment of mineral sands have a high surface area (~80 $m^2 g^{-1}$) and could contain more or less Na^+/H^+ depending on the washing stage [26–28]. Jardim et al. [26] proposed that Fe^{3+}, originated from the dissolved ilmenite mineral sand, adopts an octahedral coordination inside the lepidocrocite-like host layers exchanging partially for Ti^{4+}, forming $Na_{x-y}H_yTi_{2-x}Fe_xO_4 \cdot nH_2O$ nanosheets. This hypothesis has been recently confirmed through Mössbauer and X-ray photoelectron spectroscopies [28]. This last study also revealed that LTs nanosheets present high optical absorption in visible spectrum, similar to the one exhibited by the restacked nitrogen-doped LTs [14]. Therefore, both types of LTs, restacked nitrogen-doped LTs and $Na_{x-y}H_yTi_{2-x}Fe_xO_4 \cdot nH_2O$ nanosheets, demonstrated potential for photoinduced processes. Other potential applications of the exfoliated LTs nanosheets, in accordance to Wang et al., [11] are electrochemical and catalytic applications, dielectric devices and fabrication of polymer nanocomposites with improved mechanical and/or gas barrier properties.

There are several purposes of this report. One is to present, to our knowledge, first conclusive findings on rapid and full exfoliation by quaternary ammonium compounds of LTs nanosheets with high specific area, composed of only a few host layers and nanometric lateral dimensions while synthesized from raw mineral sands, aiming future development of exfoliated LTs-polymer nanocomposites, as well as, new pillared heterostructures [30,31]. Quaternary ammonium compounds, dimethyldioctadecylammonium bromide (2C18) and tetrabutylammonium hydroxide (TBAOH) were chosen due to their compatibility with hydrophobic polymer matrices and proved exfoliation capacity, respectively. While their structural formulae are illustrated elsewhere (Fig. S1, Supplement file) it is relevant for our study to point out that the TBA^+ is a centrosymmetric cation, while the $2C18^+$ is not

and, therefore, presents inherent polarity. The second purpose of this report is to demonstrate the viability of exfoliation of LTs with $2C18^+$ and to compare thermal stabilities of LTs-2C18 and LTs-TBA nanohybrids. To the best of our knowledge, we show for the first time the complete exfoliation of LTs with the aid of a dimethyldioctadecylammonium salt. The significance of the exfoliation with dimethyldioctadecylammonium salts resides in the opportunity to synthesize nanofillers, such as LTs-2C18 nanohybrids, compatible with hydrophobic polymer matrices and capable to support high processing temperatures which can vary from 190 °C, in the case of polyethylene, to 420 and 430 °C in the case of some polyimides and polyketones.

2. Materials and methods

2.1. Synthesis of sodium rich layered ferrititanate nanosheets from mineral sands

Pristine sodium rich nanosheets (NaLTs-NS) were synthesized by alkaline hydrothermal route from raw ilmenite sands [26,28]. In a typical synthesis, 10 g of natural Brazilian ilmenite sand, previously ball milled for 60 min, was dispersed in 400 mL of 10 M NaOH and treated hydrothermally at 130 °C for 70 h with constant stirring at 320 rpm. After cooling, the precipitated nanosheets were filtered, washed with distilled water (up to pH ~ 9) and finally dried for 5 h at 80 °C. The as-obtained NaLTs-NS have specific surface area of 75 $m^2 g^{-1}$ and contain 4.9 wt.% of sodium (corresponds to 2.12 meq Na^+ per gram of nanosheets), as determined by BET nitrogen adsorption (Micromeritics ASAP 2020) and flame photometry after dissolving in concentrated H_2SO_4, respectively.

2.2. Acid exchange reaction

The fully protonated, $H_xTi_{2-x}Fe_xO_4 \cdot nH_2O$ (pLTs-NS), were prepared by a rapid acid-exchange reaction (1 h) at room temperature. NaLTs-NS (~8 g) were re-dispersed in 600 mL of distilled water and its pH was adjusted to 1.5 through dropwise addition of 1 M HCl. After only 1 h of the magnetic stirring nanosheets were separated from solution by centrifugation and the whole procedure was repeated one more time. Finally, after washing and drying (5 h at 80 °C) of the sediment separated through centrifugation, pLTs-NS were obtained. Flame photometry confirmed that the as-prepared pLTs-NS were free of Na^+, while BET implied slight increase of the specific surface area to 85 $m^2 g^{-1}$, after acid-exchange processing.

2.3. Intercalation and exfoliation of layered ferrititanate nanosheets using quaternary ammonium compounds

Intercalation and exfoliation of NaLTs-NS and pLTs-NS were performed with dimethyldioctadecylammonium bromide (2C18), purity ≥ 98%, Sigma-Aldrich, using the following procedure: 1 g of nanosheets (NaLTs-NS or pLTs-NS) was dispersed by magnetic stirring in 50 mL of deionized water for 1 h at 60 °C. Separately, 1.15 g of 2C18 was dissolved in 50 mL of deionized water at 60 °C, and then added to the dispersion of nanosheets, resulting in a $2C18^+/H^+ = 5.5$. This mixture was agitated for 5 h using Ultra-Turrax IKA T25 disperser at 3500 rpm. The obtained colloidal suspension was then separated by decantation from the minor residual solid phase and centrifuged for 20 min at 6000 rpm. The recovered dense slurry was additionally washed with hot distilled water to remove the excess of 2C18. The centrifugation and washing stages were repeated twice. A part of the dense slurry obtained after washing was dried at room temperature, while another part was maintained as slurry. The as-obtained materials were denoted as NaLTs-2C18-o-NS and pLTs-2C18-o-NS, depending on the type of nanosheets used as the precursor. This very same fast exfoliation procedure was repeated using pLTs-NS and tetrabutylammonium hydroxide (TBAOH), purity ≥ 98%, Sigma-Aldrich, instead of 2C18, keeping