Synthesis, characterization and evaluation of Na2Ti2O5.H2O nanotubes as dye adsorber for water remediation.

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Abstract

ABSTRACT Titanium oxide-derived materials are interesting candidates for application in the catalytic photodegradation of organic pollutants. In particular, the use of one-dimensional nanostructures, derived from titanium oxide materials, exhibits greater directionality in charge conduction and a larger surface area where redox reactions can occur. Furthermore, quantum confinement effects lead to modifications in the bandgap and an increase in the oscillator force constant, resulting in more intense absorption bands compared to bulk materials. Therefore, the electronic and optical properties are strongly dependent on morphology, which allows for their rational design.

This work presents the structural and morphological characterization (XRD, SAXS, AFM, Raman), as well as the electrical and electrochemical characterization by IS means and the optical properties are evaluated in terms of diffuse reflectance UV-vis. This work investigated the structure and morphology of sodium titanate nanotubes (NaNTs), systems widely explored by different groups due to their promising applications in the energy sector. However, significant controversy persists regarding their crystal structure. This work successfully proposed a coherent structural model that explains both the complex X-ray diffraction patterns and the EXAFS absorption spectrum of the system.

Obtaining a reliable structural model is key to predicting and understanding the physical chemical properties of nanotubes. In this study, a dititanate-based structure was presented, composed of layers formed by [TiO_5] units in the form of square-based pyramids joined at their edges. This model is innovative because it deviates from the traditional approach that considers octahedral [TiO_6] blocks as the predominant components in layered titanates. DFT is used for understanding its electronic and optical behavior through DOS and dielectric function analysis, furthermore, the adsorption of methylene blue is studied on a $Na_2Ti_2O_5.H_2O$ surface.

Finally, the methylene blue adsorption is studied experimentally, as well as de adsorption kinetics. Giving place to a maximum capacity of around 220 mg/g and a pseduo second order reaction kinetics.

Keywords: itanate nanotube, methylene blue, adsorber, DFT

Introduction

Layered titanates bear a close structural resemblance to titanium dioxide, both being composed mostly of connected [TiO_6] octahedral units sharing corners and edges. In fact, the distinction between layered titanates and TiO_2 is not very clear, especially in the early literature, and the term titanium dioxide is still occasionally used to name material that should more formally be called layered titanates.

Sodium titanate nanotubes (NaNTs) are systems that have been widely explored due to their novel structure and wide range of potential applications.

These nanotubes, prepared by hydrothermal methods first by Kasuga et al. [1], consist of lamellar structures formed by [TiO_x] polyhedra that host sodium ions in the interlayer space. These materials have a very high surface area and the possibility of exchanging different ions lodged between the layers. However, there is still considerable controversy regarding the crystalline phases of these nanotubes. Several groups have proposed different lamellar phases such as $Na_2Ti_2O_5{\cdot}H_2O$, $Na_2Ti_3O_7$, $Na_2Ti_4O_9$, and even a lepidocrocite-type structure. The main reason for this controversy surrounding the crystalline phase is due to the inherent complexity of the diffraction patterns.

These nanostructures can be used as good dye adsorbers due to their great surface area and their proper physical chemical behavior. Firstly, the full characterization of the nanotubes is presented as well as a structural model in order to correlate the observed physical chemical Properties on the lab with its structure by DFT means.

It is intended to relate the methylene blue dye adsorption correlating experiment and DFT theory in order to shade some light on the adsorption mechanics.

Experimental

Synthesis and characterization:

The method used for nanotube preparation was hydrothermal synthesis under endogenous pressure, first reported by Kasuga et al. [1]. Sodium titanate nanotubes (NaNT) were prepared hydrothermally under endogenous pressure using anatase, the Sigma Aldrich® Titanium(IV) nanopowder (External ID: 232033_ALDRICH) as a precursor. 1.25 g of anatase was dispersed with magnetic stirring in 75 mL of 10 M NaOH (fill factor 2/3) in a Teflon® cartridge for the hydrothermal reactor. The reactor was maintained at 145 °C for 24 h and allowed to cool to room temperature with continuous magnetic stirring. The resulting suspension was thoroughly rinsed and centrifuged with distilled water. was repeated 10 times. Finally, the remaining solid was left to dry at 70°C overnight. Structure and morphology is studied in terms of DRX, EXAFS, Raman and TEM. Physicochemical properties are studied in terms of IS and UV-vis.

DFT calculations:

The simulations were performed using ab initio methods within the Density Functional Theory (DFT) [2,3]. The calculations were made using the VASP (Vienna ab initio Simulation Package) code. For the calculation, the projector augmented wave (PAW) method was used to account for the electron-ion interaction, the correlation and exchange functional, the generalized gradient approximation (GGA) in its PBE (Perdew-Burke-Ernzerhof) parameterization with a DFT+U approximation.

Results and discussion

It was possible to obtain a structural model that could explain the complex diffraction patterns. This model is used for performing all relevant electronic information such as DOS and dielectric function calculation, having good correspondence with experiments, validating once more the proposed model and the U value election [4].

The adsorption mechanism is studied experimentally and by DFT means showing strong physisorption process. Both planar and perpendicular arrangements were tested for the methylene blue adsorption. The experiments regarding adsorption showed a Langmuir behavior with a maximal capacity of 220 mg/g. The kinetics were of the pseudo-second order type at neutral pH. Figure 1 presents a summary of the results obtained until this moment.

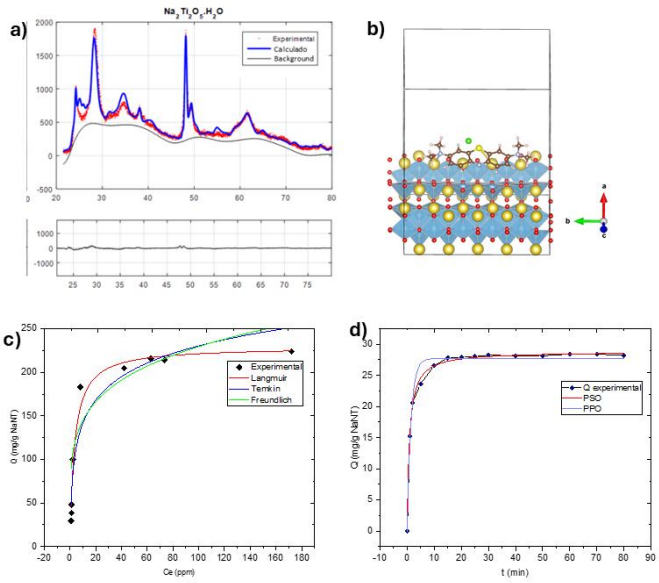

Figura 1.a) Powder diffraction pattern of NaNT and the simulated pattern for a tube using Debye method [] based on Na2Ti2O5.H2O structure [4] b) View of Na2Ti2O5.H2O DFT model surface and the methylene blue molecule adsorption showing a strong physisorption. c) Experimental adsorption isotherm for methylene blue at pH=7 fitted with several models and d) Experimental kinetics of adsorption showing and different model fitting.

Conclusions

It was possible to obtain a reliable structural model that could predict and help to understand the physicalchemical properties of nanotubes. In this study, a dititanate-based structure was presented. DFT is used for understanding its electronic and optical behavior through DOS and dielectric function analysis, furthermore, the adsorption of methylene blue is studied on a $Na_2Ti_2O_5{\cdot}H_2O$ surface. Finally, methylene blue adsorption is studied experimentally, as well as de adsorption kinetics. Giving place to a maximum capacity of around 220 mg/g and a pseudo second order reaction kinetics.

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