

Synthesis of Fe₂O₃@titanate Nanostructures with Improved Optical Absorption

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Titanate nanotubes are promising materials for photocatalytic processes due to their large superficial area and possibility of sunlight using. However, due to the large band gap energy, the absorption range of radiation is limited to the ultraviolet (UV) region, corresponding to a small part of the spectrum. Aiming to increase this range, several efforts have been done in order to decrease the band gap energy, for example, by doping with transition metals [1, 2]. Although this process can be efficient in reducing the bandgap energy it also raises the electron/hole (e⁻/h⁺) recombination rate, therefore decreasing its efficiency as a whole. One solution to this problem is the separation of the photogenerated charges immediately after their formation. In this regard, nanostructures consisting of semiconductor with attached nanoparticles show effective results, with the nanoparticles preferentially dragging the e⁻ of the e⁻/h⁺ pair before the recombination, promoting redox sites [3].

Usually, titanate with attached nanoparticles is produced by mixing both nanostructures in adequate conditions, which are then submitted to a heat treatment aiming to consolidate the hybrid nanomaterial [3]. Despite some good results have been obtained through this methodology, a poor contact between the nanostructures limits the material efficiency. Aiming to achieve a better result, this work covers the synthesis of titanate nanostructures (nanotubes and nanoribbons) with attached Fe₂O₃ nanoparticles, via a combination of hydrothermal/solvothermal processes. The objective is to grow Fe₂O₃ nanoparticles, by heterogeneous nucleation, using the titanate as a substrate, therefore, ensuring an optimum contact. At first, titanates were synthesized by alkaline hydrothermal synthesis following Kasuga's method [4]. After drying, Fe₂O₃ nanoparticles were synthesized by solvothermal method using triethyleneglicol as solvent and iron (III) acetylacetonate as precursor with titanates mixed to the solution. Structural characterization was performed via transmission electron microscopy (TEM) using a JEOL JEM 2100F operating at 200kV. Evaluation of photon absorption through diffuse reflectance spectroscopy (DRS) was performed in a Cary 500 Scan UV-VIS-NIR (Varian) spectrophotometer.

Results show that the solvothermal method was successfully applied to produce Fe₂O₃ decorated titanate, as the Fe₂O₃ heterogeneous nucleation at titanate surface. Figure 1 shows bright field TEM images of the titanates synthesized by alkaline hydrothermal method. One can see tube diameters of about 7 nm. Figures 2 shows the Fe₂O₃@titanate nanostructures. A good nanoparticle dispersion is visible as well as the good contact between nanoparticle/substrate. Nanostructures show larger optical absorption range in comparison with as-synthesized titanates, including the absorption at visible range, as can be seen in Figure 3. These results suggest that this is a promising material for photoinduced processes [5].

References:

- [1] X. Sun, Y. Li, *Chem. Eur. J.* **9** (2003), p. 2229.
- [2] E. Morgado Jr. *et al*, *Mat. Chem. Phys.* **126** (2011), p. 118.
- [3] P. Luan *et al*, *Nature* **4** (2014), p. 1.
- [4] T. Kasuga *et al*. *Langmuir* **14** (1998), p. 3160.
- [5] This research was supported by CAPES, CNPq and Faperj agencies (Brazil). We are thankful for the access to the facilities for electron microscopy of LabNano (CBPF), Brazil.

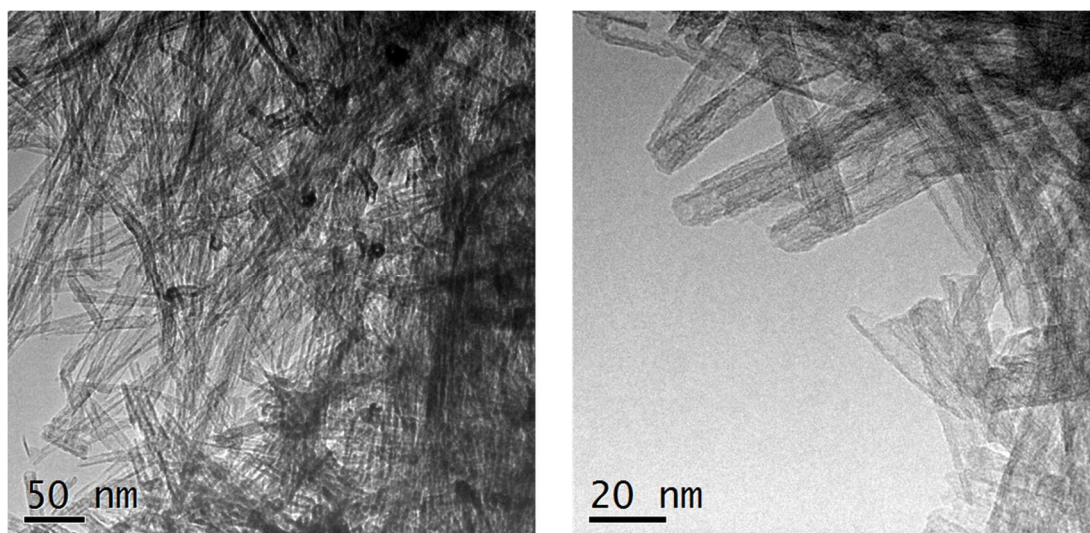


Figure 1. Titanates nanotubes synthesized by alkaline hydrothermal method.

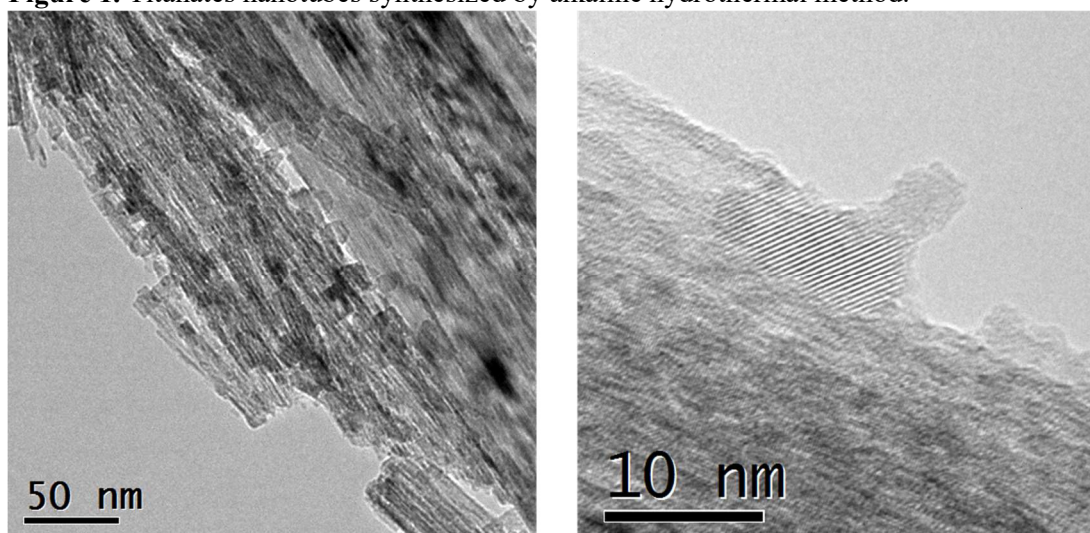


Figure 2. Fe_2O_3 nanoparticles attached at titanates nanostructures. Low magnification image displays the well-dispersed nanoparticles at titanates surface. Higher magnification displays the good contact between nanoparticle/titanate.

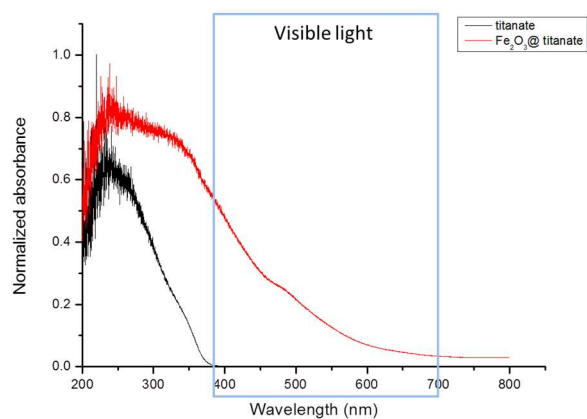


Figure 3. DRS spectra showing the higher range of absorption of Fe_2O_3 /titanates nanostructures.