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Development of ternary nanosystems MWCNT/titanate nanostructures/CeO₂ for photoelectrochemical applications

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Highlights

- Comparison between two methodologies for the preparation of nanosystems with titanate nanostructures, cerium oxides, and oxidized MWCNTs.
- Incorporation of oxidized MWCNT improves charge separation and enhances photocurrent.

Resumo/Abstract

This work developed methodologies for modifying titanate nanotubes (TiNT) to enhance their photoelectrochemical properties under simulated sunlight. TiO₂ and its derivatives are widely studied due to their photoelectric properties. TiNTs, obtained by alkaline hydrothermal treatment of TiO₂, have a crystal structure similar to sodium trititanate, allowing ion intercalation through ion exchange reactions and nanoparticle deposition on their surface. The intercalation of Ce⁴⁺ and deposition of CeO₂ nanoparticles onto TiNTs shift their bandgap from UV region to visible (~2.8 eV), but they exhibit a very fast electron-hole recombination rate, limiting charge transfer efficiency. To address this, two methodologies were proposed for preparing ternary systems of oxidized multi-walled carbon nanotubes (Ox-MWCNT)/titanate nanostructures/cerium oxide: i) physical mixture (PM) of aqueous suspensions of TiNT decorated with CeO₂ nanoparticles and Ox-MWCNTs; ii) hydrothermal (HT) synthesis of titanate nanostructures in the presence of Ox-MWCNTs, followed by suspension of the nanocomposite in cerium(IV) aqueous solution. The nanocomposites were prepared in Ox-MWCNT mass ratios of 1, 5, and 10% (w:w). Structural characterizations by XRD and Raman spectroscopy confirmed the formation of TiNTs and the modification with CeO₂ nanoparticles, without changing their structure; however, in methodology ii), the formation of titanate nanoribbons (TiNR) was observed. TEM images showed that the samples prepared by methodology i) exhibited titanate nanotubes with an external diameter of ~ 9 nm decorated with CeO₂ nanoparticles (~3 nm) and Ox-MWCNTs interacting with TiNTs-CeO₂ aggregates. For the samples produced by methodology ii), TEM images revealed nanoparticles of titanate nanotubes and nanoribbons containing CeO₂ nanoparticles deposited on their surfaces. Diffuse reflectance spectroscopy in the UV-Vis region was used to determine the bandgap of the samples from Tauc plots, indicating values between 2.83 and 3.05 eV. To evaluate the photoelectrochemical properties, chronoamperometry was used with a potential of 0.9 V in 0.1 mol L⁻¹ acetate solution (pH 4.0), with 20 s of on/off cycles. The electrodes were prepared by suspending the materials in DHP and ethanol and depositing them onto FTO. The 5C/Ti/CeO₂-MF nanocomposite showed the best result, with an increase in the current intensity of approximately 7 times compared to TiNT-CeO₂ and no transient peaks.

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