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*Short communication*

# The application of carboxylic acids on the surface of titanate nanotubes for further functionalization

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## Introduction

Recently, the accelerated development in the field of nanotechnology brought numerous advantages to many aspects of human life. This rapid growing deserves an exceptional attention as it offers substantial contribution to the world of science with its novel, brilliant nano-sized products. Titanate nanotubes (TNTs) are one of these distinctive nanomaterials which were introduced as a superior replacement for their organic counterparts (carbon nanotubes). The special characteristics of TNTs such as their high mechanical strength, good wettability and biocompatibility make them one of the most promised nanoparticles that were recently discovered (Ranjous et al, 2019; Sipos et al, 2018). Altering surface properties of these newly synthesized materials could be required for several purposes such as reducing toxicity or enhancing permeability (Chia and Leong, 2016; Soenen et al, 2010; Ranjous et al, 2021). For this reason, this study aims to functionalize the surface of TNTs with different types of carboxylic acids (trichloroacetic acid, citric acid and acrylic acid) and investigate their ability to act as possible linkers for further functionalization later with additional molecules like polyethylene glycol (PEG) which supposed to improve aqueous solubility, prolong circulation time, reduce toxicity and prevent aggregation (Lipka et al, 2010; Mano et al, 2012).

## Materials and methods

Titanate nanotubes were synthetized according to Ranjous et al, (2021), 3 types of carboxylic acids: trichloroacetic acid, citric acid (MOLAR CHEMICALS) and acrylic acid (Sigma-Aldrich) in addition to PEG 600 and PEG 6000 (Fluka AG) were used.

TNTs-trichloroacetic acid composites were prepared by adding 3 g of TNTs to 90 mL of water in ultrasonic bath for 1 hour until a homogenous suspension was obtained. This suspension was heated at 80°C in a condenser connected to nitrogen gas for 30 mins then trichloroacetic acid was added and mixed for one day.

TNTs-citric acid composites were prepared by adding 0.5 g of TNTs to 15 mL of water containing citric acid on a magnetic stirrer. The mixture was stirred for 30 mins to obtain a homogenous suspension then heated at 50°C with continuous stirring for 24 hours.

TNTs-acrylic acid composites were prepared by mixing 1 g of TNTs with 28.8 g of acrylic acid, 32 g of hexane and 8 g of water then placed for sonication for 20 mins at room temperature. This mixture was stirred at room temperature for 2 days then separated by centrifugation at 12,000 rpm for 60 min at 8°C.

TNTs-citric acid-PEG 600 composites were prepared by mixing TNTs-citric acid composites with PEG 600 at 130°C for 24 hours in an inert atmosphere condition then the mixture was cooled to room temperature and filtered.

TNTs-acrylic acid-PEG 6000 composites were prepared by two steps. First, copolymer of acrylic acid-PEG 6000 was prepared by a polymerization reaction in a water bath at 40°C with the existence of sodium sulfite and sodium persulfate as initiators. This copolymer was then bonded with TNTs after adding Na-hypophosphite as a catalyst. All the prepared composites were subjected to a washing step to remove any residues adsorbed on the surface of TNTs and finally were oven dried.

The determination of functionalization success, and the nature of TNTs-acids interactions were evaluated using Thermo Nicolet Avatar 330 FT-IR spectrometer (Thermo Fisher Scientific Ltd., Waltham, MA, USA) with a transmission E.S.P. accessory, using 256 scans at a resolution of 4 nm and applying $H_2O$ and $CO_2$ corrections.

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## Results and discussion

Trichloroacetic acid was not successfully bonded on the surface of TNTs as shown in Figure 1. On the other hand, the achieved association of citric acid and acrylic acid was evidenced by the existence of their characteristic peaks in their corresponding composites spectra. These peaks were slightly shifted as a sign of a weak interaction like hydrogen bonding between the two entities. Although the functionalization here was done successfully, this type of weak bonds is not enough for further linkage with other molecules.

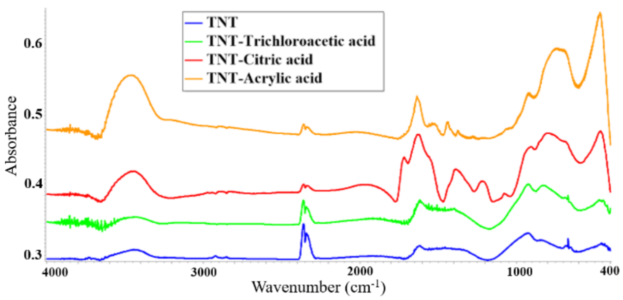


Fig. 1. TNTs and their composites with carboxylic acids

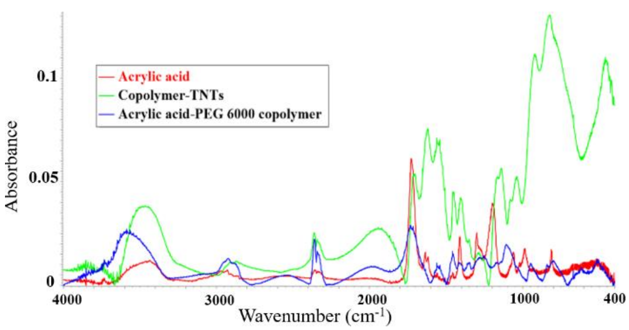


Fig. 2. TNTs functionalization with acrylic acid by two steps

For the above-mentioned reason, another approach was applied with acrylic acid to create stronger interaction such as covalent bonds as shown in Figure 2. This type of interactions could last for a longer period of time and could be of great importance in the future for further functionalization.

## Conclusion

The binding of carboxylic acids on the surface of TNTs could be done through weak interactions like hydrogen bonds but this type of functionalization is probably not enough as the functionalizing agent could detached easily from the surface. For this reason, stronger interaction is preferable which was achieved with acrylic acid using free radical polymerization and esterification reaction, respectively.

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