

Modification of Titanate Nanotubes with Transition Metals and Transition Metal-1,10-phenanthroline Complexes

D. Sović¹, D. Iveković¹, B. Zimmermann²

¹ *Laboratory for General and Inorganic Chemistry and Electroanalysis, Faculty of Food Technology and Biotechnology, University of Zagreb, Pierottijeva 6, HR-10000 Zagreb, Croatia*

² *Ruder Bošković Institute, Bijenička 52, HR-10002 Zagreb, Croatia*

In last few years, titanate nanotubes (TiNT) have attracted a lot of attention as a promising material for application in the field of photocatalysis (e.g. degradation of organic wastes) and photovoltaic's (solar energy conversion). Titanate nanotubes are an n-type semiconductor with band gap of cca. 3.6 eV. Therefore, for photogeneration of electron-hole pairs necessary for photocatalytic action of TiNT, photons with energy greater than 3.6 eV are required. Because photons with that energy correspond to the UV-radiation with wavelength shorter than 340 nm, for efficient use of TiNT as a photocatalyst it is desirable to shift the absorption of TiNT into the visible part of spectrum. In addition, modification of TiNT with transition metal ions is interesting because the incorporation of redox-active centers into the structure of TiNT might improve their catalytic properties.

In this work we investigated spectral properties of TiNT modified with selected transition metal cations (Ru^{3+} , Fe^{2+} , Cu^{2+}), as well as Fe^{2+} and Cu^{2+} -1,10-phenanthroline (Me-Phen) complexes. Titanate nanotubes were prepared by hydrothermal treatment of anatase powder in 10 M NaOH at 120 °C for 24 hours. Obtained TiNT were washed with 0.1 M HCl to convert them into the H-form (H-TiNT). Incorporation of Ru^{3+} , Fe^{2+} and Cu^{2+} cations into the structure of H-TiNT was performed by ion-exchange of H^+ with metal cations in 0.5 M aqueous solution of corresponding metal salts. Spectral properties of transition metal ions-modified TiNT were determined by UV/VIS diffuse reflectance spectroscopy. Broad absorption bands centered at 418 and 585 nm were observed for Ru^{3+} , at 463 nm for Fe^{2+} and at 818 nm for Cu^{2+} -modified TiNT.

For modification of TiNT with Me-Phen complexes three procedures were tested:

- 1) Soaking of Fe^{2+} or Cu^{2+} -modified TiNT in the solution of 1,10-phenanthroline;
- 2) Adsorption of 1,10-phenanthroline onto the surface of H-TiNT, followed by soaking in the solution of metal salt;
- 3) Adsorption of Me-Phen complex on the surface of H-TiNT directly from the aqueous solution of the complex.

In all three cases formation of Me-Phen complexes adsorbed on TiNT was confirmed by UV/VIS diffuse reflectance spectroscopy and FTIR spectroscopy. Absorption bands corresponding to Fe^{2+} and Cu^{2+} -Phen complexes were observed at 514 and 770 nm, respectively.

By monitoring the kinetics of complex formation, it was found that in the case of procedure 1 formation of complex was slow due to the migration of Me^{2+} cations from the interlayer space of TiNT to the surface of nanotubes. Procedure 3 is the simplest and the most convenient way to obtain TiNT modified with surface adsorbed Me-Phen complexes.