
**SYNTHESIS AND CHARACTERIZATION OF SODIUM TITANATE NANOSTRUCTURES
DOPED WITH Cu^{2+} , Cu^{3+} , Co^{2+} IONS AND Ag NANOPARTICLES**

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Nanostructured alkali titanates are versatile materials that possess a variety of physical and chemical properties that can be tailored allowing their use in many applications including catalysis [1] and lithium ion batteries [2,3]. Slight changes in their chemical composition, which can be achieved via ion-exchange process or *in-situ* doping, can lead to completely different physical and/or chemical properties.

In order to shed light on the basic mechanisms behind the doping of titanates, this work aims at determining the position of the dopant ions in the titanate structure when the doping is performed via *in-situ* doping or via ion-exchange processes. More specifically we address the following questions:

- (1) *in-situ* doping: do the ions accumulate between the titanate layers or do they exchange with the Ti atoms in the TiO_6 octahedra?
- (2) ion-exchange processes: do the dopant ions adsorb at the surface or do they intercalate between the titanate layers?
- (3) Can we distinguish ions located at different sites using electron paramagnetic resonance (EPR)?

To answer these questions, we focused in the study of doping of sodium titanate nanostructures (NaTiNSs). These structures are typically synthesized using TiO_2 as starting material in 10 M NaOH at temperatures between 100-200°C under hydro-thermal conditions [3]. For *in-situ* doping the starting material used was TiO_2 doped with different transition metal ions (Cu^{2+} [4], Co^{2+} , Ag^+ , Cr^{3+} [5]), *Ex-situ* doping was achieved by dispersing NaTiNSs in an aqueous solution of the desired ion. The prepared NaTiNSs were characterized by SEM, TEM, HAADF-STEM in combination with EELS and EPR. In addition, cathodoluminescence, NEXAFS and XPS were used to characterize specific properties of the samples doped with Cr^{3+} , Ag^+ and Co^{2+} .

Previously we reported that the presence of Cu^{2+} ions induces the formation of partly rolled

titanate slabs [4], whereas the presence of Cr^{3+} has no influence in the morphology of the NaTiNTs [5].

The EPR and XPS measurements showed that during the synthesis dopant ions Cu^{2+} and Cr^{3+} did not change their oxidation states. However, for Ag^+ doped TiO_2 , the $\text{Ag}^+(\text{aq})$ ions were reduced to Ag during the hydrothermal treatment. Ag nanoparticles with average size of 3 to 4 nm were found on the surface of sodium titanate nanostructures. Similar to the Cu^{2+} doping, the presence of Ag^+ ions in action mixture prevented the formation of the NaTiNTs.

As we identified different possible active sites in the doped samples, our results indicate high potential for their future application in catalysis. We will show that the sodium titanate matrix is a good host for different transition metal ions.

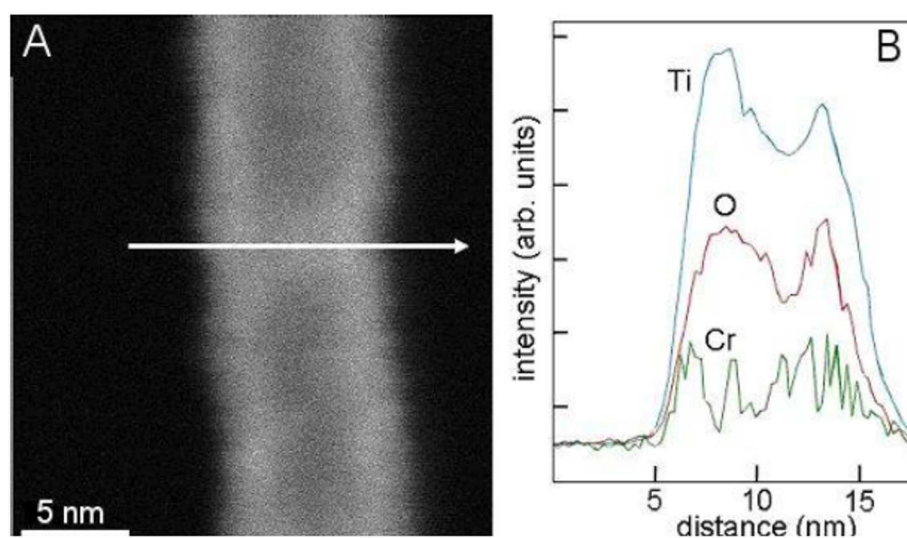


Figure 1: (a) HAADF-STEM image of a chromium-doped titanate nanotube (**Cr@NaTiNT**). (b) Ti, O, and Cr EELS for the line profile across the nanotube shown in part a.

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