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## Competitive ion-exchange of manganese and gadolinium in titanate nanotubes

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### ABSTRACT

Homogeneous Mn<sup>2+</sup> and Gd<sup>3+</sup> intercalation of scroll-type trititanate nanotubes using a post-synthesis ion exchange method is reported. Compared to Mn<sup>2+</sup>, Gd<sup>3+</sup> ion-exchange shows larger saturation intercalation levels. Upon co-doping, weak interactions between the dopant ions were found to modify the incorporated concentrations. Electron spin resonance (ESR) measurements, performed at several frequencies, confirmed the homogeneous distribution of Mn<sup>2+</sup> and Gd<sup>3+</sup>. Detailed simulation of ESR spectra identified a large spread of the local structural distortions of the occupied sites as a result of a wide range of curvature radii of the titanate nanotubes.

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### 1. Introduction

The wide range of applications of titanium dioxide (TiO<sub>2</sub>) and its biocompatibility made it the most studied oxide material in the last 30 years [1,2]. Apart from its classic use as a pigment, it turned out to enhance the efficiency of dye-sensitized solar cells (DSSCs) [3], it possesses unique photocatalytic activity [4–7], and it is the central component of the hole blocking layer in perovskite solar cells [8–10]. In addition, it is widely used in sensors [11,12], memristors [13], supercapacitors [14,15] and batteries [16]. Furthermore, the one-dimensional titanium dioxide nanotubes outperform their bulk counterpart in Grätzel-type solar cells and in photocatalytic applications, and have stimulated significant research interest since their discovery [17]. In contrast to TiO<sub>2</sub> nanoparticles, the rolled-up titanate nanotubes have a larger surface area [18,19] and the one-dimensionality in sintered systems leads to longer electron diffusion lengths in DSSCs [20]. Compared to the Degussa P25 reference material [21], i.e. nanoparticles that are mixtures of rutile and anatase, enhanced photocatalytic activity was found in these titania

nanotubes. Notably, this photoactivity turned out to depend heavily on the morphology, diameter, and annealing methods [22–24].

One of the major disadvantages of TiO<sub>2</sub> in photocatalytic applications remains, however, its large band gap of 3.2 eV giving an absorption of only about 3–5% in the solar spectrum. Doping of titanate nanotubes with metal and nonmetal ions [25], or co-doping it with Gd<sup>3+</sup> and nitrogen [26] were found to increase the photocatalytic activity up to a certain threshold. As well, doping of TiO<sub>2</sub> nanotubes leads to an increase in surface area due to the decreased particle size, dopant ions may become charge trap sites, and may act as photosensitizers [26,27,28,29]. Furthermore, in electronic and optoelectronic applications, the band gap tunability and the ability to induce impurity levels would be highly desirable. In particular, nanotubes prepared by a hydrothermal technique [30] can be easily doped using predoped TiO<sub>2</sub> particles [31], doping during the hydrothermal growth [32], or using post-synthesis ion-exchange [33].

As the intercalation takes place in the titanate phase in several cases [27–29], it is of great importance to provide information about the ion-exchange positions of the intercalated titanates. Nevertheless, it is subject to controversy [33] as to whether these synthesis routes lead to homogeneous doping of the titanate nanotubes or whether, after calcination, they result in doped TiO<sub>2</sub> nanotubes with superior photocatalytic activity. Several reports confirmed that the observed advantageous properties of titanate nanotubes upon intercalation might arise from the presence of dopant aggre-

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gates [34,35]. Furthermore, comparison of the different synthesis methods and their future scale-up is difficult as only the nominal concentrations are known and the incorporated concentrations may differ. In the case of co-doping with different dopant ions, the ion-exchange efficiencies may be correlated and interactions between dopant ions may result in the formation of aggregates. Whereas high-resolution transmission electron microscopy can identify the local distribution of dopants in a small number of nanotubes, microscopic local probes, such as the electron spin resonance (ESR) technique has the advantage to confirm homogeneity and ion-exchange efficiency, as well as for the selective identification of dopant ions in larger sample sizes. To extend our previous study [33], where  $\text{Mn}^{2+}$  was used as a dopant, here, we used  $\text{Gd}^{3+}$  as co-dopant, which is a well-established local probe in ESR studies [36,37] and has a higher oxidation state.

Here, we report the low-temperature synthesis of  $\text{Mn}^{2+}$  and  $\text{Gd}^{3+}$  co-doped trititanate nanotubes using a post-synthesis ion exchange route. As reported earlier [33], our synthesis method results in homogeneous intercalation of the co-dopants. Co-doping is studied by energy-dispersive X-ray spectroscopy (EDX), X-ray fluorescence (XRF), and ESR spectroscopies. We focus on the ion-exchange competition between the two different metal ions with different oxidation states. We determine the ion-exchange capacities both for  $\text{Gd}^{3+}$  and for  $\text{Mn}^{2+}$ . Our multi-frequency ESR study along with detailed numerical simulation of zero-field splitting tensor reveals the spatial selectivity and precise distribution of  $\text{Gd}^{3+}$  ions in trititanate nanotubes.

## 2. Experimental methods

Titanate nanotubes ( $\text{H}_2\text{Ti}_3\text{O}_7$ ) were synthesized following the method developed in Ref. [33]. During the synthesis process  $\text{Na}^+$  ions were exchanged with  $\text{H}^+$  by neutralizing the water solution of  $\text{Na}_2\text{Ti}_3\text{O}_7$  until obtaining a  $\text{pH} \approx 6.5$ , as confirmed by the EDX and XRF measurements.

To perform the ion-exchange and study the competition of  $\text{Mn}^{2+}$  and  $\text{Gd}^{3+}$ , two alternative procedures were used. In both cases,  $\text{Mn}(\text{NO}_3)_2 \times \text{H}_2\text{O}$  (Aldrich, 99.99%) and  $\text{Gd}(\text{CH}_3\text{CO}_2)_3 \times \text{H}_2\text{O}$  (Aldrich, 99.9%) were the source of  $\text{Mn}^{2+}$  and  $\text{Gd}^{3+}$  ions. As the surface potential of the titanate nanotubes remains negative even for moderately acidic solutions [38], we speculate that the choice of the anions does not affect the resulting ion-exchange efficiencies. Thus, only the metal cations are believed to play a role in setting the intercalation levels.

Upon storage, precipitation of  $\text{Gd}^{3+}$  and  $\text{Mn}^{2+}$  ions has been observed in distilled water solutions. Therefore, all the ion-exchange reactions were performed with freshly prepared salt solutions.

In the first synthesis method, 5 ml of the  $\text{H}_2\text{Ti}_3\text{O}_7$  suspension (with 100 g/l trititanate nanotube dispersed in distilled water) and respective amounts of distilled water solutions of  $\text{Mn}(\text{NO}_3)_2 \times \text{H}_2\text{O}$  (5.6 g/l with respect to  $\text{Mn}^{2+}$  content) or  $\text{Gd}(\text{CH}_3\text{CO}_2)_3 \times \text{H}_2\text{O}$  (8.7 g/l with respect to  $\text{Gd}^{3+}$  content) were mixed for 1 h at room temperature. Note that during this process the pH was always kept below  $\text{pH} \approx 9$ .

This method was used for the preparation of three samples (Mn-1, Mn-Gd-1, and Gd-1 samples, see Table 1). To further examine the competition between  $\text{Mn}^{2+}$  and  $\text{Gd}^{3+}$ , the distilled water solution of  $\text{Gd}(\text{CH}_3\text{CO}_2)_3 \times \text{H}_2\text{O}$  was introduced 20 min later than the distilled water solution of  $\text{Mn}(\text{NO}_3)_2 \times \text{H}_2\text{O}$  in the case of the equally intercalated sample (Mn-Gd-1).

As an alternative synthesis method,  $\text{Mn}(\text{NO}_3)_2 \times \text{H}_2\text{O}$  and  $\text{Gd}(\text{CH}_3\text{CO}_2)_3 \times \text{H}_2\text{O}$  salts were dissolved in 5 ml of the  $\text{H}_2\text{Ti}_3\text{O}_7$  suspension while stirring the suspension. For all three samples (Gd-2,

Mn-Gd-2, and Gd-3, see Table 1), the intercalation took place for 1 h at room temperature.

The suspension is subsequently filtered and washed with 500 ml of deionized water in order to remove the non-exchanged  $\text{Mn}^{2+}$  and  $\text{Gd}^{3+}$  remaining in the solution. Then we dried the samples at  $130^\circ\text{C}$ . Whereas titanate nanotubes are not stable in strongly acidic solutions [39], the dried powder samples are stable under ambient conditions.

For the ESR measurements at 9.4 GHz we used a commercial Bruker ELEXSYS X-Band spectrometer at room temperature for which the maximum magnetic field stands at 1.5 T. For higher frequency ESR (52, 78, 105, 157, 210, 315 and 420 GHz) we used a home-built spectrometer whose specifications are given in Refs. [40,41]. We used Mn:MgO with a known (1.5 ppm)  $\text{Mn}^{2+}$  concentration in X-band ESR as a  $g$ -factor and intensity standard. The absolute spin-susceptibility was calculated as described elsewhere [42].

Scanning electron microscope (SEM) images were taken with a MERLIN Zeiss electron microscope. The atomic concentrations of gadolinium and manganese were determined by energy-dispersive X-ray spectroscopy (EDX).

Transmission electron microscope (TEM) and scanning transmission electron microscope (STEM) images were taken with a FEI Titan Themis microscope.

X-Ray Fluorescence spectrometry was performed with an Orbis PC Micro EDXRF analyser. Gadolinium ESR spectra were simulated using the simulation software Easyspin, which allows us to simulate spectra and fit ESR data [43]. Simulation parameters include the  $g$ -factor and zero-field splitting  $D$  and  $E$ , which we retrieved from the literature [44,45]. To simulate the broadening of our spectrum, Gaussian distributions of  $D$  and  $E$  values are defined. We also included an intrinsic peak to peak linewidth broadening via the convolution of the calculated spectrum with a derivative Lorentzian function of peak to peak linewidth  $\Delta B_{\text{int}}$ . This intrinsic linewidth indicates that there exists a residual, field-independent linewidth. This is expected in the case of gadolinium because of the non-negligible spin-orbit interaction.

## 3. Results and discussion

### 3.1. EDX and XRF measurements

Six samples with different dopant concentrations were compared in our study. As shown in Fig. 1a, the typical SEM image proves that scroll-type trititanate nanotubes are produced with a prevailing tubular morphology (Fig. 1b-c) of the doped material. As shown in our previous study [33], ion-exchange positions are well-defined in rolled-up trititanate nanotubes (see Fig. 1d-e). A summary of their nominal and incorporated compositions determined by EDX, XRF, and ESR measurements is given in Table 1.

As seen in Table 1, the measured incorporated concentrations show a significant scattering for the three different experimental techniques. This discrepancy is all the more obvious at low concentrations, indicating that it might not stem from the inhomogeneous intercalation but it is due to intrinsic instrumental detection limits of EDX and XRF.

As ESR is a bulk-sensitive method, whereas both EDX and XRF are surface-sensitive techniques, the combination of the three spectroscopic techniques provides evidence of homogeneous doping in our samples. Unlike EDX and XRF, ESR is sensitive to the oxidation state, thus the oxidation states in our samples are only  $\text{Mn}^{2+}$  and  $\text{Gd}^{3+}$  states (see below).

Samples Mn-1, Mn-Gd-1, and Gd-1 were prepared by mixing a  $\text{H}_2\text{Ti}_3\text{O}_7$  nanotube suspension with a distilled water solution of known concentration (see the Experimental Methods) of  $\text{Mn}(\text{NO}_3)_2 \times \text{H}_2\text{O}$  and  $\text{Gd}(\text{CH}_3\text{CO}_2)_3 \times \text{H}_2\text{O}$  salts, whereas samples

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