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COMMENT

Comments on 'Formation and characterization of nanotubes of $\text{La}(\text{OH})_3$ obtained using porous alumina membranes'

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Abstract

New experimental evidence concerning the formation of $\text{La}(\text{OH})_3$ nanowires on anodic alumina membranes by cathodic polarization in 0.05 M lanthanum nitrate solution is provided to further support the conclusions previously reached in our work (Bocchetta *et al* 2007 *Electrochem. Commun.* **9** 683–8) and recently criticized by González-Rovira *et al* (*Nanotechnology* 2008 **19** 495305). Some unconvincing aspects of the paper of González-Rovira *et al*, according to which the same electrochemical process should lead to the formation of hydroxycarbonate nanotubes, are also discussed.

In a recently published paper [1], González-Rovira *et al* criticize our previous work [2] reporting the electrochemical growth of $\text{La}(\text{OH})_3$ and $\text{Nd}(\text{OH})_3$ nanowires (NWs) on an anodic alumina membrane (AAM) template by electrochemical reduction in 0.05 M $\text{La}(\text{NO}_3)_3$ aqueous solution. The authors of [1] claim that through a structural and morphological investigation, more detailed than that performed by us, they revealed that what we reported to be $\text{La}(\text{OH})_3$ nanowires [2] are actually lanthanum hydroxycarbonate nanotubes. After a careful reading of the paper by González-Rovira *et al* we are still convinced that we properly concluded in our paper that we prepared lanthanum hydroxide nanowires.

In order to further support our conclusions we present in figure 1 SEM micrographs up to 500 000 \times magnification showing good quality lanthanum hydroxide nanowires.

The experimental evidence reported by González-Rovira that they used to support nanotube formation in 0.05 M $\text{La}(\text{NO}_3)_3$ is reported in figures 3 and 4 in [1]. Actually, we do not see 'hollow regions' in figure 3(c) [1] and the empty regions on the side view of figure 3(d) [1] seem rather to be damaged areas of the nanostructures, while the contrast between the tube wall and its interior described by the authors in figure 4 it is not so evident.

The authors should also be careful about the experimental procedure used to separate the nanostructures from the template, which is more severe in [1] compared with that in the work they are criticizing [2]. In addition, from page 5 onwards the authors [1] generalize the conclusions about the chemical composition of the nanostructures prepared in 0.01 M $\text{La}(\text{NO}_3)_3$ solutions to those prepared in 0.05 M $\text{La}(\text{NO}_3)_3$, even though they claim that the same kind of investigation could not be performed on nanostructures prepared in 0.05 M $\text{La}(\text{NO}_3)_3$ (the only one employed in the work they are criticizing).

The x-ray diffraction (XRD) pattern for nanostructures prepared in 0.05 M $\text{La}(\text{NO}_3)_3$ reported by González-Rovira *et al* in [1] is almost coincident with that reported in our work [2], with no evidence of the occurrence of LaOHCO_3 formation. The authors are not themselves consistent: the deposited material being $\text{La}(\text{OH})_3$ in the paper title [1], 'lanthanum hydroxycarbonate' in the abstract and 'lanthanum hydroxide partially carbonated' in the conclusions.

Moreover, the only experimental evidence of the presence of small LaOHCO_3 crystals (not revealed by XRD) are the high resolution electron microscopy (HREM) and digital diffraction

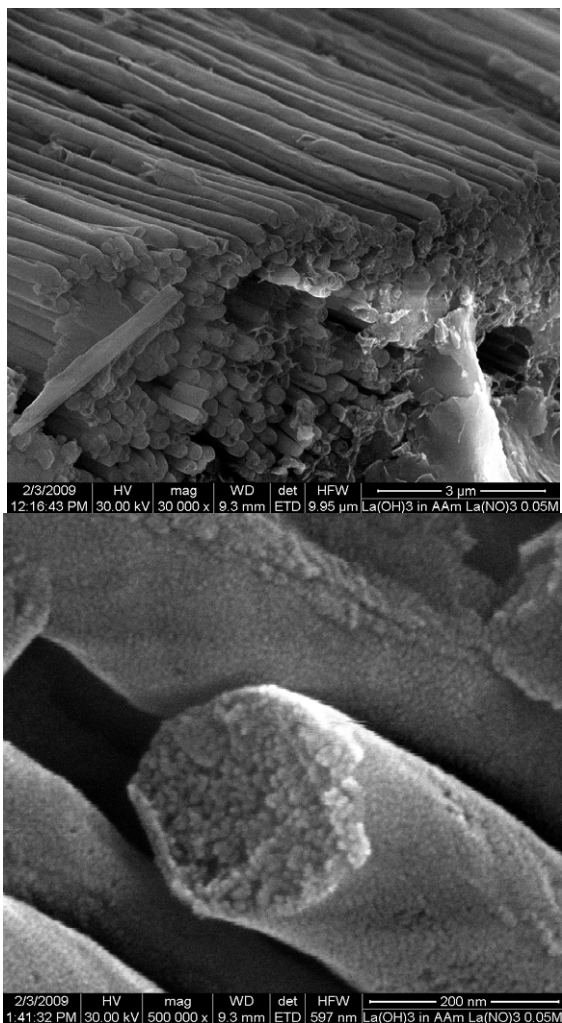


Figure 1. SEM micrographs of $\text{La}(\text{OH})_3$ nanowires prepared as reported in our paper [2].

pattern (DDP) images relating to nanostructures prepared in experimental conditions different from those used in our work [2] (0.01 M $\text{La}(\text{NO}_3)_3$ electrolyte and alumina removal

at 45 °C in 1 M NaOH). As far as we know, the carbonation is related to the interaction between highly basic tri-hydroxide with atmospheric carbon dioxide during preparation and/or handling, it affects the surface of the sample not the bulk [3, 4] and it does not hinder the dehydration process toward the corresponding oxide [5, 6]. Moreover, we did not discuss in our work [2] how $\text{La}(\text{OH})_3$ could be converted to La_2O_3 , as González-Rovira *et al* report on page 2. We just stated in the introduction that such a process is possible according to previous data [5].

Finally, a statement reported in the abstract in [1] is also rather misleading because we never asserted in our paper [2] that template assisted electrogeneration of a base should in all cases lead to the formation of nanowires. As already reported in other works relating to the same topic [7–10], the template assisted hydroxides deposition through electrogeneration of a base can lead to the formation of either nanowires or nanotubes, depending on several process parameters, and a careful investigation of this complex aspect is mandatory before reaching final conclusions.

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