Crystallization of amorphous TiO_2 nanotubes - TEM studies by in situ and ex situ heating

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Titanium dioxide (TiO_2) is a well-known material, whose many properties make it appealing in a wide and diverse range of fields both in its polymorphic and amorphous phase. Then, a full comprehension on the parameters that control the amorphous-to-crystalline transition in different conditions and on the possible phases formed represents a field of study that holds implications for basic and applicative sciences. In this framework, anodically grown TiO_2 amorphous nanotubes are a good example of the multiple application of titanium dioxide (Figure 1a), but so far their thermally-induced crystallization has been studied mainly under ambient pressure and on collective terms by techniques that require huge populations of nanotubes, thus invariably providing averaged responses. On the other hand, High Resolution Transmission Electron Microscopy (HRTEM) provides a most local and sensible tool to study these transitions at a single nanotube level. Thus, the crystallization of amorphous TiO_2 nanotubes was studied under different conditions according to *ex situ* and *in situ* approaches. Besides, different electron beam energies were used for the *in situ* investigations. The *ex situ* approach enabled us to study with unprecedented detail the early stages of crystallization for TiO_2 nanotubes heated in air at ambient pressure, showing the formation of small-sized nanocrystalline seeds and their subsequent development. [1] Conversely, the results obtained by the *in situ* approach highlighted how the combination of high vacuum and different beam energies can trigger the crystallization at different temperatures, while also providing novel insight on the structural evolution of nanosized TiO_2 polymorphs in this relatively uncommon pressure regime. To be more specific, a small group of amorphous nanotubes was first heated *in situ* to study its evolution by electron diffraction with a beam energy of 120 keV (Figure 1b, c), then the thermal treatment was repeated and the structural evolution was studied by spherical aberration-corrected HRTEM with a beam energy of 300 keV. [2] The first approach pointed out the crystallization temperatures of different TiO_2 phases; the latter provided a direct local observation of the *in situ* crystallization process and of its evolution. First, the comparison of these diverse thermally-driven crystallization processes showed the influence of pressure on the formation and evolution of different polymorphs between *ex situ* and *in situ* experiments, with anatase along with a secondary brookite population crystallizing in the former case and a mixed rutile and brookite population forming in the latter, first as seeds and then as extended domains. Second, the variation of electron beam energy in the *in situ* studies evidenced how a high-energy electron beam can become an active parameter in the amorphous nanotubes crystallization process by affecting its starting temperature through atomic knock-on effects that bring to lower such a temperature. This combination of *in situ* and *ex situ* approaches provides a broader framework to develop novel and different ways to study and exploit nanosized TiO_2 in fundamental and applicative fields.

References

[1] Stassi, S.; Lamberti, A.; Roppolo, I.; Casu, A.; Bianco, S.; Scaiola, D.; Falqui, A.; Pirri, C.F.; Ricciardi, C. Evolution of nanomechanical properties and crystallinity of individual titanium dioxide nanotube resonators. *Nanotechnology* **2017** DOI: 10.1088/1361-6528/aaa46c

[2] Casu, A.; Lamberti, A.; Stassi, S.; Falqui, A. Crystallization of TiO_2 Nanotubes by *In Situ* Heating TEM. *Nanomaterials* **2018**, *8*, 40. DOI: 10.3390/nano8010040

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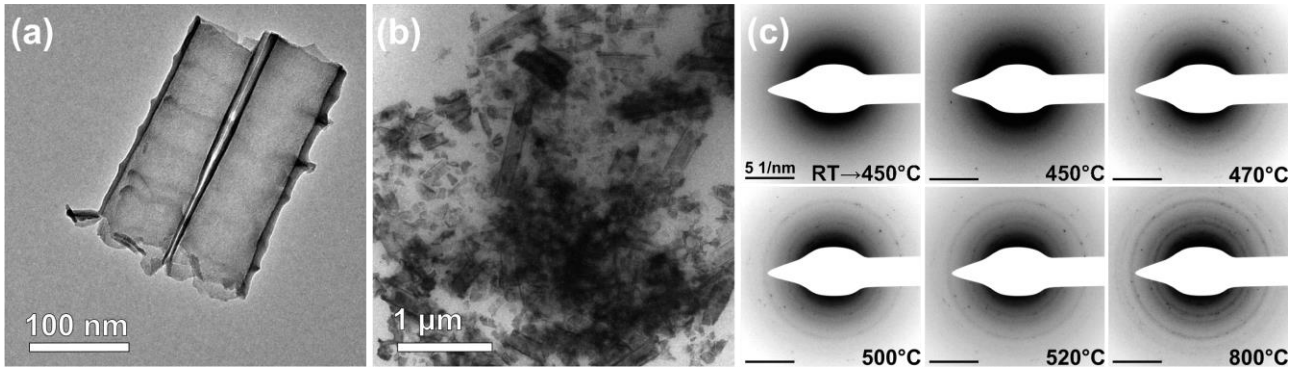

Figure 1 *In situ* SAED heating experiment: (**a**) Representative TiO_2 amorphous nanotubes at RT; (**b**) The aggregate of TiO_2 amorphous nanotubes chosen for *in situ* heating; (**c**) SAED patterns of the aggregate shown in panel (b), recorded during the *in situ* heating experiment with an acceleration voltage of 120 kV.