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Heat Treatment of TiO_2/SiO_2 Electrospun Ceramic Fibers

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Nano-TiO_2 is currently one of the most interesting topics of study in materials science and beyond, and is being used in a wide variety of applications [1]. However, producing crystalline TiO_2 nanostructures, other than simple powders, can pose significant challenges: growing such structures in the crystalline state tends to be slow and expensive, and while this can be overcome by fabricating amorphous structures quickly and cheaply, handling these materials after the subsequent heat treatment will reduce them to a powder. Dispersing TiO_2 particles on a mechanically robust support is a common method for overcoming this issue. One processing pathway for doing so is to electrospin a TiO_2/SiO_2 solution into fibers followed by heat treatment, which causes the two immiscible materials to phase separate and the TiO_2 to crystallize [2, 3]. A forthcoming publication describes how this process has recently been improved to drastically increase the TiO_2 content of such fibers [4]; this work is concerned with the details of the phase separation of the TiO_2 and SiO_2 during heat treatment and the crystallization of the TiO_2.

To this end, a Protochips Aduro single-tilt heating holder and a Gatan model 628 heating holder were used, in an FEI Tecnai F30 transmission electron microscope (TEM) operated at 300 kV, to study in-situ the behavior of electrospun TiO_2/SiO_2 fibers during heating. Fibers with Ti:Si ratios of 9:1, 3:1, 1:1, and 1:3 were observed. The fibers were heated to a maximum temperature of 1100 °C at heating rates of 5 to 10 °C/min in the Gatan holder, and to 1200 °C at a nominal heating rate of 10^6 °C/s in the Protochips holder. Electrospun fibers of plain TiO_2 were also studied this way as a point of comparison.

The diffraction patterns inset in Figs. 1a and 2a demonstrate that the as-spun material was amorphous, while the patterns in Figs. 1b and 2b are consistent with polycrystalline rutile. Interestingly, there was never any evidence of the anatase phase during these experiments, and the phase transformation to rutile occurred at a higher temperature than expected: ~1050 °C in the Gatan holder and 1200 °C in the Protochips holder. The plain TiO_2 fibers were used to rule out the SiO_2 as the cause of this behavior, and Fig. 2 shows that the TiO_2 fibers also transformed directly to polycrystalline rutile, with no evidence of anatase and no change at all below 1200 °C. There is evidence in literature that the partial pressure of oxygen during heat treatment of TiO_2 can have a significant effect on the temperature range over which the anatase phase is stable [5]; it could be that carrying out this experiment in the vacuum of the TEM column precludes the formation of anatase and increases the temperature required to obtain the rutile phase. Observations made *in situ* and *ex situ* will be compared.

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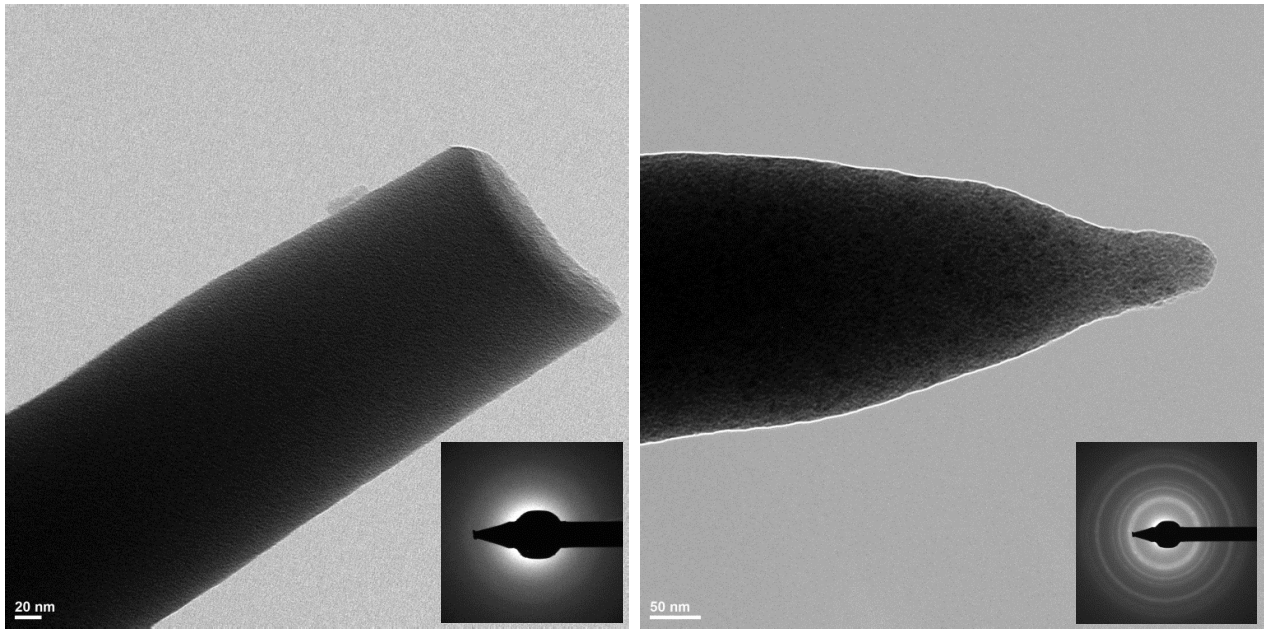

Figure 1 TiO_2/SiO_2 fibers a) before and b) after heat treatment inside the TEM; the corresponding diffraction patterns shown in the lower left corner confirm that the amorphous material has crystallized. The crystallized pattern is consistent with that of rutile.

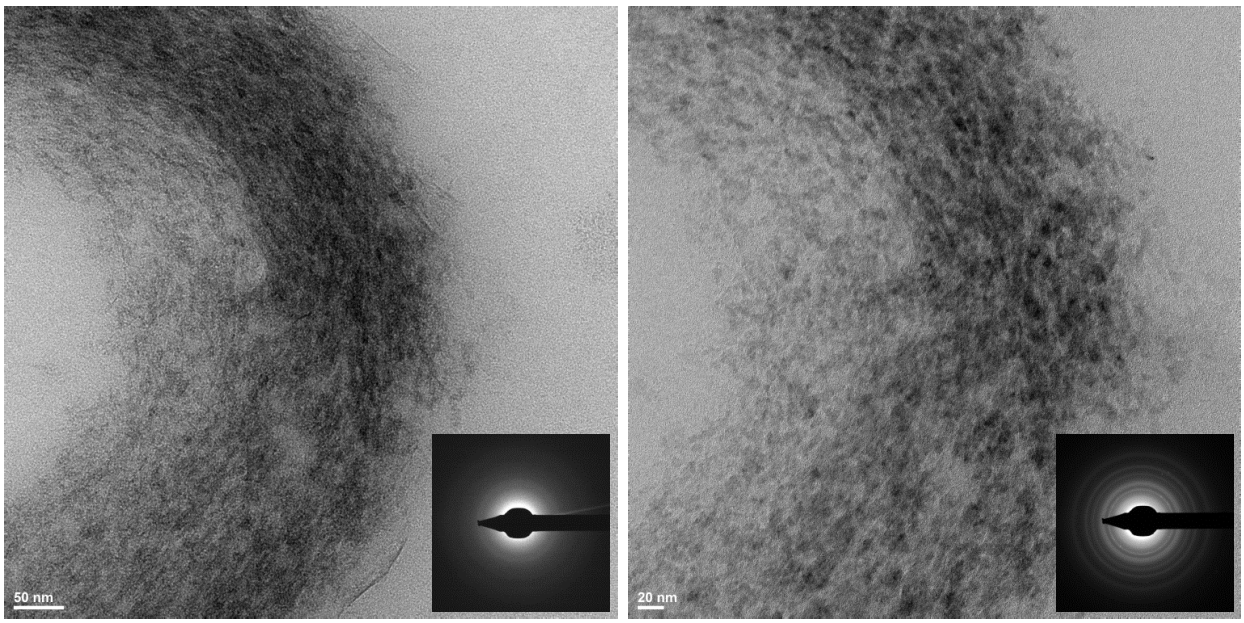

Figure 2 TiO_2 fibers a) before and b) after heat treatment inside the TEM; the corresponding diffraction patterns shown in the lower left corner confirm that the amorphous material has crystallized.

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