Water condensation on core-shell nanofibers studied using multiscale environmental electron microscopy

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Background incl. aims
Superhydrophobic, omniphobic, icephobic and self-cleaning mean advanced properties of a surface when precise control of the roughness combining different levels of topography, from micro- to- nanostructures for the called hierarchical surface [1-4]. Particularly one-dimensional nanostructured matrix allows the integration of nanowires with dimensions around several micrometers with the nanofiber surface roughness at the nanoscale. We study here hierarchical photoactive core-shell nanostructured surfaces, which wetting behaviour can be easily tuned. Understanding the mechanism of water condensation on such nanofibers at the nanoscale is crucial to design efficient systems. In this presentation, we identify their hydrophobic/hydrophilic behaviour and discuss the water condensation mechanisms using multiscale environmental electron microscopy.

Methods
Liquid-phase electron microscopy can be carried out with different systems. We used a dedicated environmental scanning electron microscope (ESEM) and an environmental transmission electron microscope (ETEM), in which different hydration states can be reached by controlling the sample temperature and the water vapor pressure.
TiO_2 core-shell nanowires were fabricated by vacuum and plasma assisted deposition techniques according to the soft template method [5]. In order to obtain the water repellent character, surface functionalization by fluorine-based grafting of the oxide surface has been employed [1]. Hydrophobic nanowires were collected by scratching the substrate and were dry-deposited onto a grid with a holey carbon membrane. The fibers were either analyzed as such, or plasma-treated to become hydrophilic. During the experiments, care was taken to minimize irradiation damage and preserve the hydrophilic/hydrophobic nature. An image processing method was developed to highlight the changes brought about by water condensation.

Results
Experiments in ESEM were performed in the STEM mode (see Figures 1a and d). Under similar conditions, where water condensates on the holey carbon membrane, the hydrophilic nature of the plasma-treated nanowires can clearly be evidenced: they are systematically surrounded by water. On the contrary, water droplets are visible on the carbon membrane but not on hydrophobic nanostructures. The presence of water onto hydrophilic surfaces but not on hydrophobic ones could be confirmed at the nanoscale using similar thermodynamic conditions in ETEM (see Figures 1b and e). The experiments were continued until water was visible around both types of nanowires (see Figures 1c and f).

Conclusion
ESEM images, obtained on a large number of core-shell nanowires, enable us to assess the reproducibility of results obtained at nanometric scale in ETEM on isolated fibers. Irradiation

of the nanostructures with the electron beam during the experiments did not modify their hydrophilic/hydrophobic character. In fact, clear differences in behavior towards water condensation are revealed at the nanometric scale. These differences will be discussed as a function of nanostructure and chemistry.

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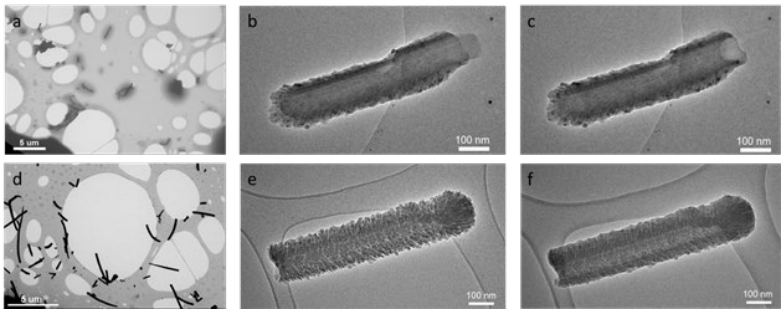
Figure caption
water condensation on core-shell TiO2 fibers. a, b, c) hydrophilic fibers. d, e, f) hydrophobic fibers. a, d) BF-STEM images in ESEM. b, e) BF-TEM images in ETEM at the initial state. c, f) BF-TEM images in ETEM on hydrated fibers.

Graphic:



Keywords:

ESEM, ETEM, liquid, in-situ, nanowire

Reference:

[1] L. Montes et al., Adv Mater Interfaces, 2021, 8, 2100767.
[2] V. Rico et al., Appl Mater Today, 2020, 21, 100815.
[3] M. Macías-Montero et al., Langmuir, 2017, 33, 6449.
[4] M. Alcaire et al., Nanoscale, 2011,3,4554.
[5] A.N. Filippin et al., Sci. Rep. 2016, 6, 20637.