Condensating water on aerosols within an environmental TEM using an open-cell cryo-holder

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Observation of liquids within a transmission electron microscope (TEM) has long been impossible owing to basic thermodynamic limitations due to the need for a high vacuum, typically 10^{-5} mbar or better, within the column of the instrument, making it impossible to maintain a liquid state at room temperature. The development of dedicated MEMS-based sealed liquid cells made possible the observation of liquids in general, and water in particular, within the transmission electron microscope but the presence of electron-transparent membranes used to seal such cells seriously hinders the capability of controlling relative humidity (RH) and to perform water condensation from a humid atmosphere. In an environmental TEM, a partial pressure can be controlled and maintained in the pole-pieces gap (where the sample holder tip containing the sample is inserted), which enables observations under gas without any sealing membranes. In this “open-cell” configuration, observing water layers is possible under a partial pressure of a few mbar as it was already perfomed in an Environmental Scanning EM (ESEM). The temperature has to be cooled down close to the dew point to insure a thermodynamic equilibrium between the solid, gas and liquid states; liquid water can then be stabilized in a temperature and pressure range of typically -5 to 10°C and 5 to 15 mbar, respectively. These experimental conditions are achievable with standard cooling TEM sample holders within the ETEM allowing, through the control of RH, direct visualization of hygroscopic growth, deliquescence and efflorescence of real or model aerosols. Such studies may eventually lead to a better understanding of the hygroscopic behaviour of atmospheric aerosols which are known to act as cloud condensation nuclei.

NaCl is among the most widespread aerosols found above oceans; we have thus used NaCl nanoparticles as relevant model aerosols in this preliminary approach. These nanoparticles were obtained by vaporizing a 1mM salt solution onto classical holey (or lacey) carbon TEM grids. We then used a Gatan/Ametek liquid-nitrogen (LN2) cryo-holder to cool down the specimen to around 0°C within a Titan ETEM G2 80-300 kV (FEI/TFS) under variable water pressure (up to 19 mbar); we could efficiently adjust the temperature by mixing LN_2 with an adequate volume of ethanol. The microscope is equipped with a SDD $XMax^N$ EDX spectrometer (Oxford Inst.) and a OneView camera (Gatan) capable of acquiring 4kx4k images at 25fps.

Experiments were performed at 80 and 300kV. A major concern was to control electron doses to avoid noticeable (ideally any) irradiation damage of NaCl during irradiation. This was achieved using an electron flux of ≈ 20 e-.$Å^{-2}$.s^{-1} and total doses < 4000 e-.$Å^{-2}$. Then, we performed water condensation/evaporation cycles to follow the evolution of NaCl cubes under different RH environments and after dissolution, their recrystallisation and redispersion on the carbon-film surface (see Figure).

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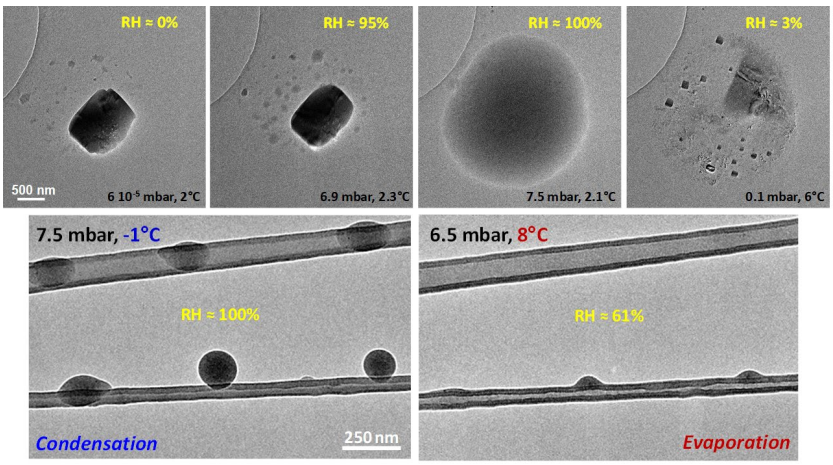

Figure: Condensation and evaporation of water on micrometer-size (top) and nanometer-size (bottom) NaCl nuclei.