Electronic Supplementary Information

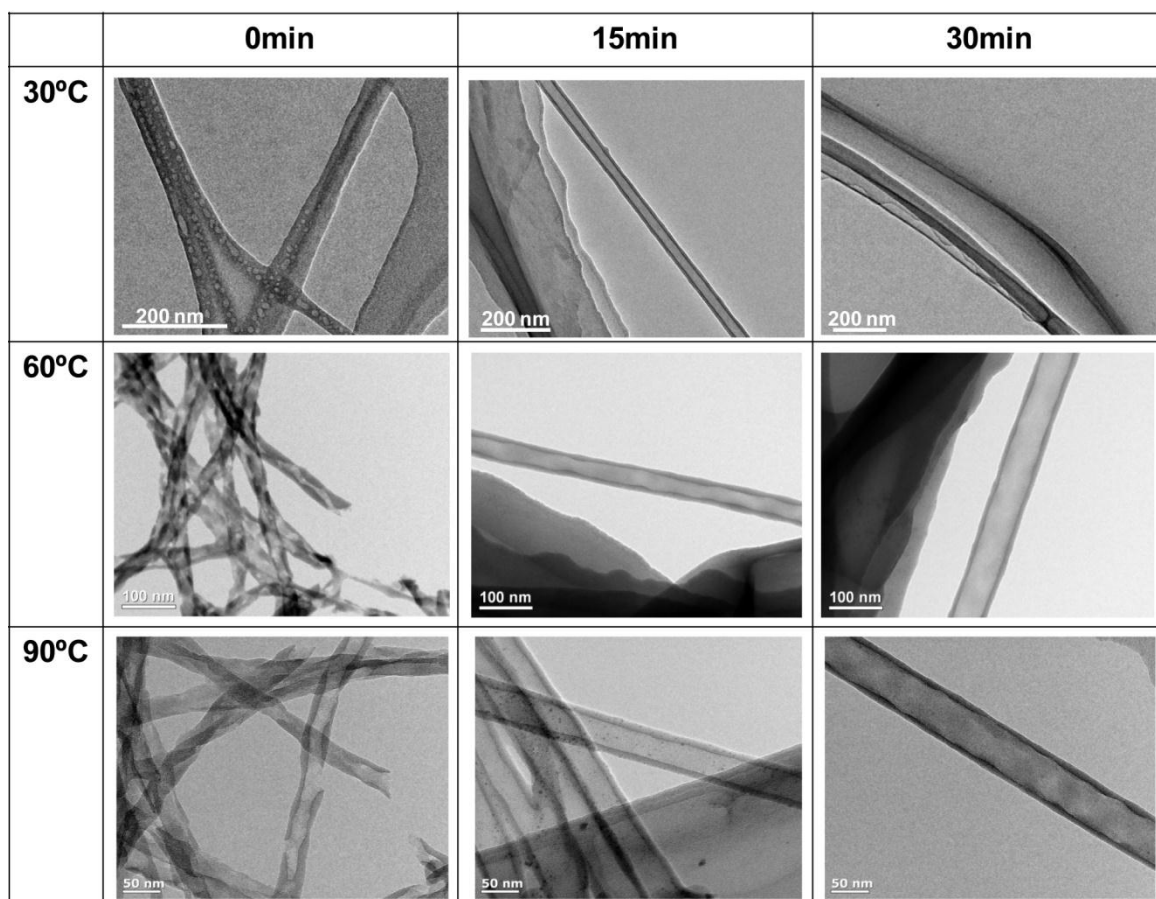|	0min	15min	30min
30°C	200 nm	200 nm	200 nm
60°C	100 nm	100 nm	100 nm
90°C	50 nm	50 nm	50 nm

Fig. S1.   TEM gallery of silica NTs obtained from our nine different experimental conditions (three temperatures of 30, 60, and 90 °C, and three pore diameter by pore widening for 0, 15, 30 min).   Sinusoidal, undulated morphologies were developed below ~30 nm in diameter for all the reaction temperatures.
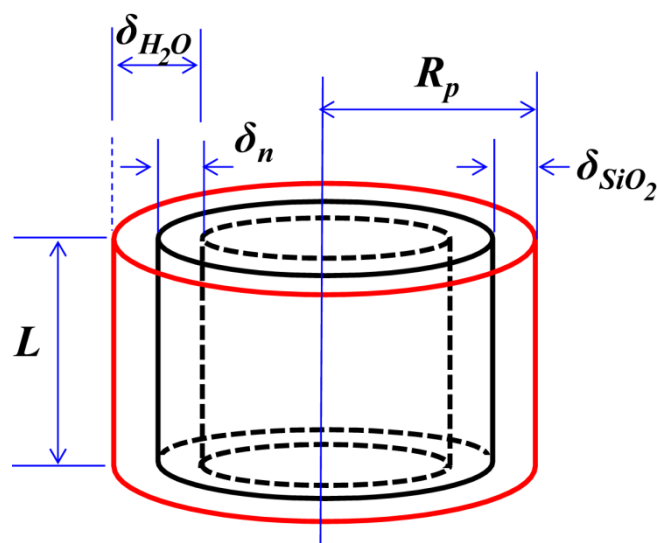
Fig. S2.   Geometry for calculating the nonlinear evolution of δ_{H_2O} in a cylindrical pore.

The red lines indicate the pore surfaces, and $\delta_{SiO_2} + \delta_n$ denotes the thickness of silica wall.

L is the unit length of pore, and δ_{H_2O} can be expressed the sum of $\delta_{SiO_2} + \delta_n$.

Estimating the thickness of water condensates.

The volume of silica tubes is assumed to be originated by consuming all the amount of H_2O

with the number of Si atoms, which was deduced from δ_{H_2O}.   We start our estimation as

follows:

$$0.39 \cdot \left\{ \pi(R_p)^2 \cdot L - \pi(R_p - \delta_{S\,i_2O})^2 \cdot L \right\} = \pi(R_p - \delta_{S\,i_2O})^2 \cdot L - \pi\left\{ (R_p)^2 - (t_{S\,i_2O} + \delta_n)^2 \right\} \cdot L$$

$$\left\{ (R_p)^2 - (\delta_{SiO_2} + \delta_n)^2 \right\} = (R_p - \delta_{SiO_2})^2 - 0.39 \cdot \left\{ (R_p)^2 - (R_p - \delta_{SiO_2})^2 \right\}$$

Therefore, we obtain eq. (4):

$$\delta_{H_2O} = R_p - \sqrt{(R_p - \delta_{SiO_2})^2 - 0.39 \cdot \left\{ (R_p)^2 - (R_p - \delta_{SiO_2})^2 \right\}}$$

Derivation of a modified Kelvin equation considering dispersion forces for cylindrical

meso- and macropores.

Condensation/evaporation of water in the walls of cylindrical macropores can be described by the well known Kelvin Equation:

$$\ln \frac{p}{p_0} = -\frac{2\gamma V_L}{rRT}\cos\theta \qquad\qquad (1)$$

with p and p_0 the vapor pressures of the curved and planar interface, respectively, γ the surface tension of the gas-liquid interface, V_L the molar volume of the liquid phase, r the radius of the cylindrical pore and θ the contact angle.

However, this equation does not take into account the influence of the dispersion forces on the interface, which may be significant in mesoporous, specially the long range forces.

To introduce this effect on the equation, we have used the work developed by K. Stephan [S1] for planar surfaces and modify it for the case of cylindrical pores. The procedure is described next.
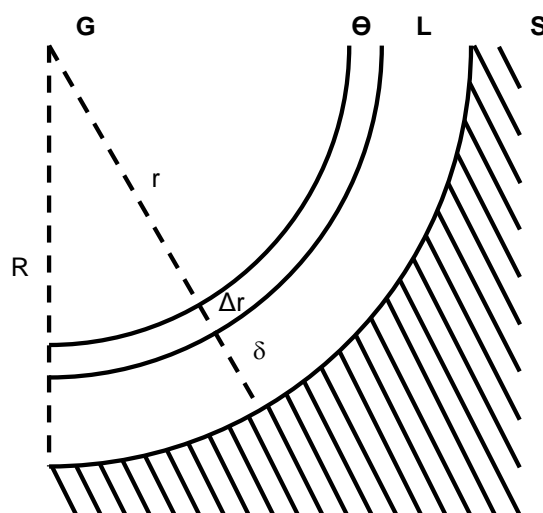

Figure S3.   Cross-section scheme of the water condensation layer in a cylindrical pore

When a cylindrical pore of radius R_p is exposed to a water vapor (Figure 5), condensation may happen to form a water layer of thickness δ and curvature K (2) on the wall of the pore. The G-L interface $\ominus$ has a thickness Δr which, under the assumption of a Gibbs interface, would equal 0. However, a water layer condensed in a mesopore wall, both δ and Δr are in the same range and this model fails.

$$K = \frac{1}{R_p - \delta} \qquad (2)$$

In mesopores, the main driving forces for the water condensation are the capillarity forces at the $\ominus$ interface and the dispersion forces exerted by the solid wall on the system. While capillarity forces rise from the uncompensated forces experienced by the molecules at the G-L interface, the dispersion forces originate from quantum mechanical phenomena and work as body forces.

The dispersion forces between the solid wall and the liquid phase can be attractive or repulsive. They are long range forces (from 0.2 up to 10 nm), being weaker with distance. Because the pore diameters used in this work are larger than 40 nm in diameter, the centre of the pore can be assumed to be almost free of dispersion forces. In general $R_p \gg \delta$, so that the dispersion forces close to the pore wall are approximately equivalent to that of a system consisting of two parallel semi-infinite planar surfaces. The potential energy per unit area of the dispersion forces in this case is given by eq. (3).

$$U_{disp} = \frac{A}{12\pi(R_p - r)^2} \qquad (3)$$

where A is known as the Hamaker constant and depends on the interacting media. It is negative for attractive forces. The equation has already been rewritten in cylindrical coordinates, with $r \equiv [0, R[$. The dispersion forces can then be derived from the potential energy as follows.

$$f_{disp} = -\frac{\partial U_{disp}}{\partial r} = -\frac{A}{6\pi(R_p - r)^3} \qquad (4)$$

where f_{disp} is the resultant of all dispersion forces acting in a unit area in the medium. These forces are compensated by an external pressure so that equilibrium condition is satisfied. Therefore, the so-called dispersion pressure (p_{disp}) is defined as:

$$p_{disp} \equiv -f_{disp} = \frac{A}{6\pi(R_p - r)^3} \qquad (5)$$

Next, consider the liquid volume element shown in Figure 6 under the influence of the dispersion forces and the dispersion pressure. The balance of the momentums acting on this volume element can be written as:

$$\rho_L f_{disp,r}^* = \frac{\partial p_{disp}}{\partial r} \qquad (6)$$

with ρ_L the liquid density and $f_{disp,r}^* = \frac{f_{disp,r}}{m}$ the dispersion forces acting on the volume element in the direction of r per unit mass.
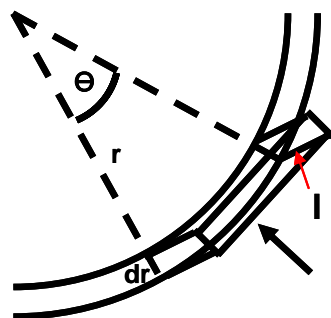
Figure S4. Volume element defined inside a pore in the liquid media

By rearranging, it is then obtained the relation

$$f^*_{disp,r} = \frac{1}{\rho_L} \frac{\partial p_{disp}}{\partial r}$$

$$f_{disp,r} = V_L \frac{\partial p_{disp}}{\partial r}$$

$$\overline{F}_{disp,r} = \overline{V}_L \frac{\partial p_{disp}}{\partial r}$$

$$\overline{F}_{disp,r} dr = \overline{V}_L \frac{\partial p_{disp}}{\partial r} dr$$

$$\overline{F}_{disp,r} dr = \overline{V}_L dp_{disp} \qquad (7)$$

On the other hand, under the next assumptions, one can derive the Young-Laplace equation

for the cylindrical pore including both the capillary forces and the dispersion forces.

- The gas phase behaves as an ideal gas, so that no interactions between the gas molecules are

considered.

- The thickness of the liquid layer δ is relatively thin compared to R_p and it is always in

equilibrium with the gas phase.

- The Gibbs assumption cannot be accepted as the liquid layer is quite thin and thus, the thickness of the interface is negligible compared to δ.

The balance of all forces acting on a shell element at the interface Θ (Figure 7) with arc length $ds = rd\Theta$, depth L and thickness Δr can be written as:
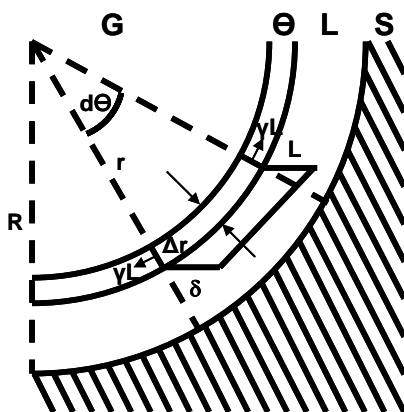
$$dF_L + dF_\theta = dF_G + dF_{disp} \qquad (8)$$

Figure S5.   Illustration of a shell element on the interface Θ with thickness Δr

The force caused by the surface tension reads as $dF_\theta = \gamma L d\theta$, with γ the surface tension.

The force caused by the liquid pressure reads as $dF_L = p_L \cdot (r + \Delta r) \cdot L \cdot d\theta$

The force caused by gas pressure reads as $dF_G = p_G \cdot r \cdot L \cdot d\theta$

And the dispersion forces read as:

$$dF_{disp} = p_{disp,\theta,L} \cdot (r + \Delta r) \cdot L \cdot d\theta - p_{disp,\theta,G} \cdot r \cdot L \cdot d\theta \approx (p_{disp,\theta,L} - p_{disp,\theta,G}) \cdot r \cdot L \cdot d\theta$$

Thus, the balance of forces is:

$$p_L \cdot (r + \Delta r) \cdot L \cdot d\theta + \gamma \cdot L \cdot d\theta = p_G \cdot r \cdot L \cdot d\theta + (p_{disp,\theta,L} - p_{disp,\theta,G}) \cdot r \cdot L \cdot d\theta$$

After arrangement of the equation, the Young-Laplace equation is obtained:

$$p_L + \frac{\gamma}{r} = p_G + (p_{disp,\theta,L} - p_{disp,\theta,G}) \qquad (9)$$

To end up in the modified Kelvin equation, the thermodynamic condition of equilibrium must be addressed.

The Gibbs-Duhem equation for a system without dispersion forces reads as follow:

$$dG = -\overline{S}dT + \overline{V}dp, \quad \overline{S}(p,T), p(\rho,T)$$

In a system with dispersion forces, because of the dependence of F_{disp} with distance, the pressure will also depend on the position in the liquid.

$$p(\rho,T,\vec{r})$$

and as a consequence

$$\mu(p,T,\vec{r})$$

The Gibbs function considering all energetic contributions is now:

$$dG(S,V,\vec{r},n) = TdS - pdV - \vec{F}_{disp}d\vec{r} + \mu dn \qquad (10)$$

with T, p, F_{disp} and μ functions of S, V, r and n

Because Gibbs equation is a homogeneous function of first order in the variables S, V, n, its Euler equation reads as:

$$G = TS - pV + \mu n \quad \rightarrow \quad dG = TdS + SdT - pdV + Vdp + \mu dn + nd\mu \qquad (11)$$

Subtracting (10) from (11)

$$SdT - Vdp + \vec{F}_{disp} d\vec{r} + nd\mu = 0 \qquad (12)$$

Since F_{disp} depends only on r (F_{disp} act in the direction of vector r), the dot product results in:

$$\vec{F}_{disp} d\vec{r} = F_{disp} dr \cos(0) = F_{disp} dr \qquad (13)$$

Now, introducing (13) first and next (7) in (12)

$$SdT - Vdp + Vdp_{disp} + nd\mu = 0$$

By arranging all the elements and dividing by the amount of substance n and introducing molar entropy and molar volume, the Gibbs-Duhem equation including the dispersion forces is obtained.

$$d\mu = -\overline{S}dT + \overline{V}dp - \overline{V}dp_{disp} \qquad (14)$$

which defines the chemical potential of the system as a function of T, p and p_{disp}.

Consider now an arc element $r_\theta d\theta$ in the water thin film with thickness δ in equilibrium with its vapor and the θ interface (Figure 8). The temperature is the same along the whole interface and at both sides of it. The pressure at the gas side is $p_{G,\theta}$ and at the liquid side $p_{L,\theta}$.

The phase equilibrium requires $\mu_L(T_\theta, p_{L,\theta}, r = r_\theta + \Delta r) = \mu_G(T_\theta, p_{G,\theta}, r = r_\theta)$

A reference system without dispersion forces can be defined far away from the pore surface ($r_\Theta \to 0$), with the equilibrium condition in this case given by $\mu_L(T_\Theta, p_{sat}, r_\Theta \to 0) = \mu_G(T_\Theta, p_{sat}, r_\Theta \to 0)$.

Since $d\mu_L = d\mu_G$,

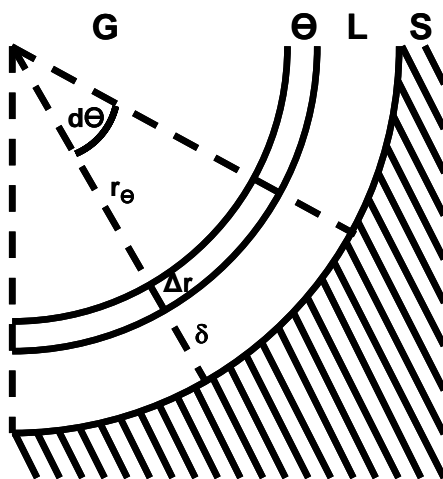$$\int_{r\to 0}^{r=r_\Theta+\Delta r} d\mu_L = \int_{r\to 0}^{r=r_\Theta} d\mu_G$$

Figure S6.   Illustration of an arc element on the interface Θ.

Using (14) now

$$\int_{r\to 0}^{r=r_\Theta+\Delta r} -\overline{S_L}dT + \overline{V_L}dp - \overline{V_L}dp_{disp} = \int_{r\to 0}^{r=r_\Theta} -\overline{S_G}dT + \overline{V_G}dp - \overline{V_G}dp_{disp}$$

$$-\int_{T_\Theta}^{T_\Theta}\overline{S_L}dT + \int_{p_{sat}}^{p_{\Theta,L}}\overline{V_L}dp - \int_{0}^{p_{disp,\Theta,L}}\overline{V_L}dp_{disp} = -\int_{T_\Theta}^{T_\Theta}\overline{S_G}dT + \int_{p_{sat}}^{p_{\Theta,G}}\overline{V_G}dp - \int_{0}^{p_{disp,\Theta,G}}\overline{V_G}dp_{disp}$$

Assuming that liquid and gas are incompressible

$$\overline{V_L}(p_{\Theta,L} - p_{sat}) - \overline{V_L}p_{disp,\Theta,L} = \overline{V_G}(p_{\Theta,G} - p_{sat}) - \overline{V_G}p_{disp,\Theta,G}$$

$$\overline{V}_L p_{\theta,L} - \overline{V}_L p_{sat} - \overline{V}_L p_{disp,\theta,L} = \overline{V}_G p_{\theta,G} - \overline{V}_G p_{sat} - \overline{V}_G p_{disp,\theta,G} \qquad (15)$$

At the interface, the Young-Laplace equation reads as

$$p_{\theta,L} + \frac{\gamma}{R_p - \delta} = p_{\theta,G} + p_{disp,\theta,L} - p_{disp,\theta,G} \qquad (16)$$

The substitution of $p_{\theta,L}$ from (16) in (15) and arrangement of all elements results in

$$p_{\theta,G} = p_{sat} + \frac{\overline{V}_L}{(\overline{V}_L - \overline{V}_G)} \frac{\gamma}{R_p - \delta} + p_{disp,\theta,G}$$

Finally, replacement of the molar volumes of gas and liquid by their densities results in the modified Kelvin equation for a cylindrical pore for the gas:

$$p_{\theta,G} = p_{sat} - \frac{\rho_G}{\rho_L - \rho_G} \frac{\gamma}{R_p - \delta} + p_{disp,\theta,G}$$

where $p_{disp,\theta,G} = \dfrac{A_{disp,\theta,G}}{6\pi(R_p - \delta)^3} < 0$

Here we assume that $\delta \gg \Delta r$ and it is neglected in the Young-Laplace equation applied to the interface, since δ is around a few tenths of nm and Δr is in the range of 1 nm.

Equivalently, it can be obtained from (16) and (15) the modified Kelvin equation for the liquid phase.

$$p_{\theta,L} = p_{sat} - \frac{\rho_L}{\rho_L - \rho_G} \frac{\gamma}{R_p - \delta} + p_{disp,\theta,L}$$

and $p_{disp,\theta,L} = \dfrac{A_{disp,\theta,L}}{6\pi(R_p - \delta)^3} < 0$

Estimation of Hamaker Constants in our systems.

Estimated Hamaker Constants for a system consisting of two dissimilar materials in the presence of a third media (water) using equation $A_{132} \approx \left(\sqrt{A_{11}} - \sqrt{A_{33}}\right) \cdot \left(\sqrt{A_{22}} - \sqrt{A_{33}}\right)$ with material 1 specified in the column, material 2 in the row and media 3 as water. Hamaker values for the system material｜air｜material are taken from references S2 and S2, as below.

$Air/Vac/Air \approx 0$

$A_{Water/Air/Water} = +3.7 \times 10^{-20}$ J

$A_{Al2O3/Air/Al2O3} = +16.5 \times 10^{-20}$ J

$A_{SiO2/Air/SiO2} = +6.8 \times 10^{-20}$ J

$A_{PC/Air/PC} = +5.1 \times 10^{-20}$ J

Table S1.　A summary of estimated Hamaker constants.

A_{1W2} $(10^{-20}$ J)	Air	SiO$_2$
Al$_2$O$_3$	-4.1	+1.5
PC	-0.6	+0.2
SiO$_2$	-1.3	

Comparison of processing times.

The processing times between the literature procedures and the present study are estimated for brief comparison, assuming the fabrication of silica NTs possessing the similar geometries each other. It is estimated by using experimental parameters when the literature processes are applied for porous alumina templates with 40 nm in pore diameter and 10 μm in pore length.   Other parameters such as evacuation time and chamber heating in the literature papers, and saturation time for humidity in the present study are commonly ruled out for simplicity.   It is noted that the types of precursor delivery such as shower head and flow reactor can also affect such a calculation.

Table S2.   A summary of compared processing times.

	Precursors	Temperature (°C)	Growth rate (nm/cycle)	**Total reaction time (h)**	References
Catalytic ALD of SiO$_2$	- SiCl$_4$ - H$_2$O - pyridine	25	0.21	**2.5**	52 [Kaus *et al.,* *Science* **1997**]
Self-catalytic ALD of SiO$_2$	-H$_2$N(CH$_2$)$_3$Si(OEt)$_3$ - H$_2$O - O$_3$	150	0.06	**10**	48a [Bachmann *et al.,* *Angew. Chem. Int. Ed.* **2008**]
Transformation of water condensates	- SiCl$_4$ - H$_2$O	30-90	7-11	**0.25**	The present work

[S1] K. Stephan, *International Journal of Heat and Mass Transfer,* **2002**, *45***,** 4715-4725

[S2] R.H. French, *Origins and Applications of London Dispersion Forces and Hamaker Constants in Ceramics*, J. Am. Ceram. Soc., **2000**, *83*, 2117–46

[S3] G.V. Franks, Colloids and Fine Particles (Chap. 5), in Introduction to Particle Technology, 2nd. Edition, edited by Martin Rhodes, Wiley, **2008**