Water adsorption on silica nanoparticles

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The atmosphere contains small nanoparticles (below 100 nm) with concentrations from few to hundreds of thousands per cubic centimeter. These nanoparticles are exposed to water vapor in atmosphere (typical relative humidity (RH) range from 30 to 100 %) that produces films on their surfaces. This water layer on nanoaerosol has major effect as it affect the scattering and absorbance of radiation. It can also have important consequences for heterogeneous chemistry in the atmosphere as the kinetics of many reactions is strongly dependent on the phase of aerosol particles (Knipping et al. 2000). The sources of the atmospheric nanoparticles are natural, e.g., mineral dust, volcanic ash and sea spray (Satheesh and Krishna Moorthy, 2005; Kanakidou et al., 2005), or human made, e.g., aerosols produced in industrial processes, biomass burning and in fossil fuel combustion (Dubovik et al., 2001).

Hygroscopic tandem differential mobility analyzer (H-TDMA) (Liu et al., 1978) is ideal for nanoparticles hygroscopic growth detection as it has capacity to measure on-line the particle diameter (nano-DMA from 3 nm) in dry and humid conditions. Figure 1 shows the schematic of the H-TDMA set-up used in this study. The hygroscopic growth factors (GF) can be then defined by the relation of particle size in humid and dry air and when studying first monolayers adsorption on these nanoparticles the GF´s need to be defined at low RH´s. In fact, a water monolayer thickness is 0.19 nm and it would result the hygroscopic growth factor of 1.004 on the particle having diameter of 100 nm and 1.04 on 10 nm, respectively. Therefore, the detecting of the monolayers based on the size change on the larger sizes is very tricky as even the minimum measurement uncertainties would shade the growth. Here, the aim is to study the hygroscopic growth factors and water monolayers adsorption on fumed-SiO_2 nanoparticles (10-50 nm) at sub saturated water vapor conditions by nano-H-TDMA.

These preliminary experiments showed that for SiO_2 nanoparticles the GFs dropped strongly at 30 nm as seen from Figure 2a. This is most probably caused by agglomerates restructuring during humidification. Figure 2b shows the water monolayer (0.19 nm) number versus RH at selected dry particle diameters 8 and 10 nm for fumed SiO_2. As expected, the monolyaers number increase with RH and particle size. In fact, SiO_2 is hydrophilic and interact strongly with the water (Saliba et al., 2001). It is proposed that first 2 - 3 monolayers on SiO2 interact with surface via hydrogen bonding with silanol groups (Verdaguer et al., 2007). The monolayers numbers defined by physisorption methods of water adsorption on flat SiO_2 surfaces (Figure 5, (broken line); Verdaguer et al., 2007) are very close the ones observed here (Figure 5, spheres and triangles).

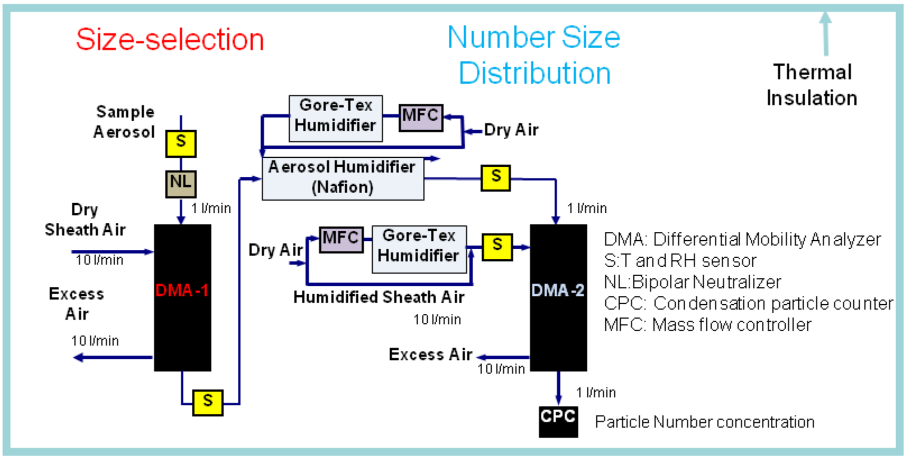

Figure 1 H-TDMA setup, first the aerosol was size selected by DMA-1 after that it was humidified in aerosol humidifier to desired RH (10 - 90%) and the humidified size distribution was measured by DMA-2 and condensation particle counter (CPC).

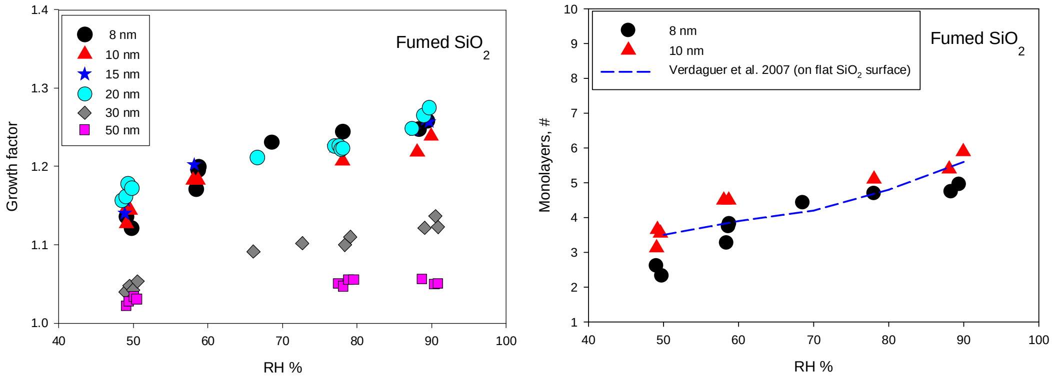

Figure 2 (a) Hygroscopic growth factor versus RH at selected dry particle diameters 8, 10, 15, 20, 30 and 50 nm for fumed SiO_2 and (b) measured monolayer number versus RH at selected dry particle diameters 8 (spheres), 10 (triangles) nm for fumed SiO_2 and for flat SiO_2 surface (adapted from Verdaguer *et al.*, 2007).

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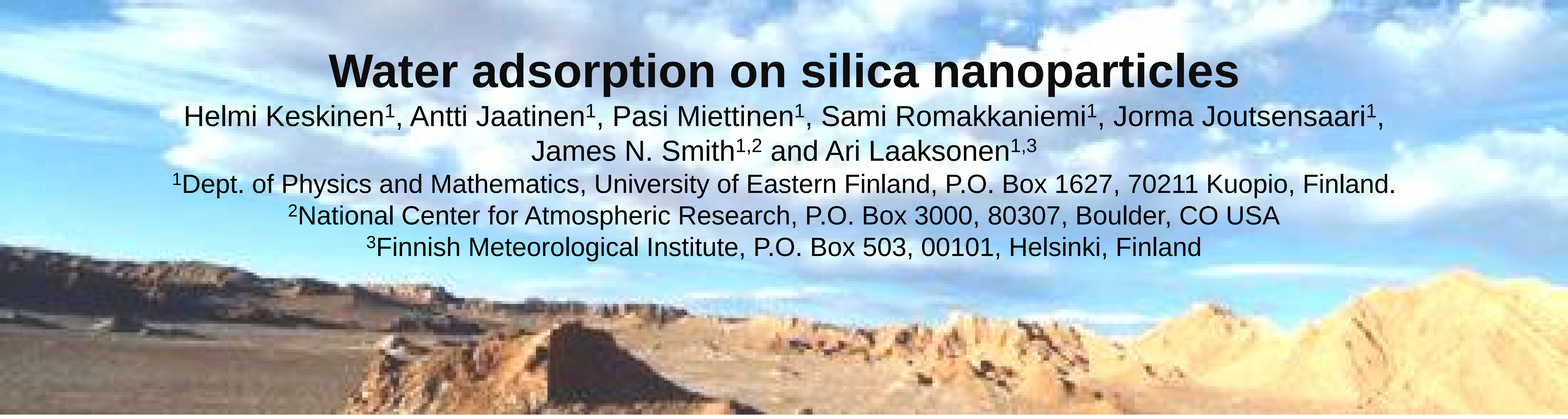

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Motivation

Silica is everywhere:

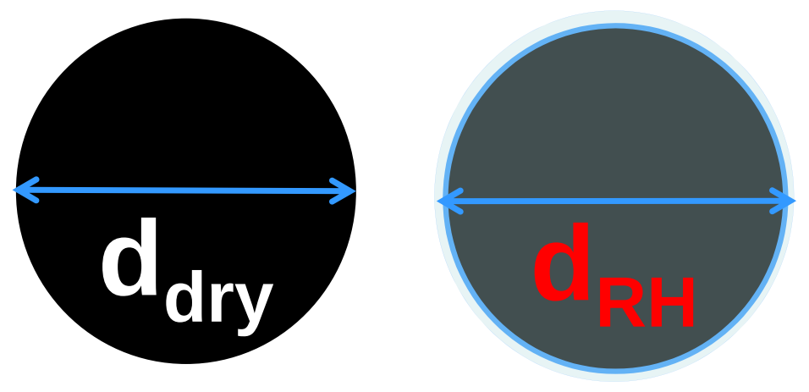
- **Natural sources:** desert dust (~80 % SiO_2), volcanic ash, biomass burning
- **Anthropogenic sources:** additive (e.g., cosmetics and food industry). E.g., nanosized fumed silica is produced more than 1 million *tons/year*

Water is everywhere:

- **Atmosphere:** nanoparticles impact on clouds and radiation
- **Breath:** nanoparticles solubility and surface properties impact on their cell interactions

Methods

Water on nanoparticles:



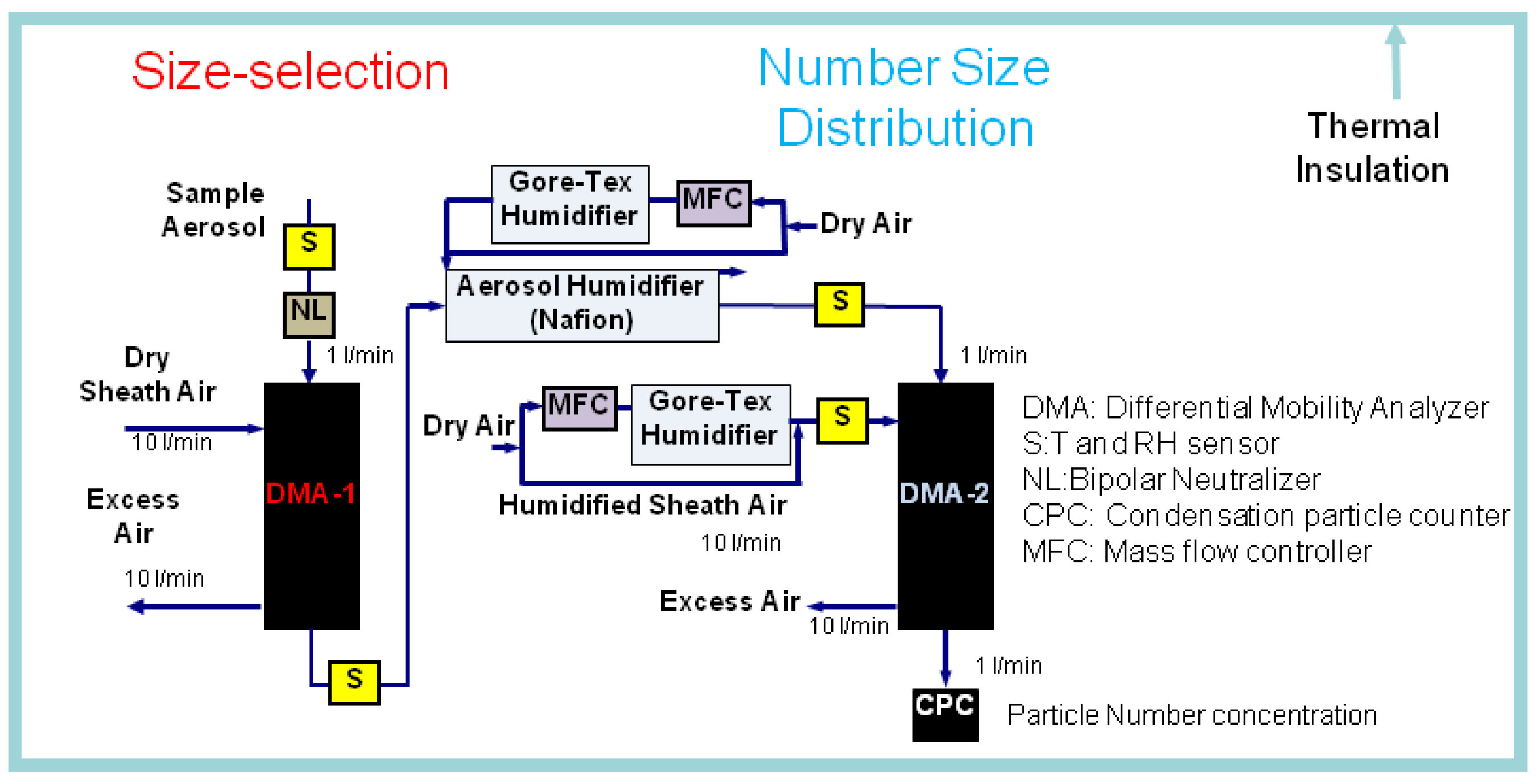
Growth Factor (GF) = d_{RH}/d_{dry}

Number of monolayers = $(d_{RH} - d_{dry})/2l_{ml}$

Water monolayer thickness is estimated to be 1.9Å

Atomized fumed-silica (d_{prim} = 7 nm) measured by:

Hygroscopic
Tandem
Differential
Mobility
Analyzer



DMA: Differential Mobility Analyzer
S:T and RH sensor
NL:Bipolar Neutralizer
CPC: Condensation particle counter
MFC: Mass flow controller

Results

Primary particles

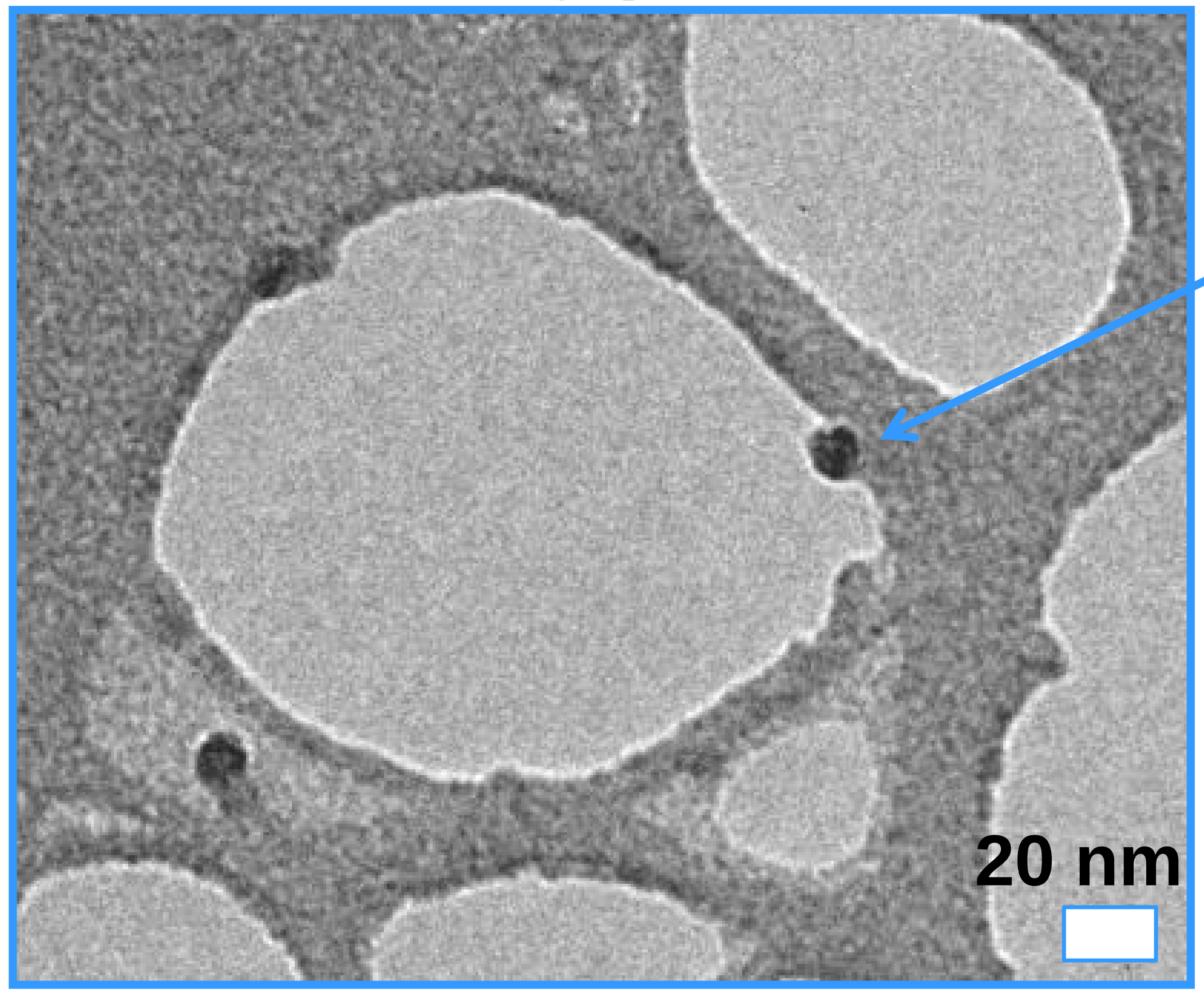


Figure 1. Transmission Electron Microscopy (TEM) photo of smaller primary particles.

Growth factors

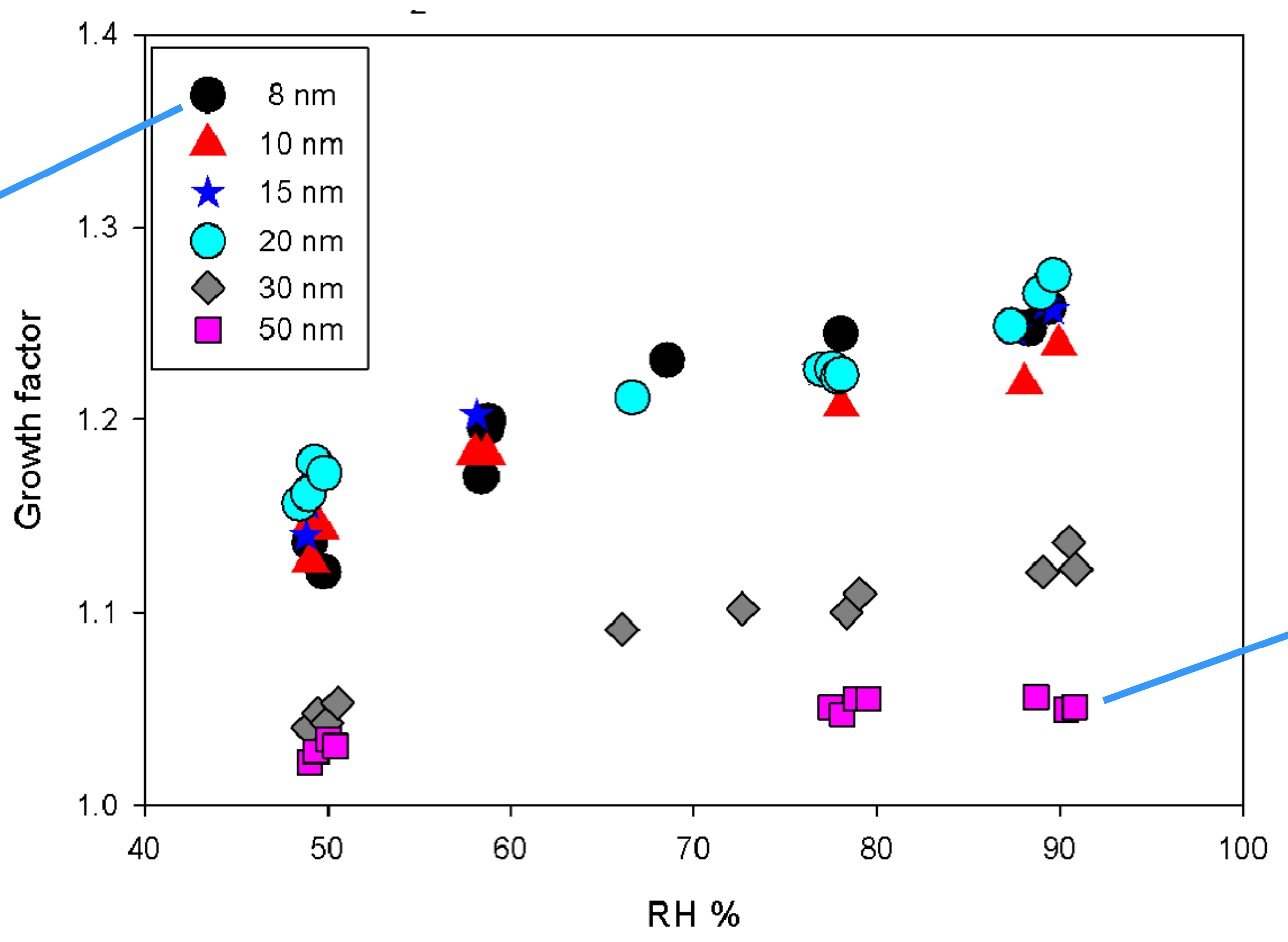


Figure 2. GF versus relative humidity (RH) at selected dry particle diameters 8, 10, 15, 20, 30 and 50 nm for fumed SiO_2.

Agglomerates

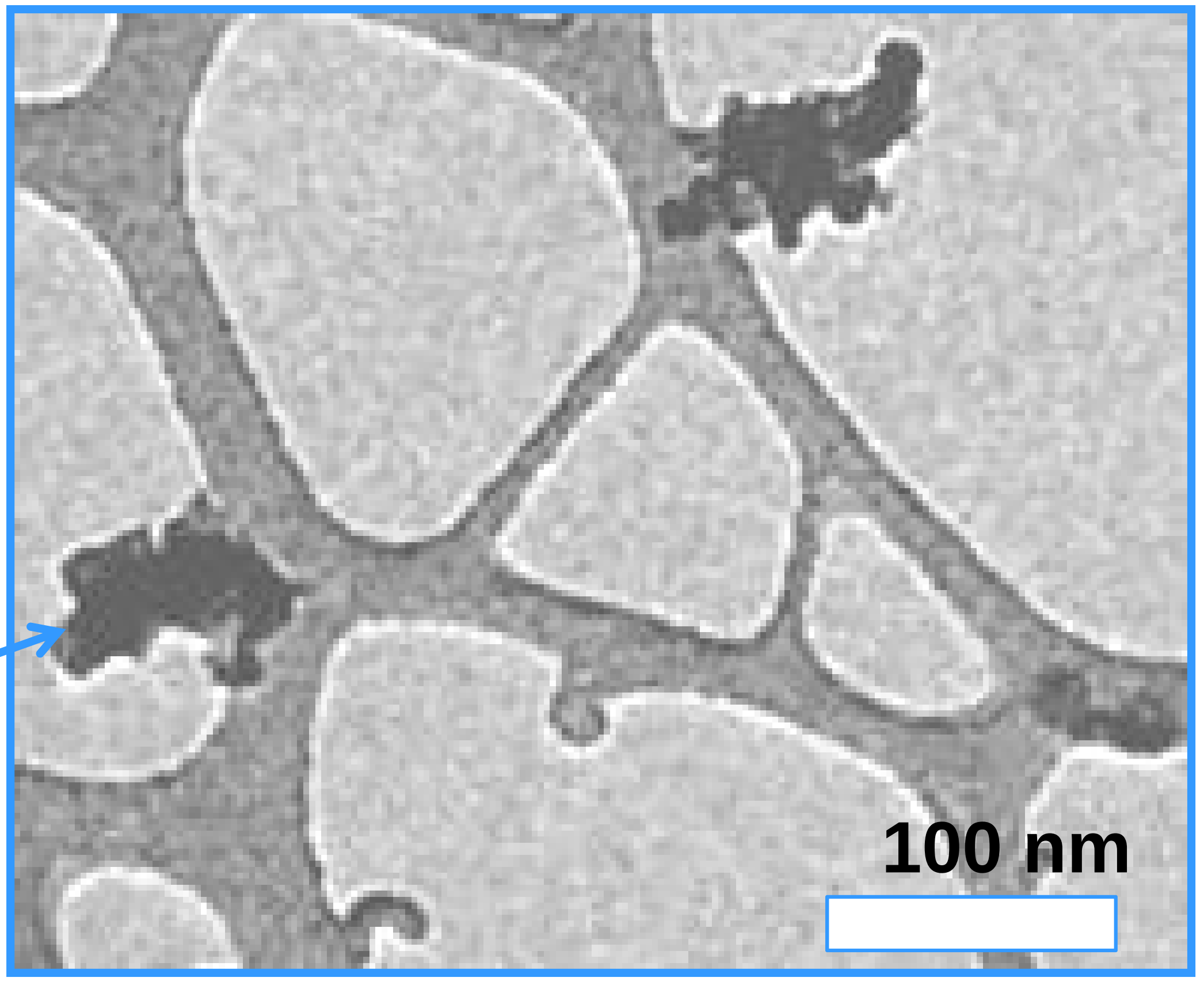


Figure 3. TEM photo of larger agglomerates.

Number of water monolayers on SiO_2 particles

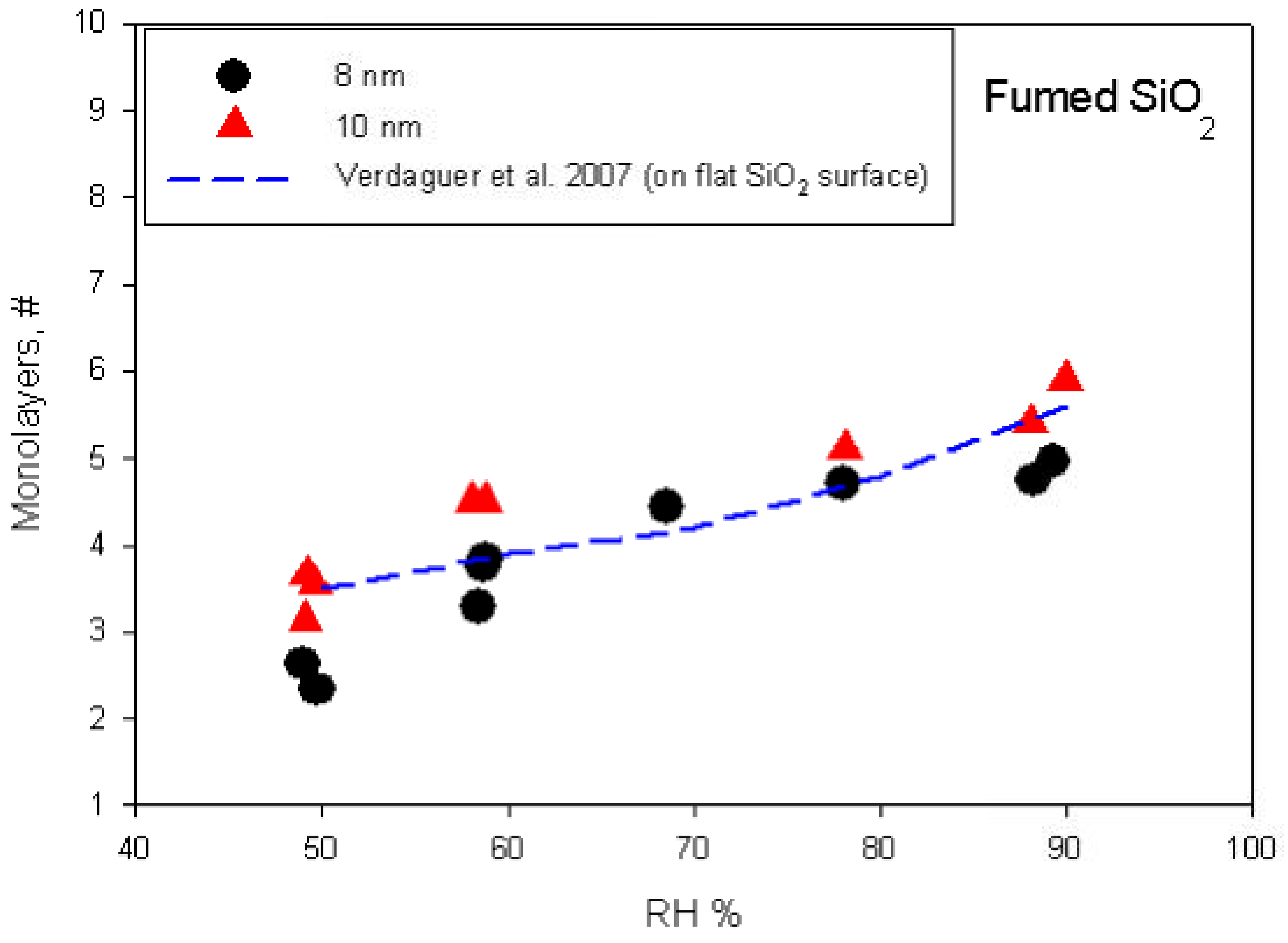


Figure 4. Monolayer number versus RH at selected dry particle diameters 8 (spheres), 10 (triangles) nm for fumed SiO_2 and for flat SiO_2 surface (adapted from Verdaguer *et al.*, 2007).

Conclusions

- **Size-selected 8 -10 nm particles were spherical**
- **From larger size fractions also agglomerates were detected**
- **Growth factors for agglomerates dropped (→restructuring)**
- **at RH = 55-90% 4 to 6 water layers were detected on 8 and 10 nm particles**
- **Water monolayer number agreed well with literature**

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