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Drying Kinetics and Particle Formation from Dilute Colloidal Suspensions in Aerosol Droplets

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Abstract

Industrial processes such as spray drying of pharmaceutical and food products often involve the drying of aerosol droplets containing colloidal suspensions into powdered microparticles of desired properties. The morphology and surface properties of the final dry products/microparticles obtained after the drying process are strongly influenced by the parameters of the initial aerosol droplet composition and the drying conditions. In particular, the final dry microparticle morphology can be dependent on the dimensionless Péclet number (Pe), which expresses the relative competition between the diffusion of the dispersed particles within the droplet and the rate of solvent loss via evaporation. In this work, we examine how control over the gas phase drying conditions and initial aerosol droplet composition can be used to influence the aerosol droplet drying kinetics in the gas phase for a range of Péclet numbers. We used a single-particle levitation instrument, the electrodynamic balance, to measure the drying kinetics of colloidal silica droplets (0.10 - 0.60 % v/v) under controlled gas phase drying conditions of temperature (263 - 326 K) and

relative humidity (0 - 90 %) and obtained Péclet numbers ranging from 4.05 - 184.5. We demonstrate that, for aerosol droplets with initially dilute feed colloid concentrations and within the constant evaporation regime, the starting composition does not strongly influence the solvent evaporation rate with the included nanoparticles (NPs) acting as spectators. However, the gas phase drying conditions, temperature, and relative humidity, directly influences the droplet temperature via evaporative cooling as well as the droplet drying kinetics and the final dry microparticle properties. With *a priori* knowledge of the droplet drying kinetics from the single droplet measurements, we further demonstrate the possibility of tailoring the morphology of the dried microparticles. Dried silica microparticles collected at $Pe = 23.8$ had dense spherical morphologies while those at the highest $Pe = 180.0$ had crumpled surface morphologies with a transition in morphology between these limiting Pe values. Our results extend the fundamental understanding of the mechanisms controlling the drying of aerosol droplets in colloidal suspensions across a wide range of application areas extending from spray drying, to the drying of respiratory fluid droplets containing bacteria and viruses, and the drying of atmospheric aerosol droplets.

Introduction

The drying of colloidal suspensions in aerosol droplets provides particles that are fundamental building blocks in many industrial applications including food processing, sprays in pharmaceuticals, inhaled drug delivery, cosmetics, ceramics and many more.¹⁻⁵ To date, spray-drying is one of the most widely used techniques to dry aerosol droplets because of its industrial popularity,^{3,6,7} scalability and the ability to control some of the parameters that determine the aerosol droplet drying process.⁸ Spray drying allows the continuous production of dry solids in

powder, granulate or agglomerate form in the aerosol phase and involves controlled drying of the aerosol droplet by contact with a warm carrier gas in a drying chamber.⁶⁻⁹ Although many successes have been reported,^{8,10-12} a lot of challenges still persist in practice for the optimization of spray drying techniques from both fundamental research and industrial scale-ups.^{6,13,14} The polydispersity in size resulting from the atomization of a liquid feed solution into a hot drying chamber and the variation in trajectories within the drying chamber (and, thus, drying rates) makes it challenging to precisely study the links between the droplet drying kinetics and the resulting particle morphology *in situ*.^{15,16}

Generally, processing techniques for most industrial spray drying applications rely on drying of aerosolized droplets that contain the desired materials (excipients or solid nanoparticles, NPs) in a dispersing solvent or liquid. In this way, the dispersing solvent evaporates during the drying process and the suspended materials dry to form granulated microparticles of diverse morphologies such as core-shell structures, doughnuts,^{8,17} folded, shriveled, hollow, dimpled or spherical dense microparticles.^{3,11,13,18,19} It is well known that the main parameters that characterize the aerosol droplet drying process and, hence, the properties of the final dried microparticle morphology can be described by the analysis of the non-dimensional parameter, the Péclet number (Pe).^{2,3,6} Pe is defined in eq. 1 as the ratio of the evaporation rate, κ , indicating the speed at which the droplet surface shrinks by solvent loss, and the diffusion coefficient, D_i , indicating the speed at which the suspended particles diffuses away from the droplet surface towards the droplet centre.^{3,6}

$$Pe_i = \frac{\kappa}{8D_i} \quad (1)$$

The evaporation rate or flux is defined as:⁶

$$\kappa = -8r_d \frac{dr_d}{dt} \quad (2)$$

where r_d is the droplet radius.

The diffusional mixing rate of the suspended particles, which can be related to the rheological properties of the aerosol droplet composition, can be estimated via the Stoke -Einstein equation as:

$$D_i = \frac{k_B T}{6\pi\mu_i r_i} \quad (3)$$

Here, $k_B T$ is the thermal energy with k_B the Boltzmann's constant and T the absolute temperature in Kelvin. μ_i and r_i are the viscosity of the solvent and the radius of the diffusing particles in the droplet, respectively.

Usually, a dried microparticle morphology can be related to the Péclet number depending on the relative dominance of the diffusional mixing rate, D_i and the evaporation rate constant, κ . If $Pe \ll 1$, the diffusive transport is the dominating transport mechanism and the drying process is considered as slow. The droplet shrinks isotropically throughout the drying process with sufficient time for redistribution of the suspended inclusions by diffusion within the drying droplet. The slow drying process results in the formation of spherical, dense microparticles.^{19,20} However, if Pe is sufficiently high, i.e. $Pe \gg 1$, convective transport dominates over the diffusive transport and the drying process is considered as fast. In this case, there is insufficient time for redistribution of the included NPs by diffusion within the droplet during the drying process and they instead preferentially form a skin or shell at the droplet surface, leading to the formation of doughnuts, shriveled or hollow dried microparticles.² It is important to highlight that a high Peclet number is necessary but not sufficient for shell formation.^{21–24}

Process parameters such as the initial aerosol droplet parameters (droplet size, type of solvent, viscosity, concentration and size of the solid NPs)^{8,25–28} and the drying conditions (drying temperature and relative humidity)^{8,11} can be optimized to achieve the required particle form for targeted applications. For example, in pharmaceutical applications, spherical, dense and crumpled

dried powdered microparticles are produced via spray drying for capsules intended for oral drug administration and for deeper lung deposition respectively.^{7,29} Experimentally, Iskandar et al.⁸ used spray drying techniques to study the influence of initial droplet size, viscosity of the droplet, drying temperature, gas flow rate, and addition of surfactant on dried microparticles morphology.

As an alternative to pilot experiments with a spray dryer, a plethora of experimental techniques^{8,9,30–32} have been developed to study some of the process parameters that are involved in the aerosol droplet drying processes and their influence on the final dried microparticle morphology. Solution aerosol thermolysis (SAT), also known as spray pyrolysis, was employed by Jayanthi *et al.*^{29,33} to study how process parameters, such as initial droplet radius, solute properties and concentration as well as ambient temperature, affect solid particle formation processes during the evaporation stages. The main advantage of spray pyrolysis is the uniformity and high purity of the dried products produced.^{33,34} However, the use of spray pyrolysis is operationally demanding because of the reaction mechanisms and thermal decomposition processes involved,³⁵ as well as the lack of ability to study droplet drying kinetics and predict or control dried particle morphology.³⁴

To circumvent the operational difficulties of interrogating the connections between final particle morphology and process parameters in a complex reactor such as a spray drier, single droplet drying experiments can provide an opportunity to more rigorously understand the droplet drying kinetics,^{15,40–45} thereby providing a route to better understand the microphysics in the much more complex drying environment. Single droplet drying techniques can be classified as contact-based techniques, non-contact techniques and the free-falling droplet method. Contact-based techniques, for example pendant drop and sessile drop methods, are those where a single droplet evaporates while suspended on the tip of a thin glass filaments^{15,36,37} or deposited on a flat

surface.^{42–44} Though a comparatively straightforward approach for monitoring droplet drying kinetics, the intrusive nature of these contact based techniques may lead to some unwanted effects. The presence of the glass filament or surface to levitate the droplet undoubtedly affects the heat and mass transfer during the droplet drying process and also affect the spherical shape of the droplet that impacts greatly on the integrity and morphology of the final dry structures formed after the drying process.

Non-contact-based methods involve the immobilization of single droplets in an isolated volume by acoustic,^{23,45,46} magnetic⁴⁷ or by electrodynamic levitation^{40,48–50} and allowed to evaporate under controlled conditions. Major advantages of the non-contact-based methods are the non-intrusive nature and the fixing of the droplet position in “*free space*” during drying that allows more convenient monitoring of droplet drying histories and morphological changes in comparison to contact based and free falling techniques. Nevertheless, some non-contact-based methods such as the use of acoustic levitation for accurate measurement of evaporation rate still poses challenges. The acoustic field, being a sequence of sharp fluctuations in air pressure alters the droplet shape and affects the heat and mass transfer rate in the droplet.^{51,52}

The free-falling droplet method^{39,53} are those where a single droplet or a chain of monodisperse droplets evaporate from the top of a tall drying chamber or glass column in a controlled air stream during free fall. Some advantages of this method are that it represents effectively what happens to an aerosol droplet during spray drying and offers the possibility to collect relatively large number of dried particles on a substrate after drying. A major drawback of this method is that it is not possible to monitor the drying histories of individual droplets during drying.

In a way, all the three techniques involved in single droplet drying are characterized by pros and cons. However, the use of electrodynamic levitation and the droplet chain method for

simulating droplet drying relevant across a broad range of application areas have been demonstrated to be of greater relevance to the study of aerosol droplet microphysics and observation of dry particle morphology, respectively.^{32,39,40,54–56} Electrodynamic levitation provides the possibility to study accurately the drying kinetics of a single droplets, whereas the droplet chain method offers opportunities for drying multiple monodispersed droplets simultaneously. In both techniques, a piezoceramic dispenser can be used to generate droplet sizes (10 - 100 μm) that can be studied under controlled gas phase drying conditions simulating the evaporation processes occurring within the spray dryer environment.

Despite the numerous studies on aerosol droplet drying, there remains a lack of quantitative data and fundamental understanding of how aerosol droplet drying process parameters directly affect dry particle formation processes and the resulting particle morphology. In this study, we explore how control over the gas phase drying conditions (gas phase temperature (T_G) and RH), taking into account the thermal effect of evaporative cooling and initial droplet composition (solid inclusion size and concentration) can be used to influence the aerosol droplet drying kinetics for a range of Péclet numbers. With *a priori* knowledge of the droplet drying kinetics from these single droplet measurements, we demonstrate the possibility of tailoring the morphology of the dried microparticles for a range of Péclet numbers. We use an electrodynamic balance capable of suspending a single charged aerosol droplet in the gas phase and subsequently probed with elastic light scattering technique. Additionally, a complementary falling droplet chain instrument for collecting dried microparticles is used. We chose pyrogenic hydrophilic nanosilica particles dispersed in water as a model system because of its many advantageous properties including low-toxicity, colloidal stability, and dispersibility in water.⁵⁷ Additionally, colloidal silica is used widely in applications such as nanoparticle research and particle formation from the drying of

suspensions,^{57,58} drug carriers,⁵⁹ catalytic support,⁵⁷ postsynthesis surface modifications, and as a fractionizing agent.⁵⁷ The final dried microparticles collected with the falling droplet chain instrument after the drying process are analyzed offline using scanning electron microscopy imaging.

Experimental Section

The drying kinetics of single aerosol droplets of hydrophilic silica NPs suspensions were studied using an Electrodynamic Balance (EDB) instrument with electrodes in a concentric cylindrical arrangement. The full experimental details for the EDB instrument have been discussed extensively in previous publications^{40,55,56} and will only be briefly reviewed here. Additionally, to relate the droplet drying kinetics with the final dry particle morphology, we used a Falling Droplet Chain (FDC) instrument⁴⁷ for temperature and humidity dependent dry microparticle collection. The surface properties and the morphology of the collected dried aerosol microparticles were analyzed offline using scanning electron microscopy (SEM) imaging.

Materials and Sample Preparation

Hydrophilic pyrogenic nanosilica (silica NPs, Wacker Chemie AG) and the solvent, HPLC Plus grade water (Sigma-Aldrich) were used as received. The silica NPs (HDK® H20) consist of primary spherical particles (12 nm diameter) sintered to form branched aggregates of size 180 nm. The branched aggregates sizes were confirmed by additional dynamic light scattering (DLS) measurements. Different initial droplet compositions with concentrations ranging from 0.10 - 0.60 % v/v homogeneous silica NPs suspensions were prepared by mixing weighed samples of the silica NPs (HDK® H20) in water followed by magnetic stirring at room temperature (293 K) for 30 minutes. The suspension was further sonicated for 30 minutes to obtain uniform mixing. At

concentrations above 0.6 % v/v, we had problems with blocking of the nozzle of the droplet-on-demand generator and, hence, were unable to study droplet compositions with concentrations above 0.6 % v/v.

EDB Droplet Drying Kinetics Measurement

The EDB used for the droplet drying kinetics measurements is operated under controlled gas phase atmospheric conditions ($T_G = 240 - 340$ K, 0 - 95 % RH). Single aerosol droplets of reproducible initial sizes (radius 28 ± 3 μm) and concentrations (0.10 - 0.60 % v/v silica NPs suspension) were dispensed by a commercial droplet-on-demand (DoD) generator (MicroFab, MJ-ABP-01 with 30 μm orifice diameter). The droplets travelled into a region (null point) of an oscillating electric field generated by an AC voltage applied to the upper and lower concentric cylindrical electrode pairs forming the EDB as in Figure 1. At the center of the trap, a humidified flow of nitrogen gas was passed over the trapped droplet at a rate of 0.03 m/s. A desired relative humidity (0 - 95 %) is achieved in the trapping region of the EDB by a controlled mixing of humidified and dry nitrogen gas flows at the appropriate ratio through the cylindrical electrodes. Since the droplet loses mass via continuous evaporation, the weight and the drag force acting on the droplet are counterbalanced with a DC voltage offset applied to the top and bottom electrodes of the EDB. Additionally, the trap temperature (250 - 330 K) is controlled by a circulating water - ethylene glycol coolant through the body of the EDB electrode mounting plates chamber. The gas phase temperature, T_G , is continuously monitored by a K-type thermocouple temperature probe held close to the trapping chamber of the EDB. The charge polarity on each droplet dispensed into the trap center is determined by a DC ring induction electrode placed at the entrance of one of the side ports of the EDB and $\sim 5 - 20$ mm away from the ejecting orifice of the DoD. In all, the magnitude of the net charge (<10 fC) on each dispensed droplet is below the Rayleigh charge

breakup limit.⁶⁰ Reproducible droplets of similar initial sizes with radius fluctuation smaller than $0.5\ \mu\text{m}$ were generated by controlling the dispenser parameter settings (pulse width, frequency, amplitude etc.). The dispenser parameters and the parameters of the AC/DC oscillating/static fields are both controlled by an in-house built LabVIEW program interfaced on a computer. A single charged aerosol droplet suspended at the trap center is illuminated with a 532 nm CW laser, and the resulting near forward elastically scattered laser light is collected over an angular range of $\sim 24^\circ$ centered at 45° to the propagation direction of the laser (see Figure 1). During the first stage of the evaporation process, when the trapped droplet is optically homogeneous, spherical, and liquid, regularly spaced interference fringes (Mie fringes) in the phase function (intensity dependence on scattering angle) are produced. The spacing between the fringes in the phase function allow the size of the droplet to be estimated using an inversion algorithm based on the geometric optics approximation to Mie theory as previously described.⁴⁰ Appropriate corrections for changes in density and refractive index as the droplet evaporates are made during the offline post-data processing.

Figure 1: The EDB experimental setup for aerosol droplet drying kinetic measurements

Collection of Dry Aerosolized Silica Particles

Falling Droplet Chain Instrument

The principles and operation of the droplet chain instrument used for the collection of dried aerosol microparticles is similar to the one described by Baldelli *et al.*^{39,53} The instrument consists of a glass column of square cross section with a collection platform for dry particle deposition at the bottom, an optical imaging system for measuring aerodynamic droplet sizes at high frame rate, and a droplet generation system composed of DoD (similar to the one used on the EDB) for injecting monodisperse droplets into the column. A basic schematic view of the column is shown in Figure 2. In this work, since the primary focus was to use the instrument for collecting dried microparticles only, with *a priori* known evaporative parameters from EDB kinetic measurements, only a brief description will be presented here. In order to match initial droplet sizes between the EDB and falling droplet chain instruments, we used the same droplet-on-demand dispenser (MicroFab, MJ-ABP-01 with 30 μm orifice diameter) with similar driving parameters to introduce a monodisperse chain of droplet into the column. The droplet chain propagates downwards through the glass column. The glass column is airtight apart from three accessible ports: a laminar gas flow inlet and outlet (for controlling the atmospheric conditions (RH) in the column), a bottom port for insertion of the dry particle deposition slide and a side opening (~ 50 mm in diameter) at the top for introducing the droplet chain into the column. The distance between the droplet delivery point from the DoD at the top of the column and the collection slide at the bottom is approximately 50 cm. Additionally, a nichrome wire coil connected to a heating power supply (linear DC Power Supply, RS PRO, UK) at both ends surrounds the column from the top to the bottom and is used to adjust the temperature in the column to a desired gas phase drying temperature.

Figure 2: Scheme of the falling droplet chain experimental setup

Temperature values are continuously recorded with two K-type thermocouples (TFE-K-20, Omega Engineering, Laval, Quebec, Canada) placed at the top and bottom of the column. For observation purposes, the droplet chain is illuminated by a vertically polarized 532 nm CW laser (ventus 532, LASER QUANTUM LTD, UK) directed by a mirror (M) from the bottom of the glass column and is modulated at the frequency of the droplet generation. The laser light also allows alignment of the droplet chain (dried aerosol particles) to free-fall gently onto the collection glass slide without hitting the walls of the glass tube and to maintain the integrity of the morphology of the dried microparticles.

Scanning Electron Microscopy (SEM)

SEM imaging was used to observe the morphology and surface properties of the dried silica particles. Prior to the SEM imaging, the deposition glass slide with the dried silica particles were mounted onto an aluminum SEM stubs, and sputter-coated with a thin layer (approximately 10 nm thickness) of silver using an Agar Scientific Combined High-resolution Coater System (Agar Scientific Ltd, UK). The SEM micrographs were taken with a Jeol IT300 SEM (JEOL Ltd, Tokyo, Japan) at 15 kV operated in high vacuum mode.

Results and Discussions

The Effect of Initial Solid Concentration on Aerosol Droplet Drying Kinetics

The initial aerosol droplet composition can be expected to have considerable influence on the characteristics and morphologies of the final dried particles mostly produced in spray dryers.⁶¹ However, for aerosol droplets with initially dilute solid concentrations as considered in this study (0.1 % v/v) and within the constant evaporation regime, the starting composition does not strongly influence the solvent evaporation/drying rate with the included solid NPs acting as spectators. Thus, the temporal evolution of the droplet surface area follows isothermally as the well-known “*R - squared law*”,⁶²

$$R^2(t) - R_0^2(t_0) = -\kappa t \quad (4)$$

where $R_0(t_0)$ is the initial radius of the droplet at $t = 0$ s and κ [$\mu\text{m}^2 \text{s}^{-1}$], the evaporation/drying rate constant. Figure 3a show the drying profiles for droplets composed of different initial silica NPs concentration in water mixtures drying into dry nitrogen gas (RH = 0 %) at $T_G = 293$ K. From $t = 0$ to $t \approx 2.3$ s, the droplets containing silica NPs dry in a similar manner to the evaporation of the pure water where the droplet radius (R) decreases progressively with time (t) until the bulk of the solvent liquid has evaporated. From $t \approx 2.3$ s, the apparent fluctuations in the reported size for

the later part of the silica NPs droplet drying profiles are a result of the silica NPs appearing at the droplet liquid-air interface introducing noise to the elastic light scattering pattern and impacting significantly on the accuracy of the sizing method.⁵⁶ Figure 3b compares the normalized droplet radius-squared (surface area) of the evaporation profiles presented in Figure 3a.

Figure 3: (a) Evaporation profiles for silica NPs colloidal droplets with; 0.10 (orange), 0.25 (blue) and 0.50 (violet) v/v % hydrophilic silica NPs in water mixtures evaporating into the same drying conditions (dry nitrogen gas, RH = 0 % and $T_G = 293$ K) compared with pure water (black line). (b) normalized radius squared (“*R - squared law*”) from Figure 3a. The drying rates constant, $\kappa / \mu\text{m}^2\text{s}^{-1}$ obtained by fitting a straight line to the first stage of the evaporation process where the “*R - squared law*” applies are $3.132 \pm 0.3 \times 10^{-10} \text{ m}^2\text{s}^{-1}$ (water), $3.132 \pm 0.3 \times 10^{-10} \text{ m}^2\text{s}^{-1}$ (0.10 % v/v silica), $3.126 \pm 0.4 \times 10^{-10} \text{ m}^2\text{s}^{-1}$ (0.25 % v/v silica) and $3.134 \pm 0.3 \times 10^{-10} \text{ m}^2\text{s}^{-1}$ (0.50 % v/v silica). The red line shows a linear fit to the 0.50 % v/v silica droplet evolution with an R-square of 0.99989.

The surface area evolutions for all the composed droplets varies linearly with time as the “*R - squared law*” which suggest that, within the constant evaporation rate regime, the droplet drying rate ($\kappa / \mu\text{m}^2\text{s}^{-1}$) can be considered constant and invariant of the number of silica NPs contained within the drying aerosol droplet.

The evaporation rate, κ , obtained by fitting a straight line to the first stage of the evaporation process for the different initial concentrations of the silica NPs droplets is very similar to the rate constant for the pure water droplet (Figure 3b), even though the change in volume leads to an increase in the NPs concentration by as much as a factor of 100. For example, the droplet with the most concentrated starting solution of silica NPs 0.5 % v/v, has an evaporation rate constant of $3.134 \pm 0.3 \times 10^{-10} \text{ m}^2\text{s}^{-1}$, within error the same as for pure water of $\kappa = 3.132 \pm 0.3 \times 10^{-10} \text{ m}^2\text{s}^{-1}$. However, it should be noted that, for aerosol droplets with increasing inclusion fractions or with higher concentrations⁶ ($> 10 \text{ % v/v}$) for industrial applications, the restriction on the redistribution of the suspended particles within the evaporating droplet lead to earlier shell formations and an increase in size of the final dried microparticle.⁹

The Effect of Temperature on Aerosol Droplet Drying Kinetics

The temporal profiles for the drying kinetics of 0.60 % v/v silica NPs droplets evaporating into dry nitrogen gas (RH = 0 %) at $T_G = 303 \text{ K}$ are shown in Figure 4a. In comparison to single component liquid droplet evaporation, the evaporation of aerosol droplets with sub-micron inclusions show diffusional mixing and interactions between the submicron particle inclusions,⁶³ as well as additional fluctuations in the resulting scattered light intensities due to spatial inhomogeneities in inclusion positions.^{46,64} As a droplet evaporates, the suspended particles, which are initially distributed evenly within the droplet, accumulate at the receding free liquid-air interface. Subsequently, capillary forces will draw the inner and the interfaced NPs together and van der Waals forces can lock and jam them in place^{20,25,63}. Here, we define the locking point time (LPT) and the radius at which the locking point time occurs (lock radius, R_L) as the onset of the

first visual skin or shell formation and morphology development²⁷ where the surface properties of the drying droplet transitions from a smooth liquid surface to a rough solid phase.

Figure 4: Evaporation profile of 0.60 % v/v hydrophilic silica droplets drying at $T_G = 303$ K into dry nitrogen gas atmosphere ($\text{RH} = 0$ %). (a) An overlay of 205 droplet measurements. The LPT occurred at approximately 1.3 s. (b) Histogram and normal distribution showing the frequency of droplet initial radius centered at 26.5 μm . (c) Corresponding histogram and normal distribution of the lock radius at the LPT. The normal distribution of the lock radius is centered at approximately 11.3 μm .

The LPT for the 0.60 % v/v hydrophilic silica NPs droplets drying at $T_G = 303$ K into dry nitrogen ($RH = 0$ %) is approximately 1.3 s (Figure 4a). After $t \approx 1.3$ s, the ensuing sporadic data points are the outcome of the intractability of retrieving the droplet radius from the interferometric light scattering method. The frequency distribution for the observed lock radius (R_L) for the 205 droplet evaporation measurements is shown in Figure 4c with the normal distribution centered at 11.3 μm . The histogram in Figure 4b shows the frequency distribution in the initial droplet radius. The normal distribution is centered at 26.5 μm , showing the reproducibility of the measurement with initial droplet radius fluctuations of less than 1 %. Apparently, the smaller narrow deviations for the initial radius distribution in Figure 4b show our control (reproducibility) of the droplet size generated by the droplet dispenser into the EDB. However, the broader deviation around the mean for the lock radius in Figure 4c characterized by the point at which the radius can no longer be calculated using the optical fringes in the phase function may be influenced by the accuracy of our sizing method (± 100 nm) and the minimum time interval (10 ms) at which the phase function is recorded. The droplet surface recession (evaporation rate) and the ability of the silica NP inclusions to redistribute within the droplet by diffusion are intimately interrelated and temperature dependent and, thus, the lock points initiating the skin formation is also inherently dependent on temperature.

In Figure 5a we report the drying kinetics (as a normalized radius ($R(t)/R_0(t_0)$)) for droplets containing 0.60 % v/v silica NPs drying into dry nitrogen gas ($RH = 0$ %) at different gas phase temperatures. As observed, increasing the gas phase temperature reduces the droplet drying time and shortens the time required to reach the lock points. The LPT for the droplets drying at $T_G = 326$ K is approximately 0.8 s compared to 11 s for the droplet drying at $T_G = 263$ K. At higher temperatures, the droplet surface recession is faster than the diffusion of the suspended solid particles in the droplet. The evaporation rate for the droplets drying at $T_G = 326$ K ($\kappa = 3.05 \times 10^{-}$

$^9 \text{ m}^2 \text{ s}^{-1}$) in dry air is 10 times higher than the evaporation rate of the droplet drying at $T_G = 263 \text{ K}$ ($\kappa = 2.87 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$). The higher evaporation rates of the droplets drying at 326 K will eventually lead to greater degree of surface enrichment of the silica NPs at the droplet surface.³ The dependence of the LPT and the lock radius (R_L) averaged over 15 droplets for each drying temperature are shown in Figure 5b along with the variability in the initial droplet radius (R_0). In Figure S1a (see Supporting Information), we show the plot of the lock radius, R_L against the initial droplet radius, R_0 for the different gas phase temperature conditions. We observe that despite the variability in R_0 as shown in Figure 5b, drying at higher gas phase temperatures lead to larger lock radius due to the shorter time required to reach the locking points.

Figure 5: Evaporation profile of 0.60 v/v % colloidal silica droplets drying at varying temperatures. (a) normalized radius (R/R_0) as a function of time for droplets drying into dry nitrogen gas at different temperatures. (b) Dependence of the silica NPs inclusions surface locking point time on temperature (blue line) with corresponding variability in initial droplet radius (dark line) and the lock radius (red line) at which LPT occurred. The shaded region in Figure 5b show the standard deviation for more than 15 droplets measurements.

The Effect of Relative Humidity on Aerosol Droplet Drying Kinetics

In most spray drying applications, the relative humidity at the outlet of the drying chamber plays an important role in determining the residual amount of solvent present in the final dry microparticle. To investigate the effect of relative humidity on colloidal droplet drying kinetics, we measured the drying kinetics of 0.50 % v/v hydrophilic silica droplets drying at specified gas phase temperature of $T_G = 294$ K into different humid RH conditions. At each RH, multiple droplet evaporation profiles were recorded to examine the reproducibility of the measurements. The evaporation profiles from many droplets recorded at $T_G = 294$ K for RH = 0 %, 40 % and 80 % are compared in Figure 6a-c. At constant gas phase drying temperature, the evaporation rate at RH = 0 %, 40 % and 80 % decreases rapidly with increasing RH.

Figure 6: Drying kinetics of colloidal droplets composed of 0.50 % v/v pyrogenic hydrophilic silica in water evaporating at $T_G = 294$ K into different humid conditions. Measurements of: (a) 186 droplets evaporating into $RH = 0$ %, (b) 101 droplets evaporating into $RH = 40$ % and (c) 31 droplets evaporating into $RH = 80$ %. Figure 6(d, e, f) show the histogram and normal distributions that correspond respectively to the number of droplets and the locking point times at which the silica NPs jammed the droplet liquid-air interface.

Ultimately, the time taken for the suspended silica NPs to lock at the droplet's liquid-air interface also increases with a decreasing evaporation rate. Figure 6d-f reports the corresponding histograms and the fitted normal distribution of the LPT for the drying kinetics in Figure 6a-c, respectively. The LPT for the droplets drying at RH = 0 %, 40 % and 80 % are centered at $t = 1.93$ s, 3.57 s and 14.48 s, respectively. Within the constant drying regime, from $t = 0$ s until the lock points, the drying time for the droplet drying at RH = 80 % is over 4 and 7 times longer than that at RH = 40 % and 0 %, respectively, indicating the possibility to control the droplet drying rates and properties of the final dry microparticles. The drying kinetics of various droplets of the same droplet composition drying at the same gas phase temperature of 294 K over a range of RH values from 0 - 90 % in steps of 10 % is shown in Figure 7a. As expected, the evaporation rate decreases with increasing RH. The corresponding LPT obtained from multiple droplets are shown in Figure 7b with the initial droplet radius and the radius at which the LPT occurred. Since an increasing RH decreases the droplet evaporation rates, the LPT also increases significantly. Additionally, the radius at which the lock occurs decreases. A plot of the variability of the lock radius over the initial radius is presented in Figure S1b to demonstrate the effect of RH on the lock radius. Evidently, droplet drying at lower RH at fixed gas phase temperatures have larger lock radius due to the shorter time required to reach the lock points as previously stated.

Figure 7: (a). Drying kinetics of droplets composed of 0.50 vol.% hydrophilic silica NPs in water mixtures at constant gas phase temperature, $T_G = 294$ K over a range of RH from 0 - 90 %. (b) Initial droplet radius (dark line), lock radius (red line) at which the locking point time (blue line) occurred. The shaded region and the error bars are the standard deviation for over 15 droplets averaged for each droplet kinetic measurement.

The Influence of Varying Temperature and Relative Humidity on Péclet Number

When considering drying of aerosolized droplets of the same initial droplet parameters (size and inclusion concentration), it can be expected that the final dry microparticle morphologies should be similar.³ However, increasing the gas phase drying temperature, as reported in Figure 5 under

a constant gas flow (RH = 0 %), could considerably change the droplet drying kinetics and, ultimately, the final shape and surface properties of the dried microparticle. An important thermophysical effect worth considering at this stage is the influence of evaporative cooling for droplets drying at different gas phase temperature conditions.^{3,66,67} Typically, in the drying stage, the droplet temperature rapidly changes (cools) from its initial gas phase temperature to an equilibrium droplet temperature (T_d), known as the wet bulb temperature as a result of heat being supplied by the gas phase environment to the droplet for vaporization. Once at the wet bulb temperature the droplet dries steadily. This steady state drying is mostly referred to as the constant rate period as the surface of the droplet remains saturated with solvent and the evaporative flux remains constant¹¹. In our study, we assume that all the evaporation rate κ obtained from the droplet evaporation kinetics are within the constant rate period (see Figure 3b) with the droplet temperature (T_d), inherently at the wet-bulb temperature.

In addition, apart from the direct influence of the temperature on the heat and mass transfer rate during the droplet drying process, the diffusional mixing rate of the included particles in the droplet is also influenced by the temperature-dependent of the viscosity of the solvent. Thus, the Péclet number (see eq. 5) is a function of the droplet temperature and explicitly dependent on the dynamic viscosity of the solvent for a given inclusion particle size (r_i). The dynamic viscosity of water decreases exponentially with increasing temperature and leads to an increase in interfacial permeability and the ease of diffusional mixing and redistribution of the suspended particles to the droplet center. An increase in viscosity can also affect the droplet lock points (time and radius) and, thus, the morphology development.⁶⁷ Here, the role of evaporative cooling and the dependence of viscosity on droplet temperature are accounted for using eq. 6.^{68,69}

$$Pe_i(T_d) = \frac{3\pi\mu_i(T_d)r_i}{4KT_d}\kappa \quad (5)$$

$$\log \frac{\mu_i(T_d)}{\mu_{20}} = \frac{A(20 - T_d) - B(T_d - 20)^2}{T_d + C} \quad (6)$$

In eq. 6, $\mu_{20} = 1.002$ mPa.s, is the viscosity of water at 20 °C (293 K) and $A = 1.1709$, $B = 0.001827$, $C = 89.93$ are constant.⁶⁸ The droplet temperature is given by eq. 7 as:^{66,70,71}

$$T_d = T_G - \frac{IL}{4\pi\beta_T Kr} \quad (7)$$

where I and L are the mass flux in kg s^{-1} and latent heat of evaporation in J kg^{-1} , respectively. β_T is transitional correction factor for heat ($\beta_T = 1$ for steady state evaporation).⁷¹ K is the temperature dependent thermal conductivity of nitrogen gas⁷² ($\text{W m}^{-1} \text{K}^{-1}$) and r the radius of the droplet. The mass flux ($I = dm/dt$) can be calculated as the slope of the mass versus time with temperature dependent density treatment. We report the plot of the temperature suppression $\Delta T = T_d - T_G$ as function of the initial gas phase temperatures in Figure S2a (see Supporting Information) with uncertainty of ± 1.5 K arising from the uncertainty in the measured evaporation rate. In dry air ($\text{RH} = 0$), and at $T_G = 263$ K, the temperature suppression reached ~ -4 K in correspondence to the slowest evaporation whereas for the droplets evaporating at $T_G = 326$ K into dry air cooled as low as -32 K during the steady state drying. This, we estimate the Pe described by Eq .5 as function of the droplet temperature rather than the gas phase temperature conditions to account for the thermal influence of evaporative cooling and steady state drying.

The dependence of Péclet number as a function of the droplet temperatures from the kinetics data presented in Figure 5 for the 0.6 % v/v colloidal silica droplet is presented in Figure S3a (top panel, see Supporting Information). The Péclet number increases approximately linear with an increase in droplet temperature from $T_d = 259$ K to $T_d = 294$ K. A lower viscosity of water at $T_d = 294$ K ($\mu_{294 \text{ K}} = 0.98$ mPa.s) will enforce less constraints on the internal mixing of the suspended silica NPs in the drying liquid droplets compared to the droplet drying at $T_d = 259$ K ($\mu_{259 \text{ K}} =$

3.12 mPa.s) under the same humid gas phase conditions. Using eq. 3 and 6, the diffusional rate at the droplet temperature $T_d = 259$ K, 272 K, 283 K and 294 K are 0.68×10^{-12} m²/s, 1.92×10^{-12} m²/s, 1.75×10^{-12} m²/s and 2.44×10^{-12} m²/s, respectively. Thus, the reduction in dynamic viscosity arising from a higher temperature will lead to an increase in the rate of diffusional mixing and a reduced time for the suspended silica NP inclusions to diffuse from the droplet air-liquid interface to the center during the drying process. However, at the same drying conditions and considering steady state drying at $T_d = 259$ K, 272 K, 283 K and 294 K the corresponding evaporation rates (i.e. $\kappa = 2.87 \times 10^{-10}$ m²/s, 7.81×10^{-10} m²/s, 1.76×10^{-9} m²/s and 3.05×10^{-9} m²/s, respectively) are over 3 orders higher than the rate at which the silica NPs diffuse to the droplet center. Coupled with the faster evaporation rate and the inadequate time for the redistribution of the suspended silica NPs to diffuse quickly to the droplet center at increasing drying temperatures, the droplet evaporation front will eventually sweep the suspended particles to the droplets liquid-air interface and ultimately result in enrichment of the droplet surface with the suspended silica NPs.

For $Pe \geq 20$, the surface enrichment of the droplets surface can be approximated as,²²

$$E_s = \frac{Pe}{3} + 0.363 \quad (8)$$

From eq 8, $E_s = 18.0$, 27.7, 42.0 and 53.3 for the droplets drying at temperatures of $T_d = 259$ K, 272 K, 283 K and 294 K , respectively. Thus, the faster evaporation rate leads to a greater degree of enrichment of the silica NPs inclusions at the droplet surface, triggering earlier skin or shell formation at the lock points. It is expected that the surface properties and morphologies of the final dried particles obtained under the conditions of higher E_s will result in the formation of low density, wrinkled, shriveled, buckled or hollow microparticles.^{3,20,73} From Figure 5b, the LPT also decreases with increase in Péclet numbers (as in Figure S3a, top panel) by increasing the gas phase drying temperature because of the higher evaporation rates. The droplet drying at lower

temperatures has later LPT and lower surface enrichment, therefore smaller normalized radius (R_L/R_0), as can be seen in the lower panel of Figure S3a. We indicate the evolution of the Péclet number as a function of increasing RH for the colloidal silica droplets drying at constant gas phase temperature of $T_G = 294$ K into different humid conditions in Figure S3b (top panel). For droplet drying at a specified gas phase temperature, Figure S2b indicates that the temperature suppression, as a results of droplet evaporative cooling, decreases and approaches the gas phase temperature with increasing RH. The evaporation rate at $T_G = 294$ K into RH = 0 %, 40 %, 70 % and 90 % are 1.42×10^{-9} m²/s, 7.80×10^{-10} m²/s, 3.34×10^{-10} m²/s and 9.89×10^{-11} m²/s, respectively. At these RHs, the corresponding droplet temperature are respectively $T_d = 278, 285, 290, 293$ K. Considering that the drying rate decrease as the relative humidity increases, the diffusional mixing rate of the silica NPs increases due to a lower temperature suppression. The Péclet number associated with the droplets drying into RH = 0 %, 40 %, 70 % and 90 % are 119.0, 52.8, 19.2 and 5.2, respectively. The Péclet number decreases as the evaporation rate decreases with increasing RH.

In Figure S3b (top panel), for RHs > 69 %, the $Pe < 20$. In such a case, the surface enrichment of the silica NPs at the droplet surface can be quantified by eq. 8 as,²²

$$E_S \approx 1 + \frac{Pe_i}{5} + \frac{Pe_i^2}{100} - \frac{Pe_i^3}{4000} \quad (9)$$

The degree of surface enrichment decreases from $E_s \approx 7.0$ at RH = 69 % to 2.3 at RH = 90 %. Consequently, drying at higher RH leads to a later LPT (see Figure 7b) and the normalized radius (R_L/R_0) is smaller, decreasing as the RH increases. In Figure S3b (lower panel), the R_L/R_0 for droplet drying at 0 % RH is approximately 0.45 compared to 0.3 for similar droplets drying at 90 % RH. This indicates that aerosol droplets drying at higher Péclet numbers will experience

structural surface transitions at earlier LPT and larger lock radii than those drying at lower Péclet numbers. Additionally, if the environment of the levitating droplet is saturated with water vapour at a given temperature, the rate of gas phase diffusional transport of water away from the droplet surface is lowered and, thus, the rate of the drying slows. Ultimately, at higher RHs, the decreasing Péclet number suggest that, the silica NPs have enough time to redistribute by diffusion throughout the droplet during the drying process, resulting in less surface enrichment and longer time for dense microparticle formation.

Relating Aerosol Droplet Drying Kinetics to Dried Microparticle Morphology

Here, we present an explicit parameterization of the Péclet number as a function of droplet temperature and RH, as described by eq. 10, for a given initial droplet composition (0.40 % v/v hydrophilic silica NPs) and inclusion size r_i at different droplet temperatures and varying RH.

$$Pe_i(T_d, RH, r_i) = \frac{3\pi\mu_i(T_d)r_i}{4KT_d} \kappa(T_d, RH) \quad (10)$$

At each chosen gas phase temperature, the drying kinetics of multiple droplets (with initial radius fluctuations less than 1 %) were measured at increasing RH values. It is important to note from eq. 10 that, at different temperatures, the RH is not a direct measure of the absolute quantity of water vapour in the surrounding environment of the levitated aerosol droplet in the gas phase due to the temperature-dependent saturation vapour pressure of water vapour.⁷⁴ Instead, it is a ratio between two known values: wet-to-dry nitrogen gas flow rates. In the EDB experiment, the mixing of wet and dry nitrogen gas flows occurs at a gas phase temperature of 293 K. Hence, to obtain an accurate estimate of the temperature-dependent relative humidity in the gas phase and its direct influence on Pe , we express the RH in eq. 10 as the ratio between the partial pressure of water vapour in the gas phase p_w , at the different gas phase temperatures and the saturation vapour pressure of

water, p_w^0 at $T_G = 293$ K (i.e. $RH = \frac{p_w}{p_w^0} \times 100$).⁵⁵ Such an approach allow us to know the amount of water vapour present in the gas phase and in the surrounding atmosphere of the droplet, and to account for the influence of water vapour variations with temperature on evaporation rates.

In Figure 8a, we report measurements of evaporation profiles of a 0.40 % v/v colloidal silica NPs droplet drying at different gas phase temperatures into humid condition of an $RH = 40$ %. Note that at $T_G = 285$ K, the vapour pressure is 1.40 kPa compared to 4.01 kPa at $T_G = 302$ K. Hence, to achieve a 40 % RH environment in the EDB at these temperature, partial pressures of 0.56 kPa and 1.60kPa are required, respectively. This corresponds to a ratio of 24 % wet to 76% dry nitrogen flow at room temperatures for 40 % RH at $T_G = 285$ K; at 302 K, this corresponds to a ratio of 69% wet to 31% dry nitrogen flow. Knowledge of these mixing ratios is crucial to establish the direct influence of the RH on Pe from kinetic measurement and the correlation of droplet drying kinetics to dry microparticle morphology. At a constant RH, the evaporation rate increases with increase in gas phase temperature. An extracted evaporation rate constant (κ) for sequential RH values obtained at increasing gas phase but varying droplet temperatures during the steady state drying process is reported in Figure 8b. The κ values were obtained from averaged 20 evaporation rate constant from 20 individual droplets drying at a different droplet temperature into varying RH conditions. Consistent with the data presented in Figure 7a and Figure S3b (top panel), the evaporation rates decrease with increasing RH. A significant decrease in the evaporation rate is also observed in Figure 8b at $T_G = 285$ K and from $RH > 50$ %. This is potentially due to associated increase in water vapour in the surrounding environment of the levitated aerosol droplet and higher uncertainties of the RH values (± 5 % from $RH > 50$ %) at gas phase temperatures below 293 K where the mixing of wet and dry nitrogen gas flows occur at the center of the EDB for higher RH values.

Figure 8: (a) Drying kinetics of 0.40 % v/v hydrophilic silica NPs droplets drying at different gas phase temperatures into constant humid condition of RH = 40 %. (b) Evolution of evaporation rate (κ) from kinetic measurements for droplets drying at different gas phase temperatures into varying humid conditions. The error bars are standard deviations from evaporation rate constants obtained from averaging 20 droplets at each measurement.

A 2D droplet temperature-RH-Péclet number (T -RH- Pe) contour map quantitatively constructed from the droplet drying kinetic measurement in Figure 8b and with eq. 10 is shown in Figure 9. Considering this T -RH- Pe process parameter space for accessible drying condition pair parameters, we can now consider the correlation with the corresponding dried microparticles morphology.

Figure 9: Temperature-RH-Péclet number map obtained from EDB kinetic measurement for a 0.40 % v/v hydrophilic silica NPs (mean diameter = 180 nm) droplet drying at different gas phase temperatures into different humid conditions. The contour map is generated with eq. 10 from 1200 individual droplet with each point representing an average data of 20 droplets from the EDB kinetic measurement. The short white dash lines are selected Pe contour lines on which Temperature - RH drying condition pair points were selected for drying experiment.

The T - RH - Pe map show that Pe increases from a minimum at $T_d = 284.6$ K and $RH = 90$ %, ($Pe = 4.05$) to a maximum at $T_d = 290.4$ and $RH = 0$ % ($Pe = 184.50$) over the range of the RH conditions. The contour lines (Péclet number line) provides unique Pe values with variable gas phase and droplet temperature - RH drying condition pairs that we will see can be evaluated to predict similar dried microparticle morphology. For example, in Figure 9, the Péclet number contour line with associated $Pe = 100.0$, can be evaluated at droplet temperatures of 275, 285, and 300 K and RH s of 0, 12, and 15 %, respectively. It seems evident in Figure 9 that, the Pe

becomes approximately independent of temperature at a fixed RH. A constant Peclet number means that the evaporation rate and diffusion rate must increase proportionately with increase in temperature. Clearly, an increased temperature leads to both an increased evaporation rate and diffusion rate (similarly as in Figure S4). The Pe collapses at $RH > 40\%$ as presented in Figure S4. This indicates that at higher temperatures ($T_G > 300\text{ K}$), the actual amount of water vapour (i.e. $RH > \sim 40\%$) present in the gas phase in the surrounding atmosphere of the droplet has very little influence upon the evaporation rate, resulting in the Péclet number purely driven by the variations in the gas phase temperature. However, we indicate that, such is not the same for the droplet temperature. In Figure S2b we show a plot of Pe at increasing RHs at a specific gas phase temperature of 285 K. A variation in RH from dry air to $RH > 85\%$ leads to a temperature depression of $\sim -10\text{ K}$ as result of evaporative cooling. The Peclet number increases with decreasing RH while the droplet temperature approaches the gas phase temperature at increasing RHs.

Surface Properties and Morphologies of Dry Silica Microparticles

In order to confirm the reproducibility and similarity of dried microparticle morphology with *a priori* knowledge of Pe values from the EDB drying kinetics measurement, we dried multiple droplets of similar initial radii from the 0.40 % v/v hydrophilic silica NPs at selected points along the Péclet number lines (white short dash lines) on the T - RH - Pe map in Figure 9 using the falling droplet chain instrument.⁵ We used the same dispenser parameters (pulse amplitude, width and frequency) similar to the droplet drying kinetic measurement for generating droplet into the falling droplet chain instrument. The droplets were dried under controlled temperature-RH conditions (as on the EDB) during their free fall down the column. The final dried silica NP microparticles collected were analyzed offline using the scanning electron microscope (SEM), as described in

section 2.3.2. We show the SEM micrographs of the silica microparticles obtained after the drying process for the selected droplet temperature-RH drying condition pairs on the Péclet number lines in Figure 10. Evidently, the SEM micrographs show dried silica microparticles of different but controlled surface properties and morphology development.

The products obtained at $Pe (T_d = 284 \text{ K}, \text{RH} = 64 \%) = 23.8$ reported in Figure 10a are dried silica microparticles of well-defined spherical shape with smooth external surfaces. Under these conditions, the drying process (see Figure 11 along path A) leads to the formation of compacted dried silica microparticles with external diameter of approximately $16 \mu\text{m}$. With increasing Péclet numbers, the dried silica microparticles show increasing surface deformations. At $Pe (T_d = 286 \text{ K}, \text{RH} = 21 \%) = 77.7$, dimples started to emerge on the surface of the dried silica microparticles with smooth surfaces (Figure 10b). The appearance of the dimples on the outer surface of the dried silica microparticles can be inferred as a result of shell deformation caused by buckling processes initiated by sol-gel transition^{2,74} at the droplet surface during the drying process. As the droplet continues to dry, the silica NPs pile up inside the droplets receding air-liquid interface and contribute to the formation and the thickness of the shell.⁷⁴ The rate at which new particles join the shell and contribute to its growing thickness during further drying processes after the critical lock points (time and radius) intimately depends on the kinetics of the drying process and the rigidity of the shell to withstand mechanical stress. In Figure 9 and from eq. 10, an increase in evaporation rate κ , leads to an increase in the Pe and the droplet surface enrichment. This suggests that shorter LPT as a result of fast evaporation rate will result in the formation of thin rigid shells of jammed particles owing to less time for the redistributed particles to join the shell during the fast-drying process as presented in Figure 11 along path E.

Figure 10: SEM micrographs of dried silica microparticles from 0.40 % v/v colloidal silica droplets produced by the droplet chain technique at increasing Péclet numbers for temperature -RH drying condition pairs. (a) Pe ($T_d = 284$ K, $RH = 64$ %) = 23.8, (b) Pe ($T_d = 286$ K, $RH = 21$ %) = 77.7, (c) Pe ($T_d = 288$ K, $RH = 8$ %) = 116.7, (d) Pe ($T_d = 292$ K, $RH = 5$ %) = 135.3, (e) Pe ($T_d = 293$ K, $RH = 4$ %) = 153.2, and (f) Pe ($T_d = 291$ K, $RH = 0$ %) = 180.0

In Figure S5, we show the dependence of the surface enrichment E_s , on the LPT for the temperature and relative humidity drying conditions from the kinetic measurements. In both gas phase conditions; the degree of the droplet surface enrichment increases exponentially with decrease in LPT as a result of increased evaporation rate. Additionally, since the relative radius (R_L/R_0) at the lock radius also scales with the Pe (see Figure S3, lower panel), it indicates that the enrichment of surface particles is high at larger relative radius. A schematic mechanistic picture illustrating the drying process and the corresponding degree of particle surface enrichment and shell thickness leading to the various morphologies of the silica microparticles is presented in Figure 11.

Figure 11: Schematic of conceptual mechanistic picture illustrating the drying process at different Péclet numbers, degree of surface enrichment with possible shell thickness based on the droplet drying rate (locking point time) and the resulting predicted morphologies of the final dried silica microparticles after the drying process. The corresponding SEM images (a, b, c, e and f) are sample images from the FDC drying experiment presented in Figure 10 (a, b, c, e and f).

The pathways in Figure 11 highlight the importance of the controlled gas phase drying conditions that defined the lock points (time and radius) and the droplet surface enrichment on dried microparticle morphology development. As thin shells are most prone to buckling,⁶² we expected dried microparticles obtained at shorter LPT/larger relative radius (R_L/R_0) and higher Péclet numbers (faster drying rate) to result in buckled, crumpled or shriveled structures with higher propensity for surface deformations as demonstrated in Figure 11 (along path E). Obviously, the initial shell formed may be only a few particles thick and is unlikely to poses enough strength to withstand pressure capable of deforming it during the later drying process.

The critical pressure capable of initiating deformation and buckling of a thin spherical shell can be given as:^{75,76}

$$p_c \propto Y_0 \left(\frac{h}{R_0} \right)^2 \quad (11)$$

where h and R_0 are the initial shell thickness and radius respectively with Y_0 , the 3D Young modulus that describes the mechanical properties of the shell. This relationship indicates that a large thin shell can be buckled easily and vice versa as in Figure 11. In Figure 10c, the dried silica microparticles obtained at Pe ($T_d = 288$ K, $RH = 8$ %) = 116.7 can be associated with the aerosol droplets that dried along path C of Figure 11 and show outer smooth surfaces with much larger dimples at the surface. Further increase in Péclet numbers as observed in Figure 10d,e based on controlled drying conditions of Pe ($T_d = 292$ K, $RH = 5$ %) = 135.3 and Pe ($T_d = 293$ K, $RH = 4$ %) = 153.2, lead to the formation of larger openings of the dimples on the structures with external tripodal surface indentations that are more pronounced on the dried silica microparticles obtained in Figure 10e. The drying kinetics of the structures obtained in Figure 10d and Figure 10e can be associated with the aerosol droplets that dried along the path C and D of Figure 11, respectively. The dried silica microparticles obtained at the highest Péclet numbers, Pe ($T_d = 291$ K, $RH = 0$ %) =

180 have crumpled surface morphologies showing predominantly the influence of higher Pe and shorter LPT on thin shell deformations during the drying process. A summary of the selected droplet temperature - RH drying condition pairs with corresponding evaluated Pe and Es values and the resulting dry silica NP microparticle surface properties and morphology are presented in Table S1 in the Supporting Information.

Conclusions

This work provides an improved understanding of the influence of gas phase drying conditions-temperature and relative humidity and aerosol droplet characteristics on the drying kinetics and morphology of dried microparticles from single droplet experiments. The use of single-particle levitation instrument, the electrodynamic balance (EDB), provides a possible approach to study precisely the influence of temperature and RH on aerosol droplet drying kinetics in the gas phase for a range of Péclet numbers ($4 < Pe < 185$). Additionally, using a complementary falling droplet chain instrument, we demonstrated that *a priori* knowledge of aerosol droplet drying kinetics from T - RH - Pe map based on EDB measurements can be used as a precursor to tailor dried microparticles of well-defined morphologies and surface properties. The microparticles resulted from higher Péclet numbers were distinguished by the obvious dimples and cracks on the outer surface. By combining the EDB single droplet kinetic measurement and the resulting dried microparticles from the drop chain experiment, we provide a mechanistic picture that illustrate the drying process and the corresponding degree of particle surface enrichment and shell thickness leading to the various morphologies of the silica microparticles. Based on these observations, it can be concluded that dried microparticle morphology and surface properties can be engineered with *a priori* kinetic data from single droplet measurements that can be used to scale up the design

and parameter optimization for most pilot spray dryer applications in the food and the pharmaceutical industries.

Supporting Information

Influence of gas phase drying conditions (temperature and relative humidity) on lock radius (R_L), droplet evaporative cooling, relative radius (R_L/R_0), Péclet numbers, surface enrichment on locking point times (LPT) and a summary of gas phase temperature – RH drying condition pairs on dried microparticles morphology.

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