Supercritical CO$_2$-assisted atomization for deposition of cellulose nanocrystals: an experimental and computational study

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Abstract Nanoparticle spray deposition finds numerous applications in pharmaceutical, electronics, manufacturing, and energy industries and has shown great promises in engineering the functional properties of the coated parts. However, current spray deposition systems either lack the required precision in controlling the morphology of the deposited nanostructures or do not have the capacity for large-scale deposition applications. In this study, we introduce a novel spray system that uses supercritical CO$_2$ to assist the atomization process and create uniform micron-size water droplets that are used as cellulose nanocrystal (CNC) carriers. CNCs are selected in this study as they are abundant, possess superior mechanical properties, and contain hydroxyl groups that facilitate interaction with neighboring materials. We fundamentally investigate the effect of different process parameters, such as injection pressure, gas-to-liquid ratio, the axial distance between the nozzle and substrate, and CNC concentration on the final patterns left on the substrate upon evaporation of water droplets. To this end, we show how tuning process parameters control the size of carrier droplets, dynamics of evaporation, and self-assembly of CNCs, which in turn dictate the final architecture of the deposited nanostructures. We will particularly investigate the morphology of the nanostructures deposited after evaporation of micron-size droplets that has not been fully disclosed to date. Different characterization techniques such as laser diffraction, polarized microscopy, and high-resolution profilometry are employed to visualize and quantify the effect of each process parameter. Numerical simulations are employed to inform the design of experiments. Finally, it is shown that the fabricated nanostructures can be engineered based on the size of the carrier droplets controlled by adjusting spray parameters and the concentration of nanoparticles in the injected mixture. Process parameters can be selected such that nanoparticles form a ring, disk, or dome-shaped structure. Moderate operational conditions, simplicity, and time efficiency of the process, and use of abundant and biodegradable materials, i.e., water, CNCs, and CO$_2$ promote the scalability and sustainability of this method.

Keywords Nanoparticle spray deposition · Supercritical-assisted atomization · Evaporation
induced nanostructure fabrication · Cellulose nanocrystals

Introduction

Deposition of nanoparticles via liquid atomization finds several practical applications in food (Huang et al. 2017), drug delivery (Singh and Van den Mooter 2016), manufacturing (Shariatnia et al. 2019), energy (Kuznetsov et al. 2011; Krebs 2009), electronics (Zhao et al. 2012), and surface coating (Phan et al. 2009). Liquid atomization is referred to as a hydrodynamic process through which a liquid jet injected via a small nozzle breaks up into several micron-size droplets upon exposure to the surrounding fluid and forms a spray. Spray deposition is a simple one-step, safe and low-cost method for coating large surface areas within few seconds to promote the efficiency and scalability, while reducing materials usage. In the nanoparticle spray deposition process, a colloidal suspension is atomized to create droplets containing nanoparticles of interest that subsequently evaporate and leave the particles on the target surface.

Various configurations of thermal sprays (Moridi et al. 2014; Barbezat 2005), electrical sprays (Fauchais, Heberlein, and Boulos 2014), and direct-write deposition (Dinh et al. 2016; Bugakova et al. 2019) are among the most common spray deposition methods that have been extensively studied. Thermal spray systems such as warm (Kuroda et al. 2015), plasma (Ke et al. 2019), and electro sprays (Pawlowski 2008) use a heat source to melt the feedstock material and spray it on a substrate using a high-speed jet. Cold spray systems where solid powders are accelerated towards the substrate, fall under the thermal spray category. Due to the harsh conditions in these sprays, coatings and substrates are limited to materials that can withstand large impact forces and are compatible with high temperature (Fauchais et al. 2015). Thermal sprays are cost effective and can cover large surface areas in a short period of time with a thickness that can range from ~ 20 microns to several millimeters. However, thermal methods lack the precision needed for coating layers with a few nanometer thicknesses, and they do not provide any control over the formation and final morphology of the deposited nanostructures (Pawlowski 2008).

Direct-write deposition techniques on the other hand, e.g. inkjet and aerosol jet printing, precisely control the deposition of colloidal droplets and formation of nanostructures on a targeted location (Le 1998; Calvert 2001). Upon deposition on the substrate, the contact line of the ink droplets pins to the substrate. As the droplet evaporation proceeds, the contact angle between the droplet and substrate decreases. As a result, a capillary flow from the center of the droplet towards the pinned contact line initiates to compensate the liquid mass loss at the droplet’s periphery (Deegan et al. 1997). This flow drags the particles and accumulates them along the edge of the droplet leaving a ring-shaped trace of particles on the substrate (Yunker et al. 2011). This phenomenon is known as the coffee ring effect (CRE) that can be exploited or suppressed to enforce a specific nanoparticle pattern on the substrate depending on the application (Deegan et al. 1997). Suppression of the CRE in direct writing methods requires costly and multi-step processes such as the use of flammable and toxic surfactants to the solvent, (Anyfantakis et al. 2015) physical and chemical modification of the substrate (Dicuangco et al. 2014; Cui et al. 2012), and imposing external forces (Mampallil et al. 2015). Inkjet printing is limited to deposition of a single or a few droplets at a time that covers a small surface area limiting the scalability of this technique. In addition, since the process parameters are set prior to print, achieving thickness and material variability, requires multiple rounds of deposition or using multiple print heads (Seifert et al. 2015). Aerosol jet printing utilizes an air-assisted atomization technique for breakup of the liquid jet stream and a specific directed nozzle to facilitate targeted deposition (Wilkinson et al. 2019). This technique is faster than inkjet printing and capable of handling a wide range of materials in moderate operating conditions (Lu et al. 2020; Paulsen et al. 2012). It also provides precise control over the thickness and profile of the material deposition with the first round of spray (Secor 2018; Mette et al. 2007). However, aerosol jet printing lacks the capability of large-scale deposition (Azarova et al. 2010; Sarobol et al. 2016). The internal design of the nozzle that directly affects the quality and dimensional resolution of the print is very complicated (Seifert et al. 2015; Jabari and Toyserkani 2015). Other limitations of this
method is low solubility of particles in the solvent and lack of control over droplet sizes (Goth, Putzo, and Franke 2011; Mahajan, Frisbie, and Francis 2013).

To overcome these limitations, supercritical-assisted atomization (SAA) has been introduced as a method that utilizes a fluid above its thermodynamic critical point to facilitate the atomization process by enhancing the nanoparticles dissolution in solvents (Reverchon 2002). SAA accelerates liquid atomization by exploiting the hybrid gas-like and liquid-like properties of supercritical fluids. High density and high diffusivity along with low viscosity of supercritical fluids enhances the dissolution of gasses into the injected mixture and reduces the surface tension between the injected liquid and the surrounding gas that both improve atomization process (Shariati and Peters 2003; Tom and Debenedetti 1991). Owing to their high diffusivity, supercritical fluids highly dissolve in the liquid mixture prior to injection and separate from the mixture in the form of gas bubbles upon injection into the surrounding environment. The sudden expansion of these gas bubbles, triggers the breakup of the liquid jet and shatters it into very fine and highly uniform droplets with a narrow size distribution compared to other spray-based techniques (Reverchon 2007). CO₂ is an abundant, degradable, nontoxic, and nonflammable gas with moderate critical temperature and pressure (31°C and 7.4 MPa) compared to other fluids, which makes it a viable option for several applications such as temperature-sensitive materials used in pharmaceutical and biological applications (Aguiar-Ricardo 2017). The high solubility of supercritical CO₂ (SCO₂) in most organic and inorganic solvents has made it the supercritical fluid of choice in SAA systems (Costa et al. 2018). Sensitivity of mixture properties to the operational conditions enables the regulation of droplet sizes and the final morphology of the fabricated particles (Della Porta, De Vittori, and Reverchon 2005). Although SAA provides great control over process parameters, it is limited to solely manufacturing micro/nanoparticles that are collected in a precipitator in the form of dry powder after atomization.

An important application of SAA is the direct deposition of nanoparticle-carrier droplets resulting from atomization of nano-colloidal suspensions exposed to SCO₂ and exploiting that process to engineer the nanostructures on a substrate. However, due to complex underlying atomization mechanisms in SAA, this potentially important application has not been fully explored in the literature to date. This knowledge gap motivated the current study where we have designed and built a novel SAA system to atomize aqueous Cellulose nanocrystal (CNC) suspension and deposit the droplets containing CNCs on a solid substrate to fabricate nanostructures with controlled size and morphology. In our previous study, we experimentally studied the effect of a wide range of process parameters on the breakup and final droplet size in the absence of nanoparticles (Shariatnia, Asadi, and Jarrahbashi 2021). In this study, we use SAA as a new large-scale delivery method for depositing CNCs and controlling the fabrication of nanostructures on solid substrates. The proposed spray deposition technique can seamlessly be adopted for several practical applications involving CNCs and other nanoparticles. The main objective of this study is to (1) understand the effect of spray parameters and colloidal suspension properties on the shape of the nanostructures formed on the substrate after droplet evaporation, and (2) use this knowledge to effectively control and tailor the architecture of deposited nanostructures.

We adopted CNCs in this study as they form a stable dispersion in water and possesses unique mechanical and chemical properties that make it appealing for a variety of applications, from 3D printing (Shariatnia et al. 2019) and manufacturing (Palaganas et al. 2017; Tang et al. 2017; Shariatnia et al. 2020) to drug delivery (Roman et al. 2009) and electronics (Grishkewich et al. 2017). CNCs with linear chain glucose units (C₆H₁₀O₅) are abundant, non-toxic, and biodegradable spindle-shaped nanoparticles obtained from plants, algae, bacteria, and marine animals (Mariano et al. 2014). CNCs contain accessible hydroxyl groups on its surface that makes them suitable for chemical modification (Moon et al. 2011). In addition, CNCs possess unique features such as low density (1.5 g/cm³), elastic modulus of 110–220 GPa, tensile strength of 3–7.5 GPa, high aspect ratio (10–100), and high surface area (Moon et al. 2011). Evaporation-induced self-assembly of aqueous CNC droplets has been widely studied for optical sensing, security labeling, food, cosmetics, textiles, and art applications (Parker et al. 2016, 2018; Gu et al. 2016). However, these studies are focused on investigating the patterns in a liquid film or a single droplet and involve time and cost-inefficient lab-scale processes. To this end, we experimentally investigate the effect
of different spray parameters and the concentration of CNCs on the mean droplet sizes and the morphology of the created nanostructure. We have leveraged computational fluid dynamics (CFD) simulations to obtain the optimum spray parameters, achieve the desired film thickness, and indicate the prime location for delivery of droplets on the substrate where minimum droplet evaporation and spray bounce-back occurs. The computational results inform the experimental system design, and thus reduce the trial-and-error process to obtain the optimum deposition outcome with minimum material waste and ensure system scalability.

**Experimental method**

**Spray setup and diagnostics**

Figure 1 shows a schematic of the experimental setup for SAA spray deposition of CNCs on a glass substrate. The spray system has two feed lines that deliver CO$_2$ and the aqueous CNC suspension to a custom-made pressure vessel. The ternary mixture, i.e., CNCs, water, and CO$_2$, mix and reside in the pressure vessel. A pump feeds the colloidal suspension into the pressure vessel, while another pump connects the CO$_2$ tank to the pressure vessel. Pressure and temperature are monitored in multiple locations along the feeding lines and inside the vessel using several pressure gauges and thermometers. The mixture is then injected into the ambient atmospheric air towards a glass substrate (VWR, micro cover glass No. 1.5).

**Materials**

Wood fiber based CNCs with an average diameter and length of 3 and 75 nm, respectively were provided by CelluForce (Quebec, Canada). The white CNC powders are produced via spray drying process and have a molecular formula of [(C$_6$O$_5$H$_{10}$)$_{22–28}$ SO$_3$ Na]$_{4–6}$.

CNCs with concentration of 0.2, 0.5, 2 wt% were dispersed in 500 mL of deionized water (DI-H$_2$O) using probe sonication (Qsonica Q125 equipped with a 12 mm sonotrode) for 30 min at a frequency of 20 kHz and 75% intensity. Sonication was performed at room temperature and the colloidal suspension was used within two hours to prevent sedimentation and ensure the quality of the dispersion. The zeta potential and hydrodynamic diameter of dissolved CNCs in DI-water were measured as $-54$ mV and 70 nm, respectively.

**Test Conditions**

Table 1 represents different test cases and corresponding experimental conditions including the concentration of CNCs in the injected suspension, injection pressure, and gas-to-liquid ratio (GLR). GLR is the ratio of the CO$_2$ mass flow rate to the liquid (nanoparticle suspension) mass flow rate measured upon feeding CO$_2$ and the liquid separately into the mixing chamber prior to injection. GLR is commonly used to represent the gas content in the injection mixture. The axial distance from the injection nozzle to the substrate is kept constant at 60 mm. The internal geometry of the nozzle is a straight, circular cylinder with an actuator.
where droplet Sauter Mean Diameter (SMD) is measured is outlined in Table 1. The average size of droplets in a spray is commonly represented by Sauter Mean Diameter (SMD) and is calculated as 

\[ SMD = \frac{D_3}{D_2} \]

where the surface diameter and volume diameter are defined by 

\[ D_s = \sqrt[3]{\frac{A}{\pi}} \]
\[ D_v = \left( \frac{6V}{\pi} \right)^{\frac{1}{3}} \]

respectively and \( A \) and \( V \) represent the surface area and volume of the droplet, respectively. All experiments were carried out at room conditions (25°C and relative humidity \( \sim 40\% \)).

**Characterization techniques**

**Microscopy**

A Leica DM6B (Leica Microsystems Inc., Germany) motorized microscope equipped with 2x-40 × objectives is used to portray the distribution of droplets on the glass substrate. Polarized light mode is applied to visualize the distribution of the crystalline CNCs that are otherwise transparent to brightfield lighting.

**High-speed imaging**

A Fastcam SA5 (CA, USA) high-speed camera equipped with a Nikon Nikkor (Tokyo, Japan) micro lens is used for diffuse back-illumination imaging of the spray development. The resolving power of this optical system correlated with the smallest feature that it can accurately capture is \( \sim 20 \mu \text{m} \). The images are captured with a frame rate of 500,000 fps and have a 128 × 64 pixels field of view.

**Laser diffraction**

A Malvern Panalytical’s laser diffraction system (Malvern, UK) with a He–Ne laser source is used for real-time measurements of the average volume-based droplet size (SMD) at different axial locations across the spray. Sampling errors and the back-end algorithms that are deployed in the system software to convert the scattered light into meaningful particle size measurements are the main limitations of these systems (Andrews et al. 2011), yet the system has a 1 Hz acquisition rate, 0.1 µm resolution, and 99% accuracy in size measurements. Measurements are captured from the diffraction pattern of the superimposed laser beam and the spray. All reported droplet sizes are at least an average of six measurement realizations.

**Profilerometry**

Bruker DektakXT Surface Profiler (Bruker Corp., USA.), which is a stylus-based surface profilometer with a vertical resolution of 1 Å, is used to map the height of CNCs deposited on the surface of the glass substrates after droplet evaporation. A stylus with a 6.5 mµ tip and 3 mg force is used for all measurements. All experiments were carried out at least six samples and the average height profile is reported.

**Rheometer**

A cone-and-plate rheometer (Anton Paar-MCR 301, Austria) is used to measure the viscosity of aqueous suspensions of CNCs with different concentrations at room temperature. All experiments were repeated at least six times and the average viscosity is reported.

**Zetasizer**

A Malvern Zetasizer Ultra (Malvern, UK) is used for measuring the diffusion coefficient of cellulose nanoparticles in water using non-invasive light scattering. All experiments were repeated at least six times and the average diffusion coefficient for each case is reported.

### Table 1 Design of experiments

| CNC concentration (wt%) | Injection pressure (MPa) | Axial distance (cm) | GLR         |
|------------------------|--------------------------|---------------------|-------------|
| 0.2                    | 3, 6, 7.5, 9             | 10, 15, 20          | 0.02, 0.05, 0.075, 0.1, 0.2, 0.5, 1, 2, 3, 4 |
| 0.5                    |                          |                     |             |
| 2                      |                          |                     |             |
Post-processing methods

ImageJ (NIH) is utilized for post-processing the microscopy images to measure the diameter of droplets. In order to measure the surface area that is coated with CNCs, we have binarized images by imposing a global intensity threshold above which the intensity was set to one and the remaining pixel intensities were set to zero. We have then used ImageJ to measure the area covered with pixels that have the intensity of one. The jet development simulation is visualized using the EnSight software package from ANSYS. In addition, the Matplotlib library in Python is utilized to plot and analyze the data from laser diffraction and profilometry techniques.

Computational method

Governing equations

Three-dimensional Computational Fluid Dynamics (CFD) simulation is carried out in the open-source C++-based CFD package OpenFOAM-2.2.x (Weller et al. 1998) to model the atomization and breakup of the aqueous suspension, formation of the liquid film deposited on the solid substrate, and the behavior of the droplets on the substrate that include stick, rebound, spread, and splash (Tsang et al. 2014). A two-dimensional domain is considered for simulating the liquid film on the solid substrate. Dynamic structure Large Eddy Simulation (LES) is implemented in this study (Mishra and Rutland 2019) to incorporate the turbulence effect of the fluid phase (liquid suspension and the surrounding gas) and Stanton-Rutland model is employed to model film formation on the solid substrate (Stanton and Rutland 1996a, b). A Lagrangian–Eulerian approach (Markt et al. 2018) is used for the spray simulation that treats the gas phase as a continuum for which a complete set of transport equations are solved while the liquid phase is considered as a discrete phase transported with the gas medium. The sub-models used for the spray simulation include the dispersion model, Kelvin–Helmholtz Rayleigh–Taylor (KH-RT) breakup model (Reitz 1987), vaporization model (Zuo 2000), Ranz-Marshall (Ranz 1952) heat transfer model, and dynamic structure turbulence model. For the sake of brevity, we only discuss the modified transport equations employed for solving the continuity (Eq. 1) and momentum for the liquid film deposited on the substrate (Eq. 2). For the details on Lagrangian–Eulerian spray simulations, the reader is referred to the authors’ earlier works (Jarrahbashi et al. 2017a, b; Jarrahbashi et al. 2017a, b). The heat transfer on the solid substrate has been neglected here to isolate the behavior of the splashing droplets upon reaching the substrate from evaporation effects. It is noted that small droplets may have a non-Newtonian behavior due to the presence of the nanoparticles; however, as the CNC concentration is low, this study assumed a Newtonian behavior.

\[
\frac{\partial \rho}{\partial t} + \frac{1}{A_{wall}} \sum_{i=1}^{N_{wall}} (\bar{V}_{film}.\hat{n})_i \delta_{i} l_i = \frac{S_d}{\rho_l A_{wall}},
\]

(1)

\[
\frac{\partial (\rho \vec{V}_{film})}{\partial t} + \frac{1}{A_{wall}} \sum_{i=1}^{N_{wall}} \bar{V}_{film}(\vec{V}_{film}.\hat{n})_i \delta_{i} l_i \otimes \hat{n}_i = - \sum_{i=1}^{N_{wall}} (\rho_l \vec{V}_{film})_i \delta_{i} l_i + \frac{M_{tang}}{\rho_l A_{wall}} + \sum_{i=1}^{N_{wall}} \bar{V}_{film} A_i,
\]

(2)

The continuity and momentum equations are presented in (1) and (2), respectively and \(A_{wall}\) is the area of the wall cell, \(\bar{V}_{film}\) is the film velocity, \(l_i\) is the substrate length at side \(i\), \(\rho_l\) is the film density, \(\delta_{i}\) is the film thickness at side \(i\), \(\otimes \hat{n}_i\) is the impingement angle, and \(S_d\) is the source term. The following equations are used to calculate the pressure as \(P = P_{cell} + P_{d}\) where \(P_{cell}\) is the free stream pressure. \(P_{d}\) is the dynamic pressure due to impingement and splashing of the droplets defined as follows:

\[
P_{d} = \rho_l \sum_{i=1}^{N_{drop}} V_{nd}^2 \frac{A_i}{A_{wall}} + \rho_l \sum_{j=1}^{N_{splash}} V_{nj}^2 \frac{A_j}{A_{wall}}
\]

(3)

where \(V_{nd}\) is the normal component of velocity of the incoming droplets and \(V_{nj}\) is the normal component of velocity of the \(j\)th secondary droplet due to splashing. \(A_i\) and \(A_j\) are projected areas of the \(i\)th incoming droplet and \(j\)th splashed droplet, respectively. \(M_{tang}\) is the tangential momentum due to the impingement and splashing of the droplets defined as follows:

\[
M_{tang} = \sum_{i=1}^{N_{drop}} (m_j \vec{V}_{z_i}) - \sum_{j=1}^{N_{splash}} \left(m_j \vec{V}_{z_j}\right).
\]

(4)

Finally, the shear force acting on the substrate due to the droplet splashing is defined as
The droplet behavior upon reaching the substrate is detected via the droplet splashing criteria suggested by Stanton (Stanton 1996) as outlined in Table 2. It indicates whether the droplets stick, rebound, or spread on the solid substrate depending on the frequency of the incoming impinging droplets. This criterion is based on the Weber number (We) that is defined as the ratio of the drag force to surface tension force acting on the droplets. The parameters given in Table 2 include \(d_i\), the diameter of impinging droplet; \(f\), the frequency of droplets impinging on the wall; \(v\), the velocity, and \(\sigma\) is the surface tension coefficient.

We will calculate the velocity of the droplets after rebound and the angle at which the droplets bounce off from the substrate. We will identify the position of the droplets based on their velocity upon impact with the substrate to predict the liquid film growth towards the edges of the substrate as the droplets stick to the substrate. The number density of the droplets bouncing off the substrate will be calculated. Finally, a Weibull distribution (1951) is used to calculate the diameter of the droplets which break down and bounce back from the surface of the liquid film on the substrate. The equations used for calculating the above-mentioned parameters are summarized in the supplementary information document.

### Table 2: Droplet splashing criteria (Stanton 1996)

| Criterion    | Formula                                                                 |
|--------------|-------------------------------------------------------------------------|
| Stick        | \(\text{We} < 5\)                                                      |
| Rebound      | \(5 < \text{We} < 10\)                                                  |
| Spread       | \(10 < \text{We} < 324d_i^{1/4}f^{3/4}(\rho/\sigma)^{1/2}\)             |
| Splash       | \(\text{We} > 324d_i^{1/4}f^{3/4}(\rho/\sigma)^{1/2}\)                  |

**Results and discussion**

**Spray formation**

It is crucial to understand the breakup mechanisms of the supercritical CO\(_2\)-assisted atomization of the aqueous CNC suspension as it creates droplets that carry and deposit the nanoparticles on the substrate. In order to fully understand the effect of different parameters on the deposition process and the created micro/nano structure, a wide range of test cases outlined in Table 1 are studied. The experiments are designed to encompass different phases (i.e., subcritical, critical, and supercritical phases) of the hybrid CO\(_2\)-water mixture. Supercritical CO\(_2\) (SC-CO\(_2\)) has a high density and is highly soluble in water around the critical point of the CO\(_2\)-water mixture, since the diffusion coefficient of CO\(_2\) significantly increases close to this critical pressure (i.e., \(\sim 7.5\) MPa). The high solubility of CO\(_2\) in water reduces the interfacial tension of the injection mixture that is shown to facilitate the atomization process (Jarrahbashi and Sirignano 2014; Jarrahbashi et al. 2016). Table 3 presents the thermophysical properties of CO\(_2\)-water mixture at sub-critical, critical, and supercritical states. Comparing these values shows that that optimum condition (high diffusion coefficient and low interfacial tension) is achieved at the critical pressure of the CO\(_2\)-water mixture and supercritical pressure. Increasing the pressure beyond 9 MPa does not further change the solubility and the interfacial tension. The translational diffusion coefficient of CNCs in water is measured using dynamic light scattering (DLS) and is plotted as a function of CNC concentration in Fig. 2. By increasing the concentration of CNCs from 0.2 to 2wt%, the measured diffusion coefficient decreases, and viscosity increases.

High mole fraction of dissolved SCO\(_2\) in aqueous CNC suspension results in the formation of a bulged core filled with CO\(_2\) in the liquid jet very close to the nozzle. The emergence of gas bubbles and depressurization into the atmospheric pressure causes bubble expansion and eventually bubble burst. The force produced by the bubble burst shatters the liquid into micron-size long and slender ligaments that eventually breakup and form small droplets (Shariatnia, Asadi, and Jarrahbashi 2021). The temporal development of the bubbles and ligaments in a region close to the nozzle (\(\sim 300\) μm downstream of the orifice exit) is
portrayed in Fig. 3. The lower interfacial tension of CO$_2$-water mixture at supercritical conditions facilitates the ligament breakup and the combined effects result in enhanced primary breakup and formation of fine droplets with homogenous size distribution that ensures a uniform distribution of the deposited nanostructures on the substrate upon evaporation of the solvent. We have detailed the breakup mechanism of the liquid jet in the same SAA system in our earlier paper (Shariatnia, Asadi, and Jarrahbashi 2021).

The droplets created through the atomization process carry the nanoparticles and place them on the substrate. The assembly of the nanoparticles and the pattern of the deposited nanostructures on the substrate are highly affected by the droplet evaporation dynamics on the substrate and the size of the droplets. As a result, it is important to understand the effect of different spray parameters (i.e., injection pressure, gas-to-liquid ratio, axial distance from injection orifice) and injection mixture properties (i.e., the concentration of nanoparticles) on the droplet average size. These analyses will aid in designing the process parameters of the spray system. The next section discusses the effect of various process parameters on the SMD of the droplets containing nanoparticles.

### Droplet size distribution

The effect of different spray parameters and physical properties of the injection mixture on the average size of carrier droplets that is especially crucial for designing the nanoparticle delivery system is discussed in this section. The laser diffraction system is used for real-time measurement of SMD at 10, 15, and

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**Table 3** Thermophysical properties of subcritical, critical, and supercritical CO$_2$-H$_2$O. (Diamond and Akinfiev 2003; Bachu and Bennion 2009)

| Pressure (MPa) | CO$_2$ solubility (mol%) | CO$_2$ diffusion coefficient (m$^2$/s) $\times 10^{-10}$ | Interfacial tension (mN/m) | Density (kg/m$^3$) |
|---------------|--------------------------|----------------------------------------------------------|---------------------------|--------------------|
| 3             | 1.35                     | 6.7                                                      | 56.5                      | 1015.2             |
| 6             | 2.15                     | 15.1                                                     | 40.8                      | 1016.1             |
| 7.5           | 2.35                     | 18.5                                                     | 36.2                      | 1018.5             |
| 9             | 2.41                     | 13.9                                                     | 33.5                      | 1020.3             |

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**Fig. 2** Diffusion coefficient of CNCs in water (left axis, dashed blue line), and viscosity of aqueous CNC suspension (right axis, solid green line) as a function of CNC concentration. nozzle, substrate, and the laser diffraction system.
20 cm axially located downstream of the nozzle. These points are selected to fully represent the whole spray plume. Figure 4 plots the measured SMD as a function of GLR for different injection pressures and axial locations. It is observed in Fig. 4a–c that for each injection pressure, the mean droplet size decreases as GLR increases and the rate of SMD reduction decreases with an increase in GLR and reaches a plateau at the GLR of 0.2. At this point, increasing GLR does not have a noticeable effect on the SMD and hence this value (i.e., GLR = 0.2) is selected for spray deposition experiments.

At each GLR and axial distance, increasing the injection pressure results in the formation of droplets with smaller sizes. This is owed to the higher solubility of CO$_2$ in water and lower interfacial tension of CO$_2$-water mixture at higher pressures as was indicated in Table 3. The combined effects enhance the primary breakup of the liquid jet due to the burst of dissolved gas bubbles and surface capillary breakup. As a result, the variation of droplet sizes by changing injection pressure is more evident in cases where measurement is performed closer to the nozzle (i.e., 10 cm axial distance in Fig. 4(a)) compared to measurements further away from the injection orifice (i.e., 15 and 20 cm from the orifice in Fig. 4(b, c)). It is also evident that for each injection pressure, increasing the axial distance between the injection orifice and SMD

**Fig. 4** SMD measurements as a function of GLR for different injection pressures and an axial distance of a 10 cm, b 15 cm, and c 20 cm from injection orifice
probe from 10 cm in Fig. 4a to 20 cm in Fig. 4c, results in smaller mean droplet sizes and their size does not vary significantly with GLR. This can be attributed to the “secondary breakup” of droplets that occurs at locations further away from the nozzle. The secondary breakup is referred to a process in which the droplets exposed to high shear forces breakup into multiple smaller droplets.

Figure 5(a) shows the measured SMD as a function of injection pressure at 1 cm axial distance with respect to the nozzle and for three different concentrations of CNCs in the suspension (i.e., 0.2, 0.5, and 2wt%). Similar to Fig. 4, increasing the injection pressure reduces the droplet sizes. The droplet sizes breakup into smaller droplets at locations further away from the orifice due to the secondary breakup. The sharpest decrease in the droplet is achieved at 7.5 MPa injection pressure that is close to the critical pressure of the CO2-water mixture. The proximity to the critical pressure enhances the diffusivity of CO2 in water and the creation of more bubbles inside water upon injection that enhances the atomization process and reduces the droplet size. Further increasing the injection pressure to 9 MPa has a negligible effect on the droplet size. This can be attributed to the maximum diffusion coefficient of CO2 in water that occurs at 7.5 MPa (Tewes and Boury 2005), which in turn results in minimum surface tension value for the water-CO2 mixture at this pressure (Bachu and Bennion 2009). In addition, increasing the concentration of nanoparticles in the injection mixture, from 0.2 to 2wt%, increases the overall size of the carrier droplets. The viscosity of the aqueous suspension increases from 1.2 to 4 mPa.s by increasing the concentration from 0.2 to 2wt% as indicated in Fig. 2. This enhancement (~ three-fold) in viscosity of the injection mixture leads to an average of ~ 54% growth in droplet sizes of the spray. It is well established that an increase in liquid viscosity results in the formation of larger droplets as it suppresses the breakup process by dampening the interfacial perturbations between the liquid and gas upon injection that eventually break it up to multiple droplets (Bouse et al. 1990; Dayal et al. 2004). The direct effect of droplet sizes on the dynamics of solvent evaporation which in turn influences the assembly of nanoparticles and architecture of nanostructures formed on the substrate is discussed in the next section.

Nanostructure patterns

In this section, we discuss the CNC patterns that form after the evaporation of the liquid droplets generated through atomization of the aqueous CNC suspension. We study the effects of different process parameters on the created nanostructure on a glass substrate. Figures 6 visualizes the polarized micrographs of otherwise transparent CNC nanostructures that are formed on the substrate upon droplet evaporation for different injection pressures. The glass substrates are 1 cm by 1 cm. Figure 6 illustrates the architecture of nanostructures for various injection pressures for 0.2wt% (left column) and 2wt% (right column) CNC concentration. The main pattern of assembled nanostructures in these top-view micrographs can be categorized in one of the three shapes: (1) ring-shape, where the majority of nanoparticles accumulate along the edge of the evaporating droplet, (2) homogenous distribution, where particles scatter across the surface area of the evaporating droplet, and (3) transition stage, where there is still a distinct ring-shape structure and some particles are also scattered within the center.
of the evaporating droplet. It is illustrated in Fig. 6(a1–d1) that regardless of the injection pressure, the droplets with diameters smaller than \( \sim 5.5 \, \text{mm} \) exhibit a homogenous distribution, while droplets larger than \( \sim 7.5 \, \text{mm} \) have generated a ring-shaped structure, and droplets with diameter sizes in between the two thresholds (i.e., between 5.5 and 7.5 mm) represent a transition between the two identified regimes. All three patterns were observed for all injection pressures as the droplet size distribution envelopes the detected thresholds. In Fig. 6(a2-d2) that illustrate droplets with a higher concentration of CNC particles (i.e., 2wt%), the homogenous distribution, transition, and ring structure occurs for \(< 9.5 \, \text{mm}, \sim 9.5–11.5 \, \text{mm}, \text{and} > 11.5 \, \text{mm} \) droplet sizes, respectively. It is noted that at least 6 images were taken at different locations of the same substrate; all of which were in great agreement with the threshold detected in these figures.

Figure 7 demonstrates the profile/height measurements of assembled nanostructures upon evaporation for droplet sizes varying from 5 to 13 mm and different concentrations (0.2wt%, 0.5wt%, 2wt%). Combined with top-view micrographs presented in Fig. 6, they provide a 3D realization of the shape of assembled CNC nanostructures. In Fig. 7, the droplets have been injected at 9 MPa. We discussed the effect of injection pressure on the nanoparticle patterns in Fig. 6 and showed that droplets with the same size and concentration shared the same pattern regardless of the injection pressure. The profilometry height measurements indicate that nanostructures represent a ring, disk, or dome shape. A ring pattern that is identified with two peaks on the height profile is referred to the accumulation of nanoparticles along the edge of the droplet (labeled as “ring” in the top view in Fig. 6). A dome forms when nanoparticles are captured at the interface during evaporation and mainly remained in the center after droplet evaporation i.e., only one peak.
is observed on the height profile. The dome structure was identified as “transition” in the top view depicted in Fig. 6. Finally, a disk pattern forms when the height profile is nearly flat at the center. This indicates nanoparticles are scattered more uniformly across the surface area of the droplet compared to the dome and ring and. The disk pattern was identified as “homogeneous” in the top view Fig. 6. Figure 7 shows that by decreasing the droplet size from 13 μm (red) down to 5 μm (blue), the assembly of particles transits from...
ring-shape to a dome-shape structure for all CNC concentrations. The 9 μm-droplet (green) represents the transition between ring to a disk-shape structure. By increasing the concentration of CNCs, the transition from a ring structure to disk occurs at larger droplet sizes. As will be discussed in the next section, the droplet size and concentration directly affects the evaporation rate of the solvent, which in turn influences the particle advection and diffusion and ultimately the nanoparticle patterns.

In summary, by controlling the droplet sizes we can engineer the desired pattern (ring, dome, disk) for different concentrations. The use of SCO₂ enables achieving a very uniform distribution of droplet sizes within the spray that facilitates achieving a uniform distribution of CNCs with the desired pattern on the substrate. The injection pressure can directly control the overall size of droplets within the spray plume and can be adjusted to the size requirements of the specific application where the spray deposition system is being used. To quantitatively demonstrate the control over the nanostructure patterns with the injection pressure Dv90 measurement using laser diffraction method is plotted vs. injection pressure for variable concentrations plotted in Fig. 8. Dv90 indicates the mean diameter size that represents 90% of the total volume of the existing liquid droplets Fig. 8 shows that at 7.5 MPa injection pressure and 0.2wt% CNC concentration, 90% of droplets are smaller than 4 μm in size. Based on the microscopic images and height profilometry, droplet sizes smaller than 4 μm will represent a homogenous nanoparticle distribution. As a result, most of the deposited nanostructures will exhibit a disk-shape structure. The information from this measurement combined with detailed discussions on the 3D architecture of fabricated micro/nanostructures have important implications in designing practical deposition systems to ensure that majority (> 90%) of droplets fall under a certain category (i.e., ring versus homogenous distribution).

Evaporation-induced nanoparticle assembly

In this section, we will explore the CNC assembly in micron-size evaporating droplets (Govor et al. 2004; Lu et al. 2013). In order to find the link between the dynamics of droplet evaporation and the formation of a specific pattern upon evaporation, two main parameters are identified: (1) droplet evaporation rate that is linked to the convective transport of CNCs as the droplet edge recedes back during droplet evaporation; and (2) the Brownian diffusion rate of CNCs in water. It has been shown that in the absence of other competing mechanisms e.g., external forces, special treatment of the substrate or solvent, the competition between the convective and diffusive transport of

![Graph](image-url)  

**Fig. 8** Dv90 as a function of injection pressure for different CNC concentrations measured at an axial distance of 15 cm and GLR = 0.2
particles dictates the final pattern after droplet evaporation (Vehring 2008). The ratio of the convective to diffusive transport of particles during water evaporation is represented by the non-dimensional Péclet ($Pe = \frac{r^2}{D_D t}$) number, where ‘$r$’ is the droplet radius, ‘$D$’ is the particle mass diffusivity in the liquid phase and ‘$t$’ is the droplet evaporation time. For millimeter-sized droplets, it has been shown (Wei 2015) that the ring pattern is typically favored for $Pe > 1$ as the convective rate surpasses the diffusive rate. A reduction in the $Pe$, which implies a diffusion-dominated transport, is known to mitigate the ring formation toward a more uniform particle distribution (Mampallil and Eral 2018).

Our SMD measurements of the spray suggest that the droplet sizes are below 20 microns for which measuring the droplet evaporation rate is experimentally very challenging. As an alternative approach, there are various mathematical and analytical models to calculate the evaporation rate of a sessile droplet (Hu and Larson 2002, 2005; Nguyen and Nguyen 2012). Larson’s model (Eq. 6), which is applicable for semispherical sessile droplets, is commonly used as one of the most accurate models that has been verified empirically (Hu and Larson 2002). This model is more accurate when the Bond number is smaller than 0.1 ($Bo = \frac{\rho g R h_0}{\sigma}$) and the capillary number ($Ca = \frac{\mu u_c}{\sigma}$) is smaller than 1. $Bo$ is the ratio of the gravitational to surface tension forces and accounts for the initial shape of the droplet whereas $Ca$ is the ratio of viscous to capillary forces and accounts for deformation of the droplet during evaporation. Here $\rho$, $g$, $R$, $h_0$, $\sigma$, $\mu$, and $u_c$ are the density, gravitational acceleration, contact line radius, initial droplet height, liquid–air surface tension, liquid viscosity, and average radial velocity due to evaporation, respectively. We first compare the experimentally measured evaporation rate for a 1 μm droplet (∼ 1 mm in radius) deposited on a glass substrate with the predictions of the Larson’s model (Eq. 6):

$$m(t) = -\pi RD(1 - H)C_v(0.27\theta + 1.3)$$ (6)

where $R$, $D$, $H$, $C_v$, and $\theta$ are the droplet radius (1 mm), water vapor diffusivity ($2.42 \times 10^{-5} \text{ m}^2/\text{s}$), relative humidity (40%), saturated water vapor concentration (West and Astle 1981) ($23.2 \text{ g/m}^3$), and droplet contact angle (0.369 rad), respectively. The contact angle is measured on an image that is taken normal to a back-illuminated droplet deposited on a solid substrate. Larson’s model predicts 709 s for a 1 mm droplet to evaporate and our experimental measurement indicated 718 s, which is in close agreement with the model prediction. The translational diffusion coefficient of CNC in DI-water measured by DLS for 0.2, 0.5, and 2 wt% concentration (Fig. 2) is $7.18 \times 10^{-12}$, $6.7 \times 10^{-12}$, and $4.3 \times 10^{-12} \text{ m}^2/\text{s}$, respectively. The diffusion coefficient reduces with concentration due to the packed space hindering the freedom of particles to transport (Van Rie et al. 2019). We use this data along with the evaporation rate obtained from Larson’s model and droplet sizes captured by the laser diffraction measurements to calculate $Pe$.

Figure 9 shows the calculated $Pe$ as a function of droplet size for different CNC concentrations. By increasing the droplet size for each concentration, the evaporation time is also increased while the diffusion coefficient is constant for the same concentration. This results in higher $Pe$ at higher concentrations. According to Fig. 9, the corresponding $Pe$ for a droplet size of 13 μm is 1.27, 1.37, and 2.13, for 0.2, 0.5, and 2.0 wt% concentration, respectively. $Pe > 1$ indicates the domination of the convective transport of CNC particles towards the edge of the droplet induced by the evaporation of DI-water and formation of a ring-shape structure as was depicted in Fig. 7. Droplets within the 6–8 μm diameter range have an average $Pe$ of 0.7, 0.8, and 1 for 0.2, 0.5, and 2.0 wt% concentration, respectively. These cases where convective and diffusion rates are almost equal were identified as the transition between ring and dome shape structures in Fig. 6.

It is noted that pure CNCs are almost hydrophilic, and thus tend to form a ring. However, various observed patterns for different concentrations and different droplet sizes imply that in addition to the particle shape, level of hydrophilicity, the droplet size, and particle mass concentration also play a role in determining the final pattern. For instance, Fig. 7 showed that for a 9 μm-droplet, the pattern changed from a ring at 0.2 and 0.5 wt% to a disk at 2 wt%. Our
results showed that increasing the ratio of mass concentration to droplet size tends to change the pattern from ring to dome as the particles are captured at the interface between the evaporating liquid and the surrounding air before they get a chance to accumulate at the droplet periphery and dry as a dome or disk after liquid evaporation.

Evaluating the effectiveness of the nanoparticle spray deposition method

Droplets created by injecting a high-pressure liquid jet toward a substrate in ambient temperature and pressure can evaporate before reaching the substrate, deposit on the substrate, or bounce back from the substrate before depositing their nanoparticle content on the substrate. Optimizing the distance between the injection orifice and the substrate at different injection conditions is necessary from two perspectives: (1) to predict and control the evaporation of the droplets to ensure most of the droplets containing nanoparticles reach the substrate before evaporation. This is important because if most of the droplets evaporate before reaching the substrate the nanoparticle content will be dispersed in the surrounding air and wasted; (2) to predict and control the splashing of the droplets that will affect the nanoparticle content and patterns left on the substrate. Figure 11 depicts a series of simulations performed to study the behavior of the spray and the resulting droplets deposited on the substrate. The black color represents the water, and the gray shows the ambient air. The droplets are observed around the core of the liquid jet due to the progression of the atomization process. The distance between the nozzle and the substrate varies from 5 to 30 cm with 5 cm increments and the tested injection pressure is 3, 6, 7.5, and 9 MPa, consistent with the experiments. The nozzle geometry selected for the simulations is consistent with the experiment (diameter of 125 μm and cone-angle of 6°). For the sake of consistency, a baseline liquid film thickness of 1 μm is set and when this thickness is achieved at any point on the substrate, it is assumed that the spray has reached the substrate. The simulations are conducted using pure water at room temperature without considering nanoparticles. Since the concentration of nanoparticles in water is very low in experiments the nanoparticles do not interfere with the spray behavior.

The spray development is visualized in Fig. 10 for the cases where the substrate is located at 10 cm axial distance from the nozzle and injection pressures are 3, 6, 7.5 and, 9 MPa. As Fig. 10 shows, increasing the injection pressure and increasing the jet momentum results in longer liquid penetration length, and thus the time taken to reach the substrate and forming the liquid film decreases from 4.8 to 2.8 ms by increasing the injection pressure from 3 to 9 MPa. The time required for the spray to reach the substrate is an
important factor in designing experiments and setting up the optimum location of the substrate. Repeating the simulations for the cases that the substrate was located at 15 and 20 cm with the same injection pressures of Fig. 10 revealed that at 20 cm, less than 1% of the droplets reached the substrate which did not result in formation of a film with 1 μm thickness. These simulations suggest that the substrate should be placed at an axial distance less than 20 cm from the nozzle to ensure a liquid film of 1 μm thickness is formed on the nozzle between 3 ms (for 6, 7.5, and 9 MPa) to 4 ms (for 3 MPa) after the start of injection. Microscopy images of the assembled CNC structures left on the substrate located at 15 cm are presented in Fig. 6.

Since droplet evaporation before the spray reaches the substrate is essential in efficiently delivering the nanomaterial to the substrate it is imperative to calculate the mass of evaporated droplet as a percentage of the total injected mass as shown in Fig. 11 for different injection pressures and nozzle-substrate distance. For each injection pressure, increasing the distance between the nozzle and the substrate increases the evaporated mass. The plots reach a plateau once the spray reaches the substrate indicating a relatively constant rates of evaporation. It is seen that for 5 and 10 cm positions, the mass loss due to evaporation of the droplets is in the range of 10–15% and 20–25%, respectively. However, the mass loss reaches 25–30% range for 15 and 20 cm from the nozzle. These observations suggest that placing the substrate at a distance lower than 20 cm below the injection orifice minimizes the mass loss due to evaporation for the explored pressure range of 3 to 9 MPa.

Figure 12 shows the variation in the percentage of the water mass deposited on the substrate for different injection pressures for substrate positioned at 5, 10, and 15 cm from the orifice. The mass of water deposited on a substrate located 5 cm below the injection point is ~ 65% of the total initial mass upon injection, whereas for a 10 cm distance, 25–30% of its initial mass is deposited. This suggests that the remaining droplets either evaporated or scattered in the surrounding air without reaching the substrate. For 20 and 30 cm nozzle-substrate distance not shown in Fig. 12, the simulations predict negligible droplet deposition on the substrate implying that most of the droplets have evaporated before reaching the substrate. At each axial location, increasing the injection...
pressure results in the delivery of higher portions of the initial mass of droplets to the substrate. However, there is a slight decrease in the deposited mass at 9 MPa injection pressure for the 10 and 15 cm cases. This is because 9 MPa injection pressure generates smaller droplets (as is shown in Fig. 4 and 5) which are more prone to evaporation before reaching the substrate. These results suggest that 6 and 7 MPa injection pressures are more appropriate for optimum spray deposition as droplets have large enough momentum to reach the substrate yet the mass of evaporated droplets is smaller than the 9 MPa case before reaching the target substrate. Satisfying these two conditions ensures more efficient delivery of the nanoparticles. In addition, comparing the experimental measurements of SMD at 7.5 MPa (Figs. 4 and 5) demonstrated a more uniform and smaller droplet size distribution.

The droplet bounce-back upon contact with the substrate is another important factor that affects the effectiveness of the nanoparticle deposition on the substrate. Figure 13 represents the water loss due to splashing from the substrate for axial distances of 5 and 10 cm. As expected, the percentage of the liquid mass bounced back into the surroundings (~0.5–1%) is higher at 5 cm where the droplets have a higher momentum upon interacting with the substrate. The mass of bounced droplets at 15 and 20 cm distance are

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**Fig. 11** Temporal variation of the percentage of the mass of evaporated droplets with changes in the distance from the nozzle to the substrate at different injection pressures.

**Fig. 12** Temporal variations of the mass of water added to the substrate with the change in injection pressures for 5, 10 and 15 cm distance between the nozzle and the substrate.
negligible, hence not depicted here. Increasing the injection pressure to 9 MPa results in higher splashing at the film interface as the droplets gain a higher momentum upon injection. While positioning the substrate closer to the nozzle may not seem ideal for a stable film formation due to increased splashing, the percentage of droplets that are lost due to the bounce-back effect is much lower than the evaporation mass loss (1% versus 20%).

Moreover, the higher number of bounced droplets will lead to higher film spread. This happens when the droplets that have already bounced from the substrate lose momentum and fall back on the substrate. The temporal variation of the surface coverage and isoscales of the covered area by the spray are depicted Fig. 14. The film area calculated for 5 cm distance between the nozzle and substrate (colored with a film thickness of 0.01 μm) is larger due to enhanced splashing and subsequent deposition. This eventually leads to higher deposition of nanoparticles and a larger film front where the nanoparticles accumulate. It can also be seen that there is no deposition for 10 cm case at 2 ms due to larger distance between nozzle and substrate as compared to the 5 cm case. Considering different behaviors of droplets (evaporation, deposition, bounce-back) relative to the axial distance of the substrate observed from simulations, it is concluded that a location between 10 and 15 cm below the nozzle and 7.5 MPa injection pressure results in a more effective and uniform nanoparticle deposition.

**Summary and conclusions**

In this study, we designed and built a novel nanoparticle spray deposition system that utilizes supercritical injection pressure: a percentage of the substrate surface covered, b iso-scales depicting droplet deposition of over 0.01 μm film thickness
CO₂ to assist the atomization process and create uniform micron-size CNC-carrier aqueous droplets and deposit them onto the substrate to form tailored nanostructures upon evaporation of water. The effect of spray parameters on formation of droplets were studied numerically and experimentally. The main conclusions from this work are summarized below.

The 1st, 4th, and 8th conclusion points provide new insights into the main breakup mechanisms of SAA system, pattern of nanostructures left on the substrate upon evaporation of water, and relationship between the size of carrier droplets and the pattern of deposited CNCs, respectively.

1. Supercritical CO₂-assisted atomization sparks two concurrent mechanisms to boost liquid atomization: reducing the liquid surface tension and enhancing CO₂ dissolution in water. The combined effect results in the formation of fine droplets with a narrow size distribution that can be used as nanoparticle-carrier droplets.

2. Laser diffraction measurement of SMD shows that in general, increasing the injection pressure, GLR, and axial distance from the injection orifice results in the creation of smaller droplets. In addition, increasing the concentration of CNCs in the injection mixture increases the overall size of the carrier droplets.

3. However, increasing the injection pressure above the critical pressure of the CO₂-water mixture (i.e., 7.5 MPa) and increasing the GLR do not noticeably decrease the droplet sizes. This means there is no need for extremely high pressures or excessive amount of assisting gas to create micron-sized droplets.

4. Microscopic visualization of the assembled nanoparticles on the substrates illustrates that morphology of nanostructures falls into three main categories: (1) ring-shape pattern, where the majority of nanoparticles accumulate along the edge of the evaporating droplet, (2) homogenous distribution or disk pattern, where particles scatter more uniformly across the surface area of the evaporating droplet, and (3) transition stage, where there is still a distinct ring-shape structure yet some particles are scattered within the edges of the evaporating droplet.

5. The profilometry height measurements combined with micrographs provide a 3D visualization of the assembled nanostructure and show that they either form a ring, disk, or dome-shaped architecture. Increasing the mass concentration to droplet size ratio shifts the morphology of assembled nanoparticles from ring to dome as the particles are trapped at the liquid–air interface before they get a chance to move towards the edge of the droplet.

6. For each CNC concentration and regardless of the injection pressure, there is a droplet size threshold range above which the assembled nanostructures exhibit a ring pattern and below that they exhibit a homogenous distribution. For concentration of 0.2wt%, the lower and upper bounds of the threshold are 5.5 and 7.5 μm, respectively while for 2wt% CNC concentration these values increase to 9.5 μm and 11.5 μm, respectively.

7. The injection pressure on the other hand dictates the size of the majority of droplets within the spray plume and can be used to design a system where the bulk of droplets fall under one of the identified nanostructure patterns.

8. The size of the carrier droplets strictly influences the evaporation rate of solvent in particle-carrier droplets upon deposition on the substrate. The evaporation rate in turn, affects the prevalence of convective to diffusive transport of particles that is represented by Peclet number.

9. The evaporation time is prolonged by increasing the droplet size for each concentration, which results in $Pe > 1$ that indicates the higher rate of convective transport of particles to diffusive transport leading to accumulation of particles along the periphery of the droplet and formation of a ring-shaped structure. At $Pe < 1$ where the diffusive movement of CNCs is dominant, a dome-shaped structure is formed for all tested concentrations. At $Pe \sim 1$, droplets fall in the transitional region where both ring and dome-shaped structures are observed.

10. Computational simulations show that considering different droplet behavior interacting with the substrate (evaporation, deposition, bounce-back) versus the injection pressure and axial distance between the substrate and nozzle, positioning the substrate at 10 or 15 cm below the nozzle and 7.5 MPa injection pressure result
in a more effective and uniform nanoparticle deposition.

**Data availability**  All the data and materials supporting the claims herein are included in the manuscript and comply with the field standards.

**Declarations**

**Conflict of interest**  The authors declare that they no conflict of interest.

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