Layer-by-Layer Spray-Coating of Cellulose Nanofibrils and Silver Nanoparticles for Hydrophilic Interfaces

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ABSTRACT: Silver nanoparticles (AgNPs) and AgNP-based composite materials have attracted growing interest due to their structure-dependent optical, electrical, catalytic, and stimuli-responsive properties. For practical applications, polymeric materials are often combined with AgNPs to provide flexibility and offer a scaffold for homogenous distribution of the AgNPs. However, the control over the assembly process of AgNPs on polymeric substrates remains a big challenge. Herein, we report the fabrication of AgNP/cellulose nanofibril (CNF) thin films via layer-by-layer (LBL) spray-coating. The morphology and self-assembly of AgNPs with increasing number of spray cycles are characterized by atomic force microscopy (AFM), grazing-incidence small-angle X-ray scattering (GISAXS), and grazing-incidence wide-angle X-ray scattering (GIWAXS). We deduce that an individual AgNP (radius = 15 ± 3 nm) is composed of multiple nanocrystallites (diameter = 2.4 ± 0.9 nm). Our results suggest that AgNPs are assembled into large agglomerates on SiO₂ substrates during spray-coating, which is disadvantageous for AgNP functionalization. However, the incorporation of CNF substrates contributes to a more uniform distribution of AgNP agglomerates and individual AgNPs by its network structure and by absorbing the partially dissolved AgNP agglomerates. Furthermore, we demonstrate that the spray-coating of the AgNP/CNF mixture results in similar topography and agglomeration patterns of AgNPs compared to depositing AgNPs onto a precoated CNF thin film. Contact-angle measurements and UV/vis spectroscopy suggest that the deposition of AgNPs onto or within CNFs could increase the hydrophilicity of AgNP-containing surfaces and the localized surface plasmon resonance (LSPR) intensity of AgNP compared to AgNPs sprayed on SiO₂ substrates, suggesting their potential applications in antifouling coatings or label-free biosensors. Thereby, our approach provides a platform for a facile and scalable production of AgNP/CNF films with a low agglomeration rate by two different methods as follows: (1) multistep layer-by-layer (LBL) spray-coating and (2) direct spray-coating of the AgNP/CNF mixture. We also demonstrate the ability of CNFs as a flexible framework for directing the uniform assembly of AgNPs with tailorable wettability and plasmonic properties.

KEYWORDS: silver nanoparticles, self-assembly, cellulose nanofibrils, layer-by-layer deposition, spray-coating

INTRODUCTION
Silver nanomaterials have attracted a wide range of interests due to their applications in catalysts (using AgNPs supported on a metal–organic framework for CO₂ conversion), antimicrobials (including AgNPs deposited on cotton fabrics and various kinds of textiles), sensors (using Ag,S nanoparticles for microRNA sensing and carbon nanotube/Au composite membrane for human-motion detection), and electronics (AgNPs-based elastic conductors and electric circuit). The tunable performance of AgNP-based devices shows a significant dependence on the structure and morphology of AgNPs at the nanoscale. Polymers, especially cellulose nanofibrils (CNFs), can provide a scaffold for assembly of metallic nanoparticles (MNP) with defined porosity and roughness, thus increasing the flexibility and ordering of the MNP layer and improving the catalytic, photonic, or electrical performance of the MNP/CNF composite nanomaterials. For example, plasmonic AgNPs were grafted onto cellulose nanocrystals to achieve remote IR actuation. AgNP ink was printed on a cellulose nanopaper with high mechanical strength and flexibility, and dialdehyde nanofibrillated cellulose (DANFC) was used to
synthesize a smooth silver layer to obtain a controlled release of antibacterials. However, the reproducible fabrication of AgNP/cellulose nanocomposites with tailorable morphology remains a challenge, which relies on a nanoscopic characterization of the self-assembly of AgNPs on and/or within cellulose nanomaterials.

Spray-coating is broadly used to fabricate functional multilayered films. Spray-coating allows for (1) controlling the morphology of the deposited layer through adjustable spraying parameters and (2) fabricating composite materials by layer-by-layer (LBL) installation of multilayered films, thus providing a facile approach for assembling multicomponent films with tailorable morphology. Grazing-incidence small-angle X-ray scattering (GISAXS) and grazing-incidence wide-angle X-ray scattering (GIWAXS) are surface sensitive characterization methods that elucidate the structure and morphology of materials at the nanoscale. In the present work, we follow the structural evolution of AgNPs on SiO2 or within the CNF layer through the combination of LBL spray-coating and GISAXS/GIWAXS techniques. Three model systems are studied as follows: (1) AgNPs are deposited on SiO2 substrates (AS) to show the assembly of AgNPs on a smooth and nonporous surface, (2) AgNP/CNF LBL film (AC) in which AgNP solution is spray-coated on a CNF thin film, which is deposited on SiO2 substrates in advance, and (3) a AgNP/CNF mixture is deposited on SiO2 substrates (AM) to study the self-assembly of AgNP/CNF composite films with AgNPs on and within the CNF network, respectively. AFM is used to visualize the topography of AgNP layers and rationalize the results from GISAXS and GIWAXS. Contact-angle measurements and transmission UV/vis spectroscopy are employed to demonstrate the potential of AgNP/CNF composite films as hydrophilic coatings with plasmonic properties.

## METHODS

### Materials and Preparation

The composition and charge density of the chemical groups of CNFs and AgNPs are significant for the intrinsic bond strength between AgNPs and CNFs in their composites. Therefore, 0.07 wt % aqueous solution of TEMPO-CNFPB with a surface charge of 800 μmol/g and a radius of around 2.5 nm was dispersed by sonication and centrifugation to prepare the CNF thin film in the AC samples. An aqueous dispersion of surfactant-free AgNPs with a final concentration of 5 ± 2 μg/mL (Figure S1) and a zeta potential of −27.5 ± 2.5 mV was produced by pulsed-laser ablation to prepare the AgNP layer in the AS and AC samples. AgNP and CNF dispersions were mixed with a volume ratio of 1:1 for preparing the AgNP/CNF composite layer in the AM samples. SiO2 wafers or SiO2-fused glass slides (Silicon Materials, USA) of 20 × 20 mm2 were used as substrates for AFM, GISAXS, GIWAXS, and contact-angle measurements. SiO2-fused glass slides were cut into 10 × 10 mm2 as substrates for UV/vis spectrum measurements. All substrates were sonicated with acetone for 15 min and then sequentially cleaned with isopropanol and ultrapure water, followed by an acid bath (87.5 mL of hydroperoxide 30%, 190 mL of sulfuric acid 96%, and 37.5 mL of ultrapure water) at 80 °C for 15 min. All chemicals were purchased from Carl Roth GmbH, Germany.

### Spray Coating

Layer-by-layer spray-coating at room temperature (23 °C) was performed by a spray-coating device (Compact JAU DSS5000, Spray Systems, Germany). CNF, AgNP, or their mixture solution was supplied by a siphon glass container connected to the spray device. Spray-coating was performed at a nitrogen gas pressure of 1 bar. The substrates were placed onto a heating plate of 120 °C. The distance between the nozzle and substrate was kept at 150 mm. Three groups of samples were prepared as follows: AgNPs deposited on SiO2 wafers (AS), a AgNP/CNF LBL film with AgNPs coated on a CNF thin film predeposited on SiO2 wafers (AC), and a AgNP/CNF mixture deposited on SiO2 wafers (AM) (Figure 1). For CNF thin films with a thickness of 200 nm, which was used as substrates for AgNP deposition in the AC samples, the deposition conditions were 0.2 s spraying and 10 s waiting alternated for 20 cycles. This is a well-established system for the investigation of the layering and self-assembly of MNPs on the AgNP/CNF interface from our previous work. Therefore, the standard CNF and SiO2 substrates provide us the basis for studying the self-assembly of AgNPs during spray-coating by directly increasing the number of spray cycles. For the AgNP layer deposition in the AS and AC samples, the parameters were slightly changed into an alternated spraying of 0.1 s and waiting of 1 s with varying spray cycles from 1, 10, 50, 100, to 150. For the AgNP/CNF mixture in the AM samples, the protocols were 0.2 s spraying and 15 s waiting for 1, 10, 50, 100, and 150 cycles. The time for spray-coating in AM was doubled in comparison to AC and AS to ensure that the same amount of AgNPs was deposited at the same number of spray cycles among the three groups. The parameters for spray-coating are also optimized in an effort to prepare the AgNP layer with high homogeneity. We adopted the following name conventions for the three groups of samples: group name-number of spray cycles.

### Atomic Force Microscopy (AFM)

The AFM images were acquired with an NTEGRA probe Nano-Laboratory (NT-MDT, Russia) in the semiconductor mode. ETALON cantilevers with a tip radius of 10 nm and a resonant frequency of 90 kHz (NT-MDT, Russia) were used for all samples. For each sample, 20 pictures of 2D topography maps were taken with a scan size of 3 × 3 and 1 × 1 μm2.
AFM data analysis, including line cuts, and average roughness were done by WSXM 5.0 software.

X-ray Scattering. The detailed morphology and crystallinity of the samples were investigated with GISAXS and GIWAXS, respectively. The X-ray scattering experiments were performed at the MII40S/P03 beamline of the PETRA III storage ring at DESY, Hamburg. The energy of X-ray was 12.85 keV (λ = 0.965 Å) with a beam size of 80 × 56 μm² (horizontal × vertical). One beam stop was used to shield the specular reflected beam. A sketch of the GISAXS and GIWAXS setup is shown in Figure S2, with α and φ representing incident and exit angles, respectively. The sample-to-detector distance (SDD) was kept at 3040 ± 2 mm in GISAXS and 115 ± 1 mm in GIWAXS measurements. 2D GISAXS data were collected by a PILATUS 300k detector (Dectris Ltd., Switzerland) with a pixel size of 172 × 172 μm² and GIWAXS data were collected by a Lambda 750k detector (X-spectrum GmbH, Germany) with a pixel size of 55 × 55 μm². The incident angle α was set at 0.42° for GISAXS and 0.11° for GIWAXS measurements.

A lateral scanning with a step size of 100 μm by moving the sample through the beam in the y-direction was used to avoid X-ray beam-induced alteration of the samples. Each GISAXS pattern was acquired for 0.1 s, and each GIWAXS pattern was acquired for 0.5 s. 1D intensity distributions were extracted from 2D GISAXS data using the Directly Programmable Data Analysis Kit software (DPDAK) v1.4.132 and fitted by minimum chi-square estimation with cylindrical and spherical form factors including a structure factor as previously reported by Schaffer et al. For GISAXS, the qz and φ plots were transformed by Grazing-incidence X-ray Scattering Graphical User Interface software (GIXSGUI) v1.7.1.38

UV/vis Spectroscopy. UV/vis transmission spectroscopy measurements were conducted on a custom build setup. For UV/vis spectra of the AS, AC, and AM samples, a SiO2-fused glass substrate (in the AS and AM samples) and a CNF thin film coated on a SiO2-fused glass substrate (in the AC samples) were used as references. We used a spectrometer (OCEAN-FX-XR1-ES, Ocean Optics) covering a range of 200–1025 nm and a balanced deuterium-tungsten light source (DH-2000-BAL, Ocean Optics). Both light source and spectrometer were connected with solarized source (DH-2000-BAL, Ocean Optics). Both light source and spectrometer were connected with solarized source (DH-2000-BAL, Ocean Optics). Both light source and spectrometer were connected with solarized source (DH-2000-BAL, Ocean Optics). Both light source and spectrometer were connected with solarized source (DH-2000-BAL, Ocean Optics). Both light source and spectrometer were connected with solarized source (DH-2000-BAL, Ocean Optics). Both light source and spectrometer were connected with solarized source (DH-2000-BAL, Ocean Optics). Both light source and spectrometer were connected with solarized source (DH-2000-BAL, Ocean Optics). Both light source and spectrometer were connected with solarized source (DH-2000-BAL, Ocean Optics). Both light source and spectrometer were connected with solarized source (DH-2000-BAL, Ocean Optics). Both light source and spectrometer were connected with solarized source (DH-2000-BAL, Ocean Optics). Both light source and spectrometer were connected with solarized source (DH-2000-BAL, Ocean Optics). Both light source and spectrometer were connected with solarized source (DH-2000-BAL, Ocean Optics). Both light source and spectrometer were connected with solarized source (DH-2000-BAL, Ocean Optics). Both light source and spectrometer were connected with solarized source (DH-2000-BAL, Ocean Optics). Both light source and spectrometer were connected with solarized source (DH-2000-BAL, Ocean Optics). Both light source and spectrometer were connected with solarized source (DH-2000-BAL, Ocean Optics). Both light source and spectrometer were connected with solarized source (DH-2000-BAL, Ocean Optics).

Contact-Angle Measurement. Wettability measurements were facilitated by an OCA35 (Data Physics, Germany) contact-angle measuring system. An automatic syringe system was used to control the volume of deionized water droplet to 5 μL. At least five droplets were measured for each sample. Microscopic images were taken from each droplet, and the contact angle calculation was done by SCA20 software (Data Physics, Germany).

### RESULTS

Surface Morphology. AgNPs deposited on SiO2, AgNP/CNF LBL film, and AgNP/CNF mixture deposited on SiO2 with 1, 10, 50, 100, and 150 spray cycles were prepared, respectively. AFM images of the AS, AC, and AM samples at 10, 50, and 150 spray cycles are shown in Figure 2a. An increase in the number of spray cycles leads to a higher Ag coverage w. The coverage w follows in series: wAS > wAC > wAM. Densely packed CNFs are observed for all AC and AM samples. We can even distinguish a nonpercolated AgNP layer above the CNF layer in the samples AC50 and AC150. In agreement with our previous studies,26,27 no preferential orientation of cellulose nanofibrils or bundles is observed in the CNF thin film (Figure 2b). It is important to note that the AgNPs form laterally elongated agglomerates due to surface diffusion in the AS50 and AC50 samples (Figure 2a, middle). However, the AgNP agglomerates assemble into circular ones due to recoalescence in the AS150 and AC150 samples (Figure 2a, bottom).
spray cycles, the average roughness values increase from $2.5 \pm 0.1$ to $3.8 \pm 0.2$ nm for the AC samples and $2.4 \pm 0.3$ to $3.6 \pm 0.4$ nm in the AM samples, whereas it increases linearly from $2.6 \pm 0.3$ to $8.0 \pm 0.5$ nm in the AS samples. This behavior is due to the fact that the CNF network favors a uniform AgNP assembly by sterically inhibiting AgNP agglomeration in the AC and AM samples, while the SiO$_2$ substrate leads to a relatively nonrestricted agglomeration of AgNPs within 150 spray cycles. The slight roughness variations between the AC and AM samples are due to the higher extent of AgNP embedding in the AM samples compared to the AC samples at the same number of spray cycles. Thus, the roughness will be less affected by spray deposition in the case of the AM samples.

To investigate the influence of CNFs on the agglomeration of AgNPs, three line cuts with a length of 1 μm are analyzed for each sample (Figure S3). Peaks of roughly $35 \pm 10$ nm appear for all samples, which correspond to the diameter of an individual AgNP. Variations in height values above 40 nm suggest the existence of Ag nanostructures with different agglomeration sizes. Figure S3a shows that the height of the main peaks of the AS10, AS50, AS100, and AS150 samples are $28 \pm 3$, $33 \pm 6$, $48 \pm 11$, and $76 \pm 23$ nm, respectively. The peak height increases with increasing number of AgNP spray cycles, which might due to that the newly deposited AgNP predominantly anchor to the existing agglomerates and assemble into larger ones. Furthermore, the average peak-to-peak distance drops from $350 \pm 270$ nm in the AS10 sample to $172 \pm 130$ nm in the AS150 sample. The increase in height and decrease in the peak-to-peak distance of AgNP agglomerates suggests a nonrestrictive agglomeration pattern of AgNPs in the AS samples.

In the AC samples, both AgNP agglomerates and individual AgNPs are well distributed on the CNF layer (Figure 2a, middle). As the number of spray cycles increased from 10 to 150, we observe an increase in the peak height from $30 \pm 9$ to $48 \pm 19$ nm and a relatively constant peak width of $130 \pm 25$ nm (Figure S3b). An explanation for these changes is that the newly deposited AgNP solution partially dissolves the previously formed AgNP agglomerates, and the detached AgNPs penetrate into the CNF substrate in the AC samples, while the dissolved agglomerates recoalesce and reassemble on the SiO$_2$ substrate in the AS samples. The agglomeration pattern of AgNPs in the AM samples is similar to the AC samples (Figure S3c). The height of AgNP agglomerates slightly increased from $36 \pm 4$ to $48 \pm 19$ nm, and the peak-to-peak distance drops from $256 \pm 43$ to $236 \pm 164$ nm as the number of spray cycles increases from 10 to 150. The lower height values in the AM samples compared to the AC samples can be attributed to the partial embedding of AgNP agglomerates within the CNF network. The larger distance in the AM samples in comparison to the AC samples is due to the 3D distribution of Ag nanostructures (including AgNP agglomerates and individual AgNPs) through the CNF network in the AM samples instead of 2D distribution in the AC samples.

The diverse morphologies of Ag nanostructures among the AS, AC, and AM samples suggest the existence of different patterns of AgNP self-assembly on smooth SiO$_2$. 

Figure 3. Horizontal line cuts of 2D GISAXS data of the (a) AS, (b) AC, and (c) AM samples at 10, 50, 100, and 150 spray cycles (details see Figure S5). The dashed lines present a fit to the data. The arrows guide the eye showing the peak evolution as the number of spray cycles increases. (d)–(i) Extracted spherical structural parameters for AgNPs. For the AC and AM samples, which contain CNFs, the cylindrical structures for CNFs and spherical structures for AgNPs are both fitted, and for comparison, only the structures attributed to AgNPs are shown. (Cylindrical structures attributed to CNFs are shown in Figure S8.) (d)–(f) show the center-to-center distance (noted as “distance” for simplification) between adjacent spherical Ag nanostructures and (g)–(i) show the radius of the Ag nanostructures, with $D_1, R_1, D_2, R_2$ corresponding to distance between and radius of AgNP agglomerates and individual AgNPs, respectively.
substrates and on/within the CNF thin film. CNFs not only provide a network structure to restrict AgNP agglomeration but also promote partial dissolution of AgNP agglomerates to form a smoother surface.

**Layer Morphology.** To characterize the layer morphology and self-assembly of AgNPs at the nanoscale, GIXAS measurements are performed for the spray-deposited AS, AC, and AM samples at 10, 50, 100, and 150 spray cycles. 2D GIXAS data are shown in Figure S4. Vertical line cuts (off-centered cuts) along the q_x direction at an offset of 0.03 nm\(^{-1}\), and horizontal line cuts along the q_y direction at the Yoneda peak position were performed (Figure S5) to extract the structural information perpendicular and parallel to the surface, respectively.

The comparison of vertical off-centered line cuts of the AS, AC, and AM samples at different spray cycles is shown in Figure S6. Qualitatively, the larger peak intensity of the AC10 than the AS10 sample is related to a higher background roughness of CNF than the AgNP layer at the early stage of spray-coating. However, after 50 spray cycles, the roughness of the AC samples becomes lower than that of the AS samples, which may suggest a lower agglomeration rate of AgNPs on CNF substrates than SiO_2 substrates. Another important factor is the partial embedding of AgNP agglomerates into the CNF layer, which is consistent with the analysis from AFM measurements. The peak intensities from 10 to 150 spray cycles are nearly consistent for the AC and AM samples. The similar trends of roughness evolution between the AM and AC samples can be rationalized by the important role of the network structure of CNFs in AgNP agglomeration. The relatively stable intensities in the AM samples indicate both the restricted agglomeration of AgNPs by the surrounding CNF matrix and a constant roughness of the spray-coated CNFs at different deposited thickness. The higher peak intensity of the AM100 than the AC100 sample is due to the lower content of CNFs in the AM samples than in the AC samples. Therefore, AgNP agglomerates could not be fully covered by the CNF matrix. The lower roughness of the AM150 than the AC150 samples may attribute to the smaller size of AgNP agglomerates, or more probably the higher embedding rate of AgNP agglomerates in CNFs within the AM samples.

In horizontal direction, two broad smeared peaks are found in the AS, AC, and AM samples, indicating the presence of two Ag nanostructures with different sizes (Figure 3a–c). In the AS samples, the peak at q_x ≈ 0.04 nm\(^{-1}\) increases and shifts toward lower values as deposition proceeds, and this is related to the size increase of a large nanostructure. We deduce that this signal originates from AgNP agglomerates. However, the peak at higher q_x values (q_x ≈ 0.21 nm\(^{-1}\)) remains nearly unchanged in position and becomes stronger with increasing number of spray cycles. This feature corresponds to the center-to-center distance between individual AgNPs. With increasing AgNP deposition in the AC samples, the scattering intensity increases primarily at higher q_x values in which the amplitude increase at q_x ≈ 0.21 nm\(^{-1}\) implies that individual AgNPs become closer in distance (Figure 3b). The peak at q_y ≈ 0.04 nm\(^{-1}\) slightly enhances and shifts to higher q_y values, suggesting that AgNP agglomerates become closer in distance and slightly decrease in radius (as revealed by the GIXAS fits in the next part, see Figure 3e,h). It is important to note that, different from AFM measurements, where a higher AgNP coverage leads to a weaker CNF signal, GIXAS is a probe that monitors the morphology both, in parallel and vertical directions. Therefore, the intensity of the CNF peaks almost does not change in the AC samples with increasing number of spray cycles as the X-ray beam penetrates the full composite film. Similar to the AS and AC samples, two peaks at q_y ≈ 0.21 nm\(^{-1}\) and q_y ≈ 0.04 nm\(^{-1}\) exist in the AM samples, corresponding to individual AgNPs and AgNP agglomerates, respectively (Figure 3c). Different from the AC samples, only a slight increase in the intensity of both the two peaks with a slight shift to lower q_y values is observed in the AM samples, indicating that the radius of AgNP agglomerates and individual AgNPs remain nearly constant regardless of the number of spray cycles and the simultaneous existence of an increasing amount of large and small structures from both AgNPs and CNFs in the AM samples.

To analyze the GIXAS data based on real-space morphological features, we fit the horizontal line cuts with a model assuming cylindrical shapes for CNF-related nanostructures and spherical shapes for AgNP-related nanostructures. The used GIXAS fit model has been proven by literature. The radius R and center-to-center distance D of these model shapes (cylinders and spheres) were varied in the fit. This model enables us to directly compare the parameters of the fitted nanostructures between GIXAS and AFM measurements. Table S1 introduces the parameters involved in the GIXAS fit. Figure 3d–i shows the fitted R and D values of the AS, AC, and AM samples. In the AS10 sample, AgNP agglomerates with R_1 = 65 ± 5 nm in a distance of D_1 = 240 ± 10 nm and individual AgNPs of R_2 = 15.0 ± 1.0 nm in a distance of D_2 = 50 ± 10 nm are found. In the AS150 sample, the agglomerates show R_1 = 90.0 ± 1.0 nm in a distance of D_1 = 190.0 ± 1.0 nm, and individual AgNPs show R_2 = 15.0 ± 0.5 nm in a distance of D_2 = 50 ± 10 nm (Figure 3d,g). Both the amplitude of AgNP agglomerates and individual AgNPs increase with continuous deposition (Figure S7), indicating that individual AgNPs increasingly contribute to the self-assembly of AgNP agglomerates, and existing AgNP agglomerates become the nuclei for adsorption of newly deposited AgNPs as spray-coating proceeds in the AS samples. Due to the complex system of AgNP–CNF nanocomposites, we fitted the CNF network before fitting AgNPs in AC and AM samples. Three cylindrical structures are identified in CNF thin films, with R_c1 = 0.0 ± 0 nm, R_c2 = 11 ± 3 nm, and R_c3 = 2.1 ± 1.0 nm and D_c1 = 73.0 ± 1.0 nm, D_c2 = 75.0 ± 1.0 nm, and D_c3 = 10 ± 3 nm (Figure S8), respectively, which agrees well with our previous results. This enables us to extract the Ag nanostructures on and within the CNF network. Based on these parameters and keeping them constant, we added the AgNP fits to retrieve their radii and distances. This reduces the number of free parameters and increases reliability of the fit. In case of the AC samples, the radius of AgNP agglomerates (R_1) slightly decreases from 90 ± 3 to 80 ± 2 nm, which demonstrates the deduced effect of partial dissolution of AgNP agglomerates from AFM measurements. The smaller radius of AgNP agglomerates in the AC than the AS samples may due to the hindering effect of the network structure of CNFs on coalescence of individual AgNPs (Figure 3e,h). Similarly, AgNP agglomerates in the AM10 sample show R_1 = 95.0 ± 1.0 nm and D_1 = 270 ± 5 nm, while in the AM150 sample, AgNP agglomerates display a radius of R_1 = 80.0 ± 1.0 nm with a distance of D_1 = 180.0 ± 1.0 nm (Figure 3f,i). Since Ag nanostructures are mainly distributed at the AgNP–CNF interface in the AC samples where partial dissolution of AgNP agglomerates primarily occurs, the dissolution effect is stronger
in the AC than in the AM samples, where Ag nanostructures are distributed through the thickness direction of the film. Therefore, the radius of AgNP agglomerates is slightly higher in the AM than in the AC samples. The distance between individual AgNPs decreases as spray-coating proceeds in the AC and AM samples, indicating a more homogeneous distribution of AgNPs on/within CNFs than on SiO₂ substrates. The GISAXS fit results generally corroborate the deduced morphology of Ag nanostructures from the AFM analysis.

Crystallinity Analysis. GIWAXS measurements are conducted to investigate the influence of the CNF network on the crystallinity of the AgNPs. Differences in the scattering patterns and relative intensities are observed among the AS, AC, and AM samples at the same number of spray cycles (Figure 4a and Figure S9a,b). Generally, two scattering peaks are observed at around \( q = 2.6 \text{ Å}^{-1} \) and \( q = 3.1 \text{ Å}^{-1} \), corresponding to \((111)\) and \((200)\) planes of the face centered cubic (fcc) structure of AgNP, respectively.\(^{35,46}\) \( q \) represents the total wave vector containing the in-plane \( q_x, q_y \) component and out-of-plane \( q_z \) component.

To probe the evolution of the crystallinity of AgNPs during spray-coating, the integrated intensity of the peaks as a function of \( q \) is extracted from the 2D GIWAXS profiles by radial integrations (Figure S10). Two scattering peaks around \( q = 2.6 \text{ Å}^{-1} \) and \( q = 3.1 \text{ Å}^{-1} \) (Figure 4b and Figure S9c,d) confirm the existence of the \((111)\) and \((200)\) planes of Ag nanocrystallites. For the AS, AC, and AM samples, the scattering intensity from the \((111)\) planes is stronger than that of the \((200)\) planes; therefore, only the \((111)\) signal (\( q = 2.6 \text{ Å}^{-1} \)) is used in the following crystallinity analysis. The relative intensity of the \((111)\) scattering peak increases with continuous spray-deposition in the AS, AC, and AM samples due to material gain (Figure 4b, Figure S9c,d). In addition to the scattering peaks of AgNPs, the peak at \( q = 1.4 \text{ Å}^{-1} \) in the AC and AM samples is identified, corresponding to the \((110)\) scattering plane of the CNFs. As expected, the intensity of the \((110)\) scattering peak of CNFs remains constant as the number of AgNP spray cycle increases in the AC samples, while it becomes stronger as the number of AgNP/CNF spray cycle increases in the AM samples, corresponding to the differential amount of CNFs between the AC and AM samples at the same number of spray cycles.

To further investigate the evolution of the \((111)\) scattering patterns of AgNPs, a Gaussian curve is fitted to the \( q \) plot in the range from \( 2.6 < q < 3.1 \text{ Å}^{-1} \) (Figure S11). The minimum crystalline size of AgNP is estimated from the full width at half maximum (FWHM) of the fitted \((111)\) scattering peak, deducing the instrumental resolution measured from LaB₆ via the adapted Debye–Scherrer formula for grazing-incidence scattering\(^{47,48}\) with a K-factor of 0.94. Within the experimental error, the minimum crystalline size of AgNPs remains constant around 2.4 ± 0.9 nm regardless of the increasing deposition amount of AgNPs or AgNP/CNF mixture (Figure 4c). Our results demonstrate that the morphology of the substrates and the amount of AgNPs or the AgNP/CNF mixture deposited have no impact on the crystallite size of AgNPs. This enables us to fabricate a homogenous AgNP/CNF film with a stable crystallinity by repetitive spray-coating.

Self-Assembly Model. Based on the comprehensive analyses of AFM, GISAXS and GIWAXS results, we summarize the morphologies of AgNPs at multiple scales (Figure 5a), the schematic structure of AgNP–CNF composites (Figure 5b), and identify three distinct self-assembly models of AgNPs in the AS, AC, and AM samples (Figure 5c). Random agglomeration predominates in the self-assembly process of AgNPs on the SiO₂ substrate. With continuous deposition, the AgNP agglomerates become larger in size and closer in distance. Therefore, the surface coverage increases, and the AgNP layer is coarsening. For the AC samples, the AgNP agglomerates are partially embedded into CNFs in the early stages of the deposition (as revealed by the distance between CNFs and the radius of AgNPs from the GISAXS fit) and begin to assemble on top of the CNF layer as deposition proceeds. This finding can be rationalized from the AFM analysis. It is observed that a small amount of AgNP agglomerates is inserted to the CNF layer, and the average distance between CNFs deduced from AFM (about 75 nm) is higher than the diameter of the individual AgNPs deduced from the GISAXS fit (about 30 nm). In the horizontal direction, the radius of AgNP agglomerates gradually decreases when spray-coating continues via partial dissolution, indicating the crucial role of the substrate morphology on the self-assembly of the AgNPs (Figure 5c, left, middle). In the case of the AM samples, CNFs self-assemble simultaneously with the AgNPs due to the coexistence of van der Waals force between Ag–Ag and electrostatic Ag–CNF interactions (Figure 5b,c, right). Similar to the AC samples, agglomeration of the AgNPs is also affected by a combination of a spatial hindering effect and stronger partial dissolution effect of the CNF matrix than in the AC samples.
than AS150 suggest that the use of CNF substrate leads to a more hydrophilic surface.49 Furthermore, the water contact angles of AC and AM samples measured after three months of storing in ambient conditions are almost the same with that measured immediately after synthesis, suggesting an excellent stability of the AgNP/CNF films. Tailorwritable wettability26,50 is crucial for the functionalization of thin films with antifouling,51 detergent-free cleaning,52 or antifogging53 properties in biomedical and industrial applications.

UV/vis spectra of the AS, AC, and AM samples at 10, 50, 100, and 150 spray cycles are examined to study the influence of CNFs on the plasmonic properties of the AgNP layer. The transmission spectrum is recorded over a wavelength range from 200 to 1025 nm. Figure 6b and Figure S13 show the comparison of the relative transmissions of the AC, AS, and AM samples at different spray cycles. The spectra are smoothed to show the features of the LSPR peak of AgNP agglomeration. The LSPR peak of AgNP emerges at around 450 to 500 nm,54−58 which could be influenced by a combined effect from the surrounding medium, size, shape, and interparticle distance of Ag nanostructures. Therefore, we attribute the dip in the transmission UV/vis spectrum to the LSPR peak of AgNPs.59,60 The spectrum from 500 to 700 nm following the LSPR peak may originate from AgNP agglomerates. For the AS samples, the LSPR peak remains almost unchanged in the position when the spray cycle increased from 10 to 150. For the AC and AM samples, the LSPR peak is slightly blue-shifted from 443 to 424 nm and 462 to 436 nm, respectively, and the transmission decreases with the number of spray cycles, which could be related to the decrease in the center-to-center distance of the AgNP agglomerates or a variation in the dielectric environment. Based on these results, we propose that the CNF network contributes to a higher LSPR intensity in the AC and AM samples by providing a uniform distribution of the AgNPs with a smaller agglomerate size and interparticle distance at the nanoscale, which is promising for optical and catalytic applications.

The novelty of this work is two-fold; on the one hand, we use CNF both as a substrate and structural framework for AgNP deposition. This demonstrates the potential of CNF for versatile, tailorable, and homogeneous nanoparticle layer fabrication on the nanoscale. On the other hand, we obtained the AgNP/CNF film not only with layer-by-layer spray-coating61 (AC samples) but also by a one-step spray-coating process (AM samples), resulting in AgNP/CNF nano-composite films with similar morphological, wetting, and plasmonic properties. The mechanism of AgNP/CNF with higher hydrophilicity and plasmonic properties is due to a more homogeneous distribution of AgNPs with specific morphologies provided by the CNF network. This contributes to a system for fabrication of AgNP layers with defined nanostructures for tailorable optical, catalytic, and other applications. The nanostructures of the AgNP layer play an important role in the applications of AgNP-based thin films. Essential structural parameters of AgNPs include the variations in the thickness of the AgNP layer, the center-to-center distance between neighboring Ag nanostructures, and the radius of Ag nanostructures. Surface roughness, which correlates to the height variations of AgNP agglomerates in the perpendicular direction, is crucial for the wetting behavior of the AgNP layer. Therefore, AgNPs spray-coated onto (the AC samples) or within (the AM samples) the CNF thin film exhibit higher hydrophilicity than AgNPs sprayed on the smooth SiO2

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**Figure 5.** Schematic diagram showing the self-assembly of spray-coated AgNPs in the AS, AC, and AM samples. (a) Deduced Ag morphologies from macroscale to nanoscale. The diameter of the nanostructures in CNFs for comparison with the center-to-center distance. (b) Sketch of the morphology of AgNP−CNF composites. (c) Self-assembly of AgNPs in horizontal and perpendicular directions with increasing number of spray cycles from top and side views.

**Figure 6.** Applications of AgNP/CNF films. (a) Water contact angles of the AC, AS, and AM samples as a function of number of spray cycles. The black line shows the exemplary raw spectra for the AC150 sample.
substrate. Furthermore, a homogeneous AgNP layer will give excellent plasmonic properties, which could be applied for label-free chemical sensing\textsuperscript{66} and wearable SERS sensors.\textsuperscript{67} Therefore, the use of CNFs provides a scaffold for the AgNP deposition, leading to a homogeneous AgNP/CNF composite film with higher LSPR intensity compared to the AgNP/SiO\textsubscript{2} film. Another potential application of the fabricated AgNP/CNF films is the antibacterial textiles.\textsuperscript{25,65}

\section*{CONCLUSIONS}

We have developed a scalable approach to assemble highly homogeneous AgNP films by spray-coating of AgNPs onto and within the CNF network. Individual AgNPs are composed of multiple crystalline domains, and the size the crystalline domain is unaffected by the substrate morphology and spray-coating process. In the lateral direction, the combined influence of partial dissolution and hindering effects from the CNF matrix lead to a decrease in the radius and center-to-center distance between the AgNP agglomerates in the AgNP/CNF films. Only a slight increase in surface roughness of the AgNP/CNF films is observed during spray-coating. Three self-assembly models for (1) AgNPs deposited on SiO\textsubscript{2} substrate, (2) AgNPs deposited on CNF layer, and (3) the mixture of AgNP/CNF deposited on SiO\textsubscript{2} substrates are developed from the comprehensive structure analysis. Our study proposes a detailed understanding on the self-assembly of AgNPs on/within CNFs and provides a novel route to obtain homogeneous MNP distributions using CNFs as a universal substrate or matrix. The smooth and uniform distribution of AgNPs lead to a high hydrophilicity and LSPR intensity in the AgNP/CNF composite films, which shows potential applications as smart sensors for detection of biomacromolecules with tailorable roughness, morphology, and wettability.

\section*{ASSOCIATED CONTENT}

\begin{itemize}
  \item Supporting Information
    The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsanm.0c02819.

    Sketch of the scattering geometry of GISAXS and GIWAXS; AFM height analysis; 2D GISAXS data; GISAXS line cuts region, GISAXS off-center vertical line cuts, amplitude evolution deduced from GISAXS fits, and GISAXS fits of CNF; GISAXS fit parameters; GIWAXS data of the AS and AM samples; GIWAXS radial-integration region; water contact-angle droplet morphology, UV/vis spectra of AS, AC, and AM samples, and additional notes on sample preparation, AFM analysis, and GISAXS (PDF)

\end{itemize}

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\begin{itemize}
  \item Author Contributions
    The research has been designed by S.V.R., P.Z., and D.S. CNF and AgNP aqueous dispersions are provided by D.S. and A.P., respectively. Q.C., C.J.B., A.C., M.G., and M.S. conducted AFM, GISAXS, GIWAXS, and contact-angle measurements. C.J.B. conducted UV/vis measurements. Q.C., S.V.R., M.S., V.K., and P.M.B. performed data analysis with support and recommendations from all co-authors. The manuscript was written with contributions from all authors.

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Notes
The authors declare no competing financial interest.

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ABBREVIATIONS
AS, AgNP deposited on SiO₂
AC, AgNP/CNF LBL film
AM, AgNP/CNF mixture deposited on SiO₂
MNP, metallic nanoparticle
AFM, atomic force microscopy
AgNP, silver nanoparticle
CNF, cellulose nanofibril
DANFC, diahyde nanofibrillated cellulose
DPDAM, directly programmable data analysis kit
GIXS, grazing-incidence small-angle X-ray scattering
GISAXS, grazing-incidence X-ray scattering
GIXSGUI, grazing-incidence X-ray scattering graphical user interface
LBL, layer-by-layer
SDD, sample-to-detector distance

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