Supplementary material - Microstructure control of electrosprayed graphene oxide thin films

Light optical microscopy (LOM)

An Olympus BX60M microscope with a Toupcam U3CMOS08500KPA digital camera was used for the LOM imaging. The built-in light source of the microscope was set to the camera icon level. The images shown in Figure 2 of the main article are all taken with a 10x magnification. The Toupcam software was set to enable autoexposure with a target exposure of 80. The color temperature was set to 6503 with a tint of 1000. Default color adjustments were used (Hue 0, Saturation 128, Brightness 0, Contrast 0, Gamma 1.00.

Image analysis method

The images of the ESD samples were used to compare different methods in the image analysis. The SEM images used a magnification of 3.0 kX for the dip-deposited samples and 5.0 kX for the ESD-coated samples. The acceleration voltage was 3.00 kV, working distance 5.0 mm, and beam current 80.0 μA. Each image covers an area of 92.3 μm by 62.2 μm. We developed an image analysis MATLAB-script that is used to test 3 different methods of peak separation. The script analyzes the chosen image and gives the percentage coverage of 0, 1, 2, and 3+ layers of GO. The script detects the peaks using the build-in function findpeaks(). The findpeaks() parameters MinPeakProminence and MinPeakDistance are used to not find too many peaks. These parameters had to occasionally be changed when the histograms are different so that too many or too few peaks are not detected. The 3 separation methods are intensity cutoff, deconvolution of peaks, and peak height. The different methods are shown in Figure S1. The intensity cutoff method has previously been used to segment SEM-images of GO thin films (1), and finds the minimum values of the intensity between the found peaks. It uses those minimum point as the separator, shown as vertical red lines in Figure S1a. The number of pixels within each separated segment are then used to find the percentage coverage. Peak deconvolution is shown in Figure S1b. The peaks are assumed to be gaussian, and the script finds 4 peaks that fit the histogram. Areas under the peaks are used to calculate the percentage coverage. The peak height method compares the top intensity of each peak as found in Figure S1a.

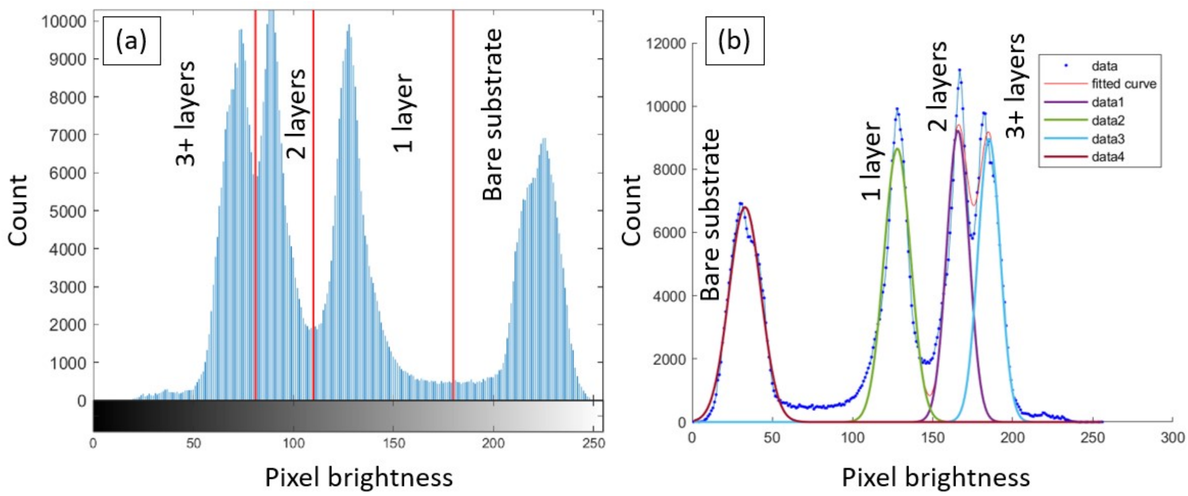

Figure S1: Example histograms of analysis methods used for separating number of GO layers. The numbers in the images denote the annotated number of GO layers. (a) The red vertical lines indicate the peak separations created from intensity cutoff. The top heights of the peaks are used for peak height results. (b) Deconvolution of data from the same sample. "data1" through "data4" indicate the 4 peaks found. Note that the x-axis is inverted for (b).

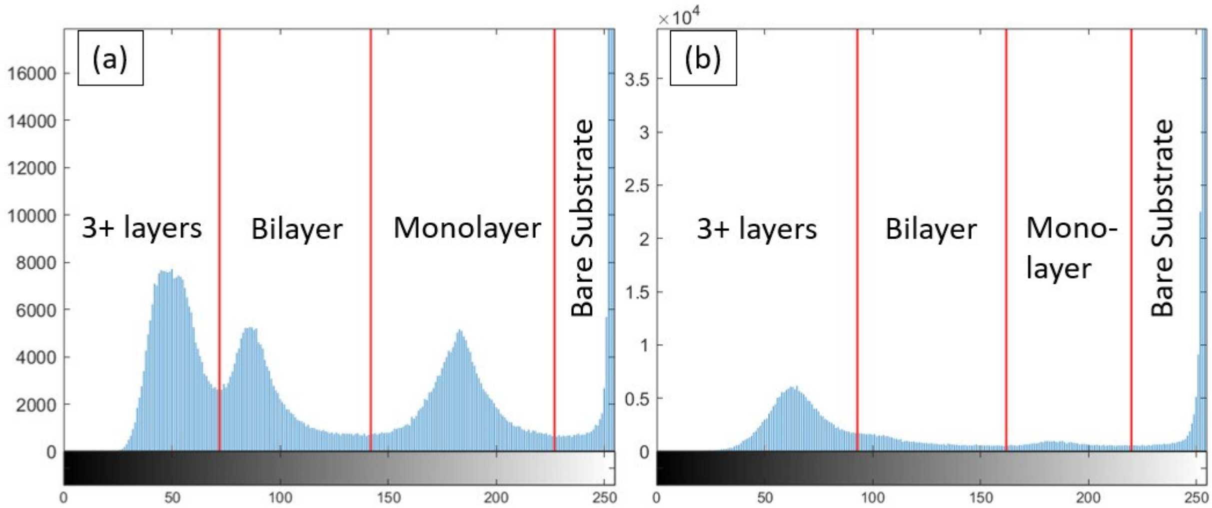

Figure S2: Examples of segmented histograms of ESD samples with a nozzle to substrate distance of (a) 2 mm, (b) 8 mm. A very low mono- and bilayered content in (b) makes segmentation a challenge. The MATLAB-script did find the peaks of histograms at 8 mm, but not at the higher distance of 12 mm.

Peak separation

Figure S3 shows the results of the different peak separation methods in the image analysis. There is an estimated difference of up to 5 percentage points between the methods.

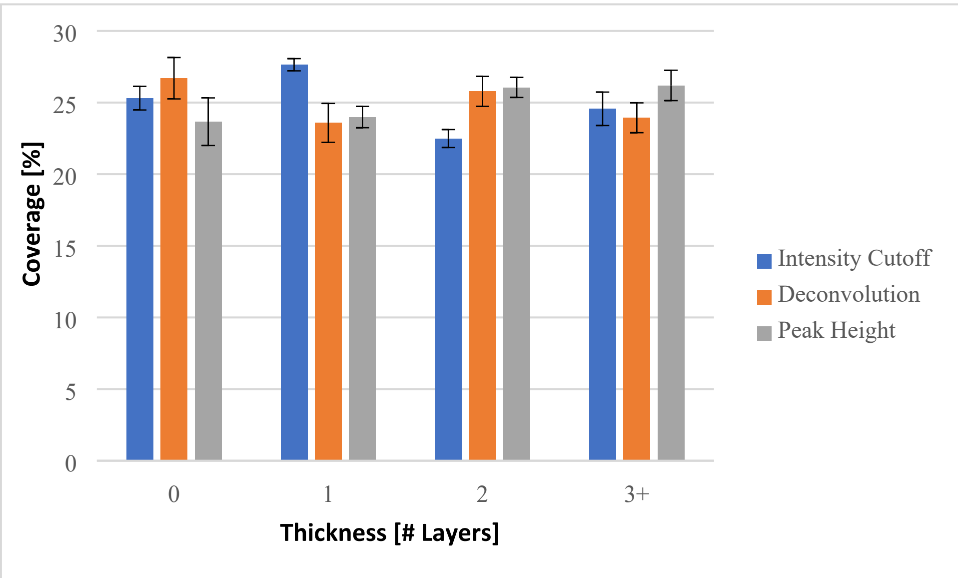

Figure S3: Comparing the coverage of ESD-samples depending on the three different analysis methods tested. The solid bars show the average of the 45 images of 5 samples, and the error bars show the 95% confidence intervals of the means.

The gaussian peaks are limited by the MATLAB-script and produce areas where the fitted curve deviates from the measured data, see Figure S4. The intensities between the peaks corresponding to SiO_2 background and 1 layers of GO is investigated in Figure S5. A small area of the image of a dip coated sample is shown in full (Figure S5a) and masked, using the built-in Image Segmenter app in MATLAB, to only show some of the pixels not accounted for between the 0 and 1 layer peaks (Figure S5c). By comparing (a) and (c) in Figure S5, we can see that the pixels between the peaks are located on the boundaries between the SiO_2 surface and GO coatings.

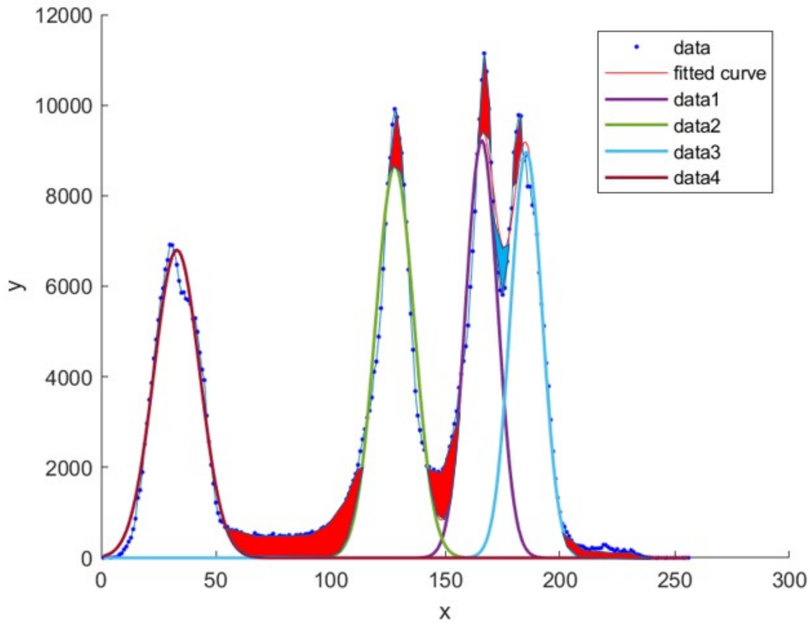

Figure S4: Histogram of pixel intensity values in a spray coated sample. Areas in red showing major segments not accounted for when deconvoluting, light blue is pixels counted but are not seen in the histogram. Note that the histogram intensities are inverted in this figure.

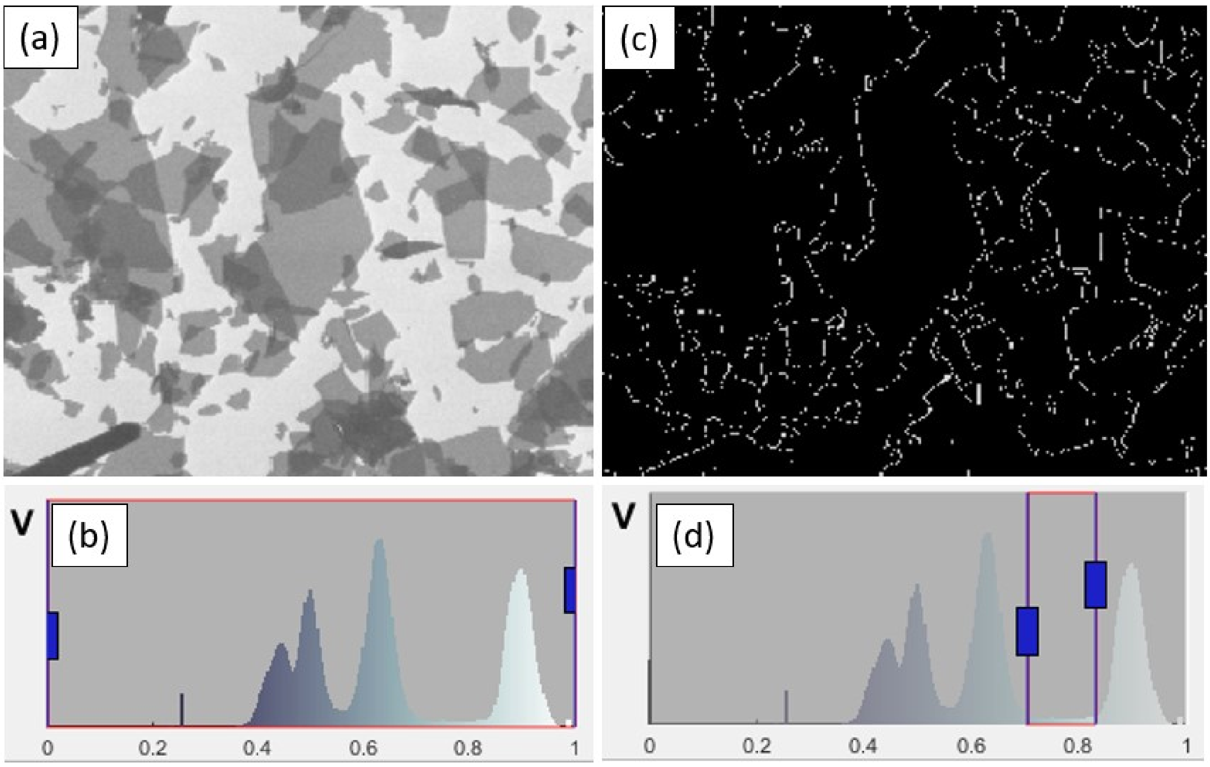

Figure S5: A small segment of a SEM image of a dip coated sample displaying (a, b) the whole intensity spectrum, (c, d) intensities between the peaks for the SiO_2 background and 1 layer of GO. The boxes in the histograms (b) and (d) decides the range of intensity pixels shown in (a) and (c) respectively.

Figure S6 shows the same example image of a dip coated sample with the approximately half of the background filtered out. This is done by intensity, so the brightest background is filtered out and shown in black. The brightest parts of the background are clustered mostly on the right side of the image and the areas tend to be sticking to the right of GO-flakes. The SiO_2 layer of the substrate is insulating, and can be causing charging effects in the SEM. It is possible that this explains the behavior in Figure S5. These effects could cause the peaks to not follow an expected gaussian peak distribution. Because of the poor fit using the fit() function from MATLAB on these peaks, the deconvolution method is not used throughout the main article of this work.

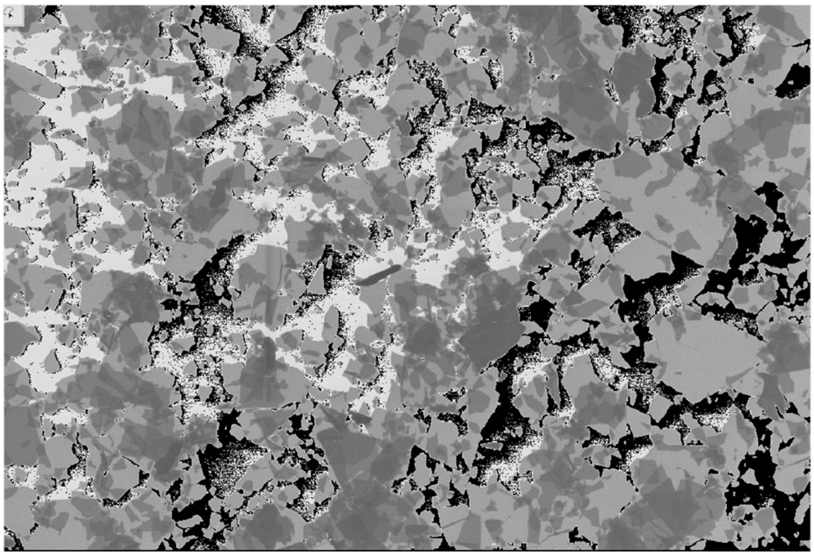

Figure S6: SEM image of a dip coated sample with the brighter half of the SiO_2 peak filtered out. Pixels with an intensity higher than the threshold are replaced with black pixels.

Figure S7 shows an example SEM image which has been segmented using the image analysis script with the intensity-cutoff method. Pre-processing of the image includes cropping the image to remove information bar and applying a 3x3 median filter through MATLAB.

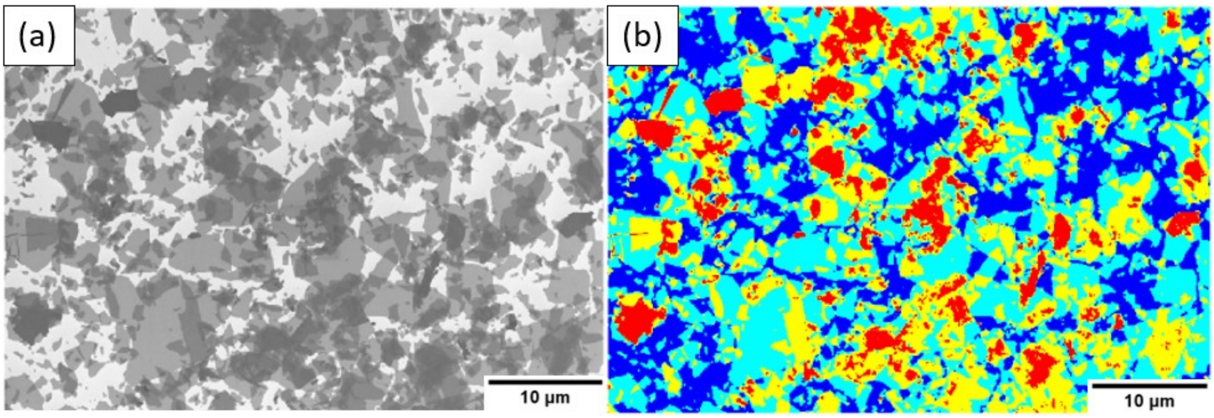

Figure S7: Sample SEM image segmented using the intensity cutoff method. (a) Cropped SEM image. (b) Segmented image using the intensity-cutoff method of the MATLAB-script that was used throughout this work. The color coding shows the number of GO-layers found for the pixel. Dark blue is bare substrate, teal is monolayered GO, yellow is bilayered GO, and red is 3 or more layers of GO.

Simulations

We created a script in MATLAB that randomly distributes “GO flakes” on a surface, and checks the statistical distribution of number of layers. The script creates individual flakes that are assigned a size, shape, position and rotation. These flakes are continuously created until a set average layer count is reached, typically from a Poisson distribution fit to experimental data.

The user sets a number of parameters that affects the results. The user chooses the size of the flakes by setting an average area in pixels and a 1-σ normal distribution of the sizes. Any flakes that the script creates with a negative size is set as having a size of 0 pixels. Flake eccentricity changes the shape of the flakes by changing the angles of the corners. An eccentricity value of 0 gives only square flakes, but can be changed to form rhombus flakes with a higher eccentricity. The chosen size and size distribution are valid for square flakes. The area of the flakes will decrease as the eccentricity of the flakes is increased, as the side length is kept constant. The user chooses the number of times the simulation is repeated.

The results are presented to the user by showing one example from the simulations. An image shows the simulated flakes on the surface by intensity, see Figure S8. A higher number of layers covering an area shows up as a darker intensity. Additionally, the statistical distribution from all simulated pixels are given as a histogram. The histogram also shows error bars if the number of simulations is greater than 1. The error bars signify 1-σ standard deviation. The most important simulation parameters are also shown in the figure shown to the user.

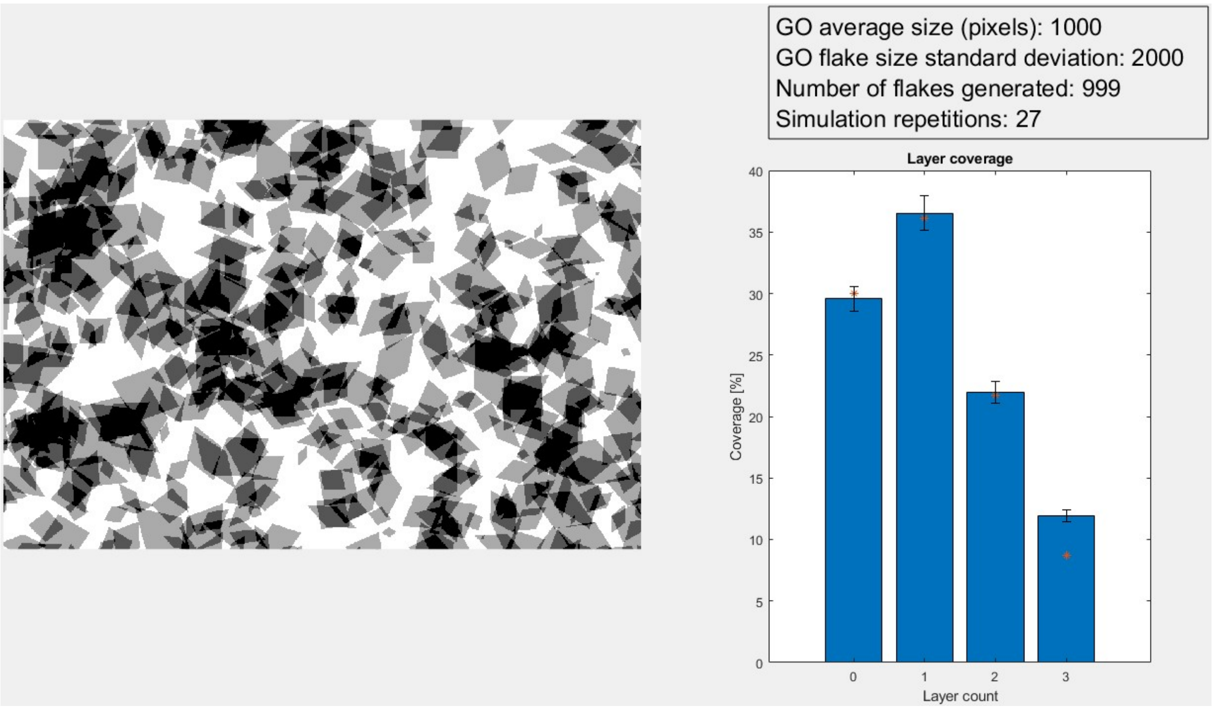

Figure S8: Simulation output as shown to the user. Here, a simulated coverage with an average layer count of 1.2. The flakes are seen as square to rhombus shapes, and the intensity corresponds to the number of overlapping flakes. A darker area means that there are more layers stacked up to 3+ layers. The white background has zero coverage and corresponds to bare substrate. The bar graph shows the area fractions of increasing overlapping layers. The "3" bar contains all layer counts 3 or higher in order to give the same information as the experimental data. The error bars show 1-σ standard deviation over 27 repeated simulations and the red stars show the Poisson distribution with the same λ-value (average layer count).

Simulation results

The simulation results give us a baseline of how a coating will look if the deposition is random. Figure S9 shows distributions of coating number of layers on the average number of layers between 1.2 up to 1.6. Included are indicators of Poisson-distribution with the expected value equal to the average number of layers. We can see that the simulation closely follows a Poisson distribution for all values. When we later compare the experimental data to a baseline, we consider Poisson distributions that are fitted to the data.

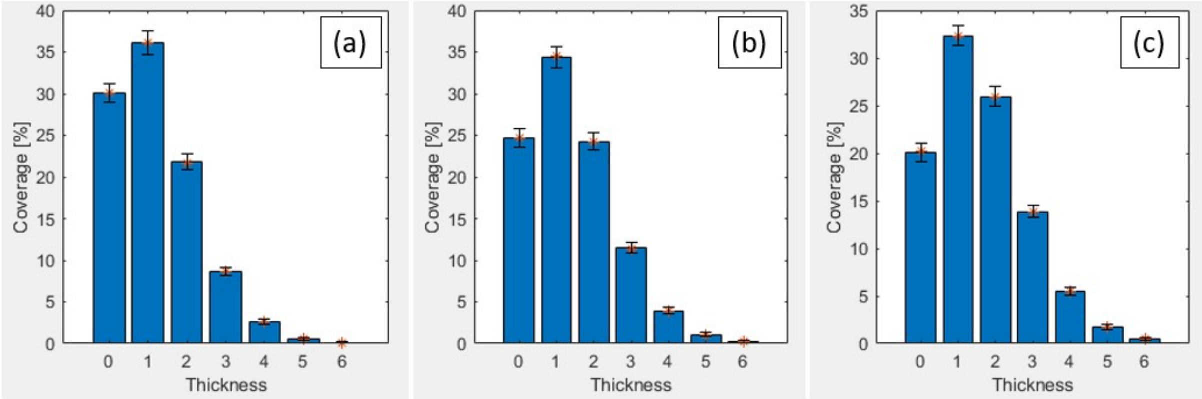

*Figure S9: Preliminary figure showing distribution of "GO" on a surface. Simulation repeated 100 times and a Poisson distribution with equal average layer thickness is shown in red * symbols. The average number of GO layers is changed between (a) 1.2 layers, (b) 1.4 layers, (c) 1.6 layers.*

Image analysis results

Figure S10 contains the compiled results from the image analysis script. Included are the experimental data as well as Poisson distributions. These Poisson distributions have been fitted to the experimental data using least-squares regression, meaning that the square of the difference between the experimental bars and Poisson bars in Figure S10 have been minimized. Then the average difference between the experimental bars and Poisson bars are presented in Figure 8a of the main article. We fit separate values of the Poisson distribution for each experimental data set so that we compare how randomly distributed the coatings are, even if the average coating thickness is different.

The error bars in the experimental values of Figure S10 show the standard deviation, and is compared in Figure 8b of the main article. The high standard deviation of ESD using a nozzle to substrate distance of 1 mm is explained by a high thickness variation in the coating. Figure S11 shows two extreme examples of this, with (a) is covered in a thicker coating of GO and (b) is mostly bare substrate.

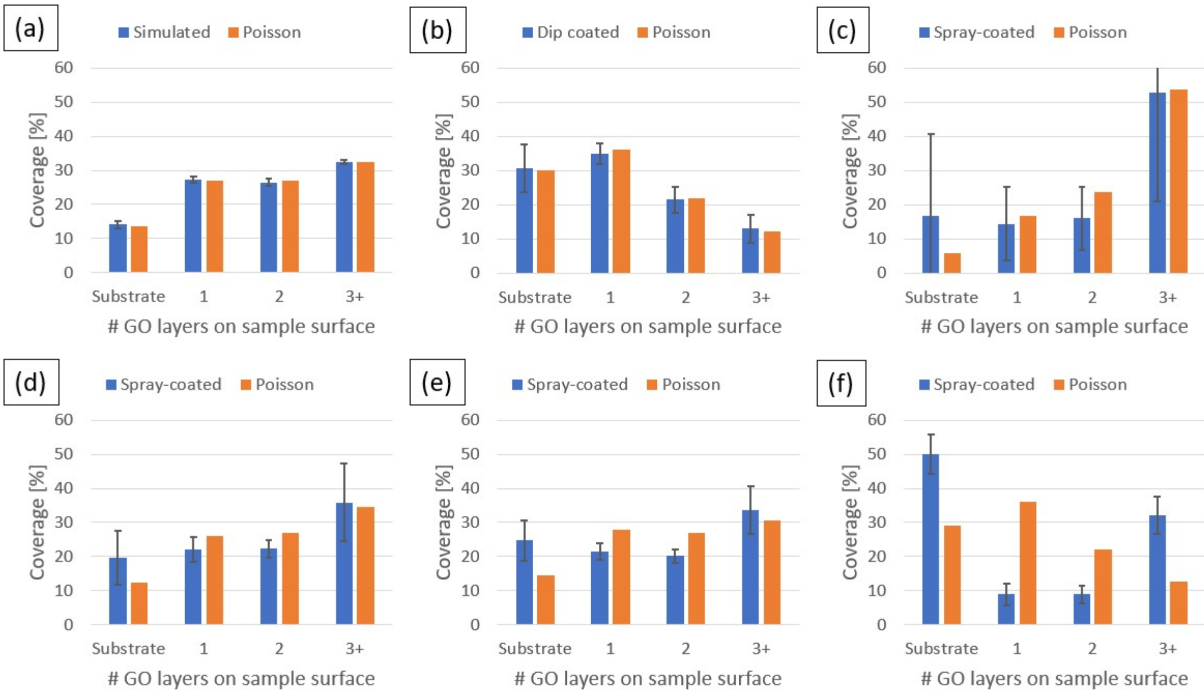

Figure S10: Comparisons between experimental results and Poisson distributions best fit to the data using least squares fitting. All error bars indicate 1-σ standard deviation of the values. (a) Results from ESD-simulations in MATLAB. (b) Dip coated substrates. (c-f) ESD coated substrates of increasing nozzle to substrate distance [in mm]: (c) 1, (d) 2, (e) 4, (f) 8.

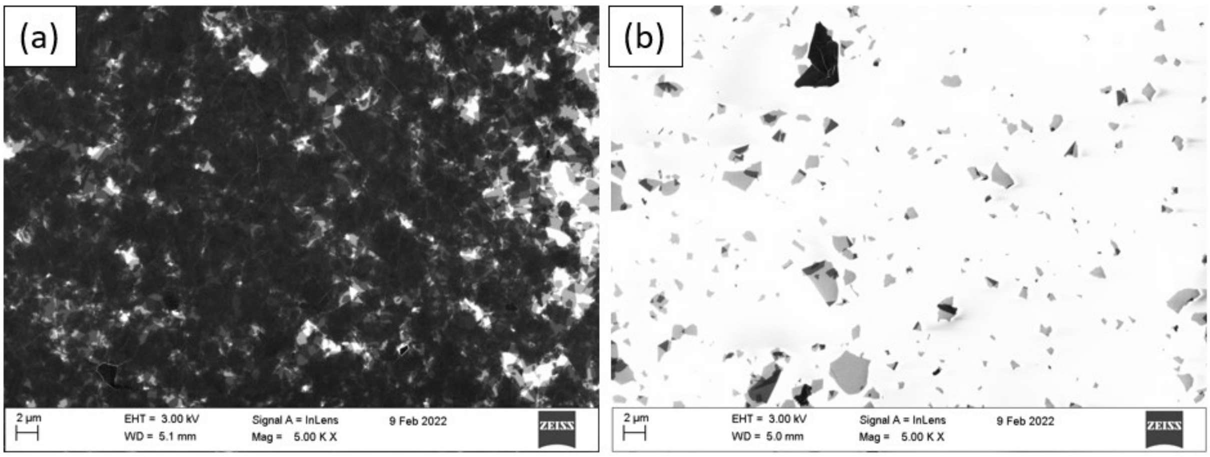

Figure S11: Images selected from the same sample ESD-coated with a substrate-nozzle distance of 1 mm. (a) Region with mostly 3+ layers of GO. (b) Region with mostly bare substrate.

References

1. Lee J, Zhou S, Chen J. Statistical Modeling and Analysis of k-Layer Coverage of Two-Dimensional Materials in Inkjet Printing Processes. Technometrics. 2020;63(3):410–20.