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Decoupled Control of Carbon Nanotube Forest Density and Diameter by Continuous-Feed Convective Assembly of Catalyst Particles

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Decoupled control of carbon nanotube forest density and diameter by continuous-feed convective assembly of catalyst particles

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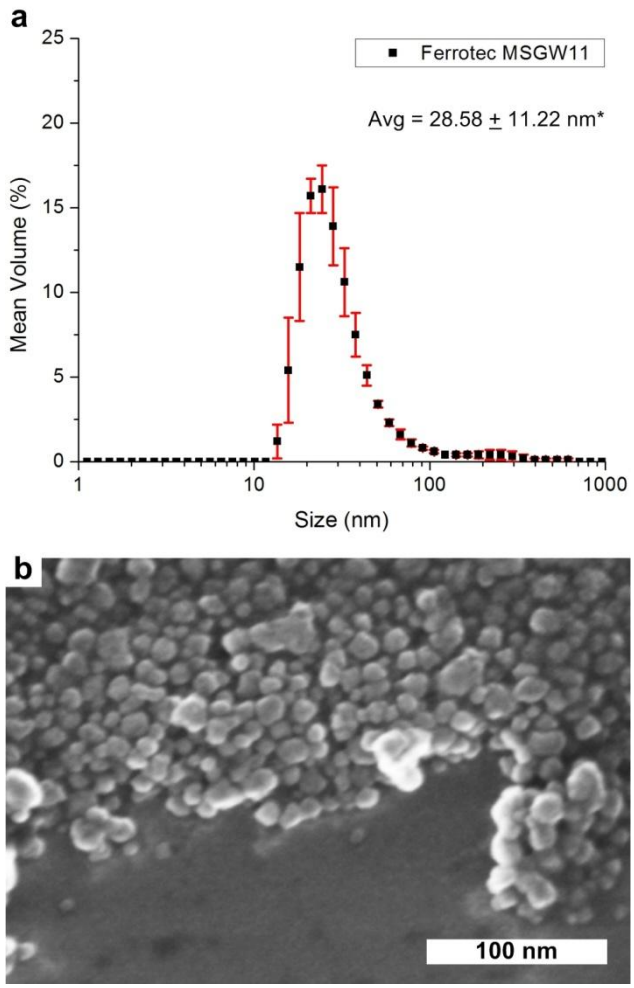

Figure S1. Particle size distribution and morphology for Ferrotec MSGW11 ferrofluid. a) DLS diameter distribution data from four separate measurements, and b) SEM of iron oxide particles from a 27.20 mg ml^{-1} solution blade casted at 25 µm s^{-1} on a substrate. * Average diameter values are based on size data ≤ 70nm (which did not significantly impact the measurement, nor did the larger particles get deposited on the substrates during blade casting).

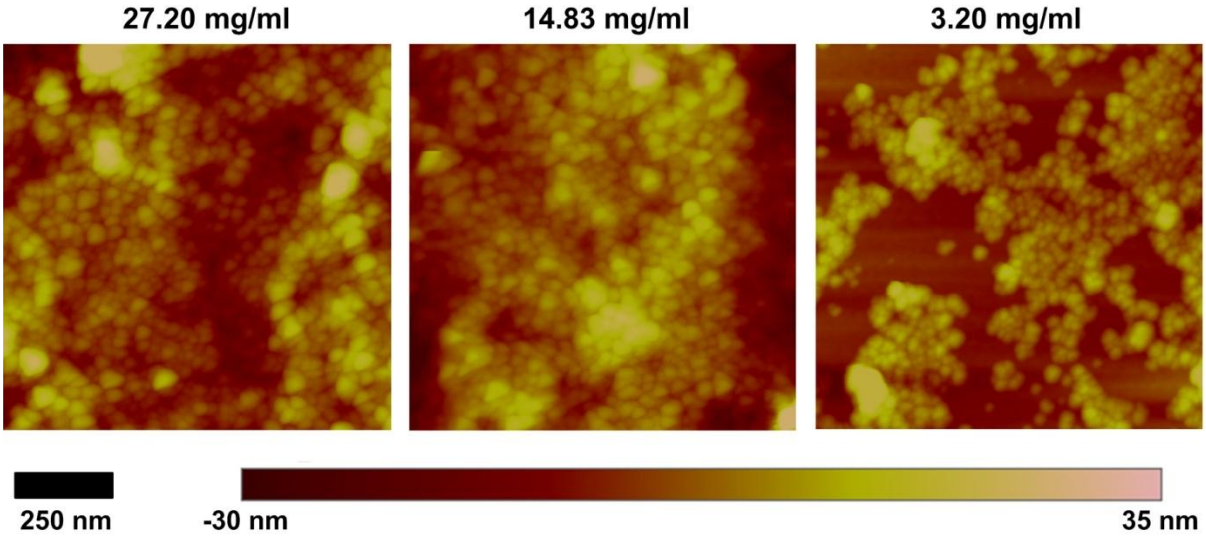

Figure S2. Iron oxide nanoparticle assembly using ferrofluid particle concentrations of 27.20, 14.83 and 3.20 mg ml^{-1} on non-treated substrates at 25 µm s^{-1}.

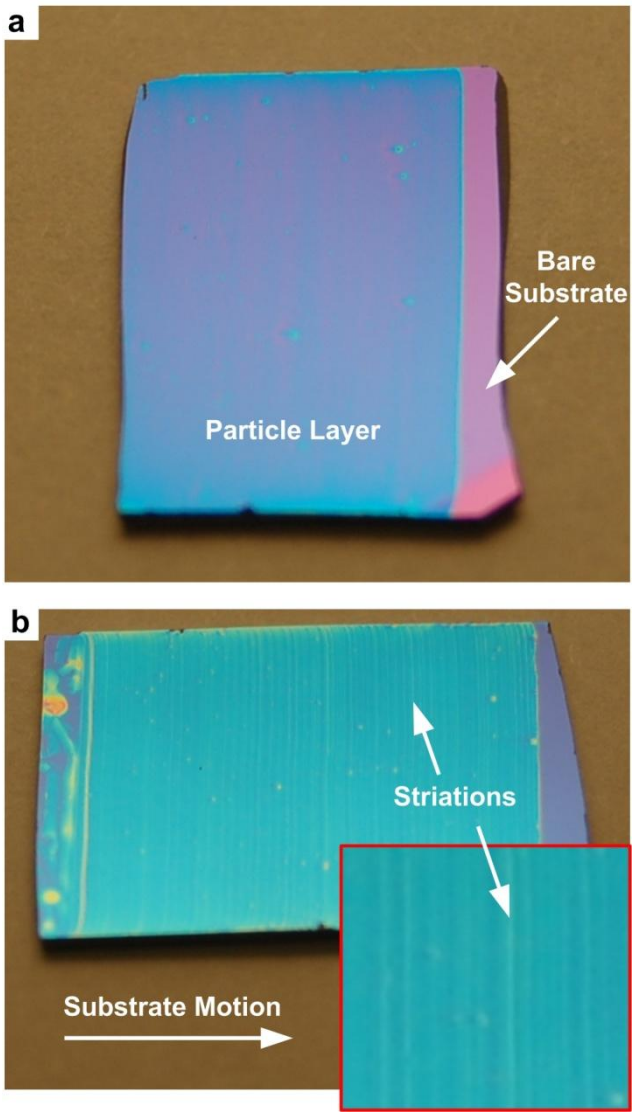

Figure S3. Optical particle layer uniformity as a result of blade casting parameters for Ferrotec MSGW11 ferrofluid. a) 3.20 mg ml^{-1} solution blade casted at 50 µm s^{-1} b) 27.20 mg ml^{-1} solution blade casted at 400 µm s^{-1} [inset: magnified image showing striations].

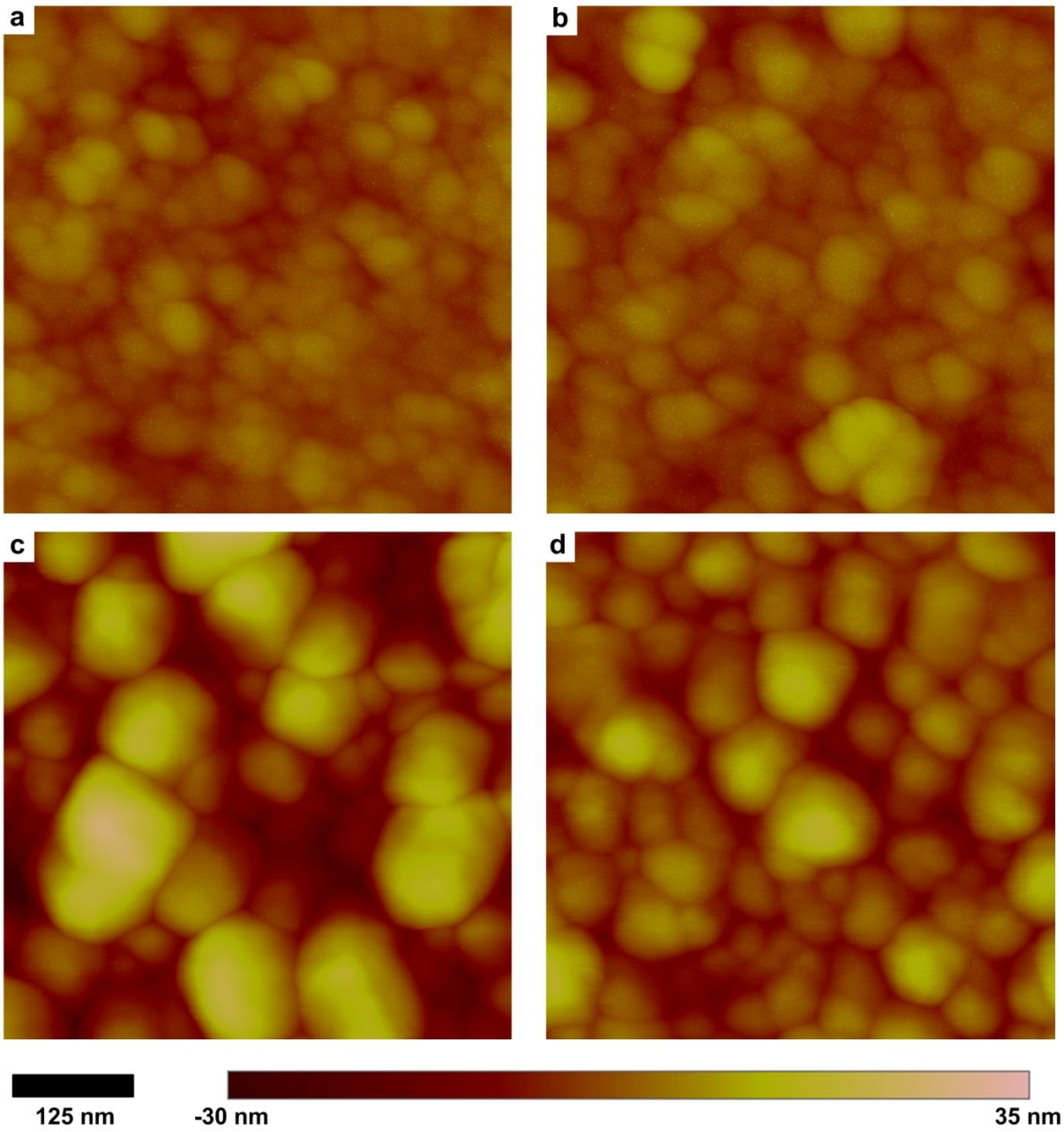

Figure S4. AFM comparison of pre and post annealed particles from a 27.20 mg ml^{-1} ferrofluid solution blade casted at 25µm s^{-1} on both plasma-treated and non-treated substrates. (a) As-cast non-treated substrate, (b) As-cast plasma-treated substrate, (c) Annealed non-treated substrate, and (d) Annealed plasma-treated substrate.

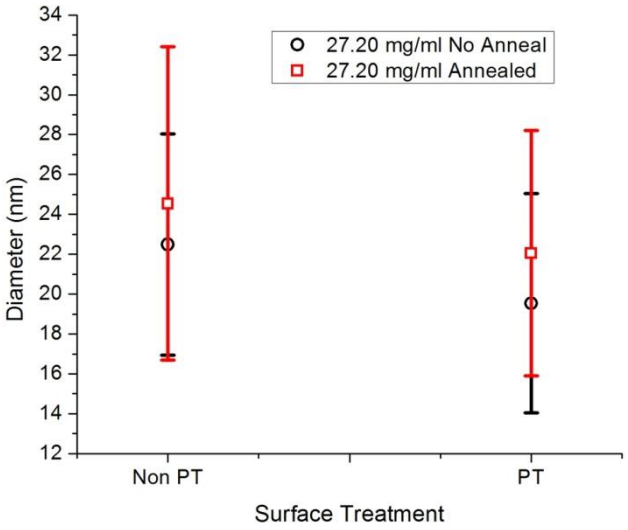

Figure S5. Analysis of iron oxide particle diameters pre and post annealing, on plasma-treated and non-treated substrates, blade casted from a 27.20 mg ml^{-1} solution at 25 µm s^{-1}.

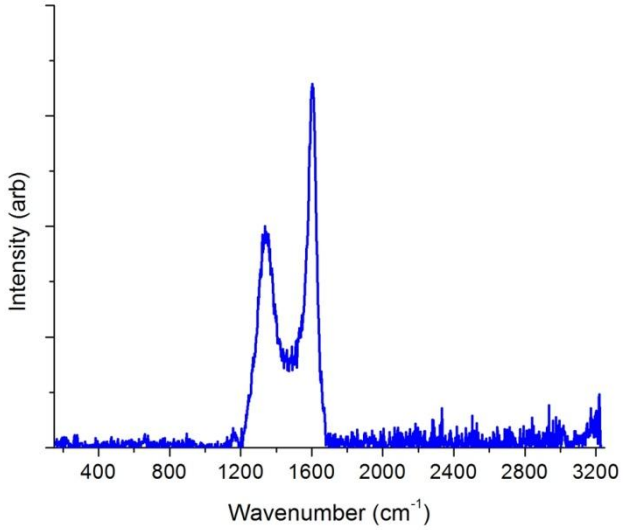

Figure S6. Raman spectroscopy of carbon "flake" structure illustrating graphitic G and D peaks.

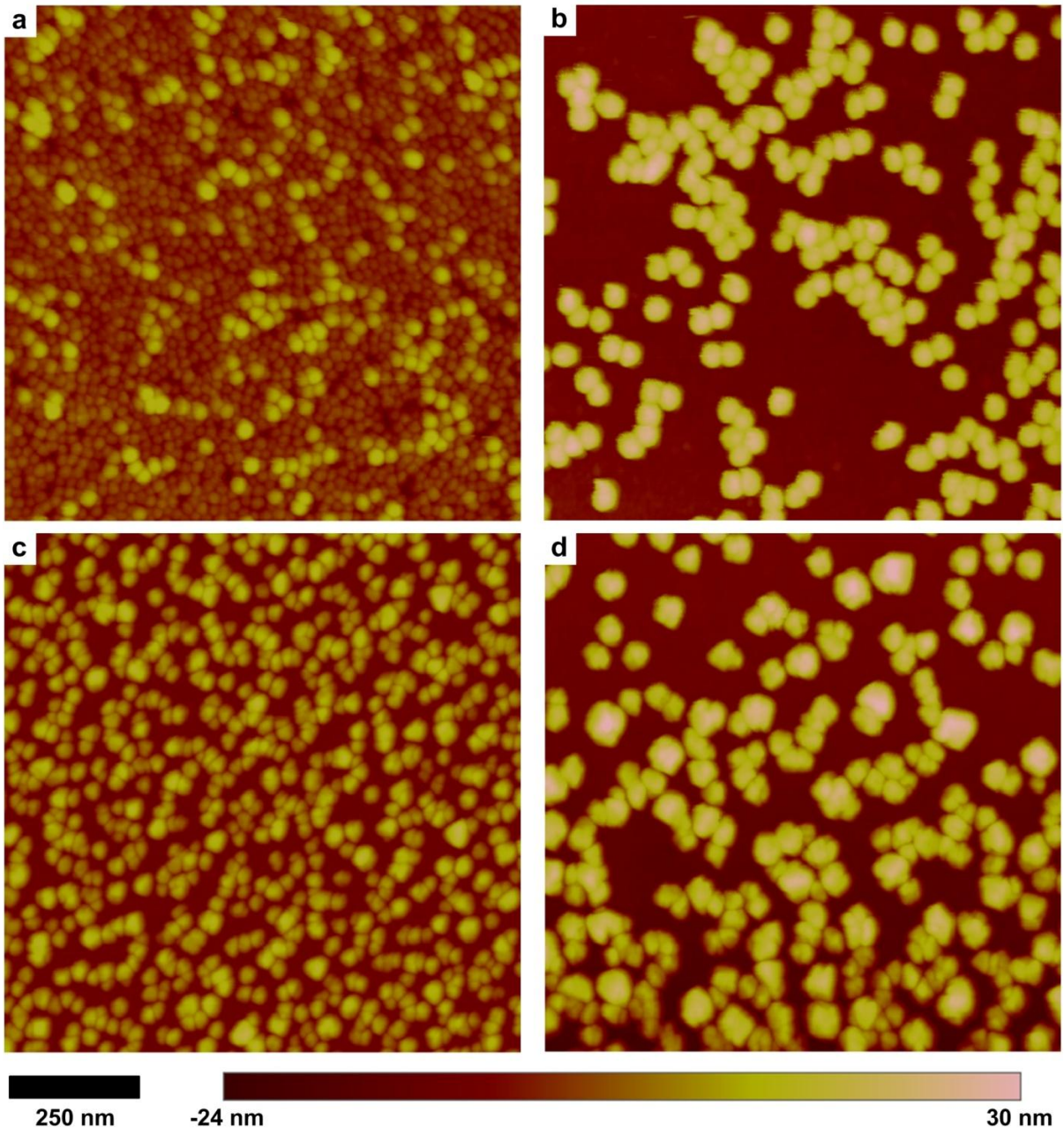

Figure S7. Coarsening of annealed particles from 3.20 mg ml^{-1} ferrofluid solutions blade casted at 25µm s^{-1}. (a) As-cast 20 nm particles, (b) As-cast 30 nm particles, (c) Annealed 20 nm particles, and (d) Annealed 30 nm particles.

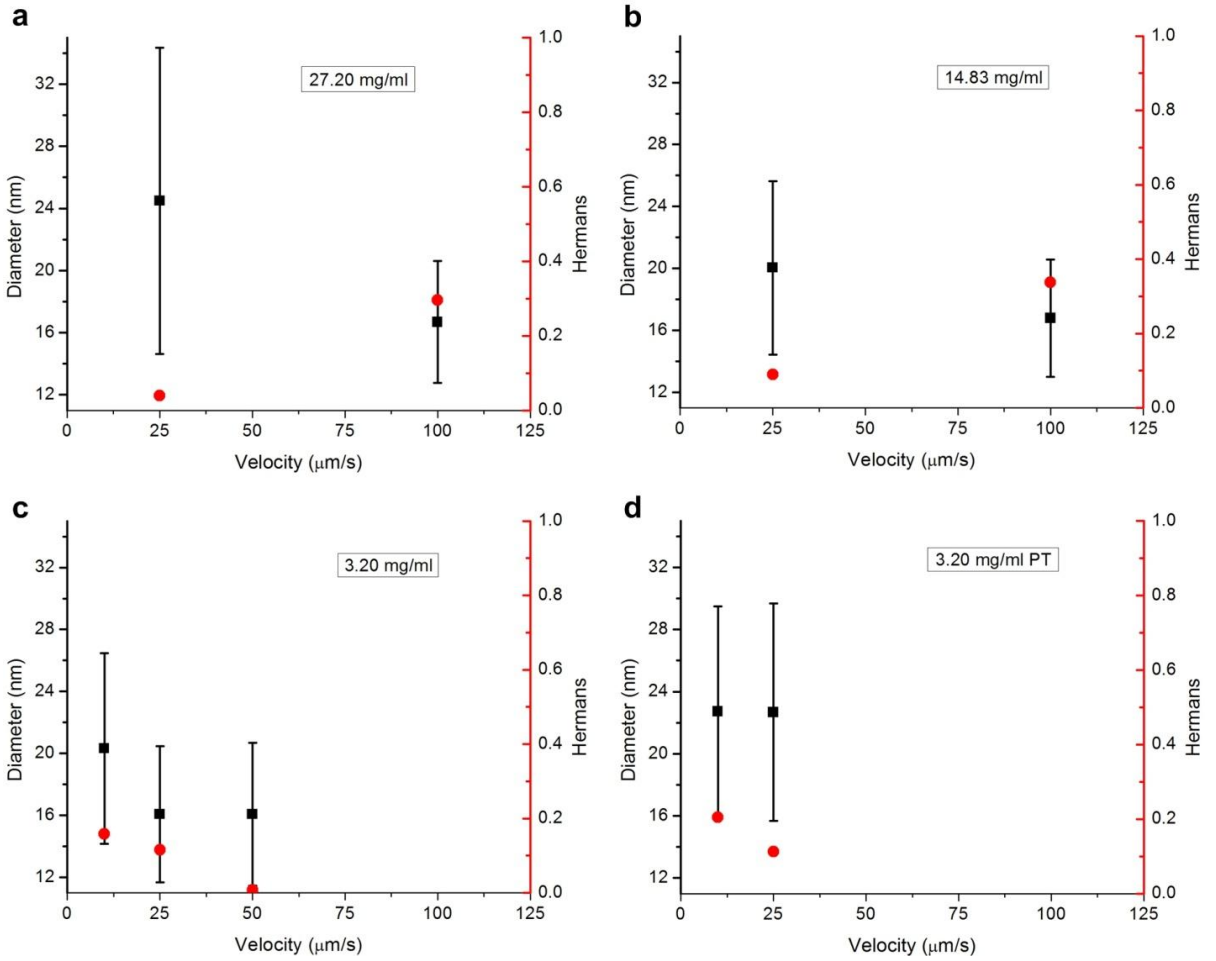

Figure S8. SAXS analysis of VACNT arrays grown with MSGW11 ferrofluid solutions of varying concentrations. (a) CNT diameters and Hermans parameter for vertical alignment of grown arrays from a 27.20 mg ml^{-1} solution, (b) CNT diameters and Hermans parameter for vertical alignment of grown arrays from a 14.83 mg ml^{-1} solution, (c) CNT diameters and Hermans parameter for vertical alignment of grown arrays from a 3.20 mg ml^{-1} solution, and (d) CNT diameters and Hermans parameter for vertical alignment of grown arrays from a 3.20 mg ml^{-1} solution blade casted on plasma-treated substrates.

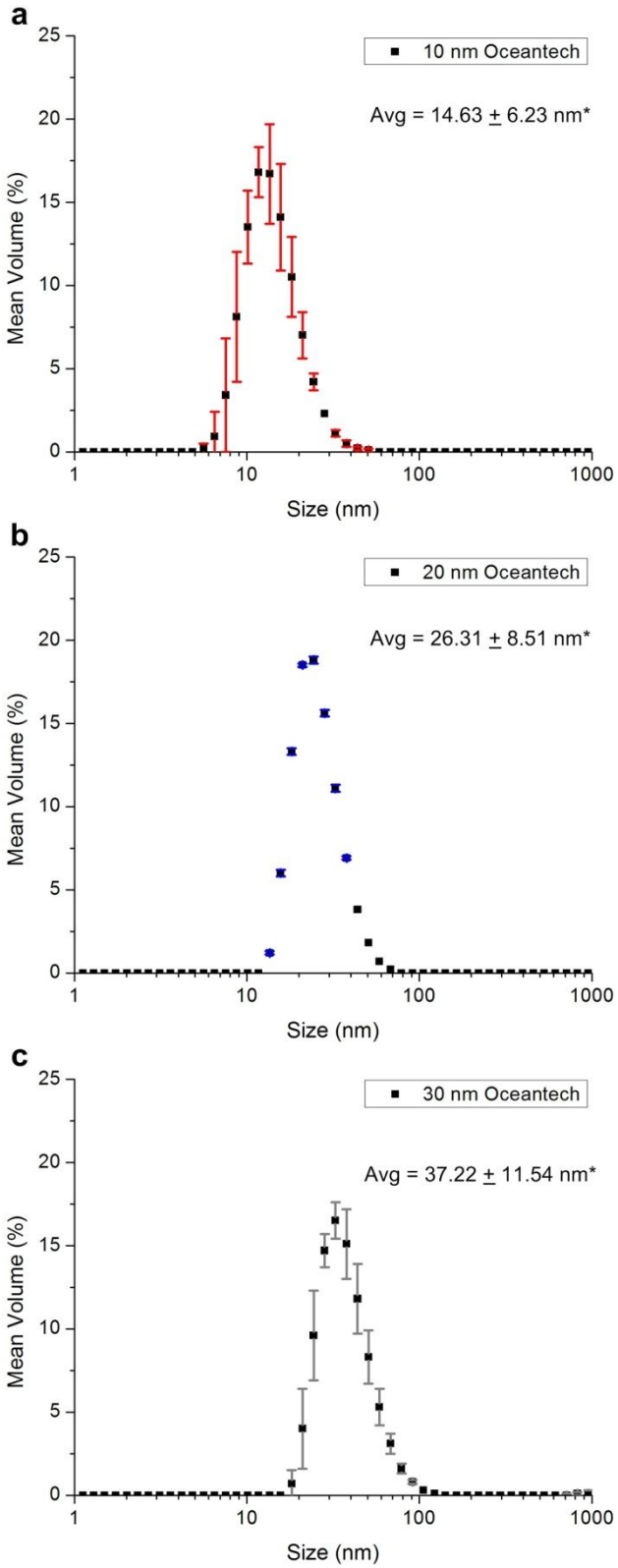

Figure S9. Particle size distributions and morphology for monodisperse Oceantech ferrofluid samples. Averaged DLS data for three runs per sample of (a) 10 nm iron oxide particles, (b) 20 nm iron oxide particles, and (c) 30 nm iron oxide particles. * Average diameter values are based on size data ≤ 70nm (which did not significantly impact the measurement, nor did the larger particles get deposited on the substrates during blade casting).

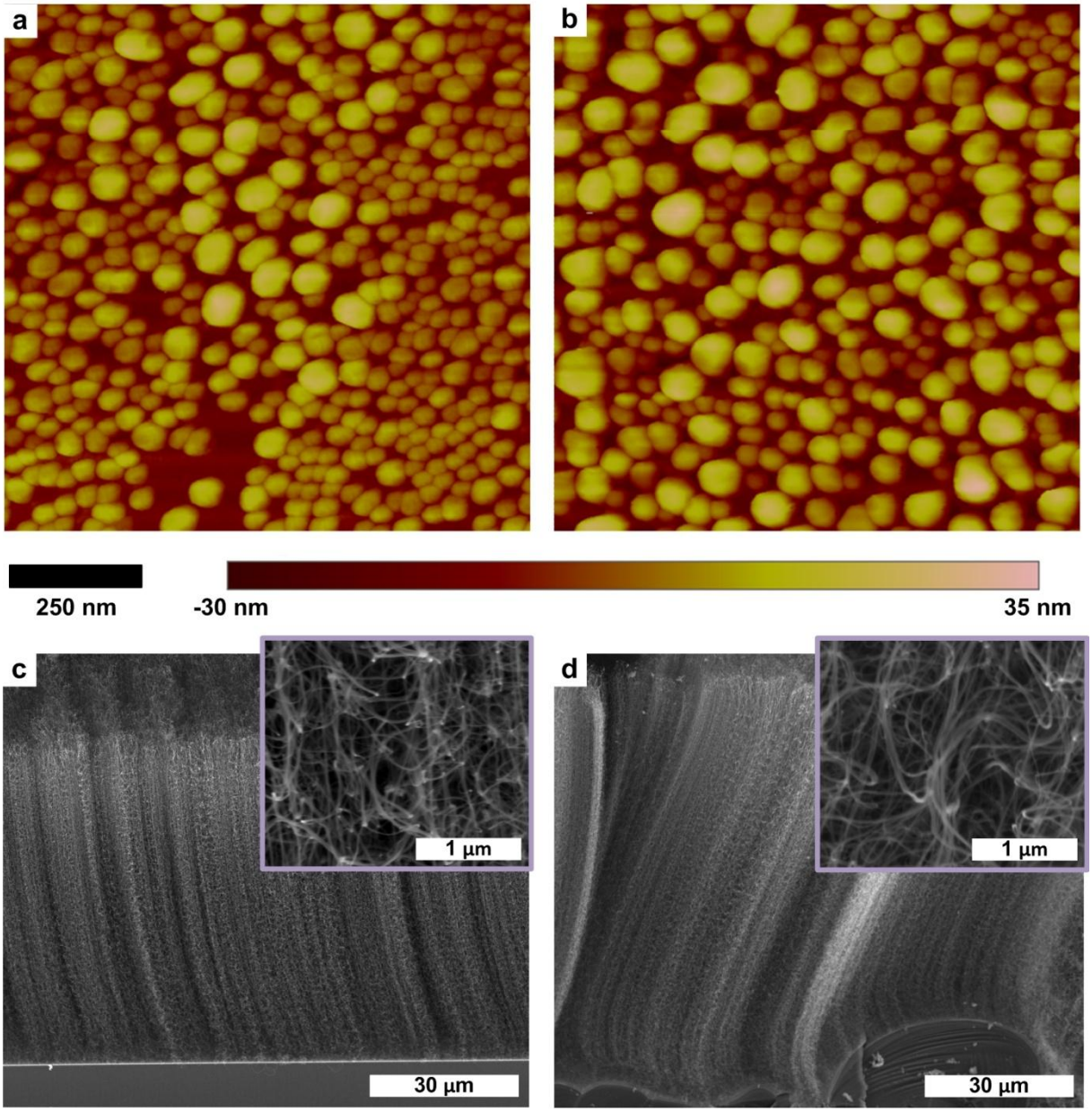

Figure S10. High-density monolayer of catalyst particles and corresponding CNT forest growth from the 30 nm nominal diameter particle solution (Fig. S9c). AFM images from annealed, blade-casted samples of (a) 3.20 mg ml^{-1} at 10 µm s^{-1}, and (b) 12.0 mg ml^{-1} at 25 µm s^{-1}. SEM images of CNT forest growth (c) and (d), from samples (a) and (b) respectively.

GOVERNING PRINCIPLES OF CONVECTIVE ASSEMBLY

The linear growth rate (v_c) of a particle monolayer, or multilayer, undergoing convective assembly is equal to:[1]

$$v_c = \frac{\beta l j_e \varphi}{h(1-\varepsilon)(1-\varphi)}, \quad (1)$$

where β is a coefficient of proportionality, j_e is the volumetric evaporation flux per unit area of the solvent, l is the evaporation length (see Supporting Information), φ is the particle volume fraction in the suspension, h is the thickness of the layer, and ε is the porosity of the array. In order to maintain a steady growth rate of a particle monolayer according to Equation 1, the relative motion speed between the blade and the substrate (v_r) must equal v_c. If $v_r > v_c$, a non-close-packed particle layer will be formed, whereas if $v_r < v_c$, multiple particle layers will be formed.

The coefficient of proportionality is defined as the ratio between the macroscopic mean velocity of the suspended particles (v_p)and that of the solvent molecules (v_s).

$$\beta = v_p / v_s \quad (2)$$

Stronger particle-particle interactions and particle-substrate interactions decrease the value of β, whereas non-adsorbing particles and dilute solutions increase β close to a value of 1. The evaporation length, l, is the ratio between the evaporation flux per unit length at the leading edge (J_{evap}) and j_e.

$$l = J_{evap} / j_e \quad (3)$$

Both J_{evap} and j_e are dependent on the local surrounding conditions illustrated by the Langmuir equation:

$$\frac{dM}{dt} = (p_v - p_p)\sqrt{\frac{m}{2\pi RT}} \quad (4)$$

where p_v is the vapor pressure of the solvent, p_p is the partial pressure of the solvent in the local atmosphere, m is the mass of a single solvent molecule, R is the ideal gas constant and T is the temperature. Dividing the Langmuir equation by the density of the solvent yields j_e.

$$j_e = \left(\frac{dM}{dt}\right)/\rho \quad (5)$$

As temperature increases, p_v increases, increasing the evaporation flux based on the Clausius-Clapeyron relation and results in an increased evaporation flux. Additionally, increases in the relative humidity of the surrounding air limits the rate at which the solvent molecules can be incorporated into the local atmosphere, which also increases p_p if the solvent is water. The use of Equation 2 has been shown to be valid for particles with diameters down to 79 nm, however, the mechanism of assembly with smaller particles still applies. While functionalized particles on the order of 6 - 11 nm have been shown to include island formation at the air-liquid interface prior to being pinned to the substrate,[2,3] the non-functionalized particles used in this study did not display the formation of islands at the air-liquid interface.

CALCULATION OF CNT NUMBER DENSITY

From the SAXS data, the arithmetic mean of the lognormal distribution of CNT diameter (D_O) within the forest, and the average wall thickness (t) of the CNTs are used to calculate the number of walls (n) for the multi-walled CNTs, assuming a wall spacing equal to the interplanar spacing of graphite (0.34 nm)

$$n = \frac{D_O - t}{0.34}, \tag{6}$$

where D_O and t are in nm. The total distance around the sum of the circumferences of each CNT wall is calculated next

$$C = \sum_{x=0}^{n-1} \pi\left(D_0 - 0.68x\right) \tag{7}$$

The height of the CNT forest (h) measured from SEM imagery, is then divided by the number of SAXS measurements collected over the forest height (s) to obtain the height of a single slice of the forest

$$\Delta h = \frac{h}{s} \tag{8}$$

Taking CNT tortuosity into account, the average length of the CNTs (L) are calculated using Δh from Equation 8 and the Hermans orientation parameter (H) that was obtained for each slice of the CNT forest via SAXS

$$L = \sum_{x=1}^{s} (\Delta h)\cos\left(\cos^{-1}\sqrt{\frac{2H_x + 1}{3}}\right) \tag{9}$$

Considering the hexagonal lattice of carbon atoms that make up the sidewall of CNTs, we can estimate the number of atoms in the average CNT within the forest. **Figure S11** shows a portion of a hexagonal lattice of carbon atoms where the unit cell is highlighted by the dotted

line. The separation between carbon atoms in this configuration is 0.142 nm, and so we can calculate the spacing between unit cells in the x and y directions (shift to blue and red positions respectively) as 0.426 and 0.246 nm respectively. With these dimensions we then calculate the number of atoms (*N*)for an average CNT (neglecting any cap) using the result from Equation 9 in nm

$$N = 4(L/0.246)(C/0.426) \quad (10)$$

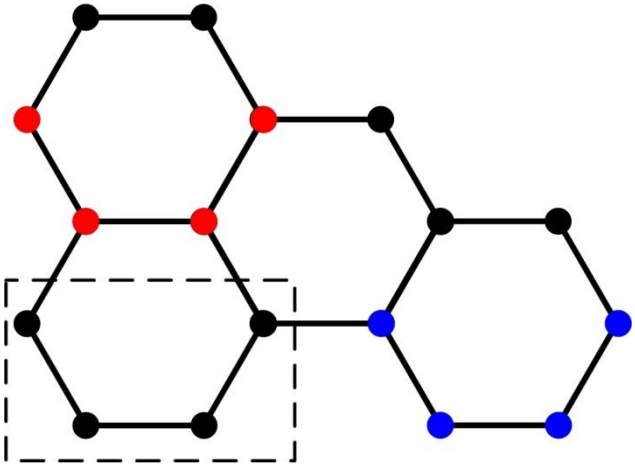

Figure S11. Hexagonal lattice of carbon atoms.

Finally, we calculate the number of CNTs per unit area using *h*, *N* and the measured volumetric density of the forest (ρ)

$$CNTs\ /area = \frac{\rho h N_A}{N(m_C)} \quad (11)$$

where N_A is Avogadro's Number and m_C is the atomic mass of carbon.

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