Electronic Supporting Information

Self-assembly of like-charged nanoparticles into Voronoi diagram

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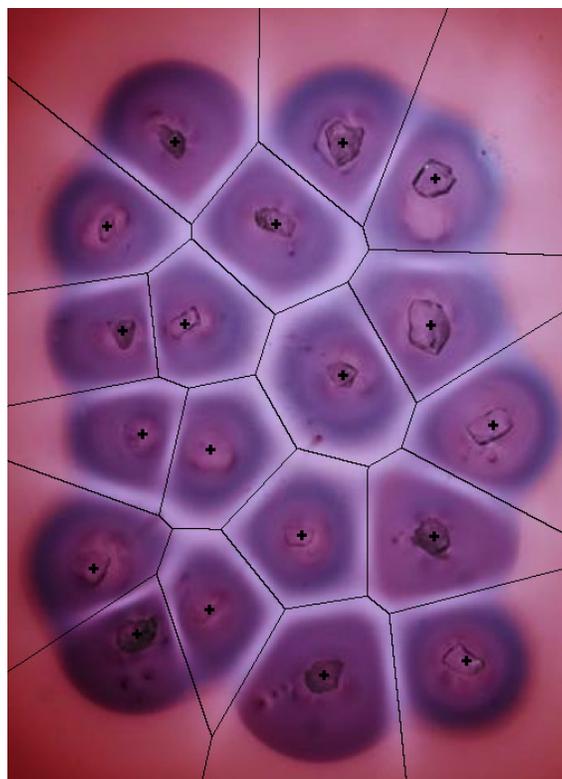
Figure S1. Comparison of a chemically generated Voronoi diagram based on nanoparticles aggregation and a geometrically generated Voronoi diagram. Black crosses and black lines correspond to the seeds/generators of the Voronoi diagram and the boundaries of the geometrically generated Voronoi cells, respectively.
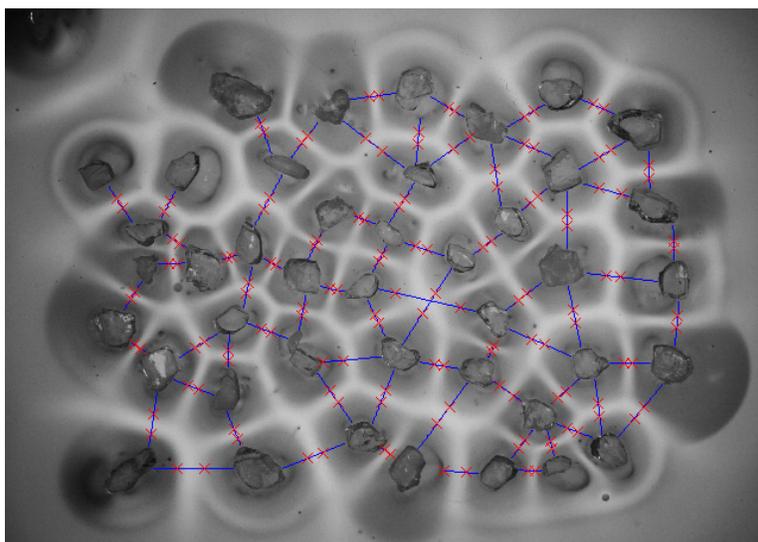

Figure S2. Determination of the distance between two pieces of crystals/seeds (L, blue lines) and the edges of the aggregation-free gaps (marked by red crosses).
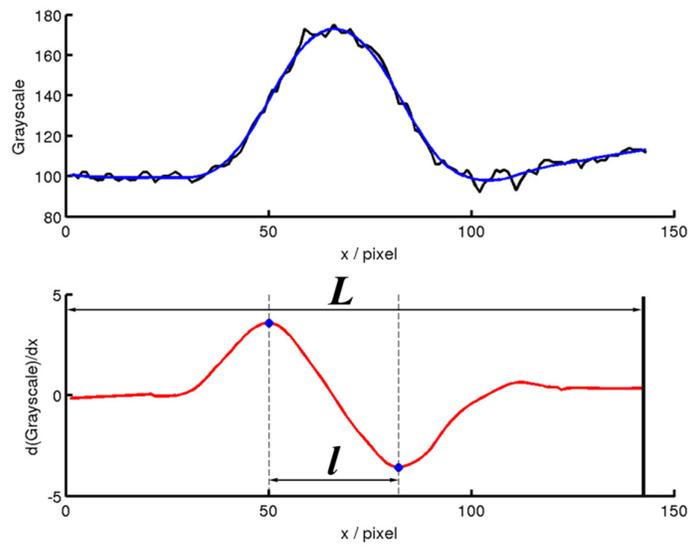
Figure S3. Grayscale analysis of the pixels along a line between two seeds (upper graph). The edges of the aggregation-free gaps were determined where the spatial gradients of the smoothed grayscale curve had extremes (below graph).

$t = 10$ s $t = 10$ min   stationary
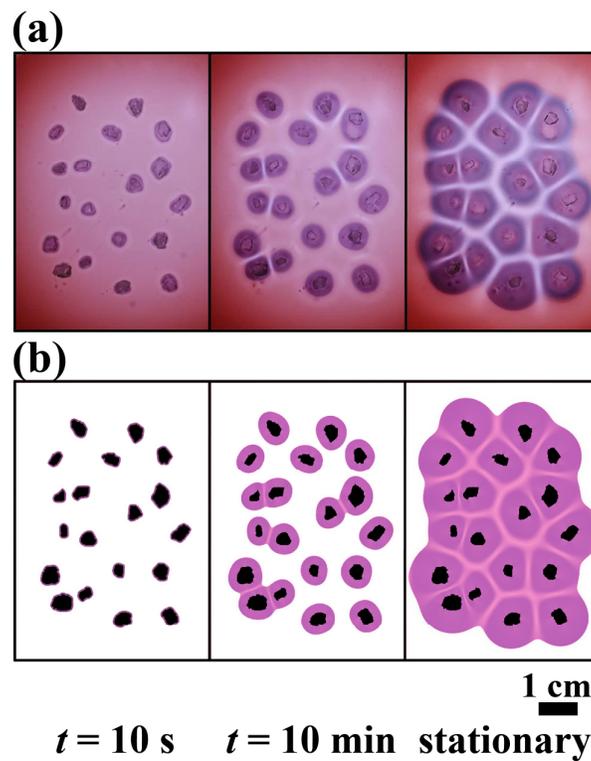
Figure S4 Evolution of a Voronoi diagram formed in an experiment (a) and in a numerical simulation (b) using bigger (~ 4 mm) sodium chloride crystals placed randomly on top of the solid hydrogel. Black regions in (b) correspond to the positions and shape of the crystals.

(a)

(b)

1 cm

$t = 10$ s $t = 10$ min stationary
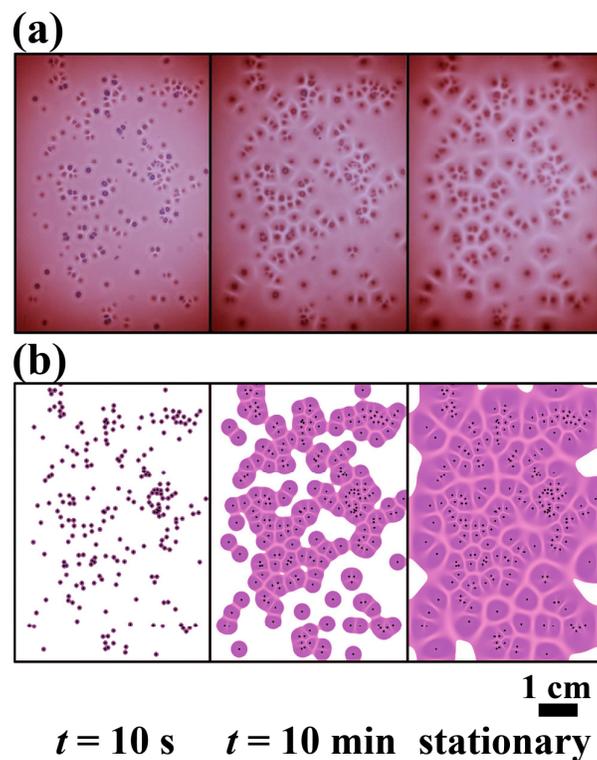
Figure S5 Evolution of a Voronoi diagram formed in an experiment (a) and in a numerical simulation (b) using smaller (~ 0.2 mm) sodium chloride crystals placed randomly on top of the solid hydrogel. Black regions in (b) correspond to the positions of the crystals.

(a) $a^* = 0.03$ M   **(b)** $a^* = 0.15$ M

1 cm
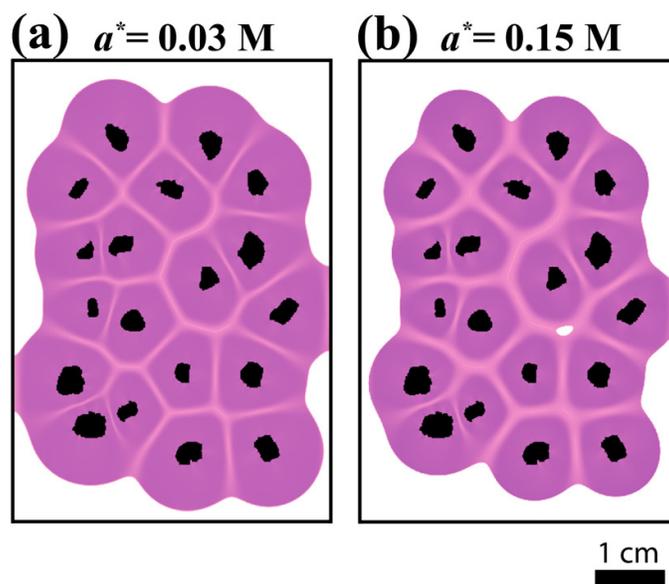
Figure S6 Calculated Voronoi patterns with different threshold concentrations for aggregation of nanoparticles **(a)** $a^* = 0.03$ M and **(b)** $a^* = 0.15$ M. The relative average error between two patterns is less than 2%. In the numerical simulations all model parameters were identical except the threshold concentration.

Calculation of van der Waals and electrostatic interaction potentials

The vdW interaction of MUA coated AuNPs can be calculated using the following equation

$$\frac{U_{vdW}(d)}{k_BT} = -\frac{A}{3}\left[\frac{r_a^2}{d(4r_a+d)} + \frac{r_a^2}{(2r_a+d)^2} + \frac{1}{2}\ln\left(1 - \frac{4r_a^2}{(2r_a+d)^2}\right)\right], \tag{1}$$

where A is the Hamaker constant for AuMUA system (4.52×10^{-19}J),[1] r_a is the radius of the particle and d is the separation distance between the particles surfaces. The radius r_a of the nanoparticle was calculated as a sum of the gold core's radius (3.25 nm) and the thickness of the MUA layer (1.60 nm).

The electric double layer repulsion was estimated as[2]

$$\frac{U_{EDL}(d)}{k_BT} = \left(\frac{r_a^2}{2r_a}\right)Ze^{-\kappa d}, \tag{2}$$

where κ is the reciprocal Debye length and Z is the interaction constant. The interaction constant can be calculated as follows

$$Z = 64\pi\varepsilon_0\varepsilon\left(\frac{k_BT}{e}\right)^2 tanh^2\left(\frac{ze\psi_0}{4k_BT}\right), \tag{3}$$

where ε_0 is the vacuum permittivity (8.854×10^{-12} Fm^{-1}), ε is the relative permittivity for water (80.1 at 20 °C), z is the valence of the ions and ψ_0 is the surface potential of nanoparticle, and it is calculated as

$$\psi_0 = \frac{2k_BT}{ze}sinh^{-1}\left[\frac{\sigma}{(8RT\varepsilon_0\varepsilon c_\infty)^{\frac{1}{2}}}\right], \tag{4}$$

where c_∞ is the bulk concentration of the electrolyte. The surface potential can be calculated from the surface charge density (σ), which is a function of ζ-potential

$$\sigma = \frac{\varepsilon \varepsilon_0 k_B T}{ze} \kappa \left[2 \sinh\left(\frac{\zeta z e}{2 k_B T} \right) + \frac{4}{\kappa r_a} \tanh\left(\frac{\zeta z e}{4 k_B T} \right) \right]. \qquad (5)$$

The zeta potential of the particles ($\zeta = -45$ mV) was obtained from electrokinetic measurements using a Malvern Zetasizer NanoZS. The total nanoparticle-nanoparticle interaction energy was obtained from Equations (1) and (2)

$$\frac{U_{total}(d)}{k_B T} = \frac{U_{EDL}(d)}{k_B T} + \frac{U_{vdW}(d)}{k_B T}. \qquad (6)$$

References

1 T. Laaksonen, P. Ahonen, C. Johans and K. Kontturi, *ChemPhysChem*, 2006, **7**, 2143–2149.
2 K. J. M. Bishop, C. E. Wilmer, S. Soh and B. A. Grzybowski, *Small*, 2009, **5**, 1600–1630.