Supporting Information

Self-assembly of Nano-ellipsoids into Ordered Structures via Vertical Deposition

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Zeta potential measurements of hematite particle:

The zeta potential of hematite particles as a function of pH at 0.0001 M NaCl concentration

(measured at 25 °C) and zeta potential of glass substrate (literature values) is shown in Fig S1.



Fig S1: The zeta potential measurements of hematite ellipsoidal particles (aspect ratio 4) and glass slide as a function of pH. The zeta potential values of glass slide are taken from Somasundaran et., al.¹

Peeling experiments:

To confirm the ordering of particles in the middle layers, the particulate film is sandwiched between two scotch tapes and the film is peeled off to visualize particle arrangement in the interior of the film. The SEM images are shown in Fig S2. From the SEM images it is clear that the particles are ordered in 3 dimensions.



Fig S2: SEM images showing the ordering of hematite nano-ellipsoids of aspect ratio 4 observed upon the vertical deposition of suspensions at pH=2 after peeling experiments.

DLVO interaction calculations:

The vertical deposition SEM images revealed that, when the particles are highly charged the particles alignment is long rang and the particles are aligned in a side by side nature. But when the particles are weakly charged the alignment is random. To understand the effect of DLVO interactions on the order and random nature, we calculated the particle-particle and particle-substrate interactions. For anisotropic particles, particle-particle (PP) and particle-substrate (PS) interactions depend on the orientation of particles. We used side by side configuration for

particle-particle interactions and particle major axis is parallel to the substrate for particlesubstrate interactions. We choose side-side configuration for the calculation of particle-particle interactions as the interactions in this configuration is relatively stronger than other possible orientations at the same center-to-center separation. The PP and PS interactions are calculated by using Derjaguin's approximation method.² This method is valid for small separation compared to the particle size. The schematic diagram of particle-particle and particle-substrate orientations is showed in Fig S3. The interaction between particles is estimated by²



Fig S3. Schematic diagram showing orientation dependent interactions: (A) Orientation of two ellipsoid particles. T_a and T_b are the closest distance points on two ellipsoid particles. The distance between two points is d. (B) Interaction between ellipsoid particle and a planar surface. Interactions depend on the distance (d) between particle and planar surface.

$$U_{p-p} = \frac{2\pi}{\sqrt{K_a + K_b + 2H_aH_b - 2S_{ab}}} \int_{d}^{\infty} w(z) dz$$
(S1)

Where

$$S_{ab} = \sqrt{\left(H_a^2 - K_a\right)\left(H_b^2 - K_b\right)}$$
(S2)

 K_i and H_i are Gaussian and mean curvature of ellipsoidal particle at point T_i (i=a,b), and w(z) is the interaction potential between the particles.

Similarly, the particle-substrate interactions are calculated by

$$U_{p-s} = \frac{2\pi A^2 B}{A^2 \sin^2 \eta + B^2 \cos^2 \eta} \int_{d}^{\infty} w(z) dz$$
(S3)

Where η is the angle between the substrate and particle, *B* and A are the length of major and minor axes of the ellipsoid respectively. The net interaction between the PP and PS is the combined effect of electrostatic repulsion and van der waals attraction. The complete DLVO force is given by

$$w(z) = \frac{2\varepsilon\phi_a\phi_b}{k}\exp\left(-\frac{z}{k}\right) - \frac{H}{12\pi z^2}$$
(S4)

Where, ε is the dielectric constant, ϕ is the surface potential on the charged surface (in case of PP interactions $\phi_a \phi_b = \phi_p^2$ and PS interactions $\phi_a \phi_b = \phi_p \phi_s$), k is the Debye length, H is Hamaker constant, and d is the surface to surface distance between the charged surfaces. The DLVO interactions of PP and PS are calculated by substituting the eq(S4) in eq(S1) and eq(S3) respectively. The zeta potential of the particle and substrate are shown in fig S1 respectively. The overall DLVO interactions for PP and PS as a function of surface to surface distance is shown in fig S4 and fig S5 respectively.



Fig S4. Particle-Particle (PP) DLVO interactions: Interactions are calculated as a function of surface to surface distance. The PP interactions are repulsive at pH 2 and attractive at pH 6.5.



Fig S5. Particle-Substarte (PS) DLVO interactions: Interactions are calculated as a function of surface to surface distance. The PS interactions are attractive at pH 2 and pH 6.5.

Reference:

- 1. P. Somasundaran, S. Shrotri and K. P. Ananthapadmanabhan, *Deposition of Latex Particles: Theoretical and experimental Aspects,* Mineral Processing: Recent Advances and Future Trends, 1995.
- 2. P. Schiller, S. Kruger, M. Wahab and H.-J. Mögel, *Langmuir*, 2011, 27, 10429-10437.