Supplementary Information for

Interaction potentials of anisotropic nanocrystals from the trajectory sampling of particle motion using *in situ* liquid phase transmission electron microscopy

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Materials and Methods:  

Materials:

Sodium oleate (>97%), hexadecyltrimethylammonium bromide (CTAB, >98%) and hexadecyltrimethylammonium chloride (CTAC, >95%) were purchased from TCI America. Hydrogen tetrachloroaurate trihydrate (HAuCl\(_4\)-3H\(_2\)O, >95%) was purchased from Acros Organics. Silver nitrate (AgNO\(_3\), >99%), sodium borohydride (NaBH\(_4\), 99.99%) were purchased from Sigma Aldrich. L-ascorbic acid (>99%) and hydrochloric acid (HCl, ≥36.5%, 12.1 M) were purchased from Alfa Aesar. All chemicals were used as received. Milli-Q water (18.2 MΩ·cm) was used in all the experiments. All glassware was cleaned using freshly prepared aqua regia (HCl and HNO\(_3\) mixed in a 3:1 volume ratio) followed by rinsing with copious amount of water.

Synthesis of gold nanorods:

Gold nanorods, 47.4 ± 2.3 nm in length and 13.8 ± 1.0 nm in diameter, were synthesized using the published method of seed-mediated growth involving a binary surfactant mixture (see Figure S1).\(^1\) The seed solution was prepared as follows: 5 mL of 0.5 mM HAuCl\(_4\) was mixed with 5 mL of 0.2 M CTAB in a 20 mL scintillation vial. 1 mL of freshly prepared 6 mM NaBH\(_4\) was injected quickly into the Au(III)-CTAB complex solution under vigorous stirring (1200 rpm) for 2 min. The stirring was stopped after 2 min and the seed solution was aged for 30 min at 30 °C.

The growth solution was obtained by first co-dissolving 6.15 g of CTAC (37 mM in the final growth solution) and 1.543 g of sodium oleate (9.9 mM in the final growth solution) in 250 mL of water at 45 °C. After allowing the binary surfactant mixture to cool to 30 °C, 12 mL of 4 mM AgNO\(_3\) and 250 mL of 1 mM HAuCl\(_4\) were added followed by the addition of
2.1 mL of 12.1 M HCl. The growth solution was kept at 30 °C under gentle stirring (200 rpm) until the solution became colorless. To initiate rod growth, 1.25 mL of 64 mM ascorbic acid was added and the solution was stirred for 1 min. Then 0.8 mL of the seed solution was diluted with 0.2 mL of water and the resulting solution was injected into the growth solution. Stirring was stopped immediately after the injection and the rods were left to grow for 12 h at 30 °C. Rods were purified by centrifugation at 7000 rpm for 30 min and concentrated to give ~15 mL Au nanorod stock solution. The aspect ratio of the rods obtained was 3.43 ± 0.30 and the transverse and longitudinal peaks in the UV/Vis spectrum were 507 nm and 730 nm respectively (see Figure S1). UV/Vis spectra were collected on a Shimadzu 3600 UV-vis-NIR absorption spectrometer.

**Sample preparation for the liquid cell experiment:**

Commercially available Poseidon 200 in situ liquid cell TEM flow holder and E-chips (Protochips Inc.) were used in this study. The microchips with 50 nm thick silicon nitride viewing windows were cleaned with acetone and methanol before undergoing plasma treatment to increase the hydrophilicity of substrate surface. 1 μL of water was then pipetted onto the bottom microchip (150 nm flow spacer) followed by loading of the top microchip. Crossed-window configuration of the E-chips gave a viewing window of dimensions 20 μm by 20 μm. Sealing against vacuum conditions was achieved with screws that tightly secured the microchips and o-rings in place. Different Au nanorod suspensions (see below) were flowed in and allowed to stabilize rather than being loaded directly as direct loading inevitably led to a significant fraction of the rods becoming immobilized on the substrate. Sample was flowed in for ~1 h to ensure that the solution inside the liquid cell was homogeneous with the solution that was being flown in. The flow was then stopped and the system was left to equilibrate for at least 15 min to preclude any effects of residual flow.
inside the liquid cell before imaging inside the TEM.

For the experiments (Figures 1-3) where Au nanorods assembled, we diluted the Au nanorod stock solution by a factor of four with Milli-Q water. This dilution step was carried out as higher CTAC concentrations resulted in uncontrolled bubble formation under the electron beam. The Au nanorod concentration used in the experiments was approximately 0.9 nM as determined from the optical density at the longitudinal resonance peak using the Beer–Lambert law. The literature value we used for the molar extinction coefficient was $\varepsilon = 4.6 \times 10^9 \text{ M}^{-1}\text{ cm}^{-1}$ which is for Au nanorods of aspect ratio 3.5. Excess reducing agents, the mildly reducing sodium oleate and the more strongly reducing ascorbic acid, are still present in the solution alongside excess CTAC. Empirically, we found that they are crucial for the stability of Au nanorods under the electron beam. Reducing agents serve as the scavenger of oxidative species (HO$_2^-$, O and H$_2$O$_2$) generated from radiolysis of water, to prevent Au nanorods from being etched. Controlled studies where we systematically varied the ascorbic acid concentration indicated that the effect of particle etching was reduced almost completely by increasing the amount of ascorbic acid in the solution for the imaging conditions used in this study. Excess CTAC (~9.5 mM) can help maintain the CTA$^+$ ligand bilayer on the Au nanorods, electrostatically stabilizing Au nanorods from random aggregation.

For the experiments (Figure 4) where Au nanorods did not assemble, we lowered the ionic strength by centrifuging the stock solution (7000 rpm for 30 min) and removing the supernatant that contained excess ions leftover from the synthesis. Au nanorods were then re-dispersed in the solution of 38 mM CTAC and the final volume was kept to be the same as the original volume of stock solution used to ensure that the rod concentration remained constant. This solution was then diluted by a factor of four with Milli-Q water before being flowed into the liquid cell.
**Ionic strength estimation:**

The estimated final ionic strength is 5 mM (Debye length 4 nm) for the sample where we observed tip-to-tip assembly and $5 \times 10^{-4}$ mM (Debye length 13.6 nm) for the sample at low ionic strength with no assembly. In this calculation, we have assumed the contribution of CTAC to the total ionic strength to be negligible and the ionic strength was approximated based on the residual ions we have after synthesis (mostly NaCl and HCl). The concentration of CTAC used was much higher than the cmc (1.6 mM) and so CTAC would be present mostly as micelles with diameter of around 5 nm. The charge on the CTA$^+$ headgroups will be screened by the chloride anions in solution and so these micelles do not act as free ions that can screen the positive charge on the gold nanorods. This assumption is corroborated by our experimental data too as the CTAC concentration was left unchanged for the low ionic strength condition (Fig. 4) and we still observed a large decrease in ionic strength (Fig. 4a).

Although our measured decay lengths are larger (16.7 nm versus 4 nm; >30 nm versus 13.6 nm) than the estimated values, they have same order of magnitude, and the trend is the same. In addition, our measured decay length is the effective decay length of inter-rod electrostatic interactions; it is not clear how this decay length is directly related to the Debye length calculated from the ionic strength. We referenced the interaction form of two charged cylindrical shapes, which provides the closest theoretical description of our experiments.

**TEM imaging:**

All TEM images and movies were obtained on Tecnai G2 20 S-TWIN TEM equipped with a Gatan Orius SC200 CCD camera. The acceleration voltage was 200 kV and the beam current density used for video collection was 61.7 and 17.3 electrons/(Å$^2$·s) for assembly and
non-assembly conditions, respectively. The electron dosage was calculated from the total pixel intensity using the conversion ratio of 10 counts in the CCD camera as being equivalent to 1 electron. Lower beam intensities were used to minimize etching for Au nanorod solutions with lower ionic strength where there are no reducing agents present to counteract the electron beam induced etching. To minimize the deteriorating effects of silicon nitride window bulging on the image resolution, imaging was carried out at the corners of the imaging window. Frame rates used for video collection were 3.25 and 4.89 fps. Video processing and analysis were done using ImageJ and MATLAB.

**Au nanorod tracking:**

We wrote Matlab codes utilizing the Matlab imaging processing toolbox to track the ends of Au nanorods. Briefly, we first read every TEM image in a TEM movie and generate its complement TEM image with reverse intensity scale, with the originally dark Au nanorods appearing bright in the complement TEM image. Then we used an optimized threshold to generate a binary image from the intensity-inverted image. Based upon the binary image, we used the built-in functions of bwboundaries.m and regionprops.m to find the outlines of the desired bright clusters, i.e. the Au nanorods in the image, and to extract the centroid and orientation of Au nanorods, which are needed to compute the tip positions of Au nanorods. For the plots in Figure 2, for a given pair of Au nanorods, each of them is selected as a reference rod, to extract all the relative position information from pairs of Au nanorods.

**Modeling of the electrostatic potential of Au nanorods:**

We model 3D Au nanorods as 2D rod shapes coated with an arbitrarily chosen charge density. We find this simple calculation sufficient for illustrating the electrostatically induced selectivity of tip-to-tip assembly.
Each Au nanorod is modeled numerically with a 47 by 14 shape matrix, with each surface element coated with one fixed “point charge”. While the choice of this charge density is arbitrary, the shape of the calculated electrostatic interaction shape is expected to stay independent of the exact charge density. The electrostatic potential between two Au nanorods at fixed positions is calculated by summing pairwise interactions of point charges, with the assumption that neither interferences nor correlations influence the potential between neighboring point charges. The point charges on interacting colloids interact via a screened Coulomb potential (Yukawa potential), where $\lambda_D(I)$ is (16.0±0.7) nm.

$$V_E(i,j,l) = \frac{1}{4\pi\varepsilon_0\varepsilon_r D_{ij}} \exp\left(-\frac{D_{ij}}{\lambda_D(I)}\right).$$
Supplementary Figures

Figure S1: Characterization of as-synthesized Au nanorods

A: TEM image of as-synthesized Au nanorods dried on a TEM grid. Scale bar is 100 nm. Due to solvent evaporation during the TEM sample preparation, Au nanorods sit side-by-side with each other, with their interparticle distance (~4-5 nm) indicating the presence of CTA\(^+\) bilayer coating on rod surfaces. B: UV-Vis spectrum of as-synthesized Au nanorod solution.

Figure S2: Brownian motions of individual Au nanorods

A: Trajectory of a typical single Au nanorod, whose color is coded according to the elapsed time. B: MSD plot showing the diffusion of Au nanorods over time.
time. B: Mean squared displacement (MSD) versus time plot for the single Au nanorod (same particle as the one in A).

**Figure S3: Analysis of end-to-end selectivity of assembled rods**

A: Schematic illustration of how tip-to-tip attachment was defined. In this study, it was defined as attachment between regions of curvature at rod tips and anything else was defined as not tip-to-tip. B: TEM image showing a large scale view of assembled rods. C: TEM image in B overlaid with red (tip-to-tip) and blue (not tip-to-tip) circles to indicate the fraction of tip-to-tip attachments. In this particular image shown, 94 are tip-to-tip (81 %) and 22 are not tip-to-tip (19 %). Note that attachments to spheres have been ignored. When this analysis was extended for 610 rod-to-rod attachments, 80 % were tip-to-tip.

**Figure S4: Radial symmetry of 2D density plot for assembled rods (Figure 2B)**
A: 2D density plot with blue and red boxes highlighting the columns/rows of data used to evaluate its radial symmetry. B: Averaged counts of the vertical columns (blue) and the horizontal rows (red) versus the radial axis. It is clear that the blue and red curves almost overlap with each other, and the same is also true for the averaged counts of data in other directions, indicating the radial symmetry of the 2D density plot. This is the reason why we have used $r$ as the only parameter for $g(r)$.

**Figure S5: Random aggregation of Au nanorods at a higher ionic strength than the condition used in Figure 1**

A TEM image (A) and schematics (B) of random aggregation of Au nanorods in a solution of 9.1 mM CTAC and 16 mM ascorbic acid.
Supplementary Movies

Movie S1: Tip-to-tip assembly from well-dispersed Au nanorods. The movie is played at 6.5 fps, 2x real time.

Movie S2: A zoomed-in view of how two rods approach each other and attach preferentially in certain relative orientations. The movie is played at 3.25 fps, the real time.

Movie S3: A demonstration movie showing how the rod ends are tracked in the intensity-inverted TEM movie. The crosses show the tracked rod tip and centroid positions. We also set a threshold for the rod aspect ratio to exclude spheres. The movie is played at 3.25 fps, the real time.

Movie S4: A TEM movie showing unassembled rods when they are at a lower ionic strength. The overlaid yellow circles show effectively the “depleted zone” within which rods start to feel repulsion from each other. The movie is played at 9.78 fps, twice the real time.

References


