

Modeling of Nanocrystal-Molecule Nanostructure Formation

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Self-assembled nanocrystal-molecule nanostructures have generated significant research interest in recent years with potential applications in molecular electronics, plasmonics and biosensing. Recently we have developed solution-based processes for assembly of plasmonic nanostructures through controlled mixing of citrate-stabilised gold nanocrystals and molecular linkers with isothiocyanate end groups; see Figure 1a. We term these nanostructures “ n -mers”, where n denotes the number of nanocrystals in the structure. Figure 1b shows high-resolution Scanning Electron Microscopy (SEM) images of individual n -mers deposited from solution. Analysis of several hundred SEM images acquired across multiple substrates yields quantitative distributions for monomers ($n = 1$), dimers ($n = 2$) and higher order n -mer nanostructures; see Figure 2a.

Here we report on development of complementary random-walk and rate-equation simulation routes to gain insight into the influences of the key processes underlying nanostructure formation. These processes include (i) adsorption of linker molecules at the nanocrystal surface; (ii) coalescence of molecule-bearing nanocrystals to form dimers, trimers and higher-order n -mer nanostructures; (iii) desorption of linker molecules (possibly leading to n -mer dissociation).

For experiments with durations up to several hours, 3-dimensional random-walk algorithms were developed to model n -mer formation. Values for the nanocrystal diffusivity were estimated using the Stokes-Einstein equation and show good agreement with experimental data^{1,2} even at the nanometre scale. “Coarse-grain” step sizes in the micron range were chosen for nanocrystals executing random walks, i.e., on the order of the mean separations between nanocrystals in solution; with corresponding time steps ~ 10 ms. Similar “fine-grain” algorithms were employed to model collision efficiencies, e.g., the likelihood of two nanocrystals or a nanocrystal and a molecule located within the same micron-scale cell “meeting” during one time step of the coarse-grain model. For the fine-grain simulations, length-scales ~ 20 -40 nm and time-scales ~ 1 -10 μ s were employed.

Figure 2a shows the measured distribution of nanostructures from a typical experiment, acquired following controlled mixing of citrate-stabilised Au nanocrystals (core diameter $d = 20$ nm) with bi-functional linker molecules over a 2 hour period. More than 2500 nanostructures were counted across multiple substrates (error bars show the 95% confidence interval). Figure 2b shows two limiting cases for the random-walk model based on the data shown in Figure 2a. One solution corresponds to a dynamic equilibrium situation, where the n -mer populations rapidly approach limiting values, which are maintained by a balance between nanostructure formation and dissociation. The second solution corresponds to a slower evolution of the n -mer distribution with a correspondingly smaller value for the ratio of the probabilities for dissociation and formation.

As the random-walk method is computationally expensive for modelling experiments over longer time scales (days to weeks), a coupled rate-equation model was also developed, based on approaches used by Venables and co-workers to model island growth at surfaces.³ This approach yields the rates of change of the monomer, dimer and higher order n -mer populations as a function of time. Good agreement with experimental data has been achieved for a time series experiment, where the evolution of the n -mer distribution for a nanocrystal-molecule solution was monitored over 7 days. Linker molecules were added at regular intervals while mixing and small aliquots of the solution were removed and diluted to quantify the

nanostructure distribution using SEM. Interestingly, the rate constants which best describe this week-long experiment are in reasonable agreement with the values extracted for dynamic equilibrium case of the random walk model described above for shorter experimental time scales (hours).

Reconciliation of the random-walk and rate-equation models is currently underway in order to extract the rate constants and corresponding activation energies for nanostructure formation and dissociation. Comparisons are also being undertaken with the results of simulations of the optical properties of monomer and dimer nanostructures since the optical properties of the nanostructure solutions reported here are measured in (almost) real-time, thus providing a potential experimental probe of the n -mer distribution evolution at the time scales at or below 1 second.

References:

- [1] Wuelfing et al., *Anal. Chem.*, **71**, (1999), 4069-4074
- [2] Xu et al., *J. Phys. Chem. C*, **111**, (2007) 32-35
- [3] Venables et al., *Rep. Prog. Phys.*, **47**, (1984), 399-459

Figures:

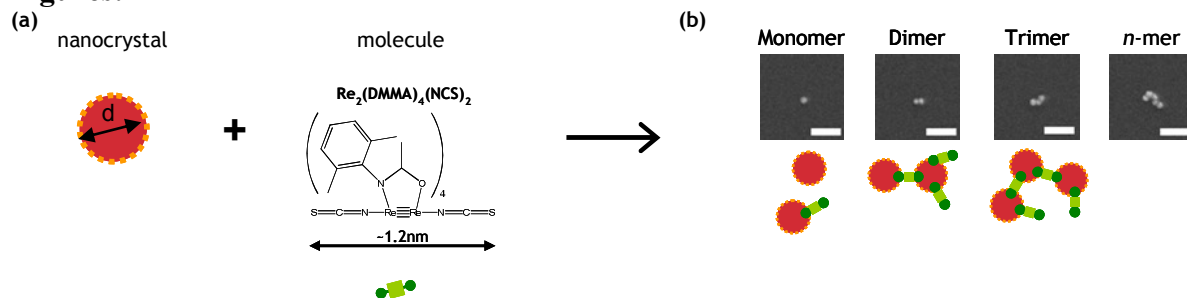


Figure 1 (a) Schematic (not to scale) of nanocrystal-molecule nanostructures formed by mixing citrate-stabilised Au nanocrystals (core diameter $d = 20$ nm) with bi-functional Re linker molecules. (b) SEM images and schematics of nanocrystal-molecule “ n -mer” nanostructures: Monomer ($n = 1$), dimer ($n = 2$), trimer ($n = 3$), etc. Scale bars: 100 nm.

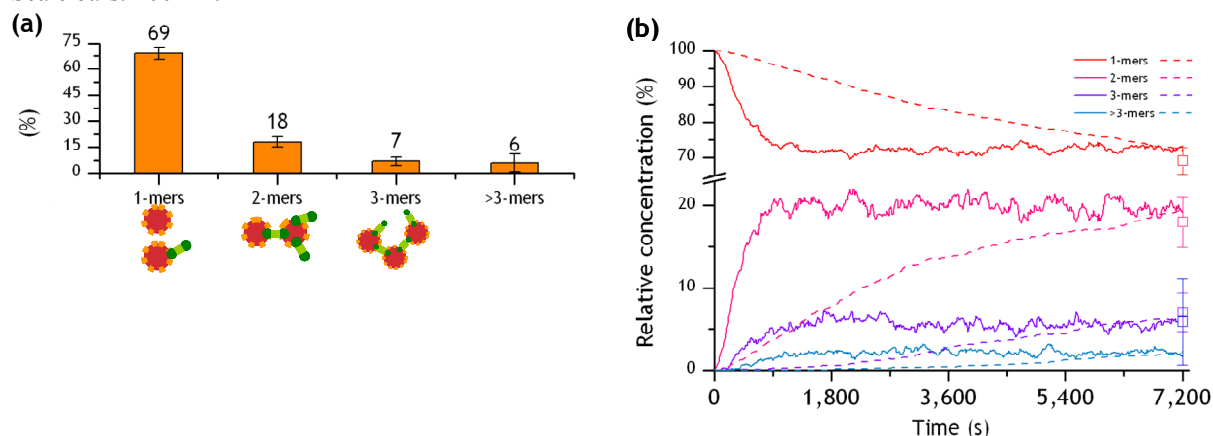


Figure 2 (a) Histogram showing the distribution of n -mer nanostructures extracted from measured SEM data: More than 2200 nanostructures were counted from 272 locations across 21 separate substrates. The error bars show the 95% confidence interval (b) Two limiting cases of the random walk model are shown which agree (after 2 hours) with the data in (a): One corresponds to a dynamic equilibrium (solid curves), where the n -mer populations rapidly approach limiting values, which are maintained by a balance between nanostructure formation and dissociation. The second case corresponds to a slower evolution of the n -mer distribution with a correspondingly smaller ratio of the probabilities for dissociation and formation.