Charge Transport in Plasmonic Nanocrystal-Molecule Nanostructures

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We report on development of 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 1. Recent results on investigation of the novel plasmonic properties of these nanostructures via measurement and simulation are presented. We term these nanostructures "*n*-mers", where *n* denotes the number of nanocrystals in the structure. Further, we report on directed assembly of nanostructures at contact nanoelectrodes and initial investigations of charge transport in these "few-molecule" devices.

Unmodified d = 20 nm Au nanocrystals showed the characteristic single nanocrystal absorbance with peak intensity, λ_{max}, at 523 nm, corresponding to the well-know plasmon resonance in gold nanocrystals; see Figure 2a. Bifunctional linker molecules were added to the nanocrystals over ~1 hour period (with a final molecule:nanocrystal ratio ~ 500:1), during which time 30 spectra were recorded. Figure 2a shows a subset of the recorded absorbance spectra (A_1, A_2… A_6) chosen to show the evolution of the optical response. Almost immediately after addition of the linkers (A_1, 2 minutes), a red-shift ($\Delta\lambda \approx 2$ nm) of the peak close to 523 nm could be observed, likely due to initial adsorption of the linkers at each nanocrystal surface. During the experiment the emergence of a second feature was observed close to 600 nm. The evolution of this shoulder can be highlighted by subtracting the absorbance data of unmodified Au nanocrystals, i.e., A_0 in Figure 2a, from the measured absorbance (A_i) at each time interval; see Figure 2b.

Figure 2c shows a histogram (dark blue data) of the *n*-mer nanostructure distribution for the solution whose absorbance (A_6) is shown in Figure 2a. The data, totalling >400 nanostructures, were extracted from analysis of >60 SEM images acquired at different locations across 4 substrates. The error bars, which show the 95% confidence interval for the analysis ($\pm 1.96\sigma$), confirm the reliability of the method to determine the distribution of nanostructures in a solution. The distribution comprises roughly 68% monomers, 20% dimers, 7% trimers and low incidences of higher order *n*-mers. Control experiments on unmodified nanocrystal solutions prepared in the same manner but without addition of linker molecules yielded the pale pink histogram data shown in Figure 2c (>100 nanostructures counted). Over 95% monomers were observed for the bare nanocrystals with a low incidence of dimers and negligible incidence of higher order *n*-mers. The statistics indicate that the nanostructures observed using SEM were formed in solution and not as a result of aggregation during drop-deposition onto the substrate or solvent evaporation.

The *n*-mer distribution extracted from SEM data suggests that the measured absorbance feature close to 600 nm in Figure 2 arises from the optical response of nanocrystal-molecule dimer or trimer nanostructures. Literature reports of simulations and optical scattering experiments on fabricated and synthesised dimer nanostructures have revealed the existence of a second peak, considerably red-shifted with respect to the plasmon peak for isolated spherical nanostructures. Simulations are currently being developed using the Generalised Multiparticle Mie method to model the optical extinction of nanocrystal dimers for electric field polarizations parallel ($E_{//}$) and perpendicular ($E_{\perp}$) to the dimer axis, respectively. Initial results for dimers comprising d = 20 nm Au nanocrystals with edge-edge separation ~ 1.2 nm (expected length for Re linkers) show two main peaks: one close to 520 nm and a second longer-wavelength peak close to 600 nm; see Figure 3. This longer wavelength feature is more prominent for case where the field polarization is parallel to the dimer axis ($E_{//}$), suggesting that the shoulder close to 600 nm in

the measured absorbance data shown in Figure 2a arises from a longitudinal excitation in the dimer nanostructures.

Full details of recent results from the plasmonics simulations, together with details of directed assembly of *n*-mers at contact nanoelectrodes and variable temperature (4 K – 300 K) charge transport in nanocrystal-molecule junctions will be presented at the meeting.
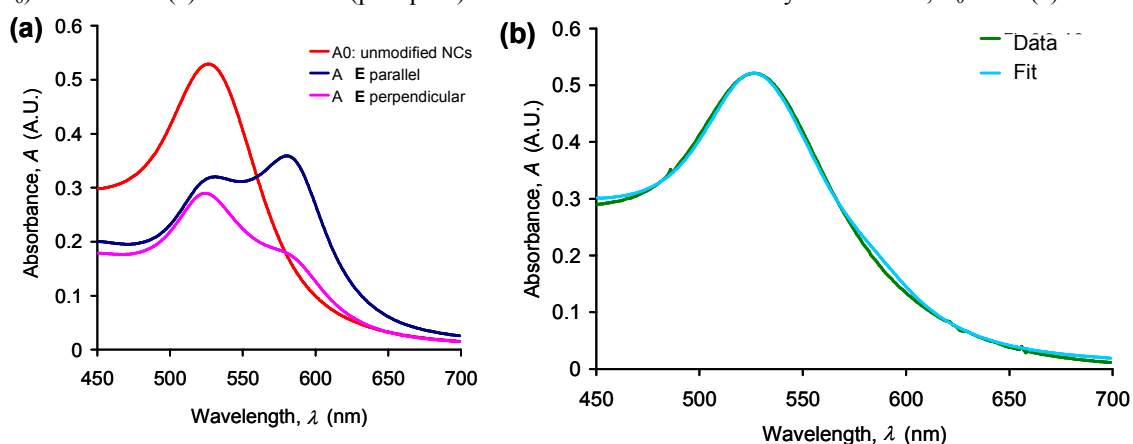
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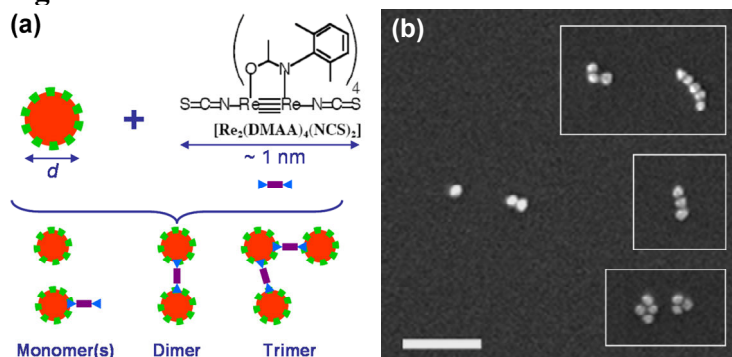
Figure 1 (a) Schematic (not to scale) of nanocrystal-molecule "*n*-mer" nanostructures formed by mixing citrate-stabilised Au nanocrystals (core diameter d = 20 nm) with bi-functional linker molecules. **(b)** SEM image showing a monomer (n = 1) and a dimer (n = 2). Insets: Higher order *n*-mers ($3 \leq n \leq 5$). Scale bar: 150 nm.
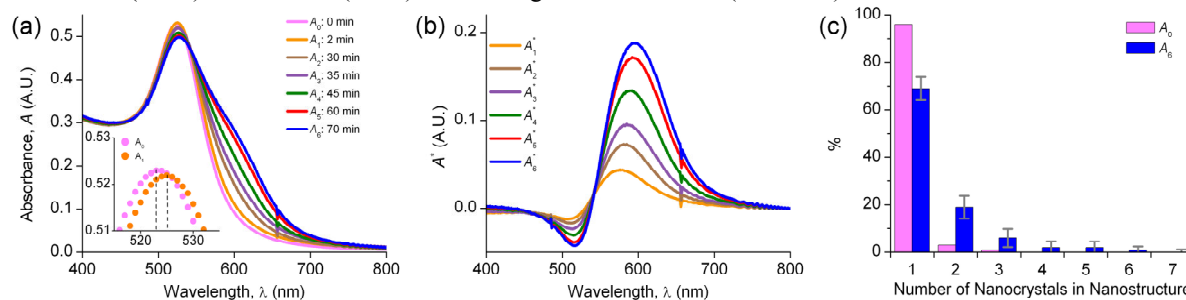
Figure 2 (a) Measured UV-Visible absorbance (A_1- A_6) of a nanocrystal-molecule solution recorded versus wavelength (λ) over ~1 hour. A_0 is the absorbance measured for the starting solution of citrate-stabilised Au nanocrystals. The inset shows the peak positions of A_0 and A_1, a 2 nm red-shift can be observed. **(b)** Relative absorbance (A^*) of the nanocrystal-molecule solutions shown in (a), following subtraction of the citrate spectrum according to: $A_i^*(\lambda) = A_i(\lambda) - A_0(\lambda)$, i = 1..6. **(c)** Histogram (dark blue) showing the distribution of *n*-mer nanostructures extracted from SEM data measured for the nanocrystal-molecule solution whose absorbance data (A_6) is shown in (a). Control data (pale pink) for an unmodified Au nanocrystal solution, A_0 from (a).

Figure 3 (a) Modelled extinction spectra for both $E_{//}$ and $E_{\perp}$ field orientations for a dimer formed from d = 20 nm nanocrystals, where the edge-edge separation of the nanocrystals was fixed at 1.2 nm. Measured extinction spectrum of unmodified d = 20 nm Au nanocrystals (A_0) and **(b)** Fit using spectra shown in (a) to measured extinction data for nanocrystal-molecule nanostructures in the early stages of formation.