ESRF	**Experiment title: SAXS study of the recognition-directed assembly of mixed metal nanocrystals in solution.**	**Experiment number**: CH-677
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Report:

Self- assembly of Nanoparticle mixtures - Ag and SiO_2 nanoparticles

In earlier studies solvent evaporation from nanoparticle dispersions (7 nm in sized Ag nanocrystals) on a substrate has shown to form ordered superstructures when adsorbed to substrate. Utilising this property the potential thus exists to assemble <100 Å heterostructures from mixed solutions of conducting and non-conducting nanoparticles.

In the pursuit of understanding the factors under which such mixed superstructures are formed mixed SiO_2 and Ag solutions were self-assembled onto a substrate and studied by SAXS. The solutions contained 9 nm sized SiO_2 nanoparticles and 6 nm sized Ag-nanoparticles modified with long chain alkanes and dissolved in $CHCl_3$. Pure solutions and mixtures were then evaporated onto mica substrates.

Figure 1 shows the SAXS spectrum of a 6 nm sized monodisperse Ag crystals. A strong diffraction peak clearly appears at about q= 0.1 $Å^{-1}$ and a second peak at about q=0.2 $Å^{-1}$. Earlier studies has shown this structure to be representative of intermediate range order and the position of the first peak to correlate with the centre to centre distance of the particles in the superstructure. In Fig 2 the spectrum obtaind from the SiO_2 -particles is also shown. Although this spectrum is find to be much less structured a clear diffraction peak at q= 0.07 $Å^{-1}$ is indicating at least short rang ordering and/or a slightly less mono dispersed sample.

Figure 2 shows the SAXS spectrum obtained from mixtures of these two solutions. Although the slight polydispersity in these samples prevent from quantitative conclustions, comparisons with the pure spectra can be used for an qualitative understanding. This must be done keeping in mind that the scattering intensity is proportional to the electron density the mixed samples is thus dominated by the scattering from the Ag particles. The first conclusion drawn is that the spectra obtained from the mixed samples are not a convolution of the spectra pure spectra in figure 2. Secondly, following the main Ag interference peak it shifts towards lower q upon addition of the SiO2-particles. Thus the mix assemblies do not contain pure SiO_2 and Ag phases. Instead a new mixed phases seams to form in which Ag and SiO_2 particles are mixed together. Further studies are on going and absorption spectra electron micrographs are cinsistent with such a picture.

The interaction between two monodisperse nanocrystals modified with a molecular substrate capable of a recognition process has been studied. The objective of the study is to determine if, in the presence of a bi-functional receptor molecule, silver nanocrystals can be self-assembled via the formation of the desired receptor-substrate complex (Figure 1).

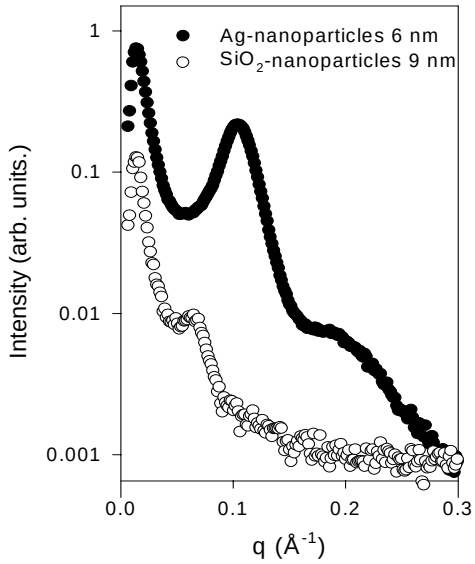

Figure 1

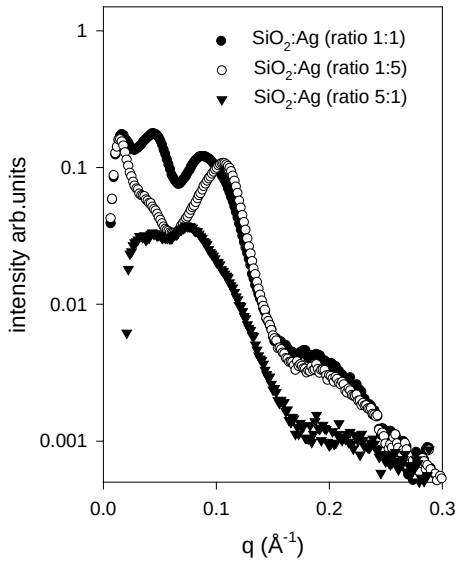

Figure 2

Self- assembly of Nanoparticle mixtures – Modified Ag Nanoctrystals

Although ordinary light scattering techniques can monitor the formation of large aggregates in solution and supply us with information regarding fractal dimensions, it does not provide structural information as to the order of these aggregates. Small-angle X-ray scattering (SAXS) is a particularly useful tool in this regard and has been used to study superlattice formation arising from self-assembly of monodisperse silver nanocrystals.

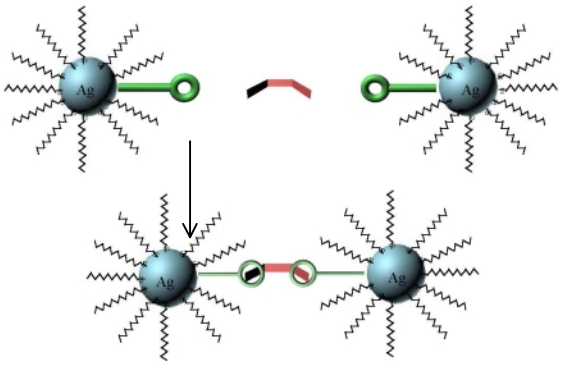

Figure 1: Nanocrystal assembly based on receptor-substrate formation.

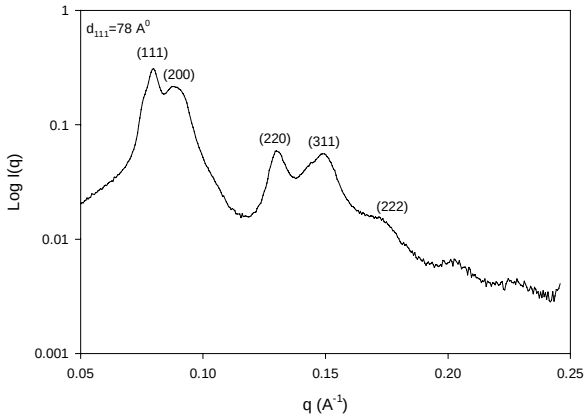

Figure 2: SAXS of superlattice formed by evaporation of a nanocrystal dispersion on a mica substrate.

Two experiments were performed. First, the degree of monodispersity had to be determined. From SAXS measurements of condensed silver nanocrystals superlattice diffraction peaks were recorded indicating an ordered arrangement of monodisperse silver nanocrystals (Figure 2). Second, the self-assembly of silver nanocrystals into a superlattice in solution was recorded. We did not observe any diffraction peaks indicative of an ordered array of silver nanocrystals in solution.

Following from these results, we conclude that the arrangement of silver nanocrystals in solution may not be close-packed, therefore precluding the observation of diffraction peaks from an ordered array. Instead, the resultant aggregate may be fractal in nature i.e. the silver nanocrystals self-assemble into an open, random structure. This is being investigated using ordinary light scattering techniques. Such information regarding the self-assembly process requires a new approach to obtaining SAXS data on this system. It is felt that this information would facilitate a worthwhile SAXS investigation of this novel system.