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Developing Chemical Strategies for the Assembly of Nanoparticles into Mesoscopic Objects

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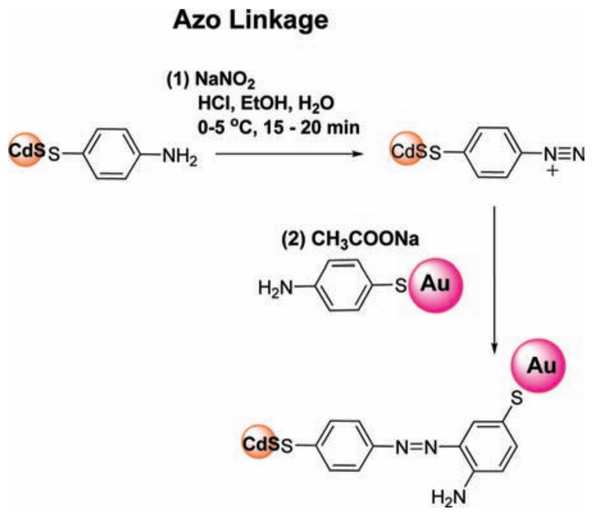
The controlled assembly of nanoparticles is potentially of broad interest in nanometrology and ultimately for device fabrication; a number of authors have reviewed this area.[1] Perhaps the most successful approaches to producing small assemblies of nanodimensional materials have involved the use of DNA, especially as described by Alivisatos.[2] Two dimensional assembly has been achieved by Keily, Brust, and Schiffrin sometimes using charged particles of different metals on a substrate.[3] Mesocrystalline assemblies provide another example of ordered arrays.[4]

There are a few papers that have delivered assembly, most often of a single type of nanoentity, by using a polydentate[5] or bioconjugate ligand.[6] Functional switches have been constructed by using such objects.[7] Chen et al. have purified dimers and trimers of gold particles bound to a block copolymer.[8] 'Nanocobs' in which small gold particles decorate the surface of a larger silver nanowire have been prepared.[9]

A slightly different paradigm is involved in making discrete objects composed of a small but defined number of nanodimensional objects. We have for some years been interested in the idea that by forming suitable bonds it should be possible to assemble individual nanocrystals to form mesoscopic entities. An early effort involved the ligand 6,6′-bipyridine with CdSe and PbS dots.[10] Eychmüller et al. reported an assembly of CdTe nanocrystals coupled via amide bonds using carbodiimide as a mediator for the reaction.[11] Another attempt was by Rao who has used 'click' derivitized gold nanoparticles to form dimers.[12]

In this paper we present our initial, and promising, results that show it is possible to create synthons from dots that under suitable (often high dilution) conditions can be assembled to form new objects. In this work, Au, Ag, CdS, and CdSe nanoparticles were synthesized and their surface coatings were modified.[13] The capping agents from the initial synthesis, such as TOPO or oleylamine, were substantially replaced by a bifunctional group, such as 11-mercaptoundecanoic acid (MUA) and 4-aminothiophenol (AmTP) by a ligand exchange reaction. This reaction was performed by adding a solution of amine capped gold nanoparticles or TOPO capped CdSe in toluene to a boiling solution of 5−10 equiv (based on gold) of thiol in the same solvent. Successful ligand exchange was confirmed by the FT-IR spectra on the products. The bifunctional capping agents are mercapto-amines, -acids or aldehydes. The 'head' of these molecules (usually sulfur) predominantly attaches to the 'soft' nanoparticle, and the 'tail' possessing a terminal reactive functional group is hence available for further reaction.

To synthesize assemblies, various functionalized dots were prepared to provide a series of reactive synthons of differing sizes. The two dots in a composite can be of the same material or of different ones; indeed analysis is somewhat easier with different types of nanoparticles in a single entity. The procedure used was high dilution synthesis with one type of nanoparticle in considerable excess over the first, the second being delivered by a syringe pump. Such reactions lead to the systematic decoration of one dot with another. In this work, two linkers were more successfully used to join the nanoparticles: (a) amido and (b) azo. We have used[14] 'Click'[15] and ester-linkage[16] reactions also, but in our hands at present the first two are the most effective. A schematic illustration of the chemistry involved is shown in Scheme 1.



Scheme 1. Amido and Azo Linkage of Nanoparticles

Amido linkages were obtained by the reaction between an acid chloride or carboxylic anhydride and an amine.[17,18] In a typical experiment, CdS nanoparticles capped with 11-mercaptoundecanoyl chloride (CdS-MUC) were obtained by dissolving 0.05 g of CdS-MUA in 15 mL of THF. Then excess $SOCl_2$ (5 mL) was slowly added into the solution of CdS-MUA, and a few drops of DMF were added as catalyst. The reaction mixture was heated at 65−70 °C and cooled after 60 min. The excess $SOCl_2$ was removed under vacuum to give the slightly yellow solution of CdS-MUC in THF. The CdS-MUC nanoparticles were then reacted with Au nanoparticles capped with 4-aminothiophenol (Au-AmTP).

The reaction between free carbonyl chloride group of CdS nanoparticles and the free amino group of Au nanoparticles resulted in the formation of an amido (CONH) linkage. Figure 1 shows some of the assemblies of nanoparticles obtained with an amido linkage including the following: CdS−CdS dimer, CdS−Au dimer, 2Au−Ag trimer, 3Au−Ag tetramer, and the assembly of one Ag dot (*ca.* 5 nm) surrounded by larger Au dots (*ca.* 15 nm) a pentamer. The different dots in the assemblies can easily be differentiated from their size in TEM images as shown in Figure 1.

Azo linkages were prepared from a diazotization reaction of an aromatic primary amine by converting it to a diazonium compound. In a typical experiment, 0.268 g (1 mmol) of CdS−AmTP was dissolved in 10 mL of ethanol. To the solution, 0.069 g (1 mmol)

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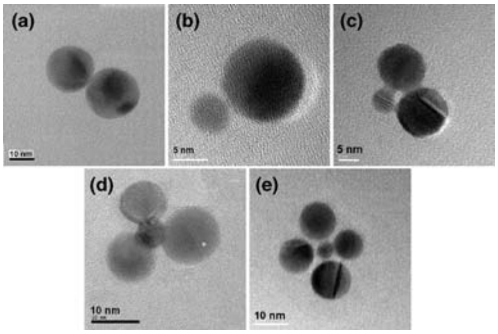

Figure 1. Typical assembly of nanoparticles with amido linkages: (a) a dimer of CdS dots (ca. 17 nm); (b) a dimer of Au (ca. 10 nm) and Ag (ca. 5 nm); (c) a trimer of Au (ca. 15 nm) and Ag (ca. 5 nm); (d) a tetramer of Au (ca. 10 nm) and Ag (ca. 5 nm); (e) Ag (ca. 5 nm) dot surrounded by four gold dots.

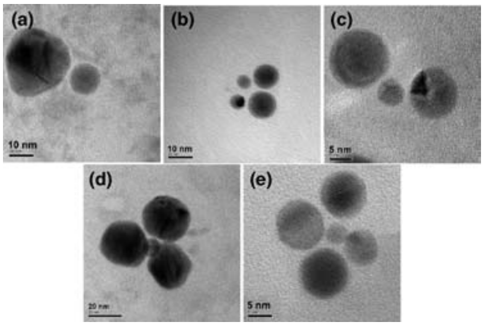

Figure 2. Typical assembly of nanoparticles with azo linkages: (a) a dimer of Au (ca. 22 nm) and CdS (ca. 5 nm); (b) pair of dimers of Au (ca. 10 nm) and CdS (ca. 5 nm); (c) trimers of Au (ca. 15 nm) and CdSe (ca. 5 nm) with small CdSe in the middle; (d) a tetramer of Au (ca. 22 nm) and CdS (ca. 5 nm) with small CdS in the middle; (e) Ag (ca. 5 nm) dot surrounded by four gold dots (ca. 15 nm).

of $NaNO_2$ in 10 mL of water was added dropwise, and then a few drops of concentrated HCl were added. The reactants were mixed together by stirring, and the temperature was kept between 0 and 5 °C for 20 min. The diazotized CdS−AmTP nanoparticles were then reacted with Au−AmTP to form an azo linkage (−N═N−).

Figure 2 shows the TEM images of the assemblies from an azo linkage between Au−AmTP and the diazonium salt of CdS, CdSe, Ag, or Au nanoparticles. The nanoparticle assemblies include the following: Au−CdS dimer, pair of Au−CdS dimers, 2CdSe−Au trimer, 3Au−CdS tetramer, and one Ag dot surrounded by four larger Au dots can be easily identified from their sizes. Figure 3 shows an azo linked trimer with a lattice spacing of 0.203 and 0.115 nm for the larger gold ((200) and (222)) and 0.215 nm for the smaller CdSe (110).

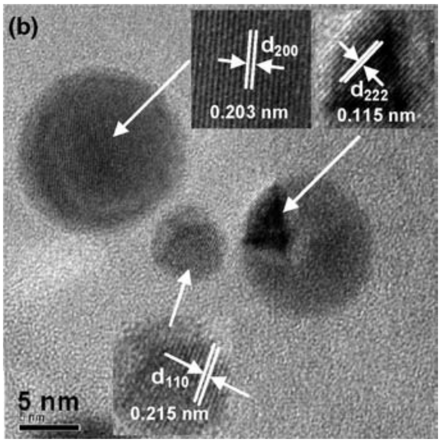

Figure 3. HRTEM images of an azo linkaged tetramer of Au and CdSe with small CdSe in the middle.

The controlled growth can only be achieved by reacting the dots at high dilutions. At higher concentrations, nanoparticles formed a network of chains for both amido and azo functionalized particles.

In conclusion, we have demonstrated the formation of covalently bound nanoparticle assemblies. By changing the concentration of one type of dots as compared to the other and/or their size ratio, we were able to control the structure of the final assembly. Several types of assemblies including dimers, trimers, tetramers, or pentamers were obtained. The assemblies formed between different types of nanoparticles were easily identified by HRTEM.

The method described in this work can lead to rational synthesis for more complex structures with potential for application in various electronic or optoelectronic applications.

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Supporting Information Available: Experimental details, TEM, HRTEM images, IR spectra of nanoparticles before and after linking reaction. This material is available free of charge via the Internet at http://pubs.acs.org.

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