Ligand-Induced Gold Nanocrystal Superlattice Formation in Colloidal Solution

X. M. Lin and C. M. Sorensen*

Condensed Matter Laboratory, Department of Physics, Kansas State University, Manhattan, Kansas 66506

K. J. Klabunde

Department of Chemistry, Kansas State University, Manhattan, Kansas 66506

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Introduction. During the past decade, nanocrystal research has been focused on two major properties of finite size materials, namely, quantum size effects and surface/interface effects.[1] A new trend, however, has emerged in the past few years to arrange the nanocrystals into two or three-dimensional superlattices.[2] The ability to synthesize nanocrystal superlattice (NCS) structures will provide a new horizon to study the collective properties due to the particle interaction and develop future optical[3] and information storage devices.[4] Several groups are striving to control nanocrystal size through size selective precipitation methods and create NCSs through evaporation of colloids containing lyophobic nanocrystals on a substrate. Face-centered cubic CdSe NCSs were synthesized through reducing the solubility of particles by slowly evaporating one component of a solvent mixture.[5] Oxide[6] and sulfide[7] NCSs were spontaneously formed by evaporating the colloid on a substrate. Linking molecules have also been used to form two-dimensional gold NCSs.[8] Narrow size latex particles and nanometer ferritin molecules were self-assembled in thin liquid films with thickness comparable to the size of the particles.[9] All these methods of forming NCSs rely on modifying the nature of the nanocrystal surface and its surrounding environment and therefore control the interaction between different particles. Other physical means such as electrophoretic deposition were also explored to form NCSs on a substrate[10a,b] and on chemically modified silica surfaces.[10c] Recently, Whetten et al.[11] used a fractional crystallization technique to create gold and silver nanoparticles with a very narrow size distribution, and NCSs with different structures were formed spontaneously after evaporating the solvent. However, exactly how important the condition of narrow size distribution in forming NCSs remains a question. Furthermore, except for the recent work involving CdSe NCSs by Murray et al.,[5] the other NCSs that have been reported so far were formed on a small substrate by evaporating the solvent. Forming NCSs of different materials directly in the colloid still remains a challenge. Although several important properties of NCSs, including dipolar coupling[12] and long wavelength shifting of the fluorescence band[5] in CdSe superlattice, have been reported, properties of NCSs remain largely unexplored. In this paper, we describe an inverse micelle synthesis[13] to create a gold nanocrystal colloid of relatively narrow size distribution. Several ligands which contain thiol, sulfide, and amino functional groups were chosen to further modify the surface of the existing gold nanocrystals. These ligands were chosen because the functional groups they contain have fairly good affinity for metal surfaces. We found that certain ligands added to the colloid will induce a spontaneous and self-size-selective NCS formation. Bulk quantities of gold NCS structures were directly synthesized in the colloid and their optical properties were studied.

Experimental Section. Didodecyldimethylammonium bromide (DDAB) was purchased from Fluka and used as received. Sodium borohydride, gold chloride (99.99%), dioctyl sulfide, and dodecanethiol were ordered from Aldrich. Gold chloride (99%) was purchased from Fisher. Toluene was purchased from Fisher and was further purified by distillation. Hexylamine was purchased from Alfa and used as received. Deionized distilled water was obtained from a Barnstead Nanopure system. Toluene and distilled water were first degassed by bubbling with dry argon gas for 2 h prior to the experiment. The degassing process is a necessary step for a well-controlled growth of nanoparticles, as pointed out by Wilcoxon et al.[13] All the synthetic steps were carried out in a dry argon environment in order to prevent chemicals from absorbing moisture. A 0.75 g portion of DDAB was dissolved in 5.2 mL of toluene to form a 0.35 M micelle solution. A 15 mg sample of gold chloride was then dissolved in 5 mL of the micelle solution by sonication to form a dark orange solution. A 17 μL aliquot of 9.4 M aqueous $NaBH_4$ solution ($[BH_4^-]:[Au^{3+}] = 3:1$) was added while the solution vigorously stirred. The solution first decolored and then turned to red after about 20 s. The mixture was stirred for 15 min to ensure a complete reaction. The gold

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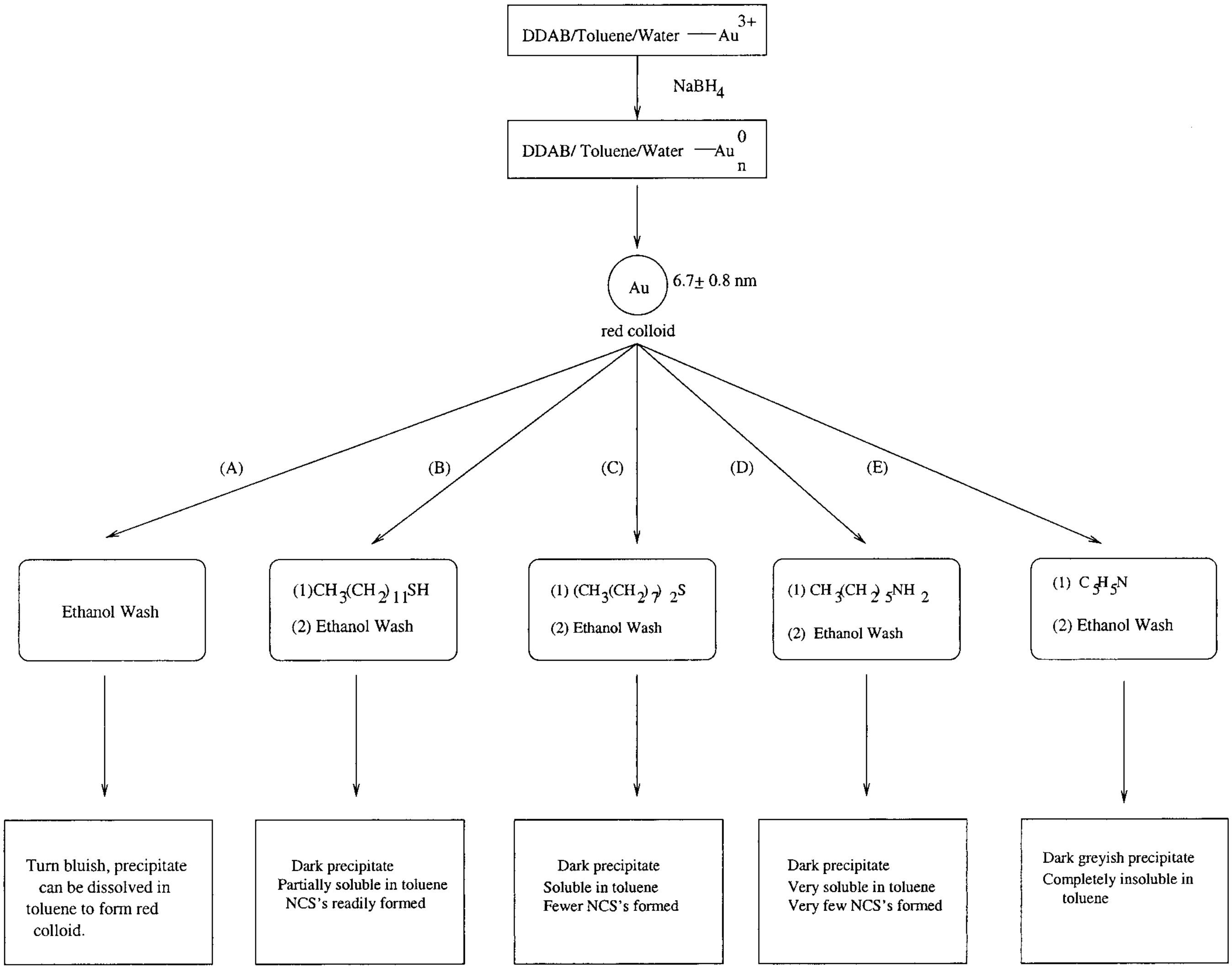
Scheme 1



colloid was then split into five portions, each with 1 mL of colloid, and the samples will be referred to as A, B, C, D, and E (Scheme 1). In sample A, 8 mL of ethanol was added, which caused a immediate change of color from red to blue. Different ligands were added to the vials for the rest of the samples prior to the same ethanol wash with [ligand]:[DDAB] = 10:1. To samples B, C, D, and E was added 0.838 mL of dodecanethiol, 1.08 mL of dioctyl sulfide, 0.404 mL of *n*-hexylamine, or 0.12 mL of pyridine, respectively, and then the samples were stirred for several minutes before adding 8 mL of ethanol. All the samples were placed on the benchtop overnight. Particle aggregates caused by the ethanol wash settled down to the bottom of the vial, leaving extra surfactant and reaction side products in the top supernatant layer. The top supernatant layer was decanted from each sample. After drying the bottom precipitate in a vacuum, 10 mL of toluene was added to each sample. A brief reflux heating was also performed to increase the solubility of all the samples.

Ligand modification was achieved for samples B–E as simply indicated by the facts that the color of the precipitate after the ethanol wash was slightly different for each sample and the solubility of each precipitate was also different. Sample A, in which the gold particles only had a DDAB coating, showed variable solubility depending on the amount of impurity ions in the system. Using 99.99% gold chloride as a starting material, the precipitate after ethanol washing would redissolve much easier than the precipitate prepared by using 99% gold chloride as a starting material. Sample B, which was ligated with dodecanethiol with possibly a coating of the remaining DDAB, had a dark precipitate and was partially soluble in toluene. After being heated under reflux, it completely redissolved into the toluene and formed a red colloid. One hour after reflux heating, the color of the colloid changed back to bluish and a precipitate started to appear. After a couple of days sitting on the benchtop, a large amount of precipitate appeared at the bottom of the vial, leaving a reddish top layer. Sample C, which was ligated with octyl sulfide, appeared to be more soluble than sample B, the amount of precipitate was considerably less after reflux heating, and settling occurred on the benchtop for several days. Sample D, which was ligated with hexylamine, completely redissolved back into toluene even without reflux heating. Sample E, which was ligated with pyridine, was completely insoluble in toluene even after reflux heating.

Results. Transmission electron microscopy (TEM) showed that the as prepared gold colloid without ethanol wash contained 6.7 nm particles with a standard

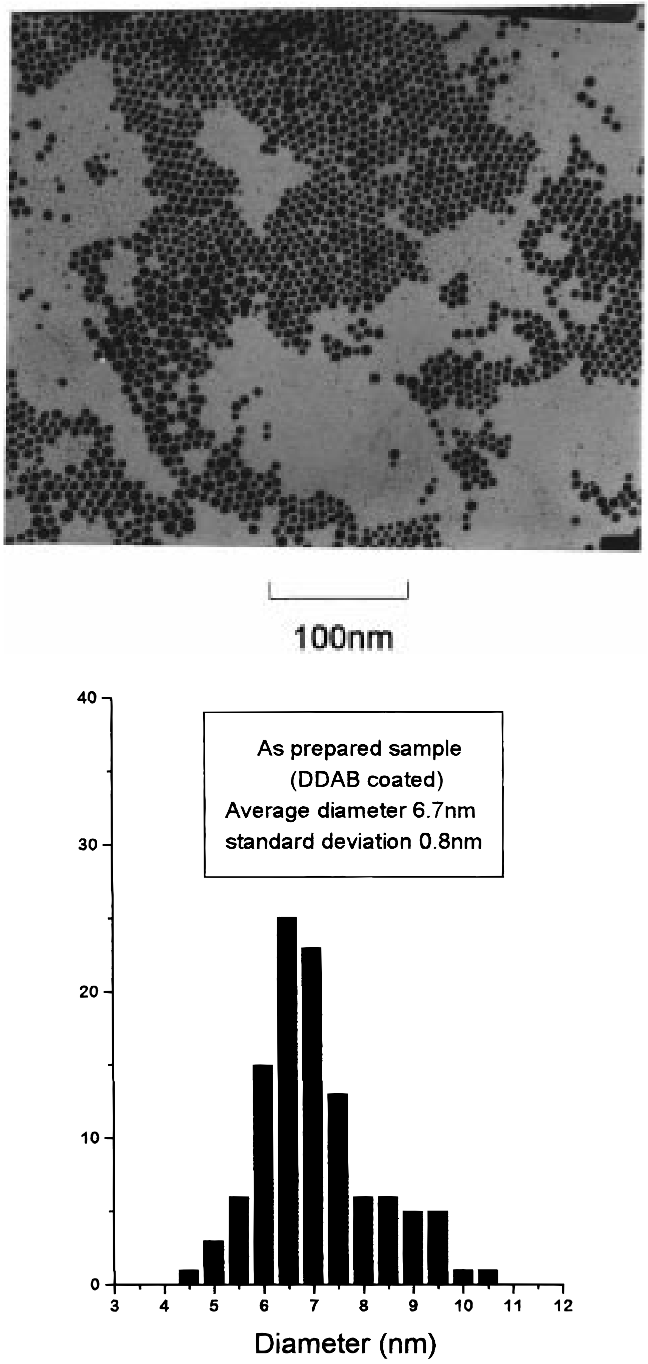


Figure 1. TEM image and histogram of as-prepared gold particles with DDAB coating before ethanol washing.

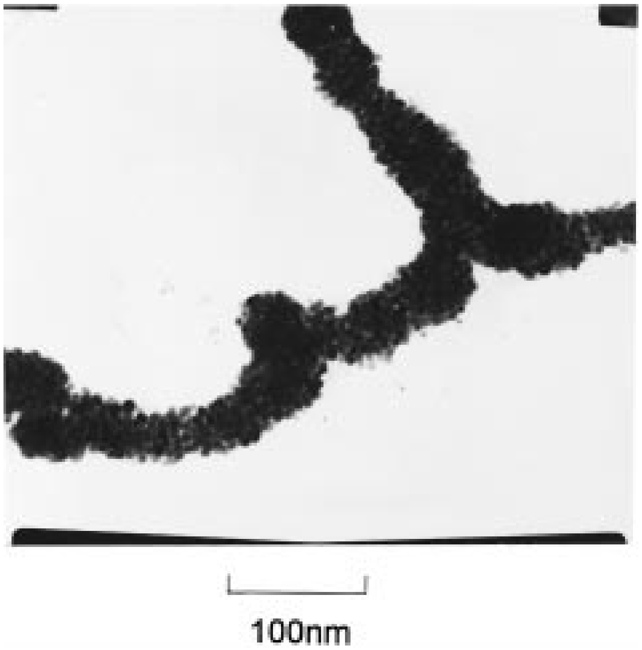


Figure 2. Random aggregates formed after ethanol wash for sample A containing a small amount of impurity ions.

deviation of 0.8 nm (Figure 1). After careful ethanol washing, in most cases, sample A coated only with DDAB can be redissolved back into toluene to form a stable reddish colloid. TEM showed it contained mainly single particles. However, with less pure gold chloride (99%) to synthesize sample A (Scheme 1), the solubility of the precipitate back into toluene was poor. In these cases, random aggregates such as in Figure 2 were obtained at the bottom of the vial. The implication is that, without ligand, the surface of the nanoparticles is more vulnerable to the attack of other impurity ions and therefore change the particle–particle interaction and cause random aggregation. Sample B, ligated with dodecanethiol, showed completely different aggregate morphology compared with sample A. The top layer of sample B contained small single particles, as shown in Figure 3a. The average size of the top layer particle was 6.0 nm, smaller than the average particle size of the as-prepared sample, and it also had a narrower size distribution (standard deviation 0.4 nm). Close-packed arrays were formed after evaporating the sample on a carbon-coated grid. The dark connected ring patches in Figure 3a also indicated formation of a bilayer of particles. The same pattern was reported by Fink et al.,[14] which was attributed to the preference of occupying 2-fold saddle sites rather than 3-fold hollow sites. The bottom layer of sample B contained a large amount of superlattice structures which were made of slightly larger particles, as shown in Figure 3b. Although these images are slightly underexposed because of the instability of the superlattice structures under a high intensity electron beam, lattice fringes can be clearly distinguished. A higher magnification revealed that these precipitates consisted of micron-sized random aggregates of spherical NCSs, each with a diameter around 130 nm (Figure 4). The fact that the dodecanethiol-ligated sample had a smaller size and narrower size distribution in the top layer and a large amount of NCS formation in the bottom layer indicates that NCS formation is a size selective process. Only the dispersion forces between large particles in the distribution of our sample were strong enough to bring these particles into close contact to form superlattice structures. The dispersional interaction between smaller particles was not strong enough to overcome the entropy loss arising from the long range ordering. Therefore, most of the small particles remained solvated in the top layer of the colloid. A close examination of Figures 3b and 4 shows that some of the smaller particles, however, do appear at the edges of the superlattice and smeared out the clear facets of the superlattices. These results corroborate well with the reported size selective crystallization process in a polydisperse system.[15] The micron-

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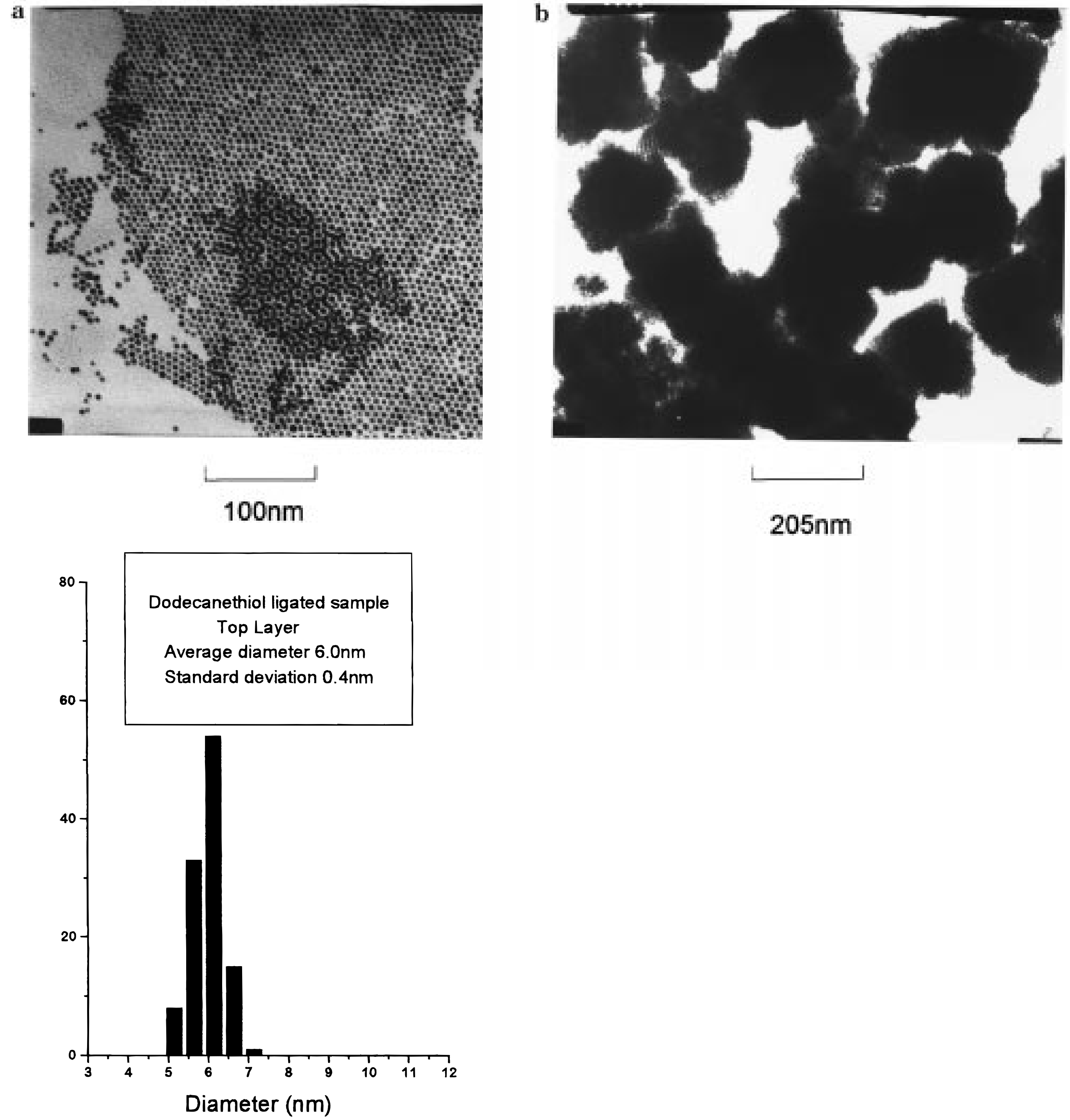

Figure 3. Dodecanethiol-ligated gold single particles and superlattice structures: (a) top layer single particles and (b) bottom layer superlattice structures.

sized NCS aggregates could be broken into single superlattice crystallites simply by shaking the colloid, as confirmed by light scattering experiments. TEM also showed that sample C (ligated with dioctyl sulfide) contained NCSs at the bottom of the vial; however, the amount of NCSs formed was signigicantly less compared with dodecanethiol-ligated sample B. Sample D, which was ligated with hexylamine, had mostly single particles witha few NCSs visible under TEM. These observations indicated that different ligands have various ability to modify the nanocrystal surface. The experimental procedures and the observations are summarized in Scheme 1.

The optical properties of both the single particles formed in the as-prepared sample and NCSs formed in the dodecanethiol ligated sample were examined by UV−vis spectroscopy. The solid line in Figure 5 shows the absorption curve for the as-prepared sample coated with DDAB prior to the ethanol wash. The sharp plasmon peak at 528 nm indicates a relative small particle size distribution, as was evident in the TEM examination. The colloid containing dodecanethiol-ligated NCSs has a broad absorption band (dashed line) from 520 to 630 nm at room temperature. The extra

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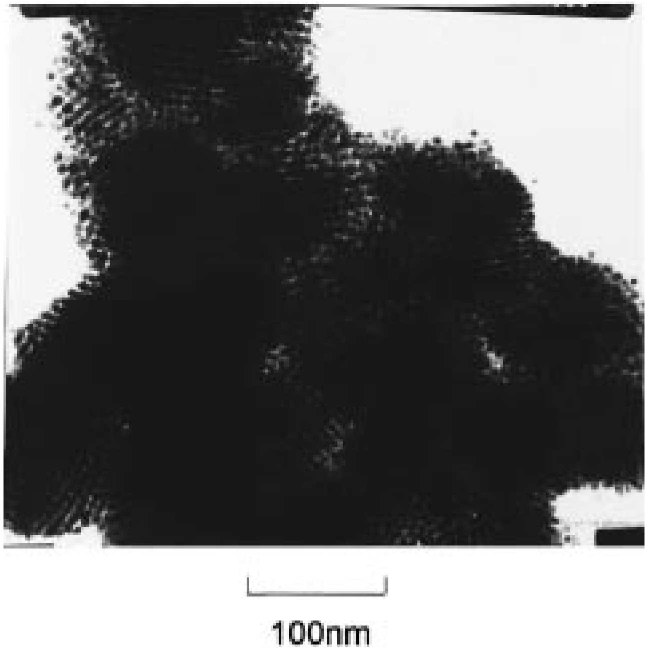

Figure 4. Higher magnification of superlatticle structure of dodecanethiol-ligated sample B.

absorption band in the low-energy region for the NCSs was theoretically predicted by Quinten and Kreibig.[16] Retardation effects and electromagnetic dipolar interaction between different particles in the NCSs caused an additional absorption band in the low-energy region. The NCSs formed in the dodecanethiol-ligated sample can also be decomposed back to single particles upon heating. The dotted line in Figure 5 shows the absorption curve of the same colloid at 100 °C, which contained superlattice structures at 25 °C. The reappearance of the single particle surface plasmon peak indicated that NCSs were broken into single particles. TEM also confirmed this conclusion. Cooling the colloid back to room temperature and settling on the benchtop for several days would re-form NCSs. Detailed studies of the thermal stability of the NCSs will be published in a subsequent paper.

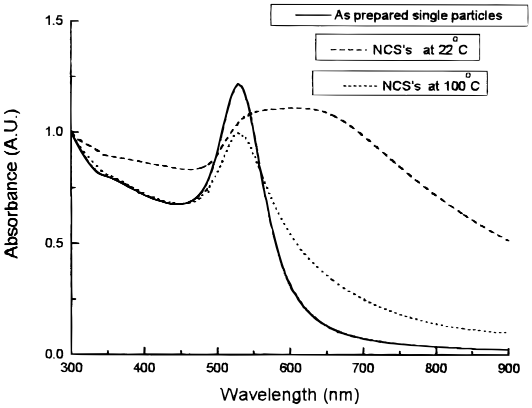

Figure 5. UV–vis absorption spectra of as-prepared DDAB-coated single particles (solid line) and superlattice structures at 22 °C (dash line) and 100 °C (dotted line).

To summarize, we have synthesized nanocrystal superlattices (NCSs) directly in a gold colloid solution through ligating the gold nanocrystal surface with certain ligands. Dodecanethiol was proven to be most effective in forming NCSs compared with several other ligands. Although the as-prepared sample had some size distribution, NCSs formation seems to be spontaneous and self-size-selective. In situ UV–vis absorption measurements show that NCSs had a broad absorption band extended toward the low-energy region compared with as-prepared single particles. Both absorption measurement and TEM confirmed that NCSs are not thermally stable. NCSs and single nanocrystals can be formed reversibly in solution by controlling the temperature of the colloid.

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