

# One-, Two-, and Three-Dimensional Superstructures of Gold Nanorods Induced by Dimercaptosuccinic Acid

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A method is described for assembling gold nanorods into one-, two-, and three-dimensional superstructures. The addition of dimercaptosuccinic acid (DMSA) into the nanorod solution was found to induce self-assembly of the latter to one-dimensional “tapelike”, two-dimensional “sheetlike” and three-dimensional “superlattice-like” structures depending on the DMSA concentration. The assembly was found to follow a smectic structure, where the nanorod long axes are parallel to each other. The rods are spaced  $8.5 \pm 0.3$  nm apart in the resulting structures, which extend over several micrometers in length. Organizations perpendicular to the grid were also found. The nanorod tapes were found to bend, and they form circular assemblies as well. The assembly and morphology of the nanorod structures were characterized by transmission electron microscopy and UV–vis spectroscopy. The effect of the DMSA concentration as well as the pH of the medium was also studied. On the basis of several control experiments utilizing similar molecules, charge neutralization of the nanorods by the carboxylic group of DMSA was found to be the principal reason for such an assembly, while the mercapto groups render additional stability to its structure. A mechanistic model of the assembly is proposed. This type of assembly would plausibly function as a plasmonic waveguide in potential nanodevices.

## Introduction

Self-assembled nanostructures find a wide range of applications in science and technology.<sup>1</sup> The interest in assembling nanoparticles lies in the fact that the collective properties of such an assembly can be different from those of the individual nanoparticles. The ability to produce monodisperse nanoparticles through simple synthetic strategies has opened up the possibility of assembling them into tailored superstructures. One-, two-, and three-dimensional (1D, 2D, and 3D) assemblies of nanoparticles have been studied extensively in recent times.<sup>2</sup> Various strategies are employed to obtain a well-ordered assembly. Nanolithographic techniques and colloidal self-assembly are the two major techniques used to get a well-ordered array. Harnessing the properties of such organized structures is a hot area of research. Assembled nanostructures are technologically important, and they find applications in many fields.<sup>3</sup> Since self-organized nanosuperstructures are too few compared to the structures produced by lithographic techniques, strong interest is shown by the scientific community to make structures using self-assembly.

In a self-assembled superstructure, the property investigated depends on the degree of order between the building blocks. Well-ordered self-assemblies from spherical metal,<sup>4</sup> semicon-

ductor,<sup>5</sup> and magnetic<sup>6</sup> nanoparticles leading to superlattices have been achieved already. Self-assembly of ligand- or polymer-stabilized nanoparticles to one- or two-dimensional arrays is well-known.<sup>7</sup> Well-structured templates are also being used to direct nanoparticle assembly in both one dimension and two dimensions.<sup>8</sup>

Compared to their spherical counterparts, anisotropic particles are diverse and fascinating because of their inherent properties such as multiple plasmon bands and light absorption in the near-infrared (NIR) regions, which open up various possible applications. In the case of nanorods and nanowires, the absorption and scattering of light give two absorption maxima, one due to plasmon excitation along the long axis, occurring in the NIR region, called the longitudinal surface plasmon (LSP) resonance, and a second due to excitation along the short axis occurring in the shorter wavelength (visible) region, called the transverse surface plasmon (TSP) resonance. Some other higher order quadrupolar interactions are also seen in the case of some anisotropic structures such as nanoprisms. Due to the enhanced electromagnetic field at the tips of these anisotropic structures, compared to their spherical equivalents, the anisotropic particles show better surface-enhanced Raman spectroscopic (SERS) activity and are also useful for fluorescence sensing applications.<sup>9</sup>

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While assembly of spherical metal particles is rather well studied, the self-assembly of anisotropic particles is comparatively poorly investigated. Assembling anisotropic nanorods, especially noble metal nanorods,<sup>10</sup> has attracted a great deal of attention because they are prospective candidates for uses such as waveguides leading to the miniaturization of devices below the diffraction limit,<sup>11</sup> catalytic motors,<sup>12</sup> etc. Lithographic techniques are widely used for producing such waveguides from gold and silver nanospheres and nanorods. An alternate way is to assemble nanoparticles on self-assembled monolayers (SAMs) to produce functional electronic devices.<sup>13</sup>

Anisotropic nanoparticles, unlike spherical particles, can align in different ways. One such assembly, especially in the case of nanorods, is an end-to-end assembly. This is attractive for several applications such as surface-enhanced Raman or fluorescence sensing applications.<sup>14</sup> Various groups succeeded in lining up nanorods in an end-to-end fashion. Van der Zande et al. were able to align rod-shaped gold particles dispersed in poly(vinyl alcohol), which was one of the first attempts to organize anisotropic particles.<sup>15a</sup> More recently Artemyev et al. made a unidirectional array of CdSe nanorods using ZnS as a template.<sup>15b</sup> Thomas et al. aligned nanorods in a longitudinal manner using amino acids, and the spectral changes that occurred were utilized for selective detection of the amino acid.<sup>15c</sup> Caswell et al. found that biological linkers can organize gold nanorods into 1D arrays.<sup>15d</sup> In all these assemblies, parameters such as relative concentrations of reagents, pH, and ionic strength have a significant effect, if the linking strategy principally depends on electrostatic forces. Carbon nanotubes were used as templates to organize nanorods in one dimension by Correa-Duarte et al.<sup>15e</sup>

Other than assembling end-to-end, nanorods can self-assemble in a parallel manner also. Such a side-to-side stacking can lead to a 2D array. In a side-to-side array, if the distances are well defined, then they are proved to be excellent at promulgating light along the nanorod–nanorod chain.<sup>16</sup> Nanorods are known to self-assemble in an air–water interface, and large-scale assembly of gold nanorods on a transmission electron microscopy (TEM) grid was reported by Nikoobakh et al.<sup>17</sup> The Langmuir–Blodgett method was used by Kim et al. to assemble gold nanorods.<sup>18</sup> Solvent evaporation on the TEM grid is also known to form a nanorod assembly.<sup>19</sup> Recently a ringlike assembly of

nanorods was reported by Khanal and Zubarev, where they used polystyrene chains covalently attached to the nanorod surface to get a well-defined shape.<sup>20a</sup> The shape-selective behavior of gold nanorods was used to fabricate an assembly by Xu et al.<sup>20b</sup> In this study, they fabricated a well-ordered array of gold nanorods on silicon wafers from a mixture of spherical particles and rods. They found that nanorods self-assemble and show shape selectivity during the assembly. Assembly of nanorods mediated by the pH changes in the medium, in which a side-by-side alignment of nanorods occurs, has been reported by Orendorff et al.<sup>20c</sup> More recently, Mitamura et al.<sup>20d</sup> reported 2D or 3D ordered structures of hydrophobic nanorods which were found to self-assemble upon the evaporation of the solvent. They accomplished this by simple surface modification of gold nanorods by replacing cetyltrimethylammonium bromide (CTAB) with (mercaptopropyl)trimethoxysilane (MPS) and subsequently with octadecyltrimethoxysilane (ODS), which made the gold nanorods hydrophobic. DNA-driven self-assembly of gold nanorods was first reported by Dujardin et al.<sup>21a</sup> and more recently by Pan et al.<sup>21b</sup> In the first report they showed how selective and reversible DNA-driven assembly of nanoparticles can be applied to nanorods. Pan et al. showed that different aspect ratio nanorods can be self-assembled using DNA as a template into 1D and 2D structures. Self-assembly of CdSe nanorods to macroscopic solids was reported by Talapin et al.<sup>22</sup> In this work, they demonstrated that the nanorods will self-organize to nematic, smectic, and crystalline solids upon diffusion of a liquid with a higher boiling point into the colloidal solution.

Nanorods have been arranged perpendicular to the substrate also. Vertical alignment of nanorods is of special interest because it will help in further minimizing the size below the lithographic limit and also because such structures exhibit single transistor behavior.<sup>23</sup> In a vertical assembly of magnetic nanorods, as the magnetic coersivity ( $H_c$ ) can be controlled along the nanorod length, such assemblies could have enormous possibilities in the area of data storage.<sup>24</sup> Several groups have tried to get vertical assemblies of nanorods. An electric field was employed in assembling nanorods perpendicular to the substrate, separately by Gupta et al.<sup>25a</sup> and Ryan et al.<sup>25b</sup> Gupta et al. found that ligand-functionalized nanorods in a polymer matrix phase separate upon the application of an electric field. Ryan et al. reported that the application of a dc electric field and solvent evaporation, combined together, will give vertically aligned nanorod superlattices of CdSe nanorods. More recently, pyrolytic graphite was used as a template for aligning CdSe nanorods into specifically aligned superstructures.<sup>25c</sup>

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In this paper we report large-scale assembly of gold nanorods in the presence of dimercaptosuccinic acid (DMSA). Well-arranged superstructures were seen on the TEM grid. The extent of arrangement and the nature of assembly were found to be dependent on the concentration of DMSA present in the system. In most of the assembly, the nanorods were found to arrange in a smectic fashion. Assembly with the long axis perpendicular to the substrate (columnar arrangement) also was found. The monodispersity of the nanorod sample and sample purity, in terms of the extent of other shapes, i.e., spheres, dumbbells, etc., present in the ensemble, was also found to affect the assembly. Nanorods were found to be stable up to a 2 mM concentration of DMSA, above which they were found to aggregate and start to settle. There was complete settling of nanorods at a DMSA concentration of 3.5 mM. The assembly was characterized by UV-vis spectroscopy and transmission electron microscopy. It may be noted that mercaptosuccinic acid (MSA)-protected spherical gold nanoparticles are known to give superlattices.<sup>2d,e</sup>

### Experimental Section

**Materials.** Sodium borohydride ( $\text{NaBH}_4$ ), DMSA, MSA, and mercaptopropionic acid (MPA) were purchased from Sigma-Aldrich. Succinic acid (SA) and butanoic acid (BA) was purchased from Merck. Tetrachloroauric acid trihydrate ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ) was purchased from CDH, India. Ascorbic acid was purchased from Hi-Media Chemicals, India. CTAB was purchased from SD Fine Chemicals. All chemicals were used as such without further purification. Triply distilled water was used throughout the experiments.

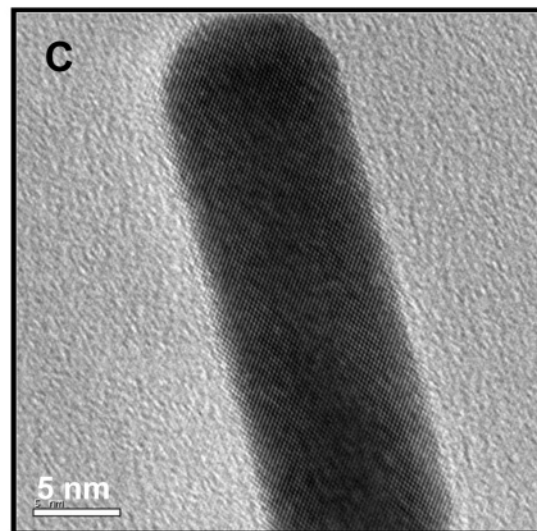
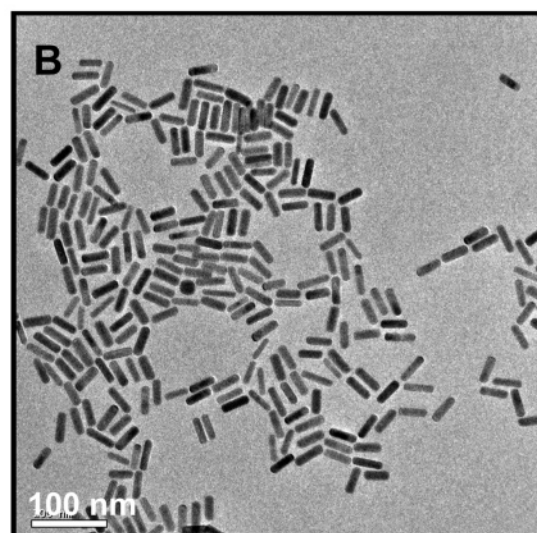
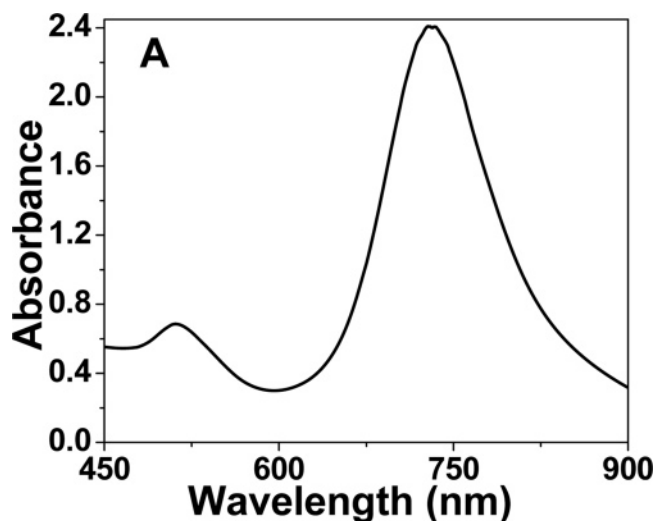
**Synthesis of Gold Nanorods.** Nanorods were made and purified as per the procedure described in our previous paper<sup>26a</sup> which followed the well-established seed-mediated method.<sup>26b</sup> First, gold seeds protected by CTAB of around 3–4 nm were prepared by the reduction of the required amounts of gold ions by ice-cold  $\text{NaBH}_4$  in the presence of CTAB. After 3 h, a calculated amount of the seeds was added to a growth solution containing specific amounts of CTAB,  $\text{HAuCl}_4$ , and ascorbic acid. The resultant solution was kept without disturbance for 24 h and examined using TEM to determine the monodispersity of the sample.

The as-prepared nanorod sample was centrifuged at 11 100 rpm for 15 min. The supernatant was discarded, and the residue was redispersed in an equal amount of triply distilled water. The sample was again centrifuged at 11 100 rpm. This was repeated twice, principally to remove excess CTAB.

**Preparation of the Self-Assembly.** The centrifuged sample was diluted to an optical density of 2.5 at 730 nm. This ensured constancy in the nanorod concentration in each centrifugation cycle. Separate 4 mL aliquots of the purified nanorod samples were taken, and different amounts of DMSA were added to the nanorod solutions such that the final concentration of DMSA in each sample was 0.20, 0.35, 0.50, 0.80, 1.00, 1.25, 1.50, 2.00, 3.00, and 3.50 mM. They were incubated at 28 °C for 24 h.

**Methods.** After 24 h, UV-vis spectra of each sample were measured using a Perkin-Elmer Lambda 25 UV-vis spectrophotometer. Simultaneously a small aliquot of the reaction mixture from each solution was dropped onto a carbon-coated copper grid and dried in the ambient conditions. These samples were examined using a JEOL 3011, 300 kV transmission electron microscope with a UHR pole piece. Detailed control experiments involving UV-vis and HRTEM were performed. Limited experiments were conducted with MSA, SA, MPA, BA, and 2,5-dimercapto-1,3,4-thiadiazole as well.

Typically HRTEM measurements were performed at 300 kV. However, lower acceleration voltages were also used. For examining the largest possible areas, images were also collected at two different modes of the transmission electron microscope. Images were taken

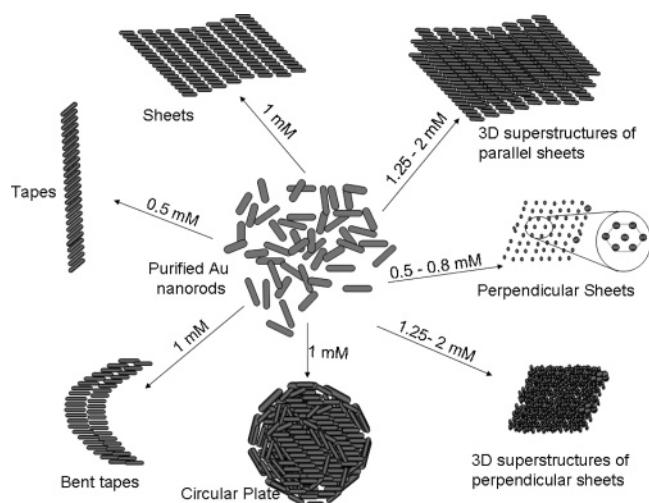


**Figure 1.** (A) UV-vis spectrum of the nanorod sample after purification, (B) low-magnification image of the purified nanorod sample showing a random orientation, and (C) lattice-resolved image of a single nanorod showing a well-structured tip and body.

in the low-magnification (Low MAG) mode of the transmission electron microscope where the condenser minilens and the objective lens were off and only the objective minilens was working. This allowed us to see a large area of the TEM grid ( $10 \times 10 \mu\text{m}$ ), over

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**Scheme 1. Various Superstructures Formed from Au Nanorods in the Presence of Different Concentrations of DMSA**

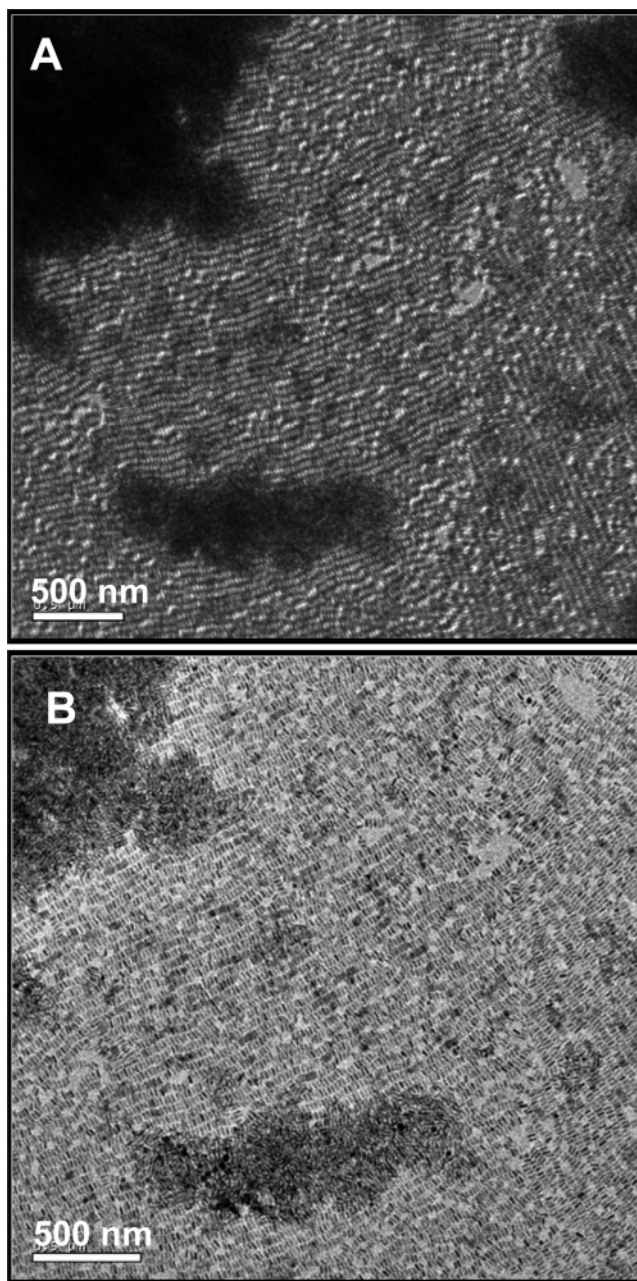


which the nanorods were arranged. However, since only the objective minilens was functional, the resolution was substantially less. Most of the images were taken in the MAG I mode, where all the above lenses were working and the images were of higher resolution (lattice resolution 1.4 Å).

$\zeta$  potentials were measured using a Malvern Zetasizer Nano ZS instrument. A WiTec GmbH, micro Raman spectrometer was used for vibrational characterization. An Ar ion laser of 514.5 nm wavelength was used to excite the sample, and the signal was collected in the backscattering geometry.

## Results and Discussion

Figure 1A shows the UV–vis spectrum of the nanorod sample after two centrifugations. The nanorod sample gave an LSP at 730 nm and a TSP at 507 nm. The aspect ratio of the nanorod sample was calculated to be 3.44 nm with a 12 nm rod diameter. The sharpness of the LSP shows the monodispersity of the sample in terms of size and shape. From the low intensity of the TSP and the absence of any feature at 520 nm, it can be understood that the amount of spherical particles present is minimal. The presence of spherical particles appears as a shoulder centered at 520 nm on the right side of the TSP of the nanorods. Figure 1B shows a large-area TEM image of the as-prepared nanorod sample. Most of the nanorods have the same size. Some (less than 1%) of the spherical particles are also seen, and the average size (diameter) of those was found to be 30 nm, which is greater than the typical nanorod diameter. The figure shows an isotropic arrangement of nanorods with small localized arrangements where rods are aligned parallel to each other. Cationic surfactants such as CTAB when present as surface-adsorbed multilayers are known to induce self-ordering of spherical gold nanoparticles.<sup>27a</sup> This is believed to be due to a balance between short-range electrostatic repulsion and interchain attraction between the CTAB tails. It is also reported that, upon concentration from an aqueous solution, higher order structures can be produced from gold nanorods of aspect ratio 4.6, if they are coated with two different cationic surfactants.<sup>17</sup> Surfactant-mediated interactions between high aspect ratio gold nanorods having uniform shape and size can result in ordered liquid crystalline arrays in concentrated suspensions, where the nanorods are arranged in a side-to-side fashion.<sup>27b</sup> However, such assemblies are observed regularly for nanorods of aspect ratio greater than 5, and smaller nanorods,



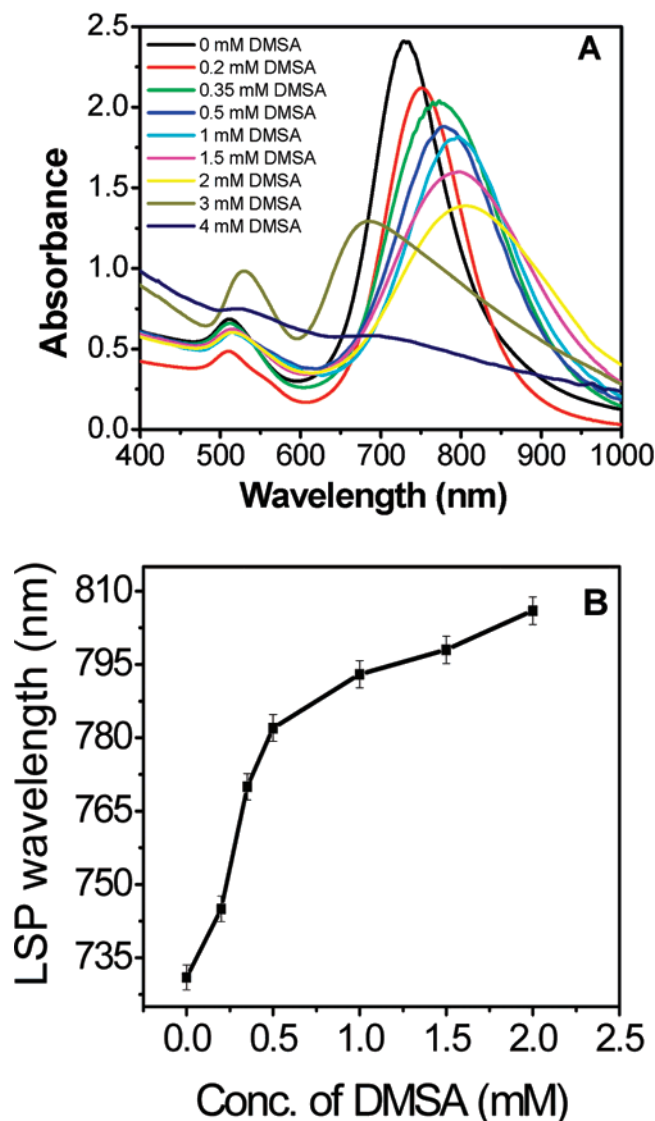
**Figure 2.** TEM images taken in the (A) Low MAG and (B) MAG I modes of the same area, showing self-assembly of nanorods, induced by DMSA (1 mM).

especially those prepared in the presence of a small quantity of silver nitrate, show a tendency to fill the available space by forming all sorts of assemblies, such as end-to-end and side-to-side, exhibiting short-range order in the vicinity but isotropic behavior over a large area.<sup>19a,c</sup> Our observations confirmed this, and it is to be noted that the local arrangement never extended beyond a few nanometers.

Figure 1C is a magnified image of a single nanorod showing the lattice structure of the nanorod. We can see clearly that the nanorod has a well-defined shape with a well-structured tip and body. The tips of the nanorods are composed of {111} and {100} facets, and the rod body is primarily composed of {110} facets.<sup>26c</sup> In most parts of the grid, the nanorods were isotropically distributed and no special preferential arrangement was seen over a large area.

We found that the introduction of DMSA into the purified nanorod solution can induce well-arranged superstructures.

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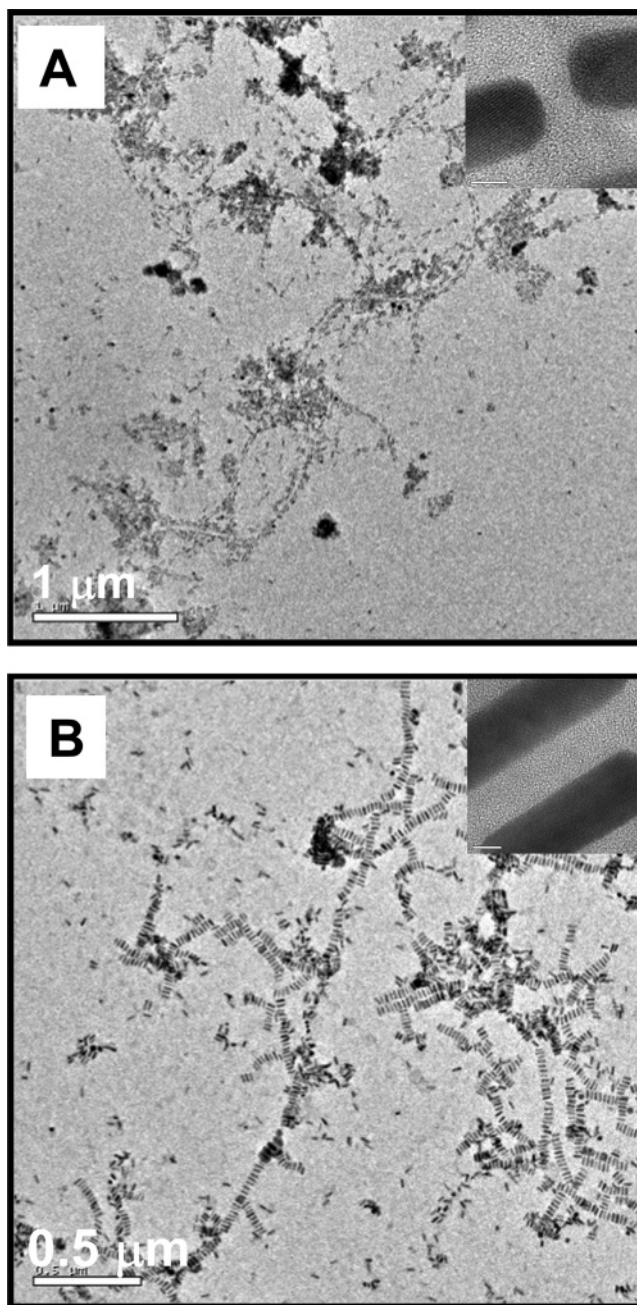


**Figure 3.** (A) UV-vis spectra of gold nanorods as a function of the DMSA concentration (keeping the total volume constant). (B) LSP wavelength against the concentration of DMSA used, showing a red shift with an increase in concentration.

Depending on the concentration of DMSA, the superstructure formed was found to vary. Scheme 1 is a pictorial representation of the various structures obtained at different concentrations of DMSA. We will discuss each one of these structures as we present the TEM images.

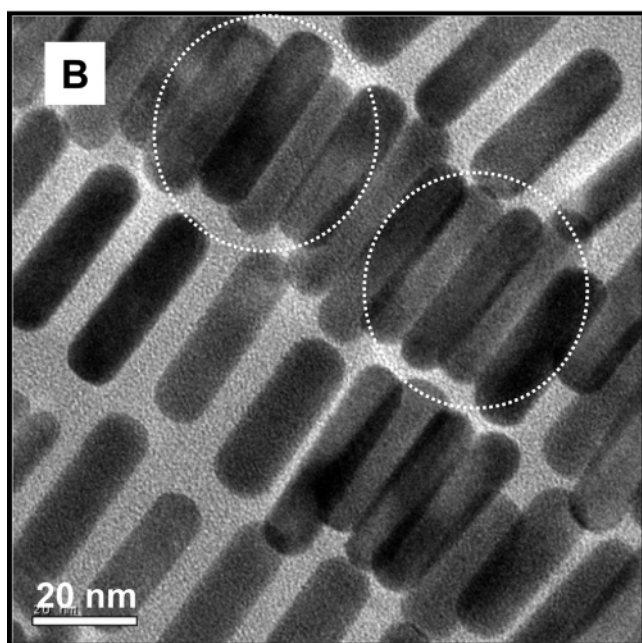
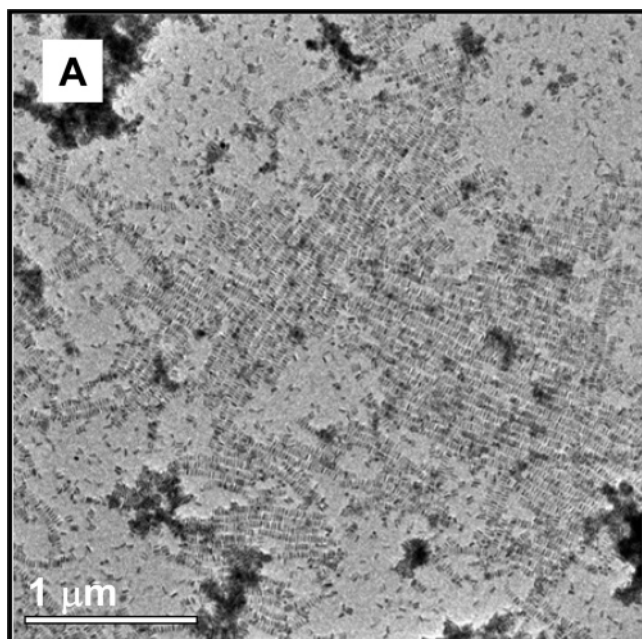
Figure 2 shows a large-area image of a well-ordered assembly obtained when nanorods were treated with DMSA. The concentration of DMSA used was 1 mM. Figure 2A was taken in the Low MAG mode of the instrument, where we can see a well-ordered assembly over a large area. More Low MAG images are given in Supporting Information Figure S1. The same area in the MAG I mode is shown in Figure 2B. There we can clearly see the individual nanorods arranged parallel to each other over a large area in a “sheetlike” or “carpetlike” manner (Scheme 1). The arrangement originates from one-dimensional sidewise assembly forming “tapes”. We can also see that the individual tapes come together side-by-side to produce a sheetlike 2D array. They can also pack one over the other to give a 3D superstructure. Such a structure can also come about from sheets.

**Effect of the DMSA Concentration on Self-Assembly.** The effect of the DMSA concentration on self-assembly of nanorods was investigated in detail. Figure 3A shows the UV-vis spectra



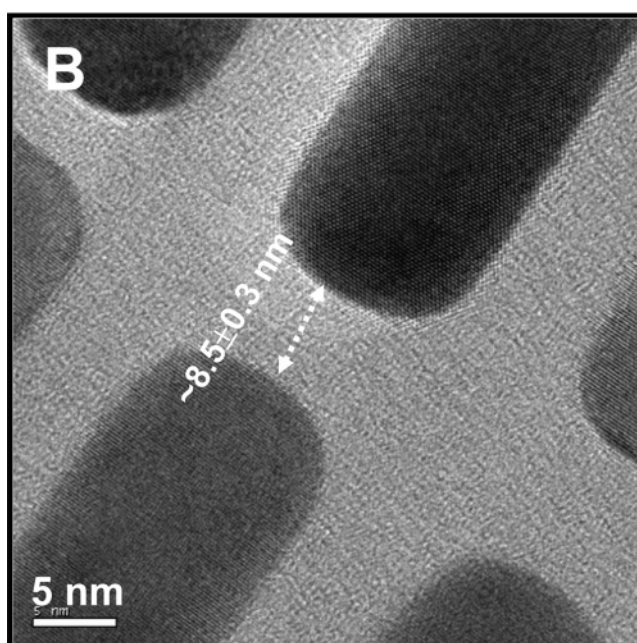
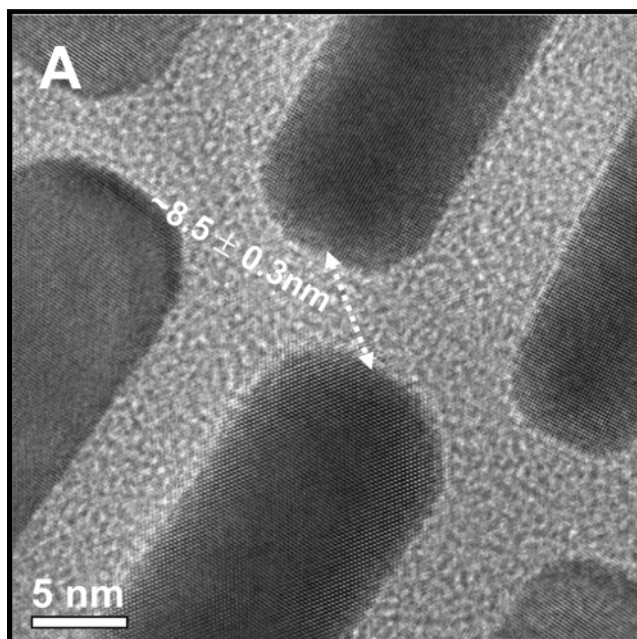
**Figure 4.** TEM images of samples with DMSA concentrations of (A) 300  $\mu$ M showing the longitudinal assembly of gold nanorods in one dimension. The inset in (A) is a lattice-resolved image of the longitudinal assembly at 300  $\mu$ M concentration. (B) Low-magnification TEM image of the sample containing 0.5 mM DMSA showing a parallel assembly of nanorods leading to a tapelike structure. The inset in (B) is a lattice-resolved image of the two nanorods arranged parallel to each other.

of Au nanorods at different concentrations of DMSA. The UV-vis spectral changes were visible immediately after the addition of DMSA into the nanorod solution. The peak position was found to be stable (after the initial shift) even after 24 h of incubation. Longer term incubation was done to ensure that an equilibrium state of the assembly was attained. We can see a gradual red shift in the LSP, whereas the TSP remains more or less constant. The red shift continues to increase as the concentration of DMSA in the solution increases. The width of the LSP also was found to slightly increase. These observations suggest that there is some interaction between nanorods, presumably due to the assembly. We saw some extent of aggregation above a 3 mM concentration



**Figure 5.** (A) Large-area image of a 2D sheetlike arrangement of nanorods obtained at 0.8 mM DMSA. (B) Magnified portion of the same assembly showing the staggered configuration of nanorods in the same plane. The nanorods in the top layer (circled) are located in the grooves of the bottom layer.

of DMSA, and a residue was found to settle. We measured the spectra of the supernatant of the above sample. The LSP was found to be greatly blue-shifted, and the TSP was slightly red-shifted. The LSP was seen as a flat band, whereas in all the lower concentrations, it was comparatively sharper. The background of the spectra was also found to increase. All these observations pointed toward aggregation. In the TEM image (Supporting Information Figure S2) we found some aggregated structures. In addition, some side-by-side aligned nanorods were seen, but they were only a few nanometers long, much smaller compared to the original long-range assemblies. At 3.5 mM concentration, the nanorod solution completely turned blue and the UV-vis spectra showed broad features characteristic of aggregation of nanoparticles with a large background due to scattering. Figure 3B is a plot showing the change in LSP wavelength with the



**Figure 6.** High-magnification TEM images of assemblies showing (A) staggered tip-to-tip alignment in consecutive tapes and (B) eclipsed tip-to-tip arrangement.

concentration of DMSA present in the nanorod solution. The purified nanorods show a strong LSP band at 730 nm. As the concentration increased, the LSP was red shifted. A shift of 48 nm was observed for 0.5 mM concentration where a well-ordered long-range one-dimensional assembly was seen. The LSP shift seemed to be greater at the beginning, and after 0.5 mM, the shift was more gradual. The LSP remained almost constant after 2 mM. Above 3 mM, the nanorods tend to aggregate.

Thiols at micromolar concentrations are known to form end-to-end assemblies of nanorods.<sup>10</sup> We also found the same trend at lower concentrations of DMSA. Figure 4A shows such an assembly which is observed at a concentration of 300  $\mu$ M DMSA. At a concentration of 200  $\mu$ M DMSA, longitudinal assembly started to appear (Supporting Information Figure S3A). As the concentration increased to 300 and 350  $\mu$ M DMSA, the character

of the longitudinal assembly was found to change. We found that more and more layers were coming together and forming the assembly. This is clearly visible in Figure 4A and Supporting Information Figure S3B. In the figures we can see 3–4 layers of longitudinally arranged nanorods coming together and forming a self-assembly. Another characteristic that can be made out from Figure 3 is the change of slope after a 0.5 mM concentration of DMSA. The slope was very sharp to begin with, and after 0.5 mM, it decreased. This can be explained by the change in the characteristics of the assembly above 0.5 mM. At 0.5 mM concentration, the end-to-end assembly was found to change into a parallel assembly (Figure 4B). This parallel assembly extended to a large length, and a “tapelike” morphology was seen at this concentration. Some tapes were several micrometers in length and some showed branching also.

According to theoretical studies, longitudinal assemblies of nanorods, in which the nanorods are arranged in an end-to-end manner, are known to produce a red shift of the LSP in the UV–vis spectra, whereas a sideways or parallel arrangement is expected to produce a blue shift.<sup>28a</sup> In our experiment, we found that both kinds of assemblies produce a red shift in the LSP, probably because side-to-side assembly also involves some end-to-end interaction over a large area. We found that there is a clear change of slope where the nature of the assembly changes, even though the trend of the red shift remains the same. The exact reason for this difference is not understood, but we believe that this is because of the extended range of the assembly compared to the structure on which the theoretical work has been done. Recent experimental work where rods were found to assemble in a side-to-side fashion, aided by antibody–antigen interactions, also suggests that side-to-side assembly can give rise to a red shift of the LSP.<sup>28b</sup> We also found that the difference between successive LSP ( $\Delta$ LSP) shifts continued to decrease, and above a 2 mM concentration of DMSA,  $\Delta$ LSP was close to zero or the LSP position was constant.

As the concentration of DMSA was increased to 0.8 mM, we found a tendency of these “nanorod tapes” to come together and self-assemble to form a sheetlike structure. Figure 5A shows a large-area image of a nanorod sheetlike self-assembly. We can see a large number of nanorod tapes coming together and self-assembling side-by-side to form a 2D structure. Each of the nanorod tapes is micrometers in length, and the 2D assembly formed covers several square micrometers in area. Interestingly, the branching of the tape seen at 0.5 mM DMSA was found to be absent, and instead a tendency to form a 2D array was observed at this concentration. Figure 5B shows a magnified image of a portion of the 2D structure. From the figure we can make out that the nanorods in the adjacent tapes are in a staggered configuration with each other. We can call it an A–B kind of arrangement within the layer. There was a tendency to form multilayers also. The most important aspect observable was that, in the second layer, the nanorods sit in the grooves of the layer below. Figure 5B shows one such instance, which is represented by dotted circles. This leads to a hexagonal packing in 3D (we will come back to this aspect later). Lattice-resolved TEM images of the assemblies clearly show the side-to-side alignment in a nanorod tape and staggered tip-to-tip alignment in consecutive tapes at this concentration of DMSA. The images are given in Supporting Information Figure S3C,D.

When the concentration of DMSA reaches 1.0 mM, we get a continuous network of gold nanorods in two dimensions. Figure

2 shows the assembly obtained at a 1.0 mM concentration of DMSA. In the images we can see a perfect 2D sheetlike structure made of gold nanorods extending to several square micrometers in area. Here also the assembly mostly follows a staggered configuration if we compare the adjacent tapes (Supporting Information Figure S4). Upon careful observation, we can see a tendency to form multilayers. At a DMSA concentration of 1.5 mM also a similar trend was observed. At 2 mM, a tendency for ordered aggregation was seen (Supporting Information Figure S5). Above 3 mM, the solution developed a blue color and the nanorods started settling. Then also a small amount of nanorods remained in the supernatant, and when analyzed with TEM, we found short-range arrangement (Supporting Information Figure S6). At a DMSA concentration of 3.5 mM, all the nanorods were found to aggregate.

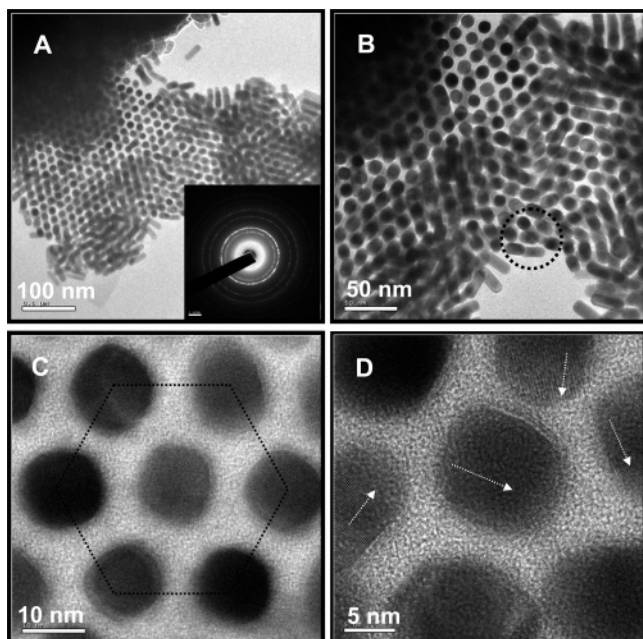
The assembly was investigated in detail using TEM. Figure 6 shows the high-magnification images of the nanorod assembly. The side-to-side distance in the assembly is approximately 8.5 nm. The distance between the two staggered tips in the consecutive tapes also was found to be approximately 8.5 nm. All distances measured came within  $8.5 \pm 0.3$  nm. Figure 6A shows the nanorods arranged side-to-side, as well as the tip-to-tip arrangement in greater detail. In most parts of the assembly, the tips were staggered to each other in the same layer as shown in Figure 6A. In some part of the grids, however, an eclipsed tip-to-tip arrangement also was seen, which is shown in Figure 6B. The extent of eclipsed arrangement was less than 2% in the whole assembly.

Axial alignment of nanorods perpendicular to the substrate is of special interest in nanoelectronic, nanomagnetic, and nanophotonic applications.<sup>24,29</sup> We were able to organize the nanorods perpendicular to the TEM grid. The axial alignment of the nanorods was visible from a DMSA concentration of 0.5 mM onward. As the concentration reached 0.8 mM, the assembly reached micrometer length, and a number of such assemblies were seen. The images shown in Figure 7 are taken from the sample having a 0.8 mM concentration of DMSA. Parts A and B of Figure 7 show perpendicularly arranged nanorods over a large area. Figure 7C shows a closer view of one such assembly. It can be seen that the assembly is hexagonal in nature. Figure 7D shows a lattice-resolved image of the tips of nanorods oriented in a perpendicular manner. Because of the higher thickness, in this orientation, it was difficult to get a well-resolved image. However, the lattice obtained suggests that the tips are composed of {111} facets, as reported.<sup>26c</sup> The lattice planes were found to be oriented in different directions or slightly twisted at an angle with respect to each other, showing a rotational disorder in the hexagonal assembly. The hexagonal ...ABAB... packing can be inferred from the data presented in Figure 6 also.

In Figure 7D we can see a diffused ring around the tip. This may be due to the fact that the nanorods may not be oriented perfectly perpendicular to the substrate, but at some angle less than 90°. Around the sides of the assemblies, we see some apparently smaller rods (Figure 7B, marked by a dotted circle) which could be nanorods oriented at lower angles (some angle between 0 and 90°) with respect to the substrate, but not oriented parallel to the substrate. We saw more rods ordered similarly around several other places also (Supporting Information Figure S7). We point out that these circular structures are not spherical nanoparticles. While there are a few nanoparticles seen, their size is large (~30 nm, Figure 1), and the diameter of the tips of

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**Figure 7.** TEM images showing the assembly of nanorods oriented perpendicular to the TEM grid (A, B). (C) High-magnification image of one such assembly showing the hexagonal nature of the assembly. (D) Lattice-resolved image of the nanorod tip, which shows rotational disorder. Arrows are parallel to the {111} lattice planes on different nanorods. Note that they are not aligned parallel to each other. The inset in (A) shows the diffraction pattern obtained from the area. The images were taken from a sample containing 0.8 mM DMSA.

the nanorods is 11–12 nm. Parts C and D of Figure 7 confirm that the size of the rods is similar to that of the nanorod (Figure 1), ruling out the possibility that this can be the arrangement formed by the nanoparticles in the crude sample. In any case, these many nanoparticles were absent in the parent sample.

Three-dimensional superstructures or superlattices are of great importance in modern technology. There are several reports of making superlattices from spherical nanoparticles, but there are only very few reports of self-assembly of nanorods to 3D superstructures. We observed that, above a 0.8 mM concentration of DMSA, the nanorods tend to self-assemble into 3D superstructures. Above a 1 mM concentration of DMSA, the assembly formed was found to be mostly 3D in nature. The extents of 2D structures formed were minimal above 1.2 mM. Interestingly, we found two kinds of 3D assemblies, one perpendicular and another parallel to the substrate. Figure 8 shows the 3D structures taken from the sample containing 1.5 mM DMSA. Parts A–C of Figure 8 show layered assemblies initiated by the perpendicular orientation of nanorods with respect to the substrate. Parts A and B of Figure 8 appear like perfect superlattices which extend to several hundreds of nanometers. Parts D–F of Figure 8 show the 3D self-assembled superstructures initiated from the parallel orientation of nanorods. We can clearly see that the nanorods are arranged parallel to each other in a layer-by-layer fashion. Interestingly, these kinds of superstructures were larger than the former type. Most of the structures seen were micrometers long. This may be due to the preferred orientation with respect to the substrate. In all samples investigated which contain a DMSA concentration above 1 mM, 3D structures of both the orientations were found. We also found in some parts of the grid, at a concentration of 1 mM, certain assorted shapes, where the nanorods were self-assembled into large circles. Figure 9 shows such structures. In most parts of the grid, the circular assemblies were associated with long tapelike assemblies. Therefore, the circular superstructure could have resulted from the long tapelike

one-dimensional assembly. The tapes may coil up to form the circular assembly, and further reorganization can result in the formation of a circular-plate-like structure. A closer look at Figure 9C gives a clearer indication toward this proposition. In the figure, we can see a circular plate starting to form from a tapelike assembly (marked by a dotted circle). We can see the tapes of gold nanorods starting to coil up and forming a circular assembly (which is only half-built and so in an open state). Therefore, we think, in addition to forming a sheetlike structure, the one-dimensional tapelike assembly of nanorods can also form circular plates, which can be several micrometers in size as we can see in Figure 9A. It is important to note that we see smaller circular plates also. Therefore, we think that the size of the circular structure formed depends on the length of the tape from which the structure is formed. Such structures can also be elongated as seen in Figure 9D. All regular structures such as 2D sheets and 3D superstructures were present to a larger extent at this concentration (1 mM). Solvent evaporation can bring about circular aggregates of gold nanorods, but such aggregates are reported to be hollow rings<sup>20a</sup> rather than circular plates.

The distances between individual nanorods were found to be larger compared to the molecular dimension of DMSA. The size of DMSA is around 0.6–0.7 nm,<sup>30</sup> but the distances found in the assembly were around 8.5 nm. Therefore, direct association of DMSA molecules on the nanorod surface can be ruled out. Gold nanorods will always be associated with a bilayer of CTAB surfactants, and upon breaking the bilayer, the nanorods will aggregate.<sup>27b,31</sup> The size of CTA<sup>+</sup> is calculated to be 2.2 nm,<sup>32</sup> but in a bilayer on a nanorod, since the tails of CTAB molecules can be interpenetrating, its thickness is calculated to be 3.9 nm.<sup>18a,32</sup> Diacids are known to produce side-by-side alignment of nanorods by charge neutralization under favorable conditions of pH.<sup>20c</sup> It is also known that DMSA can make a complex with CTAB by electrostatic interactions between the carboxylic acid group and the anionic part of the CTAB.<sup>2e</sup> It is also known that thiols will undergo oxidation to form disulfides, when in close proximity.<sup>33</sup> On the basis of all these facts, we propose a mechanism for self-assembly of nanorods as shown in Scheme 2.

The nanorods in the as-prepared sample tend to orient randomly because of the Coulombic repulsion between the CTAB bilayers in the individual nanorods,<sup>20b,27b</sup> which also protect nanorods from aggregating. It is also reported that the charge neutralization of the CTAB bilayer on the nanorod surface can induce organization of nanorods into side-by-side supramolecular assemblies.<sup>21b</sup> It has been reported that short-chain diacids which have less than six methylene groups form orthogonal monolayers on metal oxide surfaces with only one terminal acid group interacting with the surface.<sup>34</sup> Alkanedioic acid adsorption on the CTAB-coated nanorod surface is also supposed to be of the same fashion.<sup>20c</sup> Therefore, in the assembly, bridging between nanorods is possible when DMSA is adsorbed perpendicular to the surface, forming an orthogonal monolayer. When DMSA is added to the solution, the negatively charged carboxylate ion tends to neutralize the CTAB bilayer by the formation of a CTA<sup>+</sup>–DMSA complex as shown in Scheme 2. Carboxylic groups present

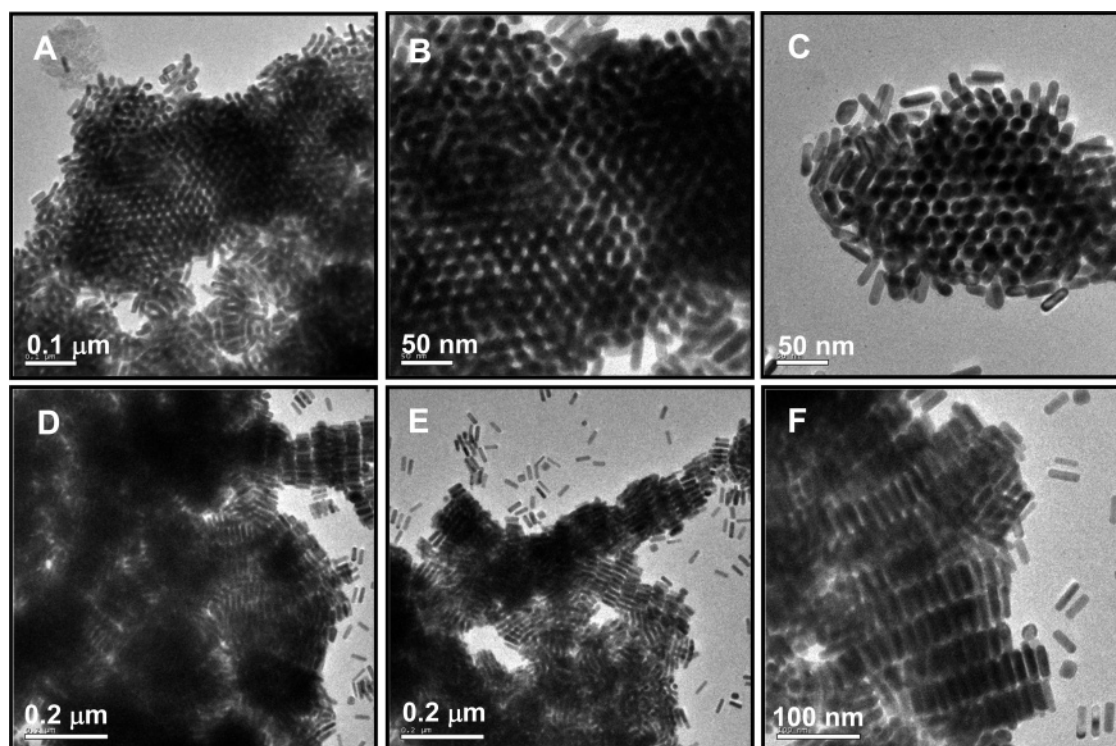
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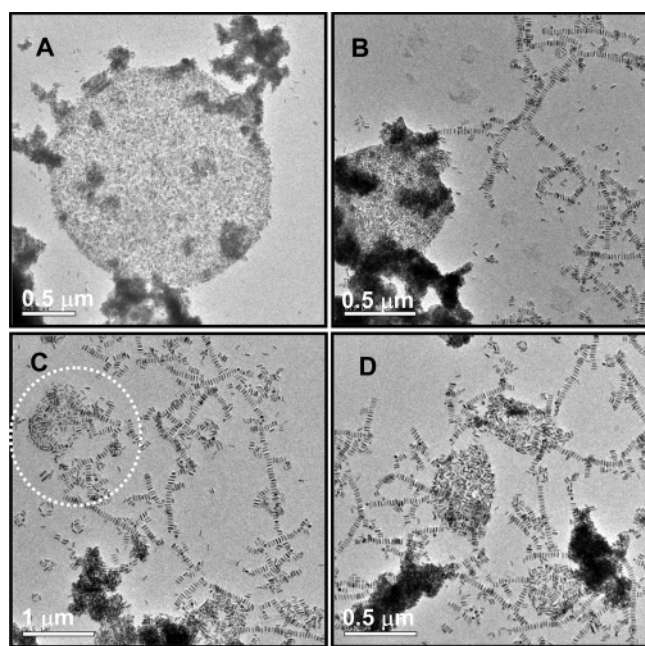
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**Figure 8.** (A–C) TEM images of 3D superstructures formed by the perpendicular orientation of nanorods. (D–F) Parallel orientation of nanorods leading to multilayer structures. The concentration of DMSA present in the sample was 1.5 mM.



**Figure 9.** (A) Circular structures formed on the TEM grid. (B–D) TEM images showing the nanorod tapes and bent tapes ending in circular plates. In (C), the area marked by the dotted circle shows a circular plate forming from the tapes.

in DMSA bring the nanorods together. In the assembly when two or more DMSA molecules come in close proximity, they can form an intermolecular disulfide bond, which in turn further stabilizes the assembly.<sup>33</sup> The concentration-dependent formation of different hierarchical structures accentuates the above arguments. It is important to note that such control of the self-assembled structures is not possible when the self-assembly is induced by surfactant-mediated interactions and drying alone.

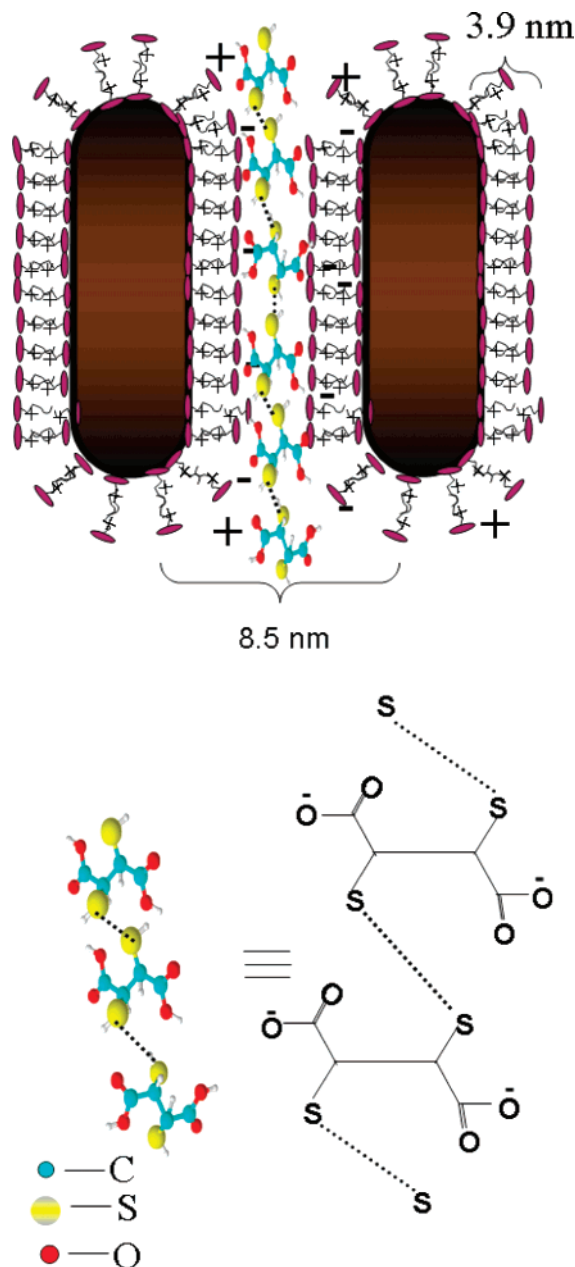
To further demonstrate the electrostatic interactions between

deprotonated DMSA and positively charged nanorods,  $\zeta$  potential measurements were carried out for nanorods at various concentrations of DMSA. Figure 10 shows the variation of the  $\zeta$  potential with the concentration of DMSA added to the solution. The  $\zeta$  potential is a measure of the effective surface charge on the nanorods, which shows the magnitude of the repulsion or attraction between particles. Nanorods in pure water are known to show a positive value due to the presence of CTAB capping on nanorods.<sup>20c</sup>

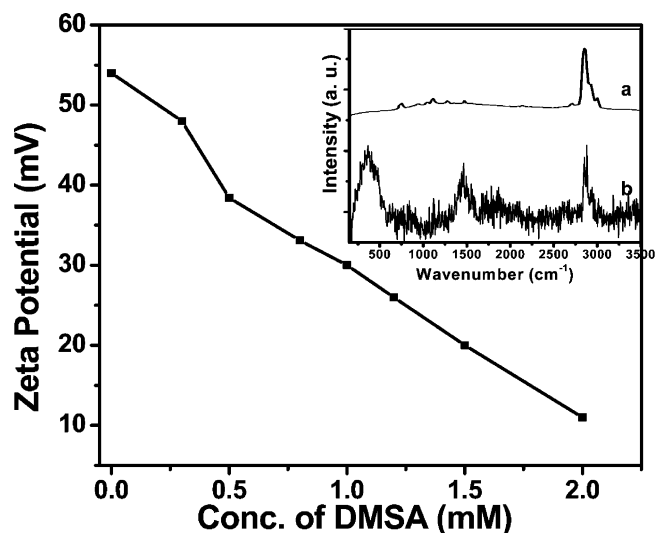
The  $\zeta$  potential of the starting nanorod solution was  $+54 \pm 4$  mV. As the concentration of DMSA was increased, it was found to decrease. Even at a concentration of 2 mM, the  $\zeta$  potential ( $+10 \pm 3.3$  mV) did not become zero, rendering the nanorods stability. However, the number of DMSA molecules is such that they decrease the overall surface charge of the nanorods, but is not enough to change the potential to a neutral or negative value. The  $\zeta$  potential of the solution decreased soon after the addition of DMSA, and no change in the  $\zeta$  potential was observed with the evolution of time. At a pH of 2 (which is below the  $pK_a$  of DMSA) the  $\zeta$  potential of the nanorods was not found to decrease. This is due to the fact that, at this pH, DMSA is in the protonated state and hence is unable to neutralize the charge on the nanorod. When 2 mM BA was added to the nanorod solution, the  $\zeta$  potential decreased to  $25 \pm 4.6$  mV (for 2 mM DMSA, it was  $10 \pm 3.3$  mV). The difference in  $\zeta$  potential between DMSA addition and BA addition is because while DMSA is a dicarboxylic acid, BA is a monocarboxylic acid. These observations strongly support the proposition that the mechanism of the assembly involves charge neutralization. The  $\zeta$  potential shows a slight deviation around 0.5 mM, around the concentration where a change is observed in the absorption spectrum (Figure 3B).

To establish the disulfide linkage between DMSA molecules, the Raman spectrum of the sample in the thin film form (dropped on a glass substrate) was measured. The concentration of DMSA in the sample used for the Raman study was 1.5 mM. The inset of Figure 10 shows the Raman spectra of the sample. Trace a

Scheme 2. Proposed Mechanism of the Assembly of Gold Nanorods in the Presence of DMSA



is the Raman spectrum of CTAB, and trace b is that of the nanorod–DMSA assembled structure. In trace b mainly three peaks can be observed. The first two peaks are centered around 2850 and 1440  $\text{cm}^{-1}$ , respectively, which correspond to alkyl C–H stretching and  $-\text{CH}_2$  deformation. Comparison of traces a and b establishes that they are due to the CTAB capping the nanorods.<sup>35</sup> This establishes that CTAB is not replaced completely and is present on the nanorod. It is reported that organic disulfide will give a Raman feature in the 450–510  $\text{cm}^{-1}$  range.<sup>36</sup> In trace b we can clearly see a peak around the 490  $\text{cm}^{-1}$  which is absent in trace a. This may be used to support the presence of disulfide



**Figure 10.** Variation of the  $\zeta$  potential with the concentration of DMSA added to the nanorod solution. All data points are averages of 20 measurements per sample. The inset shows Raman spectra of the (a) pure CTAB solid and (b) nanorod assembly at a 1.5 mM concentration of DMSA.

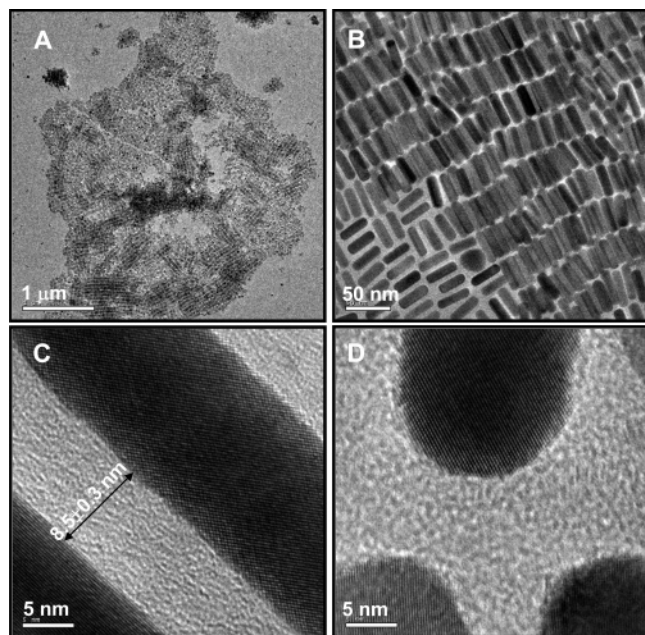
bonds in the assembly. The width of the peak suggests that it may have other contributions as well.

To verify the proposed mechanism of self-assembly, we tried to form the same assembly with MSA. There also we found a similar arrangement (Supporting Information Figure S8), but the extent and order were not as good as in the case of DMSA. In MSA, there is only one sulfur per molecule, so the formation of the extended disulfide link, while possible in the case of DMSA between several molecules, is not possible and only dimers can be formed. This may be the reason for the assembly to be not as long range as in the case of DMSA. However, the presence of two acid groups and the possibility to form a disulfide bond give rise to a similar assembly.

MPA having one mercapto and one acid group was also used. In this case, the nanorods did not assemble in any particular pattern. They were found to come closer and tend to aggregate or assemble in a rather disordered way (Supporting Information Figure S9). This further proves that at least two carboxylic acid groups are needed for the assembly. A similar reaction was tried with SA, where no mercapto group but two carboxylic acid groups exist. In SA also we found an assembly very similar to that of DMSA. The rods were seen to be arranged parallel to each other, but the assembly was comparatively of smaller range. In the case of SA, the assembly was found to be disrupted, or some kind of disorder was found after a short distance. Only some domains of well-arranged rods were seen. Figure 11 shows the TEM images of well-arranged nanorods induced by SA at a concentration of 1 mM. In Figure 11B we see that, after a small area of well-ordered assembly, the rods tend to assemble in another way, causing the structure not to extend over a large area. This may be due to the absence of disulfide bonds which may be giving additional stability in the case of DMSA and MSA. We found that, in the case of SA-induced assembly also, the side-to-side distance between the two rods matches that in the case of DMSA. This gives a strong indication that the carboxylic acid group is the principal reason for forming the assembly, as proposed. To further check the influence of the carboxylic group, we added BA, which is roughly of the same length as DMSA, to the nanorod. Even at 1 mM concentration, we did not see any preferred orientation or alignment in the nanorod sample (Supporting Information Figure S10). This was further confirmed by using

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**Figure 11.** TEM images of the aligned nanorod assembly induced by SA: (A) large-area image showing the assembly, (B) closer look of the assembly showing the ordered structure, (C) lattice-resolved image of the nanorods arranged parallel to each other, and (D) lattice-resolved image of the tips of the nanorods arranged in a staggered manner in the assembly. The concentration of SA used was 1 mM.

2,5-dimercapto-1,3,4-thiadiazole instead of DMSA for inducing the assembly, where two mercapto groups are present, but no carboxylic acid. We observed that, in this case, there was hardly any assembly and only randomly oriented rods were seen on the TEM grid (Supporting Information Figure S11). This again confirms that, as in the mechanism proposed, the carboxylic groups are the principal reason for this assembly and not the mercapto groups.

**Effect of pH on Self-Assembly.** The effect of pH on self-assembly was also tested. If the assembly is facilitated by carboxylic groups, pH changes are expected to affect the assembly. Samples containing a 1 mM concentration of DMSA were prepared at two different pH values, one above (4.4) the isoelectric point of DMSA and one below (2.3).  $pK_{a1}$  and  $pK_{a2}$  for DMSA are 3.0 and 3.9, respectively.<sup>37</sup> The pH of the purified nanorod dispersion was 5.2. When a 1 mM DMSA solution was added to it, the pH was decreased to 4.4. This can be attributed to the  $H^+$  formed in the solution by the ionization of the carboxylic acid groups in the DMSA molecule. This sample, which is the original sample, showed long-range ordering. At this pH, which is above both the  $pK_a$  values of DMSA, the carboxylic acid groups of DMSA will be fully ionized, so it can form a complex with  $CTA^+$ , neutralize the rods, and facilitate the assembly. In another sample prepared at a lower pH (2.3), the carboxylic acid

groups will not be ionized. Consequently, the formation of an electrostatic complex with  $CTA^+$  anion on the gold nanorods will not be possible, and hence, no assembly is expected. TEM of the samples confirmed this, where we find only small clusters of rods without any specific arrangement (Supporting Information Figure S12).

From the above experiments the following conclusions were drawn. First, two carboxylic groups were necessary to form the assembly. This was evident when MPA did not give any assembly and SA gave an assembly. Second, since SA itself gave a similar assembly, it is evident that the mercapto group is not directly involved in the assembly and it is also understood that thiol does not replace CTAB and gets adsorbed on the surface of the nanorods. If the thiols were directly adsorbed on the surface to give the assembly, the distance between the rods would not have been 8.5 nm. Also, SA, which does not have a mercapto group to bind, should not have given the same assembly. The distances between the rods, in the cases of both SA and DMSA, were found to be the same. This indicates that the mechanism is almost similar

in both the cases. Third, a slight change in the nature of the assembly in the case of MSA and DMSA, we believe, is due to the ability of DMSA to form an extended disulfide linkage compared to MSA, rendering extra stability to the long-range assembly formed.

## Conclusions

Large-scale self-assembly of gold nanorods was achieved by the addition of DMSA to the gold nanorod solution. Depending upon the concentration of DMSA, the rods were found to assemble into one-dimensional tapelike or two-dimensional sheetlike structures. A three-dimensional “superlattice-like” structure was also achieved. Nanorods were found to assemble parallel as well as perpendicular to the TEM grid. In some parts of the grids, the nanorod tapes were found to bend to give rise to a circular-plate-like assembly. On the basis of several supporting experiments, it was found that the charge neutralization of the rods by the carboxylic acid group is the principal reason for such an assembly. In the case of DMSA, the mercapto groups render additional stability to the assembly. On the basis of these observations, a model for the self-assembly of nanorods is proposed. The effect of the DMSA concentration as well as the effect of the pH of the medium was also studied.

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**Supporting Information Available:** TEM images of aggregates and ordered structures at various concentrations of DMSA, MSA, MPA, butanoic acid, and 2,5-dimercapto-1,3,4-thiadiazole as well as an image at pH 2.3. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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