

nitro groups in **Ib**. XPS analysis of a monolayer of **II** on silicon shows only a small loss of nitrogen ( $\approx 8\%$ ) after irradiation with  $40 \text{ mC cm}^{-2}$ . A change of the N 1s binding energy could not be detected since the chemical shifts of cyano and amino N 1s signals are virtually identical.

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## Ordered Two- and Three-Dimensional Arrays Self-Assembled from Water-Soluble Nanocrystal–Micelles\*\*

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The synthesis and self-assembly of nanocrystals (NCs) have gained much interest due to the NCs' unique size-dependent optical, electronic, and chemical properties and their potential applications in areas such as optics, electronics, catalysis, magnetic storage, and biological labeling and sensing.<sup>[1–6]</sup> To date, most work has focused on the synthesis and self-assembly of nanocrystals that are stabilized with alkane ligands ( $\text{CH}_3(\text{CH}_2)_n\text{R}$ , R = SH,  $\text{NH}_2$ , PO, etc.).<sup>[3,7,8]</sup> Such NCs can be made at fairly high quality (narrow size distribution, preferred shapes such as rod, cube, etc., and large production). These NCs are hydrophobic, and their self-assembly is limited to organic solvents. However, there are many applications requiring hydrophilic or aqueous environments, such as biolabeling and surface-enhanced Raman spectroscopy (SERS)-based NC films or arrays for biosensing.<sup>[9–12]</sup> In addition, water-soluble NCs and their ordered arrays/films provide a great oppor-

tunity for further integration into inorganic ceramic frameworks that offer the chemical and mechanical robustness needed for enhanced device functionality.<sup>[13–16]</sup> Although some NC superlattices have been fabricated through aqueous media,<sup>[17–19]</sup> the methods are limited to spherical gold NCs. Here we report a facile route to prepare ordered NC arrays self-assembled from water-soluble NC–micelles. The method is simple, widely applicable to other materials, and can be used to prepare water-soluble NCs with different compositions and shapes, such as sphere, rod, and cube, as well as their ordered arrays. Our approach involves the synthesis of water-soluble gold-NC–micelles using our recently developed surfactant encapsulation techniques,<sup>[16,20]</sup> which were conducted in an interfacially driven water-in-oil microemulsion process. The whole process takes only ten minutes. Subsequent self-assembly of NC–micelles upon evaporation of a drop of NC–micelle aqueous solution on substrates, such as a transmission electron microscopy (TEM) grid, silicon wafer, glass, etc., leads to ordered two- and three-dimensional (2D and 3D) gold-NC superlattice films (Scheme 1).

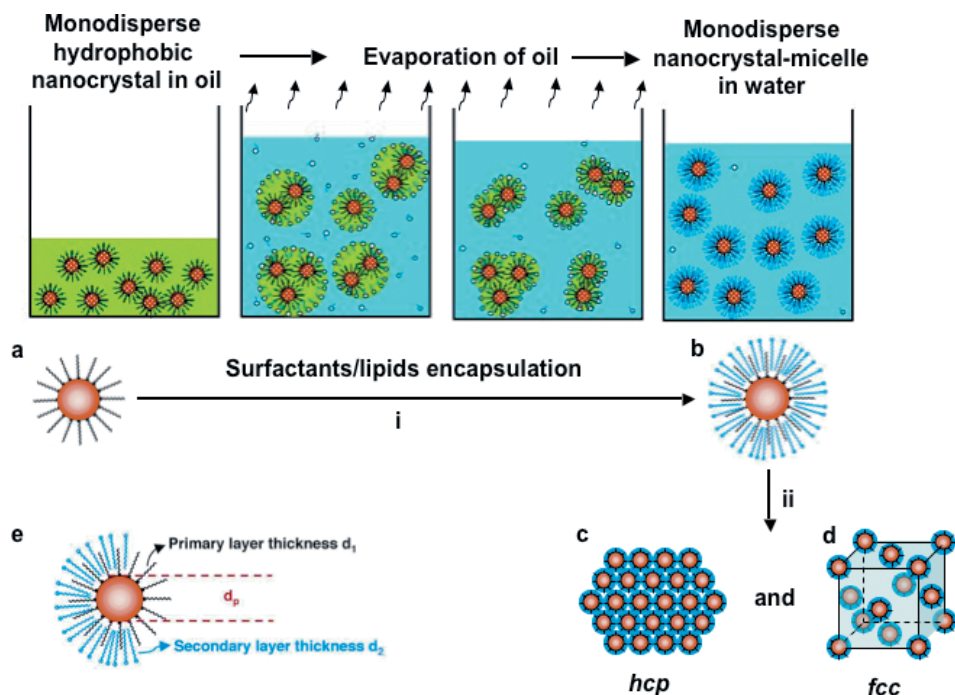
1-Dodecanethiol (DT)-stabilized gold NCs were prepared using the method of Brust et al.<sup>[21]</sup> Heat treatment at  $140^\circ\text{C}$  for 30 min followed by size-selective precipitation using the solvent/non-solvent pair of toluene/ethanol was used to further narrow the size distribution to  $\sim 7\%$ . The narrow size distribution of NCs is essential for formation of ordered NC–micelle arrays. In a typical NC–micelle synthesis procedure, a concentrated solution of monosized DT-stabilized gold NCs in chloroform was added to an aqueous solution of hexadecyltrimethylammonium bromide (C16TAB) under vigorous stirring to create an oil-in-water microemulsion. Chloroform evaporation during a heat course ( $40\text{--}80^\circ\text{C}$ ,  $\sim 10$  min) transfers the NCs into the aqueous phase (forming NC–micelle stock solution). This interfacial process is driven by the hydrophobic van der Waals interactions between the primary alkane of the stabilizing ligand and the secondary alkane of the surfactant, resulting in thermodynamically defined, interdigitated bilayer structures<sup>[22–24]</sup> (Scheme 1b).

A DT-stabilized gold NC can be envisioned as a giant hydrophobic “molecule” that can be individually encapsulated into the hydrophobic core of a surfactant micelle in water. During the formation of NC–micelles, surfactants serve as active agents to reduce repulsion between hydrophobic gold NCs and water. The thermodynamically defined, interdigitated “bilayer” structure between the primary layer and secondary layer contributes extensive energy (van der Waals interactions) to stabilize NC–micelles in water.<sup>[22–24]</sup> We conducted differential scanning calorimetry (DSC) experiments on the dried powder samples of gold-NC–micelles that were prepared using DT-stabilized gold NC and surfactants with different alkane chain lengths (C12TAB, C14TAB, and C16TAB). We observed that each sample exhibits an endothermic peak. These peaks appear at  $\sim 11.5^\circ\text{C}$  for the NC-C12TAB sample,  $\sim 47^\circ\text{C}$  for the NC-C14TAB sample, and  $\sim 72^\circ\text{C}$  for the NC-C16TAB sample; the temperature of the peak maxima increases with increasing alkane chain length. This suggests that

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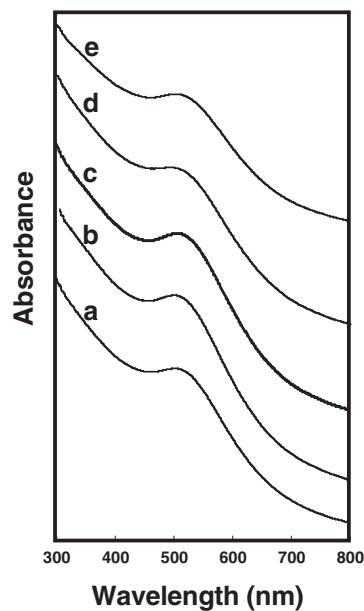
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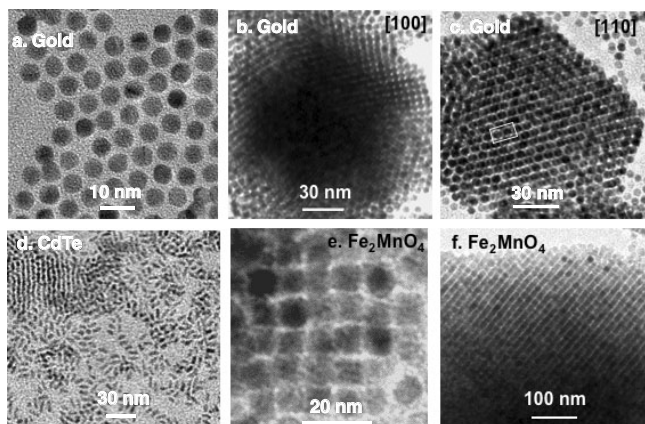
**Scheme 1.** Formation of water-soluble gold-NC-micelles through surfactant/lipid encapsulation (i) and their self-assembly (ii) into ordered 2D and 3D arrays (c and d, respectively) driven by charge interaction and hydrogen bonding. a) Addition of H<sub>2</sub>O/surfactants into oil containing monodisperse hydrophobic gold NCs leads to the formation of a water-in-oil microemulsion. b) Evaporation of the oil transfers the NCs into the aqueous phase to form NC-micelles. e) Thermodynamically defined interdigitated bilayer structures.

longer alkane chains contribute more extensive van der Waals interactions.<sup>[23,24]</sup> The advantage of the surfactant encapsulation techniques is that the interdigitated bilayer involves no chemical reactions and, therefore, would not change the physical properties (optical, aggregation, electronic, etc.) of the original NCs.<sup>[20,25]</sup>

Formation and stability of monodisperse gold-NC-micelles have been confirmed using UV-vis spectroscopy (Fig. 1) and TEM (Fig. 2). Figure 1a shows the spectra of DT-stabilized gold NCs in chloroform. The absorbance at ~520 nm corresponds to the gold surface plasmon resonance band. Figure 1b shows the spectra of gold-NC-micelles in water prepared using the cationic surfactant CTAB (CTAB: CH<sub>3</sub>(CH<sub>2</sub>)<sub>15</sub>-N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>Br<sup>-</sup>). By comparing Figure 1a to Figure 1b, we observe no difference in the positions and peak widths of the plasmon resonance band of the DT-stabilized gold NCs in chloroform and those of the corresponding water-soluble NC-micelles. This suggests that gold-NC-micelles remain monodisperse in water without aggregation, which is further confirmed by TEM (see below). Similar results in Figures 1c–e suggest that anionic surfactants, non-ionic surfactants, and phospholipids can all form NC-micelles, in addition to cationic surfactants. Advantageously, this allows the facile control of NC-micelle surface charge and functionality via functional groups, such as polyethylene glycol (PEG), hydroxyl (–OH), etc.



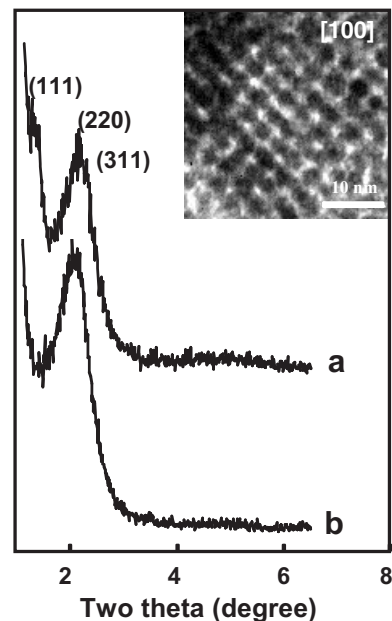
**Figure 1.** UV-vis spectra of a) gold NCs in chloroform; b) gold-NC-micelles prepared using cationic surfactant: CH<sub>3</sub>(CH<sub>2</sub>)<sub>15</sub>N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>Br<sup>-</sup> in water; c) gold-NC-micelle prepared by using anionic surfactant: CH<sub>3</sub>(CH<sub>2</sub>)<sub>11</sub>SO<sub>3</sub><sup>-</sup>Na<sup>+</sup>, SDS; d) gold-NC-micelles prepared by using non-ionic surfactant: CH<sub>3</sub>(CH<sub>2</sub>)<sub>15</sub>-(OCH<sub>2</sub>CH<sub>2</sub>)<sub>10</sub>-OH, Brij58, in water; e) gold-NC-micelles prepared using 1,2-dioctanoyl-*sn*-glycero-3-phosphocholine in water.



**Figure 2.** Representative transmission electron micrographs of ordered NC-micelle superlattices. a) 2D gold-NC-micelle arrays with hexagonal close packing; b) [100] orientation of 3D gold-NC-micelle superlattice arrays; c) [110] orientation of 3D gold-NC-micelle superlattice arrays; d) ordered CdTe-nanorod-micelle arrays; e) 2D  $\text{Fe}_2\text{MnO}_4$ -nanocube-micelle arrays; f) [100] orientation of 3D ordered  $\text{Fe}_2\text{MnO}_4$ -nanocube-micelle arrays.

The self-assembly of water-soluble gold-NC-micelles into 2D and 3D superlattice films was conducted through evaporation of drops of NC-micelle water solution onto solid substrates, such as Si wafers, glass, TEM grids. Figure 2a shows a representative TEM image of the hexagonal close-packed (hcp) 2D superlattice resulting from drying of a gold-NC-micelle solution on an amorphous-carbon-coated copper grid. The mean interparticle spacing was estimated to be  $\sim 3$  nm by direct measurement of individual spacings within well-ordered domains. The formation of ordered hcp 2D arrays, as is expected for individual, monosized NCs, further confirms that gold-NC-micelles remain monodisperse in water without aggregation.<sup>[26]</sup> In addition to spherical NCs, we extended the concept to stabilize and self-assemble NCs with other shapes, such as rods and cubes. CdTe nanorods were prepared according to Peng et al.<sup>[27]</sup> using trioctylphosphine oxide as a stabilizing agent. The encapsulation was conducted using CTAB. The TEM image (Fig. 2d) revealed that surfactant-“bilayer”-stabilized CdTe nanorods formed uniform arrays.  $\text{Fe}_2\text{MnO}_4$  nanocubes were prepared according to Zeng et al. using oleylamine as a stabilizing agent.<sup>[28]</sup> Formation of  $\text{Fe}_2\text{MnO}_4$ -nanocube-micelles was conducted using CTAB. The TEM image (Fig. 2e) shows that the  $\text{Fe}_2\text{MnO}_4$ -NC-micelles self-organize into ordered arrays with cubic symmetry.

To form 3D superlattices, a concentrated NC-micelle aqueous solution (stock solution) was directly dried on a TEM grid, Si wafer, and glass slide. Figures 2b,c show some representative TEM images of 3D gold-NC superlattices. Based on the [100] orientation in Figure 2b, the measured unit-cell parameter is  $\sim 10.6$  nm. Figure 3a shows a representative low-angle X-ray diffraction (XRD) pattern of a 3D gold-NC superlattice film prepared by drying the stock solution on a Si wafer. On the basis of face-centered cubic (fcc) symmetry, the primary peaks are assigned as (111), (220), and (311). The



**Figure 3.** X-ray diffraction patterns of 3D gold-NC-micelle arrays possessing a face-centered cubic (fcc) structure, a) with and b) without the spacer group (benzene dicarboxylate). Inset: TEM image of [100] orientation of gold-NC-micelles arrays after adding spacer molecules.

calculated unit cell parameter,  $a = \sim 11$  nm, is close to TEM results. By using concentrated  $\text{Fe}_2\text{MnO}_4$ -nanocube-micelles, 3D ordered magnetic NC arrays with cubic symmetry were also formed (Fig. 2f).

In previous work using hydrophobic NCs in organic solvents, the resulting NC superlattices exhibit two-level preferential orientation.<sup>[7]</sup> In the mesoscale (2–50 nm), the monosized NCs formed an fcc superlattice with (111) planes parallel to the substrates. In the subnanometer scale ( $< 1$  nm), the crystal structure of each NC was observed to take preferred orientation of the (111) planes parallel to the substrate. Such arrangements are believed to maximize van der Waals' interactions between neighboring NCs and the substrate.<sup>[7]</sup> Wang et al.<sup>[29]</sup> addressed preferred NC orientation using a “gear” model, in which alkane chains on similar facets preferentially form an interdigitated structure, resulting in the orientation of the NC structure. In our case, the NCs were encapsulated inside surfactant micelles with an interdigitated surfactant “bilayer” structure. The ordered gold-NC superlattice was formed directly upon water evaporation. We observed no preferred mesoscale orientation. During self-assembly, charge interactions and/or hydrogen bonding (when using non-ionic surfactants) between the NC-micelles are the only driving forces to form the NC superlattice. There is no existence of interdigitated structure between NCs, therefore, no preferred NC orientation at the subnanometer scale.

The ability to engineer interparticle spacing is crucial for the achievement of coupled properties.<sup>[2,28,30,31]</sup> Tao et al.<sup>[18]</sup> reported a hydrogen-bonding approach to control the superlattice spacing using carboxylic-acid-capped gold NCs. Based

on the characteristic of the positive charge on the gold-NC-micelles, we demonstrated the possibility of tuning interparticle spacing using a spacer molecule with two negative charges,  $-\text{OOC}_6\text{H}_4\text{COO}$ . Figure 3b shows the XRD pattern of a superlattice film prepared by adding spacer molecules into the same stock solution as for the film of Figure 3a. The average unit cell parameter ( $a \sim 12.1$  nm) is calculated based on the  $d$ -spacings from (220) and (311). After subtracting the unit cell from the sample prepared without addition of spacer molecules, the minimum resulting interparticle spacing is  $\sim 5$  Å, which is close to the simulated spacer molecular length of 6 Å, suggesting there may be on average one layer of spacer molecules between the gold nanocrystals.

In conclusion, we report a facile approach to prepare ordered gold-NC arrays from aqueous solution. Monosized, DT-stabilized gold NCs have been encapsulated inside surfactant/lipid micelles to form individual NC-micelles in aqueous media. Self-assembly of monosized NC-micelles upon water evaporation leads to 2D hcp and 3D fcc superlattice arrays on solid substrates. The robustness of this approach allows tuning of interparticle spacing through the use of various spacer molecules. In addition to spherical NCs, this approach can be extended to prepare and self-assemble water-soluble NCs with different shapes, such as nanorods and nanocubes. The formation of water-soluble gold-NC-micelles and their self-assembly into 2D and 3D superlattice arrays from water provide a novel opportunity to integrate inorganic matrices through conventional sol-gel processing for new electronics and optics, allowing the fabrication of SERS-based sensor platforms.<sup>[1,10]</sup>

## Experimental

**Synthesis of Monodisperse Gold Nanocrystals [21]:** An aqueous solution (60 mL) containing  $\text{HAuCl}_4$  (0.7 g, Aldrich) was mixed with a solution of tetraoctylammonium bromide (4 g, Aldrich) in toluene (160 mL). The two-phase mixture was vigorously stirred until the tetrachloroaurate was transferred completely into the organic layer (judged by color changes: the aqueous phase became colorless, and the organic phase became dark yellow). 1-Dodecanethiol (0.34 g, Aldrich) was added to the organic phase. A freshly prepared aqueous solution (40 mL) of sodium borohydride (0.78 g, Aldrich) was slowly added and vigorously stirred for a 20 min duration. After further stirring for 3 h, the organic phase was separated and evaporated in a rotary evaporator. Heat treatment at 140 °C was performed for 30 min. The gold nanocrystals were then purified by two cycles of precipitation, followed by size-selective precipitation using the solvent/non-solvent pair of toluene/ethanol.

In a general preparation of water-soluble gold-NC-micelles and 2D or 3D ordered superlattice arrays, cetyltrimethylammonium bromide ( $(\text{CH}_3(\text{CH}_2)_{15}\text{N}^+(\text{CH}_2)_3\text{Br}^-$ , 0.20 g, Aldrich, or other surfactants) was added to deionized water (8–12 g) to form solution A. Solution A was sonicated to completely dissolve the surfactant. 1-Dodecanethiol-derivatized gold NCs (0.30 g), or other NCs such as  $\text{Fe}_2\text{MnO}_4$ , CdTe, etc., were dissolved in chloroform (1–2 mL) to form solution B. Solutions A and B were mixed together with vigorous stirring, and the chloroform was removed by heat treatment to finish the encapsulation. A dark-colored solution (stock solution, C) was finally obtained and centrifuged at 2000 rpm for 5 min to remove any precipitates. Solution C could be further diluted for UV-vis spectroscopy or TEM

characterization. The 2D hcp superlattice was formed by using diluted stock solution C, by adding more water. The 3D superlattice films were prepared by directly drying stock solution C on glass slides, silicon wafers, and TEM grids. The 3D superlattice films could also be prepared on substrates by spin-coating or casting.

The XRD spectra were recorded on a Siemens D500 diffractometer using graphite monochromator filtered  $\text{Cu K}\alpha$  radiation with  $\lambda = 1.54$  Å in  $\theta$ - $2\theta$  ( $2\theta = 1$ – $10^\circ$ ) scan mode using step sizes ranging from 0.02 to 0.002° and dwell times of 1 to 5 s. TEM images were taken by means of a JEOL 2010 high-resolution microscope equipped with a Gatan slow-scan charge-coupled device (CCD) camera and operated at 200 keV.

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