

Synthesis of Organo-Silane Functionalized Nanocrystal Micelles and Their Self-Assembly

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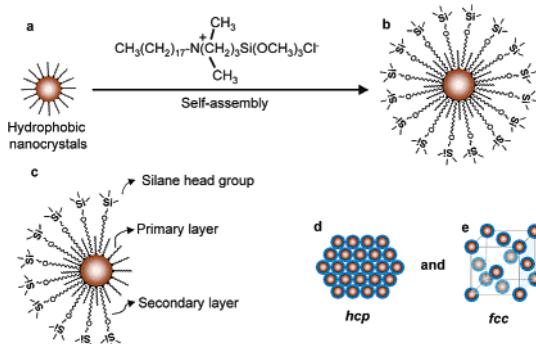
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Nanocrystal (NC) synthesis and self-assembly have received much attention due to unique size-dependent properties and new collective physical properties derived from ordered NC arrays. However to fully exploit these properties, nanocrystal functionalization is critical and essential. In general, the key to functionalize NCs is maintenance of the original physical properties of the NCs, and in many situations, it is necessary to develop flexible NC surface chemistry, allowing further, subsequent functionalization. To date, most work has focused on alkane chain functionalized/stabilized NCs prepared using hot soap^{1,2} or a two-phase approach.³ These methods can effectively make high quality NCs (narrow size distribution, preferred shape and composition, large production). Unfortunately, the alkane chains are chemically inert, preventing further chemical functionalization. In addition, these NCs are hydrophobic, precluding their direct use in bioapplications. There is an urgent need for general NC functionalization methods.

Here, we report a new synthetic route to functionalize NCs with organo-silane groups through encapsulation of monodisperse, hydrophobic gold nanocrystals within the core of silane precursor micelles. Octadecyltrimethyl(3-trimethoxysilylpropyl)ammonium chloride (precursor **1**) is an amphiphilic functional methoxysilane that self-assemble into micelles and liquid crystal mesophase.⁴ After encapsulation, the nanocrystal micelles are monodisperse, hydrophilic, and can self-assemble into 3-D ordered arrays through silane headgroup cross-linking under acidic conditions. In comparison with the previous method concerning the preparation of hybrid silica with stabilized gold NCs,^{5,6} this method is simple, general, and allows extensive further functionalization based on silane coupling chemistry.

The synthesis of organo-silane functionalized gold NC micelles was based on our recently developed surfactant encapsulation techniques.^{7,8} In a typical nanocrystal micelle synthesis procedure, a concentrated monosized 1-dodecanethiol (DT)-stabilized gold NC chloroform solution was added to an aqueous solution of precursor **1** under vigorous stirring to create an oil-in-water microemulsion. The highly volatile chloroform was then evaporated during heating at ~30 °C (~10 min), which transfers the nanocrystals into the aqueous phase, forming NC micelles. To prevent the silane groups from extensive hydrolysis, the heating process was kept as fast as possible and the temperature was kept as low as possible (~30 °C). The encapsulation was 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 (Scheme 1c), which have been used to stabilize rod- and cube-shaped nanocrystals.^{9–12}

Scheme 1. Schematic Illustrations of the Synthesis of Gold Nanocrystal Micelles with Organo-Silane Headgroups using Octadecyltrimethyl(3-trimethoxysilylpropyl)ammonium chloride as an Amphiphilic Agent^a



^a Conditions: (a) Dodecanethiol-stabilized, monodisperse gold nanocrystals. (b) Gold NC-micelles with silane functional groups. (c) “Bilayer” structure formed between the primary DT layer and the secondary amphiphilic silane layer. (d) Hexagonal closed-packed NC arrays. (e) Face-centered-cubic (fcc) packed NC arrays.

The gold NC micelles are monodisperse, as suggested by UV-vis spectra. Figure 1a shows the UV-vis spectra of DT-stabilized gold NCs in chloroform. The absorbance at ~519 nm corresponds to the gold surface plasmon resonance band. By comparison of Figure 1a–e, we observe no difference in the positions and peak widths of the plasmon resonance band of the DT-stabilized gold NCs in chloroform, those of the corresponding water-soluble NC

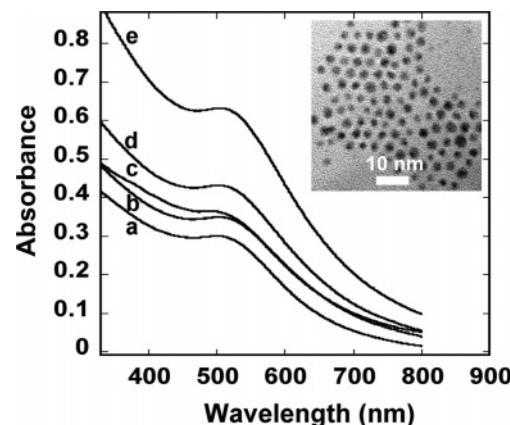


Figure 1. UV-visible spectra of (a) gold NCs in chloroform; (b) gold NC micelles prepared by using amphiphilic precursor **1** in water. (c) A film of ordered nanocrystal micelle arrays on quartz substrate. (d) Solution b after addition of HCl aqueous solution. Inset: TEM image of organo-silane functionalized gold NC micelles formed upon drying of an aqueous solution on a TEM grid. (e) Solution b after addition of methanol (v/v, 1:5).

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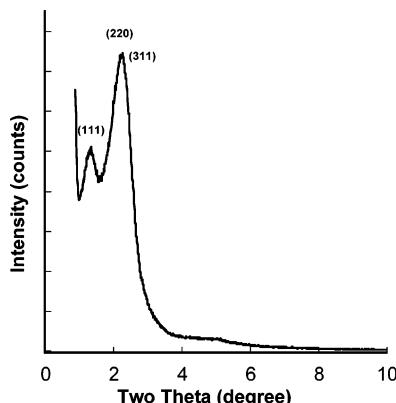


Figure 2. X-ray diffraction pattern of 3-D ordered arrays formed upon drying of NC micelle aqueous solution after addition of HCl aqueous solution.

micelles, the solid film of ordered arrays, and after addition of hydrogen chloride aqueous solution. This suggests that gold NC micelles remain monodisperse in water and the solid films without aggregation, yet the encapsulation process does not change the optical property of original DT-stabilized NCs. Figure 1 inset shows the transmission electron microscopy image of ordered arrays of NC micelles formed upon drying of a drop of NC micelle aqueous solution. The ordered hexagonal arrays, as expected for the monodisperse NCs,¹³ further indicated that the NC micelles are not aggregated.

The silane headgroups on the NC micelle surface provide reactive sites for further functionalization/grafting through siloxane chemistry.¹⁴ To demonstrate this, we hydrolyzed the silane headgroups by adding hydrogen chloride aqueous solution. Further condensation between the hydrolyzed NC micelles cross-links and organizes them into ordered arrays. Figure 2 shows the X-ray diffraction pattern of the mesophase formed. It is consistent with a face-centered-cubic (fcc) mesostructure.^{1,6} The main peaks can be assigned as (111), (220), and (310). The calculated unit cell is ~ 12.1 nm. The cross-linking was confirmed by FTIR and ^{29}Si NMR spectra (Supporting Information). Si—C and Si—O—Si bands were observed between 1000 and 1200 cm^{-1} from the FTIR spectrum. In the ^{29}Si NMR spectrum, three distinct peaks were observed at -50.1 , -59.2 , and -68.4 ppm, which account for T¹, T², T³ organo-silica species and with 4, 45, and 51% of the signal, respectively.¹⁵ It is noteworthy that for the 3-D gold NC/silica mesophases prepared by us previously using cetyltrimethyl ammonium bromide as the surfactant,⁶ a silicate precursor was needed to organize the NC micelles into ordered arrays. Here, the silane groups on the NC micelle surface, serving as both hydrophilic headgroups and functional sites, can hydrolyze, cross-link, and assemble into ordered arrays through a cooperative self-assembly process⁴ without further addition of oxide precursors. Advantageously, the silane groups can be directly used to couple with other oxides, such as TiO_2 , and form NC ordered arrays in a TiO_2 matrix that is essential for enhanced performance of nanodevices.¹⁶

We believe that this method is general and will be useful for the synthesis of silane functionalized semiconductor and magnetic NC-micelles and the corresponding 3-D ordered arrays through hydrolysis and self-assembly. We expect that the siloxane groups can be further used to graft other functional molecules for applications, such as biolabeling¹⁷ and SERS-based biosensor platforms.¹⁸ Further, through cross-linking π -conjugated organic ligand junctions, the self-assembled NC/siloxane nanostructures can be fabricated as rigid “scaffolds” to develop a useful device platform for electronics¹⁹ and sensors.¹⁸

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Supporting Information Available: Experimental details of the synthesis of gold NC and NC micelles, and FTIR and ^{29}Si NMR spectra of gold NC micelles. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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