Host–Guest Systems

DOI: 10.1002/ange.200602395

Stepwise Directing of Nanocrystals to Self-Assemble at Water/Oil Interfaces**

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The self-assembly of inorganic nanocrystals (NCs) into hierarchical structures on all length scales is pivotal for nanotechnology.[1] In this context, water/oil interfaces have gained increasing attention because their fluidity may heal defects and their rich phase separation behavior may diversify the structural complexity. The study of the attachment of micrometer-sized particles at the interface has a century-long history.[2] Nonetheless, the controlled interfacial self-assembly of NCs has been successfully realized only recently.[3–5] The appropriate surface hydrophobicity of NCs is crucial for NCs to self-assemble at the interface because of their fairly small interfacial attachment energy. This is usually realized by the proper design of the capping ligands on the NCs.[3,4] Herein, we demonstrate an alternative approach to render NCs interfacially active by entrapping their hydrophobic functional groups within the hydrophobic interior cavities of cyclodextrins (CDs). Furthermore, the functional groups on the hydrophilic exterior walls of CDs allow different NCs to be differentially directed from either the aqueous or organic phase to the interface, thus realizing stepwise interfacial self-assembly to form macroscopic heterogeneous multilayers of NCs over areas on the order of square centimeters.

CDs are characterised by having a hydrophilic exterior surface and a hydrophobic interior cavity that may include entirely or partially hydrophobic molecules through non-covalent interactions.[6] This inclusion shows a strong size selectivity. α-CDs can efficiently trap long alkyl chains, and this was used to realize the phase transfer of NCs from an organic to an aqueous phase[7] and vice versa.[8] In contrast, β-CDs have cavities of around 7.0 Å in size, which selectively trap large molecular cages such as adamantane (7 Å in diameter).[9] The specific inclusion of CDs and adamantane was used to grow multilayers of Au NCs on planar substrates layer by layer.[10]

In the present study hydrophobic 6-nm-diameter $CoPt_3$ NCs capped with 1-adamantylcarboxylic acid (ACA) and hexadecylamine (HDA) were prepared as explained elsewhere.[11] The simultaneous presence of HDA and ACA is essential for the colloidal stability of the $CoPt_3$ NCs; their partial removal leads to agglomeration of the NCs.[11] Hence one cannot render $CoPt_3$ NCs interfacially active through ligand exchange. In our study, solutions of $CoPt_3$ NCs in toluene were brought into contact with water, in which β-CDs or their derivatives were dissolved. Since the hydrophobic cavities of β-CDs or their derivatives selectively entrap the ACA group rather than the HDA,[6b,9b,c] their hydrophilic exterior walls convert the hydrophobic ACA domains on the $CoPt_3$ NCs into hydrophilic ones. The coexistence of hydrophobic HDAs and hydrophilic β-CDs or their derivatives may render the $CoPt_3$ NCs active at the interface, thus driving the NCs to self-assemble into a close-packed monolayer (Figure 1).

2-Hydroxypropyl-β-cyclodextrins (HPCDs) were used as models to demonstrate our concept because of their excellent water solubility.[12] An aqueous solution of the HPCDs (10 mM) was added to a solution of the $CoPt_3$ NCs in toluene ($0.1\ mg\,mL^{-1}$). After gently shaking the mixture, a yellow thin film formed at the water/toluene interface (Figure 2a). In contrast, no such thin film formed in the absence of the HPCDs (see the Supporting Information). The UV/Vis spectra of the bulk phases showed little detectable absorption, thereby indicating that all the $CoPt_3$ NCs were located at the interface. This result also suggests that no phase transfer occurred. Transmission electron microscopy (TEM) imaging of these thin films, transferred from the interface, revealed a

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[**] H. Zhang is acknowledged for help with the preparation of the CdTe nanocrystals. G. Zhang, J. Hartmann, O. Niemeyer, and T. Walther (CAESAR) are acknowledged for assistance with the AFM, TEM/EDX, and NMR measurements, as well as EDX mapping. We thank the Max-Planck-Gesellschaft for financial support.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

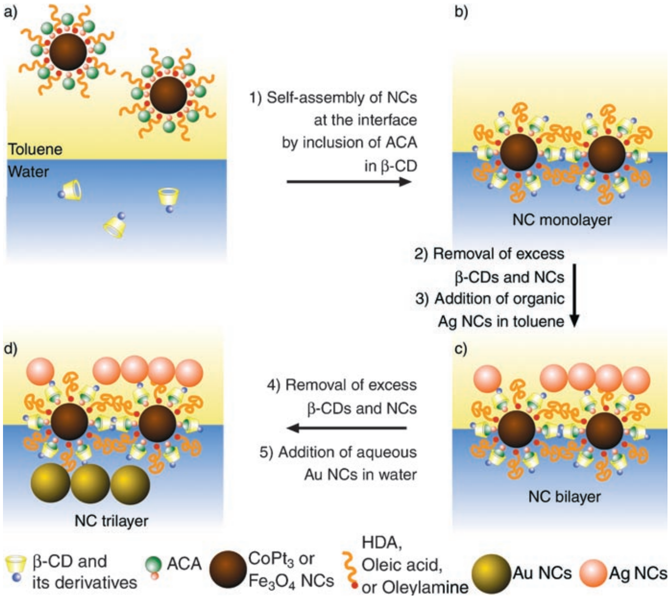

Figure 1. Schematic illustration of the self-assembly of ACA-stabilized NCs at the water/oil interface by the inclusion of ACA-capped NCs from an oil phase into CDs dissolved in water (a and b) and of the consecutive self-assembly with other hydrophilic and hydrophobic NCs into bilayers (c) or trilayers (d) based on the interaction of functional groups, such as NH_2 or SH, linked to CDs.

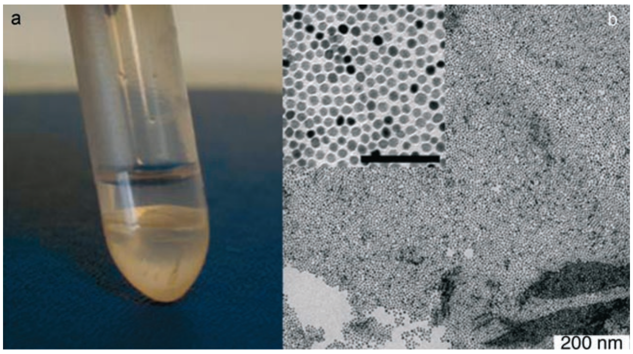

Figure 2. a) Photograph of the thin film of 6-nm-diameter $CoPt_3$ nanocrystals self-assembled at the water/toluene interface. b) TEM image of a thin film of the $CoPt_3$ nanocrystals transferred from the interface. The inset shows a high-magnification TEM image, the scale bar is 50 nm. HPCD is used for trapping the $CoPt_3$ nanocrystals at the interface.

monolayer of randomly close-packed NCs over a large area (Figure 2b).

We prepared 6-nm- and 17-nm-diameter Fe_3O_4 NCs stabilized with oleic acid and oleylamine in toluene by the oxidation of iron(III) acetylacetonate.[13] The initial capping groups of the Fe_3O_4 NCs were quantitatively replaced with ACA by ligand exchange. Incubating the Fe_3O_4 NCs in solutions of ACA in toluene at concentrations of 2, 10, and 20 mg mL^{-1} for two days resulted in the number of ACA groups per NC being 62, 128, and 199, as determined by ^{1}H NMR spectroscopy (see the Supporting Information). Note that the maximal number of ACA groups per NC is calculated as 264. The inclusion of ACA by HPCD led to the interfacial self-assembly of the Fe_3O_4 NCs (Figure 3a,b). We envisioned that the reduction in the absorbance of the Fe_3O_4 NCs in the toluene phase should be proportional to the number of NCs attached at the water/toluene interface. Accordingly, we quasi-quantitatively evaluated the interfacial attachment of the Fe_3O_4 NCs at the interface between the toluene solution and the HPCD aqueous solution at different concentrations (see the Supporting Information). Figure 3c shows that the number of HPCDs required for the entire interfacial attachment of Fe_3O_4 NCs increases with the number of ACA groups functionalizing the NCs. This underlines that the interfacial self-assembly of the Fe_3O_4 NCs predominantly relies on the inclusion of ACA by HPCD.

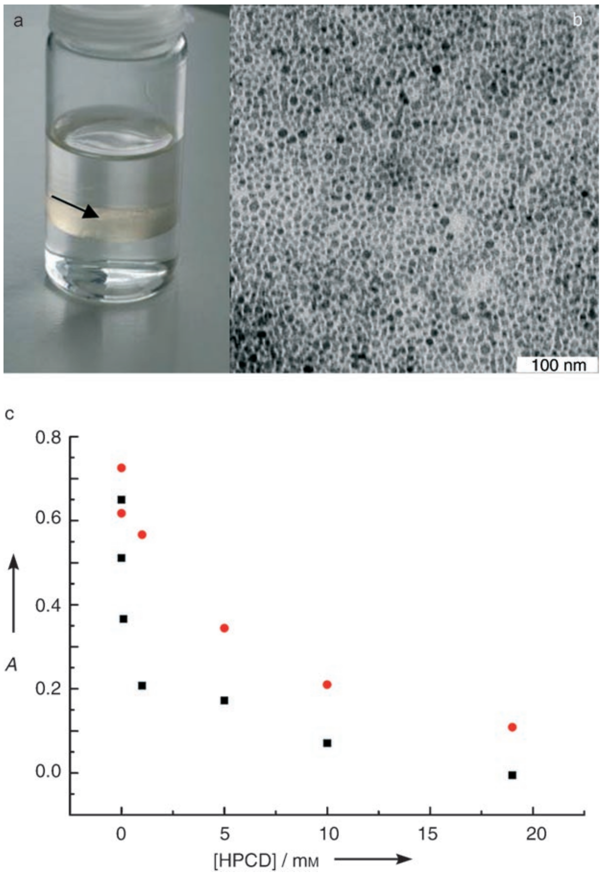

Figure 3. a) Photograph of a film derived from the self-assembly of 6-nm-diameter Fe_3O_4 NCs at the water/toluene interface and b) TEM image of the resulting thin film. The aqueous phase is 10 mM HPCD solution. The number of ACA groups per NC is 128. The water/toluene interface is highlighted by an arrow. c) Profile of the reduction in the absorption intensity of 6-nm-diameter Fe_3O_4 NCs in the toluene phase at 500 nm versus the concentration of HPCD in water. After mixing 1 mL toluene, containing 0.3 mg Fe_3O_4 NCs, with 1 mL of an aqueous solution of HPCD by shaking for 5 min, 0.8 mL organic aliquots were taken for UV/Vis absorption measurements. The numbers of ACA groups per NC are 128 (circle) and 199 (square).

Native β-CDs usually have a rather poor solubility in water because of intramolecular hydrogen-bonding interactions.[14] In the current study, the interfacial self-assembly of NCs was realized by using a rather dilute aqueous solution of β-CD (1 mM). We found that incubation at high temperature favored the formation of monolayers of NCs at the water/toluene interface: heating may weaken the intra- and intermolecular hydrogen bonding between the β-CD and the inclusion of ACA[15] (see the Supporting Information). In comparison to HPCD, β-CDs enhanced the stability of the emulsions. By staining with aqueous solutions of CdTe NCs, we found that the emulsions obtained were of the oil-in-water type (see the Supporting Information).

After the ACA functional groups on the $CoPt_3$ or Fe_3O_4 NCs had been inserted within the hydrophobic cavities of the β-CDs, the hydrophilic exterior walls of the latter were envisioned not only to result in the NCs becoming hydrophilic but also to provide flexibility for the further modification and conjugation with other materials. This encouraged us to utilize β-CDs with functional groups on the exterior walls to absorb different nanosized objects onto macroscopic monolayers of close-packed $CoPt_3$ or Fe_3O_4 NCs. Thus, heterogeneous multilayers composed of different NCs may be generated, which should be of great importance for microelectronics applications.[16] β-CDs functionalized with one SH or NH_2 group on the exterior walls, namely, mono{6-deoxy-6-[(mercaptohexamethylene)thio]}-β-cyclodextrin (SH-β-CDs)[17] and 6-monodeoxy-6-monoamino-β-cyclodextrin (NH_2-β-CDs) were recruited as new functional groups to direct different NCs to consecutively self-assemble at the water/oil interface (Figure 1). Similar to HPCDs, the NH_2-β-CDs and SH-β-CDs were able to direct ACA-capped NCs ($CoPt_3$ and Fe_3O_4) to self-assemble into randomly close-packing monolayers through the inclusion of ACA into the CD (see the Supporting Information). After the aqueous solution of SH-β-CDs was replaced by pure water, hydrophobic 6-nm-diameter Ag NCs stabilized with oleic acid were introduced into the toluene phase. The strong interaction between the SH groups on the β-CDs and the Ag NCs led to the interfacial attachment of the Ag NCs on the monolayers of the 6-nm-diameter Fe_3O_4 NCs (Figure 4 a), accompanied by the appearance of a stronger metallic luster to the film and the disappearance of the dark-yellow color in the toluene phase (Figure 3 a). TEM imaging demonstrated the formation of bilayers of close-packed NCs, but it was hard to distinguish the chemical nature of these two NCs because of their similar size and electron contrast (see the Supporting Information). Similarly, bilayers composed of 6-nm-diameter $CoPt_3$ and 12-nm-diameter Au NCs were formed at the interface by absorbing citrate-stabilized Au NCs from the aqueous phase using NH_2 groups attached to β-CDs (see the Supporting Information).

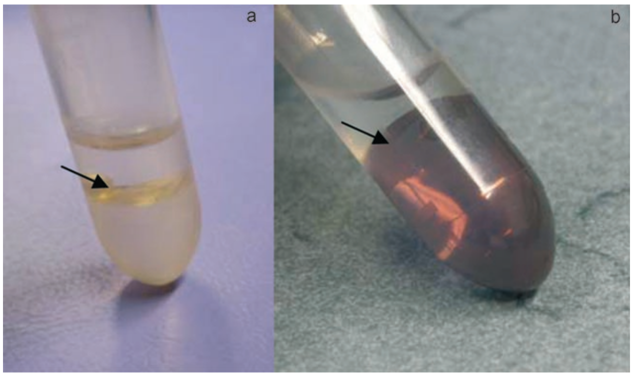

Figure 4. Photographs of the thin film obtained by consecutive self-assembly at the water/toluene interface to form bilayers of 6-nm-diameter Fe_3O_4 and 6-nm-diameter Ag NCs (a) and trilayers of 6-nm-diameter Fe_3O_4, 6 nm-diameter Ag, and 12-nm-diameter Au NCs (b). SH-β-CD is used for interfacial self-assembly. The water/toluene interface is highlighted by an arrow.

The resulting Ag/Fe_3O_4 NC bilayers are envisaged to have a hydrophobic surface in contact with the toluene, because of the free oleic acid capping the Ag NCs, and a slightly hydrophilic lower surface in contact with the water, as a result of free SH-β-CDs capping the Fe_3O_4 NCs. The free SH groups on the Fe_3O_4 NCs may be employed to attach other hydrophilic NCs from the aqueous phase (Figure 1). In the current study, 12-nm-diameter citrate-stabilized Au NCs were introduced into the aqueous phase. Figure 4 b shows that after gentle shaking, the Ag/Fe_3O_4 NC bilayer films located at the interface appear purple when viewed in the transmittance mode and golden in the reflectance mode, thus suggesting the interfacial attachment of 12-nm-diameter Au NCs. TEM imaging of broken areas of the resulting thin films revealed a trilayer structure (see the Supporting Information). The existence of different NCs was demonstrated by energy-dispersive X-ray spectroscopy (EDX) and EDX mapping (see the Supporting Information). The thickness of the trilayers was nearly 25–30 nm, which is consistent with the formation of an Ag/Fe_3O_4/Au NC trilayer (see the Supporting Information). Note that both the bilayers and trilayers remain magnetic because of the existence of magnetic NCs (see the Supporting Information).

In summary, we have demonstrated that the use of the specific inclusion of adamantane by CD can direct hydrophobic ACA-capped NCs to self-assemble into macroscopic randomly close-packing monolayers at water/oil interfaces. By introducing functional groups, such as NH_2 or SH, onto the exterior surfaces of CDs, we succeeded in directing different hydrophobic and hydrophilic NCs to self-assemble in a stepwise manner at the water/oil interface, thereby generating macroscopic heterogeneous multilayers. This result demonstrates the unique amphoteric character of the water/oil interface—being able to conjugate both hydrophilic and hydrophobic NCs from water and oil phases. Since the success of our approach relies on the molecular structure of CDs, it should pave a versatile and efficient way to the stepwise self-assembly of NCs with different chemical natures and surface wettability into macroscopic lamellar superlattices of NCs based on well-established host–guest chemistry. The trilayer films of Ag/Fe_3O_4/Au NCs, which is a magnetic NC monolayer sandwiched between two metallic NC ones, should hold immense promise in technical applications, such as magnetic information storage and processing.

Experimental Section

Aqueous solutions (0.2 mL) of β-CD or its derivatives were brought into contact with solutions of NCs in toluene (0.2 mL). The gentle shaking led to a thin film being formed at the interface and the toluene phase turning colorles. SH-β-CDs or NH_2-β-CDs were used to form heterogeneous multilayers of NCs at the water/toluene interface. After monolayers of NCs were formed at the interface, excess CDs and magnetic NCs were removed by replacing the aqueous and organic phases by water and toluene, respectively. Hydrophobic Ag or hydrophilic Au NCs were then introduced into the toluene or water phase, respectively. A gentle shaking led to bilayers of metallic and magnetic NCs at the interface. After removing the excess metallic NCs, the addition of new metallic NCs in another phase yielded metallic/magnetic/metallic trilayer films at the interface.

UV/Vis absorption spectra were recorded on a Cary 50 UV/Vis spectrophotometer. TEM images were obtained on a Zeiss EM 912 Omega microscope. EDX and EDX mapping were conducted on a Philips XL30 and a LEO 922 A electron microscope.

Received: June 14, 2006
Revised: September 7, 2006

Keywords: host–guest systems · interfaces · multilayers · nanostructures · self-assembly

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