DOI: 10.1002/anie.200604889

Nanostructures

Rings of Nanorods**

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Finding new ways to assemble nano-objects[1–6] into finite superstructures is an important task because their properties depend not only on their size and shape but also on the spatial arrangement and the degree of order among the individual building blocks. Ringlike assemblies are fairly common and have been documented for various polymers,[7–10] small organic molecules,[11] and spherical inorganic nanoparticles.[12,13] Several mechanisms have been proposed to explain the formation of rings, including the Marangoni effect,[14] the hole-nucleation mechanism,[12] "2D gas bubbles",[11] and the "breath figures" method (BF).[15] The latter mechanism takes advantage of the condensation of water microdroplets from moist air and uses them as templates. Thus, the BF method typically produces a honeycomb structure, which can be viewed as an array of air bubbles embedded into a continuous 2D matrix formed by polymer chains[16] or spherical nanoparticles.[17] One can see that if the concentration of solute is reduced, the perforated film should transform into a set of isolated rings, as was recently demonstrated in the case of linear polymers.[18] However, rings composed of anisometric nanocrystals, especially inorganic rods, have never been observed. Nearly all reports on the self-assembly of nanorods describe their packing in a parallel fashion.[19] Theoretical models also predict a side-by-side packing of rods regardless of their overall morphology.[20] In stark contrast to that, we describe herein a spontaneous assembly of hybrid gold/polymer core–shell nanorods into ringlike arrays. A systematic investigation shows that the rings of rods described here are templated by water droplets that condense on the surface of nonpolar solvents from humid air, akin to the classical BF method. The high yield and the well-defined structure of rings are a result of the presence of polystyrene (PS) chains covalently attached to the surface of the gold nanorods. The polymer shell insures high solubility of the hybrid 1D nanostructures and keeps the $\mathrm{AuNR(PS)}_n$ rods in solution during the evaporation until they are concentrated around the circumferences of water droplets. This method is surprisingly simple and can be used for organizing nanorods into circular arrays in a nearly quantitative yield.

Our recent studies revealed that carboxyl-terminated polymers can be covalently attached to phenol-functionalized gold nanoparticles under mild esterification conditions.[21] To test the versatility of such an approach, we attempted a synthesis of rodlike gold/polymer core–shell nanostructures. Unlike spherical nanoparticles, the functionalized nanorods cannot be directly prepared by reduction of gold ions in the presence of thiols. For that reason, we first prepared gold nanorods stabilized by cetyltrimethylammonium bromide (CTAB) surfactant using a modified seed-mediated growth method.[22] However, a seemingly trivial step of exchanging CTAB for a functional thiol was found to be a serious challenge. For example, the removal of either water or CTAB surfactant causes an irreversible agglomeration of nanorods and the subsequent multiple attempts to attach thiols in organic media are completely unsuccessful. In addition, many functional thiols are not soluble in water and their dispersion in an aqueous solution of CTAB-stabilized nanorods does not result in ligand exchange. After many trials, we found that dropwise addition of a concentrated solution of 4-mercaptophenol in THF directly into an aqueous growth solution of rods led to CTAB–thiol exchange and a slow precipitation of phenol-functionalized nanorods.

After centrifugal purification, $\mathrm{AuNR(SC_6H_4OH)}_n$ rods could be dispersed in dichloromethane and covalently coupled with carboxybiphenyl-terminated polystyrene ($M_w = 5000\ \mathrm{g\,mol^{-1}}$; Figure 1). The reaction proceeded within several hours after the addition of 4-(*N*,*N*-dimethylamino)pyridinium-4-toluenesulfonate (DPTS) and 1,3-diisopropyl carbodiimide (DIPC). Remarkably, the reaction could be monitored by TLC as the starting material $\mathrm{AuNR(SC_6H_4OH)}_n$ with a retention factor of $R_f = 0$ gradually transforms into $\mathrm{AuNR(PS)}_n$ product, which moves on a TLC plate as a single dark-red spot ($R_f = 0.6$ in 15% THF in $\mathrm{CH_2Cl_2}$). The product was isolated by centrifugal ultrafiltration of the THF solution using a regenerated cellulose membrane (MWCO = 30 kDa). Importantly, the complete removal of linear polystyrene was confirmed by size-exclusion chromatography of the THF-soluble $\mathrm{AuNR(PS)}_n$ product, whereas the presence of covalently attached PS arms was confirmed by ^{1}H NMR spectroscopy (see the Supporting Information). The typical weight gain of such coupling reactions is about 40%, which allows us to estimate the grafting density of PS arms (5 kDa) on gold nanorods (10 nm × 45 nm as determined by transmission electron microscopy (TEM)). The grafting density is about 2.1 chains$\,\mathrm{nm^{-2}}$, which means that approximately 3000 PS chains are covalently attached to a given nanorod (see the Supporting Information). The value of the grafting density is comparable to that reported for spherical Au nanoparticles (2.9 chains$\,\mathrm{nm^{-2}}$).[21] The presence of a dense polymer shell ensures high solubility and stability of the nanorods in organic solvents.

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[**] This work was supported by a NSF CAREER Award (DMR-0547399) and the Robert A. Welch Foundation (L-C-0003). Partial support provided by the NSF NIRT grant (CBET-0506832) is also acknowledged.

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

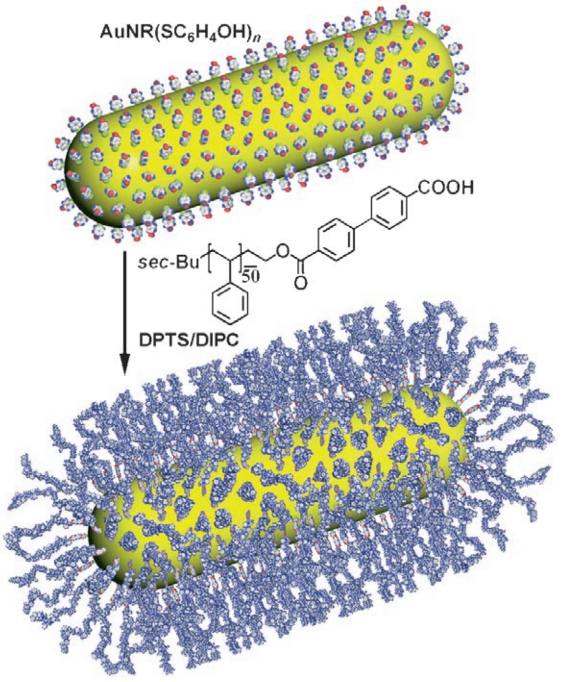

Figure 1. Synthesis of gold nanorods with covalently attached PS arms.

Examination of AuNR(PS)$_n$ by TEM revealed their unexpected and counterintuitive properties. When a carbon-coated grid is dipped in a CH_2Cl_2 solution and the drop is allowed to dry in air at room temperature, the nanorods spontaneously organize into ring structures (Figure 2). The diameter of the rings varies from 300 nm to a few microns, and their typical width is about 50 nm. In most rings the orientation of rods is random (Figure 2c,d), but at low concentration they tend to line up in a head-to-tail fashion along the circumference (Figure 2a,b). Importantly, virtually all of the rings that were found have one common feature: there are very few, if any, rods inside the rings, which is indicative of a templated process. TEM imaging at low magnification (Figure 3) revealed the presence of rings throughout the entire substrate. The yield of rings is nearly quantitative as there are very few rods either inside the rings or in the areas between them. The average size of the rings is not influenced by the concentration, and similar results were obtained when the samples were also prepared from other nonpolar solvents, such as chloroform and benzene.

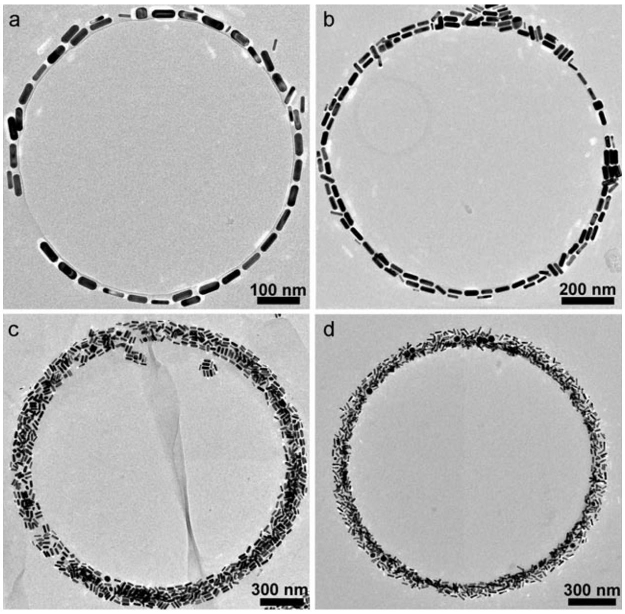

Figure 2. TEM images of rings formed by AuNR(PS)$_n$ rods from a solution in CH_2Cl_2 (1 mg mL^{-1}). See text for details.

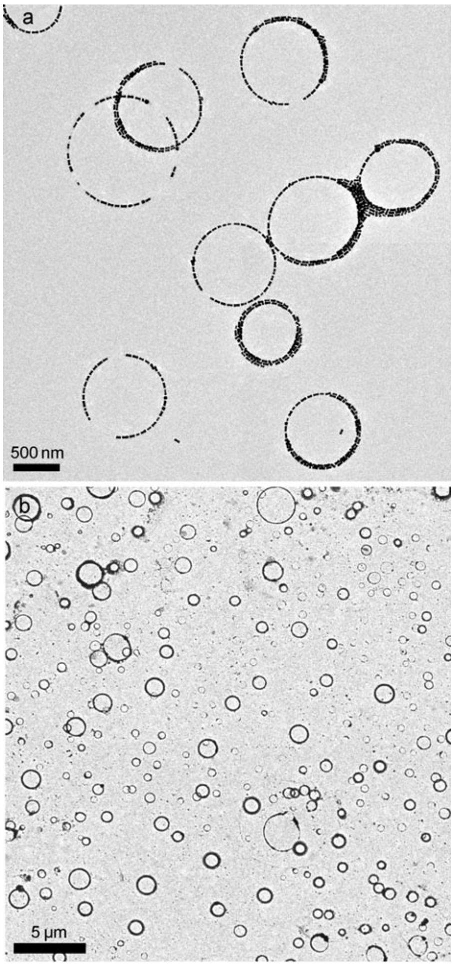

Figure 3. Representative low-magnification TEM images of rings formed by AuNR(PS)$_n$ when a carbon-coated grid is dipped into a solution of the rods in CH_2Cl_2 (1 mg mL^{-1}).

The aforementioned hole-nucleation mechanism[12] cannot explain the assembly of AuNR(PS)$_n$ rods because the rings form on very different substrates (wetting and non-wetting conditions), their size varies within a broad range, and it does not depend on the concentration. These initial data led us to hypothesize that the nanorods assemble around water droplets that can condense from the air when highly volatile CH_2Cl_2 evaporates and cools its surface below the dew point. It has been shown previously that the temperature on the surface of evaporating volatile solvents can be as low as

0 °C.[15,16] In addition, it has been proposed that microdroplets of water retain their small and uniform size and pack into a 2D hexagonal superlattice on the liquid surface of organic solvents.[23] We were able to confirm this phenomenon by direct visualization of water microdroplets condensed on the surface of a solution of AuNR(PS)$_n$ in dichloromethane, as well as on pure CH_2Cl_2, deposited onto carbon-coated TEM grids (Figure 4). The droplets, however, are not stationary and rapidly move in various directions as a result of convectional flow. As observed in the optical microscope, the droplets retain their uniform size only for a limited amount of time and undergo coalescence as soon as the organic solvent is evaporated.

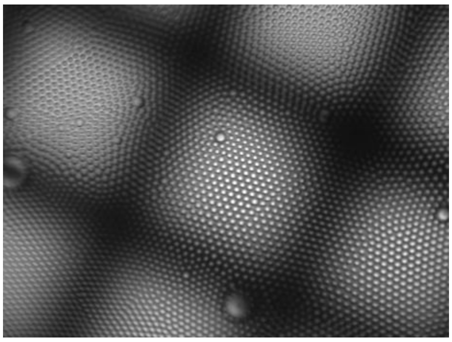

Figure 4. Optical micrograph of water droplets on the liquid surface of a dichloromethane solution of AuNR(PS)$_n$ cast on the carbon-coated TEM grid. The square windows of the copper grid in the background measure 100 μm × 100 μm.

An important control experiment was carried out in the absence of moisture. When a sample is prepared in a glove box under ultradry nitrogen atmosphere, not a single ring can be found on the substrate (see the Supporting Information). This simple experiment also proves that the formation of rings is not driven by the Marangoni effect. We also found that rings do not form from nonvolatile solvents such as toluene owing to its insufficient evaporative cooling and inability to cause the condensation of water droplets. Moreover, rings form only if the solvent is not miscible with water (CH_2Cl_2 or $CHCl_3$) and they cannot be produced from water-miscible solvents like tetrahydrofuran or acetone even though their boiling points are very close to that of chloroform.

On the basis of these data, the following mechanism can be proposed. A fast evaporation of CH_2Cl_2 leads to a condensation of numerous water droplets (Figure 5a), which subsequently land on the carbon substrate and become surrounded by a thin continuous film of the dichloromethane solution of rods (Figure 5b). Because AuNR(PS)$_n$ nanorods are highly soluble in CH_2Cl_2, they will remain in solution until its last portion is concentrated around the impervious walls of the water droplets (Figure 5c,d). At this point the temperature of the substrate will start rising back to room temperature, thus causing evaporation of the water templates and leaving behind ringlike arrays of the nanorods (Figure 5e).

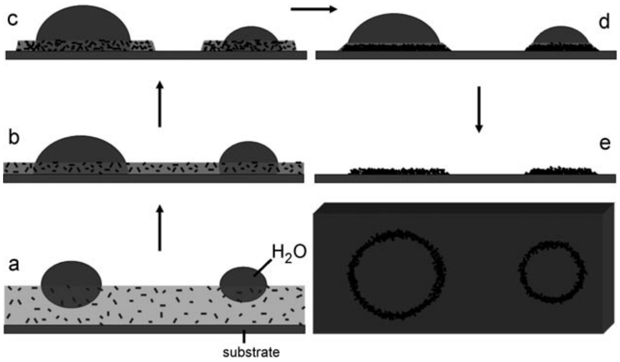

Figure 5. A schematic representation of the formation of rings templated by water droplets. See text for details.

One can directly observe in an optical microscope that the coalescence of microdroplets takes place when the majority of organic solvent is evaporated and results in a broad size distribution of rings (Figure 3b). However, the rings have well-defined structures and their overall yield is remarkably high. This is as a result of a combination of two important characteristics of the reported nanorods: The *hydrophobic nature* of PS arms prevents the nanorods from entering the interior of water templates, whereas their *high solubility* in CH_2Cl_2 ensures that they do not precipitate out of solution early and do not deposit themselves in the areas between the water droplets. The importance of the former characteristics was confirmed by examining analogous nanorods with a hydrophilic shell. We synthesized rods with covalently attached polyethylene glycol (PEG) arms (5 kDa) and found that they do not produce any rings (Supporting Information). This is because water droplets cannot stop water-soluble AuNR(PEG)$_n$ nanorods at the interface. Finally, there are two more required elements for the successful formation of rings. The solvent should be water-immiscible and volatile enough to cause an evaporative cooling below the dew point.

In conclusion, we have described a new method for the synthesis of anisometric core–shell hybrid nanorods and found an efficient way to induce their spontaneous organization into ringlike superstructures. This highly efficient and simple technique may be used to manipulate the optical properties of gold nanorods.

Received: December 3, 2006

Keywords: electron microscopy · gold · nanostructures · organic–inorganic hybrid composites · self-assembly

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