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Amphiphilicity-Driven Organization of Nanoparticles into Discrete Assemblies

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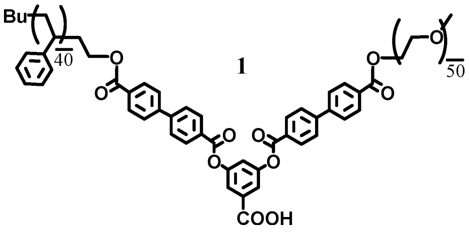
During the past decade a significant success has been achieved in the synthesis of well-defined nanosized objects, but their organization into superstructures remains a challenge.[1−3] It has been shown that the "bricks-and-mortar" strategy based on the hydrogen bonding of DNA[4] and molecular recognition of specific ligands[5] can assemble metallic nanoparticles into 3D networks. However, many existing strategies produce assemblies of NPs that are not stable in solution and precipitate soon after they form. Other approaches use various templates,[6,7] which bring a number of advantages, but also introduce certain limitations, including the dependence on size, shape, and stability of a template. Here we demonstrate that the covalent attachment of amphiphilic polystyrene-*b*-poly(ethylene oxide) molecules to the surface of gold and silver nanoparticles drives their assembly in water into one-dimensional tubular arrays that remain in solution indefinitely. This *amphiphilicity-driven self-assembly* is based on the hydrophobic effect[8] and therefore requires neither molecular recognition nor hydrogen bonding.

Our original hypothesis was based on a series of simple assumptions. Any micelle-like aggregate contains an interface between the insoluble core and the solvent-swollen corona. The interface is occupied by the junction points of the individual amphiphilic molecules. In principle, the micellization can be viewed as a process that drives the packing of all junction points into a high density array. If a micelle is cylindrical, its interface is a *tubular array* of junction points. Therefore, when a carrier of functionality, that is, a nanoparticle or a catalytic center, is covalently attached to the junction point of an amphiphile, the micellization may produce a soluble and well-defined ensemble of functional species. Because the morphology of a micelle can be tuned, all three major types of NP arrays, that is, spherical, tubular, and vesicular, may be produced, and disassembled, when necessary.

The synthesis of monofunctionalized particles,[9,10] however, is a challenging task, and we further hypothesized that the same organization would occur if a particle were a junction point of *many* hydrophobic and hydrophilic arms. Such structures can be made when V-shaped amphiphilic molecules (Scheme 1) are covalently attached to a metallic cluster (Figure 1A). The incompatible flexible arms can undergo spatial separation by wrapping around the metallic core, provided their length is *significantly* greater than half the circumference of a nanoparticle. The resulting multi-arm hybrid amphiphile would be driven to aggregate in order to minimize the entropically unfavorable contacts with water molecules (Figure 1A).

We first synthesized a V-shaped polystyrene-*b*-poly(ethylene oxide) (PS_{40}-PEO_{50}) amphiphile[11] containing a carboxylic group at its focal point (Scheme 1) and attached it to phenol-functionalized 2 nm gold and silver nanoparticles following a procedure described previously.[12] In order to induce a cylindrical morphology, we made the molecular weight of PS block (M_n = 4000 g/mol) two times higher than PEO (M_n = 2200 g/mol). When 75% (vol) of water is added dropwise to a THF solution of the amphiphilic Au-(PS_{40}-PEO_{50})$_n$ NPs and the mixture is dialyzed against DI water for 3 days, an optically transparent brown solution forms. The presence of micelle-like aggregates was confirmed by dynamic light scattering (Supporting Information, Figure S5).

Scheme 1. Chemical Structure of PS_{40}-PEO_{50} Amphiphile **1**.



TEM examination of a sample prepared from a dilute solution revealed the presence of well-defined rodlike nanoarrays of Au-(PS_{40}-PEO_{50})$_n$ NPs which measure 18 ± 2 nm in diameter and approximately 100 nm in length (Figure 1B). The individual gold nanoparticles can be seen within the cylindrical structures. The average interparticle distance is about 3 nm, which is indicative of their high packing density. Importantly, the edges of these structures appear much darker than their center, which is consistent with a tubular array of nanoparticles. This contrast suggests that the particles are residing at the interfacial surface, that is, the boundary separating the insoluble glassy PS core from the solubilizing PEO corona (not visible without staining). The observed radius of these

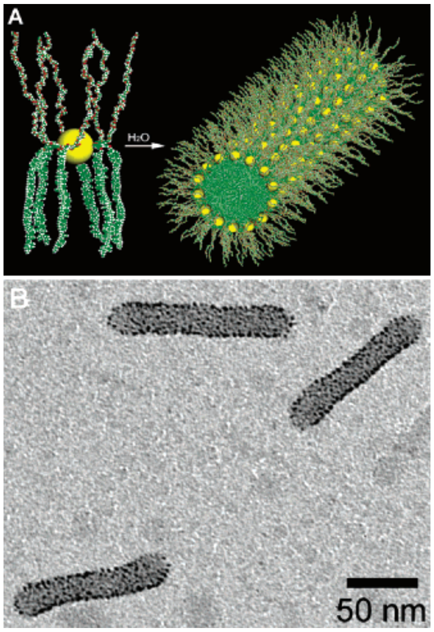


Figure 1. (A) Schematic representation of the amphiphilicity-driven self-assembly of Au-(PS-PEO)$_n$ NPs (for simplicity reasons only six PS-PEO molecules are shown); (B) TEM image of a sample prepared from an aqueous solution of Au-(PS-PEO)$_n$ NPs after dialysis of a THF/H_2O (1:3 vol.) solution against DI water.

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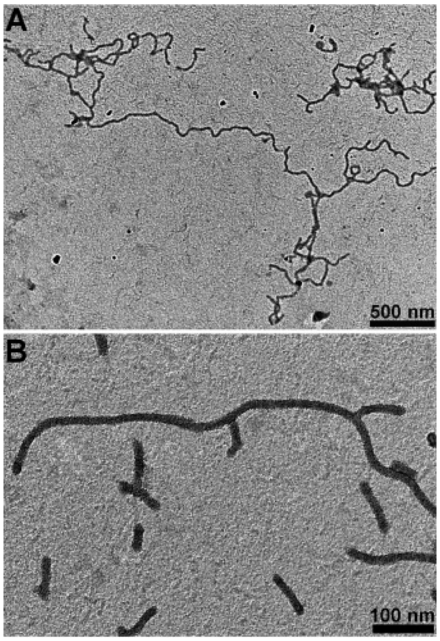

Figure 2. (A) Wormlike assemblies of amphiphilic Au-(PS$_{40}$-PEO$_{50}$)$_n$ NPs from an aqueous solution after dialysis from a DMF/H$_2$O (1:3 vol) mixture; (B) one-dimensional assemblies of silver nanoparticles Ag-(PS-PEO)$_n$ (dialysis from a THF/ H$_2$O mixture).

structures (∼9 nm) is in good agreement with the length of PS arms (∼10 nm in fully extended all-trans conformation). When the molecular weight of PS arms is reduced to 3 kDa the diameter of the core becomes ∼14 nm (Figure S7). Because polystyrene is well below its glass transition temperature (100 °C), any significant structural rearrangements either upon dilution or evaporation of water cannot occur in this system. This was demonstrated previously for micelle-like aggregates with a polystyrene core.[13−15] The addition of methanol (∼10%) to aqueous solutions reduces the average size of the arrays and leads to the formation of spherical assemblies coexisting with short rodlike structures (Figure S8)

Further investigation has shown that the size and morphology of NP arrays depend on the dialysis conditions and concentration. For example, if a solution of Au-(PS-PEO)$_n$ NPs in dimethyl formamide (DMF) is dialyzed, then much longer 1D arrays form. Such structures have the same 18 ± 2 nm diameter, but they are several micrometers long and contain Y-shaped branches (Figure 2A). These nanoparticulate morphologies can be easily disassembled and reassembled repeatedly upon addition and removal (by dialysis) of a nonselective solvent (Figures S5 and S6). Importantly, this approach is applicable to other metallic clusters, and silver nanoparticles (Ag-(PS$_{40}$-PEO$_{50}$)$_n$) were also shown to organize into 1D arrays in water (Figurea 2B and S2). In addition, the morphology can be changed from cylindrical to vesicular if the concentration of the starting DMF solution is significantly increased (from 10 to 40 mg/mL, Figure S9).

We also synthesized analogous hybrid structures with a larger metallic core (5 nm) and the same PS$_{40}$-PEO$_{50}$ arms. In that case the self-assembly does not take place and the particles form irregular aggregates in water. This result supports the initial idea that the length of the amphiphilic arms should be significantly larger than half the circumference of the particles, which is not the case in this system (10 vs ∼8 nm, respectively). In contrast, the amphiphilic Au NPs with much longer (∼50 nm) hydrophobic arms (Au(PB$_{100}$-PEO$_{115}$)$_n$, self-assemble into cylindrical structures with a much larger central core (∼32 nm) (see Figure S10).

These findings demonstrate that the hydrophobic effect can be an efficient tool for organizing metallic nanocrystals into well-defined 1D soluble arrays. The properties of such ensembles depend on their morphology and the aspect ratio. Therefore, manipulation of these parameters may provide an opportunity to control the optical and catalytic properties of inorganic nanoassemblies in water.

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Supporting Information Available: Experimental details, GPC traces, AFM and TEM images. This material is available free of charge via the Internet at http://pubs.acs.org.

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