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Self-Assembly of Amphiphilic Nanocrystals

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The self-directed assembly of molecular building blocks into extended micro- or nanostructures is an essential process in biological organisms, and is also used in many products ranging from cosmetics to drug formulations.[1–4] An important class of such self-assembled structures are vesicles, which are compartments delineated by a curved membrane enclosing a portion of the solvent. Such vesicles form the basis of autonomous living systems by providing a restricted space that defines the boundaries for cells and cell organelles and separates their internal chemical environment from their external surroundings. Membranes enclosing biological vesicles are self-assembled structures formed from glycerophospholipids, which are amphiphilic molecules with both a hydrophobic and a hydrophilic part. In dilute aqueous solutions and under suitable conditions, such as geometric packing, hydrocarbon chain stiffness, and hydrophilic–hydrophobic balance, amphiphiles naturally arrange themselves into a variety of microstructures, including micelles, bilayers, and vesicles.[5]

Synthetic amphiphilic molecules show the same tendency as biological phospholipids, but greatly extend the range of accessible molecular weights.[6] Whereas biological lipids have molecular masses of less than 1000 Daltons, there is no limit for the molecular mass of diblock copolymers.[7] Apart from diblock copolymers, many other elemental structures have been self-assembled into micro/nanovesicles, including nonionic amphiphilic molecules (niosomes),[8] dendrimers (dendrisomes),[9,10] and fullerenes.[11,12]

Förster and co-workers report the formation of vesicles from organic–inorganic hybrid systems consisting of polymer-coated fluorescent CdSe/CdS core-shell spherical nanocrystals.[13] Those organic–inorganic building blocks consist of hydrophilic polymer chain tails and a hydrophobic core, which is the fluorescent nanocrystal. Various polyethylene oxide (PEO) chains that are synthetically functionalized with several amino groups at one end bind by means of an incomplete ligand exchange to the nanoparticle surface and

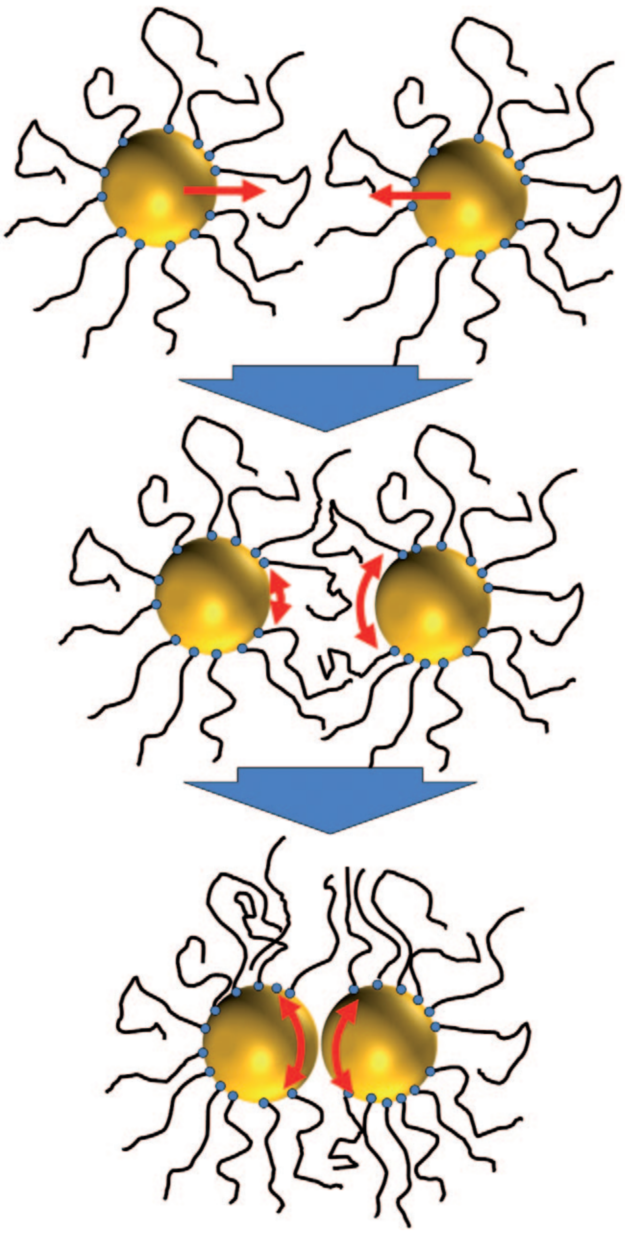

Figure 1. Proposed mechanism for the self-assembly process described by Förster et al. First, the hydrophobic nanoparticles are symmetrically surrounded by hydrophilic polymers, which are only weakly anchored onto the nanoparticles. In the event of two particles meeting, the anchor points can slide away to make room for the inorganic cores to approach more closely. Depending on the density of polymers and the strength of the anchoring, nanoparticle chains or vesicles form.

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surround the hydrophobic nanoparticles with a brush-like layer of hydrophilic flexible polymer chains. Förster and co-workers propose a novel vesicle-forming mechanism for these hybrid structures: when two particles collide, the polymeric tails redispose on the surface to make room for the cores to approach each other (Figure 1).

The polymer rearrangement relies on a weak anchoring between a few polymer amino groups (PEO-diethylenetriamine, PEO-N3) and the nanocrystal surface. The self-assembly process was inhibited by stronger anchoring of the polymers, which was achieved by increasing the number of amino anchoring points (PEO-branched polyethyleneimine, PEO-N10) or using thiol-terminated polymers.

Adjusting the density of polymer chains on the nanoparticle surface allows the resulting self-assembled structures to be modified. Upon decreasing the polymer density, the system exhibits a transition from isolated polymer-coated nanoparticles with the polymer tails facing outwards, to cylindrical neck-like aggregates with up to ten nanoparticles per aggregate, and ultimately to worm-like strings. At very low polymer chain densities, transmission electron microscopy and confocal laser scanning microscopy reveal the spontaneous formation of monolayered vesicles in which one layer of fluorescent CdSe/CdS nanocrystals makes up the vesicle wall. A combination of molecular packing considerations and general thermodynamic principles were applied to rationalize the molecular self-assembly with these surfactant-imitating organic–inorganic hybrid materials. Using geometrical relations, a change in the number of polymer chains per nanoparticle translates into drastic changes in the volume of the hydrophilic tails, the role of which determines the equilibrium structure. Depending on the packing density of the polymers and the strength of the anchoring, this process can lead to either strings of particles or three-dimensional vesicular aggregates.

There is ample potential to explore the self-assembly of polymer-coated inorganic nanocrystals into nano- and microstructures. Further complexity can be added by using anisotropic (rather than spherical) nanocrystals, such as nanorods, and exploring their assembly in different configurations, such as head-to-head or side-by-side. Another possible starting point for more detailed studies could be polymer-coated nanocrystals made from two different materials. Recently, the selective growth of gold tips on one end of a CdS nanorod was achieved.[14] Such matchstick-like particles make an intriguing building block for complex self-assembly owing to their inherent chemical anisotropy. A polymer anchored to such a matchstick particle would probably show very different affinity for the gold and the CdS parts, which should lead to interesting self-assembled structures. Other complex assemblies might arise, for instance from nanorods made of linear sections of different materials, and from heterodimers made of two spherical domains of two different materials attached to each other, each of which could be selectively functionalized with a specific type molecule. In addition to the supramolecular assemblies generated by nanoparticle organization, multiple functionalities could be introduced (for instance, fluorescence and magnetism together) owing to the specific materials of the inorganic building blocks. Thus, vesicle formation of organic–inorganic hybrid systems will most certainly be a field that should provide many more discoveries in the next years.

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