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Self-Assembly and Colloidal Polymerization of Polymer–Nanoparticle Hybrids into Mesoscopic Chains**

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The organization of polymeric colloids, inorganic nanoparticles, and polymer–nanoparticle hybrid materials into one-dimensional (1D) assemblies has been extensively investigated as a route to novel nanomaterials. Self-assembly through noncovalent associations is probably the only means to effectively put together nanoparticles, because the selective manipulation of very small, isotropic colloids in top-down approaches is difficult. One concept that has gained significant attention is using nanoparticles as colloidal monomeric entities for polymerization analogous to the polymerization of small molecules or atoms. However, it is a significant challenge to endow nanoparticles with suitable reactivity for polymerization to achieve the selective functionalization of colloids and for the efficient 1D self-assembly to give mesoscopic nanoparticle chains. Critical advances in these areas include the preparation of Janus-type nanoparticles and the differential modification of nanoparticles with discrete polymeric or small-molecule ligands. These types of nanoparticles are then capable of assembling into complex mesostructures, as a direct consequence of the noncovalent associations in the colloidal surfaces.[1]

The self-assembly of nanoparticles into extended micrometer-length mesostructures requires highly selective and directional associations that must overcome thermal fluctuations. Polymer-coated ferromagnetic cobalt nanoparticles have been used to prepare self-organized mesoscopic chains as a direct consequence of north–south dipolar associations. (Figure 1 a).[2] For nonmagnetic nanoparticles, dipole and/or charge interactions can also lead to chain formation.[3] However, continued chain growth cannot be easily achieved because of the competing "reaction" kinetics that promote branching or flocculation.

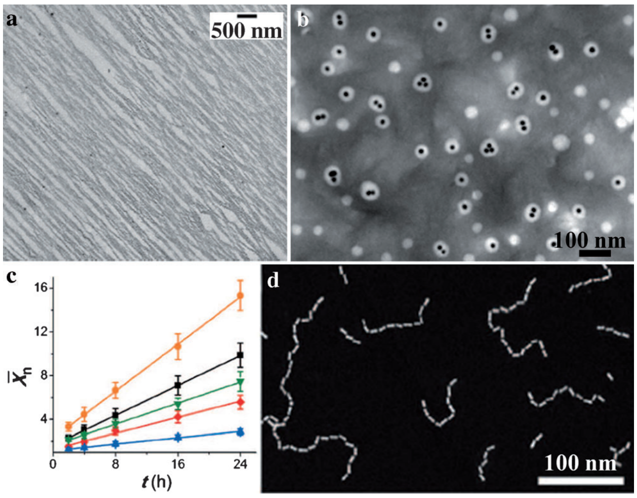

Figure 1. Examples from the literature. a) Long chains of magnetic Co nanoparticles aligned in an external magnetic field; (from Ref. [2b]); b) Au nanoparticle aggregates trapped by polymer encapsulation (from Ref. [5a]); c) Polymerization of Au nanorods at different initial concentrations; variation in the number-average degree of polymerization $\bar{X}_n$, with time t (from Ref. [6]); d) Dark-field TEM image of nanorod chains after 24 h (from Ref. [6]).

In colloidal polymerization,[4] numerous analogies can be drawn and used from the field of organic polymers. In organic polymerization, the monomers have to "find" each other by favorable stochastic collisions in order to form new chemical bonds. For colloidal polymerization, the controlled aggregation of nanoparticles can be achieved by kinetic control, where random collisions among monomers lead to clusters that associate by physical interactions such as van der Waals and hydrophobic interactions. It is conceivable that the two processes share similarities and can be balanced in their "reaction" kinetics. If so, the exploration of the aggregation kinetics, just like in polymer chemistry, will offer important insights into synthetic design.

If the aggregated clusters aggregate in a spatially directional fashion (i.e., 1D), then the aggregation kinetics can be controlled to produce 1D assemblies of nanoparticles, which should proceed by a step-growth polymerization-type process. By assuming comparable reactivity for the different sized clusters, Chen and co-workers simulated the size distribution and growth of nanoparticle aggregates.[5] In experiments, the

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polymer shells used to encapsulate nanoparticles also preserved the colloidal aggregates and the results were in reasonable agreement with the simulation (Figure 1 b). In this system, however, charge repulsion among the clusters is also present and strongly contributes to the deviation from theoretical predictions. Colloidal charge repulsion has been observed to increase with cluster size[6] and results in the enhanced electrostatic stabilization of larger nanoparticle aggregates. In a different system, Kumacheva and co-workers selectively modified the two ends of gold nanorods with polystyrene and studied their aggregation kinetics.[6] Such monomers underwent selective end-to-end aggregation following step-growth polymerization kinetics and afforded well-defined chains (Figure 1 c,d).

In a seminal report in *Angewandte Chemie*, Chen et al. used a diblock copolymer, polystyrene-block-poly(acrylic acid) (PS-*b*-PAA), to coat gold nanoparticles and induce the formation of long mesoscopic chains.[7] Under suitable conditions, the spherical polymer shells converted into cylindrical micelles. This process drove the fusion of the polymer shells and led to the concomitant assembly of nanoparticles (Figure 2 a). Here, the coexistence of monomers and long chains is a strong indication of an unusual mode of nanoparticle self-assembly, driven by the reorganization of the block copolymer ligands in solution, while also carrying Au nanoparticle inclusions. Figure 3 b shows a double-line chain after purification, where the uniformity of the chain width and interparticle spacing can be clearly seen.

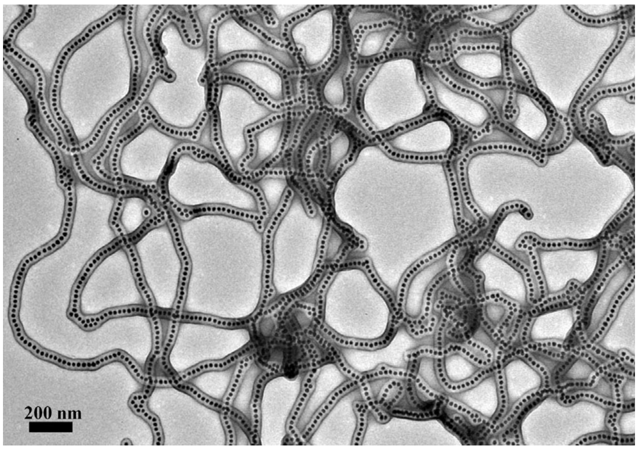

Figure 3. TEM images of single-line chains of gold nanoparticles after purification; these chains can be converted to double-line chains. The authors also provided significant morphological and kinetic evidence that the growth of the chains did not proceed by random insertion in the middle of the chains, but by selective end-on aggregation. On these premises, they discussed the mechanisms of the selective chain formation (from Ref. [7]).

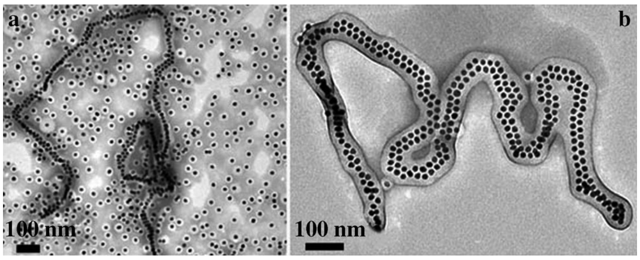

Figure 2. TEM images of double-line chains of gold nanoparticles before (a) and after purification (b) (from Ref. [7]).

Such a highly selective one-dimensional assembly of nonmagnetic nanoparticles is remarkable. Because the PS-*b*-PAA shell remains on the surface of gold nanoparticles before and after aggregation, it not only guides the linear aggregation but also confines the width of the chains. By simply tuning the DMF/water solvent ratio, single-line chains were also synthesized (Figure 3). Most impressively, the single-line chains can be converted to double-line ones by simply adjusting the solvent. Thus, the swelling of the polymer shells was critical in determining the width of nanoparticle chains.

The remarkable ability to determine the chain-growth mode in nanoparticle aggregation is a timely extension to the known step-growth methods. These modes bring our understanding in the theory of polymer chemistry into the world of nanoparticle assembly. More interestingly, Chen and co-workers utilized polymers, either as shells or end-caps, as a means to assist the nanoparticle assembly.[7] Thus, the marriage of nanoparticles with polymers will surely open up new opportunities to create “polymers” of nanoparticles.

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