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Preparation of Unique 1-D Nanoparticle Superstructures and Tailoring their Structural Features

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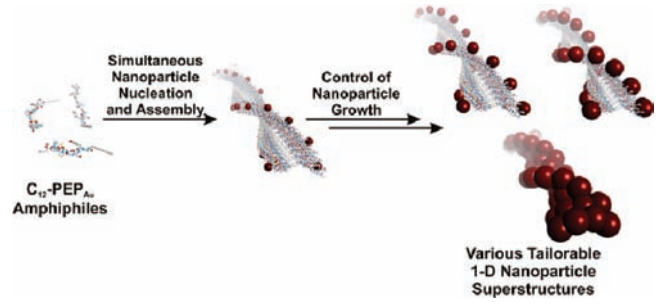
Nanoparticle superstructures have unique physical properties and potential applications in the areas of plasmonics, molecular sensing, and nanoscale electronics.[1−3] However, few methods exist for rationally controlling the assembly of nanoparticles into superstructures and precisely controlling the position and spatial arrangement of nanoparticles within such superstructures.[3−5] An ideal nanoparticle assembly method should (1) permit construction of various topologically complex superstructures; (2) allow for manipulation of the structural features of the superstructure, including nanoparticle size and interparticle spacing; and (3) allow for assembly of nanoparticles of various compositions. A method satisfying these criteria would permit preparation of functional nanoparticle superstructures with tailorable properties.

Recently, we introduced a new strategy for designing and preparing complex nanoparticle superstructures that relies on peptide conjugate molecules designed to simultaneously direct both the synthesis and assembly of nanoparticles in a single cooperative step.[6] We demonstrated that this method can be used to prepare topologically complex superstructures, such as gold nanoparticle double helices. In this contribution, we expand the capabilities of this method through examining the roles of various synthetic parameters. We explore how these parameters can be systematically adjusted to carefully tailor the structure and metrics of the nanoparticle superstructure and to ultimately yield new double-helical structures exhibiting different particle sizes and interhelical distances and new continuous 1-D nanoparticle superstructures.

Scheme 1 summarizes our synthetic approach. Within this approach, several factors can be varied to yield and tailor new nanoparticle superstructures. First, the peptide sequence, which is specific for controlling the growth of particular nanoparticle compositions, can be altered to target various compositions.[4,7] Second, the peptide secondary structure or the organic component of the peptide conjugate can be modified to direct the self-assembly into various target structures having different metrics and topologies.[4,8] Finally, since nanoparticle nucleation and growth occur during the synthesis and assembly process and because nanoparticle growth initiates from seeds assembled with the peptide superstructures, additional synthetic components and synthetic conditions, such as capping agents and reaction time and temperature, may be adjusted to control nanoparticle growth and tailor nanoparticle size and interparticle distances within the superstructure. We emphasize that all of these factors can significantly impact the properties of the resulting nanoparticle superstructure.

Here, we specifically examine how varying secondary synthetic components and synthetic conditions impacts particle size and interparticle spacing in the context of the gold nanoparticle double helix superstructure and how these factors can be adjusted to prepare other 1-D nanoparticle superstructures. C_{12}-PEP_{Au} (PEP_{Au} = AYSSGAPPMPPF) conjugates are used to direct the synthesis and self-assembly of gold nanoparticle double helices. In a typical synthesis, HEPES buffer is the principal reducing agent,[6,9,10] and

Scheme 1. Nanoparticle Synthesis and Assembly Strategy



chloroauric acid ($HAuCl_4$) dispersed in triethylammonium acetate (TEAA) buffer is the gold ion source. By introducing $HAuCl_4$/TEAA to a solution of C_{12}-PEP_{Au} in HEPES buffer, C_{12}-PEP_{Au} self-assembly and PEP_{Au}-based mineralization of gold nanoparticles occur simultaneously to yield well-organized and assembled gold nanoparticle double helices (Figure 1a).[6] We reasoned that longer reaction times may significantly impact the density of particles within the nanoparticle superstructure, because regions of exposed PEP_{Au} along the superstructure could potentially serve as sites for binding additional gold nanoparticles. By extending the reaction time to 1 day, we found that the resulting superstructures still exhibited a discernible double-helical structure, but additional nanoparticles filled the interhelical regions to yield a more continuous 1-D superstructure (Figures 1b and S1). Continued soaking (3 d) in the reaction mother liquor results in further fusion of the helices (Figures 1c and S2), and prolonged soaking (several months) yields continuous 1-D gold nanoparticle superstructures comprising large nanoparticles formed via either coalescence of smaller particles or continued reduction of Au^{3+} onto the gold nanoparticles (Figures 1d and S3).

These results prompted us to also study the influence of reaction temperature on superstructure growth. It is well-known that temperature can impact the nucleation and growth of nanaparticles. When the reaction was performed at 4 °C, gold nanoparticles form more slowly than at room temperature. In fact, a change in solution color from colorless to purple, evidence of nanoparticle nucleation and growth, was only observed after several days. Only 1-D continuous gold nanoparticle superstructures were observed (Figure S4). When the reaction was performed at 60 °C, no 1-D superstructures were observed, as the fast nucleation and growth of gold nanoparticles resulted only in the formation of random nanoparticle aggregates (Figure S5). However, it is worth noting that the gold nanoparticle double helices are robust templates for the nucleation and growth of 1-D continuous nanoparticle superstructures at high temperatures. In fact, when we transferred suspensions of double helices to a 100 °C oven to promote further nanoparticle growth and assembly, the helices remain intact and serve as templates for the construction of continuous 1-D superstructures (Figure S6). This

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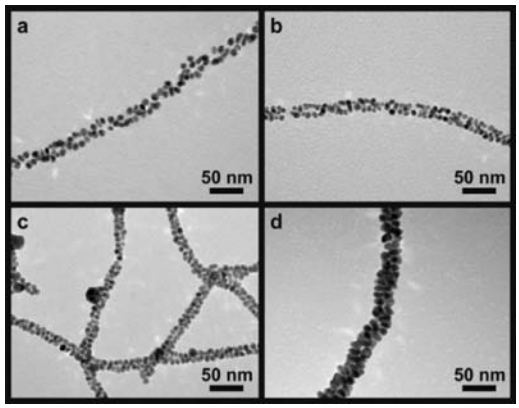

Figure 1. 1-D gold nanoparticle superstructures formed at different time scales. (a) 30 min; (b) 1 day; (c) 3 days; and (d) several months.

suggests that the gold nanoparticles comprising the double helices serve to "glue" the C_{12}-PEP_{Au} units together, preventing disassembly.

While generating dense and continuous 1-D nanoparticle superstructures may be important for nanoscale electronic applications, preparing nanoparticle superstructures in which the constituent nanoparticles are spatially segregated from one another is important for some plasmonic applications.[2] In such cases, it would be useful to control not only the placement of nanoparticles but also the particle size and interparticle spacing. We therefore investigated how the addition of secondary nanoparticle capping agents would affect these parameters. In our synthetic system, HEPES serves not only as a reducing agent but also as a weak particle capping agent in addition to PEP_{Au}.[10] Citrate is known to serve as a gold nanoparticle capping agent.[11] Therefore, we reasoned that addition of citrate to our synthesis would change the nanoparticle surface chemistry and affect nanoparticle growth, potentially leading to smaller nanoparticles. Accordingly, we added citrate to our double helix synthesis and found that, below a certain threshold amount, the addition of citrate resulted in the formation of gold nanoparticle double helices comprising monodisperse smaller nanoparticles (6.2 $\pm$ 0.8 nm) (Figures 2a and S9) compared to the particle size observed in the typical synthesis (8.1 $\pm$ 1.0 nm) (Figures 2b and S9). Interestingly, we also found that citrate resulted in larger distances between particles on adjacent helices (10.7 $\pm$ 1.1 nm) (the interhelix distance) (Figures 2a and S7) compared to those measured for double helices prepared in the absence of citrate (6.1 $\pm$ 0.4 nm).

We surmised that the larger interhelix distance could result either from the decreased particle size or from the presence of the negatively charged citrate, which could increase interparticle repulsions. To probe this further, we added adenosine triphosphate (ATP) to our syntheses instead of citrate. Like citrate, ATP is anionic and can also serve as a particle capping agent.[12] Double helices formed in the presence of ATP have a much smaller interhelix distance (5.9 $\pm$ 0.5 nm) compared to those formed in the presence of citrate, although monodisperse gold nanoparticles comprising the double helices in both cases have similar sizes (Figures 2, S8, and S9). Therefore, the magnitude of the interhelix distance is not related directly to particle size; rather, the particle surface chemistry plays a more determinant role. We have shown that particle capping agents significantly affect particle nucleation

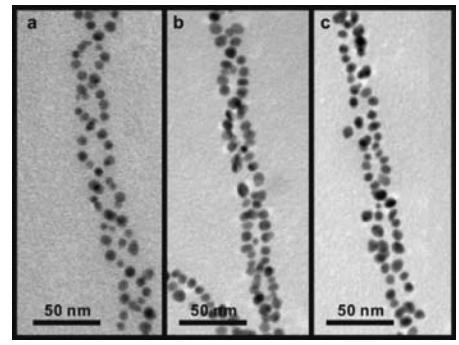

Figure 2. Tuning the structural parameters of gold nanoparticle double helices. (a) Citrate-modified synthesis; (b) typical synthesis; (c) ATP-modified synthesis. The sizes of gold nanoparticles in these double helices are uniform: (a) 6.2 $\pm$ 0.8 nm, based on 200 counts; (b) 8.1 $\pm$ 1.0 nm, based on 320 counts; and (c) 5.4 $\pm$ 0.8 nm, based on 220 counts. The distributions of the interhelix distances are as follows: (a) 10.7 $\pm$ 1.1 nm, based on 63 counts; (b) 6.1 $\pm$ 0.4 nm, based on 80 counts; and (c) 5.9 $\pm$ 0.5 nm, based on 64 counts.

and growth and interhelical distances within the nanoparticle assembly. This indicates that tuning the particle surface chemistry is a useful way to tailor the metrics and structure of nanoparticle superstructures prepared using this methodology.

In conclusion, we have shown that the described peptide-based method for the design and synthesis of nanoparticle superstructures can be systematically modified to prepare new 1-D gold nanoparticle assemblies and to carefully tailor the metrics and structures of these assemblies. We expect this methodology will enable rational design of myriad nanoparticle superstructures and systematic control of their structural attributes, key aspects for influencing their properties and ultimate applications.

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Supporting Information Available: Experimental procedures and additional supporting data. This material is available free of charge via the Internet at http://pubs.acs.org.

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