Steric Hindrance Induces crosslike Self-Assembly of Gold Nanodumbbells

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Supporting Information

ABSTRACT: In the formation of colloidal molecules, directional interactions are crucial for controlling the spatial distribution of the building blocks. Anisotropic nanoparticles facilitate directional clustering via steric constraints imposed by each specific shape, thereby restricting assembly along certain directions. We show in this Letter that the combination of patchiness (attraction) and shape (steric hindrance) allows assembling gold nanodumbbell building blocks into crosslike dimers with well-controlled interparticle distance and relative orientation. Steric hindrance between interacting dumbbell-like particles opens up a new synthetic approach toward low-symmetry plasmonic clusters, which may significantly contribute to understand complex plasmonic phenomena.

KEYWORDS: Gold nanoparticles, dumbbells, self-assembly, interparticle interactions, steric hindrance

With the focus of self-assembly gradually shifting from the use of isotropic to anisotropic nanoparticle building blocks, directional interactions will play a central role in mimicking the creation of colloidal molecules.5–3 Therefore, nonspherical building blocks are more versatile than spherical ones. The inherent chemical heterogeneity (patchiness) of anisotropic particles is likely to facilitate directional clustering via specific molecular interactions, while steric constraints imposed by the shape itself, may restrict assembly along certain directions. Thus, the combination of patchiness (attraction) and shape (steric hindrance) allows assembling nanoparticle building blocks into colloidal molecules with well-controlled interparticle distance and relative orientation.4–6 Whereas the effect of patchiness on the self-assembly of colloids has been the subject of a number of studies,7,8 the study of steric hindrance is still at an early stage. Manna and co-workers have shown that steric hindrance encoded in octopod-shaped colloids restricts assembly of the particles into intercalated chains that subsequently form hierarchical superstructures with carpetlike morphology.9 The concept of steric hindrance has also been exploited in colloids with dumbbell-like geometry. For example, silica dumbbells linked by a magnetic belt at their waist were shown to undergo assembly into chains that eventually twisted in the presence of steric constraints.4 In view of these achievements, the assembly of dumbbell-like plasmonic particles (sub-100 nm) into crosslike clusters may significantly contribute to understand complex plasmonic phenomena. In particular, understanding chiral plasmon coupling in low-symmetry clusters of gold nanoparticles may find applications in materials with anomalous dielectric properties, such as negative index of refraction materials.

However, achieving crosslike assembly is not trivial and strong lateral attractions between the particles are required to overcome the steric repulsion between the spheroidal tips. In a related work, Kumacheva and co-workers reported the synthesis of gold nanorod dimers with side-to-side relative orientation.8,10–12 Upon achieving a specific solvent composition, the intermolecular forces between the tip-grafted polymer chains, directed the particles to cluster into specific configurations.10,11 Postsynthetic processing of the clusters, however, proved difficult because the particles remain assembled in a specific solvent composition.11

Recently, several groups showed that small aggregates of hydrophobic spherical particles could be encapsulated inside polymeric micelles that help to maintain NPs organized during postsynthetic manipulation.13–20 The flagship example of such polymeric surfactants is polystyrene-block-poly(acrylic acid), PS-b-PAA, which in hydrophilic media forms so-called “crew-cut” micelles,21 because the corona-forming block (PAA) of the aggregate is very short compared to that of the core-forming block (PS). Thus, upon aggregation of the hydrophobic particles when solvent polarity is increased, the PS-b-PAA chains infiltrate at the interface between the particles surface and the solvent mixture, facilitating progressive confinement of

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the particles within the hydrophobic core. At higher water content, the organic solvent is forced out from the hydrophobic core, thereby lowering polymer mobility, which in turn leads to mechanical stress of the confined particles. The amphiphilic character of the surfactant provides colloidal stability and makes possible the postsynthetic chemical manipulation of the clusters in aqueous solution.

We have gone one step beyond by introducing a steric factor in gold nanorods through the growth of spheroidal tips, which leads to nanodumbbells (AuNDs). Hypothetically the assembly of such dumbbells can end up in a crosslike morphology if the steric hindrance between the tips is able to overcome the side-to-side attractive interactions (Figure 1). In our experiments, we first increased solvent polarity to induce the attraction between particles by decreasing the solubility of polystyrene chains grafted on dumbbell tips (hydrophobic effect), which leads to gradual assembly of the particles into doublets with parallel orientation. We then inhibited further aggregation by addition of the polymeric surfactant (PS$_{509}$-b-PAA$_{62}$), which additionally induced the mechanical stress needed to overcome steric hindrance, leading to the formation of crosslike assemblies that are unique for dumbbell-like building blocks.

The preparation of colloidal clusters starts from an aqueous solution of “standard” gold nanorods (length, 66.1 ± 5.9 nm; width, 16.1 ± 1.2 nm), stabilized with cetyl trimethylammonium bromide (CTAB). To enhance steric factors in gold nanorods, the particles were selectively overgrowth on the tips, producing dumbbell-like shape, after which the total length, width in the middle and width on the tips increased up to 87.0 ± 5.9 nm, 20.4 ± 2.0 nm, and 35.2 ± 2.0 nm, respectively (see Supporting Information, Figure S1). Next, chemical heterogeneity across the surface (patchiness) was achieved by adapting the method reported by Nie et al. in which addition of water (up to 10 wt %) to a binary nanorod dispersion in THF/DMF (1:3 w/w) induced side-to-side clustering. A gradual change of color from reddish to violet accompanied by appearance of a precipitate after two days was a first indication of particle clustering (see Supporting Information, Figure S2). Self-organization of AuND@PS was monitored via visible-NIR spectroscopy. AuNDs exhibit two different localized surface plasmon resonance bands: the longitudinal and transverse plasmon bands (LPB and TPB). The LPB in AuNDs is similar to LPB observed in nanorods, while TPB is broader and shows higher extinction (see Supporting Information, Figure S1). Differences in TPB are due to complex coupling of plasmon modes within one particle. The quadrupolar mode from the thin inner part couples with the dipolar mode on the spheroidal tips, producing a broader band. From an optical standpoint, AuNDs provide a more complete footprint as compared to nanorods and in particular when subjected to self-assembly, as both LSPR bands significantly respond to any change of the mutual spatial orientation, as observed in the present study. The LPB blue shifted by 25 nm within 8 h, while the TPB red shifted by 6 nm (Figure 2). According to the plasmon hybridization model, these shifts account for side-to-side orientation, upon which dimers decrease the overall aspect ratio as compared to individual AuNDs (blue shift of LPB, accompanied by redshift of TPB)

Time-dependent transmission electron microscopy (TEM) imaging confirmed the predictions based on the optical effects and plasmon hybridization theory. A mixture of dimers (side-to-side) and monomers was observed after 1 h of clustering time (after addition of water) and exclusively clusters containing multiple AuNDs were found after 8 h (Figure 2b). These results are in good agreement with the results by Kumacheva and co-workers. The selected mixture of THF and DMF (1:3) is a good solvent for the PS block but a bad solvent for CTAB molecules. In the initial mixture, the PS ligands are sufficiently long to stabilize the particles by steric repulsion. In the presence of water, the self-assembly of
nanodumbbells is governed by the poor solubility of both PS and CTAB, initially promoting the formation of side-to-side dimers which eventually aggregate to form larger clusters. We also studied the assembly starting from pure DMF and pure THF. Addition of water to the DMF AuND dispersion was found to result in chainlike assembly, whereas using THF large spherical aggregates were formed (see Supporting Information, Figure S3). Thus, the THF/DMF mixture was selected as the best solvent for stabilization of single AuNDs and controlled cluster formation. Nevertheless, 1 h clustering (after water addition) produced mostly dimers in parallel orientation (50%) and only 4% of crosslike clusters. The remaining population of 46% corresponded to nonaggregated monomers. The low amount of crosslike dimers indicates that attractive hydrophobic interactions between the PS-coated tips are insufficient to overcome the steric hindrance between AuNDs.

To further increase the number of crosslike dimers we exploited the possibility of using a polymeric surfactant, which was expected to compress the hydrophobic region through formation of micelle-like structures. Indeed, addition of PS$_{403}$-b-PAA$_{62}$ (in THF/DMF) to clustering particles (1 h after addition of water) was found to quench further clustering, as confirmed by the invariance of both LPB and TPB (Figure 2a, red). The growth inhibition is achieved by the tendency of copolymer molecules to encapsulate the clusters and form a uniform organic shell with the hydrophilic PAA block sticking out. TEM examination of the sample showed that the population of crosslike dimers increased to 20%, while that of side-to-side dimers decreased to 40% (Figure 3a). To further expel solvent molecules from the polystyrene core toward bulk solution, the water content was increased up to 35 wt %. The amount of crosslike dimers in solution increased then to 30% while the population of parallel doublets correspondingly decreased (Figure 3). At room temperature, however, the diffusion of solvent molecules inside the hydrophobic core is limited due to low mobility of the polymer chains (the glass transition temperature ($T_g$) for polystyrene is ca. 100 °C). Thus, thermal treatment (70 °C, 1 h) of the solution containing clusters resulted crucial to expel the remaining solvent molecules and increase molecular stress inside the polymer micelles, which allowed the AuNDs to overcome the steric hindrance, eventually converting all side-to-side dimers into crosslike clusters (60%) (Figure 3). Repetition of each experimental step of the self-assembly process under the same conditions for standard gold nanorods was found to lead to side-to-side dimers that remain unchanged upon encapsulation within polymeric micelles (see Supporting Information, Figure S4). No crosslike dimers were observed for nanorods, thus demonstrating that the dumbbell-like shape is crucial in achieving this configuration. The thermal treatment also facilitated the transfer of the dumbbell clusters into water. Although dialysis is commonly applied to transfer particles-containing polymeric micelles into hydrophilic solvents, we found that simple centrifugation and redispersion resulted sufficient to transfer our clusters into pure water. The hydrophilic PAA corona ensures the colloidal stability of the encapsulated particles in water via electrostatic repulsion ($\zeta$-potential $-37 \text{ mV}$).

The versatility of this method actually allowed us to quench particles clustering at any time. For example, the presence of PS$_{481}$-b-PAA$_{62}$ (0.55 mg/mL) in a solution of AuND@PS (THF/DMF) inhibited the formation of clusters upon water addition, leading, as expected, to encapsulation of individual AuNDs in the polymeric shell (Figure 2, black dots, Figure 4a). These results confirm previous findings reporting that the size of the particles determines whether single or multiple particles are encapsulated by the copolymer. Particles larger than 10 nm can act as templates for intercalating copolymer, leading to single particle encapsulation, whereas particles below 10 nm form small aggregates (clusters) inside the micelles.29,30 The

![Figure 3](image-url) Side-to-side dimers encapsulated inside the polymeric micelles transform into crosslike clusters. (a) Distribution of morphologies at different experimental steps. One hour after addition of water (10 wt %) the mixture contains monomers (46%), parallel dimers (50%), and crosslike dimers (4%). Addition of PS-b-PAA to the mixture increased the fraction of crosslike dimers and decreased the fraction of parallel dimers. Extra amount of water (35 wt %) and thermal treatment finally lead to conversion of all doublets into crosslike dimers (60%). Note that the fraction of monomers remains constant (~ 45%) at each experimental step. (b) TEM image of crosslike dimers.

![Figure 4](image-url) Encapsulation of particles/clusters within polymeric micelles. (a) Addition of water to an AuND@PS/PS-b-PAA mixture leads to encapsulation of single AuNDs with no clustering. (b) Quenching of the assembly process (AuND@PS in THF/DMF-H$_2$O mixture) by PS-b-PAA after 8 h leads to encapsulation of spherical assemblies.
quenching process after 8 h of self-assembly, resulted in the formation of monodisperse spherical clusters consisting of six units on average (Figure 2, blue dots, Figure 4b and Supporting Information, Figure S5). Thus, our method not only allows one to selectively induce particles attraction but also to stop the assembly process at any time.

Electron tomography analysis provided additional understanding and visualization of the crosslike dimers and the spherical clusters (Figure 5 and Figures S6, S7 in the Supporting Information). In the crosslike arrangements, we systematically found mutual orientation angles around 90°, suggesting again a strong steric repulsion between the spheroidal tips. The shortest distance between AuNDs at the central contact region (3.5 nm) corresponds to a CTAB bilayer31 (see Supporting Information, Figure S6). The fact that CTAB molecules remain on the gold surface after clustering and encapsulation supports the possibility of eventual interactions. The scale is the same for both images.

Figure 5. Three-dimensional electron tomography reconstructions of clusters encapsulated in polymeric micelles. (a) crosslike dimer, front and side view. (b) Typical cluster containing six nanodumbbell building blocks in different orientations. The scale is the same for both images.

Recent theoretical and experimental results showed that steric hindrance can selectively direct dumbbell-like particles into linear crossed stacks.4,6 Such orientation required attractive interactions, exclusively between the concave regions of the dumbbells, while noninteracting convex tips provided steric effect. In our approach, this scenario is reversed; upon addition of water, it was the polystyrene-coated tips that directed particles clustering, thereby determining doublet arrangement. The additional external force provided by micelle formation around the clusters was able to compress the clusters into an arrangement (crosslike) that was initially restricted by steric hindrance. Therefore, linear-crossed stacks were not expected under the present experimental conditions. We argue that selective surface functionalization with molecules/polymers on the concave regions could be an alternative strategy to produce similar assemblies to crossed stacks, which however remains a challenging task.

In summary, we demonstrated in this Letter that steric hindrance can improve directional interactions between nanoparticles and lead to well-defined while exotic assemblies. As a proof of concept we exploited the special morphology of dumbbell-like gold nanoparticles, which form parallel side-to-side dimers upon attractive interactions, but can subsequently undergo a transition into crosslike dimers when subjected to encapsulation within polymeric micelles. Careful control of the assembly process allowed us to achieve quasi-monodisperse spherical clusters containing several building blocks whose internal distribution was defined by packing of the dumbbell-like shape.

■ ASSOCIATED CONTENT

6 Supporting Information

Experimental part; preparation of gold nanorods; reversibility of self-assembly; effect of solvent on morphology of the assemblies; number of units (AuNDs) in spherical assemblies; and three-dimensional electron tomography reconstructions. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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