Structural Transitions in Nanoparticle Assemblies Governed by Competing Nanoscale Forces

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3 Supporting Information

ABSTRACT: Assembly of nanoscale materials from nanoparticle (NP) building blocks relies on our understanding of the nanoscale forces acting between NPs. These forces may compete with each other and yield distinct stimuli-responsive self-assembled nanostructures. Here, we report structural transitions between linear chains and globular assemblies of charged, polymer-stabilized gold NPs, which are governed by the competition of repulsive electrostatic forces and attractive hydrophobic/poor solvency forces. We propose a simple quantitative model and show that these transitions can be controlled by the quality of solvent, addition of a salt, and variation of the molecular weight of the polymer ligands.

Ensembles of inorganic nanoparticles (NPs) show collective electronic, optical and magnetic characteristics that originate from the coupling of size- and shape-dependent properties of individual NPs.1,2 A cost-efficient approach to the fabrication of nanoscale materials utilizes the self-assembly of NP building blocks and yields a broad range of nanostructures—from small clusters to large three-dimensional (3D) lattices.3,4 Control over the size and shape of these assemblies relies on our understanding of the nanoscale forces acting between NPs.5 Examples of such forces include dipole–dipole interactions,6 electrostatic forces,7 hydrogen bonding,8 hydrophobic/9 coordination10 and biospecific forces.11 Attractive and repulsive interactions between NPs may change in magnitude and compete, depending on environmental factors.

Generation of different types of nanostructures from the same type of NPs offers a route to the fabrication of stimuli-responsive nanomaterials. Typically, this strategy relies on regio-specific attachment of distinct ligands to NP surface. For example, gold and semiconductor nanorods capped with different molecules along their long side and at the tips behave as amphiphilic molecules and organize in a variety of structures, when the quality of the solvent is selectively reduced for a particular ligand type.4,12 Site-specific attachment of distinct ligands to the NP surface is achieved due to their preferential binding to a particular crystalline facet,13 which may be challenging for small, close-to-spherical NPs and/or the use of macromolecular ligands. A more beneficial approach to distinct self-assembled nanostructures would rely on stimulus-dependent competition of nanoscale forces.

Here we report this approach by controlling structural transitions between two distinct types of nanostructures: linear and 3D assemblies of charged, polymer-stabilized gold NPs. The transitions were governed by the competition of attractive hydrophobic/poor solvency forces and repulsive electrostatic forces, and were achieved by varying the composition and ionic strength of the solvent or the molecular weight of the polymer ligands.

Small, spherical 23 nm-diameter gold NPs stabilized with cetyltrimethylammonium bromide were subjected to ligand exchange with thiol-terminated polystyrene (PS) molecules, as described elsewhere.14 The number average molecular weights of the PS ligands used in the present work were 5 × 103, 1.2 × 104, 2 × 104, 3 × 104 and 5 × 104 g/mol (later in the text referred to as PS-5K, PS-12K, PS-20K, PS-30K and PS-50K, respectively). Following ligand exchange, the NPs were redispersed in N,N-dimethylformamide (DMF). A solution of NPs in DMF was colloidally stable for at least, 5 months.

The self-assembly of the NPs was induced by adding various amounts of water to the solution of NPs in DMF, thereby reducing the quality of solvent for the PS ligands.15 To screen unfavorable interactions between the solvent and the PS molecules, the NPs associated in various types of structures. We observed three types of species formed in the colloidal solution when the content of water, Cw, in the DMF/water mixture and the molecular weight, Mw, of the PS ligands were changed, namely, individual NPs, spherical 3D NP clusters (globules), and linear NP chains with occasional branches (Figure 1). For a particular range of Cw and Mw, coexistence of chains and globules of NPs was observed. The self-assembly of the NPs was “mapped” by a phase-like diagram in the Mw−Cw parameter space. The diagram in Figure 2 shows the transitions between individual NPs (I), globules (G) and NP chains (C), as well as a narrow G + C range. No self-assembly occurred for the NPs

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stabilized with low-molecular weight PS and/or in the low $C_w$ range. The ability of NPs to form globules vs. chains was determined by the interplay of $M_n$ and $C_w$. At high $M_n$ ($\geq 30000$) and low $C_w$, the formation of globules was favored, whereas for higher content of water (dependent on $M_n$), NP chains were the dominant species. The transition $G \rightarrow C$ was not sharp and occurred via a regime, in which both of the species were present.

We carried out a detailed study of the NP chains and globules. The globular assemblies were similar to 3D clusters that were formed in tetrahydrofuran by PS-stabilized gold NPs. Similar to this earlier report, in our work, NP globules assembly in solution could be monitored by dynamic light scattering and could be quenched by encapsulating the globules with a polystyrene-block-poly(acrylic acid) copolymer. The hydrodynamic diameter of the globules measured after self-assembly time, $t_{SA}$, of 1 h in the DMF/water mixture was $102.5 \pm 1.5$ nm, in comparison with $32.8 \pm 3.4$ nm, measured for individual NPs in DMF solution (Figure 3a).

With increasing concentration of water in the DMF/water mixture, the diameter of the globules (determined by analyzing TEM images) increased from ~72 nm ($C_w = 5$ vol. %) to ~84 nm ($C_w = 7.5$ vol. %). The corresponding change in the hydrodynamic radius of the globules (determined in dynamic light scattering experiments) is shown in Figure 3b.

Chains of NPs grew in a marked similarity to step-growth polymerization, with the average number of NPs in the chains increasing linearly with time, similar to our earlier work on the self-assembly of gold nanorods. The average distance, $d$, between the NPs in the chains increased with the molecular weight of PS ligands (Figure 3c), consistent with a larger polymer volume localized in the gap between the NPs. The same trend was observed for the dense NP arrays obtained by drying their solution in DMF on the TEM grid. For such arrays, the interparticle distance was consistently larger than that in the chains (Figure 3c), due to the more extended vitrified conformation of PS ligands in a good solvent. For $10 \leq C_w \leq 30$ vol. %, interparticle distance did not significantly change (Figure 3d), in agreement with our earlier work.

The structural transitions shown in Figure 2 were reversible. For example, for NPs stabilized with PS-50k, the $C_w$ transition occurred when the concentration of water in the system was reduced to ~2 vol. %. Importantly, the $C$ transition occurred via the globular state, as shown in the phase diagram in Figure 2.

The structural transitions between NP chains and globules were rationalized as follows. The resultant structure of NP assemblies was determined by the minimization of the total energy of the system, $\Delta E_{tot}$, governed by the contributions of interaction forces (favoring a compact globular structure) and repulsion forces (favoring the formation of chains) as

$$\Delta E_{tot} = \Delta E_{int} + \Delta E_{h}$$

In eq 1, $\Delta E_{int}$ is the change in energy of repulsive electrostatic interactions and $\Delta E_{h}$ is the change in energy representing a
combined effect of hydrophobic/poor solvency attraction forces (later in the text referred to as "hydrophobic forces"). We ignored attractive short-range van der Waals interactions, since over the entire range of interparticle separations hydrophobic forces dominated. A weak contribution of van der Waals forces was also supported by the absence of association of PS-stabilized NPs at low content of water in the DMF/water mixture.

Figure 4a and b illustrates the configurations formed by three adjacent NPs in the chains and globules, respectively. The type of structure was determined by the angle \( \theta \) between the lines connecting the center of the second NP with the centers of adjacent 1st and 3rd NPs. The value of \( \theta \) changed from 60° (the globular shape) to 180° (the chain shape).

The change in energy of attraction upon NP association was determined by the angle \( \theta \) between the lines connecting the center of the second NP with the centers of the 1-st and 3-d NPs (shown in b). Red and black lines correspond to the DMF/water mixtures with \( C_w \) of 5 and 15 vol.%, respectively. The energy barrier between the globular and chain configurations is to be determined. (d) Schematic of the structural transitions in NP ensembles.

The change in energy of attraction upon NP association was calculated as

\[
\Delta E_h = \Delta E_{el} = \gamma \times \Delta A
\]

(2)

where \( \Delta E_{el} \) is the reduction in the surface energy when two NPs form contact, \( \gamma \) is the interfacial tension between the collapsed PS ligands and the DMF/water mixture, and \( \Delta A \) is the change in area of this interface when two NPs associate.

The change in electrostatic energy for two associating NPs in the absence of added salt was calculated using the approximation developed for charged spherical NPs functionalized with polymer brushes19 as a logarithmic function of the surface-to-surface interparticle distance as

\[
\Delta E_{el} = \frac{\pi^2 kT}{2 l_0} \ln \left( \frac{2D - 2R}{L - 2R} \right)
\]

(3)

where \( R \) is the radius of the gold core of the NP; \( D \) is the center-to-center distance between the two neighboring PS-coated NPs; \( L \) is the center-to-center distance between the 1st and the 3rd PS-coated NPs (equal to 2D and D for \( \theta \) of 180° and 60°, respectively), as shown in Figure 4a,b; \( k \) is the Boltzmann constant and \( T \) is the absolute temperature. In eq 3, \( l_0 \) is the Bjerrum length (=\( e^2/\varepsilon \kappa T \)), the distance at which the total interaction potential of counterions is equal to the thermal energy kT, where \( e \) is the elemental charge and \( \varepsilon \) is the dielectric constant of the solvent. The NP configuration at \( \theta = 180^\circ \) was chosen as a reference. Thus eq 3 shows a logarithmic dependence of the electrostatic energy as a function of the surface-to-surface separation between NPs with respect to the 180° configuration, with separation between surfaces 2D-2R.

We evaluated the variation in \( \Delta E \) for the assembly of NPs stabilized with PS-50K in two solvent DMF/water mixtures at \( C_w \) of 5 and 15 vol.% in which the NPs assembled into the globules and the chains, respectively. For calculations, we used \( R = 11.5 \text{ nm} \), and \( \varepsilon \) of 40 and 49\(^{20}\) (corresponding to \( l_0 \) of 1.14 and 1.4 nm, respectively), and \( \gamma \) of 1.4 \( \times 10^{-3} \text{ J/m}^2 \) to 1.9 \( \times 10^{-3} \text{ J/m}^2 \) for \( C_w \) of 5 and 15 vol.%, respectively. The derivation of eq 3 and details of the calculations are given in Supporting Information.

Figure 4c shows the variation in \( \Delta E \) for two solvent compositions. For \( C_w = 5 \text{ vol.\%} \), the NP configuration with a minimum in \( \Delta E \) at \( \theta = 60^\circ \) was favored (corresponding to NP chains), due to the stronger contribution of the surface energy. For \( C_w = 15 \text{ vol.\%} \), the deeper minimum in \( \Delta E \) was achieved at \( \theta = 180^\circ \) (corresponding to NP chains), due to the larger contribution of electrostatic repulsion. Both predictions were in agreement with experimental results. We note that individually, both types of nanostructures have been reported for gold NPs, although in different systems. Chains were observed for charged gold NPs stabilized with low-molecular-weight ligands,\(^{21,22}\) while the “non-directional” attraction between PS- or DNA-capped gold NPs led to the formation of 3D lattices.\(^3\)

The schematic in Figure 4d summarizes the structural transitions in assemblies of gold NPs. Poor solvency conditions in conjunction with strong electrostatic repulsion yielded NP chains. Poor solvency conditions and weak electrostatic forces yielded globules. Improvement in the quality of solvent and reduction in \( E_{el} \) led to the C → G transition. When the quality of solvent was not sufficiently reduced, the NPs existed as individual species. Reduction in the quality of solvent did not lead to G → I transitions, because of the kinetic trapping of globular structures (see Figure 5b, Supporting Information).

We note that in the self-assembly experiments, the addition of water to the NP solution in DMF increased (although at a different rate) both \( E_h \) and \( E_{el} \) due to the reduction in solvent quality for the PS ligands and the increase in solvent polarity, respectively. To validate the argument about competing hydrophobic and electrostatic forces was further demonstrated by adding tetrahydrofuran (THF) to the NP solution in DMF/water mixture at THF/DMF volume ratios of 0.1 ≤ \( \phi_{THF/DMF} \) ≤ 1. Since the Flory–Huggins interaction parameters for PS-DMF and PS-THF solutions are 0.46 and 0.4, respectively,\(^{21,25,26}\) in the presence of THF, the quality of the solvent for the PS ligands was improved. Thus, the hydrophobic interactions between the PS-
coated NPs in the DMF/THF/water solution were weaker than in the DMF/water mixture. On the other hand, the addition of THF reduced the polarity of the mixed solvent (the dielectric constant of THF is 7.5[7]), thereby suppressing electrostatic interactions between the NPs. With increasing ratio $\phi_{\text{THF/DMF}}$ in the solution, the structure of NP assemblies changed from globules + chains ($\phi_{\text{THF/DMF}} = 0.1, \varepsilon = 42$) to globules ($\phi_{\text{THF/DMF}} = 1, \varepsilon = 31$) (Table 1).

To conclude, we have demonstrated reversible structural transitions in assemblies of polymer-coated gold NPs. We show that by tuning the delicate balance between the hydrophobic and electrostatic forces, assembly of NPs in two distinct configurations—3D globules or linear chains—can be achieved. A particular nanostructure can be realized in several ways: by tuning solvent polarity, by adding a salt, and by varying the molecular weight of the polymer ligands. Since the formation of chain or globular assemblies was governed by the interaction of ligands, rather than affected by the nature of the gold core, we hypothesize that the reported behavior is general and similar transitions can be expected for other types of charged NPs coated with polymer ligands.

**ASSOCIATED CONTENT**

Supporting Information

Synthesis of gold NPs, description of self-assembly experiments, tests of the reversibility of the structural transitions, the description of interfacial tension measurements and calculations of the change of total energy of the system. 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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**REFERENCES**


**Table 1. Effect of the Addition of NaCl and THF on NP Assembly**

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<th>$C_{\text{NaCl}}$ (mM)</th>
<th>$\phi_{\text{THF/DMF}}$</th>
</tr>
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<tr>
<td>10</td>
<td>0.1</td>
</tr>
<tr>
<td>30</td>
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<td>0.1</td>
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<tr>
<td>300</td>
<td>0.1</td>
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“NaCl and THF were added to the DMF/water solution of NPs stabilized with PS-50K at $C_N = 15$ vol. %.”