Out-of-Equilibrium Aggregates and Coatings during Seeded Growth of Metallic Nanoparticles

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Supporting Information

ABSTRACT: Although dissipative self-assembly is ubiquitous in nature, where it gives rise to structures and functions critical to life, examples of artificial systems featuring this mode of self-assembly are rare. Here, we identify the presence of ephemeral assemblies during seeded growth of gold nanoparticles. In this process, hydrazine reduces Au(III) ions, which attach to the existing nanoparticles “seeds.” The attachment is accompanied by a local increase in the concentration of a surfactant, which therefore forms a bilayer on nanoparticle surfaces, inducing their assembly. The resulting aggregates gradually disassemble as the surfactant concentration throughout the solution equilibrates. The lifetimes of the out-of-equilibrium aggregates depend on and can be controlled by the size of the constituent nanoparticles. We demonstrate the utility of our out-of-equilibrium aggregates to form transient reflective coatings on polar surfaces.

INTRODUCTION

Over the past decade, self-assembly has emerged as the method of choice for organizing inorganic nanoparticles (NPs) into higher-order architectures, which often exhibit unique magnetic,1 optical,2 catalytic,3 mechanical,4 and other5 properties. The vast majority of these materials are static,6–9 that is, once assembled, their structures cannot be easily reconfigured. Recently, increasing emphasis has been devoted to switchable NP assemblies, whose structures and properties can reversibly be modulated in response to external stimuli, such as magnetic fields, temperature, or chemical signals.10–14 A more challenging issue is designing dissipative NP assemblies, whose existence depends on the continuous availability of an energy source (typically a chemical fuel), which they consume. This mode of self-assembly is the hallmark of biological systems, which exist and function away from a thermodynamic equilibrium.15

In a classic example of a synthetic dissipative self-assembly system, Eelkema, van Esch, and co-workers used methylating agents as the chemical fuels driving the formation of transient fibrillar networks.16,17 In their design, methylation of a dicarboxylate afforded an ester that spontaneously assembled to afford fibrillar networks. However, gradual hydrolysis of the ester in the basic medium regenerated the original dicarboxylate, triggering the disassembly of the fibrils. An analogous design principle was applied by Boekhoven et al., who employed a carbodiimide as the fuel for the formation of anhydride-based gels.18 Ulijn and co-workers conceived a non-equilibrium biocatalytic self-assembly system, whereby the same enzyme could be used to rapidly form and slowly hydrolyze a tripeptide gelator, giving rise to transient hydrogels.19 Several reports have also appeared on synthetic dissipative self-assembly systems incorporating NPs as the building blocks.20–23 For example, Grzybowski et al. successfully coupled acid-sensitive NPs with previously reported pH oscillators, achieving a rhythmic assembly and disassembly of these NPs.20 Most recently, Eelkema et al. adapted their dissipative self-assembly scheme to NPs by transiently methylating and, hence, inducing the self-assembly of poly(acrylic acid)-based NPs.23

Here, we present a conceptually different route to achieve out-of-equilibrium nanoparticle assemblies, which relies on the transient destabilization of NP in solution. The destabilization is achieved in the presence of a high local concentration of a surfactant, which is released near the NP surfaces during NP growth. The surfactant molecules intercalate between the NP-bound ligands, inducing the particles to assemble. Over time, the surfactant concentration throughout the solution equilibrates, the NPs regain their colloidal stability, and the aggregates disassemble. Based on these findings, we developed a method allowing us to transiently coat transparent surfaces with reflective metallic films.

RESULTS AND DISCUSSION

Dissipative Self-Assembly during Seeded Growth of Gold Nanoparticles. Our system is based on a seed-mediated approach for the synthesis of metallic NPs.24 In one variant of seed-mediated synthesis, a metal salt is first mixed with relatively small NPs (“seeds”). The addition of a weak reductant to this “growth solution” results in the controlled growth of the seeds. Importantly, attachment of the freshly reduced metal atoms to smaller seeds is favored because of their larger curvature and higher surface energy. As a result, relatively polydisperse batches of seeds can give rise to highly size-uniform NPs. For example, gold NPs are typically obtained...
following a commonly used protocol based on reducing H\textsubscript{Au}Cl\textsubscript{4} with an excess of hydrazine in the presence of Au NP seeds, according to the following reaction equation,

\[
4\text{Au}^{III} + 3\text{N}_2\text{H}_4 \rightarrow 4\text{Au}^{0} + 3\text{N}_2 + 12\text{H}^+.
\]

The reaction is carried out in toluene in the presence of a mixture of surfactants: didodecyldimethylammonium bromide (DDAB) and dodecylamine (DDA); the latter surfactant stabilizes the NPs by forming a weakly bound self-assembled monolayer. The final NP size is determined and can be controlled by varying the molar ratio of the precursor (Au\textsuperscript{III}) to the seeds (Au\textsuperscript{0}).

We began our experiments by synthesizing 10 nm Au NPs using 6 nm NPs as the seeds (see Supporting Information for the experimental procedures). Upon dropwise (over \(\sim 10\) min) addition of hydrazine to a growth solution containing 6 nm seeds and HAuCl\textsubscript{4} (volume \(\approx 10\) mL), a series of unexpected color changes were observed. The initial red solution slowly turned purple, then rapidly became deep blue, and finally gradually regained its original red color (Figure 1a). Interestingly, the highest bathochromic shift coincided with the addition of 1.0 equiv of hydrazine. UV/vis absorption spectroscopy revealed that the red shift of the particles' localized surface plasmon resonance (LSPR) peak (\(\lambda_{\text{SPR}} \approx 525\) nm for 6 nm Au NPs) was accompanied by an increase in the absorbance in the near-IR part of the spectrum (Figure 1b, left, blue curve), indicative of NP aggregation. Indeed, NP aggregates were observed when the sample was deposited on an ultrathin carbon substrate and analyzed by transmission electron microscopy (TEM) (Figure 1c), which also confirmed that the aggregates were composed of the expanded, 10 nm NPs. These aggregates gradually disintegrated, and a red solution of non-assembled NPs was regenerated (Figure 1b, right). Interestingly, the resulting 10 nm NPs could be used as seeds for preparing larger NPs in a process that again proceeded via transient NP aggregates (Figure 2a). We verified that no aggregation took place upon adding hydrazine to a solution of 6 or 10 nm Au NPs in the absence of HAuCl\textsubscript{4} (Supporting Information, Section 2).

**Effect of Nanoparticle Size on Dissipative Self-Assembly.** To better understand the mechanism underlying self-assembly, we studied the effect of the size of the initial (i.e., seeds) and final NPs. Almost no reversible shift in the position of the LSPR band was observed when 2 nm NPs were converted into 6 nm NPs (Figure 2b). Similarly, expanding the

![Figure 1](image1.png)

Figure 1. (a) Color changes accompanying the dropwise addition of hydrazine to a “growth solution” containing 6 nm Au NPs and HAuCl\textsubscript{4}. (b) Changes in the UV/vis absorption spectra (normalized) during the initial (left) and final (right) stages of the dropwise addition of hydrazine to the growth solution. (c) Transmission electron microscopy (TEM and SEM, respectively) images acquired at different stages of the process.

![Figure 2](image2.png)

Figure 2. (a) Dynamic light scattering (DLS) profiles of the solution of Au NPs during two consecutive seeded-growth reactions. (b) Changes in the position of the wavelength of maximum absorbance of Au NP solutions during different seeded-growth reactions. (c) TEM images of 10 nm Au NPs prepared in the presence of 10% v/v methanol (left) and 50% v/v hexane (right). Note the difference in the average interparticle distance, \(d\). (d) Proposed mechanism underlying the formation of out-of-equilibrium NP aggregates.
size of 6 nm NPs into 8 nm entailed only a small (∼10 nm) shift of the LSPR peak. In sharp contrast, when the same 6 nm seeds were used to prepare larger (10 or 12 nm) NPs, we observed a pronounced yet reversible change in the optical properties of the sample (Figure 2b). These results indicate that the self-assembly behavior is largely independent of the seed diameter, and that it is determined by the size of the resulting NPs. Further insight was provided by experiments in which we treated differently sized Au NPs with increasing amounts of surfactants (DDA and DDAB). We found that the NPs remained colloidal stable irrespective of their size or the amount of DDAB in solution. Likewise, a large excess of DDA did not affect the stability of small (<10 nm) Au NPs. However, when the concentration of DDA in a solution of 10 nm (or larger) NPs was gradually increased and reached a critical level (e.g., 1.6 M for 10 nm NPs), the particles spontaneously assembled (see Supporting Information, Section 6) into aggregates similar to those observed transiently during seeded growth.

**Effect of Solvent on Dissipative Self-Assembly of Nanoparticles.** The counterintuitive finding that the stabilizer, DDA, can induce destabilization of NPs can be explained by the formation of a bilayer around the NP surfaces. Bilayer formation can have a profound impact on NP solubility, which is well-known from studies on CTAB-protected gold nanorods and spherical NPs coated with amphiphilic polymers. In our system, the intercalation of DDA between the NP-bound ligands equips the particles with terminal NH2 groups, decreasing their stability in the nonpolar (toluene) environment. To obtain further experimental support of the DDA-capped NPs, we studied the 6 → 10 nm seeded-growth process in the presence of cosolvents: methanol (polar) (10% v/v) and hexane (strongly nonpolar) (50% v/v). Following the reaction and deposition of the resulting NPs as a dense monolayer on a TEM grid, we found that the NPs deposited from the hexane-rich solution could approach one another at much closer distances (1.4 ± 0.3 nm; Figure 2c, right) compared with NPs obtained in the presence of MeOH (2.2 ± 0.6 nm; Figure 2c, left). This result can be explained by hexane readily solvating the alkyl chains of the primary DDA monolayer, thus discouraging the intercalation of extra DDA (indeed, seeded growth in the presence of hexane was not accompanied by transient NP aggregation). In contrast, in the presence of the polar MeOH the bilayer remains stable, which explains the relatively large distances between densely packed NPs.

**Molecular Dynamics Simulations.** The stability of the DDA bilayer in the different solvent systems was also investigated by atomistic molecular dynamics simulations (see Supporting Information, Section 7). In these studies, a 10 nm gold NP coated with 1467 DDA molecules (corresponding to a densely packed monolayer of DDA) was first constructed. This NP was placed in three different solvents: (a) toluene, (b) 1:9 v/v MeOH/toluene, and (c) 1:1 v/v hexane/toluene (each containing 143 mM DDA, 20% of which was protonated, in accordance with the experimental conditions), and the build-up of the secondary layer of DDA was followed. The simulations were run until the number of DDA molecules residing within 3 Å of the first DDA layer was stable. These studies revealed that DDA-capped NPs placed in toluene (pure and with 10% v/v methanol) with extra DDA could stabilize additional >400 DDA molecules (shown in blue in Figure 3a,b). However, the same NP in 1:1 v/v hexane/toluene became associated with only ∼170 additional DDA molecules (blue in Figure 3c), supporting preferential solvation of our NPs by hexane, in agreement with the experimental observations.

**Mechanism of Dissipative Self-Assembly of Nanoparticles.** Based on the above results, we propose the following mechanism underlying the formation of transient aggregates during seeded growth of NPs. First, AuIII is reduced following mechanism underlying the formation of transient aggregates during seeded growth of NPs. First, AuIII is reduced to Au0 atoms stabilized by DDA, which either attach to the existing NP seeds directly or recombine to form small, DDA-protected Au clusters, which then are added to the seeds (Figure 2d, step 1). In either case, the attachment is accompanied by the release of DDA, whose concentration near the surfaces of the growing NPs reaches a high level. Owing to this high local concentration, the DDA molecules intercalate between NP-bound DDA and form a bilayer. NPs decorated with a DDA bilayer assemble into NP aggregates by means of solvophobic interactions (Figure 2d, step 2). Over
time, as the concentration of DDA throughout the solution equalizes, NPs lose their extra layer of DDA and regain solubility (Figure 2d, step 3). This mechanism explains why no self-assembly is observed during seeded growth, which generates NPs below a certain size (<10 nm), namely, the high curvature of these small particles entails relatively large distances between the NP-bound ligands, which does not support the formation of a DDA bilayer.

It is interesting to think of hydrazine as a chemical fuel, whose decomposition drives NP self-assembly. In contrast to traditional, bistable systems, where a stimulus inducing NP self-assembly needs to be removed or is outcompeted by a counter-stimulus for NP aggregates to disassemble, our system is characterized by a spontaneous disassembly process. In other words, the addition of hydrazine drives the system to a transient, out-of-equilibrium state featuring steep concentration gradients of DDA throughout the sample, which triggers the self-assembly of NPs. To better support this picture, we performed an additional experiment (Figure 4a) in which 1.0 equiv of hydrazine was injected all at once into a solution of 6 nm seeds and HAuCl₄ at a molar ratio calculated to afford 10 nm NPs. Similar to the standard protocol involving a dropwise addition of ~7 equiv of hydrazine, transient aggregates were observed, with the highest degree of aggregation ~40 min after the injection (Figure 4b and c, bottom right). Within the subsequent ~60 min, disassembly commenced to afford a solution of non-assembled, 10 nm NPs (Figure 4c, bottom left).

Transient Nanoparticle Coatings. Next, we considered the applicability of our methodology for fabricating transient reflective coatings (Figure 5a). When the standard 6 nm → 10 nm seeded growth was performed in a glass vial with vigorous stirring, the aggregates formed a continuous golden film on the vial walls (Figure 5b). Similar to aggregates in solution (Figure 1c), these films persisted only for a specific time. To directly visualize these NP films, we performed the seeded-growth reaction in the presence of several small (5 × 5 mm) silicon wafers immersed vertically in the solution. The wafers were removed at different stages of the reaction for inspection by SEM. Images recorded at the beginning and end of the process showed a submonolayer of loosely packed NPs, which were non-specifically adsorbed onto the substrate (Figure 5c, top left and bottom left). In contrast, inspecting the wafers removed during the dropwise addition of hydrazine revealed the presence of multilayer-thick films of Au NPs, manifested as a metallic film observed with the naked eye (Figure 5b). In the future, our process could be applied to form transient conductive paths between electrodes, en route to materials exhibiting autonomously controlled, time-dependent electron transport properties.

When the same 6 nm seeds were used to obtain 8 and 12 nm NPs under otherwise identical conditions, the resulting aggregates persisted for 30 min and ~12 h, respectively. These results not only further support the mechanism shown in Figure 2d (i.e., the larger the particles, the smaller the curvature, and the more stable the bilayer, the more long-lived are the aggregates) but also, importantly, show that, by selecting for final NP size, it is possible to tune the lifetimes of transient NP aggregates.
Dissipative Self-Assembly during Seeded Growth of Silver Nanoparticles. Finally, we investigated the applicability of our methodology to NPs of other compositions. To this end, we first adapted the seeded-growth protocol to the synthesis of silver NPs with DDA as the stabilizer (Supporting Information, Section 10). First, we synthesized 5 nm, DDA-protected Ag NPs, following a previously reported procedure.36 These NPs were then used as seeds in the synthesis of 11 nm Ag NPs in toluene (see Figure 6). Specifically, we prepared a growth solution by mixing the Ag seeds with silver(I) acetate and then added a hydrazine solution in toluene dropwise. We found that similar to Au NPs, the newly expanded Ag NPs rapidly assembled into pseudospherical aggregates, which gradually disassembled to regenerate a solution of non-interacting NPs. During vigorous stirring, these aggregates deposited on the vial walls as transient silver films akin to those shown in Figure 5b for gold. Importantly, these findings suggest that our process can be adapted to NPs of various shapes and compositions, including core-shell and alloy NPs.

**CONCLUSIONS**

In summary, we identified the presence of out-of-equilibrium nanoparticle aggregates in a commonly used seeded-growth NP synthesis protocol. We showed that the formation of these aggregates could be attributed to the solvophobic interactions between the NPs induced by the formation of transient surfactant bilayers on NP surfaces. Remarkably, NPs obtained using this protocol are highly uniform in size despite the presence of the transient aggregates. Our finding could be applied to generate transient reflective coatings on polar surfaces, such as silica. In a general sense, our NP aggregates are akin to microtubules and actin filaments, which similarly exist in out-of-equilibrium self-assembled states in the presence of triphosphates as the chemical fuels. The next challenge is to explore the potential of utilizing synthetic out-of-equilibrium materials for novel applications, analogously to microtubules and related structures performing functions critical to life.

**ASSOCIATED CONTENT**

Supporting Information The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b09111.

Nanoparticle synthesis procedures, additional UV/vis absorption spectra and electron tomograms, molecular dynamics simulations (PDF)

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Notes
The authors declare no competing financial interest.

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**REFERENCES**

We previously reported that Au NPs functionalized with a thiol terminated with the NH$_2$ group are unstable in toluene: Lee, J.-W.; Klajn, R. Chem. Commun. 2015, 51, 2036.

Such clusters can be observed at the onset of hydrazine addition; see SI, Section 6.


