Nanocrystallinity and direct cross-linkage as key-factors for the assembly of gold nanoparticle-superlattices

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We report here how the crystallinity of AuNPs and the choice of binding sites of molecular cross-linkers control their aggregation.

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We report here how the crystallinity of AuNPs and the choice of binding sites of molecular cross-linkers control their aggregation. The combination of different binding moieties (N-oxides, ArF-I) and the reactivity of the particles’ facets allow control over the organization and crystallinity of the AuNP assemblies.

Nanoparticle-based superlattices are one of the most fascinating classes of materials with high technological potential and their formation attracted much interest. Gaining control over the assembly processes requires a fundamental understanding of the interactions that drive the formation of these structures. The challenge is to predict and control how specific interactions would lead to targeted structures. The assembly of NPs into ordered arrays can be induced: (I) via the manipulation of interparticle-interactions by evaporation of the solvent or gentle destabilizing of the colloidal solution. The main forces responsible for such superlattice formation are van der Waals interactions between NP cores or capping ligands. (II) Utilizing of specific noncovalent interactions between capping ligands (e.g. hydrogen bonding, halogen bonding, antibody-antigen, DNA recognitions and metallic complexation). (III) Utilization of cross-linkers that can directly bind between the NPs. Many examples are based on the use of dithiols, however the fast aggregation of the AuNPs hampers often the formation of ordered structures.

The size, shape and the morphology of NPs are important parameters that determine their optical, electronic, and chemical properties. These parameters are also known to affect the structure of ordered arrays. The effect of NP nanocrystallinity on the structure of superlattices is also of much interest. For example, Klabunde and co-workers reported the formation of face-centered cubic (fcc) type superlattices with single-crystalline AuNPs, while hexagonal close-packed (hcp) type superlattices were obtained with defective AuNPs. In another report, Pileni showed that single-crystalline and poly-crystalline AuNPs spontaneously separate in solution as the single-crystalline NPs form a superlattice.

In this work, we show how to control the level of organization of AuNP assemblies: superlattices, amorphous aggregates or separate nanoparticles. The crystallinity of AuNPs capped with dodecylamine (DDA) was used to control their reactivity towards cross-linkers to form organized assemblies. Our strategy involves the utilization of single-crystalline (SCAu) and multiple-twinned (MTAu) AuNPs and symmetrical and asymmetrical cross-linkers having two binding sites: pyridine-N-oxide and/or ArF-I (Scheme 1).

Both binding sites have not been well-explored for reactions with NPs, and their orthogonal reactivity towards the Au surfaces is reflected in the formed aggregates. The interactions of these moieties with the surface of the SCAu and MTAu AuNPs are significantly slow, therefore allowing the formation of ordered structures. We observed three levels of AuNP-arrangement: (I) superlattices obtained with cross-linker 1 having two pyridine-N-oxide, regardless of the crystallinity of the AuNPs. (II) Amorphous or crystalline structures obtained when one of the pyridine-N-oxides is substituted by ArF-I (2): single-crystalline AuNPs react with 2 to afford a superlattice, whereas the use of polycrystalline AuNPs results in amorphous aggregation. (III) The use of only ArF-I moieties (3) results in relatively small amorphous structures with SCAu AuNPs. No aggregation occurred with MTAu AuNPs.

The reaction between the NPs and the cross-linkers (1–4) were carried at room temperature by addition of 1–4 dissolved in small quantities in DCM (1) or THF (2–4) to a solution of NPs in THF. The reaction between both SCAu and MTAu and 1 resulted in highly ordered structures. Transmission electron microscopy (TEM) images taken after one day revealed the formation of large ordered arrays of NPs.

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with the nanocrystallinity of the individual particles controlling their packing (Fig. 1A–D and Fig. S2, ESI†). Fast Fourier transform (FFT) analysis of the TEM images confirmed the formation of ordered structures (Fig. 1E and H). Profile analysis reveal d-spacings of 5.7 nm and 6.0 nm for the SC\textsubscript{Au}/1 and MT\textsubscript{Au}/1, respectively, due to superlattice formed by the individual metal cores (Fig. 1F and G). The spacing is in a good agreement with NP (5.2 ± 0.3 nm) and the cross-linker (1; 1.2 nm) dimensions. A dampening of the surface plasmon resonance (SPR) band accompanied by a slight band broadening is observed by UV/Vis spectroscopy (Fig. S3A and B, ESI†).

A striking different behavior was observed upon reaction of both SC\textsubscript{Au} and MT\textsubscript{Au} with the symmetrical cross-linker 3 having two ArF-I moieties. Formation of small amorphous aggregates were observed even after 8 days (Fig. 1I and J). Differences between SC\textsubscript{Au}/3 and MT\textsubscript{Au}/3 are also reflected in the UV/Vis spectra. Dampening of the SPR band for SC\textsubscript{Au}/3 accompanied by a small red shift (≈6 nm) and peak broadening (Fig. S3C, ESI†) is observed. No significant changes in the optical spectra for MT\textsubscript{Au}/3 were observed (Fig. S3D, ESI†).

The reaction between SC\textsubscript{Au} and the asymmetric cross-linker 2 having both N-oxide and ArF-I moieties resulted in formation of ordered structures after one day as also observed for SC\textsubscript{Au}/1 and MT\textsubscript{Au}/1. The order in these assemblies is apparent from TEM imaging and FFT analysis (Fig. 2A, C, D and Fig. S4A and B, ESI†). This aggregate is less ordered than the in the case of the symmetric (I) ligand, as can be seen from the fact that the FFT shows arcs with 6-fold symmetry and not sharp spots. No aggregation was observed in the reaction between MT\textsubscript{Au} and cross-linker 2 (Fig. 2B and Fig. S5, ESI†). Aging of the reaction solutions resulted in densely ordered aggregates (SC\textsubscript{Au}/2) after eight (Fig. S4C and D, ESI†) and ten days (Fig. 2E, G and H).

One or two layers of ordered NPs sheets were observed (Fig. 2A), while in Fig. 2E more layers were added in the third dimension and the aggregate is much thicker. Smaller amorphous aggregates were observed for MT\textsubscript{Au}/2 (Fig. 2F and J). Profile analysis for SC\textsubscript{Au}/2 indicated a d-spacing of 7.26 nm (Fig. 2I). HR-TEM analysis and the corresponding FFT patterns show translational alignment among neighboring particles, and some degree of orientational order (Fig. S6, ESI†). This interparticle lattice continuation of the Au 111 planes might result from coalescence of the 2-coated AuNP upon aging. The addition of the cross-linker 2 to the solutions of SC\textsubscript{Au} and MT\textsubscript{Au} NPs resulted in a dampening of the SPR band over time (Fig. S7A and S8A, ESI†). This effect was more pronounced for SC\textsubscript{Au}/2 and is accompanied by a small red shift of ≈5 nm and band broadening.

To explore the nature of the ArF-I interaction with the surface of the AuNPs, we reacted both SC\textsubscript{Au} and MT\textsubscript{Au} with the F, Cl and Br analogues of cross-linker 2. No aggregation was observed with these systems demonstrating the role of the Au-I interaction in driving the assembly of these DDA-capped AuNPs with cross-linker 2 (Fig. S7B, S8B and S9, ESI†).
In addition, we found that the non-fluorinated derivative of cross-linker 2, also did not induce NP aggregation (Fig. S10, ESI†). Our findings are in agreement with those of Blakey et al. who demonstrated recently that iodoperfluorobenzene and derivatives thereof form metal–iodine charge transfer complexes with AuNPs. Fluorine substitution of the arene is not required in that system, but it increases the relative strength of the interaction.8

In contrast to the ArF-I moiety, the N-oxide group might act as an electron donor to the surface (δ+) of the DDA-capped AuNPs. The symmetrical cross-linker 1 forms ordered assemblies regardless of the crystallinity of the AuNPs. The symmetrical cross-linker 1 forms ordered assemblies with both types of AuNPs. However, different facets of the AuNPs can exhibit different reactivity as expressed with cross-linkers (2, 3) having an ArF-I moiety: a higher level of NP organization was observable for SC\textsubscript{Au} compared to MT\textsubscript{Au}. The use of the asymmetrical crosslinker (2) having both N-oxide and ArF-I moieties results in organized assemblies (SC\textsubscript{Au}) and amorphous aggregates (MT\textsubscript{Au}). For 3, with SC\textsubscript{Au} relatively small aggregates were observed, and no aggregation was achieved with MT\textsubscript{Au}. For the cross-linkers demonstrated, the N-oxide moiety has a larger contribution to the formation of organized AuNPs, where as the reactivity of facets is clearly expressed by using ArF-I moieties. The observed reactivity of the single-crystalline and multiple-twinned AuNPs with the cross-linkers illustrates the importance of nanoparticle crystallinity combined with molecular design to control the assembly of such systems.

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Notes and references


