Nanoparticle Self-Assembly

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Controlling the Growth of Charged-Nanoparticle Chains through Interparticle Electrostatic Repulsion**

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Nanoparticles (NPs) are envisaged as both building blocks to form advanced materials[1–3] and appropriate models to gain insight into condensed-matter physics;[4–7] this is because of their unique dimensions and the innovative physical properties derived thereof. All these promising applications of the NPs are primarily dependent on the capability of controlling their spatial coupling. Self-assembly of NPs is driven by various forces, such as van der Waals interactions, which lead to either dense and close-packed clusters or extended crystals.[8] The assembled structures are a result of a thermodynamic balance between these interactions. By capping the NPs with molecular ligands to minimize the van der Waals attractions and induce dipolar interactions, it was recently possible to tune the anisotropic interactions that dominate the course of the self-assembly process, thus leading to anisotropic self-assembly of the NPs into one-dimensional (1D) chains,[9–11] two-dimensional (2D) freestanding films,[12] or quasi-2D fractal chain networks.[13] However, the control of the anisotropic self-assembly of NPs (for example, the chain length) has been scarcely studied, which makes the thermodynamic picture revealed in the self-assembly studies hard to extend to other self-assembled systems, such as crystallization or phase transition—this is particularly true in the case of aqueous media where the electrostatic interactions are not at all negligible.

Electrostatic interactions are long-range interactions which ubiquitously exit in aqueous systems. Electrostatic repulsive and attractive interactions between charged particles are usually regarded as isotropic, thus driving the self-assembly of the particles in an isotropic crystallization fashion. Recently, Lilly et al. successfully regulated the electrostatic interactions between aqueous CdTe NPs by using dimethyl sulfoxide, thus controlling the transformation of the NPs into nanowires.[14] This result suggests an interesting but usually ignored effect of the electrostatic interactions on the anisotropic self-assembly of charged NPs in aqueous media. Here, we demonstrate the profound anisotropic character of electrostatic repulsions during the self-assembly of charged NPs in the presence of a short-range anisotropic dipolar interaction, thus endorsing the anisotropic self-assembly of charged NPs into chains. Of particular importance is the fact that tuning the electrostatic repulsion between gold NPs by using the ionic strength, and especially the polarity, of the colloidal suspensions led to a fine control of the length of the gold-NP chains, that is, the number of NPs in them.

We chose negatively charged gold NPs (with a size of 14 nm and stabilized by citrate) as the model system because the transverse configuration of their plasmon resonance is highly sensitive to the electronic coupling between particles,[15] thus enabling us to monitor the particle-chain growth in situ by using spectroscopic methods. The colloidal stability of charged particles in an aqueous medium is estimated by using the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory.[16] The total interaction potential (V_T) is expressed as the sum of the electrostatic repulsion potential (V_elec), the van der Waals attraction potential (V_vdW), the dipolar interaction potential (V_dipole), and the charge–dipole interaction potential ($V_\mathrm{charge-dipole}$) [Eq. (1)]. For monodisperse spherical NPs, V_elec, V_vdW, V_dipole, and $V_\mathrm{charge-dipole}$ can be calculated as shown in Equations (2)–(5).

$$V_\mathrm{T} = V_\mathrm{elec} + V_\mathrm{vdW} + V_\mathrm{dipole} + V_\mathrm{charge-dipole} \tag{1}$$

$$V_\mathrm{elec}(r) = 2\pi\varepsilon_\mathrm{s}\varepsilon_0\, a\Psi_0^2 \ln\{1 + \exp[-a\kappa(R-2)]\} \tag{2}$$

$$V_\mathrm{vdW}(r) = -\frac{A_\mathrm{H}}{6}\left[\frac{2}{R^2-4} + \frac{2}{R^2} + \ln\frac{R^2-4}{R^2}\right] \tag{3}$$

$$V_\mathrm{dipole}(r) = -\frac{\mu^2}{2\pi\varepsilon_\mathrm{s}\varepsilon_0\, R(R^2-4a^2)} \tag{4}$$

$$V_\mathrm{charge-dipole}(r) = -\frac{Q^2\mu^2}{6(2\pi\varepsilon_\mathrm{s}\varepsilon_0)^2\, k_\mathrm{B}\, T\, r^4} \tag{5}$$

Herein, r is the center-to-center separation of neighboring NPs of radius a ($R = r/a$), ε_s is the relative dielectric constant of the solvent (about 80 for water), ε_0 is the dielectric constant of vacuum ($8.854 \times 10^{-12}\,\mathrm{F\,m^{-1}}$), Ψ_0 is the surface potential of the particle, κ is the inverse Debye length, μ is the dipole moment, Q is the effective surface charge of the NPs, k_B is the Boltzmann constant, T is the absolute temperature, and A_H is the Hamaker constant of the particles (about 4×10^{-19} J for

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gold). The V_{dipole} of citrate-stabilized gold NPs arises from surface defects and nonuniform ligand capping which, however, is usually negligibly small. Thus, the colloidal stability of such particles is usually determined by the balance between V_{elec} and V_{vdW}. Weakening the V_{elec} between the particles by adding a tiny amount of salt usually causes aggregates, and eventually precipitates with an irregular shape (see the Supporting Information).

Here, the gold NPs were capped by using thioglycolic acid (TGA) (see the Supporting Information). Besides improving the colloidal stability of the gold NPs against salt, TGA capping also introduced Au–S bonds, which can dramatically enhance the dipole moment.[17] When a small amount of NaCl (the NaCl concentration in the NP dispersions was less than 30 mM) was added to aqueous dispersions of TGA-capped gold NPs, these dispersions remained stable for several days. Intriguingly, besides the original plasmon absorption at 520 nm, a signal found above 600 nm evolved into a pronounced band upon increasing the salt concentration. The latter signal became stronger than the former one when the NaCl concentration was 30 mM (Figure 1 a). Transmission electron microscopy (TEM) imaging of the resulting dispersions revealed that TGA-capped gold NPs self-assembled into 1D chains (Figure 1 b–d). Accordingly, the plasmon absorption band in the wavelength region of 600–800 nm should arise from a 1D transverse plasmon electron coupling between the gold NPs along the chains, similar to that observed in gold nanorods.[15] The chain length increased with the salt concentration, which suggests a correlation between the growth of the chain and the interparticle electrostatic repulsion.

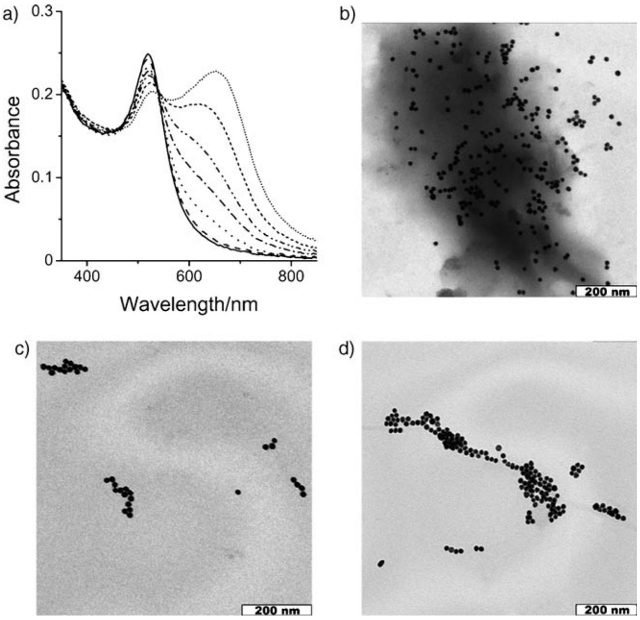

Figure 1. a) UV/Vis absorption spectra of gold-NP solutions (particle size 14 nm) capped without (——) and with (–––) TGA, and absorption spectral evolution of the TGA-capped NPs as a function of the NaCl concentration: 12.5 mM (•••••), 22.5 mM (–•–•), 25 mM (dash–dot–dotted), 27.5 mM (-----), and 30 mM (short-dotted). b–d) TEM images of the TGA-capped gold-NP self-assemblies formed in the presence of additional NaCl: b) 12.5 mM, c) 17.5 mM, and d) 22.5 mM.

According to Equations (2) and (4), a decrease in the dielectric constant of the medium surrounding the charged NPs can cause a decrease of V_{elec} while V_{dipole} increases. Thus, various polar organic solvents with a smaller dielectric constant, such as acetonitrile, ethanol, acetone, and *N*,*N*-dimethylformamide (DMF), were added to aqueous dispersions of the TGA-capped gold NPs. Similarly to NaCl, the addition of such solvents (for instance, acetonitrile) also led to a noticeable absorption band at longer wavelengths; this band became more and more pronounced as the amount of acetonitrile increased (Figure 2 a). TEM imaging clearly demonstrated that the length of the gold NP chains increased in a rather linear way upon increasing the amount of acetonitrile added (Figure 2 b–d). Preliminary modeling of the plasmon resonance of the gold-NP chains was fairly consistent with the results shown in Figure 2 a, thus confirming that the particle chains were formed in the dispersions rather than during drying (see the Supporting Information). We therefore conclude that the growth of the chain composed of TGA-capped gold NPs can be finely controlled by regulating the interparticle electrostatic repulsion.

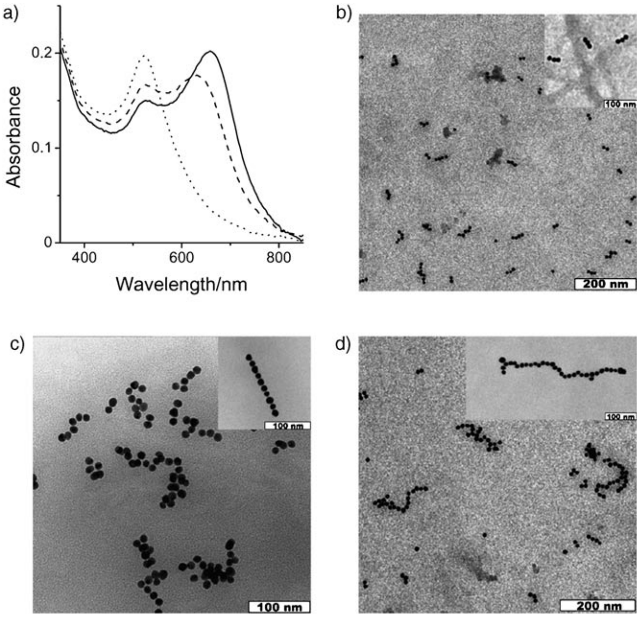

Figure 2. a) UV/Vis spectra of gold-NP dispersions in water–acetonitrile at volume ratios of 1:1 (•••••), 1:2 (-----), and 1:3 (——). b–d) TEM images of the gold-NP chains obtained using the different water–acetonitrile volume ratios: b) 1:1, c) 1:2, and d) 1:3. The corresponding high-magnification TEM images are shown in the insets.

To gain insight into the 1D self-assembly of negatively charged gold NPs, we calculated V_{elec} and V_{vdW} for TGA-capped gold NPs (size: 14 nm) with negatively charged surfaces, according to Equations (2) and (3). In our calculations, we assumed a spherical particle shape and an interparticle distance equal to twice the Debye length ($\frac{1}{\kappa}$). In a 30 mM NaCl solution, for instance, $\frac{1}{\kappa} = 2$ nm, $V_{vdW} =$

$-2.24\,k_B T$, and $V_{\text{elec}} = 4.6\,k_B T$ (at 300 K). This result indicates that V_{elec} and V_{vdW} of the NPs are of the same order of magnitude, while the former value remains larger to guarantee a better colloidal stability. Once an anisotropic dipolar attraction V_{dipole} (of the order of several $k_B T$) has been induced between the gold NPs (enhanced by the Au–S bonding of the TGA capping), the attractive forces between the NPs may overcome the electrostatic repulsion, thus leading to coupling of neighboring particles. Because of the anisotropic character of the dipolar interaction, coupling of the gold NPs is considered anisotropic, as suggested in the literature.[9–13]

Here, however, the isotropic electrostatic repulsion between the negatively charged gold NPs remained stronger, which should inhibit the growth of the NP chain.[14] To elucidate the effect of electrostatic repulsions on chain growth, we evaluated the electrostatic repulsion potential at either end of a NP chain in the proximity of an NP, $V_{\text{elec}}^{\text{end}}$, and that between the chain side and a neighboring NP, $V_{\text{elec}}^{\text{side}}$ (Figure 3). We demonstrated that once the gold NPs self-assembled into a chain, the electrostatic double layer was rearranged into a uniform layer surrounding the whole chain.[18] Based on this fact and the modified model of electrostatic interaction between elongated objects,[19] $V_{\text{elec}}^{\text{end}}$ and $V_{\text{elec}}^{\text{side}}$ between an NP chain composed of n NPs and an NP can be derived as shown in Equations (6) and (7), where ρ is the charge density, A is the surface area, n is the number of NPs ($n > 2$), and D is the length of the NP chain.

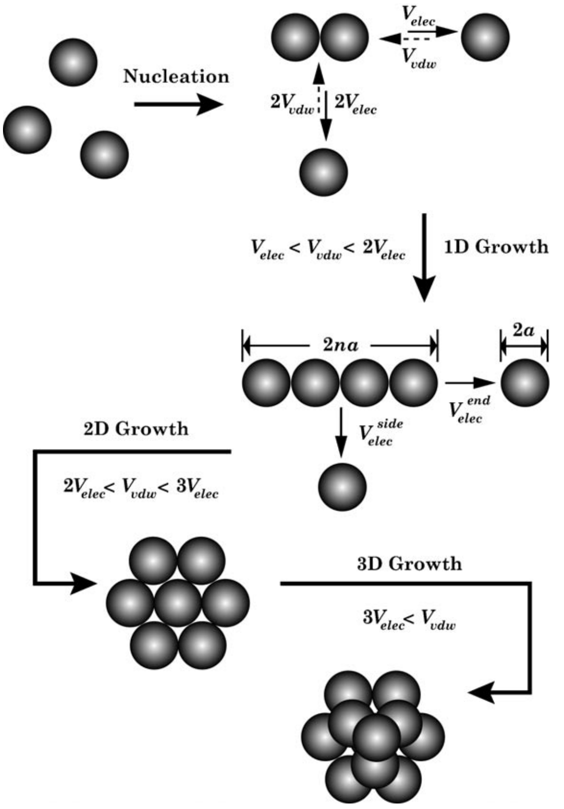

Figure 3. Self-assembly of charged particles endorsed by a balance between isotropic long-range electrostatic repulsion and isotropic short-range van der Waals attraction between the particles in the presence of short-range anisotropic dipolar attraction forces.

$$V_{\text{elec}}^{\text{end}} = \sum_n \frac{Q}{D_i} = \int_0^{D_{\text{total}}} \frac{\rho A}{Di}\,\mathrm{d}D = \rho A \ln D_{\text{total}} = \rho A \ln 2\,n\,a \tag{6}$$

$$V_{\text{elec}}^{\text{side}} = 2\rho A \ln n\,a \tag{7}$$

Comparison of Equations (6) and (7) indicates that $V_{\text{elec}}^{\text{side}}$ is always bigger than $V_{\text{elec}}^{\text{end}}$, thereby underlining the anisotropic character of the electrostatic repulsion between the NP chains and surrounding NPs. Once two NPs have coupled to form a dimer—driven mainly by dipolar interactions and van der Waals forces—the difference between $V_{\text{elec}}^{\text{end}}$ and $V_{\text{elec}}^{\text{side}}$ allows other neighboring NPs to preferentially attach to the ends of the dimer, rather than to the sides, thus forming linear NP trimers, tetramers, and eventually, 1D chains (anisotropic self-assembly of the NPs, see Figure 3). If $V_{\text{elec}}^{\text{side}}$ between NPs and NP chains becomes weaker than V_{vdW}, the NPs will start to attach to the chain sides, thus generating quasi-2D isotropic fractal aggregates, and eventually, 2D sheets (see Figure 3 and the Supporting Information).

During the endorsed anisotropic growth of the chains composed of negatively charged gold NPs (under equilibrium of different forces, namely, $V_T = 0$), the value of $V_{\text{elec}}^{\text{end}}$ should be equal to the sum of V_{vdW}, V_{dipole}, and $V_{\text{charge-dipole}}$ [Eq. (8)], while $V_{\text{elec}}^{\text{side}}$ should be kept higher to warrant chain growth and a higher colloidal stability of the chains. Accordingly, we can calculate the number (n) of NPs composing the chain by using Equation (9).

$$V_{\text{elec}}^{\text{end}} = -(V_{\text{vdW}} + V_{\text{dipole}} + V_{\text{charge-dipole}}) \tag{8}$$

$$n = \frac{\exp[-(V_{\text{vdW}} + V_{\text{dipole}})/\rho A]}{2\,a} \tag{9}$$

Equation (9) reveals a clear correlation between n and the surface charge density ρ of the particle. Note that the short-range interactions between NP chains and NPs should be equal to those between two NPs. As a result, the reduction of ρ by altering the ionic strength and/or the dielectric constant of the surrounding media can increase n, thus increasing the chain length. This is fairly consistent with our present results. The arguments given here also follow experimental and theoretical studies of Langmuir monolayers, where dipolar interactions (that is, anisotropic interactions within a plane) cause elongated lipid domains.[20–22]

In conclusion, we have used long-range electrostatic repulsions to control the growth of chains composed of charged gold NPs. Chain growth was triggered by short-range anisotropic dipolar interactions between the NPs. The colloidal stability and organization of self-assembled systems in aqueous media are always governed by long-range electrostatic repulsion forces. In this scenario, we demonstrate an interesting and non-negligible contribution of the electrostatic repulsion which—albeit usually being regarded as isotropic—can enforce the anisotropic self-assembly of charged NPs in the presence of anisotropic interactions.

Since short-range anisotropic dipolar interactions are often encountered in self-assembled systems, our findings can be easily generalized to the self-assembly of various charged pieces, thus providing a better elucidation of, for instance, the formation of irregular shapes upon aggregation of charged particles and crystallization of charged nuclei.[23]

Experimental Section

An aqueous suspension of gold NPs (with a size of 14 nm) was prepared by reduction with citrate, which was then replaced by TGA via ligand exchange. Prior to directing the self-assembly of the gold NPs using NaCl, the as-prepared gold solution (10 mL) was diluted (to 40 mL) using deionized water (8.6×10^{10} NP mL^{-1}). Afterwards, aliquots of 1M NaCl were added to diluted solutions of the gold NPs (4 mL) capped with and without TGA. The concentration of NaCl ranged between 0 and 75 mM. Additionally, different solvents—including acetonitrile, ethanol, acetone, and DMF—were added to aqueous solutions of the TGA-capped gold NPs. The additional-solvent-to-water ratios ranged from 3:1 to 1:1. Self-assembly of the gold NPs was analyzed by means of UV/Vis absorption spectroscopy (using a Cary 50 UV/Vis spectrophotometer) and TEM (using a Zeiss EM 912 Omega microscope at an acceleration voltage of 120 kV).

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