

Ionic-like Behavior of Oppositely Charged Nanoparticles

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The stability of mixtures of oppositely charged entities depends on their dimensions and is thought to be fundamentally different at molecular¹ and colloidal scales.^{2,3} For example, oppositely charged complexing ions $[A^+]$ and $[B^-]$ can remain stable in solution until reaching a certain discrete ratio $[B^-]/[A^+] = n$,⁴ at which they start to precipitate; in sharp contrast, charged microparticles precipitate continuously due to residual van der Waals forces and poor solvation of large aggregates (Figure 1a). While both molecular and microscopic regimes have been studied in detail, much less is known about the properties of mixtures of oppositely charged nanoscopic colloids—that is, colloids whose dimensions approach those of macromolecules. Recently, it has been shown that such charged nanoparticles (NPs) not only provide a flexible basis for electrostatic self-assembly of nanostructured materials but also display a range of fundamental properties unique to the nanoscale.⁵ Here, we focus on the latter aspect and study the stability of mixtures of oppositely charged, metallic nanoparticles. Using UV-vis spectroscopy, dynamic light scattering (DLS), and ζ -potential⁶ measurements, we show that the NPs are stable in solution and precipitate only at a threshold point determined by the condition of electroneutrality. Both experiments and modeling indicate that this “ionic-like” stability of nanoparticles before the precipitation point is due to the formation of charged, “core-and-shell” aggregates.

We used Au NPs and/or Ag NPs of average diameters between 3 and 11 nm (SD < 20%).⁷ Positive charges were introduced⁵ onto the NPs by coating them with a self-assembled monolayer (SAM)⁸ of *N,N,N*-trimethyl(11-mercaptopundecyl)ammonium chloride (TMA, **1** in Figure 1b, $pK_a > 13$). Negatively charged NPs were coated with mercaptoundecanoic acid (MUA, **2**, $pK_a = 6-8$ for a SAM on a curved surface⁹), 6,8-dimercaptooctanoic acid (DHLA, **3**), or asymmetric $HO(CH_2)_{11}S-S(CH_2)_{10}COOH$ disulfide (SS, **4**). The pH of MUA, DHLA, and SS NP solutions was adjusted to ~ 11 with NMe_4OH to fully deprotonate the carboxylic groups.

In a typical experiment, a stirred solution of NPs ($C = 0.2-5$ mM measured in terms of metal atoms, not NPs) of one polarity was titrated with small aliquots of a solution (0.2–5 mM) containing oppositely charged NPs. After each addition, the mixture was allowed to equilibrate for 5–10 min, and its UV-vis spectra and the value of the ζ -potential were recorded.

For all NP types, sizes, and size combinations and irrespective of the order of NP addition, the particles initially aggregated—as confirmed by DLS measurements (Figure 1c, left) and by the red-shift of the λ_{max} in UV-vis spectra (Figure 1c, right)—before rapidly precipitating at the point corresponding to the zero-value of the ζ -potential and the neutrality of the aggregates' surface charges (Figure 1d–g). In all cases, the precipitation points agreed with the charge neutrality condition determined on the basis of NP compositions.⁵

Figure 1d illustrates this for the case of 5.5 nm AuMUA added to AuTMAs prepared from the same batch of NPs. The precipitation

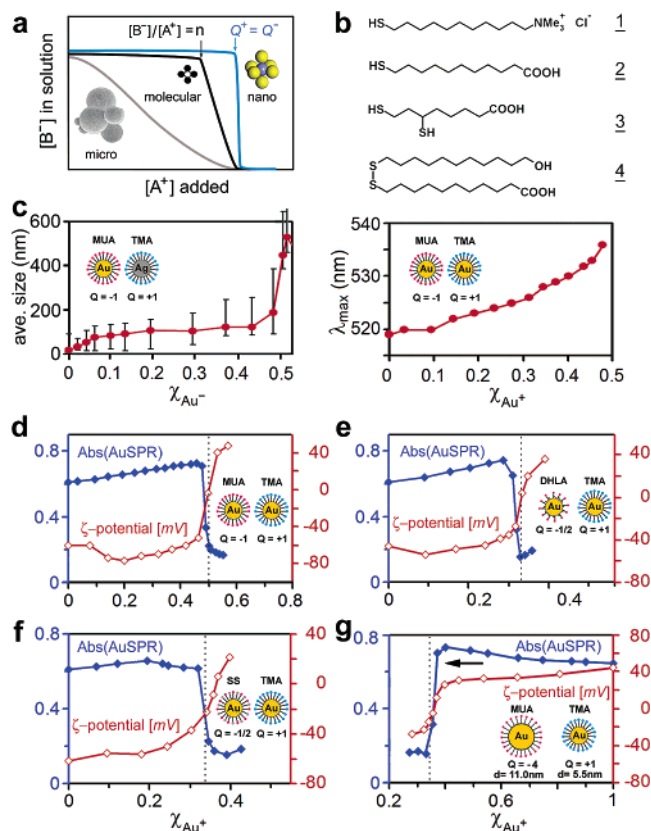


Figure 1. (a) Schematic illustration of the stability of oppositely charged ions (black curve), microparticles (gray), and nanoparticles (blue). While charged microparticles precipitate continuously, molecular ions and charged NPs remain stable up to a characteristic, threshold value. (b) Molecules used to form self-assembled monolayers on Au or Ag nanoparticles. (c) Left: average size of aggregates measured by DLS during titration of 11 nm AuMUA with AgTMAs. Right: typical red-shift of the Au SPR maximum during titration. (d–g) Intensity of the Au SPR band at $\lambda_{max} = 520-550$ nm (blue lines) and the values of the ζ -potential (red lines) for the titrations of oppositely charged Au NPs covered with different types of SAMs ($C = 2$ mM for all solutions). The types of NPs used are indicated in the inset schemes; χ_{Au^+} stands for the ratio of the gold atoms in Au NPs bearing positively charged NPs to the total number of gold atoms in the sample (also see ref 10). Dashed vertical lines give the precipitation points expected on the basis of NP compositions. The arrow in (g) indicates the “reverse” order of the titration, that is, addition of negatively charged, 11 nm AuMUA to positively charged, 5.5 nm AuTMAs.

point, χ^p , observed experimentally is 0.502 ± 0.004 and agrees with the value of 0.5 expected for NPs carrying equal but opposite charges. Similarly, the mixture of equally sized AuDHLAs and AuTMAs precipitates at $\chi^p = 0.331 \pm 0.004$ (Figure 1e) and that of AuSS and AuTMAs at $\chi^p = 0.347 \pm 0.006$ (Figure 1f). In both cases, the precipitation points are close to the anticipated $-1:2$ ratio of charges on the NPs of two types ($\chi^p = 0.333$). Finally, “reverse” addition of negatively charged 11 nm AuMUA to 5.5 nm AuTMAs

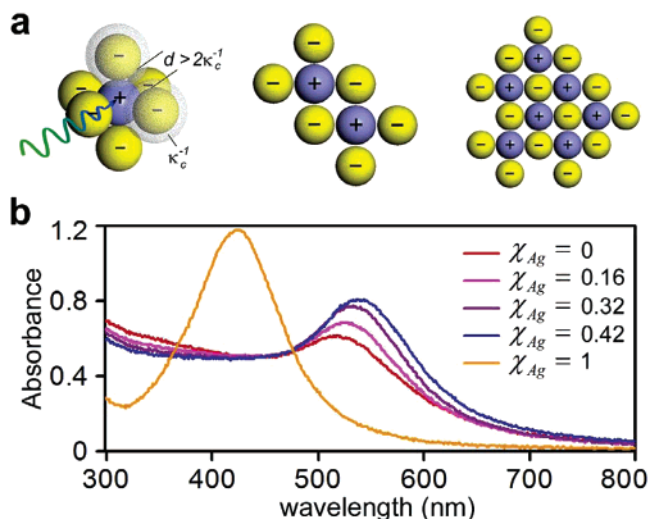


Figure 2. (a) Qualitative scheme of charged core-and-shell aggregates forming from NPs of opposite polarities at the early stages of a titration (left). As the titration progresses (middle and right), higher-order aggregates form and the shells enclose multiple NPs of both polarities. Note that the formation of shells is not energetically unfavorable, since the thickness of the Debye layer, κ_c^{-1} , around each NP is only $\sim 2\text{--}3$ nm,⁵ and the electrostatic repulsions between the like-charged shell NPs are effectively screened⁵ (for $d > 2\kappa_c^{-1}$). The wavy line illustrates the change in the wavelength of light passing through the shell. (b) UV-vis spectra for the titration of 5.5 nm AuMUs with 6.5 nm AgTMAs. The legend gives the number of Ag NP equivalents added; the spectrum of pure AgTMAs ($\chi_{\text{Ag}} = 1$) is included for reference. Note that all the way up to the titration point, the SPR band of silver at 424 nm is absent, while that of gold gradually increases.

gives the precipitation point at 0.341, close to the expected (cf. footnote 10) value of 0.333.

We further note that, even though the effective charge of NPs could depend on the ionic strength of the solution and therefore on the concentration of NPs, the magnitude of this effect within the range of concentrations studied (0.2–5 mM) is minimal.¹¹ For example, precipitation points determined for 0.2, 2, and 5 mM mixtures of AuMUA and AuTMA are respectively 0.508, 0.502, and 0.500. Overall, our experiments indicate that oppositely charged NPs precipitate when their charges are compensated and that the precipitation point can be determined with less than $\sim 3\%$ error between different experiments (provided that the solutions are well stirred and equilibrated).

The NP aggregates forming before the precipitation point are stabilized by shells composed of like-charged, “majority” NPs (Figure 2a). To show this, we first observe that, for all systems studied, the values of the ζ -potential are roughly constant before precipitation begins (cf. Figure 1d–f) and the polarity of ζ corresponds to that of the “majority” particles (cf. Figure 1d–f vs Figure 1g). Since only the “majority” NPs contribute to the surface potential, they are the only ones present on the surfaces (i.e., in the “shells”) of the assemblies. These charged shells stabilize the aggregates through solvation and mutual electrostatic repulsions. When all charges are compensated, these favorable effects are no longer operative, and the neutral aggregates precipitate rapidly.

The core-and-shell arrangement of the NPs is also congruent with the optical properties of the mixed NP solutions. The most illustrative example here is that of the titration of Au NPs with oppositely charged Ag NPs (Figure 2b). Remarkably, addition of silver particles does not give rise to any Ag surface plasmon resonance (SPR) band expected at 424 nm but, instead, causes the enhancement of the Au SPR band at 520 nm. This phenomenon can be explained on the basis of the classical Mie theory (cf.

Supporting Information), which predicts that, if the impinging light is passing through a thin shell of Au NPs before reaching the Ag NPs, its wavelength decreases by a factor that is determined by the shell’s effective refractive index (cf. Figure 2a). As a result, the Ag NPs are resonantly excited at a longer effective wavelength, $\lambda_{\text{eff}} = \lambda_{\text{intrinsic}} n_{\text{shell}}$. For the thickness of the gold shell on the order of one NP diameter, the silver particles are resonantly excited at $\lambda_{\text{eff}} \approx 520$ nm. Consequently, the silver band at 424 nm appears “extinguished”, while that of gold at ~ 520 nm is “enhanced”. Theoretical details supporting these conclusions are discussed elsewhere.¹²

In summary, we have demonstrated that oppositely charged nanoparticles of different sizes and charge ratios precipitate at the point of overall electroneutrality. Aside from fundamental interest, this unique nanoscale phenomenon provides a basis for precise determination of charges on nanoscopic objects (relative or absolute if the charge on one type of NPs used in the titration is known/standardized). We have already applied this method to the electrostatic self-assembly of nanostructured crystals,⁵ and we envision future uses of charged NPs as analytical probes for measuring ionization states of other nanoscopic objects (inorganic and organic) and for monitoring reactions occurring on the surfaces of such objects and involving charged and/or ionizable species.

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Supporting Information Available: Synthesis of the NPs and short summaries of the DLS measurements and electrodynamic Mie calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (4) This is valid if $K_f K_{sp} \gg 1$ ($K_{sp} = [A^+][B^-]$, $K_f = [AB_n^{(n-1)}]/[A^+][B^-]^n$; e.g., precipitation of AgCN occurs when $[CN^-]/[Ag^+] < 2$).
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- (7) When polydispersity was large (30–40%), the positions of the precipitation points did not change perceptibly, but the precipitation was incomplete, especially when the NP size distributions were skewed toward smaller particles. As discussed in ref 5, these small NPs stabilized the solution phase.
- (8) Witt, D.; Klajn, R.; Barski, P.; Grzybowski, B. A. *Curr. Org. Chem.* **2004**, *8*, 1763.
- (9) This estimate is based on the work of Leopold et al. (Leopold, M. C.; Black J. A.; Bowden, E. F. *Langmuir* **2002**, *18*, 978), who studied pK_a ’s of MUA SAMs on nonplanar/corrugated surfaces. For DHLA and SS molecules, the pK_a ’s are expected to be similar or even slightly lower due to sparser COOH surface groups.
- (10) Given that each NP contains n atoms, the charge per NP scales with the NP surface area, or $n^{2/3}$. Therefore, the total charge of a collection of like-charged NPs scales as (number of NPs) \times (charge per NP), that is, as $(CVn)(n^{2/3})$ or, in terms of the NP diameter, CV/d , where C is the concentration of atoms. The electroneutrality condition for monodisperse NPs having all thiols in the SAMs terminated in charged groups can be then expressed as $Q^+ = C^+ V^+ / d^+ = C^- V^- / d^- = Q^-$. From this relation, the value of χ_{Au^+} expected at the precipitation point is $d^+ / (d^+ + d^-)$ (e.g., $1/3$ for $d^- = 11$ nm and $d^+ = 5.5$ nm NPs in Figure 1g).
- (11) At pH ~ 11 , the ionic strength of the solution surrounding the charged NPs remains relatively constant (~ 0.5 mM) when the concentration of NP changes. This is so because the amount of counterions desorbed from the NPs is small compared to the amount of ions of the base used to adjust the pH, and because the solutions are allowed to equilibrate during titration. Under these circumstances, the effects of NP concentration on the titration point are small.
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