Electrostatic Self-Assembly of Binary Nanoparticle Crystals with a Diamond-Like Lattice

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Self-assembly of charged, equally sized metal nanoparticles of two types (gold and silver) leads to the formation of large, spherelite (diamond-like) crystals, in which each nanoparticle has four oppositely charged neighbors. Formation of these non–close-packed structures is a consequence of electrostatic effects specific to the nanoscale, where the thickness of the screening layer is commensurate with the dimensions of the assembling objects. Because of electrostatic stabilization of larger crystallizing particles by smaller ones, better-quality crystals can be obtained from more polydisperse nanoparticle solutions.

Crystallographic composites composed of one or more types of metallic and/or semiconductor nanoparticles (NPs) are of great interest for the development of new materials with potential applications in areas such as optoelectronics (1), high-density data storage (2), catalysis (3), and biological sensing (4). To date, methods for the crystallization of two-dimensional (2D) and 3D NP superlattices have relied on the differences in the sizes of component particles and on attractive van der Waals or hard-sphere interactions between them. This strategy has been successful in preparing several types of lattices (such as AB (5), AB₈ (6), AB₅ (7), and AB₁₄ (8)), but the all-attractive nature of the interparticle potentials limits its applicability to relatively few and usually (8) close-packed structures.

To overcome this limitation, we and others (8, 9) have focused on systems of NPs interacting via electrostatic forces; such forces provide a basis for ionic, colloidal (9), or even macroscopic (10) crystals, but, despite promising attempts (8, 11), have not been successfully exploited for controllable or predictable long-range organization of matter at the nanoscale. Here, we report electrostatic self-assembly (10) (ESA) of oppositely charged, nearly equally sized metallic NPs of different types into large 3D crystals characterized by spherelite (diamond-like) (12) internal packing, and of overall morphologies identical to those of macroscopic diamond or spherelite crystals (Figs. 1 to 4). Formation of these non–close-packed structures results from the change in electrostatic interactions in the nanoscopic regime, where the thickness of the screening layer becomes commensurate with the dimensions of the assembling particles, and is facilitated by the presence of smaller, charged NPs in the crystallizing solutions that stabilize larger NPs by what can be termed a nanoscopic counterpart of Debye screening.

We used Ag and Au NPs coated with ω-functionalized alkane thiols (13): HS(CH₂)₁₀COOH (MUA) and HS(CH₂)₁₅NMe₃⁺Cl⁻ (TMA) (Fig. 1A). These NPs were prepared according to a modified procedure (14) [see Supporting Online Material (15)] and had average diameters of 5.1 nm (with dispersity σ = 20%) for Au and 4.8 nm (σ = 30%) for Ag (Fig. 1B). We chose this pair as a model system, because the average sizes of Au NPs passivated with MUA [self-assembled monolayer (SAM) thickness = 1.63 nm (16)] and Ag NPs covered with TMA (SAM thickness ~ 1.9 nm) were very similar overall (~8.36 nm versus ~8.60 nm).

Both types of NPs were stable and unaggregated when kept in separate aqueous solutions. At the concentration used (2 mM), the pH of AuMUA solution was 9.7, so the NPs presented deprotonated carboxylate groups, and the ratio of

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Fig. 1. (A) Scheme and average dimensions (in nm) of AuMUA and AgTMA nanoparticles used as the model system. Particle compositions estimated using the method from (39) are Au₁₂₀(TMA)₃₈₀ (where L is MUA) and Ag₁₄₀(TMA)₃₄₀ (where L is TMA); the ratio of the particles’ charges Q(AgTMA)/Q(AuMUA) = -0.90. (B) Experimental, normalized size distributions of metallic cores of Ag and Au NPs; statistics are based on high-resolution TEM images of at least 500 NPs of each type. (C) Typical UV–Vis spectra for the titration of AuMUA solution (here, 2 mM, 0.4 mL) with small aliquots (40 μL, 0.1 equiv.) of AgTMA solution (2 mM; concentrations are given in moles of metal atoms). The legend gives numbers of AgTMA equivalents added. Initially, absorption of the SPR band of gold (λmax,Au = 520 nm) rises and that of the SPR band of silver (λmax,Au = 424 nm) is extinguished. Precipitation begins at ~0.7 equiv. AgTMA, and is complete when [AgTMA]/[AuMUA] ~ 0.9. The precipitation point corresponds to the formation of charge-compensated (electroneutral) complex and is consistent with an estimate derived from particle compositions: (Q(AgTMA)/Q(AuMUA))neutral = (Nₐg/Nₐ u)Q(AuMUA)/Q(AgTMA) = (3400/4100)0.9 = 0.92, where Nₐg and Nₐ u are the numbers of Ag and Au atoms in one AgTMA and one AuMUA particle, respectively). Further addition of silver NPs solubilizes the precipitate, as evidenced by the increasing intensities of SPR bands of both types of NPs (and also by visual examination of the sample). (D) (Solid curve) Progress of the titration represented by absorption coefficient ε(λmax,Au) defined in (25). The initial increase in ε is the result of close proximity of oppositely charged particles within soluble aggregates (25). Aggregation is confirmed by the red shift of the Au plasmon band maximum, λmax(Au), from 520 to ~558 nm (dashed curve). For χ > 0.5, precipitate redissolves, and λmax(Au) decreases. (E) Large-area SEM image of binary crystals obtained from AuMUA/AgTMA precipitates.
NP charges was $Q(\text{AgTMA})/Q(\text{AuMUAs}) = -0.90$ (compare Fig. 1A). When the solutions were mixed, the positively charged AgTMA anions interacted with the negatively charged AuMUAs. As suggested by the absence of the silver plasmon band centered at $\lambda_{\text{Ag}}^{\text{max}} = 424 \text{ nm}$ and concomitant growth of the gold band at $\lambda_{\text{Au}}^{\text{max}} = 520 \text{ nm}$ (Fig. 1C), the interaction involved close proximity of particles of the two types within small, soluble aggregates (15). These aggregates precipitated rapidly when the molar ratio of the NPs was near unity and the overall charge of the NPs was neutralized (Fig. 1D).

Crystals were obtained from the NP precipitate, from which the excess of ammonium salt hindering the crystallization process was removed by washing with water. Subsequently, the precipitate was dissolved in a 1:4 v/v mixture of water and dimethyl sulfoxide (DMSO), and crystals were grown by slow (~12 hours) evaporation of water at 70°C (17). This procedure yielded large numbers of regularly faceted crystals, each composed of several million NPs and with dimensions up to 3 mm in each direction (Figs. 1 and 4). When the crystals were partly dissolved in water, the ultraviolet-visible (UV-Vis) spectra showed no blue-shift of the surface plasmon resonance (SPR) of Au and an extinguished SPR band of Ag. These data suggest that (i) Ag and Au NPs in the crystals were in close proximity and (ii) that they did not amalgamate (18) during crystallization. Amalgamation was also ruled out by performing successful crystallization without heating.

The crystal structure was solved by small-angle, powder x-ray diffraction (XRD) (15). The XRD spectrum in Fig. 2A shows three peaks located at $20 = 0.801^\circ$, $1.308^\circ$, and $1.539^\circ$. This diffraction pattern characterizes the sphalerite (or diamond (15)) structure with the lattice constant $a = 19.08 \pm 0.53 \text{ nm}$ and with peak positions corresponding to Bragg reflections on planes specified by Miller indices (111), (220), and (311), respectively. The lattice constant agrees with the value of $a = 18.5 \text{ nm}$ based on scanning electron microscopy (SEM) measurements (Fig. 2B).

Also, the interparticle distance along the body-diagonal axis calculated from XRD data is $8.27 \pm 0.26 \text{ nm}$, near the value of $\sim 8.48 \text{ nm}$ estimated from hard-sphere radii of individual NPs (compare Fig. 1A) and 8.5 nm from the SEM image (Fig. 2C). Finally, both the bulk composition of the crystals as well as the identities of NPs on crystalline faces were examined via energy dispersive spectroscopy (EDS) in SEM and in transmission electron microscopy (TEM); it was found that the bulk contents of Ag and Au were approximately equal (compare (15)) and that the arrangement of surface particles was congruent with the XRD analysis (Fig. 3).

All of these experiments indicate that NPs are arranged on a diamond lattice with each NP surrounded by four oppositely charged neighbors at the vertices of a tetrahedron (Fig. 2D). This structure is closely related to that of ZnS, except that the NP “ions” have nearly identical radii. Not surprisingly, the overall crystal morphologies—including octahedral, truncated tetrahedral, truncated, and twinned octahedral, and triangular—are identical to those observed for their macroscopic diamond or sphalerite (ZnS) counterparts (Fig. 4).

Crystallization of NPs into a diamond-like structure is mediated by screened electrostatic interactions. Screening occurs because (i) the NP cores are metallic and (ii) each charged NP is surrounded by a layer of counterions. As a result, the particles interact by short-range electrostatic potentials. To show why such interactions do not lead to more closely packed NaCl or CsCl structures that might have been expected on the basis of NP charges alone, we first note that the screening length, $\xi^{-1}$, for the crystallized NPs is $\sim 2.7 \text{ nm}$ (19, 20). This short distance relative to the interparticle distance means that the electrostatic interactions can be effectively screened, and the NPs arrange themselves in the diamond-like structure.
energy of the crystals is well approximated by accounting only for the interactions between nearest oppositely and like-charged NPs.

With this simplification, crystal energies (per NP) of structures, in which each NP has \( n \) oppositely and \( m \) like-charged neighbors [e.g., \( n = 4, m = 12 \) for diamond; \( 6 \) and \( 12 \) for NaCl; \( 8 \) and \( 6 \) for CsCl (21)], can be written as a sum of favorable, \( nE_{\text{op}} \), and unfavorable, \( mE_{\text{like}}(d) \), contributions. Here, \( E_{\text{op}} \) and \( E_{\text{like}} \) denote, respectively, the energy of two oppositely charged NPs brought into contact, and two nearest like-charged NPs. The value of \( E_{\text{like}} \) depends on the separation, \( d(m) \), between the surfaces of like-charged NPs. If \( d > 2k^{-1} \), the electrostatic interaction is screened and \( E_{\text{like}} \approx 0 \); for smaller separations, \( E_{\text{like}} \) increases rapidly with decreasing \( d \) (20, 22).

In particular, for diamond structure (Fig. 4A, left), \( 2k^{-1} = d_{0} = 5.3 \text{ nm} \), and only \( E_{\text{op}} \) contributes effectively to the crystal energy, which is thus favorable (i.e., negative). In contrast, for NaCl and CsCl lattices (Fig. 5A, right), the values of \( d(m) \) are considerably smaller (3.5 and 1.3 nm, respectively), and the like-charge repulsions offset the energetic gain compared to that of the diamond lattice (\( 2E_{\text{op}} \) for NaCl and \( 4E_{\text{op}} \) for CsCl). Overall, the diamond structure has the lowest energy.

We emphasize that this effect does not scale with the size of the assembling objects. For example, with larger particles such as those recently described in (9) and (23), the characteristic separation distance between like-charged particles is much larger than the screening length, and close-packed lattices are favored. We also note that theoretical models without screening but accounting for either entropic effects (24) and/or van der Waals interactions (25–28) cannot justify the formation of a diamond lattice.

Progress of the crystallization process depends on the degree of monodispersity of the nanoparticles used. Surprisingly, polydispersity skewed toward smaller particles facilitated crystallization and gave rise to crystals of better quality. To understand this effect, we performed a series of experiments under identical experimental conditions (solvent and temperature) but with NPs characterized by various size distributions (Fig. 5B). When Au particles taken from the same, narrow distribution (\( \sigma = 20\% \)) but functionalized with either MUA or TMA were cocryystallized, the quality of crystals was poor, and a large proportion of NPs formed amorphous aggregates (Fig. 5B, left). In contrast, when one of the distributions was broader (e.g., AgTMA with \( \sigma = 45\% \)) than the other (as with the AuMUA that we used in the model system; \( \sigma = 20\% \)), large numbers of high-quality crystals were obtained (Fig. 5B, middle). Finally, when both distributions were broad (e.g., AgTMA with \( \sigma = 45\% \) and AuMUA with \( \sigma = 30\% \)), particles stayed in solution and did not crystallize at all (Fig. 5B, right). That is, some polydispersity—but not too much—aided crystallization.

These observations can be explained qualitatively on the basis of screening of electrostatic forces acting between large NPs by smaller particles present in solution. The electrostatic interaction between two large NPs can be approximated by a screened potential (29), in which the effective screening length decreases with increasing concentration of screening charge carriers (here, small NPs) and determines the stability of dispersed nanoparticles. When large NPs are surrounded by smaller, oppositely charged ones, the effective screening length is small, and the NPs interact weakly and do not aggregate (30, 31). In contrast, when no small particles are present, the screening length is large, long-range attractive electrostatic forces are strong, and flocculation (32) ensues.

Thermodynamically, the presence of small NPs shifts the equilibria between dispersed (D), amorphous-aggregate (A), and crystalline (C) phases (Fig. 5C). In the absence of small particles, the chemical potential of the dispersed phase,
mu, is—due to the electrostatic interactions—very high compared to both mu, and mu, C. In this case, the NPs either condense via flocculation or nucleate to the crystalline phase. Because the nucleation processes are less likely to occur, the condensed phase consists mostly of amorphous aggregates. Addition of small particles weakens the electrostatic interactions substantially and lowers the potential of the dispersed phase to mu, which is only slightly higher than the potentials of condensed phases A and C. Here, the effective attractive forces are sufficient to overcome the energetic barrier accompanying aggregation, but are weak enough to allow the aggregates to anneal into low-energy crystals (9, 33). The formation of the crystalline phase occurs via the nucleation/aggregation processes (34), in which a stable nucleus is formed if its radius, R, is large enough and if the gain in the bulk energy, DeltaE_{bulk} = Delta mu_{2c} R^3, dominates over the surface energy DeltaE_{surf} = sigma R^2, where Delta mu_{2c} and sigma denote, respectively, the difference in chemical potentials and the surface energy between dispersed and crystalline phases. The critical size, R_{crit}, of the nucleus that remains in suspension and serves as a seed for further crystallization is determined by the condition that the sum DeltaE_{bulk} + DeltaE_{surf}—inversely proportional to |Delta mu|—reaches its maximum value (34). Because |Delta mu_{2c}| << |Delta mu_{1c}|, crystals obtained from suspension “2” were much larger than those formed from phase “1.” Finally, if large numbers of small particles of both types are present, the chemical potential of the dispersed phase is lower than both mu, A and mu, C, and no aggregation or crystallization is observed.

Several comments are in order. We emphasize that the experimental trends cannot be explained by entropic “depletion” forces (35). In such cases, the presence of small particles would destabilize the free-floating, large particles and lead to phase separation. The electrostatic stabilization of large NPs by small ones is analogous to the Debye screening affected by high-ionic strength solutions (36, 37); in this respect, small, charged nanoparticles behave like ions. However, if the sizes and charges of the crystallizing particles were increased, one would need proportionally more small particles to provide efficient electrostatic stabilization (30). We have seen this effect in collections of 6- and 12-nm NPs that we tried to cocrystallize, where the particles kept in solution could not be stabilized even by broad distributions of small NPs. Although the screening can, in principle, be modulated by increasing the ionic strength of the crystallization medium by adding salts, these salts stabilize isolated particles and also crystallize themselves—as we verified experimentally, both of these effects hinder the formation of NP crystals.

Finally, from a practical standpoint, extension of the ESA approach to other types and combinations of NPs (e.g., magnetic or photoluminescent) may open new avenues to nanostructured materials of composite properties deriving from the unique properties of the diamond lattice (38).

Fig. 5. (A) Qualitative schemes of NP arrangements and counterion “atmospheres” in lattice structures considered [more realistic drawings of the lattices and the discussion of the m and n values defined in the main text can be found in (20)]. For diamond, the separation between the like-charged particles, d, is larger than the sum of screening lengths, 2kappa^{-1}, and the energy of repulsive electrostatic interactions is negligible. For NaCl and CsCl lattices d < 2kappa^{-1}, and the repulsions between like-charged NPs offset the energetic gain of oppositely charged interactions. (B) Effect of NP polydispersity on the quality of crystals. Graphs (i) to (iii) give normalized size distributions of the metallic cores of oppositely charged NPs used in crystallization experiments; typical outcomes of these experiments are illustrated by SEM or TEM images shown in the bottom row (scale bars correspond to 200 nm). In all cases, experimental conditions were the same, and crystallization was attempted at least five times. (i) Crystallization of similarly sized AuTMA and AuNMA gave mostly amorphous aggregates. Sparse, poor-quality crystals (100 to 800 nm) were observed in only one out of five experiments. (ii) Crystals grown from narrowly distributed AuNMA (sigma = 20%) and polydisperse AgTMA (sigma = 45%), bimodal distribution with a large fraction of smaller particles of sizes 1 to 3 nm) were large (up to 3 mm) and regularly shaped. (iii) Broadly distributed AuNMA (sigma = 30%) and AgTMA (sigma = 45%) did not aggregate or crystallize at all. (C) Effect of small particles on the stability of the dispersed, large NPs. In the absence of small particles (phase “1”), large NPs of opposite charges interact by relatively strong electrostatic forces, and the dispersed phase has a high chemical potential, mu, C. In this case, the NPs instantly flocculate to form amorphous aggregates (A). If small NPs of one type are present (phase “2”), they surround large NPs of the opposite charge and effectively screen electrostatic interactions between them. Phase “2” is characterized by a chemical potential, mu, A, much lower than that of phase “1”—as a result, large NPs nucleate and aggregate into ordered crystal structures. If small NPs of both types are present in the suspension (phase “3”), all large NPs are screened and interact very weakly. Thus, phase “3” has chemical potential lower than phases A and C, and NPs remain stable in solution.
Probing Proton Dynamics in Molecules on an Attosecond Time Scale


We demonstrate a technique that uses high-order harmonic generation in molecules to probe nuclear dynamics and structural rearrangement on a subfemtosecond time scale. The chirped nature of the electron wavepacket produced by laser ionization in a strong field gives rise to a similar chirp in the dynamics and structural rearrangement on a subfemtosecond time scale. The chirped nature of the electron wavepacket is a hitherto unexploited property in the measurement of ultrafast dynamical behavior.

The technique demonstrated here is based on high harmonic generation (HHG) from molecules. HHG is well understood within the framework of a semiclassical model, which separates the process into three distinct steps. In the first step, an intense laser pulse ionizes an atom or molecule, launching an electron wavepacket into the continuum. In the next step, the electron wavepacket moves in response to the laser electric field; it is first accelerated away from the parent ion and then returns at some later time (typically 0.5 to 1.6 fs for a laser field at a wavelength of ~800 nm) as the laser field reverses direction. The third step is the recombination of the electron with the parent ion and the emission of a high-energy photon (~10 to 500 eV) that carries away, at discrete multiples of the laser frequency, the kinetic energy gained by the electron in the process. The intensity of the radiation emitted at the moment of recombination depends upon the transition amplitude between the wave function during the HHG process.

There is currently great interest in the development of methods to probe the dynamical behavior of matter on the attosecond (1 as = 10^-18 s) time scale (1–3). It is known that the ionization of an atom or molecule by an intense laser field and subsequent electron acceleration in the field results in the formation of a chirped electron wavepacket—a “burst” of electrons with a broad range of kinetic energies that recollide with the parent ion over a range of time delays (4). However, the chirp of the electron wavepacket is a hitherto unexploited property in the measurement of ultrafast dynamical behavior.

The technique demonstrated here is based on high-harmonic generation (HHG) from extended to the nanoscale and can be used to approximate electrostatic forces acting between nanoparticles screened by counterions comparable in size (within one order of magnitude) and present in small quantities (5 fewer layers). Although quantitative analogies could thus be justified, we restrict our discussion to qualitative arguments that are sufficient to explain experimental observations.

In addition, the high-fidelity of the HHG technique allows for the measurement of complex molecular systems. For example, the high-order harmonic generation spectrum of a molecule can be used to determine the electronic density distribution within the molecule, providing information on the molecular structure and electronic states.

References and Notes
12. For crystals composed of Ag and Au nanoparticles, the lattice is isostructural with sphalerite ZnS (2G 216). For crystals made of only one type of metal cores (compare Fig. 5B), the lattice is best described as diamond (SG 227).
15. Supporting material is available on Science Online.
17. After the evaporation of the “good” solvent, the NP crystals constituted only ~0.01% v/v of the remaining solution, so crystallization cannot be attributed to confinement effects that might have been operative had all liquid been evaporated.
19. This estimate is based on the Deryagin-Landau-Verwey-Overbeek (DLVO) theory and for a 1:1 electrolyte. Specifically, g = (kF/kT)², where k denotes the number density of ions, e is the charge of an electron, k is the static dielectric constant of the medium, and e is the permittivity of vacuum. Using EDS, we determined the content of Cl⁻ to be ~5%, which corresponds to a concentration c ~ 10⁻¹⁷ M of the residual ammonium salt (NMe₄⁺Cl⁻) present in the crystal. Assuming that the effective dielectric constant of a mixture of water and DMSO filling the free space between the NPs in the crystal can be approximated as ε = ε_water + ε_DMSO/² ≈ 65, ε_DMSO ~ 2.7 nm. We emphasize that this number can only be treated as an estimate, because with NPs several nanometers in diameter, we are at the limit of applicability of the DLVO mean-field approach. At the same time, our approximation is qualitatively correct as verified by recent numerical Monte Carlo simulations of pairs of nanometer-sized charged particles (20).
25. Because each NP is covered with a SAM, the only dispersion (van der Waals) interaction that needs to be considered is that between alkyl chains of MUA and TMA thiol that form the SAMs. This attractive interaction is important only if the SAMs interpenetrate; it vanishes at distances larger than ~1 nm, and its characteristic energy is assumed to be of the same order of magnitude as the interchain—interchain interactions (22).
29. Results of recent molecular dynamics simulations (22) indicate that mean-field screening concepts can be
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