

## SIZE FOCUSING

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**Monodispersity at the nanoscale.** The difference between nanoparticles/nanoclusters and traditional colloids dates back to the early 1850s. We are all familiar with the term colloid, which is used to describe solid/liquid and solid/gas suspensions such as milk, paints, butter, smoke and smog. Although both types of materials have sizes within the nano-regime, the leading difference is the control one has over composition and morphology. In order for nanomaterials to be suitable for “bottom-up” design, their synthesis must lead to monodispersed entities with structure controlled features that will exhibit properties that are reproducible. Monodisperse Nanoparticles are arbitrarily defined as a predominately homogeneous population with >90% uniformity in size distribution. Nanostructures and nanoparticles that are >90% monodisperse exhibit some degree of atom mimicry that includes;(a) robustness suitable for mass, size characterization, (b) well defined chemical valency/stoichiometries and (c) reproducible mass/molar combining ratios when allowed to react with either sub-nanoscale reagents or other nano-elements. Reactivity is determined by functional groups present on or within the nanostructures. This > 90% monodispersity level was required in order to observe nano-super lattice crystallinity during nanoparticle self assembly.

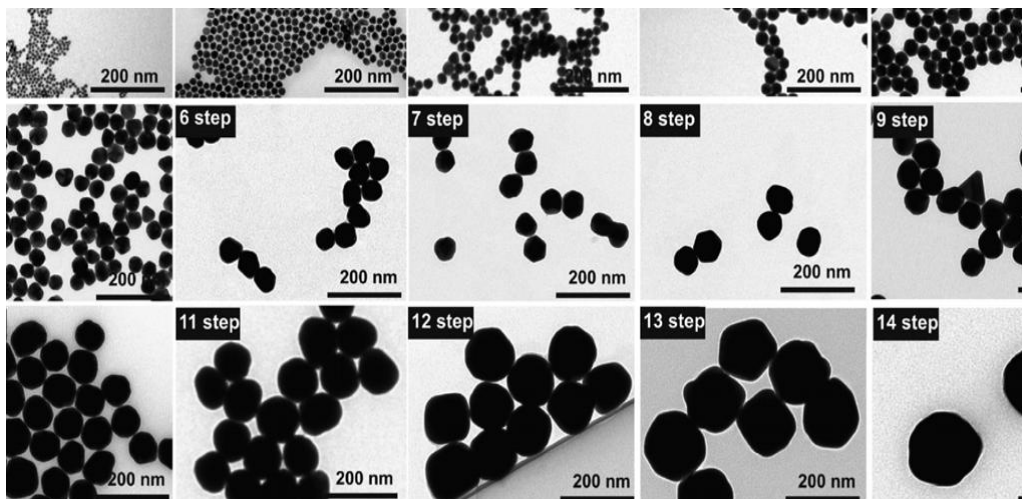
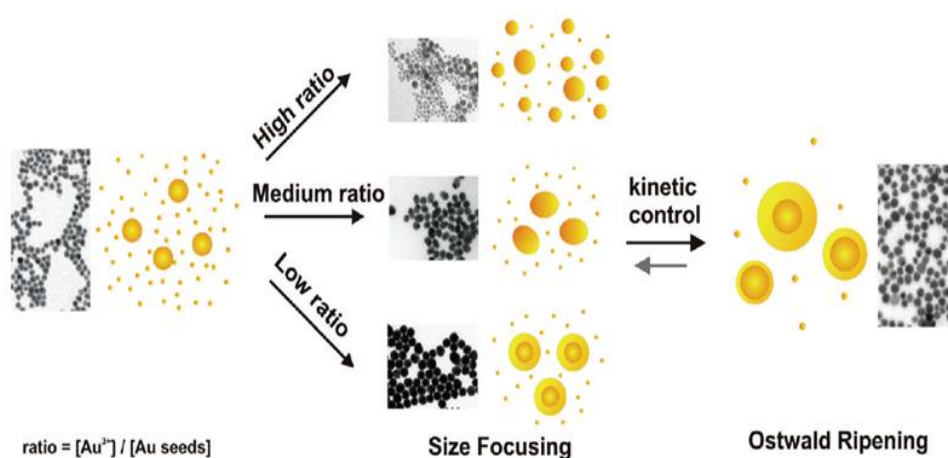


Fig. 1. Seeded growth with the dilution of the seed solution. Transmission electron microscopy images of Au seed particles and those of subsequent growth steps. The particle size increases from  $8.4 \pm 1.0$  to  $180.5 \pm 10.7$  nm, and its concentration decreases from  $\sim 3 \times 10^{12}$  /mL.

**1. Kinetically Controlled Growth of Au NCs: Size Focusing vs Ostwald Ripening [1]**  
Synthetic chemistry is the source of most nanomaterials as well as an important

knowledge base for essentially all “bottom-up” synthesis strategies, key intermediates and structural features leading to well-defined nanoparticles. Inorganic nanoparticles (NPs) made of metals, metal oxides and semiconductors, of sizes smaller than 100 nm, can be regarded as "artificial atoms" since their high density of electronic states - which controls many physical properties - can be extensively and easily tuned by adjusting composition, size and shape. The ability to predict physicochemical properties and risk/benefit boundaries enjoyed by traditional small molecule chemistry rests solidly on the existence of monodisperse nanoparticles (see ‘looking for a periodic table of the nanoparticles’ [2])

Scheme 1. Illustration of the Different Growth Pathways for the Kinetically Controlled Seeded Growth of Au NPs<sup>d</sup>



**Size Focusing Crystal Growth.** Nowadays, seeding-mediated synthesis strategies based on the temporal separation of nucleation and growth are considered to be very efficient methods to precisely control the Au NP size and shape. According to the LaMer mechanism, the growth process of NPs involves two different periods: the focusing period, where the mean radius of the particles increases rapidly and the size distribution becomes narrower and the defocusing period, where the growth rates decline sharply and the size distribution broadens. Thus, whereas at relatively high monomer concentrations smaller NPs in the distribution grow faster than larger ones (size focusing) leading to monodispersity, when the monomer concentration is depleted by growth, the distribution broadens because some smaller NPs shrink at the expense of larger ones and eventually disappear (Ostwald ripening, the phenomena, related to the Gibbs-Thomson effect, where small NPs dissolve and large ones grow).

**Is there magic number size?** A critical question is if monodispersity is achieved purely by kinetic means (the fast growing NPs catch up with the slow growing ones) or if there is some local minima where the large ones wait for the smaller ones to achieve the same diameter. The existence of local minima will justify the ease of collecting

monodisperse concentrations of NPs, but this is not necessary, and roughly, it seems that any size can be obtained.

**At which size does size focusing stop?** Small NPs are more unstable and tend to grow or dissolve faster than larger ones. At some point, NPs will grow up to one size where size focusing or Ostwald ripening will slow down and stop.

**How are size focusing and Ostwald Ripening related?** The existence of one warrants the existence of the other? NPs that can be easily grown in a size focusing regime, will suffer Ostwald Ripening if the solution is depleted of monomer? During Ostwald ripening, in sink conditions, where all the dissolved atoms are removed from the equilibrium will full NP dissolution occur? Does this mean that Au NPs smaller than 50 nm, at very diluted conditions, at 100 C, will rapidly dissolve?

[1] <http://pubs.acs.org/doi/abs/10.1021/la201938u>

[2] [https://www.nsf.gov/crssprgm/nano/GC\\_Charact08\\_Tomalia\\_nsf9\\_29\\_08.pdf](https://www.nsf.gov/crssprgm/nano/GC_Charact08_Tomalia_nsf9_29_08.pdf)