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Crystal Growth

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Increasing Complexity while Maintaining a High Degree of Symmetry in Nanocrystal Growth**

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Dedicated to Professor Soledad Penadés and Professor Manuel Martín-Lomas

Crystal growth is a complex process which originates from the solubility limits of chemical species in solution. Multiple paths can be followed from dissolved ions to solid crystals. Crystallographers know about the difficulties behind the formation of large single crystals which can be used to elucidate the structure of organometallic complexes or proteins, for example. Indeed, control over crystal growth is key to obtaining a wide variety of products but many parameters need be taken into account, such as temperature, concentration, and the presence of foreign substances which may act either as nucleation centers or as inhibitors. A particular case is the formation of crystalline nanoparticles, also known as nanocrystals. By definition, the size of nanocrystals is very small and thus the main difficulty is the modulation of the growth so that it leads to the desired size and morphology. Accurate control in the ultimate nanocrystal morphology often requires separation of the nucleation and growth stages, in such a way that nucleation is completed before growth starts and no new nuclei are formed during the growth stage.

Nanoparticles display size-dependent properties as a result of spatial confinement on the nanometer scale. Prominent examples are the optical and electronic properties of metals and semiconductors. In the latter case, confinement leads to splitting of valence and conduction bands into discrete electronic states, while the energy gap between the HOMO and the LUMO increases when decreasing nanocrystal size. In metals, similar effects can be found in the limit of very small sizes, but additionally other effects arise, such as localized surface plasmon resonances or largely enhanced catalytic activity and selectivity. Although size variations are crucial to the existence of such effects, anisotropy plays an equally (at least) relevant role. Both in metals and semiconductors, anisotropy dramatically widens the scope of the properties and phenomena which can be observed, and has motivated the design of synthetic methods toward the growth of elongated nanocrystals such as nanorods or nanowires.[1] The ideas behind inducing directional growth are mainly based on three concepts, namely anisotropic templates, facet-specific adsorption, and growth kinetics. Anisotropic templated growth has been achieved within porous membranes such as anodized aluminum oxide, but also in solutions of cylindrical micelles, for example. The adsorption of capping molecules such as surfactants or polymers has been often quoted as the reason why certain facets grow faster than others, thus leading to directional growth and anisotropy. Whereas this is rather easy to understand for semiconductors, wherein the crystalline forms are largely anisotropic and facet energies can be significantly different, it is more difficult to justify in metals because they display more isotropic lattices and uniform surface energies. Recent examples demonstrate that not only the adsorption of surfactants is relevant but also other moieties present in solution such as counterions and foreign metal ions. Finally, growth kinetics is usually determined by the nature of the precursors and thus of the reactions involved in the formation of the material forming the crystal, but also by the presence of catalysts which can affect such reactions. Obviously, these ideas cannot be considered independently, as they are closely interdependent.

Interestingly, even though nucleation and growth may happen at relatively different time scales, it has been found that complete separation of both processes, that is, synthesis of well-defined nuclei and selective (seeded) growth, provides the opportunity to define the growth conditions in a much more accurate manner, thus resulting in delicate control of the resulting nanocrystal morphology. It is important to realize that in seeded growth methods the seeds typically play a double role, that of nucleation centers and that of catalysts, so that growth originates exclusively at the existing nuclei. This feature is particularly attractive in the case of metals because metal seeds can catalyze the reduction of additional metal salts when weak reducing agents are employed. Many examples of this process have been reported, including the popular seeded-growth of gold nanorods, however, it is not yet perfectly understood.[1]

As a better understanding has been gained regarding the processes involved in nanocrystal growth, it has been possible to increase morphological complexity and a variety of branched nanoparticles have been reported, including tetrapods and multipods, but also so-called nanoflowers or nano-

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stars, among many other fancy names. Again, this increased complexity is in principle easier to implement in semiconductors since chalcogenides, such as CdSe, can display different crystalline forms and one tetrahedral zinc blende core can serve as a seed for the growth of four wurtzite arms from the four (111) equivalent faces.[2] Although a number of branched metal nanoparticles ranging from bipyramids to sharp pointed multiarm nanostars have also been obtained, the origin of branching is unclear in basically all these reports, and has hindered a rational development of such nanostructures.[3]

Interestingly, traditional chemistry concepts can often be applied to the design of nanoparticle synthesis.[4] Examples can be found not only in directed self-assembly, where single nanoparticles can be considered artificial atoms, but also in the rules applied to molecular construction. Recent examples include the growth of chiral nanostructures or the concept of protecting groups for the synthesis of Janus nanoparticles. The ideal molecular model for branched nanoparticles would be provided by dendrimers,[5] where the branching originates from functional groups which translate from one generation to the next, thereby leading to a highly symmetrical geometry. As simple as the concept may appear, implementation in colloidal nanocrystals is far from straightforward. Even when applied to the chalcogenide semiconductor system, an extremely delicate control would be required to achieve a degree of perfection that would be comparable to that in organic dendrimers.[2b] Given the current level of perfection in the synthesis of metal nanocrystals with regular (Platonic) geometries,[4] the field should be ready to tackle this problem, as long as suitable chemical reactions can be implemented for site-selective growth of subsequent dendrimer generations.

The group of Skrabalak recently reported an elegant method which leads to branching during the seed-mediated growth of metal nanocrystals.[6] The method is based on co-reduction of two metal salts, in particular $HAuCl_4$ and H_2PdCl_4, which was found to induce selective growth from the vertices of the original seeds, thus ultimately leading to uniform branching. Although the exact mechanism was not elucidated, there is a striking analogy with the anisotropic growth of gold nanorods, in which the presence of silver ions is crucial to efficient nanorod formation. The same group has now applied this method in a sequential manner to obtain dendrimer-like nanocrystals with hierarchical branching (Figure 1).[7] Indeed, the product resulting from each co-reduction step can be used as a seed to grow the next generation in such a way that branching continues in a perfectly controlled manner, at least up to the third generation. Although this is still the first demonstration of this concept, a wide range of nanostructures can be envisaged by simply varying the morphology of the initial seed, the extent of reaction in each generation or the composition, as defined by the nature of the seeds, and the co-reduced metals. One could still argue that this method has a fundamental limitation since two metals are incorporated in every single nanocrystal, thus the resulting properties will unavoidably be affected. The same argument may however be seen as an advantage, as multiple functionalities can be exploited simultaneously, such as the combination of plasmon resonances in gold and high catalytic efficiency or specific adsorption in palladium. In fact, it has been shown that such combinations can be applied to ultrasensitive plasmonic detection of hydrogen gas.[8]

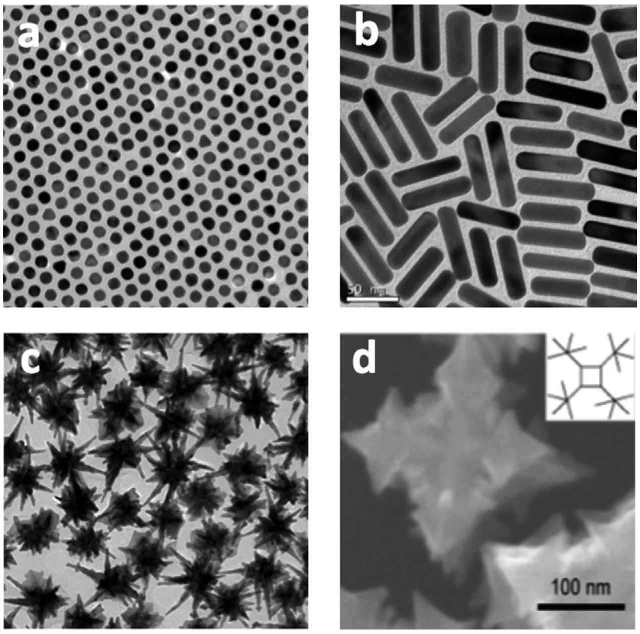

Figure 1. Electron micrographs of gold nanoparticles with increasing complexity, from spheres (a) through rods (b) to branched nanocrystals with low (c) and high (d) symmetry. For (a–c) the scale bar is 50 nm. The image in (d) is reproduced from Ref. [7].

The main conclusion to be extracted from this discussion is that we should remain open minded toward the endless possibilities which application of traditional chemistry concepts can deliver to the wide field of nanocrystal synthesis. Although much progress has been reached, we can still be amazed by new discoveries including the ability to increase complexity at the nanometer scale while maintaining a very high degree of symmetry.

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