Metallic nanocrystals synthesized in solution: a brief review of crystal shape theory and crystallographic characterization

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This article reviews the main theoretical/computational techniques and the experimental characterization methodologies that are used in the quest to investigate the shape, size, composition, and crystallography of metallic nanoparticles. Two morphological regimes are described, one governed by equilibrium thermodynamics, and another in which the shape can be controlled kinetically: in each case, the focus is on key phenomenological effects, ignoring to a large extent the specifics of the materials. For the equilibrium crystal shape, the field has recently experienced developments beyond the basic Wulff construction. For the kinetically controlled case, we argue that models informed by experiments can lead to insights into the growth mechanisms, as well as into the resulting shapes and morphologies. Experimentally, the increasing resolution of characterization techniques can inform and validate the growth models. While ex situ characterization techniques have become de facto standards for investigations of nanoparticles, in situ techniques offer significant advances in spatial and temporal resolution and help establish a fundamental understanding of growth mechanisms.

1 Introduction

Metallic nanoparticles are an ubiquitous part of current research interests due to their applications in catalysis [1–4], drug delivery [5–7], radiotherapy for malignant tumors [8], biodiagnostics [9], electronic, optical, and sensing applications [10, 11]—to name only a few of the most exciting and intensely investigated fields. On a fundamental level, the interest stems from the effects of the particle size on specific applications: the small size means that these particles can not only be effective simply as drug carriers, but also that they have different, new, and potentially useful properties compared to the bulk metal. Size is only one of the several important important ways to tune the properties of nanoparticles: the nature of the metal, its composition, along with its shape have specific effects on the chemical reactions that the nanoparticles can facilitate, both in terms of catalytic activity and reaction specificity [1, 3, 10, 12–14]. Given that some of the most widely used catalysts are noble metals, research has focused on synthesizing small particles for a variety of catalytic applications [12, 14, 15]. In addition to synthesis itself, the control over the final shape and size has also been investigated. The wide range of catalytic properties stems from the different (nano)materials and the diverse electronic properties exhibited in the vicinity of the nanoparticles’ surfaces. Specifically, the presence of different facets or combinations thereof leads to specific reactions that can be catalyzed [1, 12, 14, 15]. Interestingly, however, there is no simple, unique correlation between the catalyzed reactions and the set of facets and/or shapes of the catalytic nanoparticles. Therefore, the usefulness of the relationships between nanoparticle morphologies and the applications that they facilitate arises from the wide range of possibilities for controlling the structure and properties achievable. This control over structure and properties can be exerted by using different metals; alloys; compositions within the same alloy; morphologies (uniform or core–shell); surface passivation, termination, ad-atoms, or surfactants, etc. A small sample of these possibilities is shown in figure 1, which

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compiles a few results on different metallic nanoparticles grown by solution methods.

Often, the specifics of the synthesis method itself can lead to different nanoparticles. Although the discussion in this paper does not necessarily pertain to one synthesis process, for clarity we are focusing more on metallic nanoparticles produced in solution via wet chemical reduction (WCR) methods. WCR is a process in which zero-valent metal atoms (generated via reduction of a dissolved metallic salt) nucleate in solution forming small clusters. The clusters can either continue to grow, or dissolve; however, sufficient levels of initial saturation of the solution ensure the formation of increasingly larger clusters, which become stable crystalline nanoparticles. Figure 2 shows schematically the nucleation and growth towards final nanoparticles produced via WCR. This process has gained widespread interest since it can be used for many metals in order to generate nanocrystalline particles with controllable final sizes and with a narrow size distribution. Thus, since WCR often yields reproducible nanoparticle morphologies [19], it has been used to correlate the dependence of structure and morphology on growth kinetics. There are no uniquely established mechanisms for controlling the size and shape of the nanoparticles; specific conditions of the synthesis reactions can take the system from mainly thermodynamic to mainly kinetic regimes, with the greatest level of user control over the final nanoparticles achievable via modifications of the kinetic regimes or factors.

Leaving aside the synthesis chemistry and focusing on the stages of growth, experimental characterization techniques can show, at a minimum, the shape, size, and crystallinity of the nanoparticles – usually as a final product, and occasionally during the growth itself. Real-time tracking of growth requires in situ characterization, while the analysis of the final particles can be done either in situ or ex situ (with the latter being more common and facile). Some of the most used characterization techniques are illustrated in figure 3: X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and others discussed later in this article. Most of these techniques are very useful for characterizing nanoparticles, even though they have not been specifically designed for this purpose. Crystallography, which is understood as the application of diffraction techniques for determining the crystalline structure, takes here an additional component, that of determining the structure and orientation of the facets of a given nanoparticle. Characterization techniques, including crystallographic ones, have been key to the accumulation of knowledge relating the chemical details of the synthesis procedure with the final nanoparticle products [1, 12, 13, 20].
Fig. 3 Common experimental techniques for investigating the crystallography (XRD), the morphology (SEM, TEM), and the atomic structure (HRTEM) of nanoparticles. Reproduced with permission from Refs. [22] (XRD), [23] (SEM), and [13] (TEM, HRTEM).

On a different level, characterization is also important for supporting a physics-based understanding of the growth process. A large body of knowledge seems to fall in a thermodynamic regime in which the nanoparticle shape is given by the Wulff construction, i.e., the solution for minimization of the total surface energy at constant nanoparticle volume [21].

As such, surface energies for a set of facets (usually low-index ones), are sufficient to predict the shape of the nanoparticles with good accuracy. In contrast, in the kinetics-controlled regime, the current understanding does not benefit from a similarly complete theoretical framework that can be traced to readily computable quantities. While there exists a kinematic Wulff construction applicable for some of the experimentally relevant growth conditions, this theory assumes knowledge of the growth velocities along different directions, which cannot be obtained independently from separate calculations (the way surface energies could). Therefore, one cannot predict ab initio the growth for kinetically controlled regimes.

We have hereby come to the purpose our article. Specifically, we attempt to convey the notion that phenomenological models informed by experiments can lead to a fundamental understanding of the growth process and also to at least qualitative predictions of the final nanoparticles grown in solution. We review the basic theories of growth to identify areas where fundamental knowledge is only incipient, and to show how characterization techniques contribute to the development of the field. Knowledge of the growth kinetics, or at least of the mechanism, is important since it can be used to exert new “handles” or controls over shape, morphology and composition of nanoparticles. Where would one look for these new handles? The thermodynamic and kinetic Wulff constructions lead to a multitude of factors that affect the final nanoparticle: these factors have usually been studied independently, but their combinations may be important as well. To give an example, twinning affects the nanoparticle shape/crystallinity, and so does alloying: however, the combination between twinning and alloying has never been reported so far but represents an avenue for future shape control. If one was to pursue correlations between kinetic factors, would the current experimental techniques be sufficient to inform and/or to validate the findings? In order to make this assessment, we propose that the effects of alloying could be investigated in a more direct manner, i.e., one that allows us to use experimental knowledge for building a model or informing a kinematic Wulff construction. The interplay between different factors is intrinsically difficult to study, and the experimental information should ideally be cast into robust models, at least for cases where only one or several factors are involved. There are only a few reports of such kinetic models, recently put forth by some of us [24], as well as by other groups [25].

The remainder of this paper is organized as follows. Section 2 presents the thermodynamic Wulff construction of the equilibrium crystal shape (ECS), along with several variations. Section 3 presents the kinematic Wulff construction, first in a generic way and then using a model based on time-dependent attachment fluxes to specific facets. Of particular relevance for this journal issue celebrating 100 years of crystallography, Section 4 presents the characterization and imaging techniques currently used for gleaning information about size, morphology, specific facets and composition of nanoparticles. Section 5 summarizes our review, and reiterates specific future directions to be explored for controlling the size and shape of metal nanoparticles.

2 Equilibrium particle shape

Certain growth conditions (e.g., low supersaturation post nucleation, sufficiently slow kinetics, sufficiently large nanocrystals, possible thermal annealing, no directing agents in solution, etc.) practically lead to the formation of thermodynamically stable particles. In the WCR process, growth proceeds until the depletion of metallic salts from solution, while controlled addition of new amounts of salt can help increase the nanoparticle size. Under relatively slow growth conditions, the nanocrystals preferentially assume the equilibrium crystal shape, i.e., the
shape that minimizes the total surface energy at constant volume [21]. This is somewhat paradoxical, given that at no point during the process does the nanocrystal have constant volume: it will stop growing when the concentration of the salt decreases sufficiently, and once the growth stops there is no change of the relative extent of the facets. In other words, if thermodynamics wins over kinetics of the process, then the final shapes are very similar to those that would be determined from surface energy minimization, irrespective of the particular synthesis method but under the conditions listed above. This is by far the most used framework of understanding the shape of nanoparticles, and it will be described in some detail in the next section.

2.1 Equilibrium crystal shape: Wulff construction

When considering only discrete crystallographic planes bounding the nanoparticle, the total surface energy is

\[ \Gamma = \sum_i \gamma_i A_i, \]

where the summation is over all the facets \( i \) with normal vectors \( n_i \) of the nanoparticle, and \( \gamma_i \) and \( A_i \) are, respectively, the surface energy (per unit area) and the area of the facets indexed by \( i \) [21]. The summation is performed under the condition of constant volume, \( \sum_i h_i A_i / 3 \), where \( h_i \) are the heights (altitudes) taken from a common reference point inside the nanoparticle to their corresponding facets. Using the Lagrange multiplier technique (one multiplier for the sole constraint), the minimization of \( \Gamma \) with respect to \( A_i \) leads to \( h_i / \gamma_i = \text{constant} \). In other words, the height corresponding to any given facet is proportional to the surface energy of that facet. Knowledge of surface energies for each of the possible planar facets leads to knowledge of the ECS through the thermodynamic Wulff construction [21]: along the prescribed surface normals \( n_i \) emanating from a given origin, heights \( h_i \) are measured so as to be proportional to corresponding surface energies \( \gamma_i \), and then one draws perpendicular planes at the ends of those heights. The internal envelope of those planes constitutes the ECS [refer to figure 4(a)].

In passing, we mention that when the set of orientations present on the surface of the nanoparticles is not discrete, but instead varies as a continuous function of the polar angles, \( \gamma = \gamma(\theta, \phi) \), then the Wulff construction is similar to the one described above [26]. Usually, the polar plots of the surface energy have cusps that correspond to facets, and the regions that are between cusps lead to rounded edges between facets [figure 4(b,c)]. The particles in which rounded edges would have to form are rather large, in the range of hundreds of nanometres to microns in diameter.

2.2 Calculation of surface energies for facets of different orientations

Through the arguments made above, the problem of determining the ECS, essentially the shape of the nanoparticles in conditions dominated by thermodynamics, has been recast as the problem of knowing or determining the surface energies for all or most of the crystalline planes. If some orientations have a low surface energy, then they are likely to appear as facets of the ECS; if not, then their corresponding height \( h \) would be significantly larger than the others, and those facets will be cut-off from the ECS (e.g., imagine figure 4(a) with \( h_2 \) much greater than all other heights \( h_i \)). While this appears straightforward, the new problem of computing surface energies is not quite so. As a first step for
face-centered cubic (fcc) metals, the set of surfaces was reduced to the low-index ones, (001), (110), and (111). These are the ones that exhibit a small number of missing bonds per surface atom, are nominally flat, and hence are likely to experience a low surface stress as well. If surface stress and the effect of atomic-scale relaxation are completely neglected, then the surface energies will be simply proportional to the surface density of missing bonds. As such, the lowest surface energy would be that of (111), and the inequality $\gamma_{(111)} < \gamma_{(100)} < \gamma_{(110)}$ generally holds [28, 29]. The implication is that the shape of the nanoparticle is bounded either by (111) planes yielding tetrahedra or octahedra, or by (111) and (100) planes that generate truncated octahedra: all of these are experimentally observed shapes in a number of cases [1, 13, 20], and a qualitative consistency seems to exist between observations and the estimated surface energies of the low-index metal facets.

However, as more detailed experimental observations are reported and better determinations of the orientations and sizes of the nanoparticle facets can be performed, it becomes desirable to perform more accurate surface energy determinations. This is because the shapes are determined, according to Wulff’s construction, by the precise relative ratios of the surface energies and not simply by general inequalities between them. More accurate surface energy values have been obtained from atomic scale calculations based on either using interatomic potentials within the framework of molecular statics calculations [30, 31], or from density functional theory (DFT) total energy calculations [32–35].

For both molecular statics and DFT relaxations, computation of surface energy starts with the total energy of a periodic slab in two dimensions, with the desired surface normal and the correct periodicity of the surface in two dimensions. There are several versions of surface energy calculations depending on how many faces of the slab are considered. The simplest one is the two-facet slab, in which the surface energy is computed as the excess (with respect to perfect bulk 3-D crystal) energy per unit area that is due to exposing two surfaces:

$$\gamma = \lim_{k \to \infty} \frac{E - N_k \mu}{2A}$$

where $E$ is the total energy of the (relaxed) slab with $N$ atoms and surface area $A$, $k$ is the number of atomic layers in the slab, and $\mu$ is the bulk chemical potential. The large $k$ limit has to be taken to ensure that the two exposed surfaces do not interact significantly with each other by preventing the complete relaxation of the atoms in their vicinities.

Computations of surface energies via various potentials (usually embedded-atom method potentials, EAM) are useful for establishing trends across metals, as well as for calculations of the elastic properties of various orientations [30, 31]. At the level of interatomic potentials, the computations are virtually exact because convergence of the surface energy with the number of atomic layers is easily achievable. The drawback of these calculations is that the accuracy is deemed insufficient and that the EAM-type potentials do not cover all metals and alloys; at this point, the community has all but turned completely to using DFT calculations. Among the thorough works, Ref. [35] reports all low-index surface energies for 60 different metals using DFT. Such calculations have become standard nowadays, owing to widely available computational resources. There are still a few known pitfalls related to the convergence of the surface energy with the number of layers and with the use of the correct chemical potential [36–39].

Interestingly, despite their being at the top of the “food chain” in terms of accuracy, DFT calculations are still occasionally compared with the missing bond model [28, 29]. Enticing in its simplicity of application and not requiring any computational resources whatsoever, the missing bond model continues to be used, or at least discussed. As a recent instance of the missing bond model giving incorrect predictions, we refer to the work of Zhang et al. [34] on the shape of nickel nanoparticles. As shown in figure 5, the missing bond model is a reasonable description of the surface energies only for low-index surfaces, for which the atomic relaxations are relatively small and do not significantly alter the relative stability of different surfaces. However, in the case of high-index orientations, the DFT calculations show significant relaxations, to the point that surface energies are low enough to make it in the ECS (figure 5(c)). More subtly, sometimes it is not only the relaxation that can lead to low surface energies of high-index orientations, but atomic reconstructions at the surface as well: in this case, techniques aimed at determining the surface structure can be employed (e.g., global optimization methods [40–42]) in conjunction with DFT refinements [43–46].

Another important point in regard to surface energies and the choice method for their calculations is the fact that the DFT calculations are done at zero Kelvin, whereas the relevant surface energies for establishing the ECS are at finite temperatures. Some empirical methods have been proposed for including temperature dependence [48], but those do not appear feasible for DFT calculations. Attempting to perform molecular dynamics calculations using DFT will presently require the usage of very thin slabs, leading to errors in the surface...
energy. Conversely, the Wulff construction can be used to extract surface energies at finite temperature from experimental measurements of crystal shapes [47, 49, 50]. Figure 6 shows the differences between the surface energies extracted from experiments at finite temperatures and those computed using DFT at 0 K.

Without a doubt, the use of DFT has led to more accurate computations of surface energies and a more reliable understanding of the ECS of metal nanoparticles. However, the following challenges still remain:

(a) convergence with the number of layers is slow and often oscillatory,
(b) accurate and separate calculations of the chemical potential in bulk 3-D phase are necessary,
(c) DFT calculations are at zero Kelvin with tedious possibilities to extend to finite temperatures,
(d) the accuracy of the pseudopotentials used in DFT remains insufficient for some metals, such as those with \(f\)-electrons and (some of) those the body-centered cubic structures.

2.3 Variations of the Wulff construction

At this point, there is little room for advancement in understanding the ECS of single crystal nanoparticles. Additional effects such as the energy of the corners and edges can be included, but those are corrections and do not significantly alter the knowledge obtained from surface energies alone and Wulff construction. However, there are interesting variations of this construction, which we will discuss in this section.

2.3.1. Twinned Nanoparticles

Twin boundaries often have very low energies, to the point that they are not ruled out by thermodynamics, and can therefore appear in nanoparticles grown in solution. Figure 7 shows examples of such twins. In the presence of twin boundaries, the particle is not strictly speaking single crystal, but rather a polycrystal with low-energy grain boundaries. In this case, a modified Wulff construction was proposed based on early work by Marks [51] to understand the morphology of twinned particles. For simplicity, assume only one twin boundary that separates the nanoparticle into region A and B. The energy of the twin boundary, \(\gamma_t\), is partitioned into \(\alpha\gamma_t\) and \((1-\alpha)\gamma_t\) which are associated with the regions A and B, respectively. Here \(\alpha\) is an initially unknown value. If the nanoparticle is cut along the twin boundary, then each region is a single crystal whose shape can be determined by the regular Wulff construction under the assumption of “known” surface energies (including \(\alpha\gamma_t\) and \((1-\alpha)\gamma_t\) for the two sides of the exposed twin boundary). There are two key factors on which the shape determination in the presence of twin boundaries relies: (a) the optimal shape of the twinned nanoparticle corresponds to local
minima of the surface energy of each of the two regions (A and B), and (b) the area of the twin boundary determined from optimizing separately A and B should match. Numerical solutions for these simultaneous conditions lead to determining the mixing parameter $\alpha$ and the individual volumes of regions A and B. The extension to more twin boundaries is straightforward. While in the case of one twin boundary there always exists a solution with $\alpha = 1/2$ that is forced by the reflection symmetry at the boundary, more complex scenarios are possible for multiple twins [51].

Multiple twin boundaries (figure 7(b)) can also be addressed in a similar fashion. A key discovery made in the case of twinned nanoparticles is that, unlike in the single crystal case, the shape of the particle depends on its size. This occurs because additional strains appear at large sizes, which changes the shape that corresponds to the lowest energy structure. Barnard has modelled the presence of twin boundaries and other deviations from single-crystals in an expansion of the free energy that deals, separately, with contributions from [52]: bulk, surfaces, interfaces or twins, edges, corners, and point-defects. These terms can be introduced sequentially, and the effect of every newly included term is assessed. While tedious, this expansion method correctly predicts the relative stability of nanoparticles with twin boundaries and other defects [52]; its complexity seems to prevent widespread use. More recently, similar expansions that essentially stop at surface and interface energy terms (as opposed to including corners and edges) have resulted in a new Wulff construct for twinned nanoparticles [25]. Such models are useful as a tool to readily assess the effect of changing the surface energies (using stress, adsorbates, etc) on the thermodynamic, size-dependent, shape of the nanoparticles [53].

### 2.3.2. Substrate-supported Nanoparticles

The contact with a flat substrate may dictate the orientation of one of the surfaces or facets of the crystal, namely the one in contact with the substrate. In this case, the basic Wulff construction holds with some modifications: the substrate cuts off the spatial extent of the crystal, which means that the Wulff construction is translated in the direction normal to the substrate and scaled so as to satisfy the condition of constant volume [54]. Similarly, if the supporting substrate is not a plane, but a corner between two planes, the ensuing Wulff-type construction is also straightforward [55–57]. In all cases, the deviations from the basic Wulff construction are straightforward, and the shape of the crystal does not normally depend of its size.

### 2.3.3. Alloy Nanoparticles

An interesting variation of arises in the case of alloys. The problem is the same as in the single crystal case, with the additional complication that we must deal with two atomic species. The nanoparticle is essentially a host material, alloyed with a different species in a certain concentration prescribed globally, i.e. at the level of the entire nanoparticle. There appears to be only one main article [58] setting a theoretical framework for the ECS of alloy nanoparticles. Ringe et al. separate out the surface and volume-specific energies in a surface component and bulk component, and proceed to carrying out the same minimization that led to the original Wulff construction. The minimization is subjected to the constraint of constant volume, and in addition, the overall concentration is constrained and the mass conserved [58]. The minimization looks formally the same as the Wulff construction, with the key difference that the height $h$ of a facet does not only depend on its surface energy (which depends in turn on the concentrations of the alloy at the surface and in the volume), but also on the difference in chemical potentials between a nominal homogeneous alloy and the alloy inside the nanoparticle with the (modified, or depleted) concentration [58]. Without reproducing the detailed equations of Ringe et al., the physical explanation for the effects...
deduced for strong alloys is, in broad lines the following. The component with lower surface energy tends to segregate at the surface, and while this segregation occurs, a concentration gradient develops between the surface and the inside (volume) part of the nanoparticle: this leads to the inside having a concentration that is different than the overall concentration with which the optimization starts! This leads to the difference in chemical potentials mentioned above. If the nanoparticle is not very large, then such depletion becomes important and the heights deviate from those predicted from the basic Wulff construction. Thus, the (small) size of an alloy nanoparticle allows for a major, conceptual deviation from the basic Wulff construction: the shape depends on the size, and this dependence occurs via the compositions variation between the surface and bulk.

Figure 8 exemplifies quantitatively these findings of Ringe et al., showing the effect of composition on the aspect ratio of a cuboctahedron, measured as the ratio of the heights corresponding to the (111) and (100) facets. Furthermore, the presence of surfaces modifies their initially uniform composition either towards surface segregation of one component, or through non-uniform mixing through the bulk of the nanoparticle [58]. These findings have immediate implications for the shape control of the nanoparticles. As it turns out, the composition of the alloy itself can change its shape, and so does size (figure 8). With the community looking for avenues to design ever more clever and reproducible controls over the shape of alloy nanoparticles, this knowledge opens up new possibilities.

Some of these possibilities refer not only to the experimental control of the nanoparticles, but also to fundamental advancements. For example, depending on the alloy and the possibilities to form ordered stoichiometric compounds, the bulk material can remain a disordered alloy, while an ordered alloy (compound) may form at the surface due to spatial compositional variations at fixed overall stoichiometry. In this way, without any special efforts, we would have a core-shell nanoparticle with an ordered phase at the surface surrounding a disordered alloy in the bulk. Issues related to the structure, energy, and stress of the interface will become crucial for specific applications; one would again expect the shapes and properties to depend on size and composition.

3 Models for growth of faceted nanoparticles

3.1. Kinetic Wulff construction

During growth or dissolution, the crystal shape is given by the kinetic (kinematic) Wulff construction [26]: from a chosen origin, rays in each direction $n$ are drawn with the length equal to the growth speed in that direction, $V(n)$. Similar to the thermodynamic Wulff construction, perpendicular planes are drawn at the ends of these rays. The interior envelope of these planes gives the crystal shape at a certain time. This kinematic Wulff construction gives the shape of a particle during growth, requiring as input the growth velocity $V(n)$ as a function of the normal at the surface, $n$. Theoretically, there is no way for such a quantity to be predicted from scratch for any orientation $n$. In principle, the growth velocities could be gleaned from experiments, provided an individual nanoparticle is tracked so its complete shape is recorded as a function of time. It is the case, for example, of vapor phase epitaxy, where direct observation of growing crystals at micron scale [59] leads to complete information about the growth velocities for all relevant directions $n$ for the chosen growth conditions. However, for nanoparticles grown in solution, the difference in length scales makes similar experiments extremely difficult and rare, as they would require frequent time-lapse images of
Two intersecting facets growing at different rates $V_0$ and $V_1$. Faster growth along [001] direction can lead to a decrease in the linear dimension $b_0$ of the (001) facet and an increase in the dimension $b_1$ of the (111) facet. Reproduced with permision from Ref. [24].

3.2. Phenomenological model for facetted nanoparticles

In absence of a theoretical way to compute growth velocity along any given direction and of straightforward quantitative procedures to track size an shape during nanoparticle growth in solution, one has to rely on models for understanding the growth in solution and the ways to control it. The models would have to capture the physics of growth, and in particular the behaviour of the different facets during growth. Recently, we have put forth such a model for Pt and Pd nanoparticles [24], which we review briefly here.

As a first simplification, the model deals with discrete surface orientations and includes the effect of a directing agent (e.g., AgNO$_3$). To fix ideas, we consider two facets, (001) and (111), but the arguments can be carried out in the same manner for any two intersecting facets. Their growth rates are different because of the varying attachment rates of Pt (main metal) and Ag (directing agent) at the two surface orientations considered. It has been hypothesized that Ag hinders the attachment of Pt on the (111) orientation, but not on other orientations –or at least not to the same extent. To account for this in the model, we take different net attachment rates of the Pt atoms, $f_0$ and $f_1$, for the (001) and (111) facets, respectively. These rates are defined as the number of Pt atoms attached per unit area, per unit time. Referring to figure 9, we rationalize the growth of these two facets in terms of the net attachment fluxes. Between times $t$ and $t + dt$, the (001) and (111) facets advance outwards with velocities $V_0 = f_0/\rho$ and $V_1 = f_1/\rho$, respectively, where $\rho$ is the number density in bulk crystalline Pt. The shape at any time $t$ is given by all the facets that are present at that time. When the net fluxes for various surface orientations are different, their linear in-plane dimensions (lengths $b_0$ and $b_1$ in figure 9) will also grow at different rates. These linear dimensions can be computed from geometry, assuming that the corners and edges of the particles are atomically sharp. In the quadrilateral ABCD (figure 9), we have $AB = b_1(t + dt) - b_1(t) = -db_1$, $BC = V_1 dt$, $CD = b_0(t) - b_0(t + dt) = -db_0$, $AD = V_0 dt$, and the angle between AB and AD measures 90° - $\theta$, where $\theta$ is the angle between the [001] and [111] directions. After extending the segment DC until it crosses the line AB at C’ (see figure 9), we obtain $AB ( = db_1)$ as $AB = AC' - BC' = V_1 dt\sin\theta - V_0 dt\tan\theta$. The segment CD ( = -db$_0$) can be obtained in a similar manner, leading to expressions for time derivatives of $b_0$ and $b_1$,

$$\frac{db_0}{dt} = \frac{V_1 - V_0 \cos\theta}{\sin\theta}$$

(1)

$$\frac{db_1}{dt} = \frac{V_0 - V_1 \cos\theta}{\sin\theta}.$$  

(2)

Equations (1–2) show that different regimes can develop during growth. Interestingly, there exists a regime when $db_0/dt < 0$ and $db_1/dt > 0$, in which the characteristic length $b_0$ of the (001) facet decreases. This is depicted in figure 9, which is characterized by $V_1 < V_0 \cos\theta$. In practice, the growth velocities are time-dependent and can be directed by agents such as AgNO$_3$ that affect the growth rates on the (001) and (111) facets in different ways.

We start with the simple and reasonable assumptions that initially the characteristic lengths of the two facets are the same, and the net attachment rates to different facets are also the same. If the net fluxes $f_0$ and $f_1$ are known as functions of time, then Eqs. (1–2) can be integrated to yield the characteristic lengths $b_0$ and $b_1$ as functions of time for the entire nanoparticle evolution following the moment at which it developed facets. While time-dependent information regarding the fluxes $f_0$ and $f_1$ is hard to obtain from first-principles calculations or even from experiments, we can make reasonable assumptions to model them. For example, $f_1$ should decrease to zero fairly rapidly, which is indicative of the Ag “poisoning” of the (111) facets; $f_0$ should decrease as well, only at a much slower pace than $f_1$. We adopt an exponential
Growth model predictions for the evolution of the characteristic lengths of the (001) and (111) facets in the presence of Ag in solution. (a) Equal time constants, \( \tau_1 = \tau_0 \), leading to the presence of both (001) and (111) facets in the final shapes, i.e. cuboctahedra. (b) At higher ratio, e.g. \( \tau_1 = \tau_0 / 20 \) the (001) facets disappear and the final shape is bounded by (111) facets, i.e. octahedra. Reproduced with permission from Ref. [24].

The decay model for the two fluxes, with different time constants \( \tau_0 \) and \( \tau_1 \) (\( \tau_1 < \tau_0 \))

\[
f_{0,1} = C_{0,1} \exp\left(-t/\tau_{0,1}\right)
\]

where \( C_{0,1} \) are the initial values of the two decaying fluxes. With this model for net fluxes, Eqs. (1–2) can be integrated to yield:

\[
\begin{align*}
  b_0(t) &= b_0(0) \\
  &\quad + C_1 \tau_1 \left(1 - \exp\left(-t/\tau_1\right)\right) - C_0 \tau_0 \left(1 - \exp\left(-t/\tau_0\right)\right) \cos \theta / \rho \sin \theta \\
  b_1(t) &= b_1(0) \\
  &\quad + C_0 \tau_0 \left(1 - \exp\left(-t/\tau_0\right)\right) - C_1 \tau_1 \left(1 - \exp\left(-t/\tau_1\right)\right) \cos \theta / \rho \sin \theta
\end{align*}
\]

Depending on the time constants \( \tau_{0,1} \), several types of final shapes bound by (001) and/or (111) facets: tetrahedra, truncated tetrahedra, octahedra, and cuboctahedra. For example, when the time constants \( \tau_0 \) and \( \tau_1 \) are relatively close to one another, we obtain cuboctahedra as final shapes [figure 10(a)]. In experiments, control over the fluxes \( f_1 \) and \( f_0 \) is exercised through the concentration of the directing agent, AgNO\(_3\), in solution. In the case of Pt, Ag may attach to one or both of the (001) and (111) facets, preferentially poisoning only the (111) surface orientation (i.e., effectively blocking the growth along the [111] direction). The regime of lower Ag concentrations in solution is modeled by setting the time constants to have similar magnitudes; this leads to the presence of both (111) and (001) facets on the asymptotic shapes (cuboctahedra in figure 10). In order to have only (111) facets, we increase the difference between the time constants \( \tau_1 < \tau_0 \), thus modeling the regime of higher Ag concentration in experiments. As a result, the net flux on the (111) facets decays to near-zero much faster than the net flux \( f_0 \) on (001) facets, whose decrease is only due to the consumption of the Pt atoms from solution due to the growth of the NPs. This case is shown in figure 10(b), where the (001) facets monotonically decrease and vanish altogether past a certain moment.

### 3.3. Discussion on coupling between growth models and experiments

The utility of the model discussed in the previous section describing Pt and Pd nanoparticles with directing agents in solution appears limited, since the fluxes \( f_{0,1} \) cannot be measured experimentally. They cannot be easily derived from theoretical approaches either. As far as the predictions of shape are concerned, it is worth recognizing that the specific (exponential) form of the fluxes is not particularly important, and that other expressions for fluxes can also provide a qualitative understanding of the directed growth regimes (figure 10) if they incorporate the slow-down of the growth along [111] in some way.

However, if we are to make any reasonable quantitative predictions of size, then this model or any other should be “informed” by experiments, i.e. calibrated so as to reproduce either the majority or the distribution of nanoparticles for a small set of well-controlled experimental runs. In this way, the experimentally controllable concentrations of the precursor and the directing agent will be mapped onto the parameters of the model, i.e. the time constants that appear in the expressions of fluxes \( f_{0,1} \). Schematically, this is shown in figure 11. Such calibration is not trivial, and is yet to be achieved. It is important because it aims to endow the model with truly predictive capabilities, thus making it useful for determining various growth regimes outside the set of calibration runs. Armed with the correspondence between the time constants and concentrations in solution, the model would be used to map out all the achievable experimental conditions with very little cost, which is...
useful if the production of “tailored” nanoparticles is desired.

A note regarding the specific coupling with experiments is in order. Given that the output of the model consists in expressions for the sizes of various facets as functions of time, the calibration experiments will have to feed time-lapse information of the particle size distribution and concentrations of the precursor and directing agent. In-situ real-time measurements (e.g. via small angle X-ray scattering) of particle size distributions are probably the most suitable way to achieve the calibration of the model, while concentrations can be directly monitored in solution. This method, along with others, will be described next.

4 X-ray characterization of nanoparticles

The large ratio of surface atoms to bulk atoms in nanoparticles affects their physical, chemical, and catalytic properties. X-ray characterization is well suited to examine nanoparticles since the characteristic dimensions of both the nanoparticles themselves and their constituent crystal structure are on the same order as the wavelength of X-ray radiation. However, the relatively large number of surface atoms of each particle complicates the X-ray characterization of nanoparticles. A wide variety of methods that use high intensity X-ray sources, such as synchrotron and free electron laser sources, have been developed to overcome some of these limitations and extend X-ray characterization beyond $\theta/2\theta$ diffraction.

The aim of this review is not to provide extensive discourse on all advanced X-ray characterization techniques. Rather, this section subdivides into two (broad and somewhat overlapping) categories a few techniques of interest in examining particular features that are important for characterizing catalytic nanoparticles: (i) crystallography, structure, and size, and (ii) chemical environment and electronic structure.

4.1 Crystallography, Structure, and Size Distribution

XRD has long been a staple of materials characterization. While a majority of the characterization methodologies that follow require synchrotron radiation light sources, XRD, small, and ultra small angle X-ray scattering (SAXS/USAXS) do not. The features to which each technique is sensitive is related to the scattering vector $q$,

$$q = \frac{4\pi \sin \theta}{\lambda}$$

where $2\theta$ is the angle of between the diffracted and incident rays, and $\lambda$ is the radiation wavelength. At angles greater than $\sim 10^\circ$, XRD probes periodic structural features between 0.14 and 1.4 Å, providing information on the crystal structure through Bragg’s law of diffraction. SAXS is relevant for exploring particle size, size distribution, specific surface area, and fractal dimension for structural features ranging from 1 to 1000 nm. Such features are particularly relevant in studying catalytic nanoparticles. Figure 12 shows an example of the use of SAXS to determine particle size distributions (PSD) via the tangent-by-tangent method [60]. Furthermore, SAXS can be used to obtain real-time information about the size and size distribution of nanoparticles during growth. Recent work by Abecassis et al. [61] employed real-time in-situ probing of CdSe quantum dots to suggest that the
The rate-limiting step in the growth is the thermal activation of selenium.

By carefully tuning the incident photon energy, X-ray absorption fine structure (XAFS) measures absorption events associated with detailed electronic information, including extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES). These techniques rely on the scattering of core shell photoelectrons by neighboring atoms, and are therefore sensitive to the local atomic structure, including surface structure, rather than long-range quasi-periodic structures explored by XRD and SAXS. Analysis of XANES spectra focuses on multiple photoelectron scattering events within approximately 50–100 eV of the X-ray absorption edge, including pre-edge absorption. EXAFS explores the oscillations from scattering events at energies where XANES ends and extends several hundred eV toward higher energies.

Both XANES and EXAFS are sensitive to the radial arrangement of atoms with respect to the absorbing atom [62]. Because XANES is sensitive to multiple scattering events [63], it can contain information on more complex structures, such as bond angles and bond shortening at nanoparticle surfaces [64], than the radial distribution function calculated from EXAFS. Together, EXAFS and XANES can provide a clear picture of materials evolution during physicochemical transformation, such as particle growth [65] or, as in figure 13, electrochemical reduction of CuO [63]. XAS has been used by Chan et al. [66] to measure the kinetics of cation exchange in CdSe nanoparticles (CdSe to Ag2Se). The K-edge adsorption spectra of Se showed the progress of the cation exchange over hundreds of ms without significant intermediates. The experiments of Chan et al. demonstrate the power of microfluidic X-ray techniques for reactions in which changes in local bonding or oxidation states occur.

While much useful data may be elicited from X-ray diffraction, loss of phase information (the “phase problem”) prevents calculations of atomic positions from direct Fourier inversion of the reciprocal space diffraction data into direct space atom coordinates. In addition to the iterative “direct” methods [67], several techniques have been developed to recover this phase information and allow for determination of real-space atomic coordinates from diffraction data, among these, X-ray standing wave (XSW) atomic imaging and X-ray holography: these are summarized in figure 14.

Fig. 13  (a) XANES spectra for reduction of CuO in H2 showing a clear pre-edge peak indicative of CuI+. (b) Inverse Fourier transform of EXAFS spectra yields the real-space pair correlation function, showing the transition from Cu–O bonding at low temperatures to Cu–Cu at high temperature. Reproduced with permission from Ref. [63].

Requiring extensive sample preparation, XSW atomic imaging depends on an atomically flat, single crystal substrate of known crystallography and orientation to construct the real-space electron density of the substrate itself and any nanoparticles it supports. Specific H = hkl diffraction establishes a strong electric field with a modulation that matches the d-spacing of the selected Bragg diffractions; this provides the phase information. The X-ray fluorescence-selected atoms provide the Fourier intensity. Thus, the Fourier series is built up term-by-term from each H diffraction for atoms in the supported nanoparticle and for the substrate [68]. The result is a 3D reconstruction of the electron density of the sample.

In X-ray holography, a sample is rotated with respect to both the light source and the detector, which results in a modulation of the fluorescence intensity. The measured fluorescence must be filtered in order to eliminate shape-dependent absorption, changes to the relative orientation between crystal and detector during rotation, and Kossel lines that form from XSW. From the remaining holographic image, figure 14 (II, a-d), the real space electron density is constructed using the Helmholtz-Kirchoff formula [69].

Advances in high intensity free electron laser (FEL) photon sources allows for single shot, 3D imaging of nanoparticles, dislocations, defects, and time-dependent phenomena. X-ray coherent imaging uses femtosecond FEL pulses to expose samples to an X-ray flux beyond the damage initiation threshold, but over
such a short duration, on the femtosecond timescale, that diffraction occurs before the onset of radiation damage. These techniques are the subject of a recent review by Miao, Ishikawa, Robinson, and Murnane [70]. Although less susceptible than biological systems, nanoparticles exposed to high intensity light sources can result in radiation-induced damage [71].

4.2 Chemical environment and electronic structure

The ability of X-rays to scatter valence and core shell electrons enables a direct route to investigate the electronic structure of a sample. To examine the surface of a sample, X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) provide chemical information to a depth of ~10 nm on composition, enrichment or depletion of specific elements, and if present, the thickness of a surface coating. Resonant inelastic X-ray scattering (RIXS, also known as resonant X-ray emission spectroscopy, RXES) is able to probe the bulk of the sample, providing information on composition, as well as to even differentiate changes to an element’s chemical environment.

When an incident X-ray excites a core shell electron to produce a photoelectron, the difference in energy between the incident photon and the kinetic energy of the photoelectron is characteristic of the atomic species and the principal quantum number of the core shell (K, L, or M) from which the photoelectron was ejected. Both XPS and AES rely on the generation of a photoelectron. A monochromatic X-ray light source excites a photoelectron emission across a range of energies [71], as shown in figure 15 for CdS nanoparticles. Closer examination of these XPS peaks can reveal small changes in the electronic energy levels associated with changes in surface-level bonding. Using high resolution XPS of CdS nanoparticles, Winkler et al. correlate the effect of particle size to surface oxidation (figure 16). They reveal that, due to restructuring, the surface sulfur of small (2.7 nm) diameter CdS nanoparticles does not oxidize under the same conditions as that in larger nanoparticles [72]. As described in the previous subsection, X-ray absorption spectroscopy techniques (XAS) such as EXAFS are also sensitive to chemical environment at small length scales.

Using high intensity X-ray light sources, RIXS is able to probe more than 100 nm into the sample bulk. Near resonance, where the energy of the incident photon corresponds to the transition between a core state and an empty valence state, the absorption cross-section can increase by several orders of magnitude. In direct RIXS, a core electron is excited into an empty valence state. Subsequently, an electron from a filled conduction state decays into the core hole, emitting an X-ray photon of lower energy than the incident photon. The extreme sensitivity of RIXS allows exploration of a wide scattering phase space, from ~10 meV phonon interactions to > 1 eV
Fig. 16 High resolution XPS of CdS nanoparticles showing the disappearance of a S–O bonding orbital at small, 2.7 nm particle sizes. Reproduced with permission from Ref. [72].

crystal field splitting and charge transfer. Figure 17 demonstrates the sensitivity of RIXS; it is able to differentiate cupric cations based on the < 0.6 Å change in their bond lengths with oxygen in CuO, La₂CuO₄ (LCO), and malachite (Cu₂(OH)₂CO₃) [73].

Although only a subset of available methods, these few techniques demonstrate the ability of X-ray characterization to explore properties that are of particular interest to catalytic nanoparticles: surface structure, surface chemistry, crystal structure, presence and structure of defects and particle orientation, shape and distribution.

5 Concluding remarks

As described above, crystallographic and microscopy techniques can show the shape, size, and crystallinity of the nanoparticles – usually as a final product, and, not as frequently, during the growth itself. These techniques are used mainly to assess or characterize the final product. The thermodynamic Wulff construction and its variants remain the main framework that is currently applied to nanoparticles. While reviewing thermodynamic approaches to understanding the equilibrium shape of nanoparticles grown in solution, we encountered several issues likely to be pursued by the community in the future. First, the finding by Ringe et al. [58] that alloy nanoparticles develop a concentration difference between the surface and inside volume has led to surface energies (and hence shape, via Wulff construction) that depend on the alloy concentration; furthermore, for sufficiently small nanoparticles, the shape depends on the size as well. This is likely to be pursued for various combinations of metallic elements exhibiting various tendencies for mixing. Secondly, the effect of overall alloy concentration on the propensity to create twin boundaries or to form core–shell morphologies may appear in certain binary nanoparticles. To the extent that these effects turn out to be robust, they may be used for designing new nanoparticles.

As a common practice, sets of several characterization techniques such as those mentioned in Sections 1 and 4 are often used to complement each other in investigations of structure, morphology, and properties of nanoparticles. Regarding the kinetically controlled growth regimes, a key suggestion of this article is that the characterization techniques could be used in conjunction with phenomenological models in order to understand the effects of directing agents in solution. Theoretical models, including those presented here, usually do not focus at all on particle-size distributions but rather on shape and size. However, a future direction in modeling may consider the statistical variation of some of the
parameters; for example, the size of the nuclei should be a statistical variable for the growth model. Statistics obviously becomes important when using experimental particle-size distributions (and their variation in time) to calibrate growth models. The output of a model should then be a distribution of shapes and sizes. Such output can be compared with time-lapse particle-size distributions from experiments, first for validation of models so that they can be used in the rational design of metal nanoparticles.

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Key words. metallic nanoparticles, nanocrystals, Wulff construction, surface energies, characterization.

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