



Review

Nanocrystal conversion chemistry: A unified and materials-general strategy for the template-based synthesis of nanocrystalline solids

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ABSTRACT

The concept of nanocrystal conversion chemistry, which involves the use of pre-formed nanoparticles as templates for chemical transformation into derivative solids, has emerged as a powerful approach for designing the synthesis of complex nanocrystalline solids. The general strategy exploits established synthetic capabilities in simple nanocrystal systems and uses these nanocrystals as templates that help to define the composition, crystal structure, and morphology of product nanocrystals. This article highlights key examples of “conversion chemistry” approaches to the synthesis of nanocrystalline solids using a variety of techniques, including galvanic replacement, diffusion, oxidation, and ion exchange. The discussion is organized according to classes of solids, highlighting the diverse target systems that are accessible using similar chemical concepts: metals, oxides, chalcogenides, phosphides, alloys, intermetallic compounds, sulfides, and nitrides.

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Contents

1. Introduction	1509
1.1. Metals → metals	1511
1.2. Metals → oxides	1511
1.3. Metals → chalcogenides	1512
1.4. Metals → phosphides	1515
1.5. Metals → alloys	1515
1.6. Metals → intermetallics	1516
2. Intermetallics and chalcogenides as reactive templates.	1518
2.1. Oxides → sulfides	1520
2.2. Oxides → nitrides	1520
3. Conclusions and future outlook	1521
Acknowledgments	1521
References	1521

1. Introduction

When solids are dimensionally confined in the nanometer size regime, many interesting characteristics emerge that can be different from bulk analogs of the same material. One classic example is quantum dots, in which the carriers or excitons are confined in three dimensions and whose optical properties vary as

a function of size [1]. Similarly, the optical properties of gold nanoparticles can be tuned by adjusting the nanoparticle shape and size due to surface plasmon resonance effects [2–4]. The properties of many other materials change upon dimensional confinement as well, including magnetism [5,6], catalysis [7,8], and mechanical properties [9,10]. Importantly, the unique properties of nanoscale solids can be harnessed for a variety of applications, including information storage [11,12], medical and biological imaging [13–15], and catalysis for energy [16–18] and chemical [19] applications. Because of their size and solubility, nanoscale solids are also ideal precursors to thin films [20–22], functional devices [23], coatings [24–26], and templated materials

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[27–29] that can be formed using inexpensive benchtop solution processing techniques.

A large number of methods have been developed for synthesizing nanocrystalline solids. Physical “top down” methods such as ball milling [30,31] and laser ablation [32] are among the most straightforward, since they involve the direct size-reduction of already-made solids. While general for many classes of solids, it can be extremely difficult to control size, size dispersity, and morphology using these methods, which limits their utility. Other common synthetic strategies for nanocrystalline solids include gas-phase condensation [33,34], sputtering [35,36], and flame hydrolysis [37,38]. Thin film deposition and annealing methods can also be used to form nanoparticles supported on a substrate [39].

Chemical methods are also widely used for synthesizing nanocrystalline solids [40,41]. Among the variety of techniques used, the most common involve reduction of metal salt precursors [40], thermal decomposition of metal–organic complexes [42,43], co-precipitation [44], nucleation within inverse micelles or microemulsions [45], and solvothermal reactions [46]. Typically reactions are performed in the presence of organic stabilizers, which help to passivate the nanocrystal surface [47,48], control its size and surface chemistry for solubility and surface accessibility [49,50], and influence growth directions to facilitate shape control [51,52]. Under appropriate conditions, solution methods allow for tight control over the size and size dispersity of nanoparticles, as well as their shape [53,54]. Gram-scale quantities of nanocrystals can also be produced [55,56].

Solution chemistry methods have many advantages over non-chemical methods for nanocrystal formation, including the ability to rigorously control size, size dispersity, and shape, and also for imparting solubility as required for processing and applications. However, there are several important disadvantages of these chemical methods. For example, solution methods tend to not be materials general. While a large number of solids have been accessed in nanocrystalline form, it is often empirical results and system-dependent details that permit the synthesis of high-quality shape- and size-controlled nanocrystals, rather than more rational methods. Indeed, even chemically similar solids can nucleate and grow very differently in solution under similar conditions. Thus, while general guidelines can be rationalized, and in some cases more-detailed understanding achieved, overall the synthesis of high-quality nanocrystals is carried out on a case-by-case basis with optimization necessary for each target—each size, size dispersity, shape, and material. Some nanocrystal synthesis methods are becoming more general [57–59], but it is still difficult to achieve the on-demand synthesis of an arbitrary nanocrystal system, particularly for multi-element solids with a desired shape and size.

Because of these synthetic challenges, most high-quality nanocrystals prepared using solution chemistry methods are limited to relatively simple solids. Most high-quality nanocrystals that have been reported fall into a handful of categories with a few well-studied targets in each, such as transition metals (e.g. Au, Ag, Pt, Pd, Co), metal oxides (e.g. ZnO, Fe₃O₄, TiO₂), and metal chalcogenides (e.g. CdS, CdSe, ZnS). These and other systems that are reaching synthetic maturity have been chosen and studied for good reason, e.g. important size-dependent physical properties that are interesting targets for scientific study and also useful for emerging applications. However, from the perspective of solid-state chemistry, these systems are primitive—primarily single elements, simple alloys, metal oxides with one or two metals, and single metal chalcogenides. Applying the same synthetic concepts to more complex solids is challenging, since homogeneous co-nucleation of two, three, or more elements with controlled composition and phase formation (crystal structure) is required

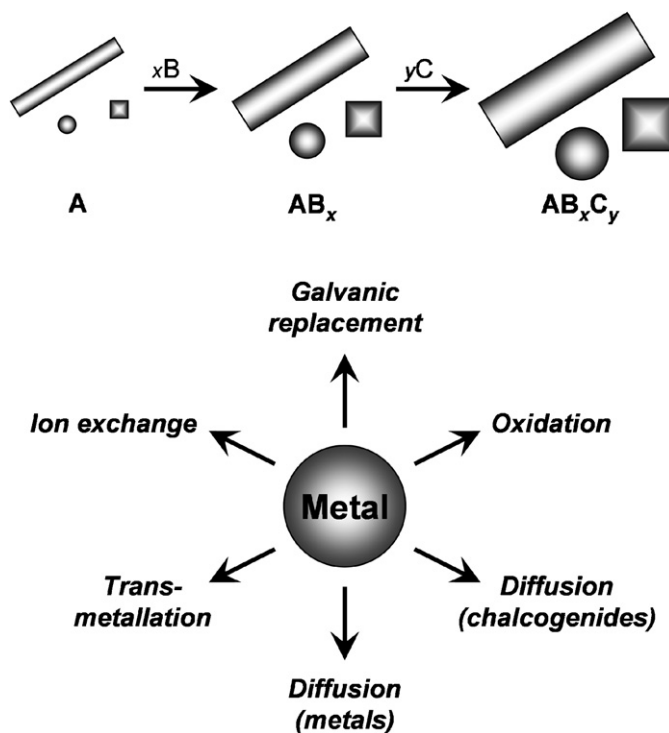


Fig. 1. Top: schematic depicting the goal of template-based nanocrystal conversion reactions—morphological and compositional retention through multiple chemical transformations that yields multi-element shape-controlled nanocrystals. Bottom: overview of common solution-based strategies for chemical transformations of nanocrystals.

in a nanometer-scale solid using soluble metal salts or metal complexes that typically have different reduction potentials, reduction kinetics, decomposition temperatures, ligand-binding affinities, reactivities, electronegativities, etc. Superimposed on this challenge is shape control, which further requires different growing crystal faces to be selectively stabilized and destabilized to facilitate anisotropic (non-spherical) growth.

Given these challenges, it would be ideal to find an alternate way of forming high-quality nanocrystals that is less complex synthetically and is applicable to a wide range of solids. One solution that addresses these synthetic challenges is the concept of “nanocrystal conversion chemistry,” which is highlighted schematically in Fig. 1. In this approach, nanocrystals that are straightforward to synthesize are used as templates that are converted, via chemical reactions, into different types of nanocrystals. The nanocrystal “reactants” serve as compositional, and in many cases morphological, templates that help to define the composition and morphology of the “product” nanocrystals.

Many types of chemical reactions are applicable to nanocrystal systems, providing a toolbox of techniques for the chemical modification of existing nanocrystals to form nanocrystals with morphological, compositional, or structural features that are otherwise challenging or impossible to prepare (Fig. 1). Galvanic replacement reactions are widely used to template the formation of metal or alloy nanocrystals [53,60–62]. These reactions proceed by sacrificially oxidizing a core metal nanocrystal by reacting it with a metal salt species that has a more positive reduction potential. Transmetalation reactions involve the reaction of a metal nanoparticle (M_1) with an organometallic complex (RM_2) and result in the formation of core–shell nanoparticles (e.g. Co/Pt) that can be further transformed to alloys and intermetallic compounds (e.g. CoPt) upon heating [63,64]. Other metal

reactions that transform metal nanoparticles into derivative solids while retaining morphology including oxidation reactions and diffusion-based reactions with chalcogenide reagents. For example, simple diffusion-mediated oxidation reactions of metal nanoparticles can be used to synthesize high-quality metal oxide nanoparticles such as CoO [65], Fe₂O₃ [66], and Fe₃O₄ [67,68]. Other diffusion-based methods can be used to convert metal nanoparticles to metal sulfides and other chalcogenides [69,70]. These strategies can also produce hollow nanocrystals via a nanoscale analog of the Kirkendall effect [69–71] that is well established in bulk solids and thin films [71,72]. Ion exchange reactions that preserve the nanocrystal framework are also applicable to certain systems, e.g. the reversible transformation of shape-controlled CdSe nanocrystals into Ag₂Se [73].

This concept article, which is not intended to serve as an exhaustive review of all nanocrystal transformations reported to date, highlights key examples of the use of chemical reactions to convert one type of nanocrystal into another. The focus is largely on solution chemistry strategies, but some dry powder processing techniques are also mentioned when appropriate. This concept of conversion chemistry using nanocrystal templates provides a straightforward framework for expanding the compositional and morphological complexity that is achievable in nanocrystalline solids using solution chemistry methods. To emphasize the potential generality of the concept and the range of systems it has been applied to, this article is organized according to classes of solids, starting with single-element systems and moving progressively to more and more complex multi-element systems. While the focus is on generating nanocrystals, these synthetic concepts are also interesting from a solid-state chemistry perspective where the generation of nanoscale solids is not the goal. The ability to carry out reactions on solids using low-temperature solution chemistry techniques, in a regime where solid–solid diffusion is not the rate limiting step in the formation of a product phase, has the potential to generate non-equilibrium solids that cannot be formed, or are not stable, using more traditional high-temperature methods.

1.1. Metals → metals

The most chemically simple nanocrystal systems are the elements, and late transition metals in particular have received the most synthetic attention. Solution chemistry methods are routinely used to synthesize high quality and often shape-controlled metal nanocrystals. Using such strategies, it is possible to generate high-quality monodisperse spherical nanocrystals of several metals, including Au [74,75], Pd [58,76,77], Ag [58,75,78], Pt [59], Ru [79–81], Co [51,82,83], Ni [84], and some post transition metals such as In [85], Bi, and Sn [86]. Some degree of additional shape control is also possible in certain cases, including Ag [54,87,88], Pd [89,90], Pt [91–93], Au [55,94], Co [42,51], and Rh [95,96]. Despite this synthetic maturity for a handful of elements, there are notable limitations. For example, while it is possible to use direct solution chemistry methods to generate metal nanocrystals with shapes that include spheres [58,97], cubes [98,99], triangles [90,100], hexagonal platelets [90], disks [101], tetrahedra [87,102], octahedra [103,104], multipods [94,105], rods [106,107], wires [107], and right-bipyramids [88], it is generally not possible to access hollow nanocrystals using this strategy. Hollow nanocrystals, which have nanocrystalline shells with no material in the center, are desirable for catalysis because of their increased surface area and their minimal use of metals in the actual nanocrystal, which is particularly important for expensive catalytic elements such as Pt and Au.

Metal nanoparticles can be used as templates to synthesize hollow metal nanocrystals through galvanic replacement reactions (Fig. 2). For example, Ag nanoparticles have been used to form hollow Au and Pt nanoparticles in aqueous and organic media. Xia and co-workers used monodisperse poly(vinylpyrrolidone) (PVP) stabilized Ag nanocubes to produce hollow Au nanocubes or nanoboxes (~100 nm) when reacted with aqueous HAuCl₄ [53]. Other morphologies of Au could also be accessed including triangles, rods, wires, and spheres, as well as Pt and Pd hollow wires [62]. In contrast to the aqueous reaction, Yin et al. [108] found that when smaller Ag nanoparticles (~10 nm) were used as templates in organic media, the exterior shape of the Au hollow structure changed from spherical to faceted or truncated octahedra. Interestingly, multi-faceted Ag nanoparticles reacted with HAuCl₄ in chloroform resulted in AgAu alloys with nanoring or nanocage morphologies [109]. Sastry et al. [110] synthesized Au and Pt hollow spheres by a phase transfer reaction of Ag nanoparticles into chloroform using octadecylamine (ODA) followed by phase transfer of aqueous HAuCl₄. Pt hollow spheres were formed in the same manner except benzyldimethylstearyl ammonium chloride was used as the phase transfer agent [110]. Co nanoparticles synthesized by NaBH₄ reduction have also been used as templates to synthesize hollow Au spheres [111], Pt spheres [112], and Au/Pt bimetallic tubular nanoparticles [113]. Under an applied magnetic field Co nanoparticles were aligned in a chain and used as a template to form hollow chains of Pt, Au, and Pd [114]. In these examples, nanocrystal conversion chemistry (predominantly galvanic replacement) facilitates the formation of metal nanocrystals with morphologies that cannot be accessed using more direct methods.

1.2. Metals → oxides

Metal nanocrystals can be converted to metal oxide nanocrystals, typically via oxidation in solution, oxidation by post-synthesis annealing, or oxidation by other methods such as an electron beam. Only the oxidation of metal nanocrystals in solution will be discussed since the focus is on solution-based nanocrystal transformations. These conversion reactions are typically carried out by exposing metal nanocrystals to a mild oxidizing agent while still in solution, under conditions where the nanocrystals remain stabilized and dispersed (Fig. 3). For example, Hyeon and co-workers used trimethylamine oxide as a mild oxidant for the conversion of Fe nanoparticles to γ -Fe₂O₃ [66]. These γ -Fe₂O₃ nanocrystals are highly monodisperse, and readily assemble into three-dimensional superlattice structures. Woo and co-workers also synthesized mixed-phase γ -Fe₂O₃-Fe₃O₄ by aeration of Fe colloids made by thermal decomposition of Fe(CO)₅ [115].

Similarly, O'Brien and co-workers synthesized Cu₂O nanocrystals by allowing Cu nanocrystals dispersed in hexanes to slowly oxidize under ambient conditions [116]. The resulting Cu₂O nanocrystals are monodisperse with tunable sizes, and as for the Fe₂O₃ nanocrystals prepared by oxidation of Fe nanocrystals [66], can assemble into three-dimensional superlattices. Hyeon and co-workers synthesized Cu₂O-coated Cu nanocrystals using a similar strategy [117], and these nanocrystals are active catalysts for Ullmann-type amination coupling reactions of aryl chlorides. Alivisatos and co-workers synthesized hollow CoO nanocrystals by oxidizing Co nanocrystals in solution via bubbling O₂/Ar [69]. They also demonstrated that this approach could be applied to core–shell structures, selectively oxidizing the Co shell to CoO in Pt-core Co-shell nanocrystals. This reaction produces catalytically active Pt nanocrystals encapsulated by a hollow shell of CoO in a complex yolk-shell morphology, which is difficult to achieve using other synthetic methods [69].

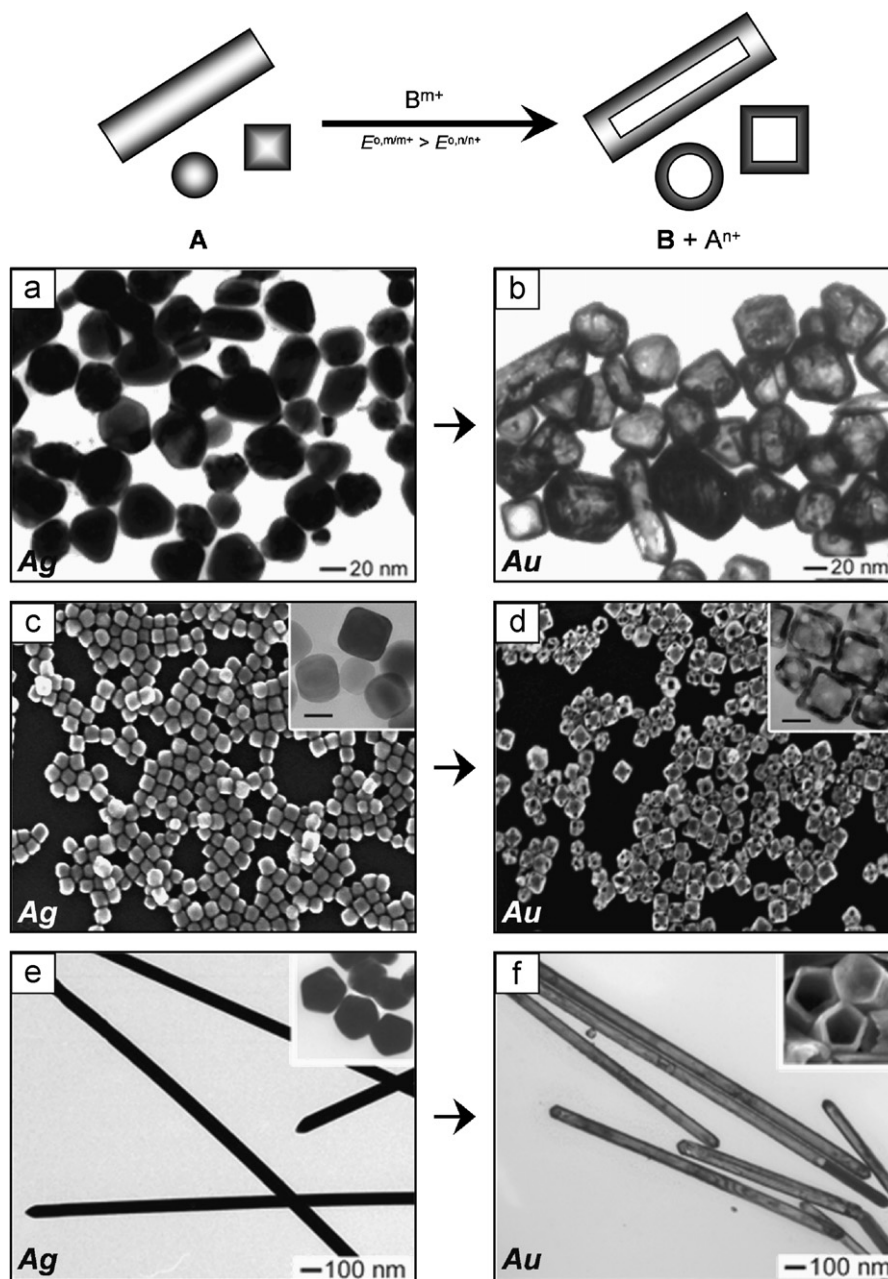


Fig. 2. Top: schematic depicting the galvanic replacement process for converting one type of metal nanocrystal into another. Bottom: TEM micrographs of representative chemical transformations of metal nanocrystals using galvanic replacement reactions: (a) Ag nanoparticles converted to (b) hollow Au nanocrystals, (c) Ag nanocubes converted to (d) hollow Au nanocubes, and (e) Ag nanowires converted to (f) hollow Au nanowires. The scale bars in the insets to panels (c) and (d) are both 20 nm. Reproduced with permission from Ref. [53b] (panels a and b, copyright 2002, American Chemical Society), Ref. [53c] (panels c and d, copyright 2005, American Chemical Society), and Ref. [61] (panels e and f, copyright 2004, American Chemical Society).

Synthesizing metal oxide nanocrystals via oxidation of metals to oxides is useful for accessing intricate morphologies and in some cases accessing phases that may not normally form under direct-synthesis conditions. However, the oxidation process can introduce twinning and polycrystallinity into the product nanocrystals that was not present in the metal nanocrystal templates. In addition, some degradation of morphology can occur during conversion of the metal to the oxide. However, this approach is complementary to direct-synthesis methods, which can also be used to produce metal oxide nanocrystals [118–123], and each can be used for designing distinct features into the product nanocrystals.

1.3. Metals → chalcogenides

Similar to the oxidation reactions, metals can be converted to metal chalcogenides using a variety of solution chemistry reactions. For example, Alivisatos and co-workers studied the transformation of Co nanocrystals to hollow Co_3S_4 and Co_9S_8 in detail (Fig. 3e and f) [69,70]. These reactions involve the diffusion of sulfur into the Co nanocrystals, usually by reacting the nanocrystals with elemental sulfur in a mixture of *o*-dichlorobenzene, tri-*n*-octylphosphine oxide, and oleylamine at 120–182 °C (although the reaction will also occur very slowly at room temperature). In addition to forming Co_3S_4 and Co_9S_8

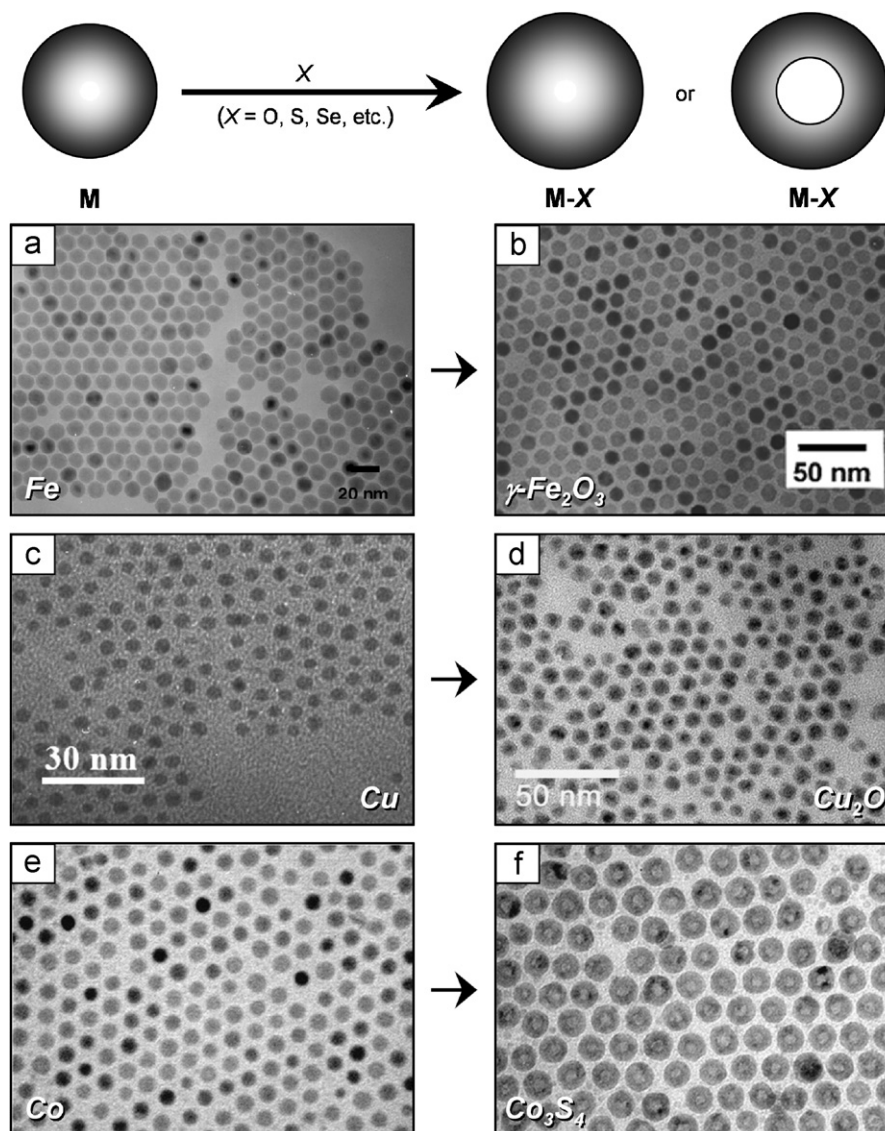


Fig. 3. Top: schematic depicting the solution-mediated reaction of metal nanocrystals (M) with O, S, and Se (X) to produce dense or hollow M-X nanocrystals. Bottom: TEM micrographs of representative chemical transformations that produce metal oxides and sulfides using solution chemistry reactions: (a) Fe nanocrystals converted to (b) γ -Fe₂O₃, (c) Cu nanocrystals converted to (d) Cu₂O nanocrystals with a thin CuO shell, and (e) Co nanocrystals converted to (f) hollow Co₃S₄ nanocrystals. Reproduced with permission from Ref. [66] (panels a and b, copyright 2001, American Chemical Society), Ref. [116] (panels c and d, copyright 2005, American Chemical Society), and Ref. [69] (panels e and f from Yin et al., Science 304 (2004) 711–714. Reprinted from permission of AAAS.)

nanocrystals, the morphologies generated by this reaction are generally hollow [69,70]. The hollow nanocrystals form via the Kirkendall effect, in which a junction between two materials with different diffusion rates results in voids forming in the material that diffuses faster [71,72,124]. In nanocrystals, these can coalesce to create a hollow particle. Similar reactions with selenium generate hollow CoSe nanocrystals [69]. An important benefit of using this method to form hollow nanocrystals is that no sacrificial template is necessary. Furthermore, monodisperse metal nanocrystals template monodisperse hollow chalcogenides, so the size and dispersity of the product can be controlled by the template. However, the products often have polycrystalline shells despite the single-crystal nature of the template nanocrystals due to the formation of multiple chalcogenide nucleation sites during the reaction [125]. Similar reactions of Ag and Cu nanowires with sulfur or Na₂S generate Ag₂S and Cu₂S nanowires [126,127].

Another approach to form metal chalcogenide nanocrystals via conversion chemistry is to react chalcogenide nanocrystals with metal reagents, rather than reacting metal nanocrystals with chalcogenide reagents as mentioned above. For example, selenium nanospheres and nanowires can be converted to a variety of metal selenides, such as Ag₂Se, CdSe, RuSe₂, and Pd₁₇Se₁₅, using reactions with metal cations in solution [125,128–130]. Single-crystal selenium nanospheres and nanorods are believed to be good templates for metal selenides because the relative atomic positions of the Se atoms do not change significantly from the parent structure to the product [128]. This topotactic relationship between precursor and product results in reasonably good retention of shape and crystallinity throughout the conversion reaction. One hypothesis for the mechanism responsible for this conversion is that Ag⁺ causes a catalytic disproportionation of Se into Se²⁻ and Se⁴⁺ [125,128]. The Se²⁻ then combines with Ag⁺ to form Ag₂Se, while the Se⁴⁺ ions form oxide byproducts. Another

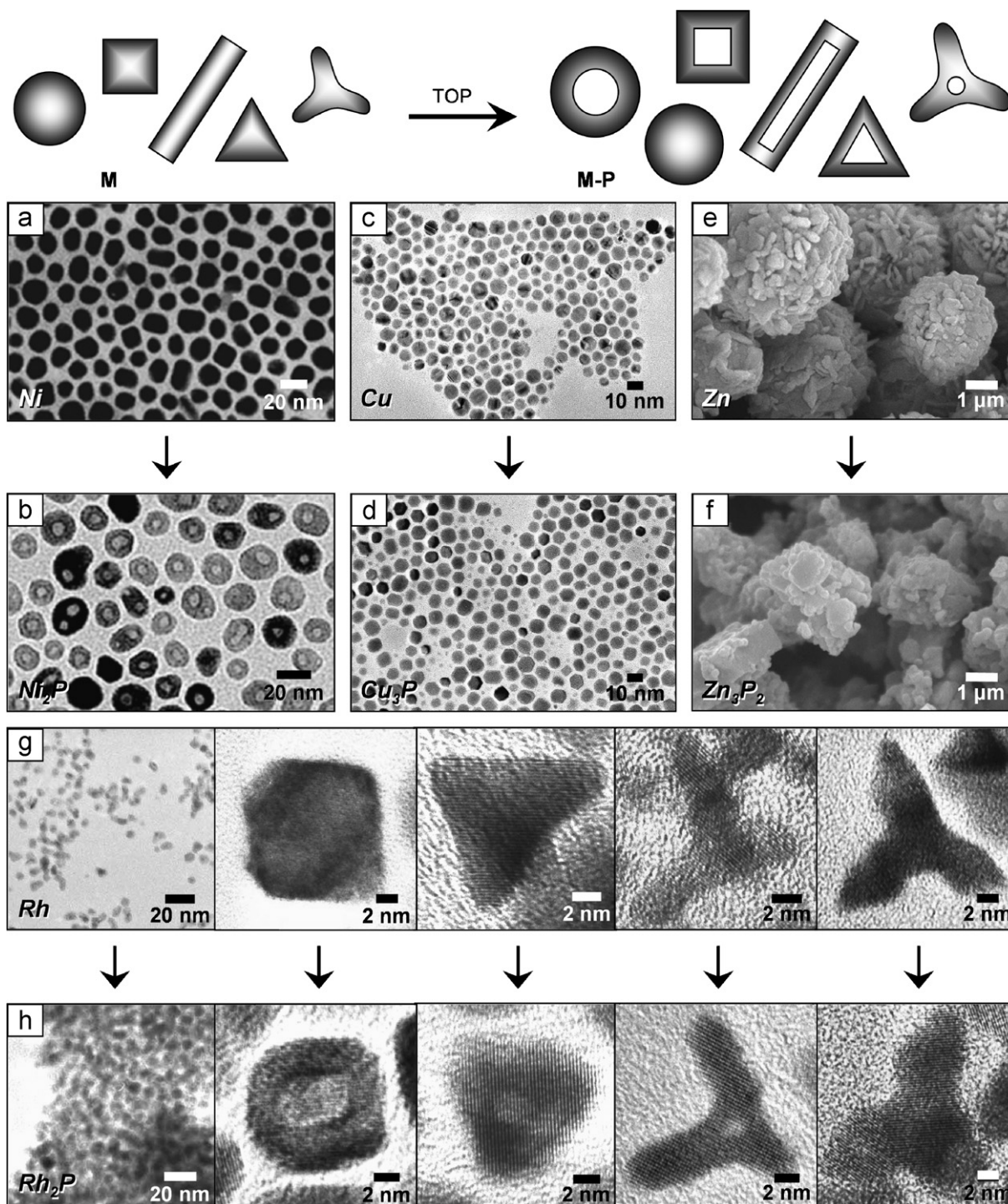


Fig. 4. *Top:* schematic depicting the shape-conserving transformation of metal nanocrystals into metal phosphides when reacted with a hot solution of trioctylphosphine. *Bottom:* TEM micrographs of representative TOP-mediated conversions of metals and metal nanocrystals into metal phosphides: (a) Ni nanocrystals converted to (b) Ni_2P nanocrystals, (c) Cu nanocrystals converted to (d) Cu_3P nanocrystals, (e) bulk Zn powder converted to (f) bulk Zn_3P_2 powder, and (g) shape-controlled Rh nanocrystals (spheres, cubes/octahedra, triangles, and two distinct types of multipods) converted to (h) shape-controlled Rh_2P nanocrystals. Reproduced with permission from Ref. [135] (panels a and b, copyright 2007, American Chemical Society), Ref. [139] (panels c–f, copyright 2007, American Chemical Society), Ref. [136] (panels g and h with 20 nm scale bars, copyright 2007, American Chemical Society) and Ref. [144] (panels g and h with 2 nm scale bars, copyright 2008, American Chemical Society).

hypothesis is that the Ag^+ is reduced to Ag^0 by sacrificial Se^0 , allowing it to diffuse into the Se crystal structure to form Ag_2Se [125].

Interestingly, when the reactions are carried out in reverse, e.g. Ag nanocrystals converted to Ag_2Se via reaction with selenium, the products are both polycrystalline and hollow [125].

The hollowing and polycrystallinity are believed to result from a Kirkendall-type diffusion mechanism, which causes small islands of Ag_2Se to nucleate on the surface of the nanocrystals, which grow larger and eventually coalesce into a solid shell around the parent nanocrystal as the core feedstock of silver is used up [125]. There are some reports of size-dependent hollowing phenomena

in which smaller nanocrystals form solid products whereas larger ones are hollow [131]. Similar Kirkendall hollowing has been observed in the transformations of Co nanocrystals to CoSe, Co₃S₄, Co₉S₈, and CoO [69,70], as discussed earlier. Other cases of observed hollowing are likely due to heating of core–shell nanocrystals to remove the selenium core [129,130,132].

1.4. Metals → phosphides

Similar to metal oxides and chalcogenides, metal nanocrystals can also be converted into metal phosphides using solution-mediated strategies (Fig. 4). For example, Khanna and co-workers converted In powder to InP via reaction with trioctylphosphine (TOP) in solution [133,134], and Chiang and Chiang [135] converted Ni nanocrystals to hollow Ni₂P nanocrystals via a nanoscale Kirkendall effect upon reaction with TOP in a mixture of oleylamine, TOP, and 1-octadecene. Building on these results, our group also studied the transformation of metal nanoparticles into metal phosphides, obtaining results similar to the Chiang group in the formation of hollow Ni₂P nanocrystals [136]. This strategy stems from the hypothesis that metal nanocrystals catalyze the cleavage of the P–C bond in TOP, which creates free phosphorus that can diffuse into the metal nanocrystal [137,138]. As such, it is potentially general for the formation of a large number of metal phosphides as nanocrystals, including those of the 4d and 5d transition metals that have not been well-studied using other synthetic approaches.

The conversion of metals into metal phosphides is quite robust, showing generality for a large number of systems, nanocrystal morphologies, and particle sizes. For example, a variety of 3d (FeP, CoP, Ni₂P, Cu₃P), 4d (Rh₂P, Pd₅P₂, PdP₂, AgP₂), and 5d (PtP₂, Au₂P₃) transition metal phosphides can be accessed as nanocrystals via reaction of the appropriate metal nanocrystals with TOP [136,139]. In addition to more than doubling the number of previously accessible nanocrystalline transition metal phosphides [136,139], this strategy provides access to metal polyphosphides (P-rich phases with short P–P bond distances), such as PdP₂, Au₂P₃ and AgP₂ [140]. Polyphosphides can be challenging to synthesize as bulk solids, yet easily form using TOP conversion chemistry. No examples of polyphosphide nanocrystals have been reported using more traditional nanocrystal synthesis strategies.

An important and useful feature of this conversion strategy for the synthesis of metal phosphides is that it can accommodate diverse metal precursors in addition to nanocrystals. For example, as reported by Khanna and co-workers [133], bulk In powder can be converted to InP, although some metal impurities remain. Similarly, we found that a variety of bulk metal powders can be converted to metal phosphides, including Ni₂P, Ni₅P₄, Cu₃P, Zn₃P₂, InP, GaP, Rh₂P, Pd₅P₂, and PdP₂ [139]. While unreacted metal impurities remain in some cases, it is possible generate phase-pure metal phosphides (within the detection limits of laboratory X-ray diffractometers) in a number of systems. This provides a low-temperature alternative to the synthesis of bulk-scale polycrystalline metal phosphides. Similarly, metal wires, foils, thin films, lithographically patterned substrates, and supported nanocrystals can also be converted to metal phosphides via reaction with TOP [139]. Of particular interest is the formation of supported Ni₂P nanocrystals, which are useful hydrotreating catalysts [141], from graphite-supported Ni nanocrystals [139], as well as the formation of thin films of Zn₃P₂, which is a semiconductor with a visible-wavelength bandgap that is of interest for solar cell applications [142,143].

Metal phosphide systems are ideal for highlighting the ability to control the morphology of the product (e.g. shape and hollow vs. dense) by reacting morphology-controlled metal nanocrystal

precursors with TOP under appropriate synthetic conditions. In the case of Ni₂P, the Chiang group was able to control the hollowing of Ni₂P spheres by varying the TOP concentration [135]. In our work, the size of the Ni nanocrystal precursor influenced whether hollow Ni₂P nanocrystals were observed: small (~5 nm) Ni nanocrystals yielded solid Ni₂P nanocrystals while larger (>20 nm) Ni nanocrystals yielded hollow Ni₂P spheres [136]. More recent work with the Rh₂P system shows that more elaborate metal phosphide nanocrystal morphologies can indeed be programmed by the morphologies of the metal nanocrystal precursor (Fig. 4g and h) [144]. For example, Rh nanocrystals with predominantly cube/octahedron, triangle, and multipod shapes can be routinely synthesized [95,96,145,146]. However, there are no reports of metal phosphide nanocrystals with these shapes synthesized using traditional direct techniques. Upon reaction with TOP, the Rh nanocrystal shapes convert to Rh₂P while retaining the shape templated by the Rh precursors [144]. Both hollow and dense Rh₂P shape-controlled nanocrystals can be generated, and variables such as stabilizing ligands, solvents, and temperature affect shape retention and nanocrystal quality [144].

1.5. Metals → alloys

Metal nanoparticles can be converted to alloys, typically through galvanic replacement reactions or through conversion of isolatable metal intermediates in one-pot reactions. Galvanic replacement reactions that use pre-made metal nanocrystals as precursors are particularly powerful, because they often provide a mechanism for controlling the morphology of the alloy nanocrystal products. For example, AgAu alloys can be synthesized by reacting pre-formed Ag nanoparticles with aqueous HAuCl₄ to produce nanoboxes [147], nanocages [148], and multi-walled nanotubes [149] with tunable surface plasmon resonance (SPR) bands. This technique has been extended to even more complex nanostructures, including multi-walled AgAu/AgPd nanotubes [150] and hollow nanoboxes of AgPd and AgPt alloys [147]. Although the formation of the AgAu alloys was initially observed as an intermediate step in the synthesis of hollow Au nanoparticles [151], the degree of alloying can be controlled in the hollow structures [151] as well as in dense analogs [152]. Subsequent work led to the synthesis of hollow AgAu nanoparticles in chloroform [109]. Hollow nanocages with pinholes and ring-like structures were observed when multiply twinned oleylamine stabilized Ag nanoparticles were reacted with HAuCl₄ in chloroform [109].

Galvanic replacement reactions have been used to synthesize other alloy nanocrystals. For example, Liang et al. [113] synthesized Au–Pt bimetallic nanoparticles with hollow linearly aggregated morphologies using magnetic Co nanoparticles as sacrificial templates. We used a similar approach to generate hollow nanospheres of a superparamagnetic CoPt alloy, reacting Co nanoparticles with K₂PtCl₆ in the presence of PVP [60]. Redox transmetalation reactions are also useful for generating alloy nanocrystals, as well as core–shell nanocrystals. For example, Park and Cheon synthesized CoPt nanoalloys through a redox transmetalation reaction between Co nanoparticles and Pt(hfac)₂ (hfac = hexafluoroacetylacetonate) [63,64], selectively generating Co–Pt core–shell nanocrystals or CoPt alloys. Evidence that CoPt nanoparticles were formed via interdiffusion of a Co core and Pt shell was provided by X-ray absorption spectroscopy (XAS) experiments [64]. This approach was recently shown to be general for the synthesis of a wide range of core–shell nanoparticles [153].

Other non-conversion methods for synthesizing alloy nanocrystals are common, typically involving the co-nucleation of two metals following reduction of metal salts and/or decomposition of

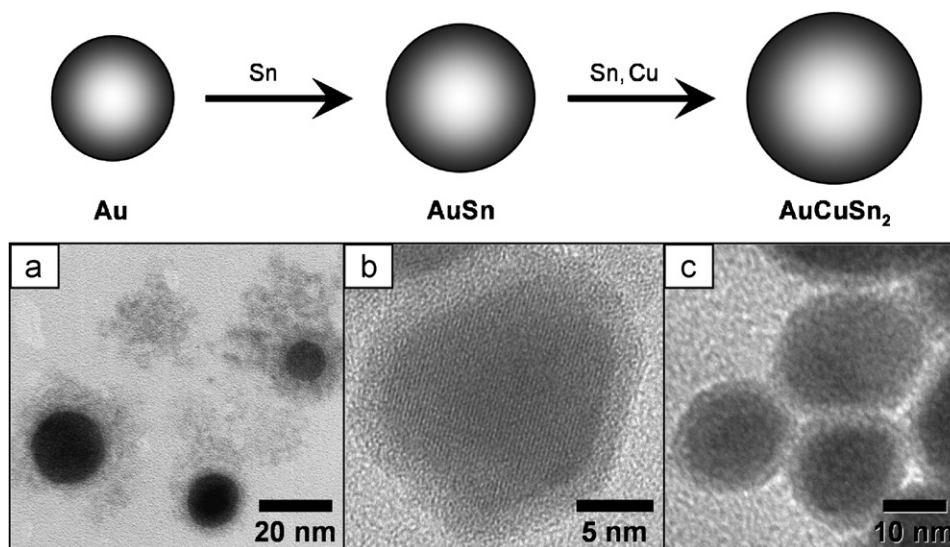


Fig. 5. Top: schematic depicting the stepwise formation of ternary intermetallic AuCuSn₂ nanocrystals. Bottom: Representative TEM micrographs characterizing each step: (a) Au nanoparticles, (b) intermetallic AuSn nanoparticles formed by reacting the Au nanoparticles in (a) with a Sn reagent in solution, and (c) intermetallic AuCuSn₂ nanoparticles formed by reacting the AuSn nanoparticles in (b) with additional Sn and Cu reagents. All nanoparticles are capped with a thin SnO₂ shell. Reproduced with permission from Ref. [156] (panels a–c, copyright 2006, American Chemical Society).

metal complexes. In some cases, mechanistic studies are performed that hint at a conversion-based reaction pathway, e.g. one metal component nucleates first, and the other reacts with it to form the alloy. Often the metal intermediate is highly reactive and short-lived (and thus often speculated to exist rather than observed). We classify such reactions separate from “conversion” reactions in the sense that they are not deliberate. That is, the reaction is not carried out specifically with a pre-formed metal nanocrystal template that is deliberately converted to a product phase. We consider this to be an important criterion for classification as a conversion reaction. However, there are examples where one-pot reactions are analyzed and isolatable metal nanoparticle intermediates are observed, which can then be made ex situ and deliberately converted (using the pre-formed or isolated nanoparticles as precursors) into the desired product. Many of the reactions discussed above were discovered in this way, e.g. the conversion of metals to metal phosphides [136,139] and the conversion of Co to CoPt alloys [60,63,64]. Reactions of Cu(OCH-(Me)CH₂NMe₂)₂ with diethylzinc (Et₂Zn) to form Cu₉₅Zn₅, Cu₇₀Zn₃₀, and Cu₃₅Zn₆₅ alloys can also likely be classified as conversion reactions, since Cu nanoparticles synthesized by decomposition of Cu(OCH-(Me)CH₂NMe₂)₂ without Et₂Zn present could also be isolated [154].

1.6. Metals → intermetallics

Intermetallic compounds represent a subset of alloys that tend to have fixed stoichiometric compositions and atomically ordered crystal structures, in contrast to alloys that are crystalline solid solutions, which usually exist over a range of compositions. In addition to alloys, metal nanocrystals can also be converted to nanocrystals of intermetallic compounds using solution chemistry methods, typically via diffusion-based processes. This pathway to intermetallic nanocrystals became apparent while studying the formation of nanoparticles of the ternary intermetallic compounds AuMSn₂ (*M* = Cu, Ni) via a modified polyol process (Fig. 5). Originally synthesized in a one-pot reaction [155], careful investigation of the reaction pathway revealed that Au nanopar-

ticles formed first (Fig. 5a), followed by diffusion of Sn into the Au to form nanoparticles of the intermetallic compound AuSn (Fig. 5b) [156]. Continued heating in the presence of additional Sn and Cu converted the AuSn nanoparticles into AuCuSn₂ (Fig. 5c). DiSalvo and co-workers observed a similar metal intermediate in the formation of PtBi nanoparticles, where Bi was formed first and allowed to react with Pt that was added separately [157].

This insight has opened the door to a large number of intermetallic compounds that are accessible as nanoparticles using solution chemistry routes (Fig. 6). Importantly, using pre-formed metal nanoparticles as reactive templates has provided a pathway to shape-controlled intermetallic nanocrystals, which are quite rare [158] and have remained a formidable synthetic challenge despite similar achievements for shape-controlled nanocrystal synthesis of other classes of solids. For example, shape-controlled nanocrystals of β-Sn can be converted to *M*-Sn intermetallic nanocrystals under conditions that maintain the shape defined by the β-Sn template [159]. The result is nanocrystals of FeSn₂ with shapes that include spheres, cubes, hollow squares, U-shaped structures, nanorods, and nanorod dimers (Fig. 6a–d). These nanocrystals are formed by reacting similarly shaped β-Sn nanocrystals with a solution of FeCl₃ under reducing conditions. This reaction facilitates reduction and diffusion of the Fe into the β-Sn. As mentioned earlier for similar reactions in the Ag₂Se system in which shape control is hypothesized to be facilitated by topotactic relationships between the precursor (Se) and the final product (Ag₂Se) [125,128], the structural relationship between β-Sn and FeSn₂ likely contributes to the retention of shape and crystallinity. The anisotropic structure of β-Sn, and the resultant different diffusion rates along the *a* and *b* axes, facilitates an anisotropic Kirkendall effect that yields interesting hollow nanocrystals, including hollow squares and U-shaped structures, as well as nanorods via Kirkendall-mediated cleavage of cube-shaped β-Sn nanocrystals [159]. Single-crystal nanorods in a large number of intermetallic systems (CoSn₃, Ni₃Sn₄, Cu₆Sn₅, Ag₄Sn, AuSn, PtSn, RuSn₂) can also be synthesized via diffusion-based conversion of β-Sn nanorods using similar chemistry (Fig. 6e–h) [160].

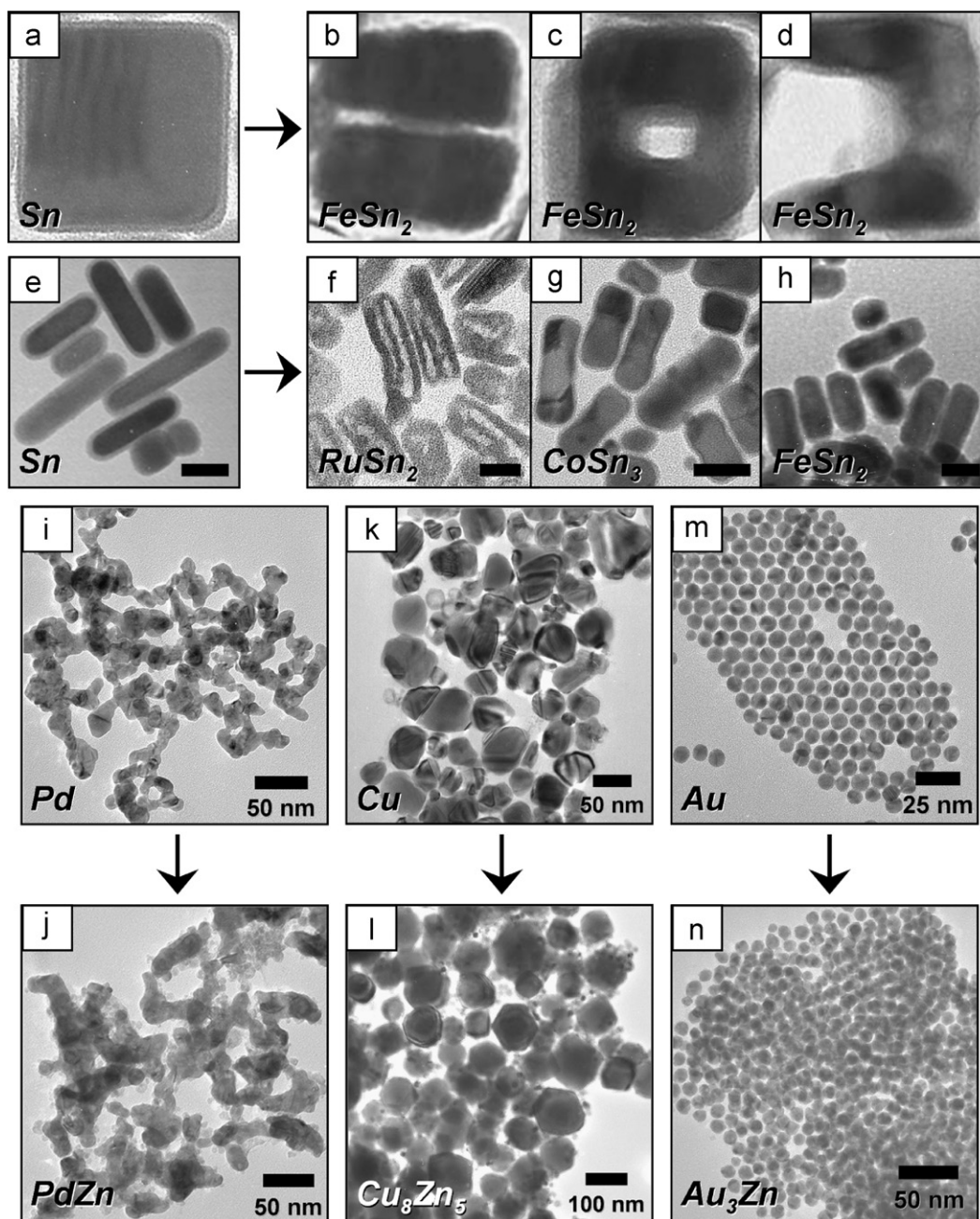


Fig. 6. TEM micrographs of representative morphology-conserving chemical transformations of metal nanocrystals into intermetallics: (a) β -Sn nanocubes converted to FeSn_2 (b) fused nanorod dimers, (c) hollow squares, and (d) U-shaped nanocrystals; (e) β -Sn nanorods converted to (f) hollow RuSn_2 nanorods, (g) dense CoSn_3 nanorods, and (h) dense FeSn_2 nanorods; (i) dendritic Pd nanoparticles converted to (j) dendritic PdZn nanoparticles, (k) Cu nanoparticles converted to (l) Cu_8Zn_5 nanoparticles, and (m) monodisperse spherical Au nanoparticles converted to (n) monodisperse spherical Au_3Zn nanoparticles. Reproduced with permission from Ref. [159] (panels a–d, copyright 2007, American Chemical Society), Ref. [160] (panels e–h, copyright 2008, American Chemical Society), and Ref. [164] (panels i–n, copyright 2007, American Chemical Society).

Interestingly, and separate from the goal of generating shape-controlled intermetallic nanocrystals via conversion chemistry, is the discovery that a variety of compounds that are traditionally difficult to prepare in bulk form can be readily accessed using this chemical strategy. For example, while the Co–Sn binary phase diagram was established decades ago, α - CoSn_3 was only discovered about 10 years ago [161,162]. α - CoSn_3 is a low-temperature intermetallic compound that is only stable up to 275 °C, and can be formed in bulk using either a peritectic reaction or a tin flux [161,162]. While α - CoSn_3 can clearly form as a bulk solid, including in single-crystal form, it is not the easiest phase to

access in the Co–Sn system. In contrast, when using the nanocrystal conversion chemistry approach, α - CoSn_3 is reproducibly the easiest phase to form in the Co–Sn system [159]. It is well known that nanoparticles can provide access to phases that are not thermodynamically stable or that are stable only at low temperatures. Our results provide additional examples of this principle, showing that this solution chemistry approach could provide another strategy for discovering and stabilizing solids that may be challenging to prepare by traditional bulk methods, that may only exist at high pressures, or that may be new. Further supporting this hypothesis is the fact that we observe the

formation of NiSn₃ using similar chemistry [159]. NiSn₃ does not appear on the Ni–Sn phase diagram [163], and likely has a structure related to that of metastable PtSn₃ (although purity issues and nanocrystallinity make structure determination difficult and inconclusive) [159]. RuSn₂, which is reported in the literature to be a metastable phase that is difficult to synthesize, also appears to form reproducibly as hollow nanorods upon reaction of β -Sn nanorods with RuCl₃ in tetraethylene glycol at 200 °C under reducing conditions [160].

Metal–zinc intermetallic compounds provide another interesting example of both conversion chemistry routes to intermetallic nanocrystals and morphological retention of the template nanocrystals (Fig. 6i–n). As discussed earlier in the conversion of metals to alloys, Cu–Zn alloys can be formed via the co-reaction of copper complexes and Et₂Zn, with the formation of a Cu intermediate that implies reaction of Cu nanoparticles with Et₂Zn to form the final Cu–Zn alloy nanocrystals [154]. We recently studied the formation of metal–zinc intermetallics in the Pd–Zn, Cu–Zn, and Au–Zn systems in order to further generalize the previously reported chemistry and to fully elaborate the crucial role that pre-formed metal nanoparticles have in defining the morphology of the product nanocrystals after conversion reactions [164]. Accordingly, dendritic Pd nanoparticle networks were reacted with Et₂Zn in a hot organoamine solvent to form intermetallic PdZn nanoparticles that retained the dendritic architecture defined by the Pd precursor [164]. Similarly, multifaceted and polydisperse Cu nanocrystals converted to Cu₆Zn₅ nanocrystals of similar morphology when reacted with Et₂Zn [164]. Finally, monodisperse spherical nanocrystals of Au were reacted with diphenylzinc to form Au₃Zn [164]. Importantly, the spherical morphology and size dispersity defined by the Au nanocrystals were retained in the Au₃Zn products. Changing the synthetic conditions could modify the morphology of the final product, inducing slight anisotropic growth and forming Au₃Zn with a “bicycle seat” morphology [164]. In all of these cases, the morphology of the precursor nanoparticles was retained upon conversion to M–Zn intermetallics via reaction with zero-valent organometallic reagents.

Conversion chemistry methods were also used to convert nanocrystalline Pt into PtBi, PtPb, PtSn, and FePt₃ via reaction with appropriate metal salt precursors under reducing conditions in polyol solvents (e.g. tetraethylene glycol) [165]. The synthetic conditions identified for these conversion reactions were then applied to Pt nanoparticles supported on Al₂O₃, CeO₂, and Vulcan XC-72 to form supported intermetallic and alloy nanoparticles of PtSn, PtPb, PtSb, Pt₃Sn, and Cu₃Pt. This demonstrates that this conversion chemistry strategy is applicable to on-support reactions, providing a pathway for transforming single-element nanoparticle catalysts into multi-element nanoparticle catalysts, which typically require higher temperature annealing to form. The formation of supported multi-metal nanoparticle catalysts directly in solution at low temperatures minimizes sintering without requiring the incorporation of deliberately added organic surface stabilizers, which can hinder catalytic activity. Using this approach, 3.3 ± 0.5 nm Pt/Al₂O₃ was converted to 5.2 ± 1 nm intermetallic PtSn/Al₂O₃, with the increase in particle size required by the addition of Sn to Pt via a diffusion mechanism [165]. Al₂O₃-supported hollow nanoparticles of PtSn could be obtained when larger (6–70 nm) Pt/Al₂O₃ nanoparticle catalysts were used as precursors, effectively merging the synthesis of supported catalysts with methods to induce Kirkendall hollowing of nanoparticles [165]. Importantly, the supported intermetallic nanoparticles are catalytically active for chemical transformations such as formic acid oxidation (PtPb/Vulcan) and CO oxidation (Pt₃Sn/graphite), making this a viable alternative method for generating useful nanoscale catalytic architectures [165].

2. Intermetallics and chalcogenides as reactive templates

The focus up to this point has been on converting single metals into other metals and derivative multi-element solids, including oxides, chalcogenides, phosphides, alloys, and intermetallics. In general, nanocrystalline solids tend to have enhanced reactivity relative to bulk solids, in part because they have a high surface area with a large fraction of coordinatively unsaturated atoms at the surface (with only weakly bound organic surface stabilizers). Thus, other classes of multi-element solids are also amenable to solution-mediated conversion reactions, in analogy to the single-element metals discussed earlier, but pushing toward structurally and compositionally more complex systems. We and others have begun to synthesize a growing library of intermetallic compounds as nanocrystalline solids [154–158,164,166–170], and these nanocrystalline intermetallics can serve as reactive templates for conversion into derivative multi-metal intermetallics, oxides, and sulfides.

The Pt–Sn system provides an instructive example of the role that conversion chemistry can play in the synthesis of nanocrystalline intermetallics [166]. Nanocrystalline PtSn can be reacted with SnCl₂ in tetraethylene glycol to form PtSn₂ via an additive diffusion-based mechanism. A similar reaction converts this PtSn₂ back to PtSn via reaction with K₂PtCl₆. When PtSn is reacted with K₂PtCl₆, Pt₃Sn forms, which in turn can be converted back to PtSn by reacting it with SnCl₂. These reaction sequences represent multi-step cyclic interconversions, and demonstrate that an intermetallic nanocrystal can serve as a chemical reagent for conversion into a derivative intermetallic nanocrystal. This reaction pathway provides easy access to nanocrystals of multiple intermetallics in a given binary system. For example, Pt₃Sn is a catalytically important intermetallic [171] that was initially challenging to form through direct polyol reactions. However, PtSn forms easily, and can be converted to Pt₃Sn via reaction with K₂PtCl₆ in tetraethylene glycol at 260 °C [166]. Similarly, nanocrystalline AuCu can be converted to AuCu₃ via reaction in tetraethylene glycol with Cu(C₂H₃O₂)₂ · H₂O at 315 °C [166]. Another important example of converting intermetallics to other intermetallics in solution is the AuCuSn₂ system that was described earlier [156]. In the reaction pathway that generates nanocrystals of AuCuSn₂, Au nanoparticles form first, which react in solution to form intermetallic AuSn nanocrystals [156]. The AuSn, in turn, reacts with additional Sn and Cu in solution to form AuCuSn₂ [156], effectively serving as a multi-step conversion reaction that transforms a binary intermetallic nanocrystal to a ternary phase.

Nanocrystalline intermetallics can also serve as reagents for conversion to multi-metal oxides and sulfides (Fig. 7). For example, intermetallic Bi₂Pd nanoparticles can serve as “single source” reagents for oxidation into the mixed metal oxide Bi₂PdO₄ [172]. This strategy takes advantage of the fact that an intermetallic compound provides the proper metal ratio and intimately mixed elements, and that the high surface-to-volume ratio of nanocrystals allows for high reactivity and facile oxidation at low temperatures. (Unlike most of the other transformations, this one involves oxidation of the dry powder by heating in O₂ or air rather than in solution.) The oxidation of Bi₂Pd to Bi₂PdO₄ occurs through a multi-step pathway, with Bi oxidizing first (350–400 °C) and phase separating to form a Bi₂O₃/Pd nanocomposite, followed by oxidation of Pd (700–800 °C) and interdiffusion to form Bi₂PdO₄ [172]. Interestingly, the intermetallic Bi₂Pd nanoparticles are cube-shaped, and this morphology persists through the oxidation as determined by both TEM (Fig. 7b and c—direct visualization of cube shapes) and XRD (Fig. 7d and e—preferred orientation consistent with cube shapes). Similarly, intermetallic Bi–Pt nanoparticles (a mixture of BiPt and Bi₂Pt) can be thermally

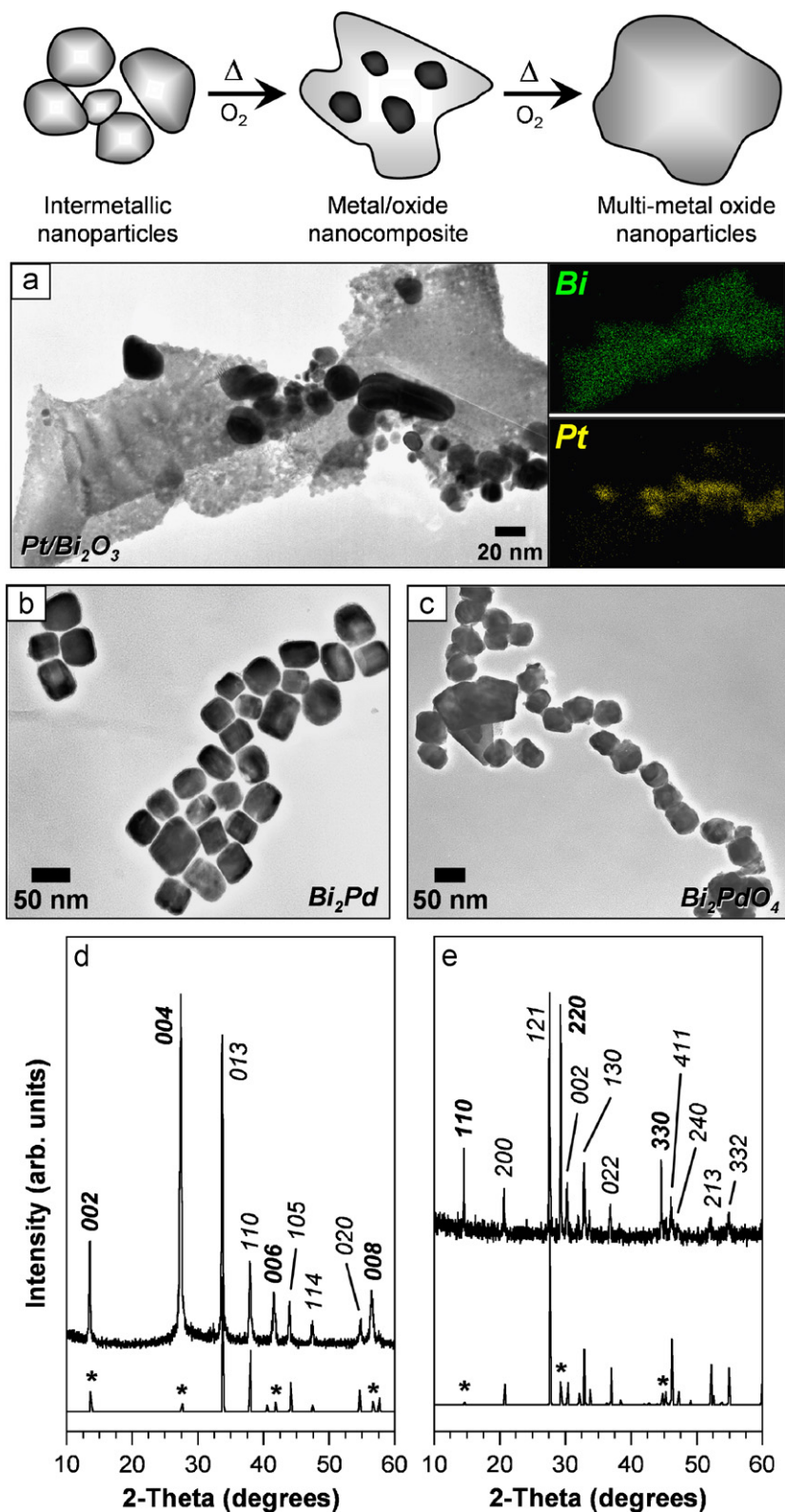


Fig. 7. Top: schematic depicting the oxidative transformation of intermetallic nanoparticles into multi-metal oxides via a metal/oxide nanocomposite intermediate. Bottom: representative TEM micrographs and XRD data characterizing the reactants, intermediates, and products: (a) TEM micrograph and semi-STEM element mapping data for the intermediate Bi₂O₃/Pt nanocomposite that forms upon oxidizing intermetallic Bi–Pt nanoparticles at 350–400 °C; TEM micrographs of (b) cube-shaped intermetallic Bi₂Pd nanoparticles and (c) cube-shaped Bi₂PdO₄ nanoparticles; powder XRD patterns for cube-shaped (d) Bi₂Pd and (e) Bi₂PdO₄ nanoparticles, showing evidence of preferred orientation that is consistent with the cubic morphology. Reproduced with permission from Ref. [172] (all panels, copyright 2007, American Chemical Society).

oxidized to form a Bi₂O₃/Pt nanocomposite and finally the fully oxidized product, pyrochlore-type Bi₂Pt₂O₇ [172]. Preliminary evidence suggests that intermetallics can be converted to mixed

metal sulfides as well. Because a large number of intermetallics are now accessible as nanocrystals, the potential exists for this strategy to be applicable to a wide range of multi-metal oxides

and sulfides via conversion chemistry. In addition, the first oxidation step that induces phase separation into a metal oxide and noble metal nanocomposite could be used as an alternative method to form supported nanoparticle catalysts. Furthermore, since the final product maintains the general morphology defined by the nanoparticles, this represents an alternative route to textured ceramics.

Metal chalcogenides can also serve as reagents for chemical conversion into derivative chalcogenides using cation exchange reactions that are typically driven by relative K_{sp} values. For example, the transformation of ZnS to Ag_2S is driven by the lower K_{sp} value of Ag_2S relative to ZnS [173]. Likewise, CuS can be made from CdS [174]. However, the reverse cation exchange can also be done, provided that an appropriate driving force is present [175]. In the transformation of Ag_2Se to PbSe, the capping ligand tributylphosphine (TBP) forms a stable complex with Ag^+ , drawing it out of the Se matrix and allowing for Pb^{2+} cations to diffuse into it to form PbSe [175]. Similarly, Ag_2Se nanowires can be converted to CdSe nanowires [176]. Moreover, Alivisatos and co-workers have shown that cyclic cation exchange transformations that preserve nanocrystal shape and size are achievable [73]. For example, CdSe spheres and rods can be converted to Ag_2Se and then back to CdSe with minimal loss of nanocrystal quality. This is also possible for the cyclic transformations of CdS to Ag_2S hollow spheres and CdTe to Ag_2Te tetrapods. The capabilities of this approach have recently been expanded to generate striped CdS/ Ag_2S nanowires by partial cation exchange [177].

2.1. Oxides \rightarrow sulfides

Metal oxides are often used as precursors to sulfides, for example the use of WO_3 and MoO_3 as precursors to the inorganic fullerenes WS_2 and MoS_2 via reaction with H_2S [178–180]. H_2S has been used as a sulfur source for a number of other reactions, including the formation of oxides via hydrothermal, solvothermal, sonochemical, electrochemical, or direct chemical methods followed by heating in the presence of H_2S [181–186].

In some cases, the oxide is reacted with different sulfur sources such as thioglycolic acid, thiourea, or elemental sulfur to produce the corresponding sulfide. For example, ZnO/ZnS, SnO_2/SnS_2 , MnO_2/MnS_2 core-shell nanostructures, and nanotubes of ZnS and SnS_2 were formed when the corresponding oxide was reacted with Na_2S and thioglycolic acid [187]. Similarly, ZnO nanorods were used to synthesize ZnS nanotubes and nanotube arrays using thioglycolic acid [188,189]. Thiourea was used as the sulfur source to produce hollow ZnS from polymer-stabilized ZnO nanoparticles [190], and also for 18-faceted Cu_7S_4 hollow nanoparticles from Cu_2O [191]. CuS nanoparticles were synthesized hydrothermally from CuO and $Na_2S_2O_3 \cdot 5H_2O$ [192]. Commercially available rare-earth oxides Pr_6O_{11} , Eu_2O_3 , and Gd_2O_3 were also converted to the corresponding monothiooxides using a solvothermal method and sulfur powder [193]. MoO_3 was converted to MoS_2 using elemental sulfur and heating to 850 °C. Other unconventional sources of sulfur have also been used to convert oxides to sulfides, including the use of boron sulfides to convert Nd_2O_3 to NdS_2 nanoparticles [194]. This strategy has been shown to be extremely general for the low-temperature conversion of oxides to sulfides [195].

Ultrasonic chemical solution procedures have also been employed to convert oxides to sulfides with appropriate sulfur sources. For example, $Zn(NO_3)_2 \cdot 6H_2O$ was reacted with NaOH and ultrasonically irradiated to produce ZnO nanocables and nanorods that were converted to ZnO/ZnS nanocables and nanotubes in the presence of thiourea [196]. Geng et al. [197] showed that ZnO could be converted to hollow particles of ZnO, ZnSe, and

core-shell ZnO/ZnS and ZnO/ZnSe nanostructures using ultrasonic irradiation.

2.2. Oxides \rightarrow nitrides

Similar to the conversion of metal oxides to sulfides, nanocrystalline metal oxides can also be converted to metal nitrides. Gas-phase reactions of dry oxide powders with NH_3 are most common. For example, Gao and co-workers have converted nanoparticles of TiO_2 , Cr_2O_3 , In_2O_3 , Ta_2O_5 , and Al_2O_3 to metal nitrides of TiN [198], CrN [199], InN [200], Ta_3N_5 [201], and AlN [202], respectively, by nitridation methods. In all cases the oxide nanoparticles converted completely to nitrides at low temperatures and short heating times while micron-scale powders did not convert completely under equivalent conditions, demonstrating the effect that nanoscale precursors have on reactivity. Other reactions with NH_3 gas at elevated temperatures have been used to produce TiN [203] and GaN [204]. In particular, reacting nanocrystalline Ga_2O_3 in the pores of an alumina membrane with NH_3 gas at 1000 °C yielded GaN nanoparticles with a diameter of 23.8 nm, which agrees well with the pore diameter of 24 nm [204]. The physical template, coupled with the conversion chemistry, is a useful method for controlling the size of the GaN nanoparticles.

Like many of the other examples of conversion chemistry, the morphology of metal oxide nanoparticle precursors can template the morphology of metal nitride nanocrystal products. For example, Hu et al. [205] reacted amorphous Ga_2O_3 nanotubes with NH_3 at 1400 °C for 1 h to generate GaN nanotubes with lengths up to 10 μm , diameters of 80 nm and wall thickness of 20 nm. While the conversion reactions mentioned up to this point

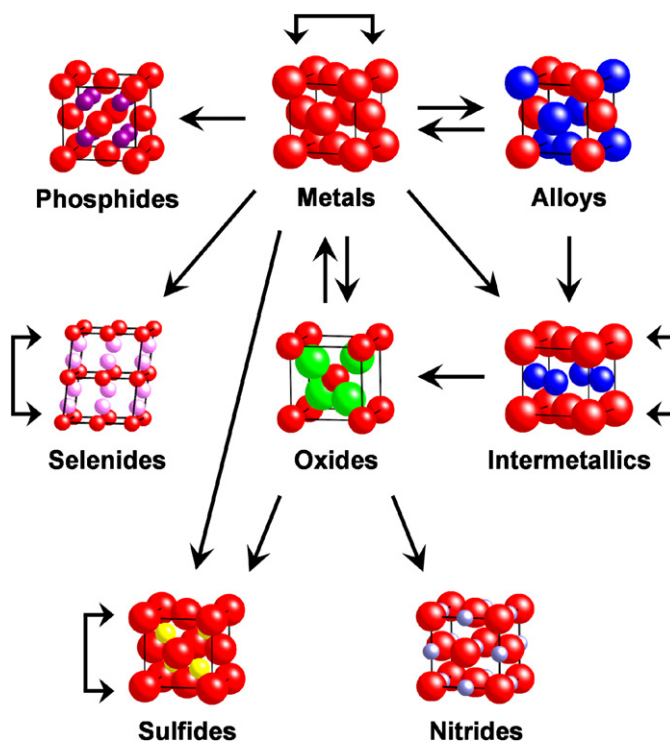


Fig. 8. Schematic summarizing the key chemical transformations that have been used to transform one type of nanoparticle into another. Some of these reactions are reversible, e.g. the conversion of metals to alloys via diffusion or galvanic replacement methods and the conversion of alloys back to metals via chemical leaching [208]. In some cases, chemical transformations within a class of solids are also achievable, e.g. conversion of one type of metal to another via galvanic replacement and conversion or metal chalcogenides into derivative chalcogenides via ion exchange.

involve nitridation of metal oxides at elevated temperatures in a NH_3 atmosphere, other nitrogen sources can also be used. For example, Buha et al. [206] reacted appropriate metal oxide nanoparticles with cyanamide or urea to form VN, TiN, AlN, GaN, NbN, TaN, and hafnium oxide nitride. Nanoparticles and nanorods could be generated, although in some cases the morphology was not preserved in the conversion reaction.

3. Conclusions and future outlook

Nanocrystal conversion chemistry—the use of pre-formed nanoparticles as templates for chemical transformation into derivative solids, often with morphological retention—has emerged as a powerful approach for designing the synthesis of complex nanocrystalline solids. The general strategy exploits established synthetic capabilities in simple nanocrystal systems (e.g. noble metals and simple metal oxides and chalcogenides) and uses these nanocrystals as templates that help to define the composition, crystal structure, and morphology of product nanocrystals. The methods used to accomplish this are diverse, including galvanic replacement, diffusion, oxidation, and ion exchange. Collectively, they comprise a powerful toolbox of chemical transformations that helps to expand the complexity of solid-state materials that are accessible as high-quality nanocrystals, and also expand synthetic capabilities in solid-state chemistry. An overview of the types of transformations and their interrelationships, highlighting the ability to interconvert (sometimes reversibly) among classes of solids, is shown in Fig. 8.

This conversion chemistry paradigm will continue to serve as a straightforward strategy for programming morphological complexity into multi-element nanocrystal systems that require simultaneous control over composition, crystal structure, and nanocrystal shape, size, and size dispersity. Likewise, these solution chemistry techniques are expanding the synthetic toolbox available to solid-state chemists, providing low-temperature strategies for the synthesis of a range of classes of solids and successfully yielding new and metastable solids in a few systems to date. These capabilities, which provide a pathway for merging synthetic techniques that are widely used in nanoscience with the more complex solids and systems that are the benchmark of solid-state chemistry, are likely to lead to the discovery of new solids and the stabilization of traditionally high-temperature or high-pressure phases under near-ambient conditions. Expansion of these ideas to other classes of solids will be important for accessing a more diverse library of complex nanocrystal systems for advanced scientific studies and emerging applications. The development of new chemical transformations will also be useful for generalizing the strategy to important systems that remain inaccessible, as well as providing access to nanocrystals and solids with previously unattainable morphologies, compositions, and crystal structures. The idea of “nanocrystal conversion chemistry,” in its variety of manifestations, has already been used successfully to generate interesting and useful materials for applications that involve plasmonics and medical and biological imaging [207]. Further implementation of this concept to more complex systems will likely expand these applications to other areas, such as catalysis, drug delivery, optics, information storage, and electronics.

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References

- [1] A.P. Alivisatos, *J. Phys. Chem.* 100 (1996) 13226.
- [2] P. Jain, X. Huang, I. El-Sayed, M. El-Sayed, *Plasmonics* 2 (2007) 107.
- [3] M. Hu, J. Chen, Z.-Y. Li, L. Au, G.V. Hartland, X. Li, M. Marquez, Y. Xia, *Chem. Soc. Rev.* 35 (2006) 1084.
- [4] M.C. Daniel, D. Astruc, *Chem. Rev.* 104 (2004) 293.
- [5] X. Liu, M. Bauer, H. Bertagnolli, E. Roduner, J. van Slageren, F. Philipp, *Phys. Rev. Lett.* 97 (2006) 253401.
- [6] F. Michael, C. Gonzalez, V. Mujica, M. Marquez, M.A. Ratner, *Phys. Rev. B* 76 (2007) 224409.
- [7] C. Burda, X. Chen, R. Narayanan, M.A. El-Sayed, *Chem. Rev.* 105 (2005) 1025.
- [8] D. Astruc, F. Lu, J.R. Aranzas, *Angew. Chem. Int. Ed.* 44 (2005) 7852.
- [9] B. Wu, A. Heidelberg, J.J. Boland, *Nat. Mater.* 4 (2005) 525.
- [10] X. Li, H. Gao, C.J. Murphy, K.K. Caswell, *Nano Lett.* 3 (2003) 1495.
- [11] S.B. Darling, S.D. Bader, *J. Mater. Chem.* 15 (2005) 4189.
- [12] F. Li, D.-I. Son, J.-H. Ham, B.-J. Kim, J.H. Jung, T.W. Kim, *Appl. Phys. Lett.* 91 (2007) 162109.
- [13] H. Lee, M.K. Yu, S. Park, S. Moon, J.J. Min, Y.Y. Jeong, H.W. Kang, S. Jon, *J. Am. Chem. Soc.* 129 (2007) 12739.
- [14] S. Mornet, S. Vasseur, F. Grasset, E. Duguet, *J. Mater. Chem.* 14 (2004) 2161.
- [15] L.M. Lacava, V.A.P. Garcia, S. Kuckelhaus, R.B. Azevedo, Z.G.M. Lacava, O. Silva, F. Pelegrini, C. Gansau, N. Buske, P.C. Morais, *J. Appl. Phys.* 93 (2003) 7563.
- [16] F. Raimondi, G.G. Scherer, R. Kötz, A. Wokaun, *Angew. Chem. Int. Ed.* 44 (2005) 2190.
- [17] X. Yao, C. Wu, A. Du, J. Zou, Z. Zhu, P. Wang, H. Cheng, S. Smith, G. Lu, *J. Am. Chem. Soc.* 129 (2007) 15650.
- [18] P.V. Kamat, *J. Phys. Chem. C* 111 (2007) 2834.
- [19] (a) Y. Li, M.A. El-Sayed, *J. Phys. Chem. B* 105 (2001) 8938;
(b) M.T. Reetz, R. Breinbauer, K. Wanning, *Tet. Lett.* 37 (1996) 4499.
- [20] X. Teng, H. Yang, *J. Am. Chem. Soc.* 125 (2003) 14559.
- [21] Y.-J. Li, W.-J. Huang, S.-G. Sun, *Angew. Chem. Int. Ed.* 45 (2006) 2537.
- [22] G. Chumanov, K. Sokolov, B.W. Gregory, T.M. Cotton, *J. Phys. Chem.* 99 (1995) 9466.
- [23] J.J. Urban, D.V. Talapin, E.V. Shevchenko, C.R. Kagan, C.B. Murray, *Nat. Mater.* 6 (2007) 115.
- [24] L. Cademartiri, G. Freymann, A.C. Arsenault, J. Bertolotti, D.S. Wiersma, V. Kitaev, G.A. Ozin, *Small* 1 (2005) 1184.
- [25] X. Xu, M. Stevens, M.B. Cortie, *Chem. Mater.* 16 (2004) 2259.
- [26] M.T. Crisp, N.A. Kotov, *Nano Lett.* 3 (2003) 173.
- [27] P. Jiang, J.F. Bertone, V.L. Colvin, *Science* 291 (2001) 453.
- [28] A. Stein, R.C. Schroden, *Curr. Opin. Solid State Mater. Sci.* 5 (2001) 553.
- [29] R.E. Schaak, A.K. Sra, B.M. Leonard, R.E. Cable, J.C. Bauer, Y.F. Han, J. Means, W. Teizer, Y. Vasquez, E.S. Funck, *J. Am. Chem. Soc.* 127 (2005) 3506.
- [30] J.E. Munoz, J. Cercantes, R. Esparza, G. Rosas, *J. Nanopart. Res.* 9 (2007) 945.
- [31] C.C. Koch, J.D. Whittenberger, *Intermetallics* 4 (1996) 339.
- [32] P. Milani, W.A. deHeer, *Rev. Sci. Instrum.* 61 (1990) 1835.
- [33] M. Raffi, A. Rumaiz, M.M. Hasan, S.I. Shah, *J. Mater. Res.* 22 (2007) 3378.
- [34] T. Haubold, R. Bohn, R. Birringer, H. Gleiter, *Mater. Sci. Eng. A* 153 (1992) 679.
- [35] J.C. Pivin, M.A. Garcia, J. Llopis, H. Hofmeister, *Nucl. Instr. Meth. Phys. Res. B* 191 (2002) 794.
- [36] Y.K. Mishra, S. Mohapatra, D. Kabirag, B. Mohanta, N.P. Lalla, J.C. Pivin, D.K. Avasthi, *Scr. Mater.* 56 (2007) 629.
- [37] A. Gurav, T. Kodas, T. Pluym, Y. Xiong, *Aerosol. Sci. Technol.* 19 (1993) 411.
- [38] S.E. Pratsinis, *Prog. Energy Combust. Sci.* 24 (1998) 197.
- [39] J.C. Nie, H. Yamasaki, Y. Mawatari, *Phys. Rev. B* 70 (2004) 195421/1.
- [40] B.L. Cushing, V.L. Kolesnichenko, C.J. O'Connor, *Chem. Rev.* 104 (2004) 3893.
- [41] A. Roucoux, J. Schulz, H. Patin, *Chem. Rev.* 102 (2002) 3757.
- [42] F. Dumestre, B. Chaudret, C. Amiens, M.-C. Fromen, M.-J. Casanove, P. Renaud, P. Zurcher, *Angew. Chem. Int. Ed.* 41 (2002) 4286.
- [43] S. Sun, C.B. Murray, D. Weller, L. Folks, A. Moser, *Science* 287 (2000) 1989.
- [44] I.H. Gul, W. Ahmed, A. Maqsood, *J. Magn. Magn. Mater.* 320 (2008) 270.
- [45] (a) M.P. Pileni, *Langmuir* 13 (1997) 3266;
(b) M.P. Pileni, *Nat. Mater.* 2 (2003) 145.
- [46] M. Rajamathi, R. Seshadri, *Curr. Opin. Solid State Mater. Sci.* 6 (2002) 337.
- [47] B. Chaudret, *Top. Organomet. Chem.* 16 (2005) 233.
- [48] T. Hanrath, B.A. Korgel, *J. Am. Chem. Soc.* 126 (2004) 15466.
- [49] C.A. Stowell, B.A. Korgel, *Nano Lett.* 5 (2005) 1203.
- [50] T. Zhang, J. Ge, Y. Hu, Y. Yin, *Nano Lett.* 7 (2007) 3203.
- [51] V.F. Puentes, K.M. Krishnan, A.P. Alivisatos, *Science* 291 (2001) 2115.

- [52] E.C. Scher, L. Manna, A.P. Alivisatos, *Philos. Trans. R. Soc. London A* 361 (2003) 241.
- [53] (a) Y. Sun, Y. Xia, *Science* 298 (2002) 2176;
(b) Y. Sun, B.T. Mayers, Y. Xia, *Nano Lett.* 2 (2002) 481;
(c) J. Chen, F. Sadki, B.J. Wiley, H. Cang, M.J. Cobb, Z.-Y. Li, L. Au, H. Zhang, M.B. Kimmey, X. Li, Y. Xia, *Nano Lett.* 5 (2005) 473.
- [54] B. Wiley, Y. Sun, B. Mayers, Y. Xia, *Chem. Eur. J.* 11 (2005) 454.
- [55] R.J. Nikhil, *Small* 1 (2005) 875.
- [56] J. Park, K. An, Y. Hwang, J.-G. Park, H.-J. Noh, J.-Y. Kim, J.-H. Park, N.-M. Hwang, T. Hyeon, *Nat. Mater.* 3 (2004) 891.
- [57] X. Wang, J. Zhuang, Q. Peng, Y. Li, *Nature* 437 (2005) 121.
- [58] N. Zheng, J. Fan, G.D. Stucky, *J. Am. Chem. Soc.* 128 (2006) 6550.
- [59] N.R. Jana, X. Peng, *J. Am. Chem. Soc.* 125 (2003) 14280.
- [60] Y. Vasquez, A.K. Sra, R.E. Schaak, *J. Am. Chem. Soc.* 127 (2005) 12504.
- [61] Y. Sun, Y. Xia, *J. Am. Chem. Soc.* 126 (2004) 3892.
- [62] Y. Sun, B. Mayers, Y. Xia, *Adv. Mater.* 15 (2003) 641.
- [63] J.-I. Park, J. Cheon, *J. Am. Chem. Soc.* 123 (2001) 5743.
- [64] J.I. Park, M.G. Kim, Y.W. Jun, J.S. Lee, W.R. Lee, J. Cheon, *J. Am. Chem. Soc.* 126 (2004) 9072.
- [65] W.S. Seo, J.H. Shim, S.J. Oh, E.K. Lee, N.H. Hur, J.T. Park, *J. Am. Chem. Soc.* 127 (2005) 6188.
- [66] T. Hyeon, S.S. Lee, J. Park, Y. Chung, H.B. Na, *J. Am. Chem. Soc.* 123 (2001) 12798.
- [67] M.F. Casula, Y.W. Jun, D.J. Zaziski, E.M. Chan, A. Corrias, A.P. Alivisatos, *J. Am. Chem. Soc.* 128 (2006) 1675.
- [68] S.G. Kwon, Y. Piao, J. Park, S. Angappane, Y. Jo, N.M. Hwang, J.G. Park, T. Hyeon, *J. Am. Chem. Soc.* 129 (2007) 12571.
- [69] Y. Yin, R.M. Rioux, C.K. Erdonmez, S. Hughes, G.A. Somorjai, A.P. Alivisatos, *Science* 304 (2004) 711.
- [70] Y. Yin, C.K. Erdonmez, A. Cabot, S. Hughes, A.P. Alivisatos, *Adv. Funct. Mater.* 16 (2006) 1389.
- [71] H.J. Fan, M. Knez, R. Scholz, D. Hesse, K. Nielsch, M. Zacharias, U. Gösele, *Nano Lett.* 7 (2007) 993.
- [72] A.D. Smigelskas, E.O. Kirkendall, *Trans. AIME* 171 (1947) 130.
- [73] D.H. Son, S.M. Hughes, Y. Yin, A.P. Alivisatos, *Science* 306 (2004) 1009.
- [74] N.R. Jana, L. Gearheart, C.J. Murphy, *Langmuir* 17 (2001) 6782.
- [75] H. Hiramatsu, F.E. Osterloh, *Chem. Mater.* 16 (2004) 2509.
- [76] S.U. Son, Y. Jang, K.Y. Yoon, E. Kang, T. Hyeon, *Nano Lett.* 4 (2004) 1147.
- [77] M. Ganesan, R.G. Freemantle, S.O. Obare, *Chem. Mater.* 19 (2007) 3464.
- [78] X.Z. Lin, X. Teng, H. Yang, *Langmuir* 19 (2003) 10081.
- [79] C. Pan, K. Pelzer, K. Philippot, P. Chaudret, P. Dassenoy, M.J. Lecante, J. Casanove, *J. Am. Chem. Soc.* 123 (2001) 7584.
- [80] N. Chakroune, G. Viau, S. Ammar, L. Poul, D. Veautier, M.M. Chehimi, C. Mangeney, F. Villain, F. Fievet, *Langmuir* 21 (2005) 6788.
- [81] G. Viau, R. Brayner, L. Poul, N. Chakroune, E. Lacaze, F. Fievet-Vincent, F. Fievet, *Chem. Mater.* 15 (2003) 486.
- [82] V.F. Puentes, K.M. Krishnan, P. Alivisatos, *Appl. Phys. Lett.* 78 (2001) 2187.
- [83] H. Bonnemann, W. Brijoux, R. Brinkmann, N. Matoussevitch, N. Waldofner, N. Palina, H. Modrow, *Inorg. Chim. Acta* 350 (2003) 617.
- [84] J. Park, E. Kang, S.U. Son, H.M. Park, M.K. Lee, J. Kim, K.W. Kim, H.J. Noh, J.H. Park, C.J. Bae, J.G. Park, T. Hyeon, *Adv. Mater.* 17 (2005) 429.
- [85] K. Soulantica, A. Maisonnat, M.-C. Fromen, M.-J. Casanove, P. Lecante, B. Chaudret, *Angew. Chem. Int. Ed.* 40 (2001) 448.
- [86] H. Yu, P.C. Gibbons, K.F. Kelton, W.E. Buhro, *J. Am. Chem. Soc.* 123 (2001) 9198.
- [87] B. Wiley, Y. Sun, Y. Xia, *Acc. Chem. Res.* 40 (2007) 1067.
- [88] B.J. Wiley, Y. Xiong, Z.Y. Li, Y. Yin, Y. Xia, *Nano Lett.* 6 (2006) 765.
- [89] Y. Xiong, Y. Xia, *Adv. Mater.* 19 (2007) 3385.
- [90] Y. Xiong, J.M. McLellan, J. Chen, Y. Yin, Z.Y. Li, Y. Xia, *J. Am. Chem. Soc.* 127 (2005) 17118.
- [91] C. Wang, H. Daimon, Y. Lee, J. Kim, S. Sun, *J. Am. Chem. Soc.* 129 (2007) 6974.
- [92] J. Chen, T. Herricks, Y. Xia, *Angew. Chem. Int. Ed.* 44 (2005) 2589.
- [93] H. Song, F. Kim, S. Connor, G.A. Somorjai, P. Yang, *J. Phys. Chem. B* 109 (2005) 188.
- [94] T.K. Sau, C.J. Murphy, *J. Am. Chem. Soc.* 126 (2004) 8648.
- [95] J.D. Hoefelmeyer, K. Niesz, G.A. Somorjai, T.D. Tilley, *Nano Lett.* 5 (2005) 435.
- [96] S.M. Humphrey, M.E. Grass, S.E. Habas, K. Niesz, G.A. Somorjai, T.D. Tilley, *Nano Lett.* 7 (2007) 785.
- [97] M. Brust, A. Walker, D. Bethell, D.J. Schiffrin, R. Whyman, *J. Chem. Soc. Chem. Commun.* (1994) 801.
- [98] D. Seo, J.C. Park, H. Song, *J. Am. Chem. Soc.* 128 (2006) 14863.
- [99] G. Chang, M. Oyama, K. Hirao, *Acta Mater.* 55 (2007) 3453.
- [100] I. Washio, Y. Xiong, Y. Yin, Y. Xia, *Adv. Mater.* 18 (2006) 1745.
- [101] V.F. Puentes, D. Zanchet, C.K. Erdonmez, A.P. Alivisatos, *J. Am. Chem. Soc.* 124 (2002) 12874.
- [102] F. Kim, S. Connor, H. Song, T. Kuykendall, P. Yang, *Angew. Chem. Int. Ed.* 43 (2004) 3673.
- [103] B. Lim, Y. Xiong, Y. Xia, *Angew. Chem. Int. Ed.* 46 (2007) 9279.
- [104] T. Herricks, J. Chen, Y. Xia, *Nano Lett.* 4 (2004) 2367.
- [105] S. Chen, Z.L. Wang, J. Ballato, S.H. Foulger, D.L. Carroll, *J. Am. Chem. Soc.* 125 (2003) 16186.
- [106] C.J. Murphy, T.K. Sau, A.M. Gole, C.J. Orendorff, J. Gao, L. Gou, S.E. Hunyadi, T. Li, *J. Phys. Chem. B* 109 (2005) 13857.
- [107] C.J. Murphy, A.M. Gole, S.E. Hunyadi, C.J. Orendorff, *Inorg. Chem.* 45 (2006) 7544.
- [108] Y. Yin, C. Erdonmez, S. Aloni, A.P. Alivisatos, *J. Am. Chem. Soc.* 128 (2006) 12671.
- [109] X. Lu, H.-Y. Tuan, J. Chen, Z.-Y. Li, B.A. Korgel, Y. Xia, *J. Am. Chem. Soc.* 129 (2007) 1733.
- [110] M. Sastry, A. Swami, S. Mandal, P.R. Selvakannan, *J. Mater. Chem.* 15 (2005) 3161.
- [111] H.P. Liang, L.J. Wan, C.L. Bai, L. Jiang, *J. Phys. Chem. B* 109 (2005) 7795.
- [112] H.-P. Liang, H.-M. Zhang, J.-S. Hu, Y.-G. Guo, L.-J. Wan, C.-L. Bai, *Angew. Chem. Int. Ed.* 43 (2004) 1540.
- [113] H.-P. Liang, Y.-G. Guo, H.-M. Zhang, J.-S. Hu, L.-J. Wan, C.-L. Bai, *Chem. Commun.* (2004) 1496.
- [114] J. Zeng, J. Huang, W. Lu, X. Wang, B. Wang, S. Zhang, J. Hou, *Adv. Mater.* 19 (2007) 2172.
- [115] K. Woo, J. Hong, S. Choi, H.-W. Lee, J.-P. Ahn, C.S. Kim, S.W. Lee, *Chem. Mater.* 16 (2004) 2814.
- [116] M. Yin, C.-K. Wu, Y. Lou, C. Burda, J.T. Koberstein, Y. Zhu, S. O'Brien, *J. Am. Chem. Soc.* 127 (2005) 9506.
- [117] S.U. Son, I.K. Park, J. Park, T. Hyeon, *Chem. Commun.* (2004) 778.
- [118] S. O'Brien, L. Brus, C.B. Murray, *J. Am. Chem. Soc.* 123 (2001) 12085.
- [119] J. Rockenberger, E.C. Scher, A.P. Alivisatos, *J. Am. Chem. Soc.* 121 (1999) 11595.
- [120] J.-W. Seo, Y.-W. Jun, S.J. Ko, J. Cheon, *J. Phys. Chem. B* 109 (2005) 5389.
- [121] D.-S. Wang, T. Xie, Q. Peng, S.-Y. Zhang, J. Chen, Y.-D. Li, *Chem. Eur. J.* (2008).
- [122] J. Park, J. Joo, S.G. Kwon, Y. Jang, T. Hyeon, *Angew. Chem. Int. Ed.* 46 (2007) 4630.
- [123] Y.-W. Jun, J.-S. Choi, J. Cheon, *Angew. Chem. Int. Ed.* 45 (2006) 3414.
- [124] A. Cabot, V.F. Puentes, E. Shevchenko, Y. Yin, L. Balcells, M.A. Marcus, S.M. Hughes, A.P. Alivisatos, *J. Am. Chem. Soc.* 129 (2007) 10358.
- [125] B. Gates, B. Mayers, Y. Wu, Y. Sun, B. Cattle, P. Yang, Y. Xia, *Adv. Funct. Mater.* 12 (2002) 679.
- [126] K. Jang, S.Y. Kim, K.H. Park, E. Jang, S. Jun, S.U. Son, *Chem. Commun.* (2007) 4474.
- [127] C. Liang, K. Terabe, T. Hasegawa, M. Aono, *Solid State Ionics* 177 (2006) 2527.
- [128] B. Gates, Y. Wu, Y. Yin, P. Yang, Y. Xia, *J. Am. Chem. Soc.* 123 (2001) 11500.
- [129] X. Jiang, B. Mayers, Y. Wang, B. Cattle, Y. Xia, *Chem. Phys. Lett.* 385 (2004) 472.
- [130] X. Jiang, B. Mayers, T. Herricks, Y. Xia, *Adv. Mater.* 15 (2003) 1740.
- [131] H. Tan, S. Li, W.Y. Fan, *J. Phys. Chem. B* 110 (2006) 15812.
- [132] Z.-Y. Jiang, Z.-X. Xie, X.-H. Zhang, R.-B. Huang, L.-S. Zheng, *Chem. Phys. Lett.* 378 (2003) 313.
- [133] P.K. Khanna, K.-W. Jun, K.B. Hong, J.-O. Baeg, G.K. Mehrotra, *Mater. Chem. Phys.* 92 (2005) 54.
- [134] N. Singh, P.K. Khanna, *Synth. React. Inorg. Met.* 37 (2007) 367.
- [135] R.-K. Chiang, R.-T. Chiang, *Inorg. Chem.* 46 (2007) 369.
- [136] A.E. Henkes, Y. Vasquez, R.E. Schaak, *J. Am. Chem. Soc.* 129 (2007) 1896.
- [137] J.-H. Chen, M.-F. Tai, K.-M. Chi, *J. Mater. Chem.* 14 (2004) 296.
- [138] F.K. Schmidt, L.B. Belykh, T.V. Cherenkova, *Kinet. Catal.* 42 (2001) 163.
- [139] A.E. Henkes, R.E. Schaak, *Chem. Mater.* 19 (2007) 4234.
- [140] H.-G. von Schnering, W. Hönl, *Chem. Rev.* 88 (1988) 243.
- [141] S.T. Oyama, *J. Catal.* 216 (2003) 343.
- [142] A.M. Hermann, A. Madan, M.W. Wanlass, V. Badri, R. Ahrenkiel, S. Morrison, C. Gonzales, *Sol. Energy Mater. Sol. Cells* 82 (2004) 241.
- [143] M. Soliman, A.B. Kashyout, M. Osman, M. El-Gamal, *Renew. Energy* 30 (2005) 1819.
- [144] A.E. Henkes, R.E. Schaak, *Inorg. Chem.* 47 (2008) 671.
- [145] N. Zettsu, J.M. McLellan, B. Wiley, Y. Yin, Z.-Y. Li, Y. Xia, *Angew. Chem. Int. Ed.* 45 (2006) 1288.
- [146] K.H. Park, K. Jang, H.J. Kim, S.U. Son, *Angew. Chem. Int. Ed.* 46 (2007) 1152.
- [147] J. Chen, B. Wiley, J.M. McLellan, Y. Xiong, Z.-Y. Li, Y. Xia, *Nano Lett.* 5 (2005) 2058.
- [148] J. Chen, J.M. McLellan, A. Siekkinen, Y. Xiong, Z.-Y. Li, Y. Xia, *J. Am. Chem. Soc.* 128 (2006) 14776.
- [149] Y. Sun, Y. Xia, *Adv. Mater.* 16 (2004) 264.
- [150] Y. Sun, Z. Tao, J. Chen, T. Herricks, Y. Xia, *J. Am. Chem. Soc.* 126 (2004) 5940.
- [151] Y. Sun, Y. Xia, *Nano Lett.* 3 (2003) 1569.
- [152] Q. Zhang, J.Y. Lee, J. Yang, C. Boothroyd, J. Zhang, *Nanotechnology* 18 (2007) 245605.
- [153] W.R. Lee, M.G. Kim, J.R. Choi, J.I. Park, S.J. Ko, S.J. Oh, J. Cheon, *J. Am. Chem. Soc.* 127 (2005) 16090.
- [154] J. Hambrook, M.K. Schroter, A. Birkner, C. Woll, R.A. Fischer, *Chem. Mater.* 15 (2003) 4217.
- [155] B.M. Leonard, N.S.P. Bhuvanesh, R.E. Schaak, *J. Am. Chem. Soc.* 127 (2005) 7326.
- [156] B.M. Leonard, R.E. Schaak, *J. Am. Chem. Soc.* 128 (2006) 11475.
- [157] C. Roychowdhury, F. Matsumoto, P.F. Mutolo, H.D. Abruna, F.J. DiSalvo, *Chem. Mater.* 17 (2005) 5871.
- [158] S. Maksimuk, S. Yang, Z. Peng, H. Yang, *J. Am. Chem. Soc.* 129 (2007) 8684.
- [159] N.H. Chou, R.E. Schaak, *J. Am. Chem. Soc.* 129 (2007) 7339.
- [160] N.H. Chou, R.E. Schaak, *Chem. Mater.* 20 (2008) in press.
- [161] A. Lang, W.Z. Jeitschko, *Metallkunde* 87 (1996) 759.
- [162] M.G. Kanatzidis, R. Pottgen, W. Jeitschko, *Angew. Chem. Int. Ed. Engl.* 44 (2005) 6996.
- [163] T.B. Massalski, *Binary Alloy Phase Diagrams*, ASM International, Materials Park, OH, 1996.
- [164] R.E. Cable, R.E. Schaak, *Chem. Mater.* 19 (2007) 4098.

- [165] J.C. Bauer, X. Chen, Q. Liu, T.H. Phan, R.E. Schaak, J. Mater. Chem. 3 (2008) 275.
- [166] (a) R.E. Cable, R.E. Schaak, Chem. Mater. 17 (2005) 6835;
(b) R.E. Cable, R.E. Schaak, J. Am. Chem. Soc. 128 (2006) 9588.
- [167] A.K. Sra, T.D. Ewers, R.E. Schaak, Chem. Mater. 17 (2005) 758.
- [168] L.R. Alden, D.K. Han, F. Matsumoto, H.D. Abruña, F.J. DiSalvo, Chem. Mater. 18 (2006) 5591.
- [169] L.R. Alden, C. Roychowdhury, F. Matsumoto, D.K. Han, V.B. Zeldovich, H.D. Abruña, F.J. DiSalvo, Langmuir 22 (2006) 10465.
- [170] A.J. Karkamkar, M.G. Kanatzidis, J. Am. Chem. Soc. 128 (2006) 6002.
- [171] M.M. Schubert, M.J. Kahllich, G. Feldmeyer, M. Huttner, S. Hackenberg, H.A. Gasteiger, R.J. Behm, Phys. Chem. Chem. Phys. 3 (2001) 1123.
- [172] F. Dawood, B.M. Leonard, R.E. Schaak, Chem. Mater. 19 (2007) 4545.
- [173] L. Dloczik, R. Könenkamp, Nano Lett. 3 (2003) 651.
- [174] A.E. Raevskaya, A.L. Stroyuk, S.Y. Kuchmii, A.I. Kryukov, Theor. Exp. Chem. 39 (2003) 303.
- [175] W. Zhu, W. Wang, J. Shi, J. Phys. Chem. B 110 (2006) 9785.
- [176] U. Jeong, P.H.C. Camargo, Y.L. Lee, Y. Xia, J. Mater. Chem. 16 (2006) 3893.
- [177] R.D. Robinson, B. Sadtler, D.O. Demchenko, C.K. Erdonmez, L.-W. Wang, A.P. Alivisatos, Science 317 (2007) 355.
- [178] Y. Feldman, G.L. Frey, M. Homyonfer, V. Lyakhovitskaya, L. Margulis, H. Cohen, G. Hodes, J.L. Hutchison, R. Tenne, J. Am. Chem. Soc. 118 (1996) 5362.
- [179] R. Tenne, L. Margulis, M. Genut, G. Hodes, Nature 360 (1992) 444.
- [180] J. Sloan, J.L. Hutchison, R. Tenne, Y. Feldman, T. Tsirlina, M. Homyonfer, J. Solid State Chem. 144 (1999) 100.
- [181] N. Elizondo-Villarreal, R. Velazquez-Castillo, D.H. Galvan, A. Camacho, M. Jose Yacamán, Appl. Catal. A: Gen. 328 (2007) 88.
- [182] G.A. Camacho-Bragado, M. Jose-Yacamán, Appl. Phys. A 82 (2006) 19.
- [183] W. Hu, Y. Zhao, Z. Liu, Y. Zhu, Nanotechnology 18 (2007) 095605.
- [184] S.K. Panda, A. Dev, S. Chaudhuri, J. Phys. Chem. C 111 (2007) 5039.
- [185] Q. Li, J.T. Newberg, E.C. Walter, J.C. Hemminger, R.M. Penner, Nano Lett. 4 (2004) 277.
- [186] Q. Li, E.C. Walter, W.E. vanderVeer, B.J. Murray, J.T. Newberg, E.W. Bohannon, J.A. Switzer, J.C. Hemminger, R.M. Penner, J. Phys. Chem. B 109 (2005) 3169.
- [187] H. Zhang, D. Yang, X. Ma, D. Que, Nanotechnology 16 (2005) 2721.
- [188] C. Yan, D. Xue, J. Phys. Chem. B 110 (2006) 25850.
- [189] Z. Wang, X.-F. Qian, Y. Li, J. Yin, Z.-K. Zhu, J. Solid State Chem. 178 (2005) 1589.
- [190] H.-F. Shao, X.-F. Qian, Z.-K. Zhu, J. Solid State Chem. 178 (2005) 3522.
- [191] H. Cao, X. Qian, C. Wang, X. Ma, J. Yin, Z. Zhu, J. Am. Chem. Soc. 127 (2005) 16024.
- [192] Y.C. Zhang, T. Qiao, X. Ya Hu, J. Cryst. Growth 268 (2004) 64.
- [193] Y. Li, Y. Huang, T. Bai, L. Li, Inorg. Chem. 39 (2000) 3418.
- [194] L.M. Wu, R. Sharma, D.K. Seo, Inorg. Chem. 42 (2003) 5798.
- [195] L.M. Wu, D.K. Seo, J. Am. Chem. Soc. 126 (2004) 4676.
- [196] H. Shao, X. Qian, B. Huang, Mater. Lett. 61 (2007) 3639.
- [197] J. Geng, B. Liu, L. Xu, F.N. Hu, J.J. Zhu, Langmuir 23 (2007) 10286.
- [198] J. Li, L. Gao, J. Sun, Q. Zhang, J. Guo, D. Yan, J. Am. Ceram. Soc. 84 (2001) 3045.
- [199] Y. Li, L. Gao, J. Li, D. Yan, J. Am. Ceram. Soc. 85 (2002) 1294.
- [200] L. Gao, Q. Zhang, J. Li, J. Mater. Chem. 13 (2003) 154.
- [201] Q. Zhang, L. Gao, Langmuir 20 (2004) 9821.
- [202] Q. Zhang, L. Gao, J. Am. Chem. Soc. 89 (2006) 415.
- [203] R. Aghababazadeh, A.R. Mirhabibi, B. Rand, S. Banijamali, J. Pourasad, M. Ghahari, Surf. Sci. 601 (2007) 2881.
- [204] G. Schmid, J. Mater. Chem. 12 (2002) 1231.
- [205] J. Hu, Y. Bando, D. Golberg, Q. Liu, Angew. Chem. Int. Ed. 42 (2003) 3493.
- [206] J. Buha, I. Djerdj, M. Antonietti, M. Niederberger, Chem. Mater. 19 (2007) 3499.
- [207] S. Skrabalak, J. Chen, L. Au, X. Lu, X. Li, Y. Xia, Adv. Mater. 19 (2007) 3177.
- [208] Y. Sun, Y. Xia, Nano Lett. 3 (2003) 1569.