

Architectural Design of Heterogeneous Metallic Nanocrystals—Principles and Processes

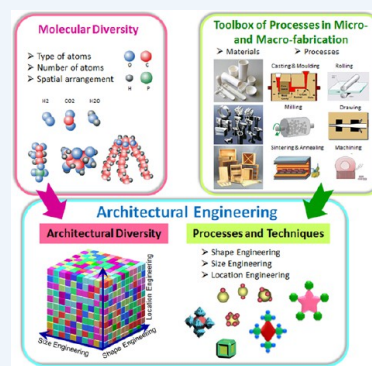
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CONSPECTUS: Heterogeneous metal nanocrystals (HMNCs) are a natural extension of simple metal nanocrystals (NCs), but as a research topic, they have been much less explored until recently. HMNCs are formed by integrating metal NCs of different compositions into a common entity, similar to the way atoms are bonded to form molecules. HMNCs can be built to exhibit an unprecedented architectural diversity and complexity by programming the arrangement of the NC building blocks (“unit NCs”). The architectural engineering of HMNCs involves the design and fabrication of the architecture-determining elements (ADEs), i.e., unit NCs with precise control of shape and size, and their relative positions in the design. Similar to molecular engineering, where structural diversity is used to create more property variations for application explorations, the architectural engineering of HMNCs can similarly increase the utility of metal NCs by offering a suite of properties to support multifunctionality in applications.

The architectural engineering of HMNCs calls for processes and operations that can execute the design. Some enabling technologies already exist in the form of classical micro- and macroscale fabrication techniques, such as masking and etching. These processes, when used singly or in combination, are fully capable of fabricating nanoscopic objects. What is needed is a detailed understanding of the engineering control of ADEs and the translation of these principles into actual processes. For simplicity of execution, these processes should be integrated into a common reaction system and yet retain independence of control. The key to architectural diversity is therefore the independent controllability of each ADE in the design blueprint. The right chemical tools must be applied under the right circumstances in order to achieve the desired outcome.

In this Account, after a short illustration of the infinite possibility of combining different ADEs to create HMNC design variations, we introduce the fabrication processes for each ADE, which enable shape, size, and location control of the unit NCs in a particular HMNC design. The principles of these processes are discussed and illustrated with examples. We then discuss how these processes may be integrated into a common reaction system while retaining the independence of individual processes. The principles for the independent control of each ADE are discussed in detail to lay the foundation for the selection of the chemical reaction system and its operating space.



1. INTRODUCTION

Many of today's technical challenges are limited by the performance of materials. In general, the properties of a material are defined by its internal configuration (arrangement of constituent atoms) and external structure (shape and size). Organic chemists have been highly successful in creating an innumerable number of diverse molecules from three basic elements (carbon, hydrogen, and oxygen) by simply changing their numbers and relative positions in the molecule. Unlike nonmetals, metallic atoms are bonded nonspecifically and therefore lack the directionality of covalent bonds and the equivalence of molecules. The level of sophistication that is possible with only metals thus looks rather limited. Recently, techniques for manipulating metals at the nanoscale have been developed, which allow the creation of new pseudometallic building units, liberating us from the bondage of the periodic table. Metal analogues of molecular-like structures, i.e., heterogeneous metallic nanocrystals (HMNCs), can be created by combining different metallic NCs directly in specific numbers and arrangements.^{1–3} HMNCs with unprecedented structural

diversity and complexity can be fabricated by a systematic approach to architectural engineering that involves, first and foremost, the rational design of the architecture-determining elements (ADEs), namely, the shape, size, and location of the unit NCs. The physical and chemical properties of nanometals are profoundly affected by these ADEs.^{1,2,4–6} Architectural engineering therefore has the potential to greatly expand the application values of nanometals by diversifying their structures and consequently the properties that can be made from a small number of metals.^{4,5,7–9}

The success of architectural engineering depends on the availability of methods and processes that can be used to fabricate these complex and diverse architectures. We can draw inspiration from some macro- and microscale fabrication processes with demonstrated capability to sculpture materials into the desired form and structure. The key is to adapt these processes, or to identify their equivalents, for nanoscale fabrication.

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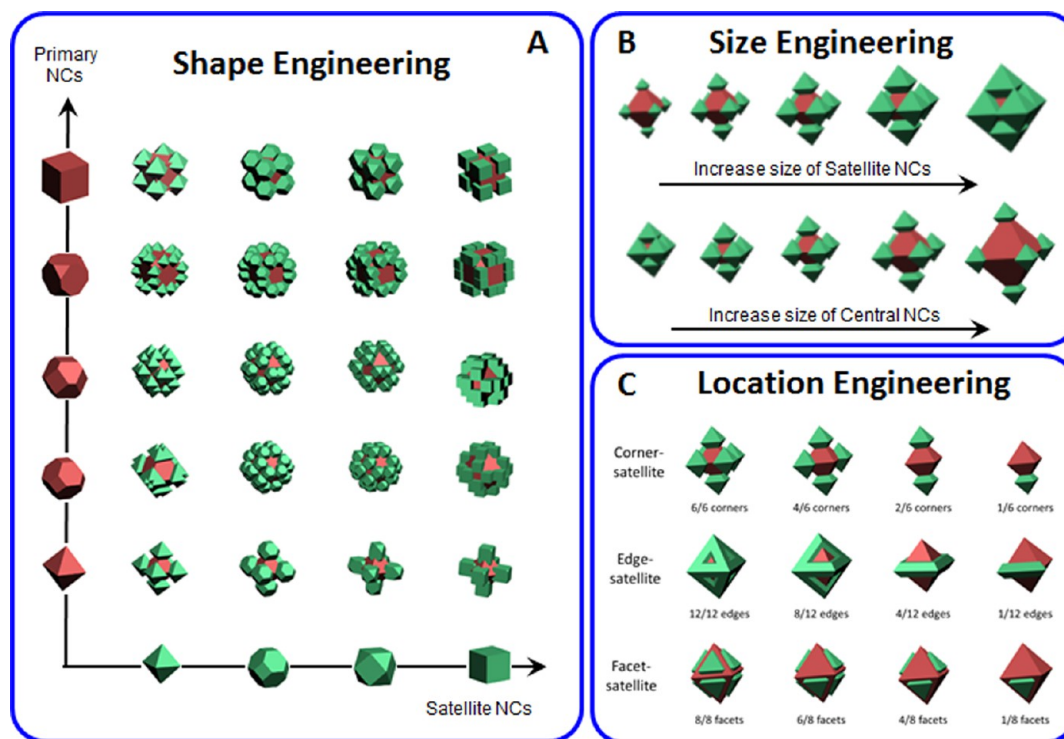


Figure 1. Illustration of the architectural diversity of HMNCs through shape, size, and location engineering using binary HMNCs as examples. (A) Shape engineering: the use of unit NCs of octahedrons, cubes, and their truncated forms with different degrees of truncation as well as satellite NCs on the corners of the primary NCs. (B) Size engineering: independent tuning of the size of satellite and primary NCs. (C) Location engineering: the selective placement of satellite NCs on the corners, edges and facets of the primary NCs.

The major problem of using these techniques in nanofabrication is the absence of physical tools and mechanical machines like those available on the macroscale to handle the materials. On the other hand, a large pool of chemical reactions and chemical interactions such as oxidation, reduction, adsorption, and desorption have been shown to be effective for bottom-up fabrication of nanomaterials. The specificity of chemical reactions can be used advantageously for ADE control.

In this Account, we first illustrate how a nearly infinite diversity of HMNC architectures may be created by engineering of ADEs. Next we discuss individual processes and techniques for engineering the shape, size, and location of the unit NCs. We then demonstrate how the various processes may be integrated into one chemical reaction system for convenience of execution without compromising the independent control of the ADEs in the HMNCs, thus leading to the control of a great variety of structural variations.

2. DIVERSIFYING HMNC ARCHITECTURES

Architectural engineering offers a systemic approach to greatly multiply the number of possible HMNC structures. Architectural engineering consists of shape, size, and location engineering. Shape engineering creates a library of polyhedral NC shapes, which form the basic building blocks (unit NCs) in an HMNC construction.^{4,10–13} Size engineering generates a continuum of sizes within a given polyhedral shape to expand the number of variations in a given HMNC design.^{6,14–16} The unit NCs can then be combined geometrically in many ways by location engineering, which diversifies the spatial relationship of the unit NCs in an HMNC structure.¹⁷ Figure 1 presents a sampling of the architectural variations made with only two types of unit NCs by shape, size, and location engineering. If the shape, size, and

relative location of the unit NCs can be independently varied, the number of ways these ADEs may be combined to form HMNC structures can indeed approach infinity.

3. SHAPE ENGINEERING

Shape engineering is the basic toolset for generating the unit NCs, which are the building blocks of the HMNCs. The key to shape engineering is the ability to alter the distribution of exposed crystallographic facets (which determines the shape geometry) by promoting selective growth in certain crystallographic directions.^{10,11} Facets perpendicular to slow-growing directions would expand at the expense of facets perpendicular to fast-growing directions. Shape engineering can be achieved by the following techniques/processes adopted from macro- and microscale fabrication.

3.1. Deposition

The principal tool for shaping nanomaterials is the deposition kinetics of the metal atoms, or equivalently, the kinetics of metal precursor reduction. The reduction kinetics determines the number of atoms available for deposition and affects their deposition characteristics. A low reduction rate limits the number of atoms available for deposition, and as a result, many of these atoms are able to select the most energetically favorable growth sites. The difference between growths in different crystallographic directions is therefore accentuated.

The metal precursor reduction kinetics can be varied through selection of the solvent, reactants, additives, and reaction conditions. Many reducing agents are available to provide a wide range of reduction power and tunability. Solvent and capping agents can affect the diffusion and delivery of the reactants and hence their effective reduction rate. Capping agents and additives may form complexes with the metal precursors to change the

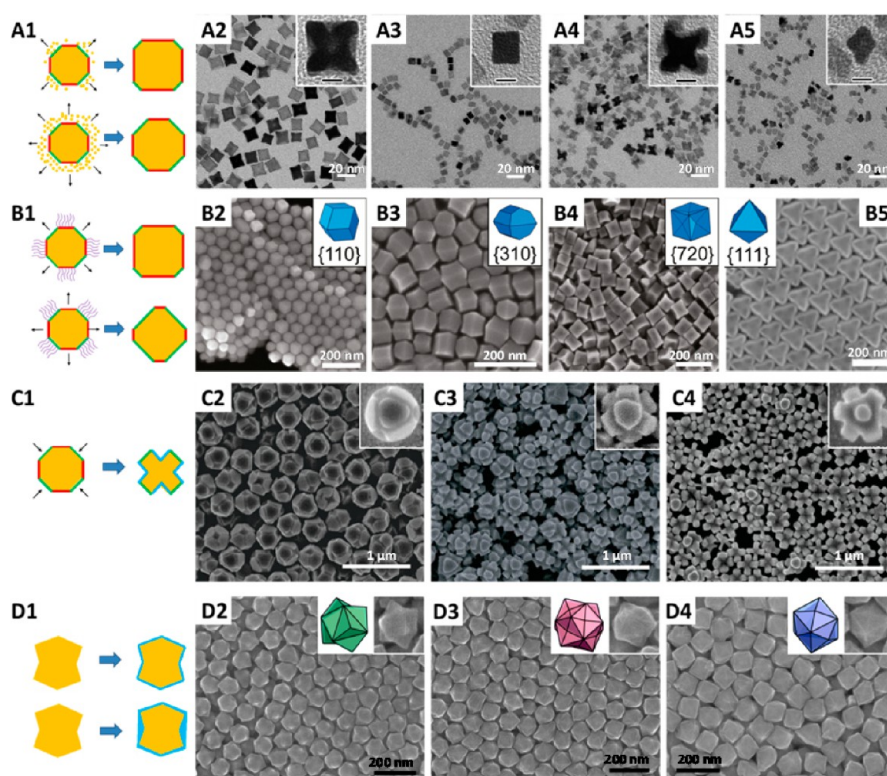


Figure 2. Shape engineering. (A) Deposition control: shaping of Rh NCs by controlling the rate of metal precursor injection. Shapes from left to right: concave cubes, cubes, octapods, and octapods in a rudimentary state. Adapted from ref 19. Copyright 2010 American Chemical Society. (B) Masking: shaping of Au NCs by varying the masking agent (Ag^+) concentration. Shapes from left to right: {110}-faceted rhombic dodecahedra, {310}-faceted truncated ditetragonal prisms, {720}-faceted concave cubes, and {111}-faceted octahedra with hollow cavities. Adapted from refs 21 and 22. Copyright 2011 and 2012 American Chemical Society, respectively. (C) Etching: Ag NCs formed by varying the etchant strength. Adapted from ref 23. Copyright 2009 American Chemical Society. (D) Templating: Au@Pd high-index NCs in {hhl}-faceted TOH, {hkl}-faceted HOH, and {hk0}-faceted THH shapes (left to right) prepared by heteroepitaxial growth of Pd facets on high-index TOH Au templates and growth kinetics control. Adapted from ref 32. Copyright 2010 American Chemical Society.

reduction potentials and/or solubility and consequently the rate of reduction.¹⁸ Reaction conditions such as temperature and solution pH can affect the reduction kinetics through their effects on the reducing power of the reducing agent and/or the dynamics of capping agent or additive adsorption. In addition, the reduction rate can also be varied by the rate of reactant injection using a syringe pump (Figure 2A).¹⁹

3.2. Masking

Masking is a microfabrication process in which a photomask with the desired pattern is used to restrain a process to occur only on the areas of the substrate not shadowed by the mask. The nanomaterials fabrication equivalent of masking is selective adsorption of chemical species on specific surface sites. The different atomic arrangements and electronic structures of the surface sites of an NC give rise to selectivity in binding affinity. Selective adsorption can reduce the accessibility of some sites to deposition of metal atoms, resulting in slower crystal growth in the affected direction and relatively faster growth of other facets to their oblivion.

A wide variety of chemical species can be used as masks. The list includes surfactants, polymers, biomolecules, and small molecular or ionic species.^{2,11} The chemisorption trends of some common masking species are known and have been used for shape control. For example, the preferential adsorption of Br^- on the {100} facets of many noble metals such as Ag, Au, and Pd have been used to promote the exposure of {100} facets

in the synthesis of nanocubes and nanobars.¹¹ Ag^+ ions are often introduced in the synthesis of Au NCs to promote the formation of more open facets such as {110} and high-index facets through the formation of a underpotential deposition (UPD) layer on the Au NC surface.^{18,20} Figure 2B shows an example of the different Au nanostructures formed by increasing the Ag^+ concentration in the reaction system.^{21,22}

3.3. Etching

Etching is used in microfabrication to remove materials from a surface. In nanomaterials fabrication, etching is the antithesis of metal deposition. Etching relies on a localized dissolution process in which certain regions of the NC surface are preferentially oxidized by a selective etchant and dissolved away into the solution.^{23,24} The etchant can be reactive paired chemical species such as $\text{NH}_4\text{OH}/\text{H}_2\text{O}_2$ ²³ or O_2/Cl^- ,²⁴ which oxidize the metal NCs, or metal ions of the less reactive metal in the galvanic pair, such as Au, Pd, and Pt ions, which can galvanically oxidize the Ag NCs.^{25,26} To initiate selective etching, the etchant has to have anisotropic reactivity that matches well with the exposed facets of the sacrificial NCs. Different etchants may induce oxidation at different surface sites.⁵ Masking can be used to inhibit or promote selective etching.^{22,27} Etching can be applied in situ with crystal growth to retard the growth rate.²⁸ It may also be used to modify the shape of a preformed NC that is susceptible to oxidative dissolution by the etchant.²³ In general, etching is used to

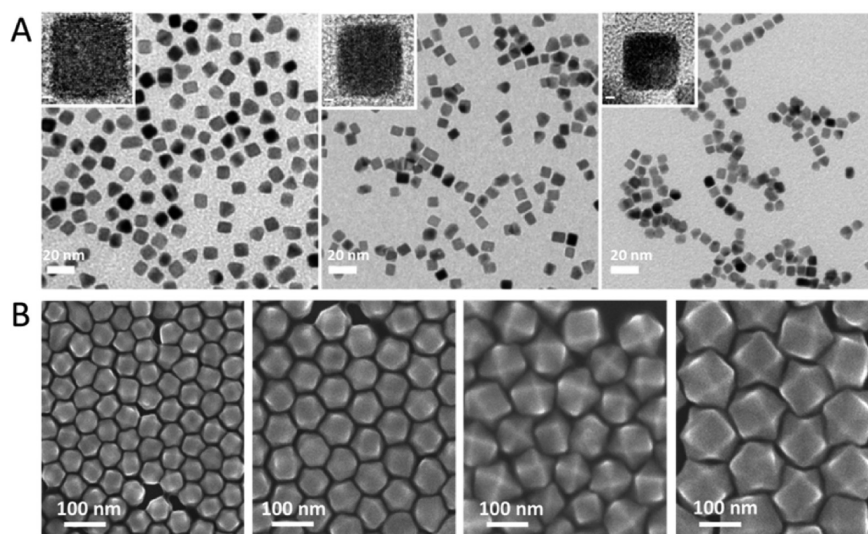


Figure 3. Size engineering. (A) Homogeneous nucleation. Pt nanocubes in decreasing sizes from left to right. Adapted from ref 6. Copyright 2009 American Chemical Society. (B) Heterogeneous nucleation. TOH Au NCs in increasing sizes from left to right obtained by a successive seed-mediated growth method. Adapted from ref 16. Copyright 2010 American Chemical Society.

create NCs with concave surfaces^{23,29} or hollow interiors.^{25,30,31}

An example of etching for shape engineering is given in Figure 2C. The etching power and selectivity were used to yield a highly anisotropic etching process for crafting of complex-shaped Ag NCs.²³

3.4. Templating

A template is an object with the desired shape that is used to guide the product formation. It is most useful to produce consistent configurations repeatedly. In nanomaterials shape engineering, a template can be used to direct the shape evolution or to transfer the shape or crystallinity of the template to a coating material where the direct synthesis of the latter into the desired shape or crystallinity may be difficult or impossible to achieve.

Template-assisted growth offers a simple and yet effective method for the preparation of high-index facets whose synthesis is difficult because of their high surface energy.^{32–35} The formation of such high-index facets is made easier by the use of preformed high-index NCs for which a method of synthesis already exists as the template to direct the growth of high-index facets of the shell component. The growth conditions for the shell component can deviate from those for the development of high-index facets on their own. The shape of the final NCs follows the shape of the high-index template when the shell thickness is uniform over the entire NC template.³³ High-index NCs with tailorable shapes and facets can also be prepared by combining the high-index templating method with other shape control techniques such as deposition kinetic control or masking. For example, we have used such combinations to prepare high-index Au@Pd NCs with customizable high-index classes (Figure 2D).³² The template may also guide the shape evolution of the shell metal through interfacial strain.^{34,35} In order to relieve the buildup of lattice strain with shell thickness, the NCs may adopt some forms of structural adjustments. The formation of high-index facets is likely an outcome of this structural adjustment.

Templates may be inert to the growth of the overlayer and thus retain their original morphology, or they may be reactive in the growth solution, where they can be etched.^{25,30} The templates in the latter case are often termed sacrificial

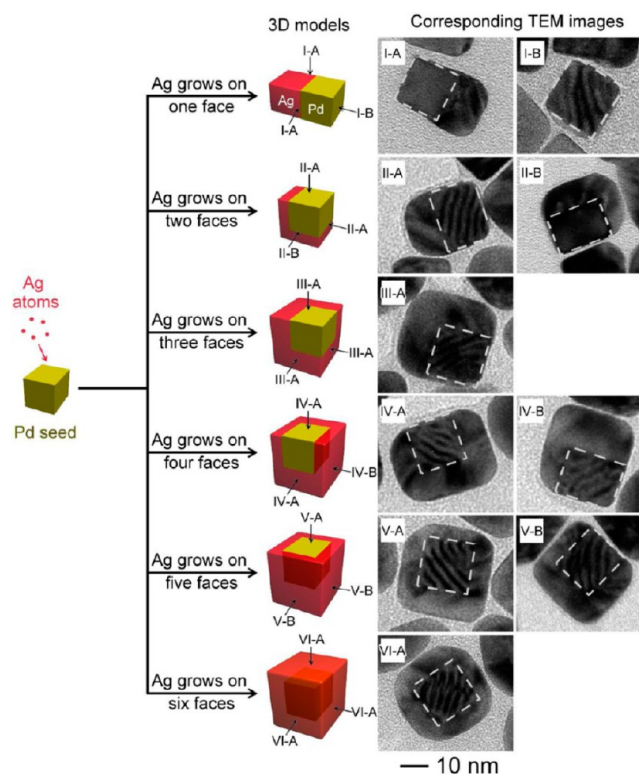


Figure 4. Location engineering by deposition kinetic control. The deposition of Ag was confined to one to six facets of a cubic Pd seed by means of carefully controlled reduction kinetics. Adapted from ref 37. Copyright 2012 American Chemical Society.

templates. Although the morphology of sacrificial templates undergoes changes during the synthesis, they still have a strong influence on the size and morphology of the final product.^{25,30}

4. SIZE ENGINEERING

Since size is almost continuously variable, size engineering of NCs can be an expeditious way to expand the diversity of

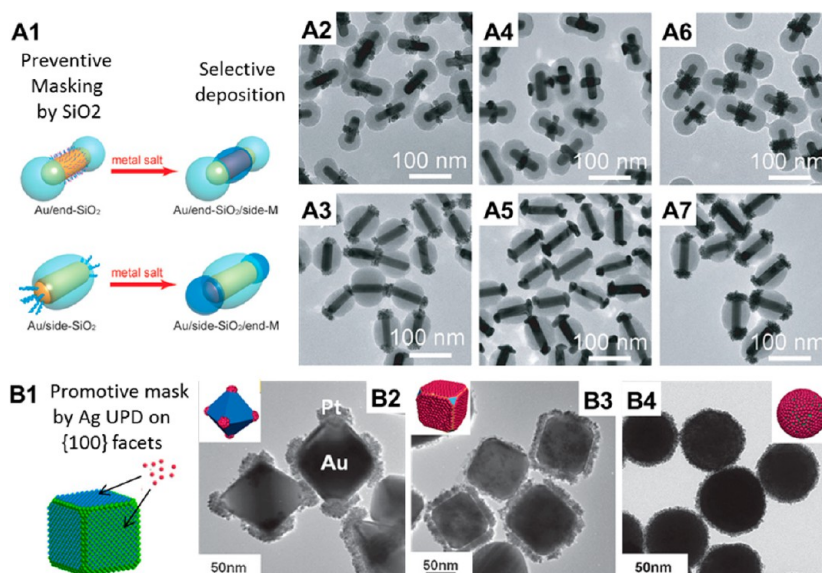


Figure 5. Location engineering by masking. (A) Preventive masking by selective deposition of silica on the two ends or the side surface of Au nanorods to prevent subsequent metal deposition there. The deposition of (A2, A3) Pd, (A4, A5) Au, and (A6, A7) Pt was confined to the middle (first row) or the two ends (second row) of the nanorods. Adapted with permission from ref 41. Copyright 2013 Wiley-VCH Verlag GmbH & Co. (B) Promotive masking by deposition of Ag on {100} facets of Au to promote the subsequent deposition of Pt. Adapted with permission from ref 43. Copyright 2009 Royal Society of Chemistry.

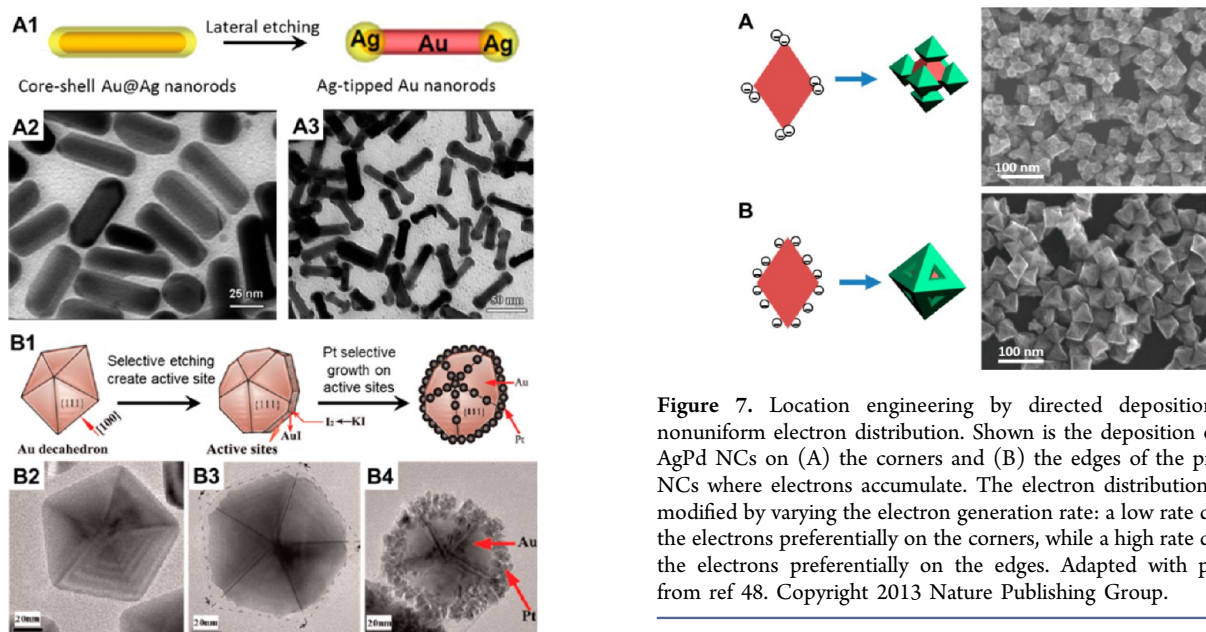


Figure 6. Location engineering by etching. (A) Lateral etching of the Ag shell in Au@Ag nanorods to form Au-Ag dumbbell HMNCs. Adapted from ref 45. Copyright 2012 American Chemical Society. (B) Etching to create active sites on edges for the edge-selective deposition of Pt on Au decahedral NCs. Adapted from ref 47. Copyright 2012 American Chemical Society.

HMNCs. NCs can grow via homogeneous or heterogeneous nucleation. In homogeneous nucleation, nucleation and growth of the NCs occur in the same environment, and the NC size is determined by the competition between nucleation and growth. Fast nucleation generates a large number of nuclei by depleting the source for subsequent growth, and hence, smaller particles are formed. The converse is true for slow nucleation, which leads to the formation of larger particles. Heterogeneous

Figure 7. Location engineering by directed deposition with a nonuniform electron distribution. Shown is the deposition of satellite AgPd NCs on (A) the corners and (B) the edges of the primary Au NCs where electrons accumulate. The electron distribution could be modified by varying the electron generation rate: a low rate distributed the electrons preferentially on the corners, while a high rate distributed the electrons preferentially on the edges. Adapted with permission from ref 48. Copyright 2013 Nature Publishing Group.

nucleation occurs when seeds are introduced into the growth environment. The NC size can be more easily controlled by varying the ratio of metal precursor to seed NCs.^{14,15} Size engineering should be carried out with minimum disturbance to shape engineering in order to preserve the desired shape in the growth environment. While size control of polyhedral NCs can be achieved by homogeneous⁶ or heterogeneous¹⁶ nucleation (Figure 3), it is more challenging to control the polyhedral size in homogeneous nucleation because the concurrent shape engineering process may also affect the nucleation and growth kinetics. By comparison, the heterogeneous method of seed-mediated growth is more able to decouple shape and size control. Hence, a succession of seed-mediated growth steps is a versatile tool since it offers better control of the reaction conditions in each step.¹⁶

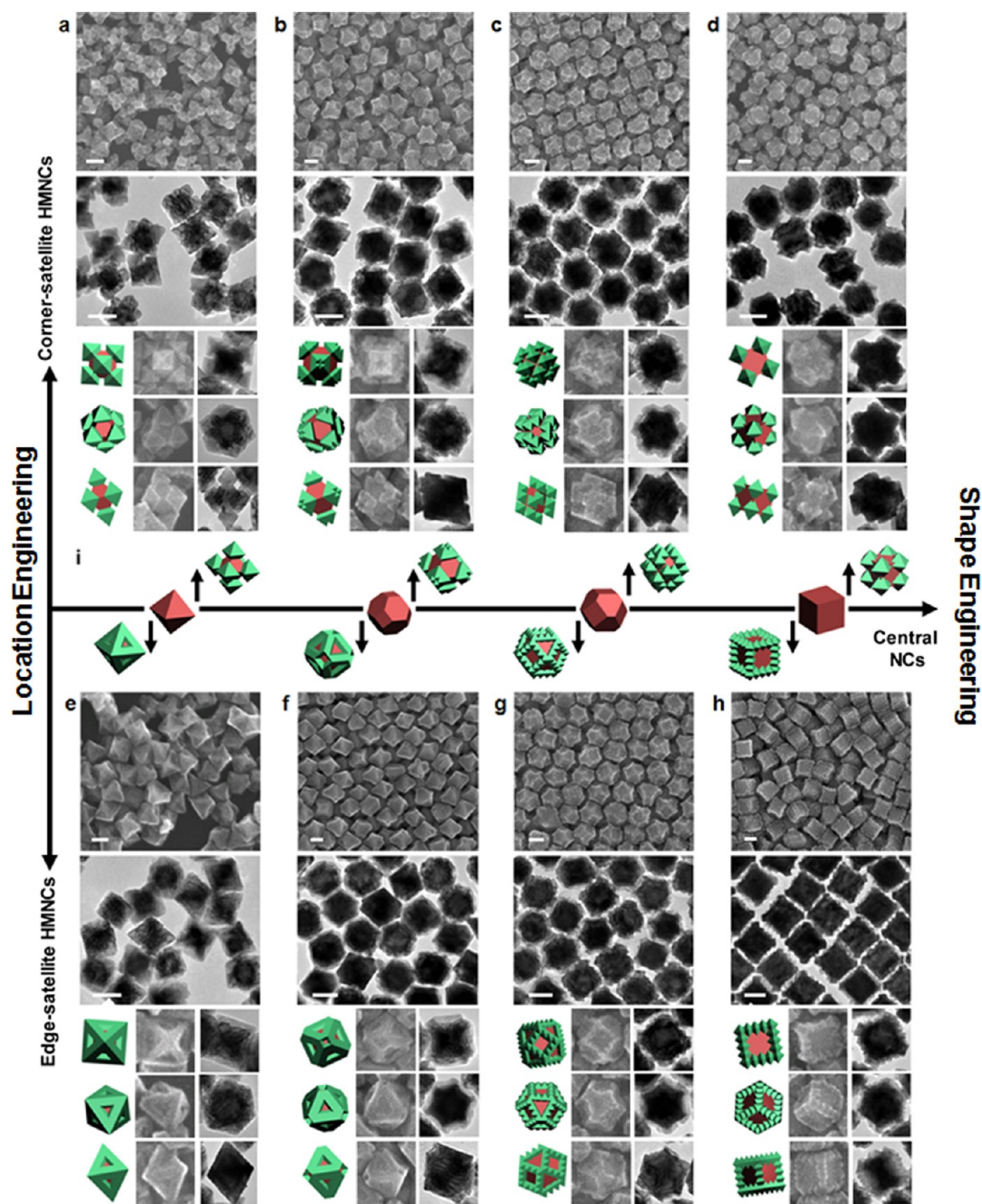


Figure 8. Architectural engineering of Au/AgPd HMNCs through location engineering (vertical axis) and shape engineering (horizontal axis) of the primary NCs. The satellite NCs were deposited on (A–D) the corners or (E–H) the edges of the primary NCs. The primary NCs were octahedrons, truncated octahedrons with small and large truncations, and cubes (from the left column to the right column). The satellite NCs were all enclosed by {111} facets.⁴⁸

5. LOCATION ENGINEERING

Unit NCs can be combined in many distinctively different ways in an HMNC. Location engineering is about the ability to identify the different deposition sites and make some of them more favorable than others. Since HMNCs are generally formed by the growth of satellite NCs on preformed primary NCs, the selective deposition of satellite NCs is often driven by the intrinsic anisotropy of the primary NC surface. Such anisotropy can be geometrical (facets, corners, and edges) or structurally related (crystallographic facets, defects, or twin planes). Many of the shape engineering processes can be used to introduce or enhance location selectivity.

5.1. Deposition Control

Similar to shape engineering, the availability of depositing atoms allows control of location selectivity. Slower reduction kinetics reduces the number of atoms for deposition and also compels them to deposit on energetically favorable sites. For example, PdAg alloy deposits selectively at the ends of Au nanorods at low reduction rates and nonselectively over the entire nanorod surface at high reduction rates.³⁶ The nucleation and growth of Ag on a cubic Pd NC can be varied from one to six facets by controlling the rate at which Ag atoms are formed (Figure 4).³⁷ Kinetic control of deposition locations can be affected by the selection of the reducing agent,³⁸ the rate of

reactant addition,^{37,39} or the concentrations of capping agent and metal precursors.^{36,37}

5.2. Masking

Location engineering can be accomplished by applying masks on specific surface sites. The selective masking can induce a preventive^{40–42} or promotive effect⁴³ on the subsequent deposition of satellite NCs.

In preventive masking, the preferential adsorption of masking agents on specific surface sites reduces the site reactivity or accessibility to reactants to inhibit the deposition of satellite NCs on the masked areas. The masking species can be a capping agent⁴⁰ or additive.^{42,43} For example, citrate passivation of the {111} facets of Ag decahedral NCs rendered the edges as the preferred locations for Au deposition.⁴⁰ Selective blocking of the {100} facets of cubic Pd seeds by Br[−] confined the overgrowth of Rh atoms to the corners and edges.⁴⁴ The masking species can also be a solid. For example, silica was selectively deposited at the two ends or in the middle of a nanorod to inhibit metal deposition at these locations (Figure 5A).⁴¹ Subsequent metal deposition could only occur on the exposed sites.

Selective masking may also provide a promotive effect on subsequent deposition of satellite NCs. For example, the preferential adsorption of Ag species on {100} surfaces of Au induced more facile Pt reduction, thereby pooling additional electrons through Ag oxidation (Figure 5B).⁴³

5.3. Etching

Selective etching is another tool for location engineering. It can be implemented using oxidative etchant pairs or galvanic replacement reactions. The former are applied to core–shell NCs with a reactive shell material for subsequent selective etching. For example, dumbbell-like Au nanorods with Ag tips were prepared by lateral etching of the Ag shell in core–shell Au@Ag nanorods with FeCl₃ (Figure 6A).⁴⁵ In selective etching by galvanic replacement reactions, a reactive template undergoes a galvanic replacement reaction with the ions of a less reactive metal. Generally, the galvanic oxidation and reduction half-reactions occur on different sites of the template surface, spatially separating the dissolution and deposition events.^{25,46} The spatially separated reaction is driven by the surface energy difference between crystallographic facets or the presence of twin defects.^{25,26,46}

Etching can also be used to create surface active sites for the subsequent anisotropic deposition of satellite NCs. For example, the edges of Au NC templates were specifically etched by KI/I₂ to create active sites (defects, atom steps, and kinks; Figure 6B)⁴⁷ for the selective deposition of Pt on the etched edges.

5.4. Directed Plating with a Nonuniform Electron Distribution

In plating, metal deposition is guided by electrons to occur on those sites rich with the latter. Location engineering of nanomaterials can likewise leverage a nonuniform electron distribution to drive the selective deposition of satellite NCs on the electron-rich sites of primary NCs. We have developed a method that can generate a nonuniform electron distribution to direct the deposition of satellite NCs on the corners or edges of primary NCs (Figure 7).⁴⁸ The method is based on the galvanic replacement reaction of a regenerable layer formed by UPD on a polyhedral NC. The electrons from the reaction move preferentially to the high-curvature sites of the primary NCs, i.e., the corners and edges of a polyhedron. The proportion of electrons migrating to the corners or edges can be altered by the kinetics of electron generation. Since corners and edges are the geometric

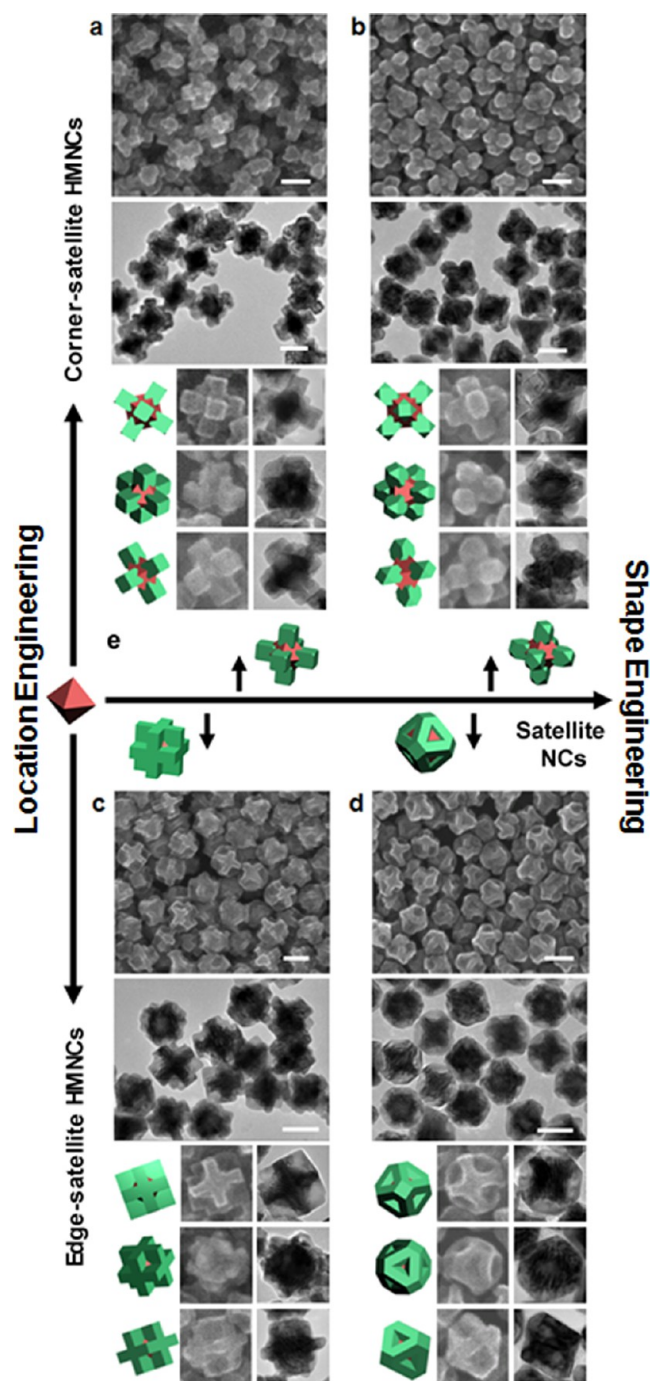


Figure 9. Architectural engineering of Au/AgPd HMNCs through location engineering (vertical axis) and shape engineering (horizontal axis) of the satellite NCs. The satellite NCs were deposited on (A, B) the corners or (C, D) the edges of the primary NCs. The satellite NCs were bound by (A, C) {100} facets or (B, D) {100} and {111} facets. The central NCs were octahedrons.⁴⁸

features of any polyhedron, this method can be applied universally to all polyhedral primary NCs without any requirement for the presence of specific features on the primary NCs.

6. ARCHITECTURAL ENGINEERING OF HMNCs

6.1. Reaction System Design

The architectural engineering of HMNCs requires the development of a robust synthesis system that can perform shape, size,

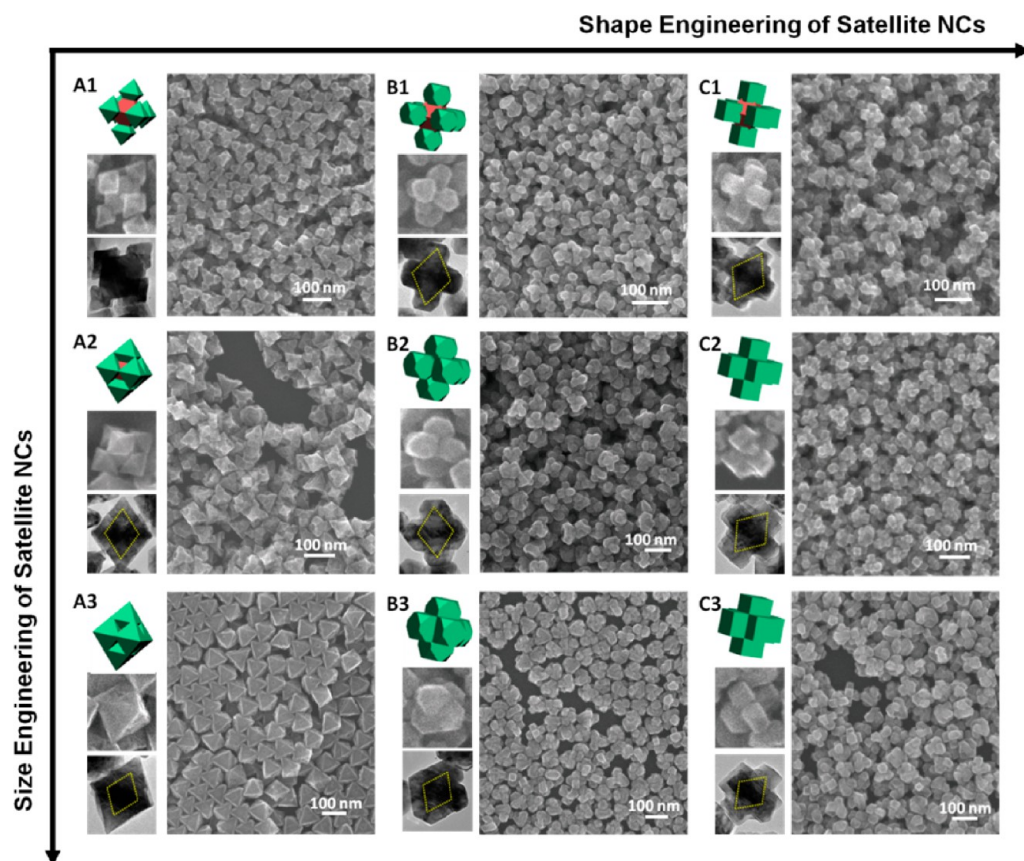


Figure 10. Architectural engineering of Au/AgPd HMNCs through shape engineering (horizontal axis) and size engineering (vertical axis) of satellite NCs. The satellite NCs were bound by (A) $\{111\}$ facets, (B) a combination of $\{100\}$ and $\{111\}$ facets, or (C) $\{100\}$ facets. The size of satellite NCs increased from row 1 to row 3.⁴⁹

and location engineering of each unit NC in the HMNCs in an *independent, rational, and systematic* way. The key is to design a reaction system capable of delinking the control of each ADE.

We have developed a strategy that enables concurrent location, shape, and size control in an HMNC.⁴⁸ In this reaction system, location engineering is driven by a nonuniform electron distribution to enable site-selective deposition (section 5.4). The shapes of the unit NCs are manipulated by a combination of reduction kinetics and masking techniques (sections 3.1 and 3.2). The sizes of the unit NCs are tuned by the relative concentrations of the metal precursors for the satellite and primary NCs (section 4). Sequential reactions allow the architectures of the primary and satellite NCs to be controlled in different steps. The strategy has been tested using Au/AgPd HMNCs as an example (Figures 8–10). The satellite NCs could be precisely located on the corners or the edges of the primary NCs. The shapes of the primary and satellite NCs could be varied between polyhedral shapes bound by $\{111\}$ facets, $\{100\}$ facets, or a combination of the two. The sizes of the primary and satellite NCs can be independently tuned. The strategy has the potential to generate a great variety of HMNC architectures.

6.2. Reaction System Control

The reaction system for architectural engineering involves several processes working in tandem to enable selective deposition to occur concurrently with size and shape evolution. The design and fabrication of HMNCs with the desired outcomes requires a good understanding of the principles of architectural control and the acquiescence of the causality between the reaction parameters and each ADE.

In the UPD-layer-induced galvanic replacement reaction system developed by us, we have identified three guiding principles for respective location, shape, and size control.⁴⁹ The three guiding principles are illustrated in Figure 11. Each principle identifies the synthesis parameter(s) related to an ADE and the ranges where they have to work in order to maintain the tunability of the ADEs. We have also shown how the synthesis parameters may be rationally controlled to build an overall complex and predesigned HMNC architecture (i.e., the ability to vary only one ADE at a time without affecting the others).

7. CONCLUDING REMARKS

HMNCs are hierarchical nanostructures that can be constructed by a systematic approach (“architectural engineering”) to attain an unprecedented degree of complexity and diversity. However, the number of HMNCs prepared to date is rather limited because of the apparent lack of efficient methods to engineer the HMNC architectures. While solution chemistry can be an extremely versatile bottom-up fabrication tool because of the flexibility in selecting the reaction system and reaction conditions, we must develop the ability to decouple the processes for individual ADE control. There are techniques that can control the shape and size of the unit NCs and their spatial relationship in an HMNC. The reaction system for the effective engineering of the architectural diversity of HMNCs should integrate these processes, which work in tandem and yet retain independent control and customizability of each ADE. Rational design and control of the reaction system is

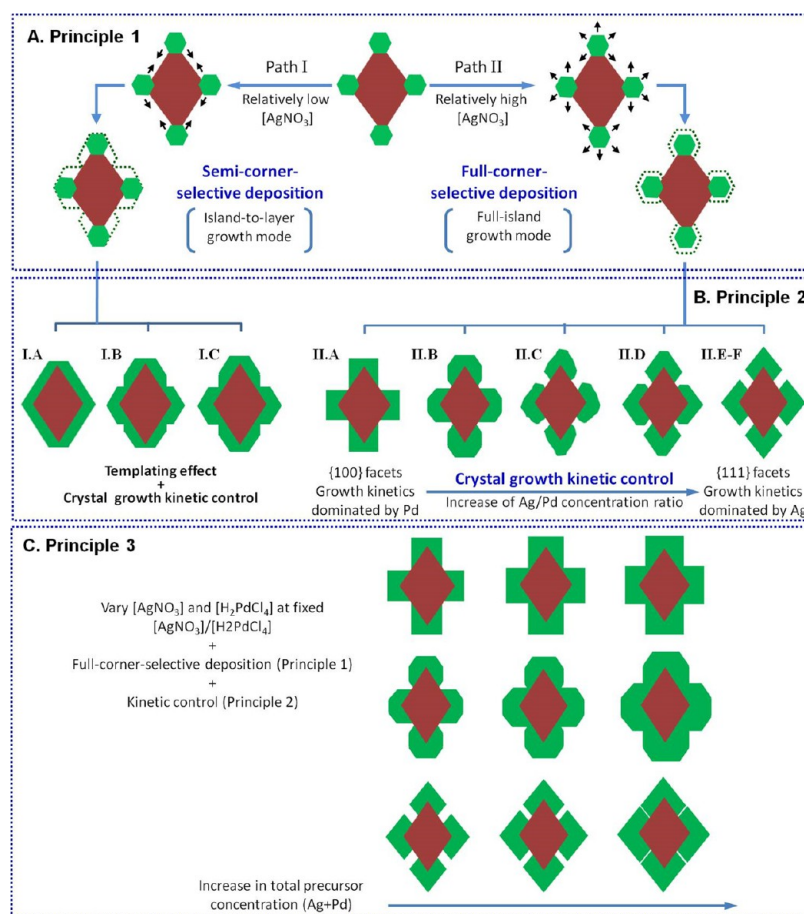


Figure 11. Principles for location, shape, and size engineering of satellite NCs in the UPD-induced galvanic replacement reaction. The deposition of corner-satellite HMNCs is used as an example. (A) Principle 1: the sustenance of the Ag UPD layer determines the deposition behavior of satellite NCs. Semi-corner-selective deposition occurs at a relatively low Ag^+ concentration as a result of island-to-layer growth (path I); full-corner-selective deposition occurs at high Ag^+ concentrations with the continual regeneration of the Ag UPD layer to support full-island growth (path II). (B) Principle 2: the shape of the satellite NCs is determined by the combined growth kinetics of Ag and Pd atoms in the full-corner-selective deposition. Varying the weights of the growth kinetics of Pd and Ag atoms (which have different preferences for exposure facets: {111} for Ag and {100} for Pd) in the combined growth kinetics changes the proportion of {100} and {111} facets. (C) Principle 3: the size of the satellite NCs may be tuned by varying the precursor concentration at a fixed Ag/Pd concentration ratio if the conditions for site-selective deposition and shape control as defined by principles 1 and 2 are satisfied.⁴⁹

conditional upon a better understanding of the controlling parameters and their interactions. Such knowledge allows the architectural complexity and diversity of HMNCs to be systematically enhanced and also increases the reliability of the architectural engineering of HMNCs. We hope that this Account will excite more materials scientists and chemical engineers to develop more effective methodologies to quickly expand the family of HMNCs.

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