

Noble Metal Nanostructure Synthesis at the Liquid–Substrate Interface: New Structures, New Insights, and New Possibilities

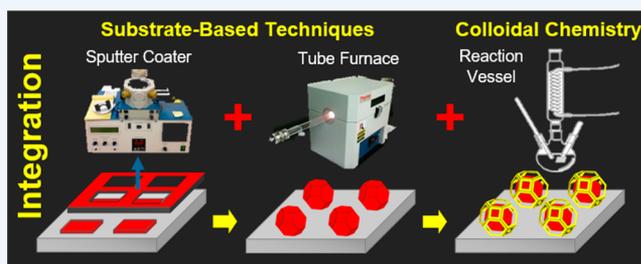
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CONSPECTUS: Modern technologically driven societies could not exist in their current form if it were not for a great many synthetic achievements reliant on solution-based chemistry and substrate-based processing techniques. It is, hence, not surprising that these same materials preparation techniques have given rise to an impressive list of functional nanomaterials including those derived from noble metals, a class of materials renowned for their extraordinary optical and catalytic properties. Acting as the foundation for substrate-based processing is a collection of techniques such as physical and chemical vapor deposition, epitaxy, self- and directed assembly, and a host of lithographic methods. These techniques allow for precise control over nanostructure placement, but where the fabrication of sophisticated architectures and sub-50 nm feature sizes are often unattainable or reliant on the use of technically demanding cost-prohibitive routes. In contrast, solution-based chemistry allows for the formation of complex nanostructures while maintaining synthetic ease, cost-effectiveness, and exacting control over monodispersity, size, shape, composition, and crystallinity. While many methods exist for the dispersal of colloids onto substrates, few are capable of achieving nanostructure ensembles where nanostructure placement allows for true long-range order as well as control over the crystallographic alignment of the nanostructures relative to each other and the underlying substrate. A more exhaustive comparison of these two approaches reveals that, more often than not, a weakness of substrate-based processing is a strength of colloidal synthesis and *vice versa*.

In this Account, we describe a synthetic strategy devised and validated by the Neretina laboratory that integrates the competencies of substrate-based techniques with colloidal chemistry and, in doing so, brings this rich and exciting chemistry and its associated functionalities to the substrate surface. The strategy takes advantage of an impressive collection of seed-mediated solution-based protocols in which dispersed seeds direct noble metal nanostructure formation along orderly reaction pathways. It, however, replaces the seed colloid with substrate-immobilized templates formed in periodic arrays where the crystallographic orientation of the templates is defined by an epitaxial relationship with the substrate. Demonstrated are syntheses at the liquid–substrate interface in which organized surfaces of crystalline templates formed through templated dewetting are subjected to galvanic replacement, preferential etching, and/or heterogeneous deposition facilitated by redox reactions in both the presence and absence of capping agents. While the protocols utilized are adapted from some of the most well-studied colloidal syntheses, in no case do they yield reaction products that are identical since the substrate inflicts asymmetries onto the growth mode. We believe that the strategy described herein not only demonstrates a family of nanostructures unobtainable through other means but also establishes a synthetic foundation that offers unprecedented flexibility, expands the palette of accessible template materials, provides a new vantage point from which complex reactions occurring in liquid media can be examined, and has the potential to underpin photovoltaic, catalytic, and sensing applications reliant on substrate-based noble metal nanostructures.



1. INTRODUCTION

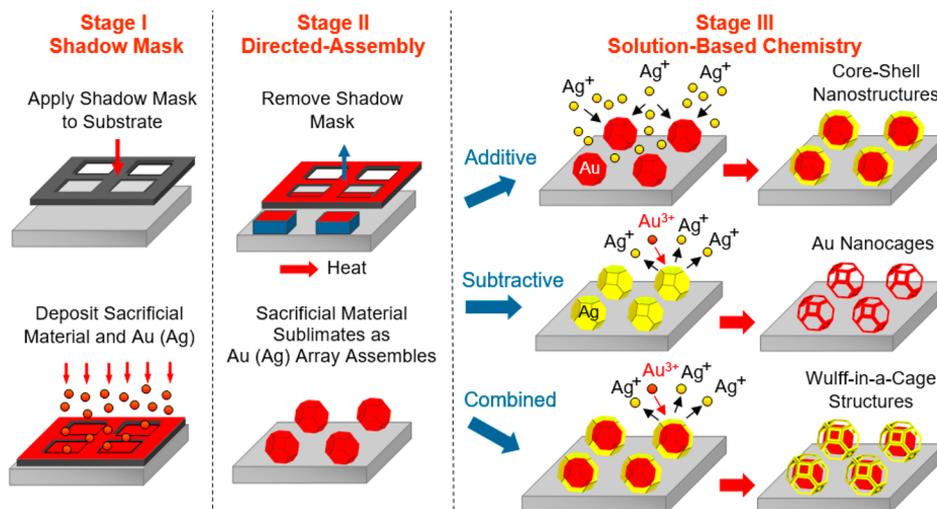
The exquisite chemical controls realizable when noble metal nanostructures are synthesized as colloidal suspensions allow for the formation of intricate three-dimensional architectures with precise control over the size, faceting, and elemental make-up. Many of these impressive synthetic achievements have been reviewed in past Accounts^{1–3} and elsewhere.^{4–7} While numerous functionalities, most notably *in vivo* biological applications,⁸ rely on the nanostructure mobility facilitated by suspensions, others require that the nanostructures be supported by a substrate in a manner that renders them immobile.⁹ With a scope that includes biological and chemical

sensors, photovoltaics, metamaterials, heterogeneous catalysis, photocatalysis, and electrocatalysis, there exists the opportunity to advance these critical applications through the advancement of nanomaterials specifically designed to promote the chemical and optical properties on which these devices are based. While the requirement for nanostructure placement at site-specific locations is often inconsequential, certain applications can benefit from the strict control required to promote cooperative

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Scheme 1. Three Stage Synthesis Strategy as It Pertains to the Synthesis of Substrate-Based Nanostructures Comprised of Au and Ag



phenomena, lab-on-a-chip capabilities, or the pixelation of electronic and photonic devices.

Substrate-based noble metal nanostructures can be obtained by first synthesizing colloidal nanostructures and then dispersing them onto the substrate surface. This method is, by far, the most versatile in terms of achieving architectural control and, hence, provides the best means to manipulate properties. The majority of the synthetic protocols are straightforward, scalable, inexpensive and short in duration, and require low processing temperatures. While numerous routes have been devised for assembling solution-dispersed structures into organized patterns,¹⁰ this capability is limited in terms of obtaining nanostructure arrays over large areas with true long-range order and high fidelity that lack registration errors. Lithographic techniques provide an alternative that is unrivalled in terms of defining accurately positioned nanostructures with well-defined shapes. While notable exceptions exist,¹¹ the nanostructures produced are typically single-element polycrystalline structures with a planar geometry, which when compared to their colloidal counterparts seem primitive. These deficiencies, along with the challenges associated with defining sub-50 nm feature sizes while meeting cost-effectiveness, throughput, and scalability requirements, place severe limitations on the use of lithographic techniques. Some limitations can be mitigated if these techniques are used in combination with high-temperature templated dewetting procedures.^{12,13} Such procedures are able to transform lithographically-defined structures into highly faceted, epitaxially-oriented crystalline nanostructures but where architectural control is limited by the fact that the assembled structures always trend toward the thermodynamically favored shape¹⁴ and by an alloying process that can frustrate the formation of bimetallic structures with well-defined interfaces.⁴

Recognizing that these various approaches all have limitations, but where they collectively satisfy the most important synthetic needs, the Neretina group devised a strategy in which they were synergistically combined such that lithography defines periodic structures, directed-assembly transforms them into single crystal nanostructures, and colloidal chemistry further transforms them into complex nanostructures.^{15–21} In this Account, we provide an overview of the synthetic achievements derived from this strategy. We place

emphasis on the uniqueness of the nanostructures formed, highlight how our studies have advanced the understanding of solution-based growth modes, and cast a glance at what the future holds for syntheses carried out at the liquid–substrate interface.

2. THE SYNTHETIC STRATEGY

Scheme 1 shows a schematic of the three-stage process used to define periodic arrays of noble metal nanostructures with complex architectures. The overall process uses (i) a lithography-defined shadow mask to fabricate nanostructured precursors at site-specific locations, (ii) directed assembly to transform them into single crystal templates with an orientation defined by epitaxy, and (iii) solution-based chemistry to transform them into complex nanostructures. The overall process can be carried out in less than 4 h, where the processing demands and instrumentation requirements for any given stage are minimal. In the first stage, physical vapor deposition is used to deposit precursors through a shadow mask. Removal of the mask leaves a periodic array of pillars consisting of a sacrificial material topped with a thin layer of a noble metal. This stage is crucial to the overall strategy in that it imposes a periodicity onto the assembly process and, by defining the number of noble metal atoms in each structure, determines the final template size and ensures monodispersity.

In the second stage, the pillars are introduced into a quartz tube furnace and subjected to a heating regimen carried out in an inert gas. While the assembly process is described in more detail in the next section, it should, at this point, be understood that the sacrificial material is lost as the noble metal atop each pillar agglomerates into a single crystal nanostructure whose orientation is defined by an epitaxial relationship with the substrate material. When acting as templates for solution-based growth modes, these structures distinguish themselves from those used in seed-mediated colloidal protocols. In contrast to seed colloids, these substrate-based templates can enter solution-based reactions with pristine surfaces or ones functionalized to promote a desired growth mode, where the requirement of having to play the dual role of stabilizing agent is lifted because nanoparticle aggregation is negated when the templates are substrate-immobilized. When a crystalline substrate is used, it can promote an ordered arrangement of

nanoparticle atoms that is commensurate with the crystallography of the underlying substrate. This so-called epitaxial relationship can give rise to the formation of nanoparticles with a specific crystallographic orientation and facilitate adhesion strong enough to resist sonication. When such templates are crystallographically aligned with the substrate it can potentially give rise to photoactive surfaces with polarization-dependent properties. The intimate contact at the substrate–template interface can promote unobstructed electron injection into the substrate material or catalytic reactions requiring the participation of both the nanostructure and its support.²² When colloids are dispersed onto a substrate, similar effects can become obstructed by capping agents or substrate surface agents that have been applied to promote adhesion. Template orientation can be manipulated by varying the crystallographic orientation of the substrate. With the assembly process being amenable to a wide variety of template materials,^{13,17} this route also expands the number of materials that are readily accessible to solution-based growth modes. Simultaneously advancing the colloidal chemistry for an equivalent number of seed materials is, in comparison, a cumbersome task.

In the third stage, the substrate-bound templates are transferred to a liquid medium in order to carry out a synthesis adapted from one of the great many solution-based seed-mediated protocols²³ able to transform arrayed templates into more intricate geometries. To date, the syntheses performed have been water-based reactions carried out in simple glassware at temperatures near the boiling point. For the purposes of this Account, these growth pathways are classified into (i) additive processes where material is deposited onto the template,^{15,16} (ii) subtractive processes where the template is consumed,^{17–20} and (iii) multistage processes that combine the additive and subtractive strategies in a sequential manner.²¹ Paramount to the overall synthesis strategy is the abundance of chemical controls offered by these solution-based growth modes that are otherwise inaccessible to substrate-based processing. Synthetic levers based on facet-specific capping,^{24,25} an interplay between kinetically and thermodynamically driven processes,²⁶ and the parametric control offered by such factors as pH,²⁷ precursor concentrations,²⁸ and the presence of solvated ions¹⁶ collectively bring unparalleled versatility to the reaction scheme.

Apart from the intrinsic advantages derived from the utilization of solution-based growth modes, there exist synergistic benefits when practicing these various techniques in combination. Significant is that substrate immobilization allows for surfactant-free syntheses or aggressive cleaning procedures capable of removing ligands from the nanostructure once a synthesis is complete. In doing so, it is possible to counteract the negative impact that ligands can have on catalytic activity,²⁹ photoluminescence,³⁰ surface enhanced Raman scattering sensitivities,³¹ the lifetime of resonantly excited hot electrons,³² and charge transfer processes between plasmonic nanostructures and an adjacent medium.³² Another key advantage stems from the fact that the reaction can be rapidly paused or terminated through the removal of the substrate from the reaction vessel or redirected by its subsequent reinsertion into a second chemical environment. Alternatively, an anchored substrate allows various reactants and byproducts to be flowed into and out of the reaction vessel. Template immobilization also facilitates the application of directional electric fields or polarized electromagnetic radiation to templates as they undergo reaction, a capability that allows for electrochemical and photochemical controls to be placed on

the synthesis. The reaction environment can also be altered by utilizing substrates that are insulating, semiconducting, and metallic, an influence that can provide an electron transfer pathway or expose nanostructures to highly asymmetric dielectric environments.

3. TEMPLATE FABRICATION

Periodic arrays of single crystal templates are fabricated using a vapor-phase directed-assembly process referred to as dynamic templating.¹³ The devised procedure is most closely connected to the solid state dewetting phenomenon (Figure 1a) in which

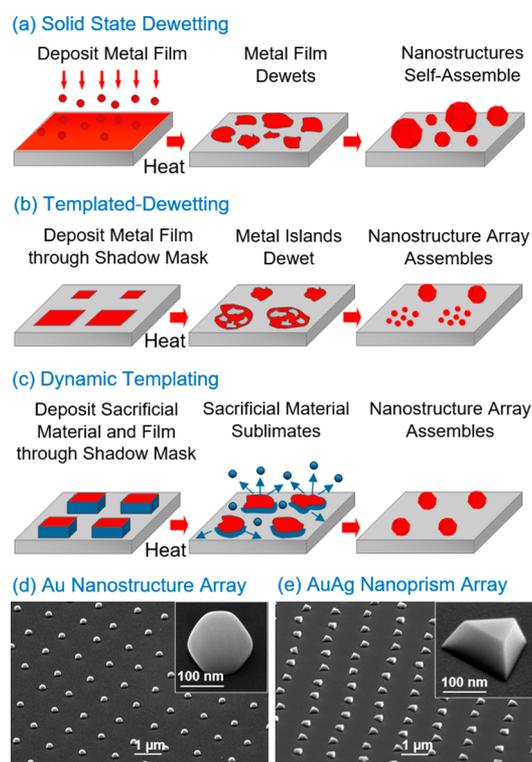


Figure 1. Schematics showing Au template formation using (a) dewetting, (b) templated dewetting, and (c) dynamic templating. SEM images of (d) a periodic array of Au templates formed using dynamic templating and (e) AuAg nanoprism-like structures formed using a kinetically driven growth mode. Adapted from ref 35, with permission from The Royal Society of Chemistry.

a continuous metal film deposited on a substrate at room temperature reorganizes into nanoscale droplets when heated. The reorganization is facilitated by the directional surface diffusion of metal atoms such that their surface energy is minimized through (i) a lowering of the overall surface-to-volume ratio, (ii) the establishment of an optimum contact angle with the substrate, and (iii) facet formation.^{12,33} This self-assembly process, while being unrivalled in terms of simplicity, is unsatisfactory from the standpoints that it yields randomly positioned structures, a substantial size distribution, and little control over the interparticle spacing.³³ These deficiencies can be alleviated by lithographically patterning the metal film into an array of island structures whose edges retract when heated to form a single nanostructure (Figure 1b, top row of templates). This templated dewetting technique, however, requires that islands be defined on length scales requiring state-of-the-art lithographic techniques if nanoscale templates are to be assembled; otherwise the islands fragment into multiple

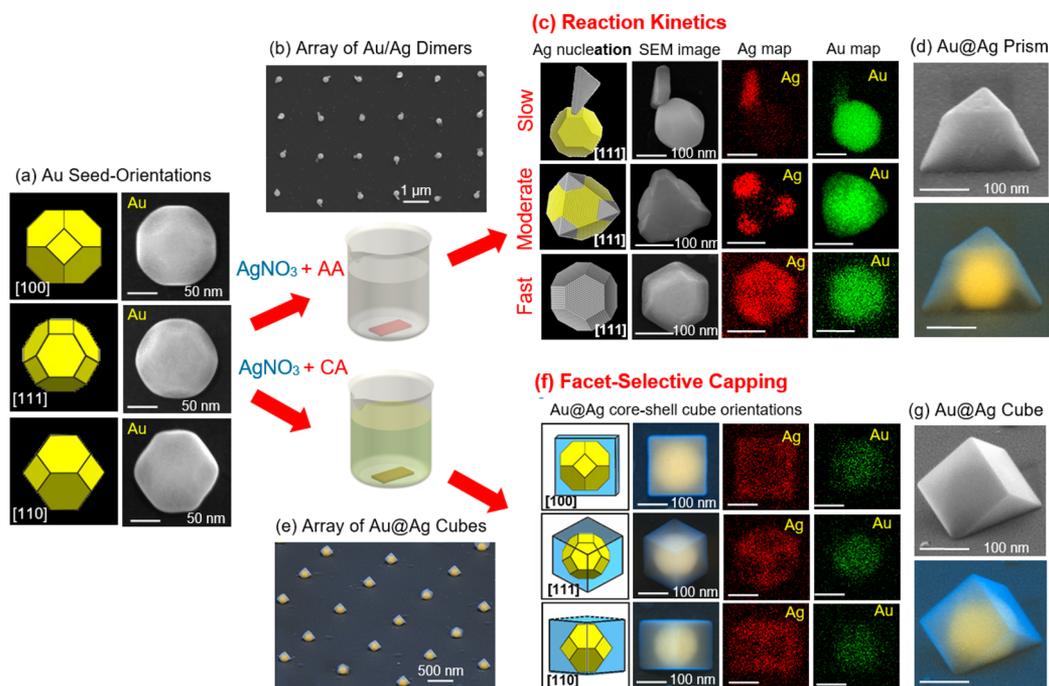


Figure 2. (a) Schematics and SEM images showing the plan-view perspective for [100]-, [110]-, and [111]-oriented Au templates.¹⁵ SEM images of Au/Ag bimetallic nanostructures as (b) an array deposited in the regime of slow kinetics, (c) plan-view schematics, images, and elemental maps for each kinetic regime, and (d) tilted-view images of a Au@Ag structure.¹⁶ Au@Ag nanocube images presented as (e) a periodic array, (f) plan-view schematics, images, and elemental maps for cubes expressing various epitaxial relationships, and (g) tilted-view images.¹⁵ Panels a and e–g adapted from ref 15. Copyright 2016 John Wiley & Sons, Inc. Panels b–d adapted from ref 16. Copyright 2014 American Chemical Society.

structures (Figure 1b, bottom row of templates). This requirement, hence, transforms a simple technique into one that is unduly complicated.

The dynamic templating route introduces a sacrificial material into the assembly process that greatly enhances the directional diffusion of the assembling atoms. It, hence, permits the assembly of metal atoms deposited over a much larger areal extent into a single nanometer-scale structure. In doing so, it allows for a periodicity to be imposed on the assembly process using shadow masks with easily manufactured micrometer-scale features, negating the need for technically demanding lithographic procedures requiring nanometer-scale control. The sacrificial material is chosen to have a high vapor pressure and, ideally, forms a low temperature eutectic with the assembling metal. Sb pedestals, for example, function as excellent dynamic templates when topped with either Au or Ag. When heated to the assembly temperature, Sb sublimation occurs rapidly from the pedestal sides while being strongly inhibited from its top surface by the deposited metal (Figure 1c). The dynamic nature of the receding pedestal edges forces the agglomeration of the metal to the center, a process that is accelerated through the formation of a eutectic since liquid kinetics promote faster diffusion processes. In the final stages of the assembly process, the pedestals disintegrate and the remaining Sb is lost to the vapor phase, leaving an array of single crystal metal nanostructures on the substrate surface. Figure 1d shows an array of Au templates fabricated in this manner. It is noted that Liu et al.³⁴ devised a related approach in which a polymer is used to direct the assembly of arrayed nanoparticles.

The templates formed using dynamic templating are fundamentally different from those used in seed-mediated solution-based protocols. The shape is largely determined by thermodynamic considerations that trend toward the formation

of truncated octahedrons, which express six square {100} facets and eight hexagonal {111} facets for face centered cubic metals, but where this so-called Wulff shape is further truncated in a plane parallel to the substrate surface.¹⁴ This truncation, which arises from surface energy minimization at the interface, gives rise to shape asymmetries that are inevitably passed onto the solution-grown structures based on these templates. As the epitaxial relationship between the metal and substrate is varied, so too is the truncation plane, a characteristic that yields a unique nanostructure architecture for each epitaxial relationship even though they all are based on the same Wulff shape. Deviations from the Wulff-shape can occur if the surface energy anisotropy between the various facets promotes a somewhat modified geometry or if kinetic factors associated with a particular synthesis acts in opposition to thermodynamic constraints. The most common deviation from the Wulff shape is a rounding that occurs at the low coordination sites where facets meet, which on an atomic length scale manifests itself as a step-terrace morphology. Kinetic effects, if appropriately manipulated, can also give rise to altered shapes such as the nanoprism-like structures shown in Figure 1e.³⁵ The degree of shape-engineering possible using such effects is, however, decidedly less than that available through solution-based syntheses.

4. ADDITIVE PROCESSES

The formation of bimetallic noble metal nanostructures through the deposition of one metal onto a preformed template of a second metal provides the opportunity to integrate materials with dissimilar physicochemical properties into a single nanostructure in a manner that offers increased functionality.⁴ We have demonstrated two substrate-based syntheses yielding bimetallic nanostructures where shape

control was achieved through (i) reaction kinetics¹⁶ and (ii) facet-selective capping agents.¹⁵ Figure 2 shows the Au seed orientations available and the structures realized using these two approaches. Both syntheses utilize a simple two-reagent redox reaction in which a reducing agent causes the reduction of dissolved Ag^+ ions, derived from AgNO_3 , onto Au templates. The key difference between the two syntheses is that the first uses ascorbic acid (AA) as the reducing agent while the second uses citrate (CA) as both a capping and reducing agent.

For the kinetically driven pathway, we monitored the overgrowth of [111]-oriented Au seeds with Ag where the reaction rate was varied to obtain three distinctive regimes allowing for slow, moderate, and fast kinetics. In all cases, AA is considered passive in terms of directing the shape. It was determined that each regime gives rise to a unique architecture (Figure 2c) characterized by Ag deposition as (i) a large protrusion off a single (100) Au facet for the slow regime, (ii) (111)-faceted pyramids formed on each of the (100) Au facets for the moderate regime, and (iii) a conformal layer for the fast regime. While the results, in many ways, mirror those obtained using the analogous colloidal syntheses, they were nevertheless unexpected. The single protrusion formed off of each template in the regime of slow kinetics (Figure 2b) was particularly surprising in that colloidal studies attributed these formations to such factors as surfactants, surface diffusion, or collision patterns, but these explanations seemed implausible in our synthesis since (i) the templates used were surfactant-free, (ii) the required diffusion would have to occur over length scales deemed unlikely, and (iii) no correlation was observed between the protrusion direction and the liquid flow pattern. We, therefore, found it necessary to formulate an alternative mechanistic framework requiring the formation of a double layer of Ag^+ and NO_3^- ions around each Au template when placed in aqueous AgNO_3 . In this scenario, an initial breach in the double layer gives rise to a Ag nucleation event that acts to strengthen the double layer at all other locations and, hence, inhibits Ag overgrowth on the rest of the Au template.

The second synthesis, which utilized citrate in the dual role of reducing and capping agent, also yielded nanostructure architectures that were quite unexpected. Figure 2f shows the Au@Ag core-shell structures obtained for Au templates oriented with their [100], [110], and [111] axes perpendicular to the substrate surface. All three orientations led to the formation of (100)-faceted nanocubes. Syntheses utilizing Ag, Pt, or Pd templates also gave rise to nanocubes. The results were surprising in light of the fact that citrate capping is associated with the emergence of an octahedral geometry with (111) facets. We noted, however, that the most commonly practiced synthetic strategy yielding octahedra utilized a three-reagent synthesis involving AA, CA, and AgNO_3 .²⁵ When AA was introduced into our synthesis as a third reagent, we also saw the emergence of octahedra. It was concluded that citrate or one of its oxidation products (possibly acetonedicarboxylate) acts as a (100) capping agent, but this ability is deactivated by small concentrations of AA. Irrespective of the mechanisms involved, this two-reagent synthesis represents the simplest synthetic route for generating core-shell nanocubes. It is also noteworthy that the substrate-based core-shell structures produced through additive processes differ from their colloidal counterparts in that they are epitaxially aligned (Figure 2e), the substrate prevents the shell material from completely encapsulating the core (Figure 2d,g), and the underlying geometry can be truncated at the nanostructure-substrate

interface as is the case for the [111]-oriented nanocube shown in Figure 2g. It is also noted that similar strategies have now been deployed by Liu et al.³⁶ and Cha et al.³⁷ to fabricate periodic arrays of substrate-based core-shell structures.

5. SUBTRACTIVE PROCESSES

Subtractive processes refer to nanostructure syntheses where the template is subjected to chemical environments that result in its partial or complete dissolution. Such syntheses facilitate the formation of hollowed architectures that are far more complex than those exhibited by the template material. Galvanic replacement reactions have emerged as one of the foremost synthetic techniques for obtaining such structures.⁵ They occur when template atoms of one metal are electrochemically driven into the solution phase by the spontaneous reduction and deposition of dissolved metal ions expressing a higher electrochemical potential than those of the template material. The reaction, shown schematically in Figure 3a as it pertains to the galvanic replacement of a Ag template by Au^{3+} ions, progresses through a series of stages characterized by (i) the dissolution of Ag^+ from the template as Au^{3+} is reduced to Au^0 and deposited on its surface, (ii) the formation of a single pit on the Au-coated template from which the interior is hollowed, (iii) the continued hollowing until the supply of pure Ag is exhausted through dissolution or alloying with Au, and (iv) the formation of side-openings due to the dealloying of Ag. Advantageous is that numerous architectures are accessible from a single replacement reaction since it can be terminated anywhere along this pathway.

By adapting well-established galvanic replacement protocols to our synthetic strategy, we have demonstrated the synthesis of substrate-based nanoshells and nanocages.^{18,19} Figure 3b shows an SEM image of an array of hollow AuAg nanoshells formed by exposing Ag templates to a solution containing Au^{3+} ions. These “nanohut” structures appear as downward facing hemispheres with a single opening at their base. Nanohuts detached from the substrate that rest on a TEM grid in an inverted geometry confirm that they are indeed hollow (Figure 3c). These asymmetric structures are unique in that the hollowed volume is enclosed partially by the nanoshell and partially by the substrate surface. Dealloying these structures leads to a morphological reconstruction resulting in the formation of nanocages with a well-defined pattern of geometric openings in the $\langle 111 \rangle$ directions of the sacrificed template. Templates with different epitaxial relationships, hence, give rise to unique nanocage configurations (Figure 3e), once again demonstrating that epitaxy plays a crucial role in the shape-engineering of substrate-based structures. Also examined was the galvanic replacement of Ag, Pb, Cu, Ni, and Co templates with Pt^{4+} ,¹⁷ reactions of intense interest due to the extraordinary catalytic activity exhibited by Pt-based nanostructures. Of note is that Pt nanoshells were synthesized from Ni and Co templates without any appreciable alloying. It is also noted that, in addition to galvanic replacement reactions, we have also demonstrated a subtractive synthesis reliant on the selective etching of Ge from Au/Ge and Ag/Ge heterodimers, a synthesis that yielded periodic arrays of hollow noble metal nanocrescents.²⁰ Another subtractive synthesis was reported by El Mel et al.³⁸ in which lithographically defined Ag nanowires were replaced with Au^{3+} to obtain AuAg nanotubes.

In addition to synthetic achievements, these studies also led to key mechanistic insights into substrate-based galvanic replacement reactions. It was determined that smooth nano-

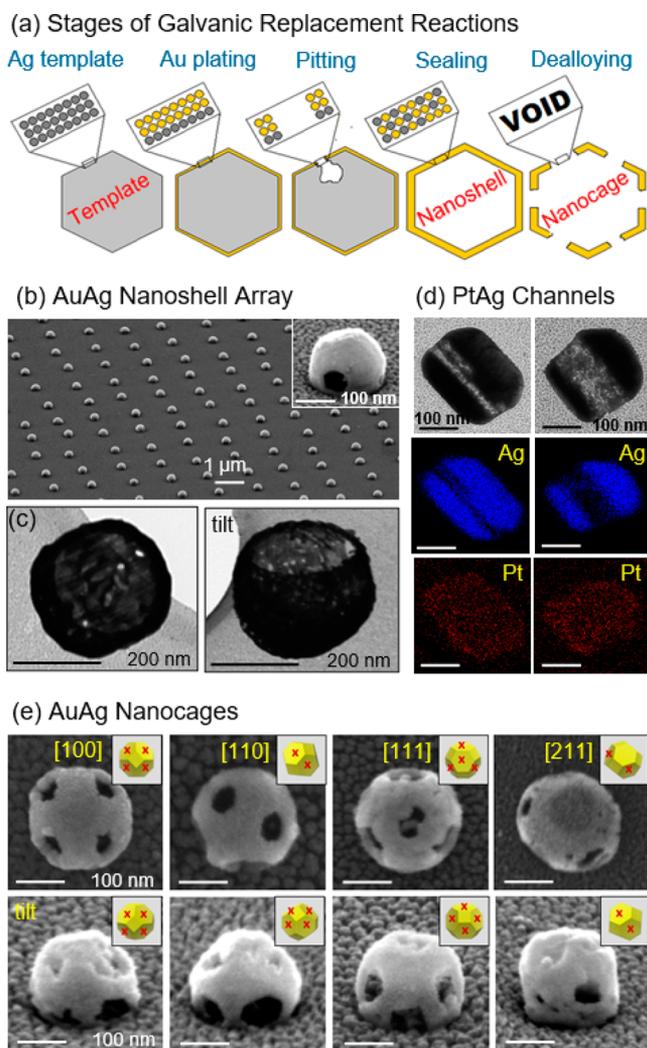


Figure 3. (a) Schematic showing the galvanic replacement of Ag templates with Au^{3+} . Images showing (b) a periodic array of hollow AuAg nanohuts, (c) inverted nanohuts resting on a TEM grid, (d) Ag templates that have been partially replaced with Pt^{2+} , and (e) AuAg nanocages derived from Ag templates with different crystallographic orientations. Panels a and d adapted from ref 17. Copyright 2014 American Chemical Society. Panels b, c, and e adapted from ref 18 with permission of Springer. Copyright Tsinghua University Press and Springer-Verlag Berlin Heidelberg 2013

shells and nanocages, such as those shown in Figure 3, could only be obtained if the surface of the Ag template was first altered by applying a thin layer of Au or Pt. The role of this layer is to passivate the highly reactive surface of the template such that the loss of Ag^+ occurs through a single breach in the passivation layer rather than from numerous locations on the template surface. Once the passivation layer is applied, the loss of Ag^+ occurs in an orderly manner that, for partially reacted templates, appears as a single hollowed channel running in one of the template's $\langle 110 \rangle$ directions (Figure 3d). The formation of such channels strongly suggests that Ag^+ is consumed in a layer-by-layer manner. The galvanic replacement of five different template materials with Pt revealed no correlation between nanoshell alloying and the degree of miscibility predicted by the binary phase diagrams of Pt with the various template materials. We proposed that the amount of alloying was instead related to interfacial stresses resulting from lattice

mismatch since compressive stresses frustrate the vacancy diffusion processes responsible for alloying in the solid state while tensile stresses enhance it.

6. MULTISTAGE PROCESSES

The sequential exposure of templates to varying chemical environments through the rapid transfer of the substrate from one reaction vessel to another allows for multistage synthetic schemes yielding complex products. In an initial demonstration, Au@Ag core-shell structures, obtained using the aforementioned additive processes, were immediately subjected to a subtractive galvanic replacement reaction utilizing Au^{3+} ions (Figure 4a).²¹ As the reaction proceeds, the Ag shell is

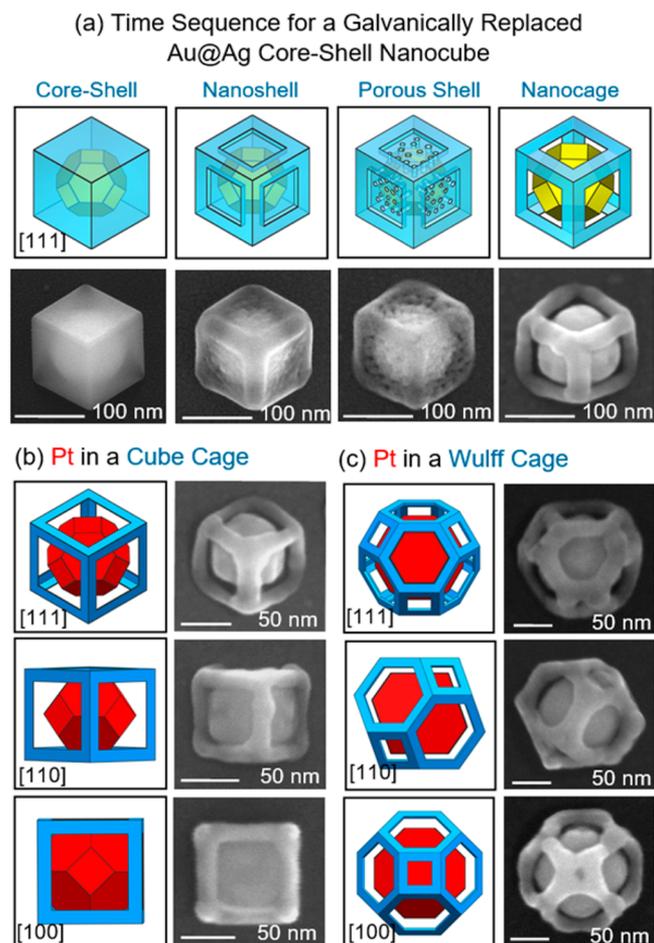


Figure 4. (a) The time evolution of a Au@Ag nanocube as it undergoes galvanic replacement. Schematics and plan-view images of Pt@void@AuAg structures derived from variously oriented Pt@Ag (b) nanocubes and (c) truncated octahedra. Reproduced from ref 21. Copyright 2015 American Chemical Society.

hollowed as Au is plated onto its surface, but the Au core remains intact. The synthesis yields a Au@void@AuAg nanocube where a well-defined gap is preserved between the Au core and AuAg shell since both are rendered immobile by the substrate. If the shell is allowed to dealloy then it initially gives rise to a thickened frame with mesoporous sidewalls. Continued dealloying causes the sidewalls to disintegrate, leaving behind a Wulff-shaped Au core confined within a cage. These “Wulff-in-a-cage” structures have also been demonstrated for the X@void@AuAg (X = Pt, Pd) configurations. Each

epitaxial relationship, once again, gives rise to a unique nanostructure architecture (Figure 4b). By merely changing the shape of the starting core-shell structure from a nanocube to a truncated octahedron an entirely different set of nanostructures emerge (Figure 4c).

The Wulff-in-a-cage synthesis, while mimicking that used to obtain nanorattle colloids,³⁹ nevertheless leads to a fundamentally distinct product in that (i) core motion is prohibited, (ii) the core does not rest against the shell, but instead forms a well-defined gap, and (iii) the void space is confined by three materials (i.e., the core, shell, and substrate) instead of two. These differences are not merely aesthetic, but instead have the potential to realize photoactive and chemically active environments that are otherwise unobtainable. With a void space allowing for the confinement of reactants by multiple noble metal catalysts as well as a catalytically active oxide, these structures could act as highly efficient nanoreactors capable of driving both single-step and cascade reactions, a capability that could be further augmented by plasmon-generated near-fields, heating, or hot electrons. Sensing modes could take advantage of plasmonic hot spots formed within the void space, hot electron injection into the substrate material, or the sensitivity of a plasmonic core to dielectric changes caused by the attachment of an analyte to a functionalized shell.

7. CONCLUDING REMARKS

Organized surfaces of complex noble metal nanostructures can be realized through the integration of substrate-based processing, vapor-phase directed assembly, and seed-mediated colloidal syntheses. Obtained from this synthetic strategy is a new class of asymmetric nanostructures that are unrealizable when these various techniques are practiced in isolation. The synthetic strategy allows for the formation of nanostructures in periodic arrays where a high degree of chemical and architectural control is exerted over the growth mode. These syntheses also open a new window through which complex reactions occurring in liquid media can be examined and from which mechanistic insights are readily obtained. While excited by our synthetic achievements and those of others, there is a recognition that this strategy has not progressed far beyond the proof-of-principle stage. We believe that there is an immense untapped potential in terms of (i) the colloidal chemistry adaptable to this strategy and (ii) the cooperative phenomena accessible when complex nanostructures are brought into close proximity or when active substrate materials transform the optical, electrical, and chemical environment adjacent to or within a noble metal nanostructure. We anticipate that when tapped it will reveal new chemistry, a distinct and rich class of nanostructure architectures, and optically and chemically active surfaces capable of supporting numerous applications. It is very much hoped that this Account will generate both interest and work in reactions carried out at the liquid-substrate interface as we are eager to discover what lies below the tip of the iceberg.

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Notes

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