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Integrated Nanocatalysts

HUA CHUN ZENG*

Department of Chemical and Biomolecular Engineering, Faculty of Engineering,
National University of Singapore, 10 Kent Ridge Crescent, Singapore 119260,
and Institute of Materials Research and Engineering (IMRE), 3 Research Link,
Singapore 117602

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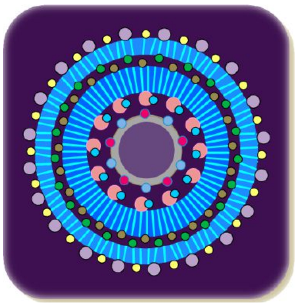

Despite significant advancements in catalysis research, the prevailing catalyst technology remains largely an art rather than a science. Rapid development in the fields of nanotechnology and materials chemistry in the past few decades, however, provides us with a new capacity to re-examine existing catalyst design and processing methods. In recent years, "nanocatalysts" has become a term often used by the materials chemistry and catalysis community. It refers to heterogeneous catalysts at nanoscale dimensions. Similar to homogeneous catalysts, freestanding (unsupported) nanocatalysts are difficult to separate after use. Because of their small sizes, they are also likely to be cytotoxic and pose a threat to the environment and therefore may not be practical for industrial use. On the other hand, if they are supported on ordinary catalyst carriers, the nanocatalysts would then revert to act as conventional heterogeneous catalysts, since chemists have known active metal clusters or oxide particles in the nanoscale regime long before the nanotechnology era. To resolve this problem, we need new research directions and synthetic strategies.

Important advancements in catalysis research now allow chemists to prepare catalytic materials with greater precision. By controlling particle composition, structure, shape, and dimension, researchers can move into the next phase of catalyst development if they can bridge these old and new technologies. In this regard, one way seems to be to integrate active nanostructured catalysts with boundary-defined catalyst supports that are "not-so-nano" in dimension. However, these supports still have available hierarchical pores and cavity spaces. In principle, these devices keep the essence of traditional "catalyst-plus-support" type systems. They also have the advantages of nanoscale engineering, which involves both high level design and integration processes in their fabrication. Besides this, the active components in these devices are small and are easy to integrate into other systems. For these reasons, we refer to the final catalytic devices as integrated nanocatalysts (INCs).

In this Account, we describe the current status of nanocatalyst research and introduce the various possible forms of design and types of integration for INC fabrication with increasing compositional and structural complexities. In addition, we discuss present difficulties and urgent issues of this research and propose the integration of the INCs into even more complex "supracatalysts" for future research.

1. Introduction

Traditional heterogeneous catalysts generally consist of active metal phases and less active or "inert" solid carriers in order to increase overall accessible working area and material utilization. In such catalysts, the active components (e.g., metal particles) normally fall within the dimensional regime of several to a few tens of nanometers,[1−3] and their processing often involves one or more of the following steps: impregnation, precipitation, coating, rewashing, ion-exchange, pulverization, drying, heat-treatment, reduction, and activation,[4] through which the metal clusters or active nanoparticles can be dispersed on the carriers. Nevertheless, conventional catalyst technology depends largely on the know-how of process implementers, and a workable catalyst is normally developed through painstaking *trial-and-error* experiments. Due to the complicated solution−solid, gas−solid, and solid−solid reactions involved in the preparation and a lack of adequate materials characterization, the process of converting the precursors to the final catalysts is mostly unclear or unrevealed due to commercial interests. In

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this sense, catalyst processing technology remains more like an art than a science.[4,5]

On the basis of surface chemistry, on the other hand, it has been well-known that the size, shape, facet, defect, dopant or promoter, and localized compositional variation of the active catalysts have significant impact on the performance of heterogeneous catalysts.[1−3] Another important consideration is the adsorbate and catalyst interaction during catalytic reactions,[6] where induced reconstruction of catalyst has also been recognized.[7] As a result, the structure and composition of catalysts may change during reactions, especially under high temperature and pressure conditions. Therefore, activation or deactivation of catalysts may take place, and the performance of catalysts could be time and process dependent. Hence maintaining the stability of catalysts is crucial.[8,9] Interaction between the catalyst and the supporting solid should not be ignored either, since a certain degree of chemical engagement between them will reduce the mobility of the catalytic metals and thus prevent them from sintering.[10,11] More importantly, synergistic effects (such as electron transfer) between the catalyst and support have been observed in many reactions,[1−3,6,7,9,12] and this must be taken into consideration during the design.

Rapid development of nanotechnology over the past decades has allowed us to view conventional heterogeneous catalysts with new a perspective.[1−3,8,9,13,14] In particular, catalytic materials can now be prepared with greater precision via nanotech-enabled processes. Noble metal nanoparticles, which often serve as active catalytic components, have been synthesized rather routinely with well-defined sizes, shapes, crystal facets, structure, and composition.[9,15−17] Such controllability could potentially lead to newer catalyst technologies. Moreover, in addition to zeolite-based microporous materials,[13,14] well-established mesoporous silica (MCM-41, SBA-15, etc.) and metal−organic-frameworks or coordination polymers can now be fabricated into desired sizes and shapes.[14,18,19] These novel porous solids will serve as host materials for the active catalyst components and provide additional functionalities.[5,18−21] Similar to Raney nickel, nanoporous metal monoliths can also serve as a new form of catalyst.[8] Moving away from traditional activated carbon and graphite, the potential now lies in incorporating catalytic nanoparticles within carbon nanotubes or onto graphene sheets,[22] making use of their well-defined porosity and surface properties.

With the above advancements, it is time for us to revisit the prevailing catalyst technology from the perspective of design, synthesis, and integration of catalytic materials. In this Account, we will touch upon some key issues and methods related to future development in this field.

2. Nanocatalysts and Integrated Nanocatalysts

Although the active components in many catalytic systems are indeed nanoscale in nature, the term "nanocatalysts" was made known to the chemical research community only in recent years, probably due to its catchy prefix related to nanotechnology. *Nanocatalysts* generally refers to suspendable nanoparticles that have catalytic activity. For example, small gold nanoparticles can be used for the catalytic oxidation of alcohols, and they are named as *nanocatalysts* these days.[9] Sometimes, the term refers just to the normal solid catalysts but with confirmation that their loaded metals or oxides are indeed of nanoscale dimensions. However, similar to organometallic complexes,[23] nanocatalysts face difficulty in recovery. Additionally, unsupported nanoparticles are likely to exhibit cytotoxicity and pose environmental threats, and they may not be ready for application. There have been only a few reports that actually mentioned the reusability of unsupported nanocatalysts, probably due to the problem of particulate aggregation after the removal of organic capping or stabilizers. In many cases, large metal particles with certain surface nanostructures are also called *nanocatalysts*, but they exhibit small specific surface areas and thus lack commercial value. In this Account, *integrated nanocatalysts* (INCs) are introduced to represent a new class of heterogeneous catalysts that are distinctly different from conventional catalysts. First, catalytically active phase(s) should be in the regime of subnanometer or nanometer in order to be termed as *nanocatalysts*. Second, to ease the separation, the nanoparticles or crystallites should be integrated into certain supporting inorganic or organic carriers or matrixes of a lower cost. Although they may still be playing secondary roles, these supports are expected to contribute to overall catalytic processes more significantly than their older counterparts. Third, such INCs are self-constraint systems; they can be suspended in a solution working as an individual catalyst or nanoreactor and can be further integrated into hierarchical superstructures collectively for gas-phase reactions as well.[24−26] For this reason, carrier units are expected to have a finite-size, say in the range of a few hundred nanometers to several tens of micrometers to be distinguished from conventional catalyst supports that have spatial dimensions in millimeter to centimeter scales.[4] Furthermore, we anticipate that the new catalyst systems would in general be complex, because synthesis of multiple active components and engineering nanostructured carriers is required. Finally, various smart features could also be included whenever needed.

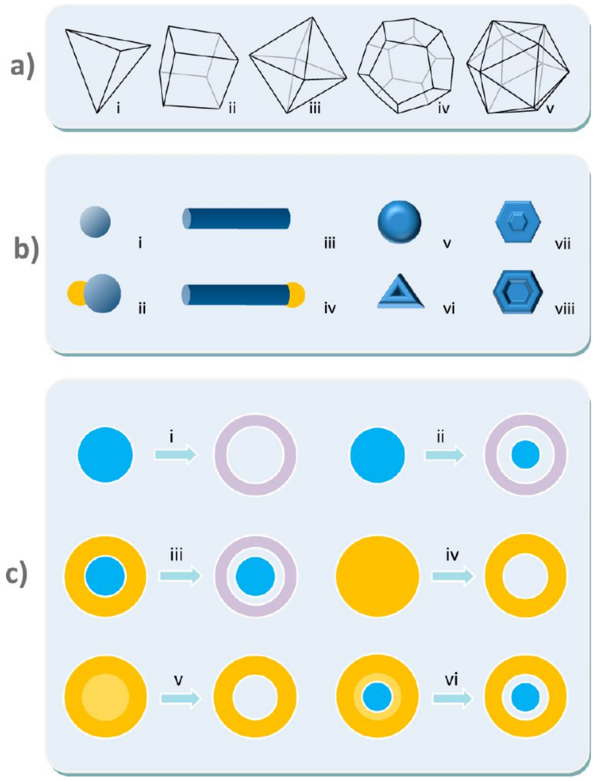

FIGURE 1. (a) Plato polyhedrons (i to v), (b) nanostructured building blocks (i to viii), and (c) hollowing schemes for nano- and microstructures (i to vi).

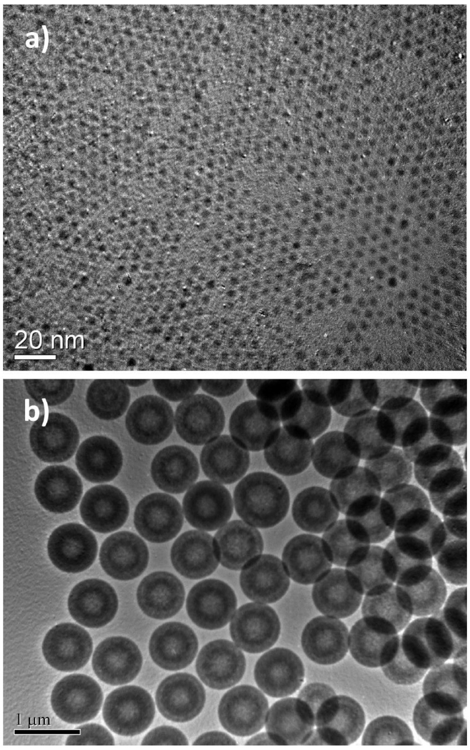

FIGURE 2. (a) Monodisperse alloy nanoparticles of $Ag_{0.8}Au_{0.2}$[30] and (b) double-shelled mesoporous SiO_2 spheres prepared through Ostwald ripening.[21]

3. Components for Integrated Nanocatalysts

By implication, integrated nanocatalysts (INCs) would be built using "bottom-up" approaches involving the self-assembly of premade building blocks. Despite being a paradigm shift from the present catalyst technology, the resultant INCs retain the essence of heterogeneous catalysts, as their configuration can still be divided into two parts, active catalysts and supporting carriers.

3.1. Active Components. Compared with commercially successful metal catalysts (e.g., Raney nickel), INCs target an even better utilization of metals. For example, colloidal noble metals and transition metals could now be prepared into faceted crystals of only a few nanometers in size; subnanometer metal clusters can also be synthesized using various appraoches.[9,15−17,27,28] Figure 1a illustrates some common crystal morphologies (e.g., five types of Plato polyhedrons) for metal and metal-oxide nanoparticles.[16,29] Small metal crystals with high Miller indices have also been prepared in recent years.[27] In general, using surface capping in synthesis is essential to prevent particles from agglomerating.[9,15,16,25,30] Because the capped metal particles are less active, a careful balance between structural stability and catalytic reactivity of metal nanoparticles must be made. In this regard, the adsorption and desorption of surface stabilizers, reactants, reaction intermediates, and final products have to be reversible in order to maintain the catalytic activity.

Apart from pure metal nanocrystals as the active components, alloy nanoparticles have also attracted significant interest, and various synthetic strategies have been in place.[9,17,30] Uniform alloy nanoparticles can now be synthesized in high yields, as demonstrated in Figure 2a.[30] Furthermore, metal nanoparticles can be deposited onto nanostructures of metals, metal-oxides, and metal-chalcogenides, resulting in a wide variety of multiphasic heterostructures.[31] In Figure 1b(i−iv), metal nanocrystals deposited on spherical nanoparticles and nanorods are depicted. Such heterostructures are comprised of two or more types of materials with small particle sizes, and they can be treated as bi- or multifunctional catalysts for tandem catalysis. In addition to regular polyhedrons or spheres, metal and metal-oxide nanocrystals have also been prepared into less common geometrical shapes (Figure 1b(v−viii)), such as disks,[32] prisms,[33] frames,[34] and hexagonal rings,[35] convex and concave structures,[36] and nanoporous monoliths.[8] With the increase in structural and compositional complexities of the nanocatalysts, the requirements of different reactions are increasingly being fulfilled.

3.2. Supporting Components. In the context of INCs, the role of carriers goes beyond support. To prevent nanocrystals from fusion, one strategy is to cap them individually with a shell of micro- or mesoporous silica.[37] The silica shell also serves as a membrane, imposing certain size restriction for molecules. Such core–shell pairs have been proven to be workable at high reaction temperatures.[37] Compared with polymer-supported or ligand-chelated nanoparticle crystals,[9,30] silica shells provide a more rigid confinement to the catalyst cores, and the resultant catalysts are able to withstand hasher environments. However, due to their small sizes, separation of these discrete core–shell catalysts can be problematic and further integration of single-core catalysts may be necessary.[24–26] In order to ensure sufficient active sites, the interior space of the core–shell structure should be enlarged so that multiple catalytic particles could be accommodated.

Along with common soft and hard templating methods, several solution-based hollowing schemes through matter relocations have been developed in recent years. The first one, galvanic displacement, is based on electrochemical redox reactions.[28,38] This is illustrated in Figure 1c(i). Investigations have been devoted to the Au–Ag pair, where Au^{3+} is reduced to Au^0 on the surface of the Ag^0 template while Ag^+ gradually dissolves.[28] The initial core material may still be retained (Figure 1c(ii)), and the formation of an interior space via electrochemistry has been investigated, including the production and synthesis of tubular structures.[38] The second scheme, Kirkendall diffusion, is operative on the grounds of the different diffusivities of metal atoms in alloys upon thermal activation.[39] This method has been utilized in nanocomposites comprised of different metals, where the formation of surface oxides or sulfides serves as an additional driving force for diffusion. Refer to Figure 1c(iii) for instance, whereby a platinum–cobalt core–shell can be turned into a yolk–shell structure when cobalt is transformed into cobalt oxide.[39] Owing to shell imperfections, reactants or products can enter or exit the nanoreactor while the platinum core functions as a catalyst. This type of single-core nanoreactor has been demonstrated to be used in ethylene hydrogenation.[39] Similarly, due to the slow diffusion of surface oxides or sulfides, direct oxidation or sulfidation on surfaces of metal particles can also be classified as such a hollowing mechanism.[40] To generate a central space, chemical etching is another useful approach (Figure 1c(iv)). In recent years, a great deal of research has been devoted to the study of silica because of its wide range of applications. Since their size can be precisely controlled, silica beads prepared by the Stöber protocol are often used as precursors.[41–43] In this type of structural transformation, sodium hydroxide has been proven to be an effective etchant to restructure solid silica into hollow spheres. A central metal nanoparticle can also be installed by preparing Stöber silica to form a metal–silica core–shell structure.[42] Recently, multiple-shelled silica spheres have been fabricated by controlled etching of pristine silica beads.[43] Furthermore, simultaneous transition-metal-ion doping and restructuring of Stöber silica have also been demonstrated.[25] One important difference between this class of porous silica spheres and the established mesoporous silica (e.g., MCM-41 and SBA-15)[18,19] is the former's open accessibility to the reactants and products despite having smaller specific surface areas. Although openly accessible macro- and mesoporous silica spheres have also been prepared through miceller-templating,[44] the silica spheres prepared via the etching possess a central interior, which will offer additional holding capacity for catalysts. The fourth hollowing approach is based on Ostwald ripening mechanism.[45–48] Due to inhomogeneity of pristine crystallite aggregates, solid evacuation can take place in the regions comprised of smaller crystallites. For example, crystallites located in the central part of a spherical aggregate are generally smaller, and upon ripening, the central matter will dissolve and redeposit onto the larger crystallites located in the outer part; an interior space is thus generated (Figure 1c(v)). Many metal oxides including doped metal oxides (e.g., Sn-doped TiO_2)[47] have been prepared into hollow spherical structures via this mechanism in recent years. Because this approach starts with aggregated crystallites, the prepared products are normally greater than 100 nm. For this reason, if one treats the hollow structure as a catalyst carrier, this approach can be used to make metal and metal-oxide core–shell or yolk–shell reactors[11,46,48] as depicted in Figure 1c(vi). More complex hollow structures can also be prepared, depending on the initial crystallite aggregative states.[45] Although it has been mainly observed in crystalline solids, ripening is operational for noncrystalline solids as well. Very recently, it has been employed in creating large interior spaces for mesoporous silica spheres, as shown in Figure 2b.[21]

Because the INCs are not entirely different from conventional catalysts, as stated earlier, a clear distinction between active components and their supports in many cases can be difficult. This is due to the complex nature of catalysts and synergistic effects under reaction conditions, especially when another catalytic material (e.g., transition metal oxides) is chosen as a nominal supporting material. In oxidative environments, for example, oxidized species of metals could be generated. On the other hand, under reducing conditions, metallic species could also be present on the surfaces of oxide supports.

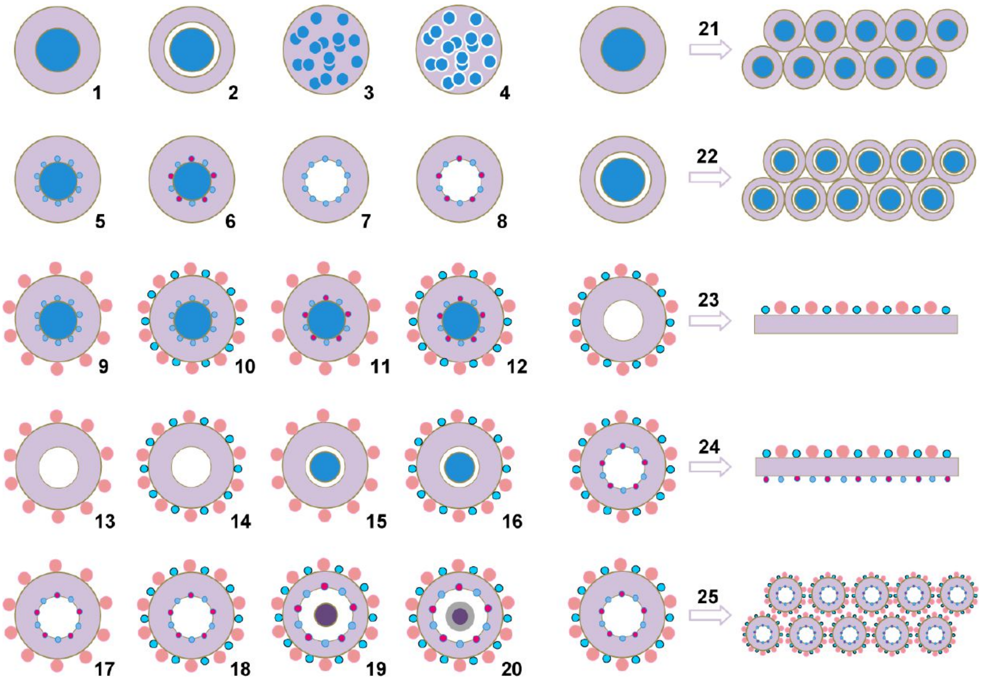

FIGURE 3. Representative forms of INCs (**1**−**20**): components in different phases are depicted as small spheres with different colors; **23** and **24** are the equivalent thin films of **14** and **18**. These INCs can be further assembled into supracatalysts (**21**, **22**, and **25**).

4. Design and Integration

4.1. Forms of Design. Similar to integrated circuit (IC) design and other architectural masterpieces, the design of integrated nanocatalysts (INCs) also require thought. Broadly, the design can be divided into two categories: compositional and structural. In this connection, chemical compositions of numerous catalyst systems have been archived in patents and chemical literature. Compositional design relies heavily on the designers' knowledge and intuition, since a great deal of working catalysts were actually found through accidental discoveries. Compared with the former, however, structural design of INCs demands more robust imagination, especially when deciding the logical order of the reaction sequence and rationalizing the architectural elements.

In Figure 3, several representative architectures of proposed INCs are illustrated. Among them, core−shell or yolk−shell structure (Figure 3, **1** and **2**) is the most common design because it reflects a primary "catalyst−support membrane" concept, which has been realized in many systems.[24] Because they are single-core and small size in nature, further integration of this type of catalysts is required (Figure 3, **21** and **22**),[24−26] as has been pointed out earlier. "Raisin bun" is another well-known structure that deserves more attention since it can entrap multiple catalytic crystals or particles within a single structural configuration (Figure 3, **3** and **4**).[49] It can also be treated as having an integrated core−shell or yolk−shell structures (Figure 3, **21** and **22**). To attain membrane function, nanocatalysts can also be hidden in the space between the core and shell (Figure 3, **5** and **6**).[20,50] When the core is removed, these nanocrystals are virtually dispersed on the inner wall of the shell (Figure 3, **7** and **8**). Furthermore, the external surface of sphere can also be utilized (Figure 3, **9**−**12**).[50] Similar to the "raisin bun", simple structures presented in Figure 3, **13**−**16**, also deserve more study[11,46] because they can support multiple catalysts. In these cases, the presence of a central cavity lightens the weight of the catalysts, which becomes equivalent to supported catalysts on a single-side film (Figure 3, **23**). Apparently, the lightweight catalysts of this type are more floatable in liquid with smaller hydrodynamic diameters compared with their film counterparts. As shown in Figure 3, **17** and **18**,[50] nanoparticles may also be integrated on the inner surface of hollow spheres. This kind of lightweight catalyst is essentially analogous to those illustrated in Figure 3, **13** and **14**, but with an additional screening function because catalysts are allocated on the inner surface of shell. Therefore, structural advantages of different catalysts are attained simultaneously. Besides, these products could also be thought of as a double-sided catalyst film (Figure 3, **24**). In Figure 3, **19**, a magnetic responsive function is introduced by adding a ferromagnetic core (e.g., Fe_3O_4) to the sphere.[20] Such a

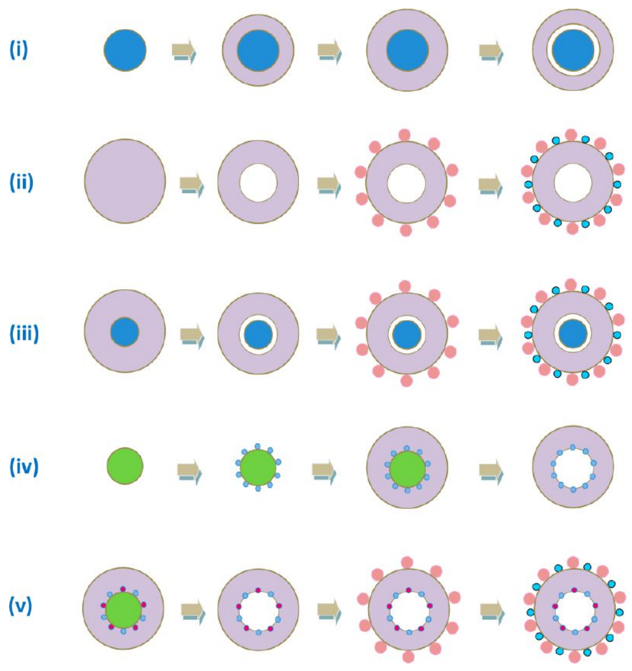

FIGURE 4. Five major types of integration of INCs (i–v): materials in different phases are depicted as small spheres with different colors.

magnetic core may be protected or turned into a catalyst support (Figure 3, **20**); multiple magnetic particles can also be loaded onto the inner or outer surface. To incorporate other smart features, light-absorbing oxides such as Cu_2O, ZnO, and TiO_2 could be used as shell materials,[11,46,48,51] powering INCs with photon energy.[46]

It is noteworthy mentioning that for illustrative purpose we merely present the spherical devices in Figure 3, because the sphere is the most common geometry adopted by particles and their aggregates. In fact, other geometries such as polyhedrons, platelets, or tubules are also suitable to be considered for the same structural analogues, as long as they have a defined solid boundary for overall materials integration (e.g., Figure 3, **25**).[22,52]

4.2. Types of Integration. In Figure 3, the "raisin bun" type of catalyst can be obtained simply by phase separation through heating or chemical transformation from solid precursors, and the resultant matrixes are often mesoporous.[49] Though many structures in Figure 3 may seem to be elaborative at the first glance, they are synthetically achievable. In Figure 4, some synthetic routes are presented. For instance, core–shell and yolk–shell structures can be easily prepared if one treats the core or yolk as a hard template (Figure 4i). Examples of this type can be found in $Au@SiO_2$, $Au@TiO_2$, and $Au@Cu_2O$ systems, in which an etching process or Ostwald ripening is responsible for the hollowing.[42,46,48] Instead of a single-core particle, multiple nanocrystals can also be loaded onto a single device through the process steps suggested in Figure 4ii.[10] There are a number of ways to introduce nanocatalysts onto the external surface of the sphere, such as organic ligand-assisted self-assembly of nanoparticles,[10,11,50] hydrothermal synthesis,[11,52] redox reactions,[53] or photoassisted reduction of metal cations.[31] Of course, the well-established impregnation method may still be adopted if it works; even state-of-the-art methods such as atomic layer deposition should also be explored. In Figure 4iii,[46,50] a more complex catalyst is also derived from the combined approaches of Figure 4i,ii. To introduce nanocrystals or particles onto the interior wall of a sphere, templating methods have been developed. In Figure 4iv, silica or polystyrene spheres (in green) can be retained or removed after the shell is formed.[20,50] Furthermore, the prepared catalytic devices may also be externally decorated with nanocatalysts, as shown in Figure 4v.[10,11,50] Depending on the application requirements and designers' perceptions, more integrative routes of this type could be further proposed.

Although the general strategies highlighted in Figure 4 use premade cores for shell deposition, the size of core particles is tunable after shell formation.[21,46] Recent progress in this area has further demonstrated new possibilities of introducing nanocatalysts into the interior space of mesoporous silica hollow spheres.[21] In Figure 5i–iii, nanocrystals such as Au and Ag can be grown inside the central cavity. On the other hand, nanoparticles can be predispersed in liquid micelles, which later serve as a soft template for shell formation (Figure 5iv). Moreover, complex shell structures can also be engineered, which results in the formation of double-shelled spheres (Figure 5v). In these hollow spheres, the interior space and exterior space are well connected through mesopores, which allows *in situ* synthesis of capsulated materials. A large variety of INCs such as $Au@SiO_2$, $Ag/Au@SiO_2$, polyaniline@SiO_2, $ZnS@SiO_2$, $Co_3O_4@SiO_2$, $Co_3O_4@SiO_2$, $TiO_2@SiO_2$, $TiO_2@SiO_2$, and $Au/TiO_2@SiO_2$ have been prepared.[21] With them as starting cores, nanocatalysts could also be deposited onto their external surfaces (Figure 4ii,iii,v), leading to even more complicated INCs.

4.3. Durability and Complexity. In actual applications, industrial catalysts normally consist of multiple active components,[4] and thus INCs with high complexity are further required especially when proposing tandem catalysis. The complex INCs in Figure 3 and their related synthetic routes in Figures 4 and 5 pose significant challenges for their synthesis. Moreover, due to complications arising from reactions, long-term durability under reaction conditions is a crucial prerequisite for INCs to be of practical use. To

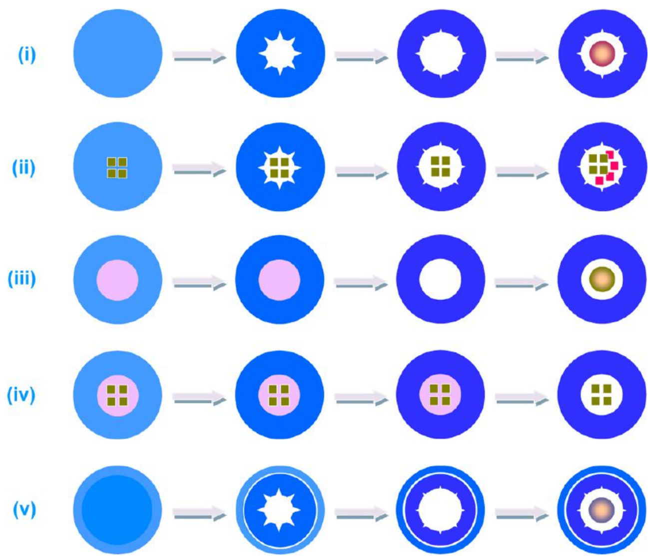

FIGURE 5. Mesoporous SiO_2-based INCs: (i) creation of an interior space through Ostwald ripening, (ii) inclusion of nanocrystals, (iii) soft-templating process, (iv) encapsulation of nanocrystals with a soft-templating process, and (v) architecture of double-shelled spheres.[21] Nanocatalysts can also be grown *in situ* (see i, ii, iii, and v). Figure reproduced with permission from ref 21. Copyright 2011 American Chemical Society.

address this issue, the workability of INCs has been examined in several cases.[11,20,21,25,37,49,54] In Figure 6a, a synthetic approach is given for converting Stöber silica spheres into a new type of porous support. The precursor SiO_2 spheres are first grafted with a layer of cationic polyelectrolyte (poly(diallyldimethyl-ammonium chloride; PDDA), which neutralizes the negative charge of SiO_2 spheres.[25] A subsequent hydrothermal treatment with a zinc source leads to the simultaneous structural transformation of SiO_2 spheres into hollow ones and diffusion of zinc into the surface phase of silica (Zn–SiO_2). ZnO crystallites and Ru nanoparticles are then grown and assembled, respectively, onto the external surfaces of the Zn–SiO_2 (see Figure 6a and Figure 4ii).[25] In Figure 6b, a series of complex Ru/ZnO/Zn–SiO_2 catalysts have been fabricated after calcination and reduction. To test their durability under harsh conditions, these INCs were further evaluated for arene hydrogenation at high temperature and pressure.[25] Compared with Ru catalysts reported in literature, the above prepared INCs (Ru/ZnO/Zn–SiO_2) exhibit superior activities in the arene hydrogenation, giving very high turnover frequencies (TOF) in the range of 1.3×10^3 to 2.0×10^4 h^{-1}.[25] It is encouraging to see that while they seem to be fragile, the Ru/ZnO/Zn–SiO_2 catalysts actually demonstrate superior activity, high robustness, and easy recovery in heterogeneous catalysis.[25] Because the synthesis of Stöber silica is a well-established process, the transformation route of Figure 7 is feasible for the large-scale preparation of this highly open support.[25] At the same time, the metal-doped SiO_2 hollow spheres can serve as a structural platform for various INCs listed in Figure 3. As another example, the "raisin bun" type of catalyst of MoO_3-embedded mesoporous carbon spheres (MoO_3@C) has shown even better catalytic performance for Friedel–Crafts benzylation of toluene with benzyl alcohol than a commercial catalyst (Amberlyst-15) under the same operating conditions.[49]

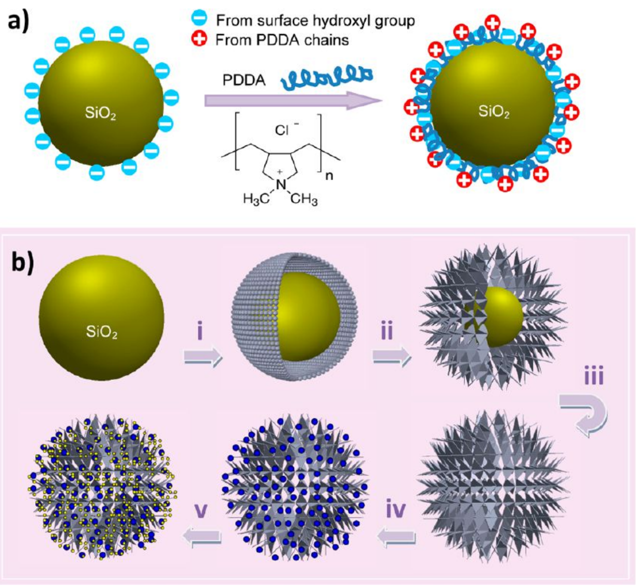

FIGURE 6. (a) Modification of SiO_2 surface with PDDA: electrostatic attraction between negative hydroxyl groups and positive PDDA. (b) Fabrication of INCs: (i) modify surface of SiO_2 (see panel a) and create yolk–shell (Zn-doped SiO_2), (ii) reduce yolk size, (iii) form plate-interlaced Zn-doped SiO_2 hollow sphere, (iv) deposit ZnO nanoparticles (blue), and (v) add Ru nanoparticles (yellow).[25] Figure reproduced with permission from ref 25. Copyright 2012 American Chemical Society.

Hence, the durability is not necessarily in conflict with complexity. Recent progress in the synthesis of multiple-shell hollow structures permits fabrication of even more complex INCs.[21,26,54] In Figure 8, for example, multishelled Cu_2S spheres have been prepared from anionic exchange using an organic–inorganic hybrid (e.g., Cu_2O/PVP) as a precursor.[26] With an increasing number of synthetic protocols,[11,21,24,26,52,53,55] new types of INCs of a higher level of complexity can be further developed in future.

In principle, the inorganic catalyst devices discussed above can be extended to incorporate organometallic catalysts and organocatalysts and even enzymatic biocatalysts. On the basis of the above discussion, a conceptual architecture is proposed herein (see Supporting Information). Starting from nanoparticles or enzyme biomolecules, for example, a mesoporous SiO_2 shell can be formed with the

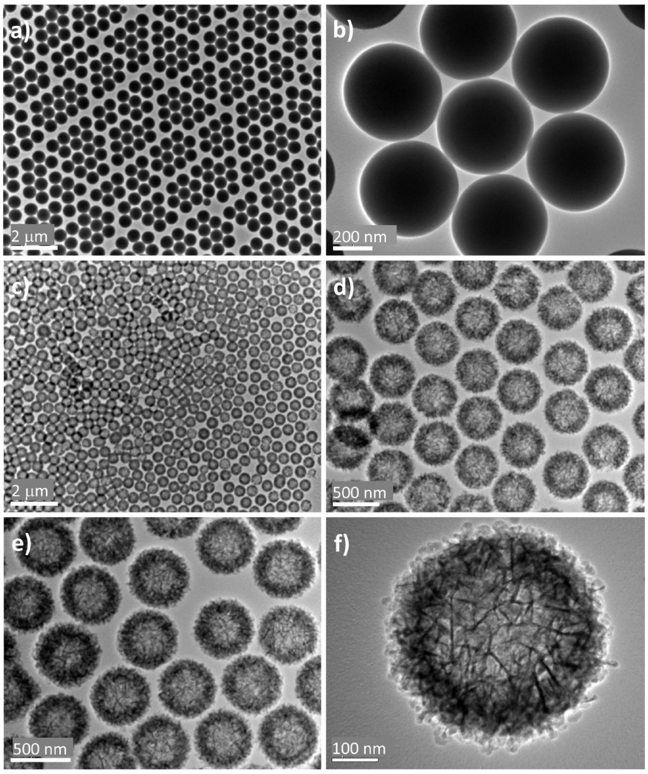

FIGURE 7. (a, b) Solid SiO_2 spheres synthesized by Stöber protocol and (c–f) porous Zn-doped SiO_2 (Zn–SiO_2) hollow spheres prepared in Figure 6.[25] Reproduced with permission from ref 25. Copyright 2012 American Chemical Society.

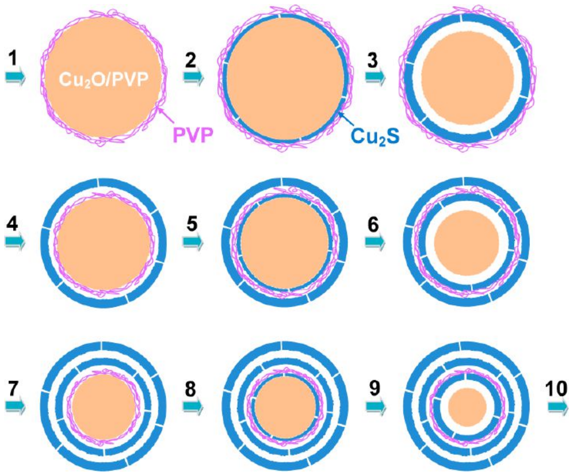

FIGURE 8. Formation of multishelled Cu_2S hollow spheres: (1) preparation of Cu_2O/PVP hybrid sphere; (2) Cu_2S formed from ion exchange; (3) continuous growth; (4) completion of the first shell. Note that 5–7 and 8–10 are similar to 2–4, which result in the second and third shells, respectively.[26] More shells can also be formed in this repeating fashion.

aid of supramolecular assemblages encapsulating the catalysts of interest. To enhance chemical reactivity and structural stability, postgrowth treatments could also be pursued. On one hand, subnanometer metallic clusters, organometallic catalysts or organocatalysts can be immobilized on the surfaces of 1D-channels sequentially by chemisorption or van der Waals interaction with the preallocated organics on the pore surfaces. Direct covalent bonding of the organocatalysts to the channel surfaces could also be considered by synthesizing designed organosilicon compounds as sol–gel precursors. Such modification and functionalization of silica substrate will create an interface between the heterogeneous catalysis and homogeneous catalysis.[23] On the other hand, a secondary shell can be fabricated, creating additional screening ability and intershell space, if desired. Furthermore, the interior space of the double-shelled spheres can also be enlarged, which can then be utilized as a working place for *in situ* synthesis of catalysts or for the incorporation of smart features. Of course, the external surface should also be fully utilized for loading either catalysts or other functional materials in such complex devices. It would be very interesting to exploit the synergistic effects arising from all the participating building parts under an identical reaction setting.

5. Future Outlook

In contrast to traditional catalyst technology, the preparation of INCs relies on the syntheses of individual catalytic components and their related integration. In the current stage, we have attained good controllability in the synthesis of building parts, but integrating them into INCs remains a difficult task. To generate assemblages among the parts, different interactive forces between nanoparticles and their depositing substrates must be present. In particular, chelating functions of the capping ligands used in nanoparticles and carriers should be carefully selected. Also, the means for interconnections among all the building parts have to be exploited. For example, thermal treatment and activation in suitable gas ambiences are crucial for forming durable and active INCs.

One important feature of INCs is that they can potentially fill the dimension gap between homogeneous catalysts and industrial heterogeneous catalysts. For catalysis in liquid phase, small-sized lightweight INCs that can be easily suspended are preferred. However, for heterogeneous catalysis in gas phase, further integration of the INCs into macroscopic objects (i.e., supracatalysts) with sizes comparable to those of commercial catalysts may be essential. Therefore, new synthetic approaches and integrative strategies should be investigated, including direct dispersion of INCs in porous supports or matrices. At the same time, evaluating the catalytic efficiency of such integrated devices under real reaction conditions is also needed, especially for tandem catalysis that requires a careful integration of multicomponent catalysts in accordance with reaction sequence.

While architectural design and synthesis are getting more and more complex, the basic functions of catalysts should not be forgotten. A good balance between the durability and complexity for INCs must be made. To achieve this, surface science techniques can be applied to understand the correlation between catalytic performance and catalyst stability. Because INCs are still relatively small, *in situ* investigations of individual INCs are feasible via the HRTEM method for observing catalyst reconstructions and XPS analysis for monitoring their surface states. The in-depth understanding acquired will allow us to select the right combinations of catalytic components, including supporting carriers. In fact, a significant volume of such knowledge has been available in the surface science literature.[2,3,6−8] For example, the catalytic reactivity of well-defined single-crystal surfaces has been extensively investigated over the past decades, which can serve as a starting point for the design and synthesis of INCs, especially for the selection of faceted metallic nanocrystals.

Synthetic integration of nanocatalysts is a grand challenge. However at the same time, this transformation of existing catalyst technology into a more sophisticated one poses a huge research opportunity to chemists for many years to come.

Supporting Information. A proposed conceptual catalyst. This information is available free of charge via the Internet at http://pubs.acs.org.

BIOGRAPHICAL INFORMATION

Professor Hua Chun Zeng obtained his B.Sc. in Chemistry from Xiamen University in 1982 and Ph.D. in Physical Chemistry from University of British Columbia in 1989. Following postdoctoral work at University of Toronto, he joined the faculty at National University of Singapore in 1991. His research interests are, at present, focused on the exploratory design and synthesis of inorganic nanostructures, with an emphasis on catalysis. He is ranked among the top 100 highly cited chemists over the period of 2000−2010 by Thomson Reuters and Times Higher Education.

FOOTNOTES

*E-mail: chezhc@nus.edu.sg.
The authors declare no competing financial interest.

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