

Nanoscale

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MINIREVIEW**Self-assembly: An Option to Nanoporous Metal Nanocrystals****Jie Ying,^a Xiao-Yu Yang,^{*a} Ge Tian,^{*a} Christoph Janiak^{*c} and Bao-Lian Su^{*ab}***Received (in XXX, XXX) XthXXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXXXX 20XX***DOI: 10.1039/b000000x**

5 Nanoporous metal nanocrystals involving both nanoscale effects and nanopore properties hold enormous promising potential for various important applications due to their unique structures, such as large surface area per unit volume and interconnected open framework. Self-assembly, as an excellent option, has been developed to control the desired structure and rational performance of nanoporous metal nanocrystals. After identifying features of their methodologies and structures, the control of synthesis based on self-assembly technique is thoroughly discussed. The development of self-assembly synthesis methodology is then presented in detail. The emerging application, mainly in catalysis, and corresponding design are finally summarized.

1 Introduction

In recent years, the morphology-controlled metal nanocrystals have been a core focus of nanomaterials chemistry because their physicochemical properties can be readily adjusted by tailoring the size and nanostructure.¹⁻⁷ These metal nanocrystals with designed functions have received particular interest for potential applications in catalysis,⁸⁻¹² electronics,^{13,14} sensing,¹⁵⁻¹⁷ photonics,^{18,19} and medicine.²⁰⁻²² However, among various morphologies, nanoporous metal nanocrystals are of particular interest in the past decade, whatever the academic study or the

potential use. Whereas materials in the range of 1-100 nm display fascinating properties that are often radically different from their bulk counterparts because of the quantum size and surface effect, the presence of nanoporosity possess high surface, unique structure, and bulk properties that underline their important uses in various fields such as ion exchange, molecular separation, and selective catalysis. Such a combination of nanopore and nanoscale in nanoporous metal nanocrystals could therefore reach the one plus one greater than two results. That would provide metal nanocrystals with the big opportunity in areas of inclusion chemistry, guest-host synthesis and molecular manipulation and reaction in the nanoscale.²³

1.1 Brief history of porous metals

Preparation of porous metals has a long history, for example, the depletion gilding by selective leaching of Cu from Au-Cu alloys.²⁴ Main approaches include dealloying^{25,26} (Fig. 1a), hard-templating²⁷⁻³⁰ (Fig. 1b) and soft-templating³¹⁻³⁴ (Fig. 1c and d), and lead co-continuous, highly order and/or intricate structures.

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The dealloying method has been observed in technologically important alloy systems since the 1920s, when nanoporous Raney metals from aluminium-based alloy were firstly used as heterogeneous catalysts.³⁵ In the 1960s and 1970s, dealloying nanoporous metals with remarkable properties were developed after the pioneer work of in-depth understanding of the dealloying process.^{36,37} The natural porous hard templates were subsequently utilized to fabricate nanostructured porous metals in the early 1970s.²⁷ Numerous artificial hard templates, such as honeycomb-like anodic alumina³⁸ and highly ordered colloidal crystals³⁹, were also exploited to produce porous metallic nanostructures in the 1990s. In templating synthesis during the same period, soft templates, especially amphiphilic molecules, were used to fabricate mesoporous metals.^{31,40,41} For example, lyotropic liquid crystals (LLC) were firstly used to prepare long-range periodic nanoporous structures in the range from several to tens nanometers in the late 1990s.³¹ Up to now, a great number of advanced strategies have been developed to rationally design and prepare nanostructured porous metals. The particle size on the nanoscale has been one of the goals of structure control of metal materials, to get superior properties compared with their bulk counterparts. Nanoporous metal nanocrystals were firstly reported via a surfactant mediated method by Song *et al.* in 2004.⁴² Dendritic Pt nanocrystals were obtained by self-assembly of platinum seeds in the presence of surfactant. Since then, self-assembled surfactant molecular aggregates or supramolecular assemblies were generally employed as the structure-directing agents to build-up porous nano-architectures in the final metal materials. Careful control of the synthetic condition, such as surfactant, reducer, precursor, temperature, pH value, can be utilized to adjust the composition, pore structure, particle size, and morphology of nanometals. With the development of nanofabrication technology, much progress has been made in self-assembly based synthesis strategies, such as self-assembly combining hard template, dealloying, self-etching and galvanic replacement. Novel nanostructures and morphologies were designed and synthesized, resulting in intricate structures and excellent performances. The extent of the structure control is generally at the desired alloy with an emphasis on tailoring their properties. These synthetic materials were widely applied, especially in catalysis, by controlling multiple functions (composites variety) at the atom length scale, whereas the molecular separation, selectivity and transport properties of materials are controlled through manipulation of nanoporous

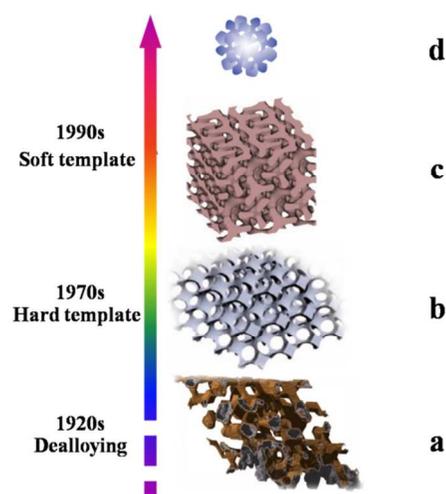


Fig. 1 Scheme to show the development of various methods for the synthesis of nanoporous metals. (a) Reproduced with the permission from ref. 25. (b) Reproduced with permission from ref. 30. (c) Reproduced with the permission from ref. 33. (d) Reproduced with permission from ref. 34.

structures and morphologies at nanometer and micrometer length scales.

1.2 Development of self-assembly to porous metals

Self-assembly, as a common phenomenon throughout nature and technology, has attracted enormous interests by countless scientists and engineers over the past decades.⁴³⁻⁴⁵ It is also a simple and effective method for controlling the structure and performance of ensembles of individual components. The rational design of components, which organizes themselves into a desired structure, is the key factor to utilization of self-assembly method.

Numerous metals, porous structured in 0D, 1D, 2D, 3D, have been prepared by self-assembly (Fig 2). For instance, an ordered porous Pt 3D mesostructure was obtained after removal of carbon in a mesoporous Pt-C composite, which formed from the self-assembly of block copolymers with ligand-stabilized Pt nanoparticles.⁴⁶ Porous metal 2D films were fabricated to ordered arrays in the nanometre-to-micrometre size range by colloidal crystal templating.^{47,48} Bismuth 1D nanotubes were spontaneously formed from layered bismuth in solution by a rational low-temperature synthetic route.⁴⁹ These metal structures



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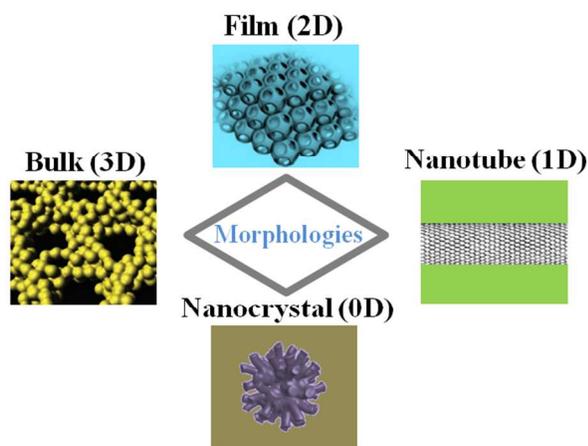


Fig. 2 Scheme to show various porous metals prepared by self-assembly. Right: bulk (3D). Reproduced with permission from ref. 46. Top: film (2D). Reproduced with permission from ref. 30. Left: nanotube (1D). Reproduced with permission from ref. 49.

share a core structural unit of a 0D nanocrystal, which could be ensembled to higher dimensional structures. The interactions between the excitons, magnetic moments or surface plasmons of individual units would lead to new electronic, magnetic and optical properties. Moreover, only ensembles of 0D nanoparticles can perfectly exploit their collective properties and quantitative prediction of their structural features. For example, the lack of models depicting the kinetics and statistics of the 1D self-assembly does not allow the quantitative prediction of their structural features. So a better understanding of the self-assembly to nanoporous metal nanocrystals is essential for the design and synthesis of metallic materials with desired structures and properties. Using different surfactant templates to synthesize nanoporous metal nanocrystals is a straightforward strategy. It is important to understand the micelle formation, which plays a key role in the build-up of the porous structure and dispersion of the nanocrystals in the process. For example, the rising of temperature is availing to micelle formation of ionic surfactants, resulting in successful self-assembly of the metal precursor. The surfactant templating has therefore been a basic technique or



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an inseparable part of other self-assembly based techniques. Through combination with other methods, such as hard templating and dealloying, self-assembled metal nanocrystals with different morphologies and fine porous structures can be easily obtained. For instance, metal nanocrystals with a hollow interior and porous dendritic shell were synthesized by a combination of self-assembly and dealloying.⁵⁰

Nowadays, the self-assembly method has been utilized to synthesize numerous metal nanocrystals with novel porous structures for various metals, such as Pd and Pt,^{34,51-53} which exhibit excellent performance as catalysts and electrocatalysts. Methods based on self-assembly for synthesis of different metal nanocrystals with porous structures are summarized in Fig. 3 and Table 1. Metal nanocrystals with porous interiors represent a promising new class of nanomaterials due to their unique structures, physicochemical properties, and great potential for



Fig. 3 Various methods based on self-assembly for the synthesis of nanoporous metal nanocrystals.

Table 1 Methods based on the self-assembly for synthesis of different metal nanocrystals with porous structures.

Classifications	Methods	Structures	Compositions
Directed self-assembly strategies	Direct surfactant-mediated synthesis	Branched nanoporous structures	Pt, ^{42,52-59} Pd, ⁵¹ PtPd, ⁶⁰ PtNi, ⁶¹ AuPd, ⁶² AuPdPt ⁶³
	Seed-mediated synthesis	Dendritic heteronanostructures, porous single-crystalline nanoparticles	Pd, ³⁴ PtAu, ⁶⁴ PtPd ^{65,66}
Development of synthesis strategies	Self-assembly and hard template	Mesoporous monocrystalline nanoparticles	Pt ⁶⁷
	Self-assembly and dealloying	Wormhole nanostructure, nanocages with dendritic shells	PtNi, ^{68,69} PtPd ⁵⁰
	Self-assembly and self-etching	Nanocages, nanoskeletons	Co ⁷⁰
	Self-assembly and galvanic replacement	Nanocages, nanoboxes	PtCu, ⁷¹ AuAg, ⁷² PdAg, ⁷³ PtAg ⁷³

Table 2 Various applications of metal nanocrystals with porous structures.

Catalysis	Types	Features
Chemical reactions	Oxidation reaction ⁶⁴ Hydrogenation reaction ⁵² Suzuki coupling reaction ^{34,51} Hecking coupling reaction ⁷⁴	High percentage of atoms on the surface; better stability; highly accessible surface active sites; large number of surface reaction sites
Electrochemical reactions	Oxygen reduction reaction ^{61,66,68,69} Methanol oxidation reaction ^{50,53,60,62,71,75}	Entire surface readily accessible to reactants; little diffusion resistance for reactants; sufficiently high durability; superior tolerance to undesirable agglomeration of the active sites; relatively good poison tolerance; good thermal stability; sufficient active sites; excellent surface permeability; abundances of corner and edge sites

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various applications (Table 2). Since many progresses have been achieved in the development of metal nanocrystals with porous structure, it is necessary to give an overview of recent advances on these novel nanostructures to promote further developments in this exciting research area.

A global view on the organization of this minireview is illustrated in Fig. 4. Firstly, we present the methodological features (Six Simple features; see section 2.1) and structural features (such as chemical composition, porous structure, morphology, surface area, crystallinity and particle size; see section 2.2) to self-assembled nanoporous metal nanocrystals as well as their control synthesis (various effects of surfactant, reducer, precursor, temperature and pH value; see section 2.3). Next, the methodological development by combining self-assembly with other methods, such as hard template, dealloying, self-etching and galvanic replacement, will be addressed (see section 3). Finally, we review some examples to discuss the effects of porous structure, composition, and morphology to performance of nanoporous metal nanocrystals in catalysis (see section 4).

2 Self-assembly method to nanoporous metal nanocrystals

Self-assembly to nanoporous metal nanocrystals has been widely studied. Features in both methodology and structure will be briefly summarized in this section. Then, the control of synthesis,

such as effects of surfactant, reducing agent, precursor, temperature and pH value, will be specifically addressed.

2.1 Features of self-assembly to nanoporous metal nanocrystals

“SS” (Six Simple) features in the self-assembly synthesis of nanoporous metal nanocrystals can be identified.

Simple precursor. The precursors are metal salts and metal acetylacetonates with or without a co-reactant depending on the desired chemical compositions. Very pure metal materials can be produced and adjusted by precursors. Moreover, highly crystalline phases are present in the final products starting with just these precursors.

Simple reducing agent. Only one reducer is often needed, for example, AA (ascorbic acid) for most examples in aqueous solution. Alloy materials can be directly obtained by co-reduction using the same reducer.

Simple synthesis procedure. Self-assembly provides a facile and low cost method for control synthesis of nanoporous metal nanocrystals, which could be spontaneously formed by surfactant-assisted reduction of the precursors. Moreover, the synthesis procedure is being simplified. For example, one-pot synthesis has been widely developed.

Simple synthesis condition. All of the reaction conditions are mild, such as low temperature and ambient pressure. Most of the examples are synthesized only in aqueous solution. No very strong acid and base are used, only nitride acid for few examples.

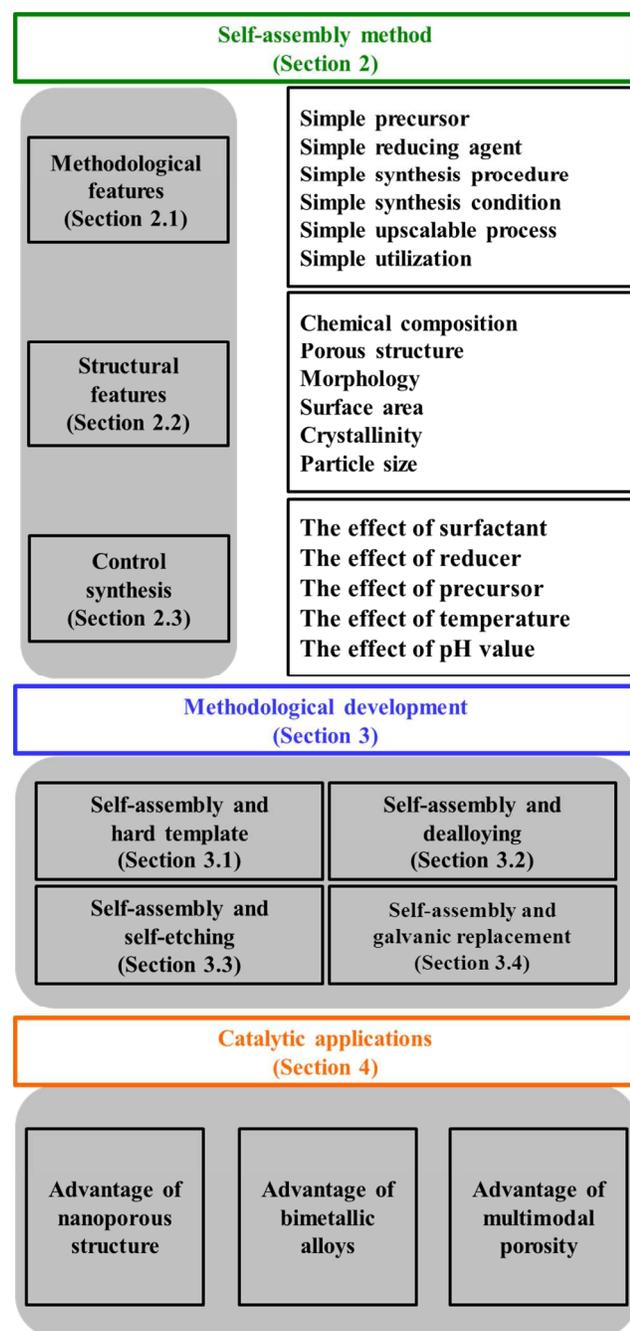


Fig. 4 Diagram outlining self-assembly method to nanoporous metal nanocrystals, development of synthesis methodology and catalytic applications of nanoporous metal nanocrystals.

Simple upscalable process. It is easy to large-scale production, mainly not requires high temperature and organic solvents. There is also no complex or harsh post-treatment. That means process reducing, time saving and cost cutting, will be very important to upscalable processes.

Simple utilization. The as-synthesized products can be directly used as catalysts only by a simple centrifugation and washing process. Due to their small nano-size, the products are easily utilized in many applications, such as hybrid material and host-guest chemistry. Furthermore, it is easy to form ensembles through controlling the spacing and alignment of these individual

nanocrystals.

2.2 Structural features of nanoporous metal nanocrystals

From a chemistry point of view, these nanoporous metal nanocrystals with various compositions, porous structures and morphologies are targeted. These characteristics are detailed below.

Chemical composition: Main compositions are Pt, Pd, and their alloys. Galvanic replacement can introduce other metals, such as Au, Ag and their alloys. Only one example is on Co by self-etching.

Porous structure: Most samples present an open framework and uniform pore size. The three porous structures of branched pores, hollow pores and perpendicular pores, are mainly obtained.

Morphology: Spherical structure, nanosheet structures, core-shell structures and cubic cages.

Surface area: Often around between $20 \text{ m}^2\text{g}^{-1}$ and $80 \text{ m}^2\text{g}^{-1}$. Introduction of secondary porosity can improve the surface area.

Crystallinity: Usually high crystalline degree, even in twist porous structure.

Particle size: Good uniformity and size-control in the range of several nanometers to near one hundred nanometers.

2.3 Control of self-assembly synthesis of nanoporous metal nanocrystals

Detailed investigation of the synthesis could provide useful insight into controlling the nanocrystal pattern and nanoporous textural properties, implying the precisely adjustment of advanced function. We will view the effects of general synthesis conditions, including surfactant, reducer, precursor, temperature and pH value.

The effect of surfactant. The surfactant plays a pivotal role in the synthesis of nanostructures with well-defined shape, uniform size and dispersed particles. The surfactant is also adaptable to effective create porous structure in the fabrication of metal nanocrystals.

The first attempt to prepare nanoporous metal nanocrystals, in which platinum salts were reduced by ascorbic acid in the presence of a surfactant to form nanodendritic structures, was demonstrated by Song *et al.*⁴² The porous structures of the Pt nanocrystals exhibited notable surfactant-dependent properties. In solutions of small surfactant assemblies (SDS and Brij-35 micelles), dendritic Pt nanoparticles are formed, whereas dendritic sheets dendritic disklike nanosheets or dendritic sheets in the form of solid foamlke nanomaterials are obtained in the presence of large liposomes. Following the work, non-ionic surfactants with different molecular structures (e.g. Pluronic F127, Brij 700, Tetronic 1107, PVP and PVP-co-VA) were used to fabricate similar Pt nanodendrites (Fig. 5a-e),^{55,57} indicating that the exact molecular structures or groups of nonionic organic molecules does not seem necessary to obtain the structure of Pt nanodendrites.

The above-mentioned results suggested that the surfactants should be a critical factor to branched structures, but have no obvious effect to particle size, pore size and pore structure. However, a novel perpendicular porous structure was very recently developed through the proper choice of surfactant, reported by Huang *et al.*⁵¹ As shown in Fig. 5f, the mesoporous nature of the Pd nanocrystals can be easily exhibited and this type

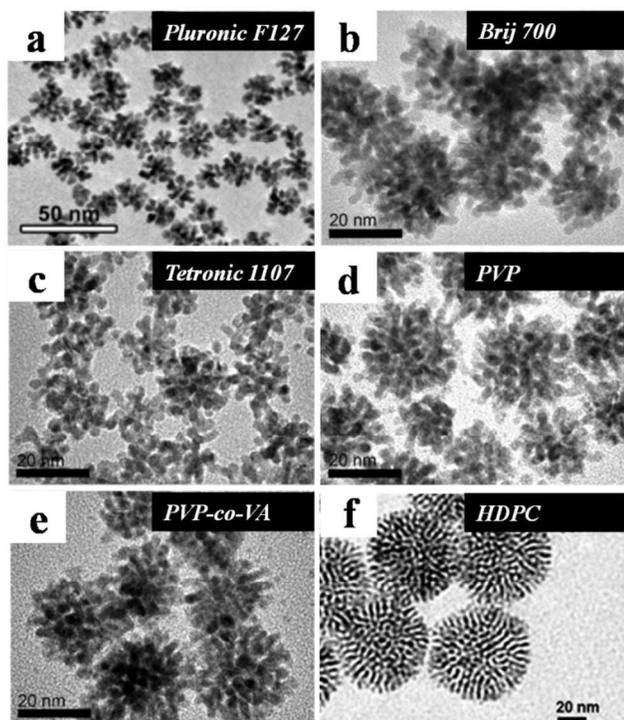


Fig. 5 Branched porous nanocrystals synthesized by various surfactants. (a) Pluronic F127. Reproduced with permission from ref. 55. (b-e) Brij 700, Tetronic 1107, PVP and PVP-co-VA. Reproduced with permission from ref. 57. (f) HDPC. Reproduced with permission from ref. 51.

of novel mesoporous Pd nanoparticles consists of many nearly parallel branches to form perpendicular pore channels. In this wet-chemical synthesis, the selection of hexadecylpyridinium chloride (HDPC) as surfactant and structure-directing agent is a crucial factor for the formation of mesostructured Pd nanocrystals with perpendicular porous structure.

The effect of reducer. The choice of a proper reducer is a key factor for the synthesis of nanoporous metal nanocrystals. Weak reducers are usually necessary for the formation of nanoporous structures. For example, Pt nanoparticles with branched structures have been obtained in an aqueous surfactant solution when ascorbic acid (AA) was used as the weak reducing agent, whereas cuboctahedral or cubic Pt nanoparticles were obtained when the reducing agent was sodium borohydride (NaBH_4), a strong reducer.⁵² It is presumed that the weak reducing agent is more suitable for the synthesis of porous metal nanocrystals in aqueous-phase reaction under mild conditions, because the reduction process is more difficult to control when using strong reducing agents but can be better controlled when weak reducing agent is used. The results from Mohanty *et al.* also confirmed the effect of the weak reducer in the synthesis of branched metal nanocrystals.⁷⁴ Au, Pt and Pd nanoflowers with a large number of branches were synthesized by using AA as reducing agent, while spherical nanoparticles were synthesized when using NaBH_4 as reducing agent.

In principle, the synthesis method towards porous monometal can be extended to prepare core-shell bi- and trimetallic

nanocrystals with nanoporous shells by utilizing the different redox potential of metals as the metal species with higher redox potential are reduced first. In other words, nanoporous nanoalloy can be one-pot synthesized by co-reduction using the same reducer. For example, solid Au@porous Pd bimetallic nanocrystals could be obtained with the same procedure for the synthesis of mesoporous Pd nanocrystals as mentioned above but using HAuCl_4 as additional precursor.⁵¹ Au@Pd@Pt triple-layered structured nanocrystals consisted of a compact Au@Pd core and dendritic Pt shell were also formed by co-reduction of HAuCl_4 , Na_2PdCl_4 and K_2PtCl_4 .⁶³ Moreover, the particle size of nanoporous metal nanocrystals can be tuned by adjusting the concentration of reducing agent. With increasing of the concentration of AA, the particle sizes were decreasing.⁵¹

The effect of precursor. The metal salt and metal acetylacetonate precursors are reduced to generate the final metal products. In general, redox potentials and amounts of the precursors directly influence metallic types and ratio of the final nanoalloys.

Currently, an innovative strategy, namely seed-mediated growth, has been developed to prepare branched porous metal nanocrystals, in which introduction of the second preformed seed precursors, not only can be used to synthesize a nanoalloy by the further growth of secondary metal, but also can be adjusted to control the particle size. For instance, PtAu bimetallic nanodendrites were successfully prepared by using 11 nm gold nanocrystals as seeds for the subsequent growth of Pt branches by reduction of $\text{Pt}(\text{acac})_2$ in a decahydronaphthalene/oleylamine mixture.⁶⁴ PtPd bimetallic nanodendrites have also been synthesized by reducing K_2PtCl_4 in an aqueous solution at 90 °C in the presence of preformed truncated octahedral Pd nanocrystals as seeds.⁶⁶ Monometal nanoparticles with branched porous structures could be also obtained by using the same metal as seeds. The single-crystalline branched Pd nanocrystals were synthesized by means of small Pd nanoparticles as seeds.³² Moreover, the size of the porous Pd nanocrystals could be tailored from 14 to 53 nm by adjusting the concentration of the seed. In these examples of seed-mediated growth method, the precursor seeds play an important role in the synthesis of branched porous metal nanocrystals, since the particle size and shape of these nanocrystals are difficult to control without using the preformed uniform and well-defined seeds.

The effect of temperature. As we mentioned in the above subsection, many nonionic surfactants were used to synthesize branched metal nanocrystals at room temperature. However, ionic surfactants, such as cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS), are not available for the synthesis of Pt nanodendrites in the same synthesized system.⁵⁷ The reason is the formation of floccules or precipitation by these ionic surfactants at a low temperature. This problem has been solved by raising the temperature of the reaction solution, as porous Pt nanoparticles have been obtained by using the ionic surfactant C_{14}TABr as structure-directing agent in aqueous solution at 70 °C.⁵² The porous metal nanocrystals synthesized by using ionic surfactants can be ascribed to the increased solubility of ionic surfactants with increasing temperature, which can effectively avoid the formation of floccules or precipitation.

In addition, temperature adjustment is another way to control

the particle size of nanoporous metal nanocrystals. For example, the average sizes of porous Pd nanoparticles were 101 nm, 82 nm and 51 nm when the reaction temperatures were 20 °C, 35 °C and 50 °C, respectively.⁵¹

5 The effect of pH value. The pH value of a solution has also been studied as an effect on the growth of nanoporous metal nanocrystals. Spherical metal nanoparticles, instead of metal nanodendrites were formed under the same condition, except the solution pH value was increased from 5.0 to 7.5.⁷⁴ The pH-mediated formation of metal nanodendrites here can be ascribed to the varied self-assembly behavior of sodium N-(4-n-dodecyloxybenzoyl)-L-isoleucinate (SDBIL: an amino acid based surfactant) in different pH value. In an acidic pH (5.0-6.0), SDBIL tends to slowly form long fibrous aggregates, which can

10 guide the growth of metal nanoparticles in an anisotropic manner, forming nanodendrites. SDBIL spontaneously forms spherical vesicles in alkaline pH (7.0-8.5) and, thus, leads to spherical metal nanoparticles.

3 Development of synthesis methodology

20 Self-assembly methods can be easily combined with other strategies for the fabrication of nanomaterials with specific structure and function. Developments in the self-assembly method have widened the panel of available methodologies to nanoporous metal nanocrystals with a remarkable control of

25 structure and function. The expected method not only allows the successful fabrication of novel porous structures, but also can easily modulate the shape of these porous nanocrystals. A significant development is that this self-assembly method was extended to combine with other strategies for the fabrication of

30 nanoporous metal nanocrystals with specific structure and function. Such a combination taking advantage of different structures and properties at the macroscopic or microscopic scale has been spotlighted for future developments of nanometal design. So, in this section, we identify the process, advantages, features

35 and mechanisms of these advanced synthesis strategies, including the combination of self-assembly with hard template, dealloying, self-etching and galvanic replacement. The detailed structures and corresponding compositions of these metal materials obtained by the combined strategies will be given.

40 3.1 Combination of self-assembly and hard template

Hard template synthesis is a common and effective method for the preparation of nanoporous metals with ordered structures.⁷⁶ It can also be utilized to prepare metal nanocrystals with an ordered porous structure.

45 In a typical replication procedure, the ordered nanoporous structure of a hard template (commonly porous silica or porous carbon) can be replicated by precursor infiltration and hard template removal. Mesoporous monocrystalline Pt nanoparticles have been synthesized by Yamauchi *et al.* in a novel hard-templating method.⁶⁷ The growth procedure of mesoporous Pt nanoparticles in a KIT-6 template is illustrated in Fig. 6a. An aqueous solution of K_2PtCl_4 was first filled into the mesoporous silica templates, KIT-6 or SBA-15, followed by chemical reduction of K_2PtCl_4 into Pt using aqueous AA as a reducing

50 agent. Ordered Pt replica structures were finally obtained after the removal of the silica by HF corrosion (Fig. 6b, c). The reducing

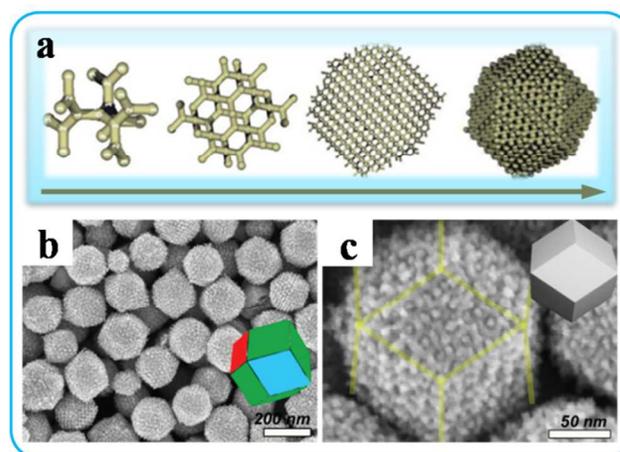


Fig. 6 (a) Computer simulation of Pt growth in 1a-3d mesostructure assuming that the Pt deposition occurs by tracing the channels of KIT-6 template outward from the nucleation center with a uniform speed. (b) Low- and (c) high-magnification SEM images of the obtained mesoporous Pt nanoparticles prepared with mesoporous silica KIT-6. Reproduced with permission from ref. 67.

65 agent, AA, plays a vital role in the successful synthesis of mesoporous Pt nanoparticles with uniform size, whereas Pt with irregular morphology deposited on the outer surface of the mesoporous silica when sodium borohydride (SBH) and dimethylaminoborane (DMAB) were used as reducing agents

70 instead of AA. The size and shape of the mesoporous Pt nanoparticles can be controlled by adjusting the reduction time and varying different mesoporous silicas as templates, respectively. To date, various nanoporous metals with novel structures have been synthesized in hard templates. However, the

75 prepared morphologies of nanoporous metals are limited to powders or films, very few can form metal nanocrystals with porous structures.

3.2 Combination of self-assembly and dealloying

Dealloying, also known as selective dissolution of one or more components out of an alloy, is a widely used approach to creating porous metal nanostructures.^{26,75-77} On this basis of morphology control of metal nanocrystals, dealloying provides a versatile approach to additionally endow as-synthesized metal nanocrystals with nanoporous structure by post-etching.

85 Generally, the porous metal nanocrystals synthesized by combination of self-assembly and dealloying have a two-step process. Two or multi-component metal nanocrystals with uniform and well-defined structures were firstly prepared by self-assembly method, and then endow the metal nanocrystals with

90 unique porous structure via selective dissolution of the less-noble component from the as-prepared nanocrystalline alloys. As shown in Fig. 7a, compact PtNi nanocrystals with intermetallic structures could be given porous interiors by dealloying of Ni.⁶⁹ PtNi nanoparticles were first synthesized in octadecylamine

95 solution (Fig. 7b). Then most of the Ni in the PtNi nanoparticles was chemically etched away by using an excess amount of concentrated nitric acid as oxidant, forming PtNi nanoporous nanoparticles with an average pore diameter of 2 nm (Fig. 7c). Core@shell structure can also be generated by dealloying after

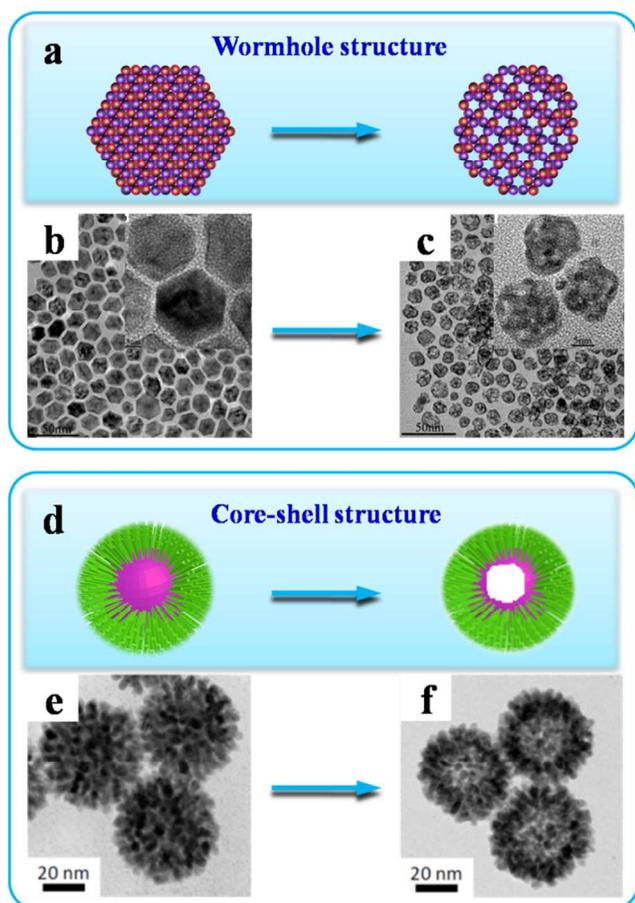


Fig. 7 (a) Schematic illustration of the formation of nanoporous PtNi alloy. TEM and HRTEM (insert) images of (b) PtNi nanoparticles and (c) nanoporous PtNi alloys. Reproduced with the permission from ref. 69. (d) Schematic illustration of the formation of dendritic PtPd nanocages. TEM image of (e) dendritic Pt-on-Pd nanoparticles and (f) dendritic PtPd nanocages. Reproduced with permission from ref. 50.

self-assembly (Fig. 7d). Yamauchi *et al.* prepared a novel metallic nanocage with a hollow interior and porous dendritic shell by this two-step procedure.⁵⁰ Pt-on-Pd nanodendrites with a Pd interior and dendritic Pt exterior were first prepared in aqueous solution at room temperature by using the block copolymer Pluronic P123 as surfactant and AA as reducing agent (Fig. 7e). Then the PtPd dendritic nanocages with hollow interiors and dendritic exteriors were fabricated by the selective dissolution of the Pd core using an excess amount of concentrated nitric acid (Fig. 7f).

3.3 Combination of self-assembly and self-etching

Although the combination of self-assembly and dealloying (also called post-etching) method has been proven as very effective and versatile to synthesize numerous nanoporous metal nanocrystals, disadvantages of high cost and complicated synthetic procedures hindered their practical applications. A new one-pot synthesis of nanoporous metal nanocrystals by combination of self-assembly and self-etching has also been developed.

Yao *et al.* firstly used the one-pot synthesis to produce a hollow structured metal nanocrystal.⁷⁰ Cubic cobalt

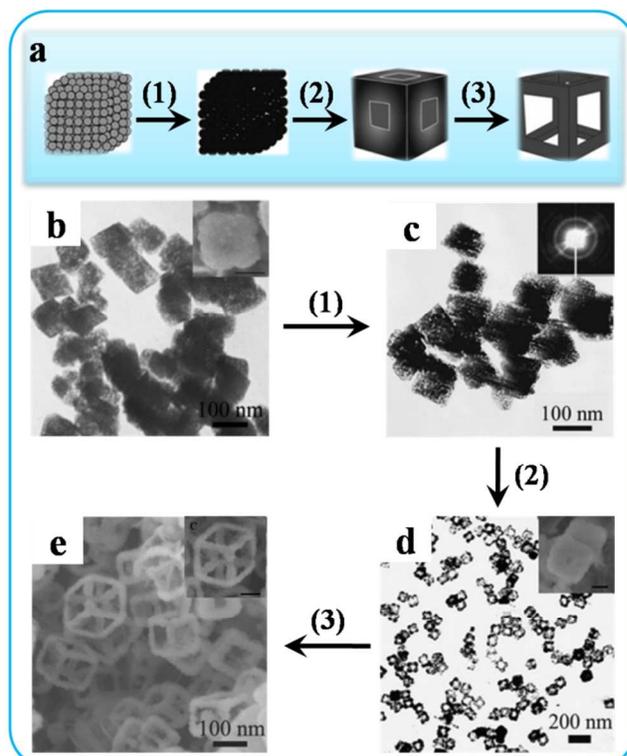


Fig. 8 (a) Scheme of the overall shape evolution: formation of Co cube-like aggregates (step 1), cubic Co nanocages (step 2) and Co nanoskeletons (step 3). TEM and SEM images of the products with different morphologies obtained at different reaction stages: (b) cubic CoO aggregates, (c) Co cube-like aggregates, (d) cubic Co nanocages and (e) cubic Co nanoskeletons. Reproduced with permission from ref. 70.

nanoskeletons were prepared by mixing cobalt acetate tetrahydrate and sodium fluoride in ethanol solution at 180 °C for 48-60 h. Cubic Co nanocages and nanoskeletons can be easily obtained by simply adjusting the reaction time (Fig. 8a). At the initial stage of reaction, CoO nanoparticles self-assembled into cube-like nanostructures (Fig. 8b), followed by quick in situ reduction to cubic Co aggregates (Fig. 8c). Hollow Co cubes (Fig. 8d) were gradually formed from cubic aggregates with noncompact structure and the shell changes from polycrystalline to single-crystalline because of Ostwald ripening. As the reaction continues, the six surfaces of the Co nanocages were eroded by NaF-assisted facet-selective corrosion, forming cubic Co nanoskeletons (Fig. 8e). In the synthetic system, fluoride was necessary for the formation of these novel hollow structures, while Co nanocages and nanoskeletons can be prepared when NaF was substituted by KF, whereas Co spheres were obtained when NaBr or NaCl were used instead of NaF.⁷⁰

3.4 Combination of self-assembly and galvanic replacement

Galvanic replacement offers an extremely effective route for the synthesis of metal nanocrystals with controllable hollow interiors and porous walls. In this typical synthesis, a relatively less-reactive metal is reduced by the core metal rather than reducers to form hollow nanostructures with a wide range of different morphologies, such as nanoboxes, nanocages, nanoshells and

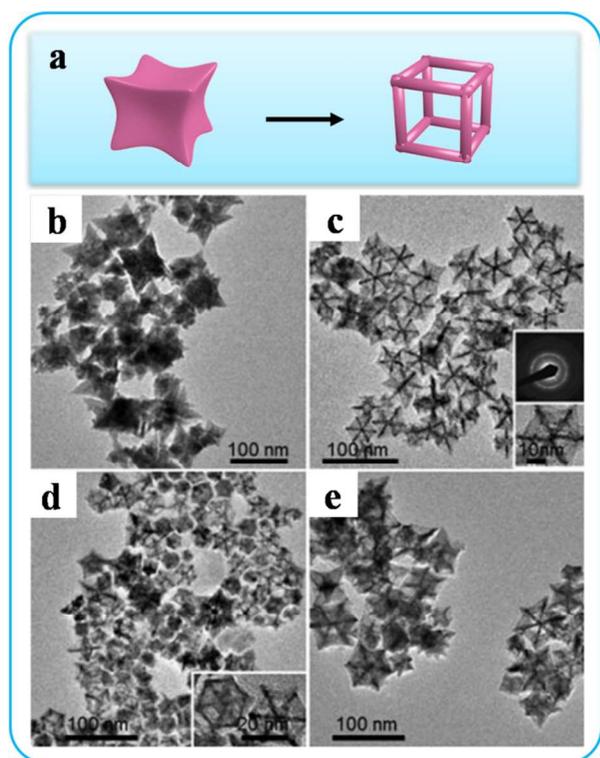


Fig. 9 (a) Schematic illustration of the formation procedure of PtCu₃ nanocages. TEM images of products obtained with different reaction times: (b) 12 h; (c) 20 h; (d) 28 h; and (e) 36 h. Reproduced with permission from ref. 71.

nanotubes.^{72,73,80-84}

Cubic intermetallic PtCu₃ nanocages were obtained by Lou *et al.* via a one-pot solution synthesis.⁷¹ The synthesis is performed in oleylamine solution containing chloroplatinic acid hexahydrate, copper acetylacetonate and CTAB at 170 °C for 24 h. The morphologies of the intermediate nanocrystals produced at varied reaction times were measured to investigate the formation mechanism of these PtCu₃ nanocages. As shown in Fig. 9, uniform solid nanoparticles were formed after reaction for 12 h (Fig. 9b). The products with nanocage structure can be clearly observed when the reaction times were 20 h (Fig. 9c) and 28 h (Fig. 9d). Fig. 9e shows the morphology of the products which obviously did not change anymore when further increasing the reaction time to 36 h. The formation of these novel bimetallic PtCu₃ nanocages can be reasonably attributed to the galvanic replacement of Cu in the nanocrystals with Pt species during the reaction. Notably, CTAB, as a structure-directing and stabilizing agent also plays a crucial role in the formation and dispersion of the PtCu₃ nanocages.⁷¹

4 Catalytic applications

Metal nanocrystals with porous structures are highly promising catalysts in numerous chemical and electrochemical reactions.⁸ Due to high surface area and rich edge/corner atoms, the porous metal nanocrystals are greatly favorable for enhancing catalytic performance and reducing metal consumption, which is particularly important for noble-metals.

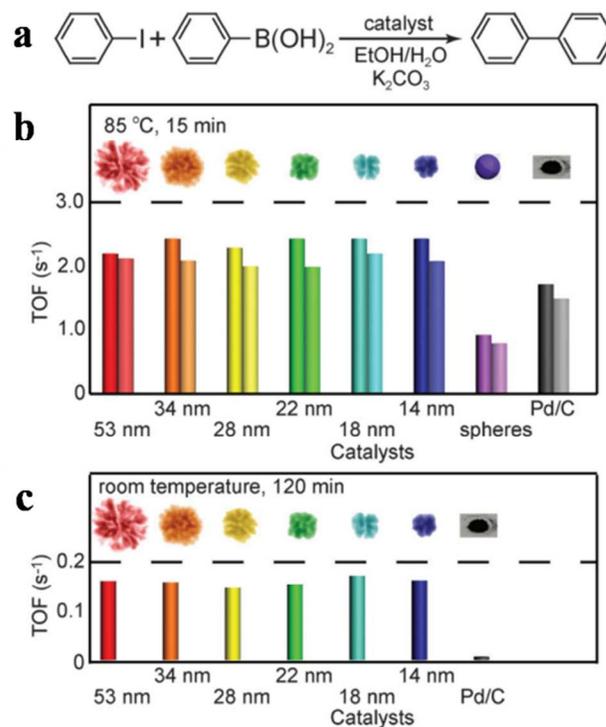


Fig. 10 Turnover frequency (TOF) values of the Pd-based catalysts for the coupling between iodobenzene and phenylboronic acid. (a) Reaction equation. (b) TOF values at 85 °C for 15 min. For each catalyst, the left column shows the TOF value in the first run, and the right one indicates the TOF value in the second run. (c) TOF values at room temperature for 120 min. Reproduced with permission from ref. 34.

Metal nanocrystals with nanoporous structures show superior catalytic performance over solid metal nanoparticles with specific shape. For example, porous Pt nanoparticles prepared by using C₁₄TABr as a structure-directing agent showed much higher catalytic activity for ethylene hydrogenation than the cubic and cuboctahedral Pt nanoparticles, owing to their higher surface area than the cubes or cuboctahedra.⁵² Recently, porous single-crystalline Pd nanoparticles prepared by using CTAB as the stabilizing agent in aqueous solutions displayed higher catalytic activities for the Suzuki coupling reaction than Pd nanospheres and commercial Pd/C nanoparticles both at 85 °C and at room temperature (Fig. 10).³⁴ The high catalytic activity of the porous Pd nanoparticles was ascribed to the large surface area and high concentration of coordinatively unsaturated surface atoms.

One of the techniques to improve the activity of nanometal catalysts is the partial introduction of a secondary metal to yield bimetallic alloys. Control of composition is therefore an important path. Porous alloy nanocrystals would also reduce the consumption of noble metal. For instance, PtPd nanodendrites with a dense array of Pt branches on a Pd core, as electrocatalysts for oxygen reduction reaction (ORR) (Fig. 11a), shown a mass activity (on the basis of equivalent Pt mass) of 2.5 times and 5.0 times than that of the Pt/C catalyst and the Pt-black catalyst, respectively.⁶⁶ Additionally, the PtPd nanodendrites also exhibited superior specific activity, which is 3.1 to 3.4 times than

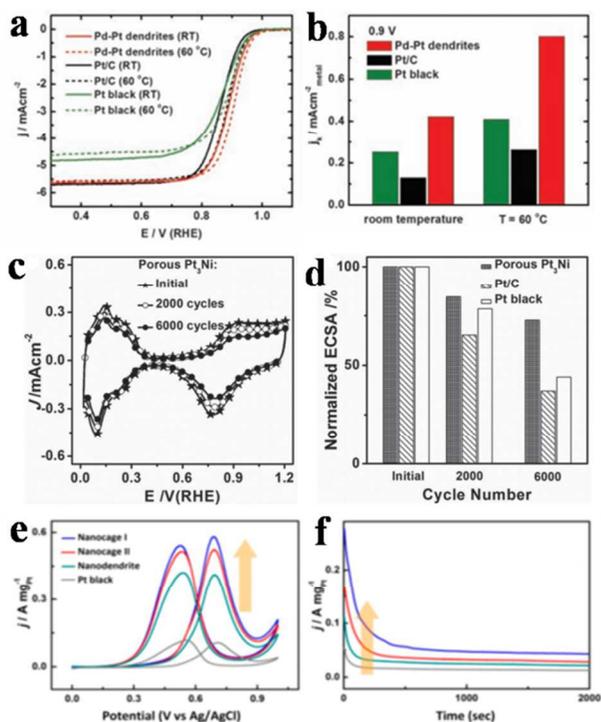


Fig. 11 (a) Oxygen reduction reaction (ORR) polarization curves for the PdPt nanodendrites, Pt/C catalyst, and Pt black recorded at room temperature and 60 °C in an O₂-saturated 0.1 M HClO₄ solution with a sweep rate of 10 mV/s and a rotation rate of 1600 rpm. (b) Specific activity at 0.9 V versus RHE for the PdPt nanodendrites, Pt/C catalyst, and Pt black. Reproduced with permission from ref. 66. (c) Cyclic voltammetry (CV) curves for porous Pt₃Ni nanocrystals after prolonged cycles of CV. The durability tests were carried out at room temperature in O₂-saturated 0.1 M HClO₄ at a scan rate of 50 mV/s. (d) Loss of electrochemically active surface area (ECSA) of porous Pt₃Ni nanocrystals, Pt/C catalyst, and Pt black after potential sweep cycles. Reproduced with permission from ref. 61. (e) CV curves and (f) chronoamperometric curves for methanol oxidation reaction catalyzed by nanocages I, nanocages II, nanodendrites, and Pt black in an aqueous solution containing 0.5 M H₂SO₄ and 1 M methanol. The chronoamperometric curves are recorded at 0.6 V. Reproduced with permission from ref. 50.

that of the Pt/C catalyst and 1.7 to 2.0 times than that of the Pt-black catalyst at room temperature or 60 °C (Fig. 11b). The high activity of PtPd nanodendrites can be ascribed to the high surface area and the exposure of particularly active facets on the Pt branches. Recently, Pt₃Ni nanocrystals with highly porous features also exhibited much better performance (mass and specific activities) than that of the Pt/C catalyst and the Pt-black catalyst,⁶¹ owing to the high surface area, rich steps/corners atoms, and the interconnected 3D nanostructures. Furthermore, the porous Pt₃Ni nanocrystals also presented better durability than the Pt/C and the Pt-black catalysts (Fig. 11c, d) due to the unique structures and alloy effect.

For the catalysis reactions occurring in porous nanometal, the porous structures strongly influence catalytic activity. The single-sized nanoporous metals have received interest in heterogeneous

catalysis in mentioned above. However, materials presenting multimodal porosity have an even higher interest, particularly for catalysis application, where optimization of the diffusion and confinement regimes is required.⁸⁵⁻⁹¹ For instance, PtPd nanocages with hollow interiors and porous dendritic exteriors, prepared by chemical etching of Pd cores from preformed dendritic PtPd nanoparticles,⁵⁰ exhibited a mass activity of 1.4 times higher than that of preformed PtPd nanodendrites and 5.3 times higher than that of Pt black for the methanol oxidation reaction (Fig. 11e). The activity of this PtPd nanocage was the highest catalytic activity among the previously reported Pt-based materials. In addition, the mass current densities of the nanocages were also higher than that of nanodendrites and Pt black in chronoamperometric investigation recorded at 0.6 V for 2000 s (Fig. 11f). This high catalytic performance of the PtPd nanocages was attributed to their sufficient accessible active sites at both interior and exterior porous structures.

5 Summary and outlook

In this minireview, we provide a brief overview of recent developments of metals nanocrystals with novel nanoporous structures. The methodological and structural features along with the control of synthesis, including surfactant, reducer, precursor, temperature and pH value, are summarized. Developments of synthesis methodology by combining self-assembly with other methods, such as hard template, dealloying, self-etching and galvanic replacement, are discussed. The fascinating properties and corresponding applications in catalysis due to the novel porous structures of metal nanocrystals are also demonstrated, which indicating the synthesis of metal nanocrystals with porous structures is of great importance in both academia and industry.

Recent years have witnessed rapid and significant progress in the synthesis of nanoporous metal nanocrystals. Self-assembly offers a most effective and facile option in the controlled synthesis of nanoporous metal nanocrystals. However, the studies in this field are still at the infancy stage and many issues need to be addressed, mainly including ordered porous structure and size-controlled pores, multiple compositions and regular morphologies. In order to face the challenges and make great progresses, in our opinion, researches on nanoporous metal nanocrystals should be developed toward the following directions. (1) Further developing of synthetic strategies. The self-assembly method can be easily combined with other strategies for the structural fabrication and functional control. Self-assembly with two or even more approaches can be exploited to precisely fabricate the intricate structure and regular morphology. Furthermore, one-pot synthesis, having many advantages such as process reducing, time saving and cost cutting, will be most important for the future synthesis of nanoporous metal nanocrystals. (2) Precise controlling of the porous structures. Highly ordered porous metal nanocrystals are mostly preferred, avail to high molecules selectivity in selective catalysis. Fine tuning of the pore size is also of technological importance in applications, such as host-guest chemistry. (3) Precise controlling of the morphology of nanocrystals. Metal nanocrystals with controlled regular morphology can maximize the expression of active facets toward a specific reaction. However, the metal nanocrystals with a regular morphology and ordered porous structure have not been

created so far. Porous nanometals with specific morphology could meet the big demand for future development of metals materials with fine structures. (4) Fine adjusting of multiple compositions. Like bimetal nanocrystals, multi-component metal nanocrystals could also bring us a big surprise in properties and applications. It is very difficult to fabricate nanoporous nanometal materials with more than two components due to the big difference of redox potential and few choices of the co-reducers. More examples in bi-, tri-, tetra-, pentametal etc. should be made, that means multi-functions. And very fine adjustment of these multi-components is very important to fascinating applications, especially in catalysis. (5) Further extending of applications. The nanoporous structure and rich active atoms in metal nanocrystals have been greatly favorable for enhancing catalytic performance. As a unique kind of metal material with both advantages of nanopores and nanocrystals, it is worth to expect scientists to find more emerging applications in the future such as sensing and imaging. (6) Precise controlling of multi-dimensional assemblies. Because of collective properties and quantitative prediction, ensembles of nanoporous metal nanocrystals could exhibit new properties in a wide field that are different to those of individual nanoporous metal nanocrystals. Control of multi-dimensional assemblies will be a very spotlight research field.

Despite significant progress in the synthesis of metal nanocrystals with porous structures based on self-assembly, deeper insights into the growth mechanisms involved in the synthesis of these novel structures are not rigorously understood. Precise structural control of porous metal nanocrystals is also not very easy. Therefore, further studies are needed to better understand the growth mechanism of porous metal nanocrystals. With the continuous development of new synthesis approaches and nanofabrication techniques, it is no doubt that remarkable advancements on porous metal nanocrystals and their properties will be achieved.

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