Review

Weiqing Zhang and Xianmao Lu*

Morphology control of bimetallic nanostructures for electrochemical catalysts

Abstract: Bimetallic nanostructures with well-defined shapes have shown distinct and advantageous catalytic properties compared to their monometallic counterparts. The use of bimetallic electrocatalysts may improve activity and durability, in addition to the possibility of reducing the loading of precious metals. A variety of bimetallic nanocrystals with different shapes has been reported in recent years. Their activities toward electrochemical catalytic reactions such as oxygen reduction and alcohol oxidations have been intensively studied. In this review, we discuss some latest developments in the morphology-controlled synthesis of Pt- and Pd-based bimetallic nanocrystals with shapes such as nanoden- drites, polyhedra, porous hollow structures, and core shells, as well as their applications as electrochemical catalysts.

Keywords: bimetallic nanostructures; electrochemical catalysts; shape-selective growth.

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1 Introduction

Bimetallic nanostructures have received tremendous attention in recent years. This is because nanocrystals composed of two metals, either in the form of homogeneous alloy or heterogeneous mixture, have shown distinct and advantageous properties compared to their monometallic counterparts. For catalytic applications, in particular, bimetallic nanostructures have emerged as an important class of electrocatalysts for a number of reactions including oxygen reduction reaction (ORR), alcohol (methanol or ethanol) oxidation reaction (MOR or EOR), and formic acid oxidation reaction (FOR). The purpose of incorporating two metals in catalysts is manifold: (1) to improve catalytic activity; (2) to lower the loading of the more precious metal; and (3) to enhance durability or resistance to poisoning.

Using bimetallic catalysts to achieve improved activities toward various electrocatalytic reactions have been well investigated. For example, it has been demonstrated that Pt,Ni(111) surface is 90-fold more active for the ORR than carbon-supported monometallic Pt nanoparticles [1]. To date, a large number of bimetallic nanostructures with various compositions and morphologies have been reported to show enhanced mass- or surface-specific activities toward ORR, AOR, or FOR [2–4]. This enhanced electrochemical performance of bimetallic nanostructures relative to nanocrystals of single metal have been mainly attributed to the following reasons. First, the introduction of the second metal (M₂) may change the geometric structure of the nanocrystals consisting of the first metal (M₁) due to the different bond lengths of M₁-M₁, M₁-M₂, and M₂-M₂. This change in geometric structure will affect the adsorption energy and bond breaking mechanism of the chemical species on the catalyst surface. For instance, when Pt-based alloys are used as the catalyst for ORR, an optimum spacing of Pt-Pt will lead to the highest electrocatalytic activity by allowing favorable dissociative adsorption of O₂ [5]. Formation of alloy also changes the surface atomic arrangement. For alcohol or formic acid oxidation reactions on Pt-based catalysts, it has been predicted that one of the most effective methods to improve activity is to reduce the number of three neighboring Pt sites by alloying with another metal. This approach will minimize the formation of CO species that block catalytically active sites [6]. The second reason for the enhanced activity is due to the change in electronic structure, which in turn will affect the binding energy of the chemical species such as oxygen and CO species on the catalysts. It has been shown that maximum electrocatalytic activity can be obtained when the adsorption energies of the reactive species and the blocking intermediate species are in balance. The adsorption energies of different species on the catalyst surface can be governed
by the electronic structure of the bimetallic structures. For ORR on Pt-based bimetallic alloy surfaces, the $d$-band vacancy can be increased, causing strong metal-O$_2$ interaction that weakens the O-O bonds. Based on this theory, a so-called volcano-type relationship between the ORR activity and oxygen binding energy has been reported [7]. This theory has been employed to predict the electrocatalytic activity of bimetallic surfaces and to screen a large number of bimetallic alloy catalysts [8]. For alcohol and formic acid oxidation reactions, the formation of adsorbed CO intermediate species (CO$_{ads}$) on the catalytic surface largely affects the catalytic activity. The change in electronic structure caused by the second metal may lower the adsorption energy of CO$_{ads}$ on the bimetallic catalyst to prevent the CO species from blocking active sites.

Some precious metals are excellent electrocatalysts for various oxidation and reduction reactions. The cost of these metals, however, is prohibitive and prevents one from exploiting their broader applications. This is especially true for Pt, which is the most expensive metal and shows excellent catalytic activities toward nearly all the important fuel cell catalytic reactions including ORR and MOR. To lower the loading of such costly metals in electrocatalysts without sacrificing activity has been an imperative task for researchers in this area for many years. One of the most effective approaches toward this goal is to add a low-cost second metal to form bimetallic structures. In addition to the possibility to achieve higher activity, the use of 3$d$ transition metals such as Cu, Fe, Co, Ni would considerably lower the overall cost of the catalysts, although some associated issues such as leaching of the more active metal in the long run may also arise.

Catalyst poisoning is another critical problem that may be alleviated by using bimetallic nanostructures. Pt, for example, is highly susceptible to CO, C, and S poisoning – these poisonous species may block the active sites of the catalysts and significantly reduce the activity over time. By adding another metal, it is possible that oxygen-containing surface species may be formed at lower potentials. These species will facilitate the oxidation of CO. For example, Pt-Ru alloy has been studied intensively for MOR as Ru can dissociate water $\rightarrow$ form adsorbed OH (OH$_{ads}$). These OH$_{ads}$ will then diffuse on the catalyst surface and react with CO$_{ads}$ to form CO$_2$. In addition to Ru, a number of metals including Mo, Sn, Ge have been proposed and investigated as promoters for AOR and/or FOR to reduce CO poisoning [2, 9].

## 2 Morphological control of bimetallic nanostructures

### 2.1 Shape-dependent electrocatalytic activity

Controlling the shape of the metallic nanostructures has strong implications on their catalytic activities. This is because nanocrystals with different shapes profiles may have different exposed facets. As the number of neighboring atoms and dangling bonds on the catalytic surface change with the exposed facet, the catalytic activity of nanocrystals is highly facet-dependent. For instance, Pt nanocrystals terminated with high-index (730) facets have shown unusually high activity for electrooxidation of formic acid and ethanol [10]. This facet-dependent effect on catalytic activity, which is also applicable to bimetallic nanostructures, is mainly caused by both the surface geometry and surface electronic structure that vary with facets. It should be noted that the catalytic activities for bimetallic surfaces of different facets might follow a different order compared to that of their monometallic counterparts. For example, it has been well-established that for Pt surface, the ORR activity in perchloric acid increases following the order of Pt(100)<Pt(111)<Pt(110). For the Pt$_3$Ni alloy, however, it increases as Pt$_3$Ni(100)<Pt$_3$Ni(110) (Figure 1A) [1]. In addition to the facet effect, lattice strain may also impact the electronic structure of the catalyst and contribute considerably to the ORR activity [13]. This can be attributed to either the compressed or stretched lattice at the crystal domain boundaries that exhibit different electronic structures. For example, Yang et al. found that Pt$_3$Ni icosahedral and octahedral nanocrystals exhibit significantly different ORR activities, although both shapes are terminated with (111) facets [11]. The mass- and area-specific activities of Pt$_3$Ni icosahedra are much higher than those of octahedra with a similar size. This difference is explained based on the density functional theory (DFT) calculations that show different adsorption energies of hydroxyl group (OH) on the edge of icosahedral and octahedral nanoparticles because of the different percentage of edge atoms relative to the atoms on the whole surface (Figure 1B) [11].

For the bimetallic alloy nanostructures, the surface atomic distribution of the two metals is another variable that may influence the catalytic activity. The atomic distribution can be manipulated by changing the atomic ratio or by tuning the degree of alloying of the two metals. In a study by Dimitrov and coworkers, it is found that Pt-Cu
nanocubes terminated with \{100\} facets exhibit superior activity toward \text{FOR} compared to Pt spherical nanocrystals, which are generally enclosed by both \{100\} and \{111\} facets [14]. In addition, the catalytic activity of the bimetallic Pt-Cu nanocubes can also be changed by varying the Pt:Cu ratio – the FOR activity reaches maximum when the Pt to Cu ratio is 80:20. In another work, Choi et al. prepared composition-controlled Pt$_x$Co alloy nanocubes ($x$=2, 3, 5, 7, and 9) [15]. They found that among all the Pt$_x$Co nanocubes with different compositions, Pt$_3$Co exhibited the highest specific activity toward ORR. This finding is attributed to the different oxygen-binding energies on the catalytic surfaces of the different Pt to Co ratios. Instead of changing the composition, Han et al. manipulated the surface atomic distribution of bimetallic nanostructures by forming either alloy or core-shell structures with two metals at the same atomic ratio (Figure 1C) [12]. Their results showed that Au-Pd alloy nanocrystals have higher mass-specific activity than Au@Pd core shells. It is believed that this enhancement effect of alloy Au-Pd
octahedra is caused by both the change in electronic structure and the improved CO removal ability.

2.2 Shape-selective growth of bimetallic nanostructures

Typically, the preparation of bimetallic nanostructures with controlled shape is more complicated than monometallic ones. Although a variety of studies have been reported for the shape-selective growth of monometallic nanocrystals and reasonable understanding regarding the growth mechanisms has been obtained in recent years [16, 17], the rules that have been discovered for monometallic nanocrystals generally cannot be simply applied to bimetallic cases. This is because the involvement of the second metal in the reaction has significant effect on both the nucleation and growth stages of the nanostructures – the reaction kinetics may be altered by introducing the precursor of the second metal to the reaction system, causing either slower or faster nucleation; the deposition mode of the second metal on the surface of the seeds will interfere with the further growth of the first metal due to the change in surface energy and lattice strain of the nanocrystals; the interaction of the surfactant with the surface of nanocrystals composed of single metal or two metals are also different due to the different binding strength of the functional groups with the two metal atoms. All the above factors will complicate the shape-controlled synthesis of bimetallic nanostructures. Over the past couple of decades, some design rules or synthetic protocols have been successfully developed for monometallic nanocrystals [16]. For bimetallic nanostructures, however, controlling their shape is still, by and large, based on trial-and-error approach, although a few generalized methods applicable for some particular bimetallic systems have started to emerge [18–23].

To date, several synthetic methods have been developed for shape-selective growth of bimetallic nanostructures. The first method is co-reduction. This is a relatively simple method that involves the use of two metal precursors – one for each metal, a suitable reducing agent or multiple reducing agents that may convert the metal ions into their atomic form, and surfactants that bind to the nanocrystal surface to mediate their size and shape. Depending on the reduction rate and the interaction of the two metals, either heterogeneous structures such as dendritic or smooth core-shell nanocrystals or homogeneous alloy nanocrystals may be formed (Figure 2A). A large number of core-shell nanocrystals with a metallic core surrounded by a shell of the second metal have been synthesized via this approach [6, 24]. The formation mechanisms of core shell or dendritic structures in Pt-based bimetallic systems have been discussed in detail in a recent review of Yang and coworkers [25]. During the reaction, because of the different reduction rates or concentrations of the metal precursors, the atoms of one metal may be generated first and nucleate to form seeds for the deposition of the second metal. In general, to form a bimetallic core-shell structure, certain requirements should be met. First, the lattice mismatch between the two metals should be small enough so that not much lattice strain is introduced when the second metal (M₂) is growing on the surface the first metal (M₁). In addition, the surface energy change, which is determined by the surface energy of M₂ and the interfacial energy between M₁ and M₂, should be smaller than the surface energy of M₁. Therefore, the growth of M₂ on the surface of M₁ will follow the Fran-van der Merwe (FW) mode to give a core-shell structure. Co-reduction may also lead to the formation of dendritic nanostructures. When the lattice mismatch of the two metals are large, or the sum of the surface energy of M₁ and interfacial energy is larger than the surface energy of M₂, a so-called Volmer-Webber (VW) growth mode takes place, causing the formation of “islands” of M₁ on the M₂ nanocrystal surface. If continuous growth of M₁ on the “islands” is allowed, these “islands” will eventually develop to form a dendritic structure. Co-reduction method is also one of the most common approaches to prepare homogenous bimetallic alloy nanocrystals. This can be achieved by manipulating the reaction kinetics to allow proper reduction and growth rates of the two metals.

Template-directed growth is another important synthetic method for the formation of bimetallic nanostructures. For this approach, shape control can be relatively more easily compared to the co-reduction method mainly because metal templates with different shapes can be used to guide the growth of the nanostructures. Based on the relative reactivity of the two metals and other reaction conditions such as the use of reducing agent, the formation of the bimetallic nanostructures can follow either galvanic replacement reaction (GRR, Figure 2B) or seed-mediated deposition pathway (Figure 2C). GRR is a powerful method to form bimetallic hollow structures. Typically, GRR-based synthesis involves the use of metal nanostructures as sacrificial templates to react with ions of a more noble metal. Owing to the difference in electrode potentials of the two metals, the nanostructured metal templates will be dissolved, and the more noble metal ions will be reduced to the elemental form, which subsequently deposits onto the surface of the templates. Depending on a number of factors such as similarity in crystal structures, degree of lattice mismatch, and difference in metallic bonding strengths, a conformal or a
nonconformal growth of the second metal may take place on the surface of the template to form a shell, while the first metal is continuously consumed from the core. In the end, a structure with a hollow interior and a shell composed of either just the second metal or the alloy of both metals can be formed. To date, a wide variety of bimetallic or trimetallic hollow nanostructures have been prepared via GRR [26, 27]. Depending on the composition and reaction conditions, these nanostructures may exhibit either smooth or rough surfaces. For catalytic applications, the nanostructures with porous and rough surfaces are more interesting as a larger surface area may be expected from these structures. Another mechanism is seed-mediated deposition of the second metal on the nanocrystal surface of the first metal. This type of growth may be achieved under the following conditions: (1) the reduction potential of the second metal is more negative relative to the first metal, so the template composed of the first metal will not react with the precursor of the second metal but mainly serves as the substrate for the deposition of the second metal; or (2) even though the first metal is more reactive than the second metal, when a relatively strong reducing agent is present in the reaction, the second metal ions tend to be reduced by the reducing agent instead of the nanostructured template of the first metal. In this case, the reaction kinetics directs the reduction pathway of the second metal so that a galvanic replacement reaction will not occur. The template of the first metal is reserved for the deposition of the second metal. Depending on the rate of the deposition, the amount of the precursor, the physical properties of the two metals including the lattice constants and metal-metal bond strength, the deposition of the second metal may lead to the formation of a conformal monolayer/multiple-layer coating, clustered nanoparticles that give rough and porous surfaces, or thick coating that changes the geometry of the nanocrystals.
In the next section, we will discuss some of the latest developments in the synthesis of bimetallic nanostructures with well-controlled shapes and their applications in electrocatalytic reactions. Considering the large body of work in this area, it is not realistic to include all related studies in this review. Therefore, we focus on very recent reports in the past 3–4 years with emphasis on Pt- and Pd-based bimetallic nonspherical nanocrystals. For the work that is not covered, readers may refer to other recent reviews [3, 4, 23, 28, 29].

3 Case studies

3.1 Bimetallic dendritic or particle-on-particle structures

Bimetallic dendritic nanostructures have attracted significant attention for electrocatalytic applications. This is because these dendritic (or branched/particle-on-particle) structures with rough surfaces may provide much improved surface areas and/or high density of defects compared to nanocrystals with smooth surfaces. Typically, dendritic bimetallic nanostructures can be prepared with metal seeds as the template followed by the growth of nanoparticles of another metal on their surface. The metal seeds can be either pre-prepared as in template-directed synthesis or formed in situ as in co-reduction method. Sometimes, a soft template can be employed to guide the growth of the dendritic or branched structures. Pt- and Pd-based dendritic nanostructures have been mostly studied due to the excellent catalytic property of the two metals. In general, the metal seeds are composed of either noble or more active transition metals such as Pd, Au, Cu, Co, or Ni. The formation of Pt or Pd nanoparticles can be either through a simple reduction pathway or via a galvanic replacement reaction mechanism, depending on the relative redox potentials of these metals and the presence of reducing agents such as ascorbic acid and trisodium citrate. As mentioned earlier, the growth mode of Pt or Pd on the metal seeds is determined by a few factors including lattice mismatch, change in surface energy, and nucleation rate. Briefly, in the case when there is large lattice mismatch between the two metals, high surface energy excess that favors heterogeneous nucleation on the surface of the metal seeds, or fast nucleation rate of the second metal, the growth will proceed following the so-called VW mode to give particle-on-particle morphology. Owing to the facile synthesis, there have been a large number of Pt- and Pd-based bimetallic dendritic structures with various compositions and morphologies (Table 1).

3.1.1 Pt-Pd nanodendrites

Pt-Pd bimetallic dendritic nanostructures have been intensively studied due to the superior catalytic properties of both Pt and Pd metals in various reactions such as oxygen reduction, methanol oxidation, and formic acid oxidation. Xia et al. obtained Pt-on-Pd bimetallic dendritic structures by reducing K₂PtCl₄ on cuboctahedral Pd nanocrystals (Figure 3A–B) [35].

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on Pd core are bounded with {111}, {110}, and high-index {311} facets. These nanostructures were tested for ORR and showed mass activities 2.1 and 4.4 times higher than Pt/C and Pt black reference catalysts, respectively (Figure 3C). The enhanced electrocatalytic activity for ORR was attributed to the large surface area and rich active facets of the branched Pt structures. The growth mechanism of the Pt-Pd dendrites was also investigated in a later study of the same group [36]. It was found that at the very beginning of the reaction, Pt homogeneous nucleation took place with heterogeneous nucleation – while homogeneous nucleation led to the formation of tiny Pt nanoparticles, heterogeneous nucleation of the tiny particles via oriented attachment gave Pt branches. Similar Pt-on-Pd bimetallic dendritic nanostructures were also obtained via a sequential synthetic method reported by Yang and coworkers (Figure 3D–E) [37]. In their synthesis, Pd nanoparticles were prepared first by decomposing palladium acetylace- tonate. The resultant 5-nm Pd nanoparticles were then employed as seeds for the growth of 3-nm Pt nanoparticles to give Pt-on-Pd dendritic heteronanostructures. They studied the electrocatalytic activity and stability of the
Pt-on-Pd dendritic nanostructures supported on carbon black for ORR. The area-specific activity of Pt-on-Pd dendritic structures was almost twice that of Pt black reference catalyst (Figure 3F) [37]. Meanwhile, the Pt-on-Pd dendrites showed an unusually high long-term stability – when cycled between 0.6 and 1.0 V for 30,000 times, the Pt-on-Pd dendrites showed an electrochemical surface area (ECSA) loss of only 12%, which is in stark contrast to a loss of 39% for Pt black. Both methods developed by Xia group and Yang group for the preparation of Pt-Pd dendritic nanoparticles are based on seeded growth – in which Pd nanoparticles are formed before they are used as seeds to direct the growth of Pt nanoparticles on their surfaces. In a later work, Yamauchi and coworkers discovered a simple and mild co-reduction pathway for the preparation of Pt-on-Pd nanodendrites [38]. In their synthesis, Pluronic P123 was used to assist the reduction of K₂PtCl₄ and Na₂PdCl₄ simultaneously at room temperature. It was found that Na₂PdCl₄ can be reduced faster than K₂PtCl₄; therefore, Pd nanocrystals were formed first and acted as in situ-generated seeds for the deposition of Pt. The resultant Pt-Pd bimetallic nanodendrites were composed of Pd cores and Pt dendritic shells (Figure 3G). It was found that the copolymer Pluronic P123 also acted as template for the formation of Pt branches. The Pt branches grown on Pd core mainly showed (111) facets that are highly active for electrocatalytic oxidation of methanol. Comparison of MOR activities of Pt-on-Pd dendrites with different compositions indicated that nanocrystals obtained at larger Pt/Pd ratios have better electrocatalytic performance (Figure 3H) [38].

### 3.1.2 Pt-Au nanodendrites

Although Au alone is not an active catalyst for fuel cell applications, Adzic et al. found that when small Au clusters were decorated onto Pt nanocrystals, the resulting bimetallic structure exhibited extremely high durability toward ORR [50]. In the meantime, various studies have also shown that Au nanostructures decorated with Pt nanoparticles can show good activity and durability for electrocatalytic reactions. To this end, a number of Au nanostructures have been employed as seeds to grow Pt-Au bimetallic dendritic structures. As Au is nobler than Pt, a reducing agent has to be used to induce the formation of Pt on Au template. For example, Han et al. synthesized Au@Pt dendritic core-shell heterostructures using Au nanoparticles with shapes including cube, rod, and octahedron as seeds (Figure 4A–C) [31]. While all dendritic Pt shells formed on Au cores with different shapes exhibited larger ECSA than that of Pt dendrites prepared without Au,
those grown on Au octahedron showed the largest ECSA. The mass activities of ORR for the dendritic Pt shells on different Au templates decreased following the order of Au octahedron > rod > cube. These results indicate that the electrocatalytic performance of the Au@Pt bimetallic nanostructures is dependent on the core morphology. Furthermore, the Au@Pt core-shell nanostructures also exhibited better durability compared to the monometallic Pt dendrites. The improved durability of the Au@Pt bimetallic heterostructures was attributed to the incorporation of Au core to the dendritic structures.

Similar Au@Pt dendritic core-shell nanostructures were also prepared by Yamauchi et al. with a one-step co-reduction method with Pluronic F127 block copolymer as the surfactant [32]. In a nearly parallel work, Wang et al. used Pluronic F127 to synthesize noncompact Pt-on-Au dendritic nanoparticles [34]. Later, Yamauchi and coworkers improved this surfactant-assisted method by applying ultrasonic treatment to decrease the Au@Pt particle size and narrow the size distribution [33]. The resultant Au@Pt dendritic nanoparticles showed a Brunauer-Emmett-Teller (BET)-specific area twice as large as that of the Pt dendritic nanoparticles when normalized to Pt mass loading. They also found that the electrocatalytic activity of the Au@Pt dendritic core shells for MOR can be tuned by changing the ratio of Au:Pt – when the molar ratio Pt: Au was 1:1, the Au@Pt dendrites showed an optimum peak current density approximately four times higher than that of monometallic Pt dendritic nanoparticles [33].

In addition to Au nanoparticles, one-dimensional (1-D) Au nanowires have also been used as template to form Au@Pt dendritic structures. Zheng et al. obtained 1-D Au@Pt core-shell dendrites with dense and tiny Pt dendrites decorated on Au nanowires via a seed-mediated method (Figure 4D–F) [30]. This self-supported Au@Pt dendritic structure exhibited much enhanced electrocatalytic activity and better stability for ORR compared to Pt/C. Compared to nanoparticle-based templates, 1-D Au nanowires as support for Pt catalyst can form a nanowire network, which allow efficient electron transfer.

### 3.1.3 Pt-M nanodendrites (M=Ni, Co, Cu, etc.)

To lower the loading of precious noble metals in electrocatalysts, considerable efforts have been made by various groups to prepare Pt-M (M=transition metals such as Cu, Co, Ni, etc.) bimetallic nanostructures. The replacement of noble metals with earth-abundant transition metals may significantly lower the cost of electrocatalysts. In addition, the more active transition metals may also serve as an oxophilic element in the catalysts. This approach has a strong impact for the preparation of electrocatalysts resistive to CO poisoning as the presence of an oxophilic element in Pt-based catalysts can facilitate the formation of oxygen species on the catalyst surface. To date, a number of Pt-M dendritic structures have been synthesized via co-reduction or the seeded growth method. For example, Zhao et al. obtained Pt-Cu bimetallic nanodendrites by co-reduction of H₂PtCl₄ and CuCl₂ in the presence of Pluronic F127 block copolymer and formic acid (Figure 5A–B) [41]. The resultant Pt-Cu nanodendrites exhibited higher electrocatalytic activity for MOR than the commercial Pt/C catalyst. Also based on a co-reduction approach, Gu et al. synthesized Pt-Co dendritic alloy nanoparticles that showed an ORR activity 4.5 times higher than that of Pt/C catalyst (Figure 5C–F) [40]. Seeded growth has also been employed to form Pt-transition metal nanodendrites. For example, Li et al. reported the preparation of highly branched Pt-Ni bimetallic nanobundles via a seed-based diffusion synthetic route [39]. In their synthesis, branched Pt nanostructures were formed by reducing H₂PtCl₄ in octadecylamine. These pre-formed Pt structures were then used as seeds to allow the diffusion of Ni species that were generated by reducing Ni(NO₃)₂. The resultant Pt-Ni bimetallic nanobundles were rich in step surface and showed an MOR activity 3.6 times higher than that of Pt nanoparticles. The enhanced activity was attributed to both the high-density surface active sites and the incorporation of Ni in the structure. In addition, the Pt-Ni nanobundles also exhibited better stability than Pt nanoparticles – 55% of the initial peak current density was retained after 4000 cycles for Pt-Ni, while only 10% was obtained for Pt nanoparticles after the same number of cycles (Figure 5G–I). More importantly, tolerance to CO poisoning was also significantly improved – CO stripping experiments confirmed that the oxidation potential of CO on Pt-Ni nanobundles shifted negatively by 0.06 V relative to that of Pt nanoparticles, indicating that CO species on the Pt-Ni surface can be removed more efficiently [39].

### 3.1.4 Pd-M nanodendrites

Pd-based bimetallic nanostructures with dendritic morphology have also been intensively studied. In an earlier work of Han et al., they synthesized Pd-Au alloy nanoflowers using ascorbic acid to reduce Pd and Au precursors. By varying the ratio of Pd to Au, bimetallic nanoflowers with three compositions, namely, Au₃Pd, Au₆Pd, and Au₃Pd₆, were obtained [42]. Later, with hydrazine instead of ascorbic acid as the reducing agent, the same group synthesized
dendritic Au-Pd nanoflowers as catalysts for ethanol oxidation reaction (Figure 6A–B) [43]. The results showed that all Pd-Au nanoflowers with different Au to Pd ratios exhibited enhanced electrocatalytic activity and stability relative to Au and Pd nanoparticles. Au-Pd dendritic core shells have also been prepared by various researchers. For instance, Wiley et al. obtained Au-Pd dendrites consisting of an Au core and a Pd dendritic shell through a seed-mediated growth method [45]. Also, via a seed-mediated method at room temperature, Su et al. synthesized Au-Pd core-shell nanodendrites with Au polyhedral nanocrystals as the template (Figure 6C–D) [46]. They compared the electrocatalytic activity of the Au-Pd dendrites for MOR with that of Au-Pd alloy nanoparticles. Very recently, hexadecylpyridinium chloride has been used as a soft template to grow Au-Pd porous nanostructures. This structure exhibited a distinct morphology compared to the other reported dendrites – the pore channels of the Pd shell are perpendicular to the Au core (Figure 6F) [48].

### 3.2 Bimetallic alloy nanocrystals with polyhedral shapes

Shape-selective growth of bimetallic alloy nanocrystals with well-defined facets has dramatically emerged in recent years. To date, Pt-M and Pd-M bimetallic nanocrystals with various polyhedral shapes such as cube, octahedron, and icosahedron have been prepared by a number of research groups. Some general methods in tuning the shapes have
been developed. Thanks to the availability of a broad range of bimetallic nanocrystals with controlled shapes, uniform sizes, and well-defined facets, advances in understanding both the growth mechanisms and the effect of different facets on catalytic activities have evolved rapidly (Table 2).

### 3.2.1 Bimetallic alloy nanocrystals with cubic shape

#### 3.2.1.1 Pt-Pd nanocubes

Wang et al. synthesized Pd-Pt bimetallic alloy nanocubes with monodisperse size and tunable composition via the co-reduction method in an aqueous medium (Figure 7A–C) [58]. These Pd-Pt nanocubes exhibited enhanced electrocatalytic activity toward FOR compared with Pd sub-10 nm nanocubes and commercial Pd black. The maximum peak current of the Pd-Pt nanocubes was obtained at a Pt content of 25.6 at.%. In addition to the co-reduction method, galvanic replacement reaction as a synthetic approach can also be used to give Pd-Pt bimetallic cubic nanostructures. Xia et al. synthesized Pd-Pt concave nanocubes via Br-assisted galvanic replacement reaction using Pd nanocubes as template to react with PtCl$_6^{2-}$ [59]. It was found that because Br ions preferentially adsorb on the
Table 2: List of Pt- and Pd-based bimetallic alloy nanostructures with polyhedral shapes, their synthetic methods, and catalytic reactions.

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<th>Metal 1</th>
<th>Metal 2</th>
<th>Morphology</th>
<th>Synthetic method</th>
<th>Reference and catalytic reactions</th>
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<td>Octahedra</td>
<td>Co-reduction</td>
<td>FOR [12]</td>
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<td>Pd</td>
<td>Trisoctahedra</td>
<td>Co-reduction and seed-mediated method</td>
<td>[71]</td>
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<tr>
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<td>Convex polyhedra</td>
<td>Co-reduction and seed-mediated method</td>
<td>EOR [72]</td>
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<td>Co-reduction</td>
<td>EOR [73]; MOR, FOR [74]</td>
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<td>Octopods</td>
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<td>[75, 76]</td>
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<tr>
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<td>Co-reduction</td>
<td>[75]</td>
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<tr>
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<td>Pd</td>
<td>Nanocubes</td>
<td>Co-reduction</td>
<td>[77]</td>
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\{100\} facets of Pd nanocrystals, they could facilitate the galvanic replacement reaction on \{100\} facets of the Pd template. The Pd-Pt concave structures with different Pt contents were obtained and those with 3.4 wt% Pt showed four times ORR activity as that of the commercial Pt/C catalyst.

Yan et al. also took the advantage of the preferential adsorption of small ions such as Br or I as facet-selective agent to prepare the sub-10 nm Pt-Pd nanocubes [60]. The Pt-Pt concave structures were tested for MOR and showed an activity 1.3 and 2.9 times higher than that of Pt-Pd nanotetrahedra and commercial Pt/C catalyst, respectively. The enhanced electrocatalytic activity of Pt-Pt nanocubes relative to tetrahedra was attributed to the different reaction pathways of MOR on \{100\} and \{111\} facets [60]. Again, with the assistance of different halide ions such as Cl and I as the shape-directing agent, Huang et al. obtained Pt-Pd nanocubes. The composition of the Pt-Pd nanocubes can be controlled by changing the molar ratio of the starting precursors (Figure 7D–F) [62]. It was found that the catalytic performance is highly dependent on the shape of the Pt-Pd structure – the optimum activity was achieved when the Pt-Pd nanocubes were bounded with \{100\} rather than \{111\} facets [62].

3.2.1.2 Pt-M nanocubes (M=Co, Ni, Cu, Fe, Mn, Zn)

In addition to Pd, many transition metals such as Co, Ni, Cu, Fe, Mn, and Zn have also been intensively studied to form cubic alloy with Pt. For instance, Choi et al. synthesized composition-tunable Pt-Co (x=2, 3, 5, 7, and 9) alloy nanocubes in a co-reduction approach via changing the amounts of Co precursor and found that the electrocatalytic performance on ORR highly depended on the Co composition (Figure 7G–U) [15]. Also via a co-reduction approach, Xu et al. synthesized uniform Pt-Cu nanocubes (Figure 8A–C) [14]. It was found that the use of multiple capping agents, including tetraoctylammonium bromide (TOAB) and oleylamine, played a key role in controlling both the shape and the size of the nanocubes.
formation of the cubic shape was attributed to stabilization of the Br ions that preferentially adsorb on {100} facets of the Pt-Cu nanocubes. Meanwhile, oleylamine was important in stabilizing the Pt and Cu clusters at nucleation stage. At growth stage, oleylamine synergistically controlled the cubic shape with TOAB. The electrocatalytic activity of the Pt-Cu nanocubes for MOR was evaluated in comparison with spherical Pt-Cu and Pt nanocrystals with similar sizes. It was found that the current density of Pt-Cu nanocubes was 1.4 and 5.3 times higher than those of Pt-Cu nanospheres and Pt nanocrystals, respectively, indicating that the electrocatalytic activity of Pt-Cu nanostructures is highly dependent on their facets [14]. In a later work of the same group, they further tuned the composition of the bimetallic Pt$_x$Cu$_{100-x}$ nanocubes ($x$=54–80 atom%) and investigated the electrocatalytic activity and long-term stability for FOR [55]. It was found that Pt$_{54}$Cu$_{46}$ nanocubes exhibited the best electrocatalytic performance compared to the nanocubes containing less Pt. Using a one-pot hydrothermal process,
Yan et al. also prepared Pt-Cu nanocubes and concave nanocubes via a galvanic replacement reaction approach assisted by Br ions \[56\]. The Pt-Cu concave nanocubes were bounded with multiple \{hk0\} high-index steps and facets. The Pt-Cu concave nanocubes exhibited a higher specific activity for MOR than the Pt-Cu nanocubes, Pt nanocubes, and Pt/C catalyst.

Fang et al. conducted a series of work to investigate the preparation of Pt\(_{3}\)M nanocubes (M = 3-D-transition metals including Co, Fe, and Ni) (Figure 8D–L) \[51–53\]. In their syntheses, tungsten hexacarbonyl \([W(CO)\_6]\) was used to control the nucleation and growth. Meanwhile, oleylamine and oleic acid with different ratios were used as both the solvent and surface stabilizer to obtain a cubic shape. \([W(CO)\_6]\) was found to play a critical role in morphological control for the formation of cubic shape. This is because the introduction of \([W(CO)]\) mediates the reduction of Pt\(^{2+}\) ions at the nucleation and growth stages via the reaction of Pt\(^{2+}\) + W\(^{6+}\) \(\leftrightarrow\) W\(^{n+}\) + Pt\(^{0}\). Therefore, the reduction of Pt\(^{2+}\) is slowed down to facilitate a steady crystal growth with sustained feedstock of Pt \[52\]. The resultant Pt\(_{3}\)M nanocubes exhibited better electrocatalytic activity for MOR and FOR relative to spherical Pt\(_{3}\)M or Pt nanocubes \[52, 53\]. This is because of slow CO adsorption and facile CO desorption on the surface of nanocubes \[53\].

Also, as an effort to reduce the Pt loading and to improve CO poisoning tolerance, Murray et al. synthesized Pt-Mn nanocubes with uniform size via a co-reduction method (Figure 8M) \[57\]. The Pt-Mn nanocubes were obtained via hot injection of Mn\(_{2}\)(CO)\(_{10}\) into a solution containing Pt(acac)\(_2\), oleic acid, and oleylamine. However, when Mn\(_{2}\)(CO)\(_{10}\) was added into the reaction solution instead of hot injection, Pt-Mn nanoparticles instead of nanocubes were formed. The Pt-Mn nanocubes exhibited enhanced ORR activity three times higher than the commercial catalyst. It was also found that the ORR activity...
of Pt-Mn was both shape- and electrolyte-dependent – the \{111\} facets of Pt-Mn showed higher ORR activity than \{100\} facets in HClO$_4$, while the opposite was observed in H$_2$SO$_4$ [57]. In another work, the same group also investigated the growth of monodisperse PtZn nanocubes and nanospheres (Figure 8N) [61]. The Pt-Zn nanocrystals exhibited much improved tolerance of CO poisoning in MOR compared to other Pt-M bimetallic nanocrystals.

3.2.2 Bimetallic alloy nanocrystals with other polyhedral shapes

3.2.2.1 Pt-Pd alloy polyhedra
Pt-Pd bimetallic nanocrystals with tetrahedral and octahedral shapes bounded by \{111\} facets have also been prepared by various researchers. For instance, Yan et al. obtained sub-10 nm Pt-Pd tetrahedra using Na$_2$C$_2$O$_4$ to stabilize \{111\} facets of Pt-Pd tetrahedra (Figure 9A–B) [60]. The resultant Pt-Pd tetrahedra showed better stability toward MOR than that of Pt-Pd nanocubes and commercial Pt/C catalyst. Huang et al. also obtained Pt-Pd octahedra and tetrahedra instead of nanocubes by switching the shape-directing agent from I$^-$ to Cl$^-$ ions (Figure 9C–D) [62]. Park et al. reported a polyol process to grow octahedral Pt-Pd nanoparticles in aqueous solution [66]. The octahedral Pt-Pd nanoparticles are well-defined alloy nanocrystals with dominant \{111\} facets. They further tuned the composition of the Pt-Pd alloy nanoparticles to form Pt$_x$Pd$_y$, Pt$_x$Pd$_y$, and Pt$_x$Pd$_y$ octahedra [67]. Among the alloy nanocrystals with different compositions, octahedral Pt$_x$Pd$_y$ exhibited much enhanced electrochemical performance for ORR relative to Pt$_x$Pd$_y$ and Pt$_x$Pd$_y$.

3.2.2.2 Pt-M (M = Ni, Cu, Au) alloy polyhedra
Following a similar synthetic approach of Pt$_x$Ni nanocubes, Fang et al. also prepared Pt$_x$Ni nanoctahedra by changing the injection rate of the Ni precursor (Figure 10A–B) [54]. It was found that while slow injection

Figure 9 (A–B) Pt-Pd tetrahedra. Adapted with permission from Ref. [60]. Copyright 2011 American Chemical Society. (C–D) Pt$_{52}$Pd$_{48}$ octahedra/tetrahedra. Adapted with permission from Ref. [62]. Copyright 2012 American Chemical Society.
Figure 10  (A–B) Pt,Ni octahedra. Adapted with permission from Ref. [54]. Copyright 2010 American Chemical Society. (C–D) Pt,Ni truncated octahedra. Adapted with permission from Ref. [63]. Copyright 2010 American Chemical Society. (E) Pt3Ni icosahedra. Adapted with permission from Ref. [11]. Copyright 2012 American Chemical Society. (F–G) Pt-Cu hexapods. Adapted with permission from Ref. [78]. Copyright 2013 Nature Publishing.
of Ni precursor facilitates the growth of nanocubes, fast addition causes the formation of octahedra. The Pt₃Ni octahedra bounded by (111) facets showed much-enhanced electrocatalytic activity for ORR compared to Pt₃Ni nanocubes and Pt nanocubes. Yang et al. also employed a facile co-reduction approach to prepare Pt₃Ni truncated-octahedra (Figure 10C–D) [63]. In their synthesis, adamantane-carboxylic acid (ACA) or adamantane-acetic acid was added to mediate the reaction kinetics. They studied the effect of the alkane-chain length of amines on the shape controlling of Pt₃Ni. It was found that three different amines including octadecylamine, hexadecylamine, and dodecylamine resulted in truncated-octahedra with yields of 70%, 90%, and 100%, respectively. This trend indicates that short-alkane-chain amine favors the formation of truncated-octahedra. In a subsequent work, Yang et al. systematically studied the effect of reaction parameters including capping agent, reducing agent, and reaction time on controlling the shape of the Pt₃Ni nanocrystals [64]. They further investigated the electrocatalytic performance of Pt₃Ni nanocrystals with 70%, 90%, and 100% of truncated octahedra for ORR in alkaline medium. It was confirmed that the Pt₃Ni (111) surface has much higher ORR activity than (100) surface.

In addition to octahedra, multiple-twinned icosahedral nanocrystals are also bounded by {111} facets. Yang et al. reported several types of Pt-M (M= Au, Ni, and Pd) alloy icosahedral nanocrystals synthesized in solution by using carbon monoxide gas as both the reducing agent and the capping agent to stabilize {111} facets (Figure 10E) [11]. It is interesting that although both icosahedron and octahedron are bounded by {111} facets, the ORR activity of Pt₃Ni icosahedra was found to be higher than that of the octahedra. To understand the difference in ORR activity of Pt₃Ni with different shapes but same facets, they conducted density function theory (DFT) calculations and molecular dynamics (MD) simulations, which suggested that the diffuse elastic strain present at the twin boundaries within icosahedral nanocrystals should be the main reason of the difference in ORR activity between Pt₃Ni icosahedra and octahedra [11].

In addition to the abovementioned cubic, octahedral, and icosahedral nanocrystals, other polyhedral shapes of Pt-M alloy nanocrystals have also been reported. For example, based on a one-pot strategy, Li et al. synthesized bimetallic Pt-Cu hexapod nanostructure with high-index {112} facets (Figure 10F–G) [78]. A growth mechanism for the formation of Pt-Cu hexapods was proposed. It is believed that Pt-Cu nanocrystals with rhombic dodecahedral shape were generated first at the beginning of the reaction. Following etching of the apaxes and facets led to the concave hexapod nanostructure. The bimetallic Pt-Cu hexapod concave nanocrystals exhibited an electrocatalytic MOR activity 2.5 times higher than that of commercial Pt black [78].

### 3.2.2.3 Pd-Au alloy polyhedra

Using co-reduction method, Han et al. synthesized Au-Pd rhombic dodecahedra (RDs) in aqueous solution in the presence of cetyltrimethylammonium chloride (CTAC) (Figure 11A) [69]. It was found that both the reaction kinetics tuned by the use of ascorbic acid as the reducing agent and the selection of surfactant played critical roles in controlling the facets of the Au-Pd nanocrystals. At slow reduction rate or when CTAC was replaced with other surfactant, RDs were not obtained. The Au-Pd RDs were enclosed by 12 (110) facets and exhibited an enhanced mass-specific activity toward EOR 6 times higher than that of Au-Pd nanocrystals bounded with (111) facets (Figure 11B). They also synthesized octahedral Au-Pd alloy and Au@Pd core-shell nanostructures via the co-reduction approach (Figure 11C) [12]. The octahedral Au-Pd alloy, Au-Pd core shell, Pd and Au nanocrystals were employed to compare the electrocatalytic activity for formic acid oxidation. The results showed that the Au-Pd alloy octahedra exhibited the best electrocatalytic activity and stability among all the nanocrystals with identical shape and size (Figure 11D) [12]. They further conducted selective etching of the {100} facets by Br ions for the Au-Pd alloy octahedra to form octapodal Au-Pd alloy nanocrystals, which exhibited enhanced electrocatalytic activity for ethanol oxidation [70]. Following a seed-mediated and co-reduction method, the same group also obtained trisoctahedral (TOH) Au-Pd alloy nanocrystals enclosed with {441} high-index facets [71].

Another systematic study regarding the evolution of Au-Pd alloy nanostructures was conducted by Skrabalak et al. [68]. In their work, Pd-Au alloy nanostructures were synthesized via a coupled seed-mediated and co-reduction method. First, tiny Au seeds (<10 nm) were prepared to grow larger Au cores. Then the Au cores were used as a template for the growth of Pd-Au alloy via co-reduction of additional Au and Pd precursors by ascorbic acid in the presence of CTAB. With the decrease in the Au:Pd precursor ratio, branching became obvious, and octopods were formed finally (Figure 11G). When pH values were decreased at fixed Au:Pd precursor ratios, four kinds of nanostructures including octopodal, concave, cuboctahedral, and octahedral nanocrystals were produced (Figure 11H). It was found that while Au:Pd precursor ratio determines the final nanocrystal morphology, the
pH can affect the reaction reduction rate and may also cause etching of Au cores via Au(III)-CTAB complexes. Therefore, the interplay of these two mechanisms led to the formation of nanostructures with systematically varied morphologies [68].

### 3.3 Porous/hollow Pt- and Pd-based bimetallic nanostructures

Bimetallic nanoparticles with porous or hollow structure possess large surface area and have shown great promise as electrochemical catalysts. Typically, porous bimetallic nanostructures can be generated via galvanic replacement reaction or dealloying method. In a typical galvanic replacement reaction approach, nanotemplates composed of a more active metal are reacted with the precursor of the second metal. Based on the different reduction potentials, the second metal is reduced and deposited onto the templates at the expense of the first metal to form hollow structures. Another method is based on dealloying of bimetallic nanostructures. The bimetallic alloy nanostructures can be prepared first via methods such as the co-reduction of two metal precursors. Afterwards, dealloying will be performed using methods such as electrochemical etching or chemical leaching by adding an etchant that
can dissolve the more active metal from the alloy. With the dissolution of the more active metal, a porous structure can be generated (Table 3).

Based on the galvanic replacement reaction approach, Wang et al. synthesized ultra-long Pt-on-Pd nanowires consisting of small Pt nanobranches supported on Pd nanowire. In their work, Te nanowires were first obtained and used as sacrificial templates for the synthesis of Pd nanowires via the replacement reaction between Te and H₂PdCl₄. Subsequently, the preformed Pd nanowires were used as seeds to direct the growth of Pt nanobranches via the reduction of K₂PtCl₄ by ascorbic acid. Owing to the branched structure, the Pt-on-Pd nanowires showed a high ESCA (90.7 m² g⁻¹) and much enhanced electrocatalytic activities for MOR relative to the commercial Pt/C catalyst (Figure 12A–C) [79]. Porous Pt-Pd bimetallic nanostructures have also been obtained via the replacement reaction between Pd nanocrystals and Pt precursors. In a recent work, Han et al. applied Pd octahedra and nanocubes as template to synthesize Pd-Pt bimetallic octahedral and cubic nanocages via the reaction between Pd and K₂PtCl₄ in the absence of other reducing agents [80]. They also found that if a small amount of ascorbic acid was added as a reducing agent to facilitate the reduction of Pt precursor, dendritic hollow nanocrystals instead of nanocages were obtained. Once a large amount of ascorbic acid was introduced, the final structures were octahedral and cubic core-shell dendrites. They further employed the Pd-Pt nanostructures with different morphologies as electrocatalysts for ORR. The results showed that the Pd-Pt nanocages have better performance than Pd-Pt dendritic hollow or core-shell structures. It is also interesting to note that all the structures obtained from octahedral templates showed better electrochemical performance than those obtained from nanocubes (Figure 12D, E) [80].

Lu et al. reported the synthesis of Pt-Ag bimetallic nanostructures with a controlled number of void spaces via a tailored galvanic replacement reaction (GRR) (Figure 12F–G) [81]. Ag nanocubes were employed as the template to react with Pt ions in the presence of HCl. The use of HCl in the GRR caused rapid precipitation of AgCl, which grew on the surface of Ag nanocubes and acted as a removable secondary template for the deposition of Pt. The number of nucleation sites for AgCl was tailored by controlling the amount of HCl added to the Ag NCs or by introducing PVP to the reaction. This strategy led to the formation of Pt/Ag hollow nanoboxes, dimers, multimers, or popcorn-shaped nanostructures consisting of one, two, or multiple hollow domains. Owing to the presence of large void space and porous walls, these nanostructures exhibited high surface area and improved catalytic activity for MOR.

Li et al. developed a general dealloying approach to form nanoporous Pt-Ni and Pt-Co nanoparticles [19]. In their work, bimetallic nanocrystals were prepared first using a so-called noble-metal-induced-reduction method. Subsequently, the less noble component (Ni or Co) of the nanocrystals was selectively dissolved with nitric acid to create a porous structure. The resultant nanoporous particles exhibited relatively high BET surface areas (∼60 m² g⁻¹) and ECSA (∼85 m² g⁻¹), indicating that these bimetallic nanostructures are promising electrochemical catalysts.

### 3.4 One-dimensional bimetallic alloy nanorods or nanowires

One-dimensional bimetallic nanostructures including nanorods and nanowires may exhibit superior electrocatalytic activities compared to nanoparticles. This is because this type of structures may allow efficient electron transfer

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**Table 3** List of porous/hollow Pt- and Pd-based bimetallic nanostructures, their synthetic methods, and catalytic reactions.

<table>
<thead>
<tr>
<th>Metal 1</th>
<th>Metal 2</th>
<th>Morphology</th>
<th>Synthetic method</th>
<th>Reference and catalytic reactions</th>
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<td>MOR [81]</td>
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<td>MOR [81]</td>
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<tr>
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<td>Dealloying</td>
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<td>ORR [86]</td>
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</table>
due to the interconnected conductive pathways. Similar to monometallic nanowires/nanorods, 1-D bimetallic nanostructures can be formed based on either template-directed growth or oriented attachment mechanisms (Table 4). For template-based methods, the template can be either soft templates such as micelles formed from surfactant within certain solvents or inorganic templates such as nanowires of an active metal (e.g., Te). Oriented attachment of nanoparticles is another approach for the formation of 1-D bimetallic nanostructures. In this approach, small metallic nanoparticles collide in solution and fuse together along one direction by forming metallic bonds at the interfacial sites to grow into nanowires.

Sun et al. reported a synthesis of ultrathin FePt and CoPt nanorods/nanowires in hot organic solution containing oleylamine and octadecene (Figure 13A–C) [18]. The length of the nanorods/nanowires can be tuned by varying the volume ratio of oleylamine and octadecene. It was believed that oleylamine self-organized into a micelle-like structure within octadecene solvent as soft template and directed the growth of FePt or CoPt nanowires. Also, with octadecene as the solvent, Schaak et al. synthesized CuPt nanorods with tunable lengths and aspect ratios in the presence of oleylamine and oleic acid (Figure 13D–G) [88]. It was found that the activity of CuPt nanorods for CO oxidation was much higher than that of commercial Pt/Al₂O₃ catalyst. Yang et al. also developed a general soft template method for the preparation of ultrathin Pt-M (M=Pd, Ru, Au, Fe) alloy nanowire networks [87]. In their method, the nanowires were grown...
within the micelles formed in a two-phase (water-chloroform) system with CTAB as a soft template.

Nanowires composed of two metals have also been prepared using hard templates such as Te nanowires. Based on this method, Dong et al. obtained ultrathin Pd-Pt and Pd-Au nanowires [91]. In this work, Te nanowires were employed as both sacrificial template and reducing agent to react with precursors of Pd, Pt, or Au. The electrocatalytic performances of Pd-Pt nanowires with different ratios of Pd to Pt were tested for ethanol and methanol oxidation reactions. It was found that Pd_{45}Pt_{55} has much higher activity than that of Pd_{80}Pt_{20} and Pd_{93}Pt_{7} nanowires as well as Pd nanowires, Pt nanotubes, and Pd/C catalysts [91].

![Table 4](chart.png)

Table 4 List of one-dimensional Pt- and Pd-based bimetallic nanostructures, their synthetic methods, and catalytic reactions.

<table>
<thead>
<tr>
<th>Metal 1</th>
<th>Metal 2</th>
<th>Morphology</th>
<th>Synthetic method</th>
<th>Reference and catalytic reactions</th>
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<td>Co-reduction</td>
<td>[18]</td>
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<td>Pt</td>
<td>Nanowire networks</td>
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<td>[87]</td>
</tr>
<tr>
<td>Ru</td>
<td>Pt</td>
<td>Nanowire networks</td>
<td>Soft template</td>
<td>[87]</td>
</tr>
<tr>
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<td>Pt</td>
<td>Nanowire networks</td>
<td>Soft template</td>
<td>[87]</td>
</tr>
<tr>
<td>Fe</td>
<td>Pt</td>
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<td>Soft template</td>
<td>[87]</td>
</tr>
<tr>
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<td>Pt</td>
<td>Nanowires</td>
<td>Co-reduction</td>
<td>CO oxidation [88]</td>
</tr>
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<td>Cu</td>
<td>Pt</td>
<td>Nanotubes</td>
<td>Galvanic replacement reaction</td>
<td>[89]</td>
</tr>
<tr>
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<td>Pt</td>
<td>Nanowires</td>
<td>Oriented attachment</td>
<td>[90]</td>
</tr>
<tr>
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<td>Pd</td>
<td>Nanowires</td>
<td>Galvanic replacement reaction</td>
<td>MOR, EOR [91]</td>
</tr>
<tr>
<td>Au</td>
<td>Pd</td>
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<td>Galvanic replacement reaction</td>
<td>MOR, EOR [91]</td>
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<tr>
<td>Au</td>
<td>Pd</td>
<td>Porous tubes</td>
<td>Electrochemical deposition</td>
<td>EOR [92]</td>
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</tbody>
</table>

![Figure 13](image.png)

Figure 13 Fe_{55}Pt_{45} NRs and NWs with a length of (A) 20 nm, (B) 50 nm, and (C) 200 nm. Adapted with permission from Ref. [18]. Copyright 2007 Wiley. CuPt nanorods with average lengths of (D) 12.6, (E) 27.8, (F) 37.1, and (G) 55.5 nm. Adapted with permission from Ref. [88]. Copyright 2009 American Chemical Society.
The orientated attachment mechanism has been exploited for the growth of bimetallic nanowires. It was found that for bimetallic systems, the attachment of nanoparticles to form 1-D nanowires only takes place at certain ratios of the two metals. For example, Yang et al. studied the formation of PtAg worms via oriented attachment of small PtAg nanoparticles [90]. It was concluded that the formation of nanowires only happened when the molar ratio of Pt and Ag approached to 1. When either Pt or Ag became the dominant component in the alloyed nanostructures, sphere-like or faceted nanoparticles instead of wires were obtained under the same reaction conditions. They also investigated the growth mechanism of PtAg wormlike nanowires through DFT calculation and MD simulation. Based on both experimental results and simulation calculations, it was determined that the oriented attachment of PtAg nanoparticles to form nanowire was caused by the interplay of thermodynamic and kinetic factors [90].

### 3.5 Bimetallic core-shell nanocrystals bounded by high-index facets

High-index faceted bimetallic core-shell nanostructures have emerged as an important class of electrocatalysts in the past few years. Nanocrystals enclosed by high-index facets may exhibit higher catalytic activity relative to those bounded by low-index ones due to the high density of kinks and steps present on high-index facets. However, the preparation of bimetallic nanostructures terminated with high-index facets is not an easy task as these facets are thermodynamically unstable and tend to disappear along the nanocrystal growth process. Only until recently have some synthetic strategies been developed by a few research groups based on co-reduction or seed-mediated growth methods to prepare bimetallic core-shell nanocrystals terminated with high-index facets (Table 5).

Using Au nanocubes as seeds, Huang et al. prepared Au@Pd core-shell nanocrystals with tetrahedral (THH) shape bounded by high-index (730) facets (Figure 14A) [95]. They found that a number of factors, including the lattice mismatch between Pd and Au, the use of CTAC as the surfactant, the right reaction temperature, and oxidative etching caused by Cl- and O species, were attributed to the formation of the high-index facets. They further prepared Au@Pd core shells with concave octahedral and octahedral shapes by lowering the temperature to prolong the reaction time (Figure 14B). The electrocatalytic activities of these core-shell nanostructures for EOR were investigated in alkali solution. The results showed that the tetrahedral core-shell structures exhibited much enhanced electrocatalytic activity over that of octahedra and concave octahedra. This enhancement was believed to be caused by the high-index (730) facets [95].

Yan et al. also obtained Au-Pd core-shell trisoctahedral (TOH) and tetrahedral (THH) nanocrystals via seed-mediated method by using Au octahedra and tetrahedra as growth seeds. The prepared TOH and THH Au-Pd nanocrystals are bounded with (730) and (221) high-index facets, respectively. These nanostructures showed much improved catalytic activity for Suzuki coupling reaction relative to Pd and Au@Pd nanocubes (Figure 14C) [96]. Lee et al. also employed Au TOH nanocrystals to grow Au@Pd core shells. They found that, with carefully controlled reaction kinetics, Au@Pd core shells with different geometries including THH bounded by \( \{hk0\} \) facets, concave TOH bounded by \( \{hhl\} \) facets, and concave hexoctahedron (HOH) bounded by \( \{hkl\} \) facets were produced (Figure 14D) [97].

<table>
<thead>
<tr>
<th>Metal 1</th>
<th>Metal 2</th>
<th>Morphology</th>
<th>Synthetic method</th>
<th>Reference and catalytic reactions</th>
</tr>
</thead>
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<tr>
<td>Au</td>
<td>Pd</td>
<td>Core-shell concave nanocubes</td>
<td>Seed-mediated method</td>
<td>[93]; EOR [94]</td>
</tr>
<tr>
<td>Au</td>
<td>Pd</td>
<td>Core-shell cuboctahedra</td>
<td>Seed-mediated method</td>
<td>[93]</td>
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<tr>
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<td>Pd</td>
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<td>Seed-mediated method</td>
<td>EOR [95, 93]</td>
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<tr>
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<td>Pd</td>
<td>Core-shell tetrahedra</td>
<td>Seed-mediated method</td>
<td>EOR [95] [96] [97]</td>
</tr>
<tr>
<td>Au</td>
<td>Pd</td>
<td>Core-shell trisoctahedra</td>
<td>Seed-mediated method</td>
<td>[96, 97]</td>
</tr>
<tr>
<td>Au</td>
<td>Pd</td>
<td>Core-shell octahedra</td>
<td>Co-reduction method</td>
<td>[98]</td>
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<tr>
<td>Ru</td>
<td>Pd</td>
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<td>[99]</td>
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<td>Seed-mediated method</td>
<td>[20, 100]</td>
</tr>
<tr>
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<td>Pd</td>
<td>Symmetrically branched</td>
<td>Seed-mediated method</td>
<td>[101]</td>
</tr>
<tr>
<td>Au</td>
<td>Pd</td>
<td>Core-shell concave trisoctahedra</td>
<td>Seed-mediated method</td>
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</tr>
<tr>
<td>Au</td>
<td>Pd</td>
<td>Core-shell concave hexoctahedra</td>
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<td>[97]</td>
</tr>
<tr>
<td>Ag</td>
<td>Pd</td>
<td>Eccentric nanobars</td>
<td>Seed-mediated method</td>
<td>[20, 100]</td>
</tr>
</tbody>
</table>
In a systematic study of morphological evolution of nanocrystals, Huang and coworkers prepared concave Au@Pd core-shell nanocubes bounded by high-index \{410\}, \{510\}, \{610\}, \{720\}, and \{830\} facets (Figure 14E) \cite{93}. In their work, Au octahedral nanocrystals were employed as growth seeds to deposit Pd shell. Among the different shapes, including Au@Pd core-shell octahedra, truncated octahedra, cuboctahedra, truncated cubes, and concave cubes obtained by tuning the amount of Au octahedral seeds, only concave cubes exhibited high-index facets. The appearance of high-index facets was attributed to the release of lattice strain by forming a thicker coating of Pd at the corners of the cubes. In another work, Zhang and Xu also synthesized Au@Pd concave nanocubes via seed-mediated method using truncated Au octahedra as seeds \cite{94}. They found that, due to the presence of high-index facets, the concave nanocubes possessed much enhanced electrocatalytic performance for EOR compared to Pd/C, Pd nanoparticles, and Pd black \cite{94}. In addition to nanocrystals with concave shape profile, Au@Pd core shells with convex polyhedral shape have also been investigated. For instance, Han et al. synthesized convex Au@Pd core-shell polyhedra via a combined co-reduction and seed-mediated method (Figure 14F) \cite{72}. 

![Figure 14](image-url) (A–B) Au-Pd core-shell tetrahexahedra, and concave octahedra. Adapted with permission from Ref. \cite{95}. Copyright 2010 American Chemical Society. (C) Au-Pd core-shell tetrahexahedra. Adapted with permission from Ref. \cite{96}. Copyright 2011 American Chemical Society. (D) Au-Pd core-shell trisoctahedra. Adapted with permission from Ref. \cite{97}. Copyright 2010 American Chemical Society. (E) Au-Pd core-shell concave nanocubes. Adapted with permission from Ref. \cite{93}. Copyright 2011 American Chemical Society. (F) Au-Pd core-shell convex polyhedra. Adapted with permission from Ref. \cite{72}. Copyright 2012 Wiley.
In their synthesis, Au octahedra were used as growth seeds. When Au and Pd and precursors were reduced with ascorbic acid simultaneously, the deposition of the two metals led to the formation of Au@Pd core shells with convex hexoctahedron-like structure bounded with high-index \{12 5 3\} facets. This convex polyhedral core-shell nanostructure exhibited much enhanced electrocatalytic activity on EOR relative to the hexoctahedral, cubic, and octahedral Au@Pd nanocrystals. The enhanced activity was attributed to both the presence of the large number of catalytically active sites such as atomic steps and kinds on the nanocrystal surface, as well as the modified electronic structure of Pd shell caused by the Au core.

### 4 Conclusion and outlook

In this review, we have discussed some recent developments in the synthesis of Pd- and Pt-based bimetallic nanostructures with controlled shapes, as well as their applications in electrochemical catalytic reactions such as MOR, EOR, FOR, and ORR. Our emphasis is on the different shapes including dendritic structures, alloy, or core-shell polyhedra enclosed by low- or high-index facets, nanoporous particles, and 1-D nanowires/nanorods that have been obtained via synthetic approaches such as co-reduction, seed-mediated method, galvanic replacement reaction, and template-directed method. It should be noted that this is a fast-evolving research area and a large number of bimetallic nanocatalysts of different shapes and compositions are emerging rapidly.

Despite the fast progress in the synthesis of bimetallic nanostructures as electrochemical catalysts, challenges still remain in the following directions:

1. Fundamental understanding of the growth process for bimetallic nanostructures. For monometallic nanocrystals, reasonable understanding has been gained about how various factors such as reaction kinetics, surfactants, and presence of anionic or cationic species may influence the nucleation and growth stages and the final shape of the nanocrystals. The introduction of the second metal in such syntheses complicates the growth process. In the co-reduction synthesis, the formation of atoms of the second metal will influence the nucleation and the growth of the first metal. After the formation of the nuclei, the deposition of the two metals on the surface of the seeds will compete with each other. This is also true for template-directed growth. The surface atomic distribution of the two metals will affect the binding of surfactants – so the facet-selection rules of a given surfactant established for monometallic nanocrystals may not be applicable to the bimetallic ones. All these factors need to be systematically studied in bimetallic nanocrystal systems for a better understanding of their growth process.

2. Development of general synthetic method. Owing to the lack of clear understanding of the nanocrystal growth in bimetallic systems, current syntheses of such nanostructures to give certain shapes are highly system-specific, meaning that a successful method (including the use of certain reducing agents, surfactants, and other shape-influential species) for the growth of bimetallic nanostructures for two metals is unlikely to be applied to a system of two different metals to generate the same shape. Owing to the large number of combinations of bimetallic systems, many more experiments need to be conducted to form the desired shape and optimized catalytic activity for a specific reaction. Therefore, some general methods applicable to various bimetallic systems are highly desirable.

3. Size reduction of bimetallic nanostructures with well-defined shapes. Current synthetic approaches to form bimetallic nanocrystals with controlled shapes generally give relative large particle size. This is because the exposed facets need to be well developed to define the shape of the nanocrystals. Large particle size will reduce the utilization of the catalysts. Therefore, reducing the size of bimetallic nanoparticles while maintaining their desired facets, especially those catalytically more actives ones, should be pursued.

4. Improvement on the stability. As the formation of bimetallic nanostructures involves the use of a less stable metal, leaching over time of the active metal becomes a critical issue associated with bimetallic catalysts under either acidic or basic environment that is typical for electrochemical reactions. Manipulating the composition and structure of the catalysts to avoid rapid leaching and to improve long-term stability is an important task for the development of such catalysts with meaningful applications.

5. Establishment of the relationship between the catalytic activities of bulk metal surface and nanocrystals. This is important for both monometallic and bimetallic nanocrystals. Some fundamental studies of catalytic activity for reactions such as ORR and MOR have been conducted on single crystal surface of bulk metals. Often, the activity obtained on bulk metal surface cannot be translated to that...
on nanocrystals with the same facets due to reasons such as the presence of surface adsorbed species on nanocrystals, different lattice strains of bulk and nanocrystal metals, change in the atomic distribution of nanocrystals, etc. Experimental techniques that may closely relate the activities on bulk metal and nanocrystal surfaces should be developed.

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