A Comprehensive Review on Controlling Surface Composition of Pt-Based Bimetallic Electrocatalysts

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Abstract
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A comprehensive review on controlling surface composition of Pt-based bimetallic electrocatalysts

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With increasing energy demands worldwide, significant efforts have been made to develop superior electrocatalysts for efficient energy conversation systems. Among all the electrocatalysts exploited, Pt-based bimetallic nanomaterials stand out by virtue of their high catalytic activity and relatively low cost due to the introduction of non-precious metal component. It should be noted that electrocatalytic reactions only take place on the surface of catalysts, so investigations of the surface composition of Pt-based bimetallic nanomaterials are very necessary for practical electrocatalysts. In this review, we summarized recent studies on controlling the surface composition of Pt-based bimetallic catalysts for the oxygen reduction reaction (ORR), formic acid electro-oxidation, and ethanol electro-oxidation. The controlling strategies, including the chemical method and the electrochemical method, are discussed. The impacts of surface composition compositions on the electrocatalytic
performance are also discussed. Finally, the challenges and future directions for controlling the surface composition of Pt-based bimetallic nanomaterials are addressed.

1. Introduction
The energy demand is expected to rise 36% over the immediate need by 2030.[1] With the severe environment pollution and shortage of fossil fuels, clean and efficient energy sources are strongly appealed by researchers. Fuel cell is a green energy device with converting chemical energy into electrical energy, which has attributed increasing attention.[2-4] In particular, proton exchange membrane fuel cells (PEMFCs), direct formic acid fuel cells (DFAFCs) and direct ethanol fuel cells (DEFCs) have been regarded as a series of promising power devices, which show high efficiency and high energy density.[5-9] Although the fuels are different, all of them contain an anode (fuel electro-oxidation), a cathode (oxygen reduction) and an electrolyte;[10,11] the rates of these oxidation or reduction reactions are strongly depended on electrocatalysts, which determine the energy conversion efficiency.[12-15] Among these metal electrocatalysts, platinum (Pt) exhibits the best activity for formic acid electro-oxidation, ethanol electro-oxidation and oxygen reduction. However, pure Pt electrocatalyst faces several severe shortages, which limit its wide application in fuel cells. First, for formic acid and ethanol electro-oxidation on pure Pt, the poisoning phenomenon (poison intermediates adsorption) usually happens on the surface of Pt, which will significantly decrease its electrocatalytic performance.[16-20] Second, for cathodic reaction, the oxygen reduction on pure Pt is sluggish.[21-24] Third, Pt is noble metal, which is limited reserve in nature. Therefore, how to reduce the Pt content and at the same time maintain its electrochemical performance are critical to achieve the commercialization of fuel cell.
Bimetallic nanomaterials play an essential role in electrochemical energy conversion and storage, such as in fuel cells and metal-air batteries.\textsuperscript{[25-27]} Unlike their monometallic counterparts, bimetallic nanomaterials ordinarily present better performance beneficial from synergistic effects, which means that the electrochemical performance of the whole will be superior than the sum of its parts.\textsuperscript{[28-30]} In the case of the noble metals (especially Pt), their high cost and scarcity are obstructing the commercial viability of fuel cells.\textsuperscript{[31-34]} Reducing the Pt loading without compromising its performance is the target of electrocatalytic investigations.\textsuperscript{[35-37]} The typical approach is to incorporate with another metal, which could obtain better performance with much prolonged duration than the traditional commercial Pt/C. There are a great quantity of works on Pt-based bimetallic electrocatalysts, such as alloying Pt with 3d-transition metals, including Fe,\textsuperscript{[38, 39]} Co,\textsuperscript{[40-42]} Ni,\textsuperscript{[43, 44]} and Cu\textsuperscript{[45, 46]}. PtM (M = Fe, Co, Ni, etc.) bimetallic nanomaterials have been demonstrated to be promising electrocatalysts, which strategic enhancement and development of the performance of commercial Pt/C electrocatalyst; and fundamental researches have shown that the enhanced catalytic activity originates from the modified electronic structures and geometric structures of Pt in these alloy catalysts.\textsuperscript{[47-49]}

It is a remarkable fact that these electrocatalytic reactions merely occur on the surface of the electrocatalysts.\textsuperscript{[28, 50]} Thus, the surface constituents of electrocatalysts determine the adsorption/desorption behaviors of the reactants and intermediates during the electrochemical reaction. Therefore, the catalytic reactions mechanisms and efficiencies strongly rely on the surface composition of these catalysts.\textsuperscript{[51-54]} Based on this view, the goal, reducing the Pt loading without a loss of catalytic performance, is able to be achieved by tuning the compositional segregation of the bimetallic electrocatalysts surface. Some studies have been carried out to control the surface composition of bimetallic nanomaterials, involving the formation of the Pt-skin
structure and Pt-rich surface.\textsuperscript{[55-58]} There are four forces that could drive segregation at the surface of bimetallic nanomaterials: (1) two different atoms (A and B) that are mismatched in atomic size will cause strain energy between A and B atoms. Because of the lattice mismatch, the larger one tends to occupy the surface sites; (2) the element with lower surface energy migrates to the surface of bimetallic nanomaterials; (3) the size and temperature also affect the surface composition. Smaller dimensions and higher temperature could increase the atomic diffusion distance and expedite the diffusion rate, so as to finally affect the alloying process; (4) Adsorbent (such as CO \textsuperscript{[59, 60]}) that could bind strongly to one element will pull the element out to the surface. These factors enable the feasibility of controlling the surface composition of bimetallic nanomaterials. Nevertheless, it is not easy to tune the surface composition of bimetallic nanomaterials; in actually, these factors all contribute to the surface composition of nanomaterials. This means the surface composition of bimetallic nanomaterials could be modified by the nanomaterials size, reaction temperature and the adsorbent. For example, the size of Au-Ag nanomaterials could induce its surface segregation phenomena.\textsuperscript{[61]} Meanwhile, for PtNi bimetallic nanomaterials, different atmospheres and annealing temperatures will result in various of surface composition.\textsuperscript{[62]} There are only a limited number of experimental works in the field of PtM bimetallic nanomaterials, however, which are far from sufficient to understand the fundamental principles controlling the surface composition in PtM bimetallic nanomaterials.\textsuperscript{[28]}

With the purpose to fill in this gap, in this review, we systematical and comprehensive summarize the widely used methods to control the surface composition of PtM bimetallic nanomaterials and their electrocatalytic reactions applications. Controlling the surface composition is a critical issue for PtM bimetallic nanomaterials, which plays an important role in their electrochemical properties. The approaches to tune the surface composition of PtM bimetallic nanomaterials are discussed, and how these PtM
bimetallic nanomaterials influence electrocatalytic reactions, such as the oxygen reduction reaction (ORR), and formic acid and ethanol electro-oxidation reaction, are discussed in details. Significant attentions are also paid on our current understanding on the synthesis mechanism and their electrocatalytic application, to explore their fundamental design principles. We hold the view that controlling the surface composition is a challenge but also an opportunity for the advancement of PtM bimetallic nanomaterials.

2. Controlling the surface composition of PtM bimetallics

2.1. Chemical method

The chemical method is an effective strategy to synthesize specific surface composition of PtM bimetallics, which is easy to scale up.\(^{[63, 64]}\) Currently, the most commonly used chemical methods to control the surface composition include the controlled thermal treatment method (CTTM), the wet chemical method \textbf{and the combination of these two methods}. CTTM is a simple method to tune the surface composition of bimetallic nanomaterials and is suitable for large-scale production.\(^{[65]}\) By controlling the H\(_2\) reduction temperature and time, core–shell structured Pt–Pt\(_3\)Co nanoparticles with 2–3 atomic-layer Pt shells (Pt\(_3\)Co@Pt) could be obtained,\(^{[66]}\) even Pt-skin on Pt\(_3\)Co (or Pt\(_3\)Ni) bimetallic materials.\(^{[67, 68]}\) \textbf{Figure 1a} is a schematic illustration of the Pt-skin of Pt\(_3\)Ni bimetallic nanomaterials synthesized using CTTM.\(^{[68]}\) The precursor mixtures (containing Pt precursor and Ni precursor) usually are dispersed into solvents, and then these mixtures are ultrasonicated before the solvents evaporate. Finally, by controlling the thermal treatment, Pt-skin on well-dispersed Pt\(_3\)Ni bimetallic nanoparticles can be obtained. The reason why CTTM could tune the surface composition is that there is a general trend in the surface segregation
phenomena in the bimetallic nanomaterials.\textsuperscript{[69-71]} Pt has negative segregation energy, and Ni (or Co) has positive segregation energy; hence, Pt tends toward surface segregation.\textsuperscript{[68, 72-74]} Nevertheless, without enough energy, Pt cannot segregate on the surface of the bimetallic, and the surface compositions tend to be in the form of PtM alloys.\textsuperscript{[68]} The common strategy is that, when the precursor mixture is reduced, high temperature is applied into the reaction system, which will offer enough energy to form a Pt-skin or even a 2-3 atomic-layer Pt-shell (Figure 1b-1g). Moreover, the thermal treatments also provide a powerful strategy to synthesis of the nanoparticles coated with carbon shell. As shown in Figure 1h,\textsuperscript{[75]} when disordered PtFe nanoparticles are synthesized, dopamine hydrochloride solution is applied to coated polydopamine. Finally these mixtures are treated by thermal annealing, the N-doped carbon-coated PtFe nanoparticles obtained. Meanwhile, this high temperature also could help disordered PtFe nanoparticles to form order phase.

CTTM is a powerful method to control the surface composition, but when faced with some nanomaterials with specific shapes, it may be quite helpless, because the high temperature treatment could ruin the specific shape.\textsuperscript{[76]} The wet chemical method is then a good choice, which can effectively exploit the structural evolution of bimetallic nanomaterials.\textsuperscript{[77]} It is well known that the experimental conditions in the synthesis process, such as the growth time, solution temperature, pH, and precursor ratio, could all significantly affect the degree of alloying and the composition of the bimetallic nanomaterials.\textsuperscript{[29, 78-81]} Thanks to the abundant literature from many research groups around the world, there is an extensive collection of work on the synthesis of bimetallic nanomaterials with Pt surface segregation. For example, Niu et al.\textsuperscript{[82]} reported the evolution of phase segregation from Ni-rich shells to Pt-rich shells by controlling the growth time, as shown in Figure 2a. The grown time is a vital factor, and by effectiveness controlling it, the surface compositions of bimetallic nanomaterials could be
tuned from Ni-rich shells to Pt-rich shells.\textsuperscript{82} Moreover, apart from the growth time, the growth temperature also has an effect on the bimetallic nanomaterials. By adjusting the reaction temperature, Pt-covered bimetallic nanomaterials could be obtained.\textsuperscript{83} In addition, the reducing agents also play an influence on the surface composition of nanomaterials. A good example is that during the preparation of PtPb nanoparticles progress, when ascorbic acid is applied as reducing agent to replace phenol, PtPb nanoplate with ~1.0 nm Pt shell thickness could be obtained.\textsuperscript{84} Moreover, the amount of surfactant and precursors also has a significant influence on the surface composition of PtM bimetallic nanomaterials.\textsuperscript{85-87} For example, by controlling the amount of cetyltrimethylammonium chloride (CTAC) and Co(acac)\textsubscript{2}, Pt-rich facets and ordered intermetallic hierarchical Pt\textsubscript{3}Co nanowires could be obtained.\textsuperscript{40} Moreover, two steps reduction method is also a great way to control the surface composition: firstly, prepare the seed; then the containing the Pt precursor is added into the seed solution, and reduced by reducing agent.\textsuperscript{88, 89} Zhang et al. also pointed out that, by controlling the molar ratio between Pt and Pd, and the solution pH, and then using the one-step microwave heating method, Pd@Pt core-shell nanostructures could be easily obtained.\textsuperscript{90}

Despite wet chemical method merits, it also face a mainly problem to solve, that is the surface atoms are usually random. To precise tune the surface composition of nanomaterials, when PtM nanomaterials are prepared by wet chemical firstly, they could be treated at the thermal treatment. For example, Chen et al.\textsuperscript{91} used PtNi\textsubscript{3} nanopolyhedra (~20.1 nm) as starting materials. The PtNi\textsubscript{3} nanopolyhedra were transformed by storing them in hexane under ambient conditions for 2 weeks. Pt\textsubscript{3}Ni nanoframes were then obtained; because the PtNi\textsubscript{3} nanopolyhedra were eroded from the interior to the surface to form hollow structures. These hollow Pt\textsubscript{3}Ni nanoframes were thermal treated and then Pt-skins obtained, as shown in Figure 2b. Meanwhile,
the atmosphere of the thermal treatment is significantly impact the surface composition of the nanomaterials. When Pt-Ni nanowires, prepared by wet chemical method, are annealed in the H₂/N₂ (5 : 95), the Pt-Ni nanowires have minimum phase and structure changes. By contrast, when the thermal annealing is in air, the high density of NiOₓ/Pt₃Ni interfaces could be obtained. Chemical dealloying, combing chemical method with thermal treatments, is an powerful strategy to acquire a Pt-rich surface, even a Pt-skin surface on bimetallic nanomaterials. By selecting an appropriate PtM bimetallic as starting precursor and then dissolving the surface of the non-Pt component in an acid medium, a Pt-skeleton on the PtM was obtained. Finally, these Pt-skeletons on PtM bimetals were annealed at 400 °C, forming a multilayered Pt-skin on the PtM bimetallic, as shown in Figure 2c. To investigate the chemical dealloying mechanism, Lai et al. applied extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) observations to study the dealloying process of Pt-Co. They found that the Co-Co bonding dissolved gradually during the chemical dealloying procedure. Furthermore, the Pt-skin feature was damaged if the chemical dealloying lasted too long. This is because the electrolyte could go through the Pt-skin surface into the core and dissolve the Co. Interestingly, by selectively dissolving non-Pt metal in the electrochemical dealloying process, we could obtain porous/hollow bimetallic nanomaterials. For example, Wang et al. immersed Cu₃Pt/C ordered intermetallic nanomaterials in 1 M HNO₃ for 2 days under continuous magnetic stirring, and a porous Cu₃Pt/C structure was obtained.

2.2 Electrochemical method

Compared with the chemical method using common reducing agents and surfactants, the electrochemical method represents a simple and versatile route to the preparation of
Pt surface segregation on bimetallic nanomaterials. Galvanic replacement, driven by the difference in electrochemical potentials between a sacrificial metal and another metal ion, usually is applied for the synthesis of Pt monolayers. For example, a series of Pt monolayers on bimetallic nanomaterials was acquired by the galvanic displacement of a Cu monolayer by Pt, as shown in Figure 3a. It is an excellent way to reduce noble metal content by using the nonnoble metals as cores; in additional, the nonnoble metals cores would also affect the electronic structure Pt monolayer, maintaining a high activity.

Electrochemical modification is also usually applied to the synthesis of nanostructures with a different element decorating Pt surfaces. The surface modification is also known as “electrocatalysis by adatoms”, which modify Pt surfaces with adsorbed second atoms. For example, Bi could decorate tetrahexahedral Pt nanocrystals by means of voltammetric cycling in a solution containing Bi$^{3+}$. By controlling the number of cycles, different Bi coverage of tetrahexahedral Pt could be obtained, and the Bi coverage could be evaluated by the blockage of hydrogen adsorption charge:

$$\theta_{\text{Bi}} = 1 - \theta_{\text{H}}$$

(1)

When this strategy is applied to the PtM bimetallic nanomaterials as electrocatalysts, we could obtain electrocatalysts with various surface compositions from Pt-rich to Pt-lacking.

It is notably that in acid solution, some nonnoble metal could dissolve from PtM bimetallic electrocatalysts, which lead to that the morphology and surface structure of PtM will change after electrochemical scanning. Cui et al. have demonstrated that for Pt$_x$Ni$_{1-x}$ octahedra, under the electrochemical condition, Ni will selectively leached and favours the formation of Pt-rich structure, as shown in Figure 3b. The nonnoble metal dissolution will reshape the electrocatalyst morphology, and it provides us with a new strategy to synthesize different surface compositions of bimetallic nanomaterials,
that is electrochemical dealloying method. In general, the PtM bimetallics are electrochemically dealloyed by potential cycling between 0.06 and 1.0 V (vs. reversible hydrogen electrode (RHE)) for a number of cycles in acid based solution.\textsuperscript{[111]} The ratio of Pt to M in the starting precursor and the size of PtM nanostructures have a significant effect on the final bimetallic structures. Gan et al.\textsuperscript{[111]} used an electrochemical dealloying method to dissolve Ni in PtNi, PtNi\textsubscript{3}, and PtNi\textsubscript{5}; and they found that there is a trend towards enrichment of Ni near the surface in spherical particles of dealloyed (D)-PtNi\textsubscript{3} and D-PtNi\textsubscript{5} bimetallics, resulting in the formation of Ni-enriched inner shells; nevertheless, the D-PtNi presents a core–shell structure, as shown in Figure 4a. The electrochemical dealloying of non-noble metals from PtM bimetallics could alter the surface electronic structure of Pt shells, and finally affect their activity.\textsuperscript{[101]}

Oezaslan et al\textsuperscript{[112]} studied the processes occurring at the atomic level during the electrochemical dealloying of Pt-Co and Pt-Cu precursor bimetallic nanomaterials, and they found that there are three distinctly different size-dependent types of morphology, as shown in Figure 4b. Therefore, the surface composition of bimetallic nanomaterials after electrochemical dealloying will be slightly dependent on size: for small nanoparticles, they will form core-shell nanoparticles;\textsuperscript{[95]} in the case of larger particles, porous multiple core-shell particles will emerge. These numerous voids could increase the electrocatalysts surface area, and result in higher activity.\textsuperscript{[95]}

3. Application of Pt surface segregation of PtM bimetallic nanomaterials

3.1 ORR

Fuel cell is a promising green energy technology; nevertheless, the scarcity and high cost of Pt catalysts hinder its commercialization. In addition, the sluggish kinetics of cathode reaction (ORR) is also one of main challenges for commercial viability of fuel
Basis on these factors, it is of significant interest to develop more active electrocatalysts, and meanwhile get a deeply understand of the ORR mechanism. In general, the ORR follows two types of reaction mechanism: direct four electron reduction or two electron reduction. In an acid medium, for the four-electron reduction pathway, O$_2$ is reduced and combined with H$^+$ to form H$_2$O; the overall reaction is shown in Eq. (2):

$$O_2 + 4H^+ + 4e^- = 2H_2O$$

The two electron reduction mechanism is generally disfavoured in practical operation for the ORR as involving the intermediate H$_2$O$_2$:

$$O_2 + 2H^+ + 2e^- = 2H_2O_2$$

$$H_2O_2 + 2H^+ + 2e^- = 2H_2O$$

A well accepted reaction mechanism, which intermediate H$_2$O$_2$ could be stable intermediate species, was first presented by Wroblowa et al.$^{[117]}$ as shown in Figure 5a. Density functional theory (DFT) results indicate that this direct four electron reduction also occurs through different possible intermediates. As shown in Figure 5b, there are three main mechanisms in an acidic medium.$^{[118]}$ For mechanism 1, firstly, O$_2$ adsorbs on the electrocatalyst surface, and then, by breaking the O-O bonds, surface-absorbed hydroxyl groups could be obtained. This pathway is favoured for proton exchange membrane fuel cells (PEMFCs) above the other two mechanisms. Based on this mechanism, it is extremely important to tune the Pt surface composition of bimetallic nanomaterials for the ORR. This is because the substrate metals are promising for modifying the electronic structures of the Pt surface, and will significantly affect the performance of these electrocatalysts towards the ORR.$^{[119]}$ A good example is a report of Stamenkovic et al.,$^{[120-122]}$ where they controlled the surface composition of Pt$_3$M bimetallic nanomaterials (M = Co, Ni, and Fe) to achieve: 1) a random surface, which was made up of Pt and M distributed randomly; 2) a Pt-skeleton surface, which
consisted of 75% Pt and 25% M; and 3) a Pt-skin surface, which was composed of 100% Pt. The Pt-skin structure of Pt₃Co, with Co enrichment in the second layer, exhibited the best activity among the three Pt-skin Pt₃M bimetallics in 0.1 M HClO₄, which was 4 times as high as for pure Pt. The reason of the enhancement for the Pt-skin structure is that OHₐd has a more positive potential on the Pt-skin surface; and this electronic structure is induced by the second outermost M element. In addition, they also provided evidence that the enhancement order is Pt-skin > Pt-skeleton > Pt random.

It is well known that alloying could alter the electronic properties of Pt; in turn, it can change the adsorption properties of Pt and thus enhance the performance of bimetallic nanomaterials. Meanwhile, the non-noble-metal alloy elements also affect the activity of the bimetallic nanomaterials. For example, the activity of Pt₃Co, experimentally measured, is better than those of Pt₃Ni, Pt₃Fe, and Pt₃Ti, although the DFT results indicate that the activity of Pt₃Ni is better than that of Pt₃Co, shown in Figure 6a. The structure of atoms on the surface also plays an important role in the ORR electrocatalyst performance. To identify how the different crystal facets of Pt₃M will affect the ORR performance, single-crystal electrodes with Pt-skin of Pt₃Ni (111), Pt₃Ni (100), and Pt₃Ni (110) were introduced into this reaction. The three outermost layers of these three catalysts are identified as follows: the innermost is Pt-rich, with 87% Pt; the second outermost is Ni-rich, with a Ni content of 52%; the outer layer is Pt-skin, with 100% Pt. The ORR activity of the three different possible facets is as follows: Pt-skin of Pt₃Ni (100) < Pt-skin of Pt₃Ni (110) < Pt-skin of Pt₃Ni (111). Meanwhile, the ORR activity of the Pt-skin of Pt₃Ni (111) is 10-fold more active than the current state-of-the-art Pt (111) and commercial Pt/C catalyst, as shown in Figure 6b.

Furthermore, Huang et al. surface-doped the Pt-skin surface of Pt₃Ni octahedral particles with transition metals (M-Pt₃Ni/C, M= V, Cr, Mn, Fe, Co, Mo, Re, and W) to
investigate their ORR performance.\textsuperscript{128} Although when the oxygen binding energy of Pt\textsubscript{3}Ni (111) is about 0.2 eV less than that of Pt (111), its ORR activity could reach maximize.\textsuperscript{126} DFT results indicated that the oxygen binding energies of the sites near the edge are too strongly, and the sites near the facets are too weakly; surprisingly, Mo atoms tend to occupy the subsurface positions near the edges, which will modify the oxygen binding energies closer to the 0.2 eV, and enhances the stability and activity of Pt\textsubscript{3}Ni/C, as shown in Figure 6c. Mo-Pt\textsubscript{3}Ni/C showed the best ORR performance, with a mass activity of 6.98 A/mg\textsubscript{Pt}, which is 73 times higher than that of commercial Pt/C (0.096 A/mg\textsubscript{Pt}).

3.2 Formic acid electro-oxidation

The H\textsubscript{2}-polymer electrolyte membrane fuel cells restrict by the potential dangers in the transportation and use of H\textsubscript{2}, and low energy density.\textsuperscript{129-131} The direct formic acid fuel cell (DFAFC) has drawn much attention due to the fact that formic acid processes several significant advantages, such as lower crossover through Nafion\textsuperscript{®} membranes and less toxicity.\textsuperscript{132-136} At room temperature, formic acid is liquid, which is easy transport; besides, it is environment friendly, which is approved as a food additive by the US Food and Drug Administration.\textsuperscript{137, 138} It is well known that formic acid electro-oxidation takes place on Pt-based electrocatalysts via the dual-pathway reaction mechanism. Two reaction mechanisms are possible\textsuperscript{139, 140}: one is the direct pathway mechanism:

\[
\text{HCOOH} = \text{CO}_2 + 2\text{H}^+ + 2e^- \quad (5)
\]

And another is the dual pathway mechanism:

\[
\text{HCOOH} = \text{CO}_{\text{ad}} + \text{H}_2\text{O} = \text{CO}_2 + 2\text{H}^+ + 2e^- \quad (6)
\]

It is widely accepted that for pure Pt, formic acid electro-oxidation proceeds through the dual pathway, with the formation of poisoning intermediates. Studies have found that the
poisoning intermediates always form on at least two or more contiguous Pt surface sites, which blocks the direct electro-oxidation of HCOOH.\cite{141,142} Therefore, exploring highly active catalysts that are capable of direct electro-oxidation of HCOOH is heavily dependent on tuning the surface composition of bimetallic nanomaterials.

Abruña’s group demonstrated that Pt/Bi$_{\text{ads}}$ and PtBi intermetallics could enhance the catalytic activity of Pt electrodes towards formic acid oxidation.\cite{143,144} Feliu’s group also demonstrated that the Bi$_{\text{ads}}$ could yield the so-called “third body effect”, and with increasing Bi coverage, HCOOH would be electro-oxidized to CO$_2$ without the poisoning intermediates.\cite{145,146} Li et al.\cite{147} introduced a reliable synthetic method that enables PtBi intermetallic to be supported in ordered mesoporous carbon voids, and realised excellent catalytic performance for HCOOH electro-oxidation. Furthermore, Zhang et al.\cite{65} explored how the different surface composition from Bi-rich to PtBi intermetallic surface of PtBi bimetallic nanomaterials could affect the formic acid electro-oxidation. PtBi intermetallic with a Bi-rich surface showed higher mass activity and more stability than unmodified PtBi intermetallic and pure Pt/C towards HCOOH electro-oxidation, and in situ Fourier transform infrared spectroscopy (FTIRs) indicated that both PtBi intermetallic via direct electro-oxidation, as shown in Figure 7a. DFT results offered a detailed mechanism of Bi:\cite{148}: for PtBi intermetallic, HCOOH is first physisorbed on Bi, and then deprotonated and chemisorbed in the form of HCOO$^-$, without barrier; as a consequence, these two processes could happen simultaneously. Moreover, the C-H bond of HCOO$^-$ favourably depends on configuration of Bi, and then is cleaved on the neighbour Pt sites, forming CO$_2$, as shown in Figure 7b.

PtPd,\cite{149-151} PtPb,\cite{152,153} PtCu,\cite{154,155} PtRu,\cite{156,157} PtAu,\cite{158,159} and PtFe\cite{160,161} ect bimetallic nanomaterials also have been proved to be excellent catalysts for HCOOH electro-oxidation. When tune the surface composition of PtPb (or PtPd) bimetallic nanomaterials also could
obtain different activity towards HCOOH electro-oxidation. For example, when the atomic ratio of Pd : Pt is to 6: 1(Pd₆Pt₁), it would achieve highest mass activity in HCOOH electro-oxidation among Pd₄Pt₁, Pd₂Pt₁, Pd₁Pt₁ and Pt/C.[153] Tuning the surface composition of bimetallic nanomaterials could also yield an amazing effect. A good example is that, by tuning the surface of Pt₃Ni from Pt-skin to Ni-rich, the mass activity in the ORR is decreased but increased in that of the HCOOH electro-oxidation.[68] In addition, in situ FTIR spectra demonstrated the electro-oxidation of HCOOH on a Ni-rich surface of Pt₃Ni takes place via the direct pathway, without forming poisoning intermediates; however, the Pt-skin structure of Pt₃Ni goes through the dual pathway mechanism, formation of poisoning intermediates, as shown in Figure 8.[68]

3.3 Ethanol electro-oxidation

Direct ethanol fuel cells (DEFCs) represent one of the most promising renewable energy applications, which have many obvious advantages, such as low toxicity, high energy density, and inexhaustible availability from biomass, when compared with the proton exchange membrane fuel cell.[162-164] The mechanism of ethanol electro-oxidation on Pt-based catalysts has been well studied,[165, 166] and it is established that the CH₃CH₂OH electro-oxidation involves two parallel oxidation pathways: one is the complete oxidation pathway (C1 pathway) and another is the partial oxidation pathway (C2 pathway).[167-170]. The detail of the mechanism is shown in Figure 9a: the C1 pathway with the transfer of 12e⁻ is accompanied by breaking the C-C bond, resulting in the formation of CO₂ or CO₃²⁻ or HCO₃⁻. For the C2 pathway, ethanol is incompletely electro-oxidized to acetate, with the transfer of 4e⁻. Although DEFCs have great potential, CH₃CH₂OH electro-oxidation on most electrocatalysts proceeds through the C2 pathway, leading to the formation of acetate as the final oxidation product;[171, 172] according to previous reports, at room temperature, the percentage of electrocatalysts for CH₃CH₂OH oxidation that work through the C1 pathway is only 1%, since
breaking the C-C bond is kinetically hindered.\cite{167, 170, 173} It is very eager to explore the high activity electrocatalysts, going through the C1 pathway.

The surface composition of Pt based electrocatalysts will have a great influence on its capability to split C-C bonds. For example, when Pt and Rh are introduced onto a SnO\(_2\) surface, SnO\(_2\) could strongly adsorb H\(_2\)O and interact with Pt and Rh to form M-OH, making it highly active for CH\(_3\)CH\(_2\)OH oxidation.\cite{174} Meanwhile, Rh atoms could form bonding to ethanol and intermediates, which will favour the C-C bond splitting. In a word, the synergistic reactions exist in such multicomponent systems, which could help improve the performance of these catalysts.\cite{175} To evaluate the function of Rh, cubic PtRh with different atomic ratios of Pt to Rh were studied by Rao et al.\cite{176} They demonstrated that the CO adsorption ability on Rh is strong, and Rh atoms in PtRh bimetallic nanomaterials could promote the breaking of the C-C bond of CH\(_3\)CH\(_2\)OH, and Pt\(_1\)Rh\(_1\) showed higher activity and better performance towards the splitting of C-C bonds to complete CH\(_3\)CH\(_2\)OH oxidization into CO\(_2\) than other ratios of Pt to Rh, as shown in Figure 9b.

Nevertheless, the production of Rh is extremely low, even lower than that of Pt. Rational design of electrocatalysts, which can reduce cost and simultaneously allow them to work via the C1 pathway, is a very profound objective for the ethanol oxidation reaction (EOR). It is widely believed that PtSn bimetallic catalysts are active towards CH\(_3\)CH\(_2\)OH electro-oxidation, providing OH\(_{\text{ads}}\) to remove CO\(_{\text{ads}}\) and CH\(_{\text{x,ads}}\), but inactive towards breaking the C-C bond of CH\(_3\)CH\(_2\)OH to form CO\(_2\).\cite{177, 178} Nevertheless, Du et al.\cite{179} found that, by controlling the surface PtSn to create Pt\(_{46}\)-(SnO\(_2\))\(_{54}\) core–shell particles, CH\(_3\)CH\(_2\)OH could be electro-oxidized into CO\(_2\), and the rate of CO\(_2\) generation is 4.1 times that of commercial Pt/C, as shown in Figure 9c.

PtPd\cite{180-182}, PtAu\cite{183, 184}, and PtW\cite{185} bimetallic nanomaterials also were investigated for CH\(_3\)CH\(_2\)OH electro-oxidation. Nevertheless, studies on controlling the surface composition of
these bimetallic electrocatalysts to improve CH$_3$CH$_2$OH electro-oxidation are rare. It is a significant chance but challenge to explore the mechanisms of the surface composition of a bimetallic on ethanol electro-oxidation. In addition, not all Pt-rich surfaces of Pt-based bimetallics are able to assist splitting the C-C bond of CH$_3$CH$_2$OH. For example, although Pt$_3$Co with a Pt-skin structure could improve the activity towards CH$_3$CH$_2$OH electro-oxidation, *in-situ* FTIR and DFT results demonstrated that this Pt-skin structure mainly causes the reaction to go through C2 pathway: it promotes incomplete oxidation of CH$_3$CH$_2$OH over breaking the C-C bond, leading to higher CH$_3$COOH production than CO$_2$ generation.$^{[67]}$ The core-shell bimetallic nanomaterials have drawn great deal of attention due to the fact that it could enhance their electrocatalytic activity resulting from the electronic effect and geometric effects.$^{[186-188]}$ For example, the Au-Pt core-shell nanowires, with various Pt shell thickness, have been introduced into ethanol electro-oxidation to improve Pt utilization.$^{[189]}$ It demonstrated that the highest ratio of Au : Pt as 2.6 : 1.0 (Au$_{2.6}$Pt$_{1.0}$) presented the best activity among these Au$_{1.8}$Pt$_{1.0}$, Au$_{1.0}$Pt$_{1.0}$, and Pt/C. The enhancement of ethanol electro-oxidation of these Au-Pt core-shell nanowires could be attributed to the synergistic effect from the Au core, which also processed a better activity towards CO electro-oxidation. Further, Song et al.$^{[190]}$ demonstrated that Au-Pt core-shell bimetallic nanomaterials with thicker Au cores showed better activity than that of thin Au cores towards ethanol electro-oxidation in alkaline medium.

4. Conclusions and prospects

In this review, we have focused on recent progress made in controlling the surface composition of Pt-based bimetallic nanomaterials as electrocatalysts for the ORR, formic acid electro-oxidation, and ethanol electro-oxidation. The key concept of these reports is to achieve the goal of high activity and low Pt content via the synthesis of
nanoparticles with Pt surface segregation; another objective is to deepen understanding on electro-catalytic mechanisms of these PtM nanomaterials. On the basis of these results, we can draw the following conclusions:

(1) There are two tactics to tune the surface composition of bimetallic nanomaterials: the chemical method and the electrochemical method. The chemical method is easy to realize large-scale production; and the electrochemical method can accurately control the reactive potentials.

(2) The surface composition of bimetallic electrocatalysts has great effects on their performance. For the ORR, Pt-rich or Pt-skin PtM bimetallics could yield better activity and stability. In contrast, this structure may be unsuited for formic acid and ethanol electro-oxidation, because they would go through the dual pathway or incomplete oxidation mechanism on Pt-rich or Pt-skin structures.

On the other hand, it is great potential to develop various strategies for controlling the surface composition of PtM bimetallic nanomaterials. Herein, we spotlight some insights into the current challenges and future directions.

1. The controlled synthesis of PtM bimetallic nanomaterials with specific surface compositions and structures will be a very significant future direction. Both the chemical method and electrochemical method provide us with feasible strategies to tune the surface composition of PtM bimetallics, but the synthesis mechanisms remain unclear. The process of many reactions is controlled by both kinetic and thermodynamic effects; and our understanding of them is still at a nascent stage; because it is hard to measure the kinetic and thermodynamic parameters in practical synthesis. Surprisingly, in-situ TEM offers us an effective technique to observe the synthesis process for nanomaterials. Based on the in-situ instrument, we could obtain an in-depth understanding of the synthesis mechanism, leading to rational design of specific surface compositions.
2. A bimetallic electrocatalyst is not perfect. In practical electrocatalytic reactions, a bimetallic electrocatalyst could effectively improve the activity towards the ORR, but it may be poisoned for formic acid electro-oxidation. Part of the problem is that different electrochemical reactions take place via various reaction mechanisms; thus, they require bimetallic nanomaterials with specific electronic structures. The electrocatalytic reactions only take place on the surfaces of electrocatalysts; therefore, the electronic structure of the electrocatalyst surface could determine the mechanism or pathway during the reactions. As could be expected, DFT is becoming more and more powerful in predicting what electronic structure of bimetallic nanomaterials is required for a given reaction. Future studies should also focus on including DFT as a powerful resource to design the surface composition of bimetallic nanomaterials.

3. To date, there are numerous studies on the application of PtM bimetallic nanomaterials as promising electrocatalysts, such as for the hydrogen evolution reaction (HER). We believe that rational design of the surface composition of various bimetallic nanomaterials extend their applications in different electrocatalytic reactions.

Conflicts of interest

In accordance with our policy on Conflicts of interest please ensure that a conflicts of interest statement is included in your manuscript here. Please note that this statement is required for all submitted manuscripts. If no conflicts exist, please state that “There are no conflicts to declare”.

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Acknowledgements

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References


Figure 1. a) A schematic illustration of CTTM method to prepare Pt-skin structure of Pt₃Ni/PC: The precursors H₂PtCl₆ and NiCl₂ precursors was mixed with porous graphitic carbon; then the mixture was reduced by H₂. Reproduced with permission.© 2015 Elsevier Ltd. b) Atomic-resolution ADF-STEM image of 2-3 atomic-layer Pt-shell of Pt₃Co/C after Richardson-Lucy deconvolution (the yellow arrows indicates this nanoparticles exist a Pt-rich shell). There is a smaller nanopartice overlaps the lager nanoparticles in the lower left. The unit cell with inset this project demonstrate that it along the [001]. c) The diffractogram image of this nanoparticle. d) A group of super lattice of this nanoparticle. e) the simulated image of ordered Pt₃Co along [001] axis from the ADF-STEM image in b. f) the idealized nanoparticle multislice simulated from ADF-STEM image of this nanoparticle in b. g) The idealized atomic structure of the Pt₃Co core–shell nanoparticle. The white
and blue spheres in e.g. present Pt and Co atoms, respectively. Reproduced with permission. Copyright 2015, Nature Publishing Group. h) Schematic synthesis diagram of carbon-supported and N-doped carbon-coated ordered fct-PtFe NPs.

Figure 2. a) The schematic illustration of the four representative stages, corresponding with obtained TEM images of these four samples during the evolution process from PtNi$_3$ polyhedra to Pt$_3$Ni nanoframes: first solid PtNi$_3$ polyhedra (A), then PtNi intermediate (B), and the hollow Pt$_3$Ni nanoframe (C); finally annealed Pt$_3$Ni nanoframes with Pt-skin structure (D) supported on a high surface area carbon.
b) 1–6, HAADF-STEM and EDS mapping images of the nanoparticles with various growth times of 3 min (1), 10 min (2) and 30 min (3), and their corresponding chemically corrod ed products (4–6). In the 3 min stage, the bright signal in the HAADF-STEM image indicates the Pt-rich arms. For the 10 min stage and 30 min stage, the bright signal in the HAADF-STEM image demonstrates it processes Pt-rich edges of the dodecahedron and it is constructing the nanoframe. As for the EDS mapping images, the green indicates Pt element, and the red present Ni element. It could demonstrate that Ni element is distributed in all first three types: 3 min stage, 10 min stage and 30 stage; Pt element is dispersed in the arms. The scale bar in all images is 6 nm. Reproduced with permission.\textsuperscript{[75]} Copyright 2016, Nature Publishing Group. c) The HAADF-STEM images with corresponding their theoretical simulation of PtNi/C in different evolution: (1) the representative HAADF-STEM images along the [110] axis; (2) the intensity line analysis, with background subtracted, extracted from the regions as marked in HAADF-STEM images; (3) composition line analysis (normalized from the Pt–L peaks) obtained by EDX scanning across these individual nanoparticles; (4) the overview of these nanoparticle at different evolution; and (5) the cross-sectional views of the nanoparticles, as describe by an atomistic nanoparticle simulation. The as-prepared (left) nanoparticle, then the acid treated (middle), finally the acid treated/annealed (right) of PtNi/C nanocatalysts in the figure is also organized in columns, respectively. Reproduced with permission.\textsuperscript{[81]} Copyright (2011), American Chemical Society.
Figure 3. a) a model for the synthesis of Pt monolayer catalysts on non-noble-metal – noble-metal core–shell nanoparticles. Reproduced with permission.\textsuperscript{[90]} Copyright (2005), American Chemical Society. b) a schematic illustration of these Pt\textsubscript{x}Ni\textsubscript{1−x} nanoparticles surface and morphology varies after the electrochemical activation (numeric potential cycles) and electrochemical stability tests corresponding to obtained particles. Reproduced with permission.\textsuperscript{[98]} Copyright 2016, Nature Publishing Group.
**Figure 4.** a) Structural models (bottom) and corresponding elemental line scans along the lines shown in the insets (top) of core–shell fine structures of dealloyed Pt$_x$Ni$_{1-x}$ catalysts with distinctly different compositions. Reproduced with permission.$^{[59]}$ Copyright (2012), American Chemical Society. b) Illustration of the evolution of the size-dependent morphology and composition of dealloyed Pt–Cu and Pt–Co particle electrocatalysts. Reproduced with permission.$^{[100]}$ Copyright (2012), American Chemical Society.
Figure 5. a) reaction pathways proposed for the ORR. Reproduced with permission.\textsuperscript{105} Copyright (1976), Elsevier Ltd. b) schematic illustration of free energy levels of the ORR taking place on a Pt (111) surface via three different mechanisms at 0.8 V. Reproduced with permission.\textsuperscript{106} Copyright (2013), American Chemical Society.
Figure 6. a) the electrochemical activity v.s. the d-band center related to Pt. The black colour presents the electrochemical activity expected from DFT resultes, and the red colour presents the experimental measured electrochemical activity. Reproduced with permission. Copyright (2006), WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. b) an effect of the electronic surface properties and surface morphology on the kinetics of the ORR. The comparison of Pt₃Ni (hkl) surfaces with the corresponding Pt (hkl) surfaces (the electrochemical specific activity of pure Pt is marking as a horizontal dashed gray line). The electrochemical specific activity is expressed as $i_k$ (a kinetic current density) measured at 0.9 V v.s. RHE reference electrode. The d-band center position of these Pt₃Ni (hkl) and Pt (hkl) surfaces surfaces are measured from ultraviolet photoelectron spectroscopy (UPS) spectra, which are listed in the lowest to be compared. Reproduced with permission. Copyright (2007), the American Association for the Advancement of Science. c) the electrochemical
performance of these transition metal (M) doped octahedral Pt₃Ni/C electrocatalysts corresponding with the commercial Pt/C electrocatalyst: (A) Cyclic voltammograms (CVs) of Mo-Pt₃Ni/C, Pt₃Ni/C, and Pt/C electrocatalysts carried out at room temperature in N₂-saturated 0.1 M HClO₄ media, the scanning rate of 100 mV/s. (B) the ORR performance of Mo-Pt₃Ni/C, Pt₃Ni/C, and Pt/C nanocatalysts carried out at room temperature in an O₂-saturated 0.1 M HClO₄ solution, with a rotation rate of 1600 r.p.m. and a sweep rate of 10 mV/s (C) The different kinetic current densities activity at 0.9 V for these various transition M doped Pt₃Ni/C nanocatalysts: the top is electrochemically active surface area (ECSA), the middle is specific activity, and the bottom is mass activity, which are normalized to the ECSA and the mass of Pt given, respectively. (D) the Ni₁₁₋₇₅Pt₃₉₈ NC and (E) the Mo₇₃Ni₁₁₄₃Pt₃₃₅₇ NC are the mean site occupancies of the second layer of, which are determined by the Monte Carlo simulation. The color triangle of the occupancies are shown on the right. The outer layer is shown in small spheres. (F) The binding energies for the single oxygen atom on these fcc and hcp sites in the Mo₆Ni₄₁Pt₁₇₈ NC (111), related to the lowest binding energy. Pt atom is shown in gray spheres, and oxygen sites are shown in colored spheres. (G) The transforming binding energies from the Ni₄₇Pt₁₇₈ NC is substituted by Mo atoms, formation a Mo₆Ni₄₁Pt₁₇₈ NC, corresponding to the energetically favored sites in the second layer. Reproduced with permission. [¹¹⁶] Copyright (2015), the American Association for the Advancement of Science.
Figure 7. a) CVs of catalysts in 0.1 M HClO₄, 50 mV s⁻¹: (A) Pt/C, (D) PtBi intermetallic and (G) Bi-rich surface of PtBi intermetallic; CVs of formic acid electro-oxidation on three nanocatalysts before (black) and after (red) 3600 s j-t curves at -0.05 V in 0.1 M HCOOH + 0.1 M HClO₄, 10 mV s⁻¹: (B) Pt/C, (E) PtBi intermetallic and (H) Bi-rich surface of PtBi intermetallic; in situ FTIR spectra of three nanocatalysts for formic acid electro-oxidation (C) Pt/C. (F) PtBi intermetallic. (I) Bi-rich surface of PtBi intermetallic. $E_R = -0.25$ V, and $E_S$ were changed from -0.20 to 0.90 V with a 0.1 V interval. Reproduced with permission.⁵⁹ Copyright (2015), Elsevier Ltd. b) HCOO fragment adsorbed on the Bi-Pt(111) surface (above) and final products in the oxidation of formic acid (below). Reproduced with permission.¹³⁶ Copyright (2014), American Chemical Society.
Figure 8. a–c) the model of Pt-skin of Pt₃Ni/PC, Pt₃Ni alloy and Ni-rich of Pt₃Ni/PC. d–f) in-situ FTIR spectra of three nanocatalysts for formic electro-oxidation in 0.1 M HClO₄ + 0.1 M HCOOH solution on Pt-skin of Pt₃Ni/PC, Pt₃Ni alloy and Ni-rich of Pt₃Ni/PC. $E_R = -0.25$ V, and $E_S$ were changed from $-0.20$ to $0.70$ V with a $0.1$ V interval. g) comparison of ORR
mass activities for Pt/C, Ni-rich of Pt$_3$Ni/PC, Pt$_3$Ni alloy and Pt-skin of Pt$_3$Ni/PC at 0.9 V

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a

CH$_{x,\text{ad}}$ + CO$_{\text{ad}}$ → 2CO → 2 CO$_2$ or CO$_3^{2-}$ or HCO$_3^-$

C1- pathway

-CH$_2$CHO

C2- pathway

CH$_3$CH$_2$OH → CH$_3$CHO → + OH$_{\text{ad}}$ → CH$_3$COOH

CH$_3$CHOH$^-$ → CH$_3$COO$^-$

b

(A)

\( j / \text{mA cm}^{-2} \)

E / V vs SCE

Pt$_x$/Rh$_y$/GN
Pt$_x$/Rh$_y$/GN
Pt$_x$/Rh$_y$/GN
Pt$_x$/Rh$_y$/GN
Pt$_x$/GN
Pt$_x$/GN
Commercial Pt/C
Rh/GN

(B)

\( j / \text{mA cm}^{-2} \)

t / s

Pt$_x$/Rh$_y$/GN
Pt$_x$/Rh$_y$/GN
Pt$_x$/Rh$_y$/GN
Pt$_x$/Rh$_y$/GN
Pt$_x$/GN
Pt$_x$/GN
Commercial Pt/C

(C)

CO$_2$

Pt$_x$/Rh$_y$/GN
Pt$_x$/Rh$_y$/GN
Pt$_x$/Rh$_y$/GN
Pt$_x$/Rh$_y$/GN
Pt$_x$/GN
Commercial Pt/C

(D)

CO$_2$/CH$_3$COOH

\( \text{CO}_2 / \text{CH}_3\text{COOH} \)

Pt$_x$/GN
Pt$_x$/Rh$_y$/GN
Pt$_x$/Rh$_y$/GN
Pt$_x$/Rh$_y$/GN
Pt$_x$/Rh$_y$/GN
Commercial Pt/C

(C)

CO$_2$ partial pressure (mmHg)

0.5% CO$_2$/99.5% N$_2$
1% CO$_2$/99% N$_2$
5% CO$_2$/95% N$_2$

Time (min)

0 10 20 30 40 50 60

CO$_2$ partial pressure (mmHg/m$^2$)

Pt$_x$/Sn$_y$/C intermetallic
Pt$_x$/Sn$_y$/C intermetallic
Pt$_x$/C
Pt$_x$/C-Sn$_x$O$_y$
Pt$_x$/C-Sn$_x$O$_y$
Pt$_x$/C-Sn$_x$O$_y$
Pt$_x$/C-Sn$_x$O$_y$
Pt$_x$/C-Sn$_x$O$_y$
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**Figure 9.** a) The proposed reaction mechanism for CH$_3$CH$_2$OH electro-oxidation on pure Pt catalyst. Reproduced with permission.$^{[147]}$ b) Comparison of (A) CVs and (B) $j$–$t$ carried out at 0.3 V with various atomic ratio Pt$_x$Rh$_y$/GN (GN = graphene) and Pt/C catalysts, in 0.1 M CH$_3$CH$_2$OH + 0.1 M HClO$_4$ solution at room temperature and with a sweep rate of 50 mV s$^{-1}$; (C) *in-situ* single potential alteration FTIR spectra of CH$_3$CH$_2$OH electro-oxidation for Pt$_x$Rh$_y$/GN and Pt/C catalysts, $E_R = -0.25$ V, $E_S = 0.6$ V, in 0.1 M CH$_3$CH$_2$OH + 0.1 M HClO$_4$ solution; (D) the ratio between integrated intensity CO$_2$ (complete oxidation pathway) and intensity CH$_3$COOH (partial oxidation pathway) as a function of the different potential for various electrocatalysts. Reproduced with permission.$^{[156]}$ Copyright (2014), The Royal Society of Chemistry. c) CO$_2$ microelectrode responses in various CO$_2$ gas environments (left); and ECSA-specific partial pressure of CO$_2$ ($P_{CO2}$) of Pt/Sn and Pt catalysts (right). Reproduced with permission.$^{[159]}$ Copyright (2014), American Chemical Society.