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Nanoscale

Review

Recent Advances in Noble Metal Based Composite Nanocatalysts: Colloidal Synthesis, Properties, and Catalytic Applications

Yong Xu\textsuperscript{a}*, Lei Chen\textsuperscript{a,\textdagger}, Xuchun Wang\textsuperscript{3}, Weitang Yao\textsuperscript{b,\textdagger}, Qiao Zhang\textsuperscript{a,\textdagger}

This Review article provides a progress report on the synthesis, properties and catalytic applications of noble metal based composite nanomaterials. We begin with a brief discussion on the category of various composite materials. We then present some important colloidal synthetic approaches to the composite nanostructures, in which major attention has been paid to the bimetallic nanoparticles. We also introduce some important physiochemical properties that are beneficial from the composite nanomaterials. Finally, we highlight the catalytic applications of such composite nanoparticles, and conclude with remarks on prospective future directions.

1. Introduction

Catalysis is of fundamental importance to the chemical industry. The ultimate goal of catalysis research is to understand the catalytic process at the molecular level and design catalysts with desired activity and selectivity.\textsuperscript{1} With the development of nanotechnology over the past several decades, it is widely accepted that nanoparticles tend to show better catalytic performance than their bulk counterpart because of their smaller particle size as well as the “nano-effect” originated from the small size. As a result, many synthetic methods have been developed in order to prepare nanoparticles with controllable morphologies and narrow size distribution. For example, noble metal nanoparticles (Au, Ag, Pd, Pt et al.) have received increasing interest due to their unique physiochemical properties and their potential applications in various fields, such as biomedicine,\textsuperscript{2,4} sensing,\textsuperscript{5,5} surface-enhanced Raman scattering (SERS),\textsuperscript{6,7} photothermal therapy,\textsuperscript{8,9} and especially catalysis.\textsuperscript{10-16} To date, researchers are able to synthesize noble metal nanoparticles with various shapes and controllable dimensions, including zero-dimensional,\textsuperscript{17-19} one-dimensional,\textsuperscript{20-24} two-dimensional,\textsuperscript{25-29} and three-dimensional nanoparticles,\textsuperscript{30,31} in an elegant manner. And one can tailor the properties of noble-metal nanostructures and thus improve their performance in catalysis by controlling their size, shape, composition, and interfacial interactions.\textsuperscript{13,32}

Recently, it is gradually realized that a single-component material usually does not meet all the requirements in terms of high activity, high stability, high selectivity, etc. On the other hand, more and more attention has been paid to composite nanomaterials that made of two or more components. Because the composite nanomaterials combine the functions of individual component and can overcome the limitation of single component in catalytic application.\textsuperscript{33,34} Among various composite catalysts, bimetallic catalysts have gained much attention and have been widely used in many applications.\textsuperscript{35} For instance, bimetallic catalysts have been widely used for the oxidation, hydrogenation, hydrogenolysis and reforming reactions.\textsuperscript{35} Recently, the applications of composite catalysts have been extended to biomass chemical industry which is regarded as a promising supplement to the petroleum industry.\textsuperscript{36}

Up to now, the synthesis of composite nanocatalysts with tailored morphologies and tunable compositions has been achieved via diverse approaches, leading to a significant progress in nanocatalysis during the past decades.\textsuperscript{38-51}

Based on different mixing patterns, composite catalysts can be roughly divided into three major categories: core-shell nanostructures, heterostructures, and alloyed nanostructures, as shown in Figure 1. There are many sub-groups under each major category. For example, there are four general components that can be engineered to prepare various core-shell nanostructures.\textsuperscript{52} First, regarding the overall architecture, one can prepare concentric yolk-shell nanostructures or anisotropic structures. Second, by tuning the number as well as the components of the core particle, one can prepare core-shell nanostructures with either single-core or multi-core or multi-component core. Third, by engineering the shell nanostructure, we can obtain core-shell nanostructures with single-shell or multi-shell or porous shell. Finally, by tuning the interface, one can synthesize core-shell nanostructures with different interfacial properties, which is critical for the development of nanocatalysts with improved performance. Because there are many different types of composite nanostructures, we are not going to describe too much detail on the sub-groups of each major category.
In this review article, we seek to describe and discuss recent advances in the synthesis, properties and applications of noble metal based composite nanocatalysts. We will first review the recent advances in the synthesis of noble metal nanocomposites. Major emphasis will be put on the colloidal synthesis of bimetallic nanostructures. Then, we will focus on some unique physiochemical properties of the nanocomposites, especially the plasmonic and catalytic properties. At last, the promising catalytic application of noble metal based nanocomposites is presented with an emphasis on bimetallic, tri-metallic, and metal-oxide composites.

2. Colloidal Synthesis

The synthesis of noble metal based composite nanocatalysts is generally more complicated than mono-metallic catalysts. In order to obtain composite catalysts with desired structures as well as desired properties, many factors should be taken into consideration, including crystal structure of each component, the relative strength of the bond among different elements, surface energy, relative atomic sizes, capping ligand, electronic effects, and so forth. During the past two decades, the synthesis of composite catalysts has attracted great attention. Hundreds of papers are published in this field every year. Composite nanomaterials can now be prepared via various approaches, including colloidal synthesis, CVD method, atomic layer deposition (ALD) method, electrochemical approach, and so on. In this Review article, we will mainly focus on the colloidal synthesis of composite nanostructures. Our major attention will be paid to the bimetallic nanostructure systems. Less attention will be paid to metal-oxide or metal-salt systems.

Chemical reduction method Noble metal nanoparticles are generally obtained by chemical reduction method in the presence of an appropriate surfactant (e.g., citrate) or polymeric ligands (e.g., polyvinylpyrrolidone, PVP) that can passivate the surface of nanoparticles and prevent them from aggregation. Although the procedure for synthesizing composite nanoparticles using chemical reduction method is similar with that for mono-metallic nanoparticles, it is more difficult to control the co-reduction process of mixed metal ions because of the difference in the reduction potentials and inherent chemical nature. In general, simultaneous reduction processes were used to prepare alloyed composite metal nanostructures, while sequential reduction processes were used to prepare core-shell nanostructured composites. Therefore, a suitable reducing agent is critical for obtaining the controllable composite nanoparticles.

Sodium borohydride (NaBH₄) is a strong reducing agent that can enable a rapid nucleation and growth of noble metal nanoparticles, and has been widely used for preparing the composite catalysts. Wang and co-workers reported a protocol for generating monodispersed Cu-Pt and Cu-Au composite nanoparticles, in which metallic ions could be reduced sequentially by NaBH₄ to form nanocomposites. However, strong reducing agents can generally cause a quick and less controllable reduction of metal ions. To get better control over the reaction kinetics as well as the products, some mild reducing agents, such as ethylene glycol and diethylene glycol (also called polyol process), citrate/sodium citrate, ascorbic acid, formic acid, 2-thiopheneacetonitrile, polymers, and oleylamine, have been used to obtain monodisperse composite nanoparticles in solution. In this condition, a mild reducing agent can rapidly reduce one metal with higher reduction potential that tends to form a core, while the second metal is reduced at later stage and deposited on the surface of the core, thus to form the core-shell nanostructure. For example, noble metals ions (e.g., Pt) can be effectively reduced by a mild reducing agent (i.e., octadecylamine) first, while the transition metal ions (e.g., Ni, Zn, Co, Cd and In) will be reduced later due to their lower reduction potentials. Li and co-workers have done excellent work in preparing these composite nanoparticles. By using this method, many noble metal based composite nanoparticles with different nanostructures have been synthesized, including Cu-Pt, Co-Pt, Ni-Pt, In-Pd, Zn-Pt and In-Pt nanocomposites (Figure 2). Hydrogen can also be used as a mild reducing agent when the composite catalysts are prepared by co-precipitation or impregnation. For synthesizing the composite catalysts, a supporter with large surface area (e.g., Al₂O₃, SiO₂ and zeolites etc.) is usually needed. The noble metal precursors are directly deposited on the supporter, followed by a further calcination for the thermolysis of metal precursors to form metal oxides. And the hydrogen is used to reduce the oxides to obtain the supported catalysts. For example, Su and co-worker have prepared Pd/Au bimetallic catalysts supported on the mesoporous silica nanoparticles (MSN) by an impregnation approach. The active
noble metallic components reduced by hydrogen are highly dispersed on MSN with a tunable molar ratio from 0.1 to 0.4 (Figure 3).

**Figure 3.** HRTEM images of (a) MSN, (b) Pd/MSN, (c) PdAu0.1/MSN, and (d) PdAu0.3/MSN catalysts. STEM (e) and HRTEM (f-h) images, with corresponding electron diffraction pattern (inset in h) of the optimized PdAu0.3/MSN. Reproduced with permission from ref. 79. Copyright 2012, Elsevier Inc.

**Thermal decomposition method**  The decomposition of a mixture of organometallic compounds or labile noble-metal salts at elevated temperature is a widely used approach to synthesize noble metal based composites.80-83 This approach is usually conducted in non-aqueous media under inert atmosphere. Compared to aqueous synthesis of bimetallic nanoparticles that conducted in water, this method has some advantages, such as narrower size distribution and more tunable compositions of product. For example, noble metal nanostructures can be combined with a lot of transition metals, which is usually not available in the aqueous phase synthesis.84-86 In addition, introducing a small amount of oxygen into the prepared bimetallic nanoparticles can be used to make metal-metal oxide composites.

Sun et al. have prepared monodispersed Fe-Pt composite nanoparticles from the precursors of Pt(acac)2 and Fe(CO)5 through thermal decomposition method in the presence of oleic acid and oleylamine.87 The ratio of Fe and Pt in the composite nanoparticles can be systematically tuned by altering the concentration of Pt(acac)2 and Fe(CO)5. Thomas and co-workers have synthesized bimetallic nanoparticles of Ru-Pd, Ru-Sn, Ru-Pt, Ru-Cu, and Ru-Ag by the decomposition of organometallic clusters at around 200 °C for 2 h in vacuum.88 Bronstein’s group has synthesized Pt-Fe nanoparticles by using a two-step process, in which the iron nanoparticles were pre-synthesized via a thermal decomposition at 200 °C, followed by a second thermolysis of Pt(acac)2 in the presence of oleic acid and oleylamine at 285 °C. The two phases of Pt and Fe in obtained nanoparticles are composed in the manner of side by side (Figure 4).88 Pan et al., synthesized carbon supported Pd-Pt composite nanoparticles with small particle size and the single-phase fcc disordered structure using the precursors of Pd(CH3COO)2 and Fe(CH3COO)2 in the absence of additional stabilizers, giving an excellent electrocatalytic activity for the oxygen reduction reactions (ORR).84 This method has been extended to use other precursors including PdCl2,86, 89 and [Pd(NH3)4]2(NO3)285,90 to generate Pd-based composite catalysts.

**Figure 4.** TEM images of (a) Pt-Fe2, (b) Pt-Fe3, (c) Pt-Fe4, and (d) HRTEM images of the Pt-Fe3 sample. The three insets show zoom-in views of individual NPs. Yellow and green arrows indicate different domains in a single particle. Reproduced with permission from ref. 88. Copyright 2014, American Chemical Society.

In addition, the thermal decomposition method has also been used to synthesize Au-based89 and Ag-based91 composite nanoparticles. Lee’s group has recently synthesized the Ag-Cu bimetallic nanoparticles through a two-step process.91 Cu(acac)2 was thermally decomposed at 220 °C to form Cu nanoparticles in the presence of oleylamine. AgNO3 was subsequently added and was further reduced by Cu through the galvanic displacement reaction. Highly monodispersed Ag-Cu composite nanoparticles with a narrow size distribution were obtained, giving a decreased O2 adsorption energy comparing with pure Cu (Figure 5).

**Figure 5.** (a) TEM image of the Ag-Cu nanoparticles synthesized at 220 °C for 2 h (initial Cu nanoparticle nucleation and growth) and 180 °C for 6 h. (b) Characterization by XRD of the synthesized Ag-Cu nanoparticles. (c) HRTEM image of a nanoparticle. (d) SAED pattern of the Ag-Cu nanoparticles. (e) Schematic illustration of the synthesis of Ag-Cu nanoparticles. Galvanic displacement and reduction of Cu occur due to the difference in Ag and Cu redox potentials and oleylamine-based thermal decomposition.
respectively. Reproduced with permission from ref. 91. Copyright 2014, American Chemical Society.

**Biosynthesis method** Biosynthesis methods have been suggested as promising alternative synthetic routes for synthesizing nanoparticles because they do not require additional chemical reagents or complex experimental apparatus. At the beginning, people are trying to utilize the biomass extracts as the reducing agent as well as the capping ligand to prepare metallic nanocomposites. 92 Li group used *Cocumen Platycladi* leaf extract as reducing agent to synthesize Au-Pd 93, 94 and Au-Ag 95, 96 composite nanoparticles. The composition and particle size of the obtained nanoparticles were determined by the concentration of *Cocumen Platycladi* leaf extract. 95 Recently, other biomass extracts, including mahogany leaves, 97 micro-algae, 36 Neem (*azadirachta indica*) leaf, 39 *piper pedicellatum* C.DC, 100 *Fusarium oxysporum*, 101 and chloroplasts, 102 have been explored to synthesize noble metal based composite nanoparticles. Besides, microorganisms have also been used for synthesizing the noble metal based composite nanoparticles. Avalos and co-workers have reported a biosynthetic method for the production of Ag-Au composite nanoparticles by using the fungus *N. crassa*. It is found that the size and composition of the composite nanoparticles can be controlled by the fungus. 103

Biomimetic synthesis is another important route for obtaining nanostructures. 104 Numerous biological systems, such as proteins 104-108 and DNA, 109-111 have been used to direct the growth of noble metal based composite nanoparticles. For example, Monika et al. reported that uniform and size-tunable bimetallic Ag-Au nanowires can be obtained by using artificial DNA templates via a two-step metallization process. 111 Rotello and co-workers have synthesized Fe-Pt composite nanoparticles through DNA-mediated "bricks and mortar" self-assembly process. It is reported that the magnetic properties of the assemblies can be altered by the enhanced structure and increased spacing in the bio-nanocomposite assembly. 112 Additionally, virus is considered as an attractive template for constructing and organizing the nanostructure, because it has the capabilities of molecular recognition and self-assembly. 113, 114 Belcher and co-workers have reported the synthesis and self-assembly of Au-Co3O4 and Au-Ag nanowires using virus. The synthesis and self-assembly of nanoparticles have shed light on the development of lithium ion battery (Figure 6). 115, 116

![Figure 6. Characterization of CTAB-stabilized Au0.5Ag0.5 alloy nanowires on p8#9 virus. (a, b) TEM images of Au0.6Ag0.4 nanowires, (c, d) TEM images of Au0.6Ag0.33 nanowires, and (e, f) TEM images of Au0.5Ag0.5 nanowires. Reproduced with permission from ref. 113. Copyright 2010, American Chemical Society. (g) Visualization of the genetically engineered M13 bacteriophage viruses. P8 protoplast containing a gold-binding motif (yellow) were doped by the phagemid method in E4 clones, which can grow Co3O4. (h) TEM images of the assembled gold nanoparticles on the virus, (i, j) TEM image of hybrid nanowires of Au nanoparticles/Co3O4. Reproduced and adopted with permission from ref. 116. Copyright 2006, American Association for the Advancement of Science.](image-url)
reports that make bimetallic nanoparticles have been found. The pioneering contributions were reported by Mizokoshi and co-workers, who have prepared Au-Pd bimetallic nanoparticles and Au@Pd core-shell nanostructure by using sonochemical method. In the subsequent publications, some other noble metal based composite nanoparticles, including Pd-Cu, Pt-Sn, Pt-CO, Pt-Pd, Au-Ag, and Ag-Pd, have been synthesized by using sonochemical methods.

**Radiolysis method** In this method, metallic ions are reduced by solvated electrons irradiate by γ-ray radiation. The γ-ray determines the rate of reduction and hence the final structure of composite nanoparticles. Radiolysis is an efficient method for reducing metal ions to obtain noble metal based composite nanoparticles, including Ag-Au, Cu-Ag, Pt-Ag, Pt-Au, Ag-Ti, Pd-Al, Pd-Au, Pt-Au, Au-Ni, and Cu-Pt nanoalloys.

**3. Properties**

A unique and attractive feature of composite nanoparticle is that one can integrate multi-functions into one single unit or even create some properties that cannot be obtained by simply mixing different components. In this part, we will highlight some interesting properties, including surface plasmon resonance, magnetic, and catalytic properties, that are beneficial for the catalytic applications.

**Surface plasmon resonance (SPR) properties**

Studies on the optical properties of noble metal nanoparticles can be dated to 1857 when Michael Faraday prepared various gold colloids with different colors. We now understand that the different colors are caused by surface plasmon resonance (SPR), which occurs when a metallic nanoparticle of appropriate size interacts with incident photons in such a way as to confine the resonant photon within the dimensions of the nanoparticles. These unique optical properties have inspired promising applications of noble metal nanoparticles. To better understand the plasmonic properties, some theories or methods have been proposed to simulate the collective excitation of electrons in metallic particles, including Mie theory, discrete dipole approximation (DDA), boundary element method (BEM), T-matrix, and finite differences in the time domain (FDTD). Gold and silver nanoparticles are the most widely studied noble metal nanoparticles for investigating optical properties of metallic composite nanoparticles, because their SPR peaks are located in the visible region. It is well known that the SPR peak of nanoparticles is highly dependent on their shape, composition, and architecture.

**Figure 7.** TEM images, illustrations (insets), HAADF-STEM images, and EDX mapping analyses of Ag nanocubes after reaction with two different volumes of 0.2 mM aqueous HAuCl₄ solution in the absence of ascorbic acid: (A) 1.0 and (B) 1.5 mL. (C) Scheme of the coreduction of silver nanocube and Au. (D) UV-vis-NIR spectra of aqueous suspensions of Ag nanocubes before and after reacting with different volumes of 0.2 mM aqueous HAuCl₄ solution in the absence of ascorbic acid. Reproduced with permission from ref. 162. Copyright 2014, American Chemical Society.

A critical factor to determine the overall plasmonic properties of composite nanoparticles is the ratio of each component. For example, Kim and co-workers have investigated the LSPR properties of individual AgAuAg nanorods using the dark-field spectroscopy technique. The scattering spectra of such heterostructures show longitudinal resonance wavelengths that are nearly insensitive to the relative composition of Ag and Au, suggesting that the plasmonic properties are determined by the overall geometrical arrangement as well as the composition of the hetero-metallic nanostructures. Chen et al have investigated the plasmonic properties of the star-shaped Au-Ag bimetallic nanoparticles, in which the SPR wavelength of the composite nanoparticles is strongly dependent on the ratio of gold and silver. Yang and co-workers have studied the plasmonic properties of Ag-Au hollow nanocubes prepared through the galvanic reaction between silver nanocubes and HAuCl₄, showing that the SPR wavelength of the Ag-Au hollow nanocubes could be tuned by adjusting the addition of gold source (Figure 7).

Recently, it is realized that one can tune the SPR peak by engineering the architecture of composite nanomaterials, e.g., core-shell, 3D architectures, etc. For instance, the coupling effect between gold and silver nanoparticles can significantly enhance the plasmonic properties, which may be affected by the compositions and structures. For core-shell nanostructures, it has been reported that the outer shell determines the overall character of the optical response. A gold core within a silver shell leads to a distinct red-shift of SPR wavelength. A single outer layer of Ag
produce an Ag-like resonance even in a gold-rich structure.\textsuperscript{167-169} To better understand the coupling effect of the core and shell, Donoval and co-workers have calculated the effects of silver shell on the overall plasmonic properties of Au@Ag core-shell nanostructures. Theoretical results indicate that an increasing of silver ratio in the shell leads to a blue-shift of SPR wavelength.\textsuperscript{170} Maye’s group have investigated the effects of Au-Ag alloy shell on the plasmonic properties of Au@Au-Ag composite nanoparticles, suggesting that the plasmonic properties could be tuned by altering the processing temperature, alloy composition as well as the alloy thickness.\textsuperscript{171, 172} In addition, the effects of shell on optical properties have also been proved by Singh and Soni through the preparation of Al@Al\textsubscript{2}O\textsubscript{3}@Ag@Au core-shell nanostructures with multilayer shells, in which the SPR wavelength could be systematically tuned by altering the composition of Au in nanostructures.\textsuperscript{173}

Additionally, it has been reported that metallic dimers and their decoupling from the substrate in a three-dimensional (3-D) design can further improve their SERS performance. Krahe’s group recently synthesized 3-D Au-Ag nanostar dimer in ring structures (NSDiR) through electron-beam lithography method. It is demonstrated that the electromagnetic field enhancement is significantly enhanced because of the efficient decoupling from the substrate, indicating that the plasmonic properties can also be affected by the interactions between composite nanoparticles and substrate (Figure 8).\textsuperscript{174}

**Figure 8.** (a) Schematic illustration of a Ag-Au 3D-NSDiR structure. (b) Normal-incidence SEM image of Ag-Au 3D-NSDiR structures. (c-d) Magnified image of a Ag-Au 3D-NSDiR structure with 55 size at normal incidence and at 52° tilted view, respectively. (e-g) Electric field distribution of a Au nanostar dimer, a AgAu nanostar dimer, and a AgAu nanostar dimer in a ring (3D-NSDiR), respectively, in the x-y plane. (h) Magnified view of a 3D-NSDiR from (g). The scale bars represent the field enhancement, with an incoming field $E_0$ equal to 1. Reproduced with permission from ref. 174. Copyright 2014, American Chemical Society.

Investigations on plasmonic properties of noble metal based composite nanoparticles have been extended to a number of noble metal based composite nanoparticles, including: Au-Pd,\textsuperscript{175-178} Ag-Pt,\textsuperscript{179} Au-Cu,\textsuperscript{180-182} Au-Ni,\textsuperscript{183} Ag-Cu,\textsuperscript{184} Ag-Pd,\textsuperscript{178} Cu-Pd,\textsuperscript{185} Fe-Pd,\textsuperscript{186} and Rh-Pd,\textsuperscript{187} which may inspire some promising applications of noble metal based composite nanoparticles.

**Magnetic properties**

Magnetic metal elements (e.g., Fe, Co, Ni) have two 4s outermost electrons and unsaturated 3d electron shell, which induce rich physicochemical properties, such as specific magnetic and catalytic performances.\textsuperscript{188, 189} The combination of noble metals with magnetic metals has shown great scientific significance, since the multifunctional nanostructures may provide some promising physicochemical properties.\textsuperscript{190-193} For example, it is well known that magnetic 3d metal clusters exhibit the phenomenon of giant magneto-resistance (GMR) when they are mixed with nonmagnetic metals or even insulators. These GMR materials have shown promising applications in magnetic sensing and recording, resulting in the studies of composite nanoalloys between magnetic 3d metals and nonmagnetic 4d (e.g., Rh, Pd, Ag) or 5d metals (e.g., Pt, Au).\textsuperscript{201} The magnetic properties of composite nanoparticles among noble metals and magnetic metals have been widely investigated during the past decades.\textsuperscript{194-202} Investigations on the magnetic properties of Fe-Ag composite nanoparticles with different ratios of Fe and Ag, including Fe\textsubscript{50}Ag\textsubscript{50},\textsuperscript{197} Fe\textsubscript{75}Ag\textsubscript{25},\textsuperscript{197} Fe\textsubscript{50}Ag\textsubscript{50},\textsuperscript{203} Fe\textsubscript{25}Ag\textsubscript{75},\textsuperscript{197} Fe\textsubscript{25}Ag\textsubscript{75},\textsuperscript{204} and Fe\textsubscript{25}Ag\textsubscript{75},\textsuperscript{204} suggest that the magnetic properties of composite nanoparticles are strongly dependent on the interactions between the different elements as well as structural arrangement (Figure 9). The studies of magnetic effects of noble metal based composite nanoparticles have been extended to other systems, such as Fe-Pt,\textsuperscript{205, 206} Fe-Pd,\textsuperscript{207, 208} Fe-Au,\textsuperscript{209} Au,\textsuperscript{210} Ag,\textsuperscript{211} Ni-Au,\textsuperscript{212} and Ni-Pt.\textsuperscript{213}

In addition, the manipulation of magnetic properties can be achieved by controlling the morphologies of composite nanoparticles. The studies of Fe-Au nanorods indicate that the performance of magnetic tweezers and high gradient magnetic separation can be improved by the manipulation of magnetic properties.\textsuperscript{214} Other shapes of composite nanoparticles, including core-shell nanostructure,\textsuperscript{215-217} nanocat,\textsuperscript{218} and sandwich,\textsuperscript{219-221} have also been reported for investigating the magnetic properties of noble metal based composite nanoparticles.
Catalytic properties

Noble metal nanoparticles have been widely used in catalysis due to their unique catalytic performance. However, the application of monometallic noble metal catalysts has been seriously impeded by several factors, including high cost, low stability, low selectivity, etc. It is realized that the catalytic performance of noble metal nanoparticles can be significantly improved by incorporating some other components to form composite nanostructures. The composite nanoparticles can potentially achieve the catalytic performance that unprecedented with their parent metals because different components may have synergistic effects to obtain a new functional catalytic system.

Compared to single component noble metal nanocatalysts, the composite nanocatalysts possess several advantages. First, the incorporation of non-noble metals into noble metal based catalyst is helpful for cutting the cost, since the high price has become a major concern for all commercial technologies. Many non-noble components, including Cu, Zn, and oxides generally act as promoters or supporters in composite catalysts, which can greatly decrease the content of noble metals. Additionally, the formation of composite nanomaterials can improve its stability by “diluting” the noble metal component. Second, composite catalysts can significantly enhance the catalytic performance due to the synergistic effects among different components. For example, the strong-metal-support-interaction (SMSI) between a metal catalyst and the support has proven to be very important for a lot of catalytic reactions. Third, the stability of composite nanomaterials can be improved by properly engineering its composition as well as architectures. For instance, a core-shell nanostructure that composed of a metallic core and a thermally stable shell shows much better thermal stability because the shell can separate the metal nanoparticles and prevent the agglomeration. Fourth, composite nanoparticles may provide some additional functions by adding some specific components. For example, Xu and co-workers synthesized the Fe@Pt core-shell nanoparticles for ammonia borane oxidation. The composite catalyst could be magnetically recycled because of the magnetic properties of iron. This kind of idea has been extended to some other systems, including Au-Co, Au-Fe, Ag-Fe, Pd-Fe, Rh-Fe, and Pd-Co. Further discussion on the catalytic performance of the composite nanoparticles is presented in Section 4.

4. Catalytic applications

As mentioned in the previous section, composite nanocatalysts show improved catalytic performance, including higher activity, longer lifetime, lower cost, and higher selectivity. Over the past several decades, various noble metal based composite nanocatalysts have been reported. In this Section, we will highlight some typical composite nanocatalysts, which can be roughly divided into three categories: bimetallic, tri-metallic and metal-oxide composites.

4.1 Bimetallic catalysts

Pt-Pd catalyst  Pt-Pd composite catalysts have been widely studied for their potential application in oxygen reduction reaction (ORR), since Pt is the most effective catalyst to facilitate both hydrogen oxidation and oxygen reduction in a proton-exchange membrane (PEM) fuel cell. Xia’s group synthesized Pd-Fe bimetallic nanodendrites consisting of a dense array of Pt branches on a Pd core for the oxygen reduction reactions. The catalytically exhibited relatively large surface areas and particularly active facets toward the oxygen reduction reaction, showing 2.5 times higher activity on the basis of equivalent Pt mass than the state-of-the-art Pt/C catalyst and five times higher activity than the Pt-black catalyst (as shown in Figure 10).

Figure 10. Comparison of electrocatalytic properties of the Pt-Pd nanodendrites, Pt/C catalyst (E-TEK) (20% by weight of 3.2-nm Pt nanoparticles on carbon support), and Pt black (Aldrich) (fuel cell grade). (A) CV curves recorded at room temperature in an A 0.1M HClO solution with a sweep rate of 50mV/s. (B) Specific ECSAs for the Pt-Pd nanodendrites, Pt/C catalyst, and Pt black. (C) ORR polarization curves for the Pd-Pt nanodendrites, Pt/C catalyst, and Pt black.
catalyst, and Pt black recorded at room temperature and 60°C in an O₂-saturated 0.1 M HClO₄ solution with a sweep rate of 10 mV/s and a rotation rate of 1600 rpm. (D) Mass activity and (E) specific activity at 0.9 V versus RHE for these three catalysts. (F) CV curves for the Pt-Pd nanodendrites before and after accelerated durability test. Reproduced with permission from ref. 244. Copyright 2009 the American Association for the Advancement of Science.

Another account from Xia group describes Pt-Pd nanocages with hollow interiors and porous walls that exhibits both higher activity and selectivity for the preferential oxidation (PROX) of CO in excess hydrogen than those of Pd nanocubes and the commercial Pt/C (Figure 11 A-B).121 The investigations on mechanism of Pt-Pd composite catalysts suggest that the catalytic performance of Pt-Pd composite nanoparticles strongly depends on their compositions and structures. For example, Hong et al.247 have demonstrated that Pt-Pd nanocages with porous walls and dendritic hollow structures could enhance the catalytic performance of Pt-Pd alloy catalyst in oxygen reduction reactions (Figure 11 C-D), while Yin et al. have presented the enhanced electrocatalytic activity and durability of Pt-Pd tetrahedrons and cubes in ORR applications (Figure 11 E-F).248

**Figure 11.** Plots of (A) activity and (B) selectivity as a function of reaction temperature for CO preferential oxidation in the presence of hydrogen on Pd-Pt alloy nanocages of 8, 12, and 20 nm in size, Pd nanocubes of 18 nm in size, and the commercial Pt/C catalyst. Reproduced with permission from ref. 121. Copyright 2011 American Chemical Society. (C) H₂O₂ yield plots and (D) ORR polarization curves for the Pd-Pt bimetallic NCs and Pt/C obtained using a RRDE in O₂-saturated 0.1 M HClO₄ at scan rate of 10 mV s⁻¹ and a rotation rate of 1600 rpm. Reproduced with permission from ref. 247. Copyright 2012 American Chemical Society. (E) Stable CV curves obtained for the Pt-Pd NCs, NTs, and Pt/C in the electrolyte of 0.1 M HClO₄ and 1 M CH₃OH at the sweep rate of 50 mV/s. (F) CV curves obtained after 4000 additional cycles. Reproduced with permission from ref. 248. Copyright 2011 American Chemical Society.

**Pd-Ni** The introduction of Ni element can significantly improve the catalytic performance of Pd catalysts. For example, Justus and co-workers have synthesized cavity-conform Ni-Pd nanoparticles for catalytic hydrogenation of dialkyl ketones. The catalytic performance of the composite Pd-Ni catalysts is highly dependent on the compositions, giving a much higher activity than the pure Pd or Ni catalysts (Figure 12).249 Recently, the Kawai group has also shown that Pd-Ni bimetallic catalysts exhibited a higher activity than Pd towards the reduction of p-nitrophenol, even when the number of Pd atoms in Pd-Ni bimetallic nanowires was lower than pure Pd nanowires.250 Son and co-workers have investigated the catalytic performance of Ni@Pd core-shell for Sonogashira coupling reactions.251 Pd-Ni composite catalysts have also been used for the decomposition of methane to hydrogen and carbon nanofiber.252

**Figure 12.** Reduction of cyclohexanone (0.18 mg Pd (0.52×10⁻⁴ mol %), 350 µL, 60°C, 24 h) and cycloheptanone (0.36 mg Pd (0.8×10⁻⁴ mol %), 500 µL, 60°C, 48 h) at 20 bar H₂; w/o = without catalyst. Reproduced with permission from ref. 249. Copyright 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

**Pd-Cu** Pd-Cu bimetallic tripods with different compositions have been synthesized by a chemical reduction method and used for the catalytic oxidation of formic acid. The obtained Pd-Cu tripods have highly accessible (211) facets on the side faces, which are expected to be an excellent catalyst for the electrocatalytic oxidation of formic acid. Although only a minor difference between the catalytic activities of Pd₃₋₄Cu₃ and Pd₈₋₉Cu₁₀ was observed, the Pd-Cu tripods exhibited substantially enhanced (almost eight folds per unit mass of Pd) catalytic activity towards the electro-oxidation of formic acid, comparing with the commercial Pd black (Figure 13).228

**Figure 13.** Cyclic voltammograms of the Pd-Cu tripods with different Pd to Cu ratios, together with that of commercial Pd black. The curve was recorded at room temperature in an aqueous solution containing 0.5 M HCOOH and 0.5 M HClO₄ at a sweeping rate of 50 mVs⁻¹. The current was normalized to the corresponding (a) mass of Pd and (b) ECSA, respectively. RHE: reversible hydrogen electrode. Reproduced with permission from ref. 228. Copyright 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

A core-shell Cu@Pd core-shell catalyst for formic acid oxidation was prepared by Li and co-workers by decorating Pd shell on the surface of Cu nanowire. Results from high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) indicate that Cu only exists in the core part of the nanowire, while Pd is mainly distributed in the shell part. The Cu@Pd core-shell nanoparticles exhibit good catalytic activity because of the synergetic effects of Cu and Pd (Figure 14).252 Pd-Cu/Al₂O₃ catalysts have been prepared by Anderson and co-workers through impregnation method for selective acetylene hydrogenation.229

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optimized ratio of Cu and Pd in composite catalyst is about 50:1, giving a high acetylene conversion of 99 % and ethylene selectivity of 70 % at low temperature (100 °C). The enhanced activity is attributed to hydrogen dissociation on Pd with spill over to neighbouring Cu sites where the reaction takes place. 253 Gao and co-workers recently prepared montmorillonite (MMT)-supported Pd-Cu catalysts with narrow size distribution and well-controlled compositions for Sonogashira coupling reactions. The MMT@Pd/Cu material exhibit catalytic activity superior to MMT@Pd and MMT@Cu, giving a highest yield of products of 97 %. 254

Figure 14. (A) TEM images of Cu@Pd nanowires. (B) Formic acid oxidation test of Cu@Pd/C and commercial Pd/C (N2-saturated 0.1 M HClO4, 2 M HCOOH, Scan rate: 50 mV/s). The HAADF-STEM image of Cu@Pd nanowires (C), corresponding element mapping images of Cu-L (D), Cu-K (E), Pd-L (F), Pd-K (G), the 3d graphic illustration (H), and EDS line-scan analysis (I, J). Reproduced with permission from ref. 252. Copyright 2014 Elsevier Ltd.

Pd-Au  Pd-Au composite nanoparticles have been studied for a number of different catalytic applications. Fortunelib and co-workers have investigated the CO oxidation process by using a combination of analytic-potential and first-principles density functional theory (DFT) calculations, suggesting that the composition of Pd-Au nanoparticles have a strong effects on the CO absorption and catalytic performance. 255 Hutchings et al. showed that Au/Pd-TiO2 catalysts give very high turnover frequencies (up to 270,000 turnovers per hour) for the oxidation of alcohols, mainly because the addition of Au to Pd nanocrystals improved the overall selectivity (Figure 15 A-B). 42 The mechanism of the promotional effect of Au in a Pd-Au catalyst has been investigated by Goodman and co-workers. Results show that the role of Au is to isolate single Pd sites that facilitate the coupling of critical surface species to product, while inhibiting the formation of undesirable reaction by-products (Figure 15 C-D). 16

Figure 15. (A) Benzyl alcohol conversion and selectivity to benzoaldehyde with the reaction time at 373 K and 0.1 MPa pO2. Squares, Au/TiO2; circles, Pd/TiO2; and triangles, Au-Pd/TiO2. Symbols indicate conversion, and open symbols indicate selectivity. (B) Au-Pd/TiO2 catalyzed reactions at 363 K, 0.1 MPa pO2, for cinnamyl alcohol (squares) and vanillyl alcohol (circles). Solid symbols indicate conversion, and open symbols indicate selectivity to the corresponding aldehydes. Reproduced with permission from ref. 25. Copyright 2006 the American Association for the Advancement of Science. (C) Vinyl acetate (VA) formation rates (TOFs) as a function of Pd coverage on Au(100) and Au(111). The two insets show Pd monomers and monomer pairs on the Au(100) and Au(111) surfaces. (D) Schematic for VA synthesis from acetaldehyde and ethylene. The optimized distance between the two active centers for the coupling of surface ethylenic and acetate species to form VA is estimated to be 3.3 Å. With lateral displacement, coupling of an ethylenic and acetate species on a Pd monomer pair is possible on Au (100) but implausible on Au(111). Reproduced with permission from ref. 16. Copyright 2006 the American Association for the Advancement of Science.

Shim et al. investigated the electrocatalytic activity of spongelike nanoporous Pd-Au structures. The catalytic activity and stability of the Pd-Au catalyst are characterized for the oxygen reduction reactions in alkaline media. It is reported that the Pd-Au composite catalyst exhibited enhanced catalytic stability and comparable catalytic activity for the oxygen reduction reactions compared to the Pd-20/C and Pt-20/C products. 256 Pd-Au catalysts have also been used for selective hydrogen production via HCOOH decomposition by Mullins et al. It is found that the HCOOH molecules are activated by Pd atoms at the surface. Pd atoms that reside at Pd-Au interface sites favour the dehydrogenation of HCOOH, whereas at Pd(111)-like sites favour the dehydration of HCOOH, suggesting that the catalytic performance of Pd-Au catalysts on the decomposition of HCOOH can be tailored by controlling the arrangement of surface Pd and Au atoms. 257 Feng and co-workers have recently reported the catalytic oxidation of 1,2-propanediol with O2 to lactic acid over hydroxylapatite nanorod-supported Au-Pd bimetallic nanoparticles (Au-Pd/HAP).
under atmospheric pressure. It is reported that the electron transfer between Au and Pd atoms can significantly enhance the catalyst performance, giving a maximum lactic acid selectivity of 97.1% and 1,2-propanediol conversion of 96.6%.²⁵⁸

**Au-Pt** Au-Pt composite nanoparticles have been used as efficient catalytic materials in fuel cell reactions. Sunvitch and co-workers have established a direct correlation between the surface compositions of Au-Pt nanoparticles and their catalytic activities on CO and methanol oxidation. It is found that the intrinsic activities of Au-Pt nanoparticles with the same bulk composition of Au₀.₅Pt₀.₅ can be enhanced by orders of magnitude through simply controlling the surface composition. The phenomena can be attributed to the weakened CO binding on Pt in discrete Pt or Pt-rich clusters surrounded by surface Au atoms (Figure 16).²⁵⁹

![Figure 16](image_url)

**Ru-Pt** Ru is another very important element for enhancing the catalytic performance of Pt-based catalysts on a variety of fuel cell reactions.²⁶⁰-²⁶⁸ In direct methanol fuel cells, Pt catalysts can be easily poisoned by CO, while Ru can help remove CO via preferential oxidation and thus improve the catalytic performance of Pt-based catalysts. Hence, Ru-Pt composite nanoparticles have been widely used for the production of fuel cell electrodes. Manos and co-workers have investigated the Ru-Pt core-shell nanoparticles for preferential oxidation of carbon monoxide in hydrogen. It is found that Ru-Pt core-shell nanoparticles exhibit a much higher catalytic activity than traditional Pt-Ru composite, monometallic mixtures of nanoparticles or pure Pt particles (Figure 17).²⁷¹ Density functional theory studies suggest that the enhanced catalytic activity of the core-shell nanoparticle originates from a combination of an increased availability of CO-free Pt surface sites on the Ru@Pt nanoparticles and a hydrogen-mediated low-temperature CO oxidation process.²⁶⁹ Oldfield et al. have investigated the CO tolerance in a Pt/Ru fuel cell by using solid-state electrophoresis (EC) NMR. Results show that the addition of Ru can weaken the metal-CO (d-n*) bond and lead to a lower activation barrier to CO thermal diffusion in the Pt/Ru domains.²⁷²

Besides, the catalytic performance of Ru-Pt composite catalysts is strongly dependent on the compositions and morphologies.²⁷³ For example, an account from Navaneethan and co-workers has studied the effects of structure on catalytic performance, showing that 10-fold higher for Ru-Pt alloy shells and 5-fold higher for Pt-enriched shells compared with the pure Pt catalyst.²⁷⁴ Johansson et al. have synthesized the Pt-Ru catalysts with various compositions of Ru for the CO oxidation and methanol oxidation reaction. It is found that the activity is low for pure Pt and it gradually reduced with increasing Ru content from 29% up to 100%.
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15.2

\( \text{Pt-lectivity of 96% even when the } \)

\( \text{suggesting that higher steam/carbon } \)

\( \text{Au atoms appear to block the high reactivity edge and kink sites on } \)

\( \text{activity toward low } \)

\( \text{enhanced activity and stability in the generation of hydrogen, giving } \)

\( \text{Au nanoparticle catalysts have been } \)

\( \text{at 170 }^\circ \text{C. (b) } \% \text{ formation of } H_2 \text{O (open symbols) and } \% \text{ CO conversion (filled symbols) plotted against } \)

\( \text{to block the formation of carbonate and thereby increase the catalytic } \)

\( \text{Ni@SiO}_2 \text{ catalyst exhibits enhanced activity and stability in the generation of hydrogen, giving } \)

\( \text{high oxygen reduction } \)

\( \text{before and after } \)

\( \text{enhance activity and stability than pure Ni. The } \)

\( \text{Another important factor for enhancing the stability of Au-Ni catalysts is that } \)

\( \text{Pt-Rh alloy nanoparticles have also been used in methanol electrooxidation reaction because of the } \)

\( \text{Rh catalysts with well-defined alloy formation, uniform particle size and shape, and high-index facets exhibit improved electrocatalytic activity and stability in comparison with spherical Pt-Rh and pure nanoparticles.} \)

\( \text{Farrauto and co-workers have investigated the catalytic performance of Rh-Pt catalyst on steam reforming of sulfur-containing dodecane, suggesting that higher steam/carbon ratio positively favours the stability of catalyst.} \)

\( \text{Pt-Sn/SiO}_2 \text{ bimetallic catalysts have been prepared by Basset and co-workers for propane dehydrogenation. It is found that the inactive Sn on the surface of Pt nanoparticles can isolate the active Pt atoms, resulting in the enhanced catalytic performance on the dehydrogenation of propane.} \)

\( \text{Xiang and co-workers have studied the catalytic performance of various supported Pt-Sn catalysts for propane dehydrogenation, suggesting that supports are quite important for enhancing catalytic activity and stability.} \)

\( \text{addition, many reports show that mixing non-noble metals to replace or decrease the noble metal can not only increase the catalytic performance, but also decrease the cost of catalyst preparation. For example, Linic and co-workers have demonstrated a low-cost Ag-Co surface alloy nanoparticle for oxygen reduction reaction, in which cheap metals have been used to replace conventional Pt-based catalysts. Comparing with the conventional Pt catalyst, the performance of Ag-Co bimetallic catalysts reaches over half of the area-specific activity of Pt catalysts and is more than a fivefold improvement over pure silver nanoparticles at typical operating potentials.} \)

\( \text{The Au-Pt-Sn/SiO}_2 \text{ catalysts show much higher activity and stability in comparison with spherical Pt-Rh catalysts and Pt-Sn/SiO}_2 \text{ catalysts, reaching a monometallic Pt remains in the baseline in this temperature range and does not light off until 170 }^\circ \text{C.} \)

\( \text{The main effect of Au is to enhance activity and stability in the generation of hydrogen, giving the highest hydrogen production in the shortest time compared with Au@SiO}_2 \text{ catalyst and Ni@SiO}_2 \text{ catalysts.} \)

\( \text{Au on the Au/Ni(111) surface is to block the formation of carbonate and thereby increase the catalytic activity toward low-temperature CO } \)

\( \text{Au-Ni composite catalysts have much higher activity and stability than monometallic Ni and Au catalysts. For example, Jiang and co-}

\( \text{Au-Ni@SiO}_2 \text{ composite catalysts with higher catalytic activity and better durability toward the hydrolysis of ammonia borane. It is found that Au-Ni@SiO}_2 \text{ catalyst exhibits enhanced activity and stability in the generation of hydrogen, giving the highest hydrogen production in the shortest time compared with Au@SiO}_2 \text{ catalyst and Ni@SiO}_2 \text{ catalysts.} \)

\( \text{The Au-Ni nanoparticles supported on SiO}_2 \text{ and TiO}_2 \text{ have also been studied by Keane in catalytic hydrodechlorination. The TiO}_2 \text{-supported Au-Ni catalysts exhibit much higher specific hydrodechlorination rates and distinct selectivity than the SiO}_2 \text{ systems, suggesting that the support is one of the critical factors to obtain catalysts with excellent activity and stability.} \)

\( \text{The structure and reactivity of } \text{SiO}_2 \text{ and MgAl}_2 \text{O}_4 \text{ supported Ni-Au nanoparticle catalysts have been reported by Alfons and Jens by using a combination of } \text{in situ } X\text{-ray absorption fine structure, transmission electron microscopy, and } \text{in situ } X\text{-ray powder diffraction. It is found that Au-Ni composite particles exhibit much higher activity and stability than pure Ni. The Au atoms appear to block the high reactivity edge and kink sites on the small Ni particles, and thus lower the probability of adsorbed carbon to form graphite and carbon whiskers.} \)

\( \text{The introduction of a second non-noble metals can significantly enhance the catalytic activity of monometallic catalysts.} \)

\( \text{Figure 18. (a) Conversion of propane (X, green) and selectivity (S, blue) for propane during propane dehydrogenation on the } \text{Al}_2\text{O}_3 \text{ support, Pt, } \text{Pt}_2\text{Ga, and Pt}_2\text{GaK catalysts for each of the eight successive dehydrogenation cycles. The exact values of } \text{X and } S \text{ for the first, second, and eighth cycle. (b) Long-term stability experiment with the Pt}_2\text{GaK catalyst, which was cycled for ca. 1500 h.} \)

\( \text{Figure 17. Catalytic results of core-shell and alloy Pt-Ru particles. (a) TPR results for the different Pt-Ru catalysts showing } H_2 \text{O formation versus temperature for } H_2 \text{ feeds contaminated by 0.1% CO by volume. The } H_2 \text{O yields are plotted as } \% \text{ maximum formation based on the limiting reactant } O_2 \text{. With complete CO conversion in the 0.1% CO feed, the maximum formation of water is 90%. The monometallic Pt remains in the baseline in this temperature range and does not light off until 170 }^\circ \text{C. (b) } \% \text{ formation of } H_2 \text{O (open symbols) and } \% \text{ CO conversion (filled symbols) plotted against temperature for the core-shell (black) and alloy (red) nanoparticles catalysts for } H_2 \text{ feeds contaminated by 0.2% CO. In these feeds, the maximum } H_2 \text{O yield is 80% when CO is preferentially oxidized. CO is normalized to its inlet concentration. Reproduced with permission from ref.} \)
times over a 14 day period. Reproduced with permission from ref. 284. Copyright 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

**Phase segregation of bimetallic nanoparticles** An interesting study conducted by Somorjai and co-workers demonstrated that the composition of bimetallic nanoparticles can be varied by changing the reaction condition. They studied both Rh$_{0.5}$Pd$_{0.5}$ and Pd$_{0.5}$Pt$_{0.5}$ nanoparticles under oxidizing, reducing, and catalytic conditions by using x-ray photoelectron spectroscopy at near ambient pressure. Under oxidizing condition (100 mtorr NO or O$_2$), Rh$_{0.5}$Pd$_{0.5}$ nanoparticles has a Rh-rich shell with most of the Rh in the oxide form. Under both catalytic condition (100 mtorr NO and 100 mtorr CO) and reducing condition (100 mtorr CO or hydrogen), the shell become more Pd-rich (Figure 19)\(^{191}\). The composition change and oxidation states change are highly reversible. The reversible segregation phenomena in bimetallic nanoparticles have been ascribed to the surface energy in the metals and oxides. The surface energy of Pd is relatively lower than that of Rh, while Rh oxide is more stable than Pd oxide. As a result, Rh atoms tend to stay outside under oxidative condition and migrate into the core under reductive condition. As a comparison, no substantial segregation of Pd or Pt atoms was found in Pt$_{0.5}$Pd$_{0.5}$ nanoparticles.

**Figure 19.** (Top) Evolution of Rh (Rh$^0$ + Rh$^{2+}$) and Pd (Pd$^0$ + Pd$^{2+}$) atomic fractions in the Rh$_{0.5}$Pd$_{0.5}$ NPs at 300°C under oxidizing conditions (100 mtorr NO or O$_2$) and catalytic conditions (100 mtorr NO and 100 mtorr CO) denoted in the x axis. (Bottom) Evolution of the fraction of the oxidized Rh (left y axis) and Pd atoms (right y axis) in the examined region under the same reaction conditions as the top part of the figure. All atomic fractions in this figure were obtained with an x-ray energy of 645 eV for Rh3d and Pd3d, which generates photoelectrons with a MFP of ~0.7 nm. Schematic diagrams above the top of the figure show the reversible segregation of Rh and Pd under alternating oxidizing and catalytic conditions. The y-axis data points for reactions 1, 3, and 5 have an associated error of ±0.03; for reactions 2 and 4, the error bar is ±0.02. Reproduced with permission from ref. 191. Copyright 2009 the American Association for the Advancement of Science.

### 4.2 Tri-metallic catalysts

Recently, the preparation of composite catalysts with more components has attracted some attention, because it is believed that such complicated systems might show unprecedented catalytic performance. For example, Hungria and co-workers have reported the application of tri-metallic Ru$_{0.5}$Pt$_{0.5}$Sn nanoparticles in single-step conversion of dimethyl terephthalate (DMT) into cyclohexanediomethanol (CHDM). It is believed that Sn in the composite catalyst plays a key role in anchoring the particle owing to its oxopelicitic support, which in turn diminishes the tendency for the nanoparticles to sinter.\(^{284}\) Pt$_{0.5}$Ni$_{0.5}$Au tri-metallic catalysts have been synthesized by Li group for the Suzuki Miyaura coupling reaction and reduction of nitrobenzene using formic acid. It was found that the catalytic performance can be significantly improved by sophisticated decoration with the third metal (Figure 20).\(^{285}\)

**Figure 20.** (a-c) SA-corrected HRTEM images of (a) Pt$_{0.5}$Ni$_{0.5}$Au$_{0.5}$, (b) Pt$_{0.5}$Ni$_{0.5}$Au$_{0.5}$, and (c) Pt$_{0.5}$Ni$_{0.5}$Au$_{0.5}$. (d-f) Elemental mapping of (d) Pt$_{0.5}$Ni$_{0.5}$Au$_{0.5}$, (e) Pt$_{0.5}$Ni$_{0.5}$Au$_{0.5}$, and (f) Pt$_{0.5}$Ni$_{0.5}$Au$_{0.5}$. Conversion as a function of time in the Suzuki-Miyaura coupling reaction (g) and reduction of nitrobenzene using formic acid as a hydrogen source catalyzed by tri-metallic catalysts containing 0.5 atom %Pt (h). Reproduced with permission from ref. 285. Copyright 2013 American Chemical Society.

Tri-metallic Au-Pd-Pt nanostructures are highly active and fairly stable when employed as anode catalysts for electro-oxidation. Wang and Yamauchi have synthesized tri-metallic Au@Pd@Pt core-shell nanoparticles as an efficient catalyst for methanol oxidation reaction. It is found that the pseudo-inserted Pd-Pt alloy can serve as catalytic sites, while the Au cores serve as only the seed for subsequent deposition of the Pd inner layer and Pt outer shell.
Another account shows that very few Au atoms (the surface atomic ratio of Pt/Pd/Au is 15:102:1) on the surface of tri-metallic Au@Pd@Pt concave nanocubes lead to excellent catalytic performance on ethanol electro-oxidation due to the synergistic effects among the metals. 297

Pt based tri-metallic nanoparticles have also been used for oxygen reduction reactions due to their high activity for fuel oxidation and oxygen reduction reactions. 298-300 Xia’s group recently reported tri-metallic Pd@Pt-Ni core-shell octahedra catalysts for oxygen reduction reactions. It is found that the Pd@Pt-Ni/C catalyst shows an oxygen reduction reaction mass activity of 12.5-fold higher and a specific activity of 14-fold greater than that of the state-of-the-art Pt/C catalyst after HAC treatment. 301 The introduction of Ni into Pt based catalysts can effectively increase the specific activity because Ni can tune the d-band center and surface structure of Pt. 302, 303 Furthermore, the metal of Co can increase the activity of Pt-Pd towards the oxygen reduction reactions, giving enhanced mass activity, specific activity, durability and methanol tolerance in the oxygen reduction reaction compared with commercially available Pt black. 304, 305 Sun and co-workers recently reported Ag/CuPd and Au/CuPd tri-metallic nanoparticles for oxygen reduction reactions, giving a mass activity of about 0.20 A/mg and 77.6% of their activity after 48000 s-t test, which are more efficient than the commercial Pt catalysts (Figure 21). 306

As a result, we can understand the underneath mechanism, which in turn, help us design and make new catalysts. In this section, we will highlight some metal-oxide composite system, including TiO2, ZnO, Al2O3, SiO2 and CeO2. 307

Metal-TiO2 TiO2 is an important semiconductor with a relatively wide band-gap (~3.2 eV for anatase TiO2), which usually can utilize only UV light. Recently, it is realized that one can make Au/Ag-TiO2 hybrid nanostructure to extend the absorption to longer wavelength by utilizing the SPR property of Au or Ag. In addition, the metal component can help to separate the electron and hole and thus improve its catalytic property.

For example, Yang and co-workers have studied the catalytic performance of Au-TiO2 for oxidizing CO under visible light irradiation. 307 It is found that the visible light can promote the preferential oxidation of CO over Au-TiO2 catalyst comparing with Au-Al2O3 catalyst (Table 1). The irradiated light may result in more O2•− species on TiO2 surface, which is considered as the critical factor in photocatalysis of CO via a so-called Au-assisted Mars-Krevelen mechanism. 308 Liang and co-workers have studied the oxidation of methanol to methyl formate on Au-Ag-TiO2 catalyst under UV irradiation. It is found that Au-Ag-TiO2 catalysts exhibit superior photocatalytic performance in terms of high methanol conversion of 90% and methyl formate selectivity of 85%. 309 Llorca and co-workers have reported hydrogen production from the photolysis of ethanol-water over Au/TiO2 catalyst, the catalytic performance was strongly depended on catalyst loading, temperature, contact time and water to ethanol composition. 310 Gao and Yin recently synthesized Au/TiO2 photocatalysts by depositing pre-synthesized colloidal Au nanoparticles with well-controlled sizes to TiO2 nanocrystals and then removing capping ligands on the Au surface through a delicately designed ligand-exchange method. The obtained catalyst has a very clean surface, showing a superior activity in both dye decomposition and water-reduction hydrogen production (Figure 22). 311

Table 1 Catalytic performances for oxidizing CO in the absence or presence of H2 over Au/TiO2 and Au/Al2O3 at 20 °C under visible light irradiation or not, respectively.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Conversion of CO (%)</th>
<th>Conversion of H2 (%)</th>
<th>Selectivity of CO oxidation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No light</td>
<td>Light</td>
<td>No light</td>
<td>Light</td>
</tr>
<tr>
<td>Au-TiO2</td>
<td>64.1</td>
<td>79.6</td>
<td>-</td>
</tr>
<tr>
<td>Au-Al2O3</td>
<td>23.6</td>
<td>25.2</td>
<td>-</td>
</tr>
<tr>
<td>Au-TiO2</td>
<td>30.3</td>
<td>37.1</td>
<td>8.6</td>
</tr>
<tr>
<td>Au-Al2O3</td>
<td>23.5</td>
<td>25.1</td>
<td>1.3</td>
</tr>
</tbody>
</table>

4.3 Metal-Oxide Composite Catalysts

Long before the rising of nanotechnology, people were able to make various metal-oxide composite catalysts. With the development of nanotechnology, we are able to make composite nanocatalysts with well defined shape, composition, and interface.
Figure 22. Photocatalytic hydrogen generation from the TiO$_2$-Au(x)-y nanocomposites under visible-light illumination in a period of 6 h. Bare P25 and Au-TiO$_2$ nanocomposites obtained by the DP method (DP-x; x, annealing temperature, °C; Au loading, 6 wt %) were employed as the control materials. (a) Illumination conditions: $\lambda > 515$ nm, 100 mW cm$^{-2}$. (b) Illumination conditions: $\lambda > 390$ nm, 100 mW cm$^{-2}$. (c) Photocatalytic hydrogen production from the photocatalyst TiO$_2$-Au(6)-10 in 4 cycles; illumination conditions: $\lambda > 515$ nm; 100 mW cm$^{-2}$. Reproduced with permission from ref. 311. Copyright 2014 American Chemical Society.

Yin and co-workers have designed and fabricated a sandwich-like structured composite, in which Au nanoparticles are sandwiched by a silica core and a titania shell (as shown in Figure 23).\textsuperscript{161} The addition of suitable amount of Au nanoparticles can significantly improve the photocatalytic performance of TiO$_2$. It is demonstrated that the sandwich structure shows much better performance in the photodegradation of organic dyes under direct sunshine than commercial P25 even when the loading of Au is only 5000 ppm.

Figure 23. (a) Schematic illustration of the fabrication process of SiO$_2$@Au@TiO$_2$ sandwich-structured composite catalyst; (b) Typical SEM image of the composite catalyst. (c) Elemental mapping of a single particle, with the distribution of individual elements shown in the bottom row. Adapted with permission from Ref. 161. Copyright 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

Additionally, metal-TiO$_2$ catalysts demonstrate exceptional catalytic activity for a wide range of reactions, such as CO oxidation, olefin epoxidation, hydrocarbons decomposition, and water gas shift (WGS) reaction.\textsuperscript{322,323} For example, Li and Zeng have studied the reaction of CO with lattice oxygen atoms at the Au$_{1-x}$TiO$_2$ interface by using Born-Oppenheimer molecular dynamics (BOMD) simulation, suggesting that the M-VK mechanism is likely more favoured for relatively fluxional Au clusters, whereas the L-H mechanism is more favored for robust Au clusters.\textsuperscript{320} Boughton and co-workers have reported a well-dispersed small Au-Ag composite catalyst on TiO$_2$ nanobelts that exhibited unique properties including high thermal stability, large surface area, high permeability, low density, and tailorable shape and size, giving an enhanced catalytic performance toward aerobic oxidation of benzyl alcohol.\textsuperscript{321} Alberto and co-workers have prepared Au-Ag/TiO$_2$ catalysts by using deposition-precipitation method for the oxidation of CO. It is found that the Au-Ag/TiO$_2$ catalysts exhibit significantly higher activity and stability in CO oxidation, which can bear a high temperature of 550 °C.\textsuperscript{322}

Metal-ZnO ZnO is also an important semiconductor. Metal-ZnO composites have been widely used in catalysis. Ravishankar and co-workers synthesized Au-ZnO nanohybrids by rapid microwave-assisted synthesis for CO oxidation. It is found that the presence of Au-Zn and Au-O bonds on the interface leads to the formation of anionic and cationic Au sites, which can significantly enhance the activity of the Au-ZnO catalysts.\textsuperscript{323} Wanchantheu and co-workers have prepared Au-ZnO catalysts through photodeposition method for CO oxidation. It is found that the small nanoparticles with a size of 1-2 nm can efficiently catalyze the preferential oxidation of CO.\textsuperscript{324} An account from Wang and co-workers have investigated the adsorption of CO on Au-ZnO catalyst through Fourier transform infrared (FTIR) spectroscopy in an ultra-high-vacuum (UHV) system. The proposed mechanism claims that O$_2$ absorbs on the Au/ZnO interface and reacts with the adsorbed CO to form the OC–O$_2$ intermediate complex, accompanied by charge transfer from substrate to Au cluster. Different carbonate species are produced via interaction of formed CO$_2$ with surface oxygen atoms on ZnO.\textsuperscript{325} The first-principle investigations of Au catalysis on 2D one-atom-thick ZnO nanosheets on CO oxidation indicate that the planar structure (P2) of Au$_x$ cluster on 2d ZnO sheets exhibits high catalytic performance with a low reaction barrier of around 0.3 eV.\textsuperscript{326}

Metal-ZnO nanoparticles have also been used as photocatalysts. For instance, Singla and co-workers have studied the photocatalytic activity of Au@ZnO core-shell nanostructure by the degradation of methyl orange (MO) dye and oxidation of methanol under visible irradiation, showing that the photocatalytic activity increased by the plasmonic Au core.\textsuperscript{327} A similar enhancement has been reported by Wang and co-workers who have investigated the plasmonic heating effect of Au-ZnO on CO$_2$ reduction under visible light illumination. It is found that the conversion of CO$_2$ and the selectivity of products can be readily controlled by adjusting the light intensity (Fig. 24).\textsuperscript{328}

Figure 24. Catalytic CO$_2$ conversion rate as a function of laser intensity of (a) Au-ZnO under cw 532 nm illumination, with corresponding catalyst temperature due to plasmonic heating.
Ag-Al₂O₃ Ethylene epoxidation is a process in which ethylene and oxygen react to form ethylene oxide (EO), which provides a gateway to produce ethylene glycol, ethanolamines, detergents, and many other chemicals in chemical industrial. Silver is the only heterogeneous catalyst that can achieve reasonable selectivity to EO. Linic’s group has studied the ethylene epoxidation reaction by using Ag catalysts and suggested that heterogeneous composite Ag catalysts are more selective in partial oxidation of ethylene to form EO than conventional Ag catalysts. Another account from the Linic group reported that the plasmonic silver nanostuctures can concurrently use low-intensity visible light (on the order of solar intensity) and thermal energy to drive the ethylene epoxidation reaction. The so-called visible-light-enhanced catalytic process is quite important for ethylene epoxidation reaction to improve the catalytic performance by combining the thermal energy and laser irradiation. Conventional catalysts are driven by thermal energy, but high temperature may decrease the selectivity for the desired products because they are easily thermally activated on the catalyst. On the other hand, high operating temperature is another challenge for the stability of catalyst which may decrease or even lose the activity through carbon deposition and sintering. Mechanistic studies show that the plasmonic Ag nanocubes supported on Al₂O₃ (Ag-Al₂O₃) can yield chemically useful energetic electrons when irradiated with visible light, and these electrons can synergistically drive the ethylene epoxidation reaction with thermal energy (shown in Figure 25).

Figure 25. Plasmon-enhanced oxidation reactions. a. The rate of ethylene epoxidation at 450 K in the dark and with visible illumination. A significant enhancement in the rate caused by visible-light illumination was observed. b. Rate enhancement (left axis, blue circles) calculated by dividing the rate of the photothermal process by the rate of the thermal process as a function of temperature. On the right axis black triangles show the rate of photothermal epoxidation and red squares show the rate of thermal epoxidation as a function of temperature. c, Selectivity to EO for the thermal and photothermal processes as a function of reaction rate. The two processes show identical selectivity at a given rate. d. Rate enhancements, calculated dividing the rate of photothermal by the rate of the pure thermal process, for CO and NH₃ oxidation as a function of temperature. Error bars in the plots represent the standard deviation of the systematic errors in the collection of mass spectrometer data. Reproduced with permission from ref. 328. Copyright 2013 Royal Society of Chemistry.

Pt-SiO₂ Porous SiO₂ is a common supporter for synthesizing composite catalysts. A great number of mesopores in the SiO₂ can provide spaces for confining metal nanoparticles with specific size. The strong confinement effects of mesoporous SiO₂ can prevent the sintering of nanoparticles even under harsh conditions. The Pt-SiO₂ catalysts have been widely used in the past decades on hydrogenation reactions. Recently, Somorjai and co-workers studied the catalytic processes on Pt-SiO₂ catalysts during 1-butadiene hydrogenation by using in situ sum frequency generation vibrational spectroscopy (SFGVS), suggesting that calcination is effective in removing the capping agent PVP, and the SFGVS signal can be generated from the metal surface to monitor the catalytic processes. Zhang’s group reported a facile and scalable process to prepare graphene-nanosheet-supported Pt nanoparticles covered by mesoporous SiO₂ layers. The SiO₂ outer layer can restrain the π-π stacking interactions among graphene nanosheets and prevent the aggregation and restacking of graphene nanosheets. In addition, the confinement effects of mesoporous SiO₂ can prevent the sintering of Pt nanoparticles. These robust catalysts show high catalytic activity, high stability under high-temperature calcination, and excellent recycling and reusability towards gas-phase and solution-phase reactions.

Au-CeO₂ CeO₂ is one of the most efficient supports for low-temperature oxidation of molecular CO due to its oxygen storage capacity. Camellone and Fabris have investigated the mechanism of CO oxidation on Au/CeO₂ catalysts, suggesting that the single gold atoms could promote the oxidation of CO on CeO₂ (111) surface. The reversible Au⁹⁵/Au and Ce⁹⁵/Ce⁵⁷ reductions assist the formation of surface O vacancies, and molecular oxygen can seal these vacancies to form activated O₂ species, leading to a local rearrangement of the AuO₄ unit activated by an energy barrier of 0.55 eV. CO reacts with these O₂ species without activation energy to form CO₂ and recover the initial stoichiometry of the Au₄Ce₁₂O₄ system. Another similar account for the CO oxidation mechanism on CeO₂-supported Au nanoparticles by using density functional theory (DFT) has been reported by Henkelman et al. They have compared CO oxidation by a Au₁₅ nanoparticles supported on CeO₂ (Au₁₅@CeO₂-2TO) and partially reduced CeO₂ with three vacancies (Au₁₅@CeO₂-3VAC), giving three possible mechanisms as follows: (1) activating the M-V mechanism of CO oxidation by lowering the energy of CO₂ production, (2) increasing the number of oxygen vacancies in the CeO₂ surface that bind and supply O₂ for the second half of the M-V mechanism, and (3) increasing the concentration of reduced metal ions, which act as anchoring sites for O₂ molecules.
5 Conclusion and Outlook

In this Review article, we have discussed the recent advances in noble metal based composite nanocatalysts. Incorporating another or many other components into a noble metal nanoparticle to form a composite can significantly improve its catalytic performance, such as activity, selectivity, and stability. We have mainly focused on the colloidal synthesis of bimetallic nanoparticles. With the development of nanotechnology, composite nanoparticles with desired shape, size, and physicochemical properties can be obtained through various approaches. We then highlighted some unique properties, especially SPR properties and magnetic properties, that are beneficial for the catalytic performance of nanomaterials. To the end, we have summarized some important catalytic applications of bimetallic, tri-metallic, and metal-oxide composite nanocatalysts.

One of the remaining challenges in this field is the characterization of nanocatalysts in the real reaction conditions. Although impressive progress has been achieved in understanding model reaction systems under some extreme condition, such as ultra-low pressure and low temperature, it is still very difficult to understand the phenomena under real reaction conditions, e.g., high temperature and high pressure, due to the limitation of characterization tool. For example, although a lot of enhanced properties of composite catalysts have been ascribed to the synergistic effect, it is not clear where the synergistic effect comes from and how we can design a structure that will have the effect. To reveal the synergistic effects of various elements, some in situ spectroscopic investigations and advanced characterizations are required to directly “see” the catalytic process. One of the potential techniques might be that based on synchrotron radiation. Since the aqueous phase reactions are more complicated, gas-phase reactions may be more easily to handle.

Another challenge is how to cut the cost of noble metal based catalysts to fulfill the requirement of industrial applications. To decrease the cost, one needs to decrease the content of noble metal. Recently, main-group and non-noble metal catalysis has attracted more and more attention. However, noble metals are still necessary for a lot of applications. A possible solution to this question might be the advanced nanotechnology that can not only understand the reaction phenomena, but also can make better composite catalysts. For example, it is not easy to control the bonding property of composite nanoparticles from the atomic scale. If one could achieve the atom-to-atom fabrication of catalyst, we may be able to make excellent catalyst with low cost in a more sustainable way.

In terms of the stability of shape- and composition-controlled nanocatalysts, more researches should be conducted. Although a lot of composite catalysts with significantly enhanced catalytic performance have been reported by controlling their morphology and composition, the long-term stability is still a big concern. Recently, coating the active and unstable nanoparticle with a porous and stable shell to form a core-shell nanostructure has proven to be an effective way for some specific catalyst systems.

But most synthetic strategies are tedious and time-consuming. More researches need to be done along this direction.

In a short summary, noble metal based catalysts have attracted increasing attention due to their excellent catalytic performance. We have tried to present an up-to-date overview of this field; however, it is impossible to take into account all contributions to the field. We hope that this critical review can inspire researchers pursuing in the area of catalysis and nanotechnology to design the noble metal based composite catalysts with excellent activity, low cost, and stability.

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Notes and references


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Biography

Dr. Yong Xu obtained his PhD degree in Chemical Physics from University of Science and Technology in 2013 under the supervision of Professor Quanxin Li. From 2011 to 2012, he was a joint PhD student at Laboratori Nazionali di Frascati, Istituto Nazionale Di Fisica Nucleare (LNF-INFN), Italy, under the supervision of Professor A. Marcelli. He joined Shanghai Advanced Research Institute, Chinese Academy of Sciences (SARI-CAS), as an assistant researcher in 2013. Now he is a postdoctoral fellow in the college of Nano Science and Technology at Soochow University, working with Professor Qiao Zhang. His current research interest focuses on the synthesis and catalytic application of noble metal nanomaterials.

Lei Chen was born in Jiangsu, China, in 1992. He obtained his B.S. degree in Polymer Materials and Engineering from Soochow University in 2014. Now he is a graduate student at Soochow University under supervision of Professor Qiao Zhang. His current research interest focuses on the synthesis of noble metal nanoparticles and their application in catalysis.

Xuchun Wang was born in Shandong, China, in 1990. He obtained his B.S. Degree in Chemistry from Soochow University in 2014. Now he is a graduate student at Soochow University under the supervision of Professor Qiao Zhang. His current research interest focuses on the colloidal synthesis and catalytic applications of noble metal nanoparticles.

Dr. Wei-Tang Yao obtained his PhD degree in Inorganic Chemistry from University of Science and Technology of China in 2005 under the supervision of Professor Shu-Hong Yu. He was a postdoctoral fellow in the Division of Nanomaterials and Chemistry at Hefei National Laboratory for Physical Sciences at the Microscale from 2005 to 2007. He was a postdoctoral fellow at the Max Planck Institute of Colloids and Interfaces, Germany, working with Dr. Cristina Giordano and Prof. Markus Antonietti (2008-2009). From 2009 to 2010, he joined Domen-Kubota Lab, University of Tokyo, as a Postdoctoral Researcher. From 2010 to 2014, he was appointed as an associate professor in the Department of New Energy, Hefei University of Technology. Since 2015, He became a faculty member of Southwest University of Science and Technology. His current research interest focuses on the studies of II-VI semiconductor nanomaterials, hybrid materials, functional metal nitrides, and conducting rubber ambers, and their related properties.
Dr. Qiao Zhang received his Ph.D. in physical chemistry from the University of California, Riverside, in 2012 under the supervision of Prof. Yadong Yin, then worked as a postdoctoral fellow at the University of California, Berkeley and the Lawrence Berkeley National Laboratory, under the supervision of Prof. A. Paul Alivisatos and Prof. Gabor A. Somorjai. In 2014, he became a faculty member of Soochow University. His research interests include synthesis and utilization of nanostructured materials for applications in fields such as catalysis, photonics, and biomedical research.