# Ordered Macroporous Bimetallic Nanostructures: Design, Characterization, and Applications

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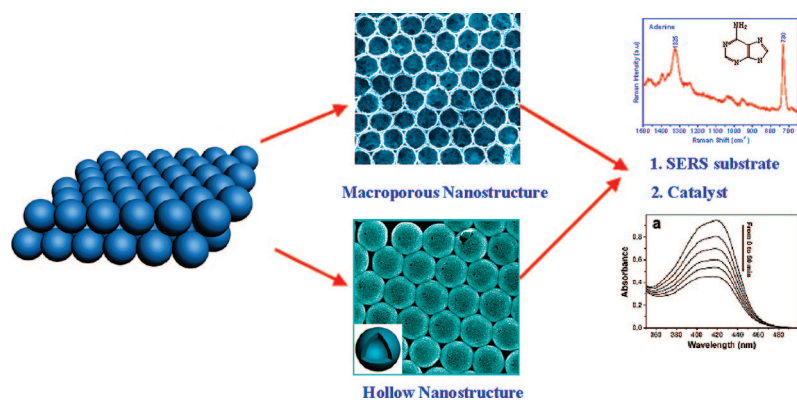
Ordered porous metal nanomaterials have current and future potential applications, for example, as catalysts, as photonic crystals, as sensors, as porous electrodes, as substrates for surface-enhanced Raman scattering (SERS), in separation technology, and in other emerging nanotechnologies. Methods for creating such materials are commonly characterized as "templating", a technique that involves first the creation of a sacrificial template with a specific porous structure, followed by the filling of these pores with desired metal materials and finally the removal of the starting template, leaving behind a metal replica of the original template. From the viewpoint of practical applications, ordered metal nanostructures with hierarchical porosity, namely, macropores in combination with micropores or mesopores, are of particular interest because macropores allow large guest molecules to access and an efficient mass transport through the porous structures is enabled while the micropores or mesopores enhance the selectivity and the surface area of the metal nanostructures. For this objective, colloidal crystals (or artificial opals) consisting of three-dimensional (3D) long-range ordered arrays of silica or polymer microspheres are ideal starting templates. However, with respect to the colloidal crystal templating strategies for production of ordered porous metal nanostructures, there are two challenging questions for materials scientists: (1) how to uniformly and controllably fill the interstitial space of the colloidal crystal templates and (2) how to generate ordered composite metal nanostructures with hierarchical porosity. This Account reports on recent work in the development and applications of ordered macroporous bimetallic nanostructures in our laboratories. A series of strategies have been explored to address the challenges in colloidal crystal template techniques. By rationally tailoring experimental parameters, we could readily and selectively design different types of ordered bimetallic nanostructures with hierarchical porosity by using a general template technique. The applications of the resulting nanostructures in catalysis and as substrates for SERS are described. Taking the ordered porous Au/Pt nanostructures as examples for applications as catalysts, the experimental results show that both the ordered hollow Au/Pt nanostructure and the ordered macroporous Au/Pt nanostructure exhibit high catalytic ability due to their special structural characteristics, and their catalytic activity is component-dependent. As for SERS applications, primary experimental results show that these ordered macroporous Au/Ag nanostructured films are highly desirable for detection of DNA bases by the SERS technique in terms of a high Raman intensity enhancement, good stability, and reproducibility, suggesting that these nanostructures may find applications in the rapid detection of DNA and DNA fragments.

Introduction

The design of ordered porous metal materials has developed into an increasingly important research area in recent years as driven by their widespread applications for example, as catalysts, as photonic crystals, as sensors, as electro-optical devices, as fuel cells, in separation technology, as porous electrodes, and as substrates for surface-enhanced Raman scattering (SERS).[1–3] In nearly every case, success strongly depends on the availability of porous metal materials with specific pore sizes, compositions, and structure. In general, porous metal materials can be classified into three distinct categories according to their pore size: microporous (pore size <2 nm), mesoporous (2 nm < pore size < 50 nm), and macroporous (pore size >50 nm) systems.[4] From the viewpoint of practical applications, ordered metal nanostructures with hierarchical porosity, namely, macropores in combination with micropores or mesopores, are of particular interest because macropores allow large guest molecules to access and an efficient mass transport through the porous structures is enabled while the micropores or mesopores enhance the selectivity and the surface area of the metal nanostructures. Especially, if such structures are extended to bimetallic nanomaterials, this is of importance since the properties of one metal may be altered and improved by the addition of another.

Methods for the fabrication of ordered porous metal nanostructures are commonly characterized as "templating". Herein, the term templating refers to a technique that involves first the creation of a sacrificial template with a specific porous structure, followed by the filling of these pores with desired metal materials and finally the removal of the starting template, leaving behind a metal replica of the original template (Figure 1). The architecture and the pore size of the resulting porous metal materials thus rely directly on those of the starting template. There are several properties of colloidal crystals (or artificial opals) that make them particularly attractive for use as starting templates: (1) colloidal crystals themselves are two-dimensional (2D) or three-dimensional (3D) long-range ordered arrays of silica or polymer microspheres, and therefore they can produce well-defined metal replicas that preserve their key feature of long-range periodic structure; (2) the pore size of the resulting metal replicas can be easily tuned by varying the diameter of the building blocks such as silica or polymer microspheres, enabling the design of ordered metal nanostructures with adjustable pore size; (3) the terminal groups on the surface of the silica and polymer microspheres can be tailored to facilitate uniform metal deposition

in the interstitial space of colloidal crystal templates. As will be discussed below, these three attributes play a pivotal role in generating highly ordered bimetallic nanostructures with hierarchical porosity.

With respect to the colloidal crystal templating strategies for production of ordered porous metal nanostructures, there are two challenging questions for materials scientists: (1) how to uniformly and controllably fill the interstitial space of the colloidal crystal templates and (2) how to generate ordered composite metal nanostructures with hierarchical porosity. Several attempts have recently been reported to successfully perform uniform deposition of metal into the interstitial spaces of colloidal crystal templates, including metal nanoparticle infusion,[5] metal infiltration,[6] electroless deposition,[7] convective assembly of metal nanoparticles,[8] electrochemical deposition,[9] and metal salt precipitation with subsequent hydrogen reduction.[10] In particular, the latter two methods can be extended to generate ordered bimetallic macroporous materials. Nonetheless, these approaches provide little control over the deposition procedure and thus invariably lead to a nearly complete infiltration of the interstitial space of the colloidal crystal templates.

Recent work on metal nanoshells by Halas et al. and our groups may provide important insights into solving these problems.[11,12] The methods typically begin with the grafting of an appropriate reagent onto silica spheres through covalent bonding, followed by the mixing with much smaller gold nanoparticles, producing a gold nanoparticle film on the surface of the silica spheres. These gold-coated silica spheres are then used for further gold (or other metal, see below) growth. During this process, the small gold nanoparticles on the surface of silica spheres serve as catalysts for electroless metal deposition, enabling a complete coverage of the silica spheres with metal. This strategy is promising for achieving uniform and controllable metal deposition into the voids of the colloidal crystal templates, because the electroless metal deposition can be controlled to occur only on the surface of the silica spheres due to the presence of the small gold nanoparticles. However, as opposed to isolated silica spheres, the colloidal crystals are ordered arrays of silica spheres where the interstitial areas are curved, narrow, and not readily accessible, which makes uniform and controllable metal deposition into them even more challenging.

In this Account, we present our recent efforts involving a general colloidal crystal template technique for the selective fabrication of bimetallic nanostructures with hierarchical poros-
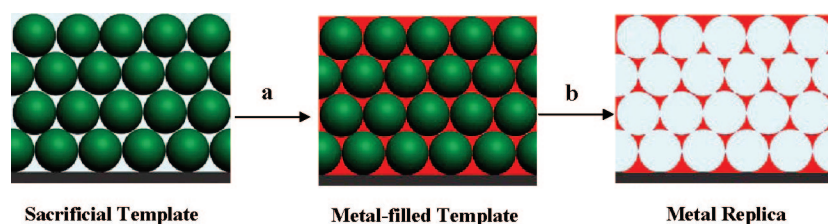
FIGURE 1. Schematic illustration of the templating technique to the ordered porous metal nanostructures: (a) metal filling; (b) template removal.
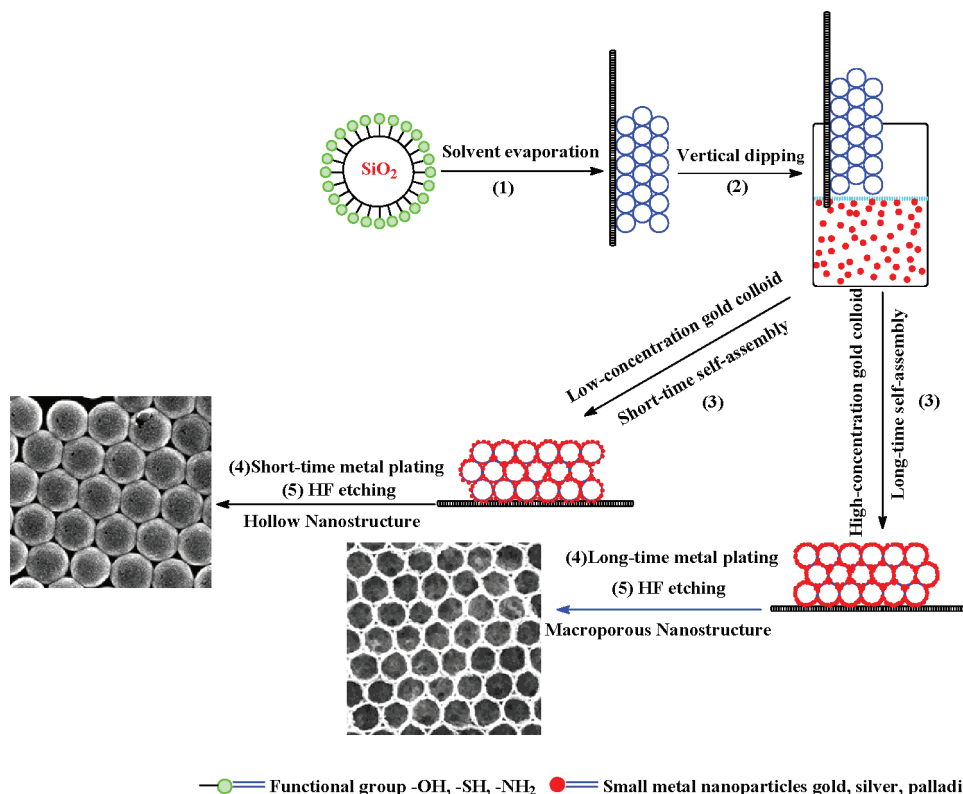

FIGURE 2. Schematic diagram of the synthetic procedure for ordered bimetallic nanostructures with hierarchical porosity.

ity. First applications of such structures in SERS and in catalysis are also demonstrated.

## Making Bimetallic Nanostructures with Hierarchical Porosity

An overview of our preparative strategy is schematically shown in Figure 2 and will be outlined in detail in this paragraph.

1. Modification and Assembly of Monodisperse Silica Microspheres. Silica is one of the most commonly used materials to fabricate colloidal crystals because it is possible to synthesize highly monodisperse spherical particles of this material with size variations of below 5% and diameters controllable in the range from tens of nanometers to several micrometers. Importantly, the surfaces of the silica spheres are usually terminated with silanol groups ($-Si-OH$), enabling covalent grafting of versatile functional groups such as $-NH_2$,

$-SH$, $-COOH$, $-NCO$ and $-CHO$ onto their surface for different purposes. Alternatively, these functional groups can be introduced into the surface layer of polymer spheres such as poly(methyl methacrylate) (PMMA) and polystyrene (PS) by adding the appropriate component to the monomer solution before polymerization. The silica microspheres described below are produced using an improved Stöber growing procedure.[13] At the end of the synthesis, the particles are modified with 3-aminopropyltrimethoxysilane (APTMS) molecules. After careful washing, the resulting APTMS-modified silica microspheres are dispersed in anhydrous ethanol. Slow evaporation of the solvent generates high-quality colloidal crystal films on a vertically held substrate. The size distribution of the silica microspheres is the key parameter in yielding 3D long-range ordering while interactions between the microspheres and the substrate also play an additional role in this ordering.

2. Incorporation of Metal Nanoparticles. To ensure a controllable and uniform deposition of metal in the interstitial space of the colloidal crystal, it is important to first attach small metal nanoparticles onto the surface of the APTMS-modified silica microspheres within the preformed colloidal crystal. This step can be easily performed by immersing the colloidal crystal template into an aqueous solution of small gold nanoparticles. In this procedure, 3-nm citrate-stabilized gold nanoparticles are chosen instead of others mainly based on the following considerations: First, they can be easily and reliably prepared in this size range, and they are desirable for further metal plating. Second, no further heating is required to remove organics from the gold surface, which is of great importance for the successful fabrication of the ordered hollow nanostructured films.

Scanning electron microscopy (SEM) images clearly show that after the incorporation of the small gold nanoparticles the colloidal crystal film still retains its original hexagonal packing, and 3D ordered arrays of APTMS-modified silica microspheres are revealed from the cleaved edge of the colloidal crystal film (Figure 3a). Higher magnification SEM images demonstrate a substantial coverage with gold nanoparticles on the surface of the silica microspheres. These small gold nanoparticles are well separated from each other on the surface, and no obvious particle aggregation is observed (Figure 3b). The prevention of nanoparticle aggregation within the 3D ordered colloidal crystal (3DOCC) film can be ascribed to the unique structural properties of the 3DOCC film in which the largest voids for the infiltration of small gold nanoparticles are about 45% of the size of the APTMS-modified silica microspheres and by this being much larger than the gold nanoparticles.[14] From higher magnification SEM images, the coverage of the silica spheres with gold nanoparticles is estimated to be approximately 27%, which is consistent with the previously reported coverage of gold nanoparticles on planar amine-modified surfaces of solid substrates.[15] The quality of the gold-coated 3DOCC film sensitively depends on the kind of functional molecules employed and the size and concentration of the gold nanoparticles. When OH-terminated silica microspheres were used as building blocks for the fabrication of gold-coated 3DOCC films nanoparticle aggregation was clearly observed in the interstitial space of the 3DOCC film and on the surface of the silica microspheres, which is undesirable for further metal plating. As discussed below, a high concentration of gold nanoparticles leads to the formation of mesoporous structures consisting of interconnected nanoparticles in the interstitial space of the 3DOCC film besides the gold nanoparticle film on the surface of the silica
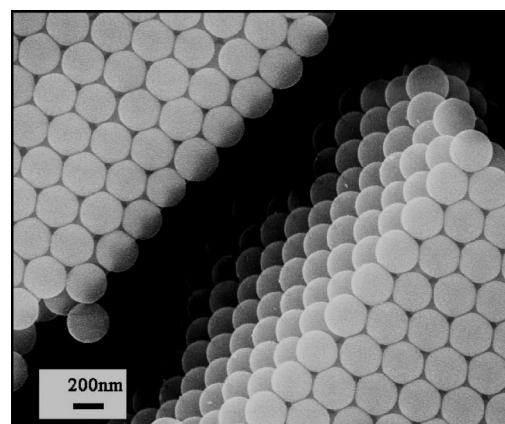
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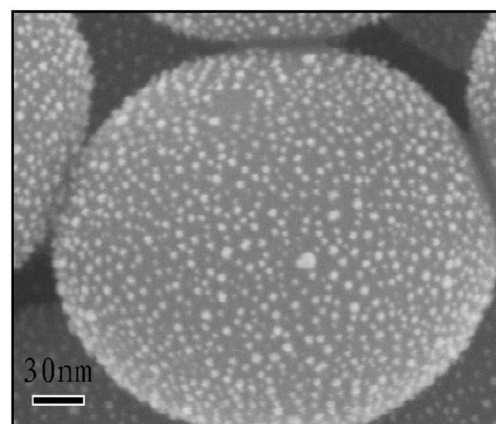
(b)

FIGURE 3. (a) SEM image of a 3D gold-coated silica colloidal crystal film and (b) a corresponding high-magnification image.

microspheres. Our initial attempts to organize 12-nm gold nanoparticles into a 3DOCC films was less successful most probably because these particles are too large to infiltrate them completely into the whole interstitial space of the 3DOCC film and electrostatic repulsive forces exist between the larger particles, which leads to lower coverage with gold nanoparticles being disadvantageous for further metal plating.[16]

In addition to the gold nanoparticles, many other metal nanoparticles including silver and palladium can be introduced into the 3DOCC films for designing different kinds of bimetallic nanostructures. The approach for incorporating small silver nanoparticles is similar to that used for gold nanoparticles: 3-mercaptopropyltrimethoxysilane (MPTMS)-modified silica microspheres are used as building blocks for the assembly of the 3DOCC template. Subsequent immersion into an aqueous solution of 4-nm citrate-stabilized silver nanoparticles results in the successful incorporation of silver nanoparticles in the 3DOCC film. Nevertheless, it should be mentioned that there is a disadvantage for use of silver nanoparticles for fur-

ther metal deposition. Upon exposure to metal anions such as $AuCl_4^-$, $PtCl_6^{2-}$, or $PdCl_4^{2-}$, a part of the silver nanoparticles oxidize to Ag^+ cations and metal anions are reduced to yield zero-valent metal nanoparticles. Due to the presence of Cl^- ions in the growing solution, Ag^+ cations may further react with them to produce AgCl precipitates. As for the incorporation of small palladium nanoparticles, it is not necessary to first modify the surface of the silica microspheres with other functional groups. We directly immerse the 3DOCC film into the aqueous solution of the PVP-stabilized palladium nanoparticles, yielding palladium nanoparticle-coated 3DOCC films. To prepare different kinds of nanostructures, different immersion times and different concentrations of the aqueous metal nanoparticles are required.

3. Metal Plating and Removal of the Template. The colloidal crystal template loaded with the small metal nanoparticles is dipped into a metal plating solution for further metal deposition. During the plating process, the small metal nanoparticles can serve as seeds to accelerate the reduction of metal ions.[17] For many metals, their plating solutions are commercially available. The detailed plating procedures that are often used in our work for gold, silver, platinum, palladium, and copper can be found in refs 18–22, respectively.

The metal plating procedures are of utmost importance for producing high-quality ordered porous metal nanostructures as desired, since they determine the quality and the structure of the resulting materials and hence their properties. For example, when the mirror reaction solution rather than the just-described silver plating solution is used to deposit silver metal, the interstitial space of the gold-coated 3DOCC film is unevenly filled and thus upon removing the template poor-quality macroporous Ag/Ag nanostructures are obtained. The choice of the metal plating procedures to be employed is determined by several factors including their reactions in the presence of the 3DOCC films loaded with small metal nanoparticles, the desired size of the particles used as "building blocks" in the resultant materials, and the ability to remove the template without destruction.

Temperature is another important factor that determines the quality of the resulting metal materials. For instance, low temperature is advantageous for uniform and controllable deposition of Pt and Pd metals in the interstitial space of the 3DOCC films because low temperatures make a slow reduction reaction process possible, evidenced by a slow color change of the 3DOCC film loaded with small metal nanoparticles.

Removing the silica template with dilute HF solution yields self-supporting flakes with brightly colored reflections. They can be transferred onto desired substrates with little damage. Since the silica template is removed at room temperature, shrinkage of the pores is avoided. By carefully combining the above-mentioned parameters, the colloidal crystal template technique can be used to selectively produce different types of ordered bimetal nanostrucutres with hierarchical porosity.[20]

4. Resulting Structures. Ordered macroporous structures are the most typical examples that are prepared by the colloidal crystal template technique. A SEM top view of the macroporous structure formed via our strategy is demonstrated in Figure 4a. The resultant material exhibits relatively uniform porosity with hexagonal close packing, and the size of these pores match that of the starting silica microspheres, indicating that negligible shrinkage of the metallic structure occurs. Furthermore, it is noted that there are three dark regions inside each pore corresponding to the air spheres of the underlying layer, revealing that these spheres are indeed close-packed. The small nanoparticles around the large pores in the original interstitial space, yielding a mesoporous structure, can be clearly observed in corresponding higher magnification images (see inset).

Ordered hollow metallic nanostructures are another kind of important porous material. We found that if we properly tailor the experimental conditions, the method presented above is also applicable for the production of such materials.[20] Strictly speaking, the ordered hollow metal nanostructures discussed herein also belong to the macroporous structure according to their pore size. Nevertheless, these materials exhibit their unique structural characteristics that differ strongly from the ordered macroporous metal nanostructures mentioned above, and thus we list them as a separate type. Compared with the ordered macroporous metal nanostructures, the ordered hollow metal nanostructures have been less extensively studied, probably because of the difficult preparation. SEM investigations show that after removal of the colloidal crystal template, both the long-range ordering and the spherical shape are well preserved from the starting template (Figure 4b,c). Because the original template can be produced from silica microspheres with different sizes, the resulting nanostructures exhibit a tunable hollow volume. The hollow structure character of these materials is evidenced by inspection of the broken spheres seen in Figure 4b,c. A closer look reveals another interesting feature, namely, the existence of a hole with an average diameter of about 20 nm in almost every hollow sphere. These holes are arranged in order and the distances between neighboring holes equals roughly the center-to-center distances of the hollow metallic spheres. Higher
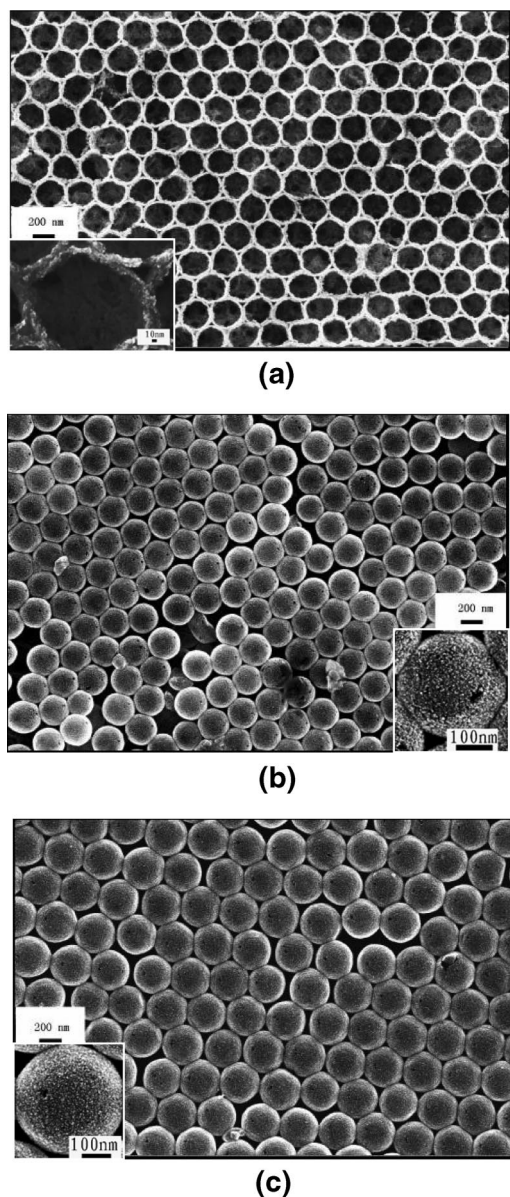
FIGURE 4. (a) SEM image of an ordered macroporous Au/Pt nanostructure and SEM images of ordered hollow Au/Pt nanostructures produced using (b) 277 nm and (c) 300 nm silica colloidal crystals as templates. The insets show the corresponding high-magnification images. Adapted from Lu et al.[20]

magnification SEM images show that these hollow spheres consist of many interconnected small nanoparticles (<10 nm in average diameter). The nanoparticle framework of the as-prepared materials provides yet another level of porosity that gives the structure a very high surface area, as the size of the small pores and the overall surface area are determined by the size of the Au/Pt nanoparticles.

5. Formation Mechanism. Previous studies showed that when the colloidal crystal template was immersed into a concentrated aqueous solution of gold nanoparticles, small gold nanoparticles were deposited in the interstices of the colloi-

dal template by an infiltration process, forming a mesoporous structure around the silica spheres. Since the porosity allowed the solvent to flow freely through the deposit, the pores could be nearly completely filled with gold nanoparticles.[5,8]

The situation is different in the present work. After modification of the silica spheres with the appropriate molecules, these molecules are grafted onto the surface of the silica spheres heading their functional groups such as $-NH_2$, $-SH$, and $-COOH$ outward. The immersion of this modified colloidal template into an aqueous solution of small metal nanoparticles leads to an intense coverage of metal nanoparticles on the surface of the silica spheres. If the concentration of the metal nanoparticles is relatively low and the immersion time is comparatively short, the assembly of the metal nanoparticles on the surface of the silica spheres should be predominant. A small quantity of residual metal nanoparticles in the interstices of the colloidal template can be removed by rinsing with deionized water (or by deposition on the surface of the silica spheres during the N_2-drying process). Subsequent electroless deposition of other metal occurs only on the surface of the silica spheres, and thus the removal of the colloidal template leads to the production of ordered porous bimetallic nanostructures constructed from hollow spheres. In contrast, if the concentration of the metal nanoparticles is relatively high and the immersion time is relatively long, besides the assembly of the metal nanoparticles on the surface of the silica spheres, a larger amount of them are found in the interstices of the colloidal template. Together with those on the surface of the silica spheres they associate into a larger mesoporous structure. The subsequent metal deposit leads to an almost complete infiltration of the pores of the colloidal template. By removing of the colloidal template, macroporous bimetallic nanostructures with hierarchical porosity are gained.

Applications

1. Catalysis. The ordered bimetallic nanostructures with hierarchical porosity may exhibit some unusual properties in comparison with their solid counterparts with the advantages of high surface areas, periodicity, and saving of material, and thus they may yield many promising applications. For instance, Hyeon et al. demonstrated that hollow Pd spheres possess excellent catalytic activity in Suzuki reactions and could be recycled without loss of the catalytic activity.[23] Therefore, it is only natural to explore their catalytic properties.

The ordered bimetallic Au/Pt (Au/Pd, Ag/Pt, Ag/Pd, Pd/Pt) nanostructures with hierarchical porosity discussed above are particularly desirable candidates for catalytic applications for the
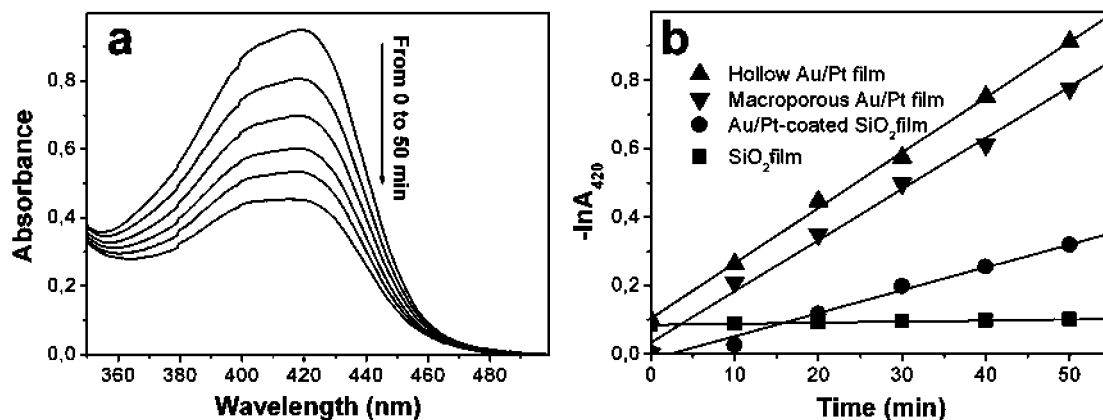
FIGURE 5. (a) Spectroscopic evolution of $Fe(CN)_6^{3-}$ in the presence of an ordered hollow Au/Pt nanostructure and (b) pseudo-first-order plots in the presence of different nanostructures. Adapted from Lu et al.[26]

following reasons: (1) these nanomaterials possess uniform macropores (typically a few hundred nanometers) with periodic arrays, bicontinuous networks, and highly accessible surface area, allowing efficient mass transport through the pores and less diffusional resistance to active sites; (2) these nanomaterials are hierarchical macroporous–mesoporous structures; this specific structural characteristic gives these materials a very high surface area and enhanced selectivity; (3) the catalytic performance of these nanomaterials may be improved by adjusting the molar ratio between the constituting elements.

We investigated the catalytic performance of the as-prepared nanostructures by a typical redox reaction between $Fe(CN)_6^{3-}$ and $S_2O_3^{2-}$ as described in ref 24.

$$Fe(CN)_6^{3-} + S_2O_3^{2-} \rightarrow Fe(CN)_6^{4-} + 1/2S_4O_6^{2-} \quad (1)$$

Figure 5a shows spectroscopically the evolution of $Fe(CN)_6^{3-}$ upon the reaction with $S_2O_3^{2-}$ in the presence of the as-prepared ordered hollow Au/Pt nanostructure. The absorption spectrum of $Fe(CN)_6^{3-}$ suffers an evident change in the band peak intensity from 0 to 50 min. For reaction 1, pseudo-first-order kinetics could be used to evaluate the catalytic rate.[25] The resulting pseudo-first-order plot of $-\ln A_{420}$ versus time gives a good straight line (Figure 5b). Here A_{420} stands for the absorbance of $Fe(CN)_6^{3-}$ at 420 nm. The rate constant for the reaction in the presence of the ordered hollow Au/Pt nanostructure is determined from the slope of the straight line to be 1.62×10^{-2} min^{-1}. For comparison, the same reaction has been applied to investigate the catalytic properties of the other samples. The rate constants are determined to be 1.49×10^{-2} min^{-1} for the macroporous Au/Pt nanostructure, 6.71×10^{-3} min^{-1} for the Au/Pt-coated SiO$_2$ film, and 3.21×10^{-4} min^{-1} for the bare SiO$_2$ film. All samples are on a silicon wafer (0.8 cm × 0.8 cm) and are examined under similar experimental conditions at 35 °C. It is

evident that both the ordered hollow Au/Pt nanostructure and the ordered macroporous Au/Pt nanostructure exhibit better catalytic ability due to their special structural characters.[26]

We also investigated the effect of the molar ratio between Au and Pt on the catalytic performance of the ordered hollow Au/Pt nanostructures. The experimental results demonstrate clearly that their catalytic activity was improved by increasing the content of gold vs platinum. Our studies have not progressed far enough to allow us to extract quantitative correlations between the rate constant and the gold content, but this will obviously be a fruitful avenue for further investigation.

2. Surface-Enhanced Raman Scattering (SERS) Substrates. The need for SERS substrates with good stability, easy and reproducible preparation, and large intensity enhancement has been well recognized in its practical applications. Recent studies show that highly ordered porous metal (Au and Ag) nanostructured films prepared by a colloidal crystal-template method can provide an excellent platform for this purpose.[8,26,27]

The SERS enhancement mechanisms can be roughly divided into two kinds, namely, electromagnetic field enhancement and chemical effects.[28–30] The detailed description for electromagnetic field enhancement and chemical effects can been found in several excellent review articles and books.[20,28] The SERS Stokes signal, $P_{(Vs)}^{SERS}$, can be estimated according to the following equation.[30]

$$P_{(Vs)}^{SERS} = N\sigma_{ads}^R |A(\nu_L)|^2 |A(\nu_S)|^2 I(\nu_L)$$

where $I(\nu_L)$ is the excitation laser intensity, σ_{ads}^R is the Raman cross section of the target molecules, N is number of molecules involved in the SERS process, and $A(\nu_L)$ and $A(\nu_S)$ are field enhancement factors. This equation shows that the SERS signal enhancement is proportional to the fourth power of the

field enhancement factor.

Ordered porous metal nanostructures possess several advanced features that are particularly well-suited for a SERS signal enhancement. First, as discussed earlier, tunable hierarchical porous structures can provide high surface areas that allow more analyte to adsorb and thus an increasing the number of target molecules N. Second, a long-range periodicity has been demonstrated to improve their performance as SERS substrates. According to Gaponenko, the photon density of states redistribution may readily occur in periodic porous metal nanostructures, which leads to an increase of the density of optical modes and thus to a superior enhancement of the Raman intensity of the target molecules.[31] Third, in metal nanostructures, collective electron oscillations known as plasmons can be excited by light. If the excitation is confined near to the surface of metal nanostructures, it is called a surface plasmon.[28–33] In this case, many crevices are generated between these macropores during the preparation process, which is particularly desirable for the SERS effect. It is known that SERS is a very local phenomenon occurring at crevices or in the pores of a rough surface. Excited by the incident radiation, a collective surface plasmon is trapped at these crevices, creating a huge local electric field at these sites and by this increasing field enhancement factors $A(\nu_L)$ and $A(\nu_S)$.[32,33] According to Xu et al., an electric field enhancement of 10^{10} could be achieved between two nanoparticles with a 1-nm spacing. These local resonant plasmon modes at long-range ordered crevices are able to produce an enhancement of as large as 10^7 in the Raman intensity of the target molecules adsorbed at these particular crevices.[33] Fourth, the walls within ordered porous metal nanostructures consist of many interconnected nanoparticles, thus providing another level of porosity that gives the structure an even higher surface area. Importantly, a large electric field enhancement can also occur between these neighboring nanoparticles, allowing for a further increase of SERS signal intensity. Fifth, chemical effects may result from the interactions between chemisorbed probe molecules and hot electrons that are produced through plasmon excitation.[30] A "roughness" constructed by periodic crevices and walls consisting of interconnected metal nanoparticles is very desirable for chemical effects because they can provide pathways for the hot electrons to the probe molecules, thus increasing the Raman cross section of the target molecules.[30]

SERS applications of ordered porous metal nanostrutured films are investigated in our group.[27] We selectively prepared an ordered macroporous Au/Ag nanostructured film and an ordered hollow Au/Ag nanostructured film as described ear-
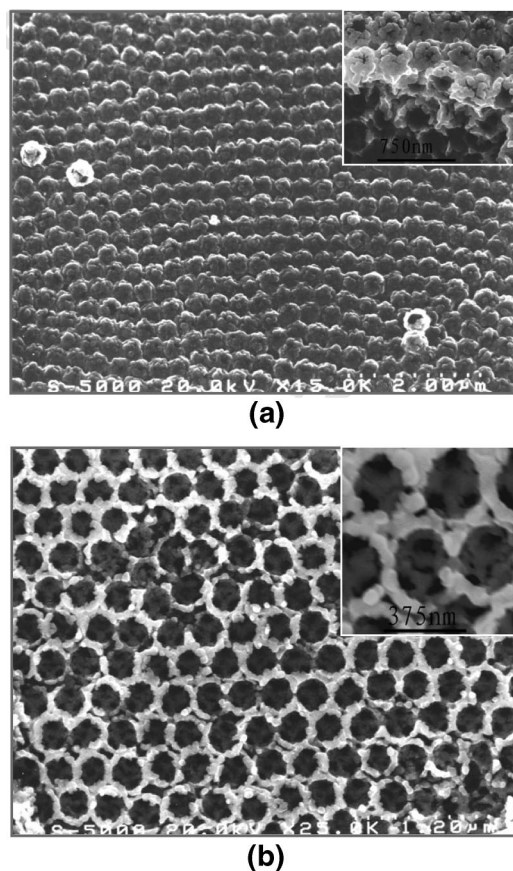
FIGURE 6. SEM images of (a) an ordered hollow Au/Ag nanostructure and (b) an ordered macroporous Au/Pt nanostructure produced using 267-nm silica colloidal crystals as templates. The insets show the corresponding high-magnification images. Adapted from Lu et al.[27]

lier. A SEM investigation reveals that after removal of the silica template by HF etching both the long-range ordering and the spherical shape from the original template are well preserved in the as-prepared porous metal nanostructures. In the hollow nanostructures, relatively uniform Au/Ag shells are constructed by many larger interconnected nanoparticles in the size range of 50–80 nm, leading to the formation of a rough surface (Figure 6a), and importantly, such a particle size range is very efficient for SERS excitation at 514.5 nm. The hollow feature of the as-prepared samples is evidenced by the broken Au/Ag shells. In the case of the macroporous nanostructures, it is noted that the open voids and the walls consisting of larger interconnected aggregates of nanoparticles form pore structures (Figure 6b). These pores are well-ordered in a hexagonal packing, and such ordered structures can extend several hundreds of micrometers. Their performance as SERS substrates is evaluated by using rhodamine 6G (R6G) as a probe molecule. For comparison, a silver film is also produced via the "mirror reaction" because such a film can exhibit high SERS intensity for R6G molecules.[34,35] SERS signals corre-
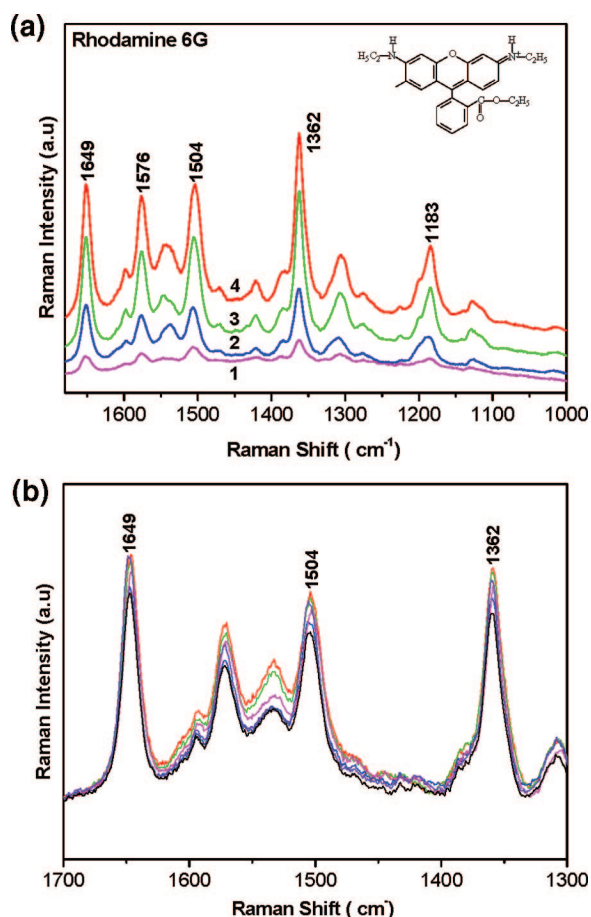
FIGURE 7. SERS spectra of (a) 50 nM R6G on different substrates (1, a Ag film prepared by the mirror reaction; 2, an ordered Au/Ag-coated silica film; 3, an ordered macroporous Au/Ag nanostructured film; 4, an ordered hollow Au/Ag nanostructured film) and (b) 20 nM R6G on the different points of an ordered hollow Au/Ag nanostructured film. Adapted from Lu et al.[27]

sponding to R6G are observed in either case, but clearly the porous Au/Ag nanostructured films exhibit the highest SERS signal intensity (Figure 7a). In addition to the large intensity enhancement, it is also found that the SERS spectra are highly reproducible on these porous nanostructured films (Figure 7b). One of the important potential applications of the SERS technique is the rapid detection of DNA fragments. Unlike fluorescence techniques, the SERS technique does not require any labeling step because it is a technique of vibrational spectroscopy that gives detailed fingerprint information of DNA bases.[36] To explore the capability of the as-prepared porous Au/Ag nanostructured films for the detection of DNA fragments, DNA bases, including adenine and cytosine, are chosen as a target molecules. Primary experimental results show that these porous metal nanostructured films are highly desirable for detection of DNA bases by SERS technique in terms

of high Raman intensity enhancement, good stability, and reproducibility.[37]

Summary and Outlook

The studies discussed in this Account have demonstrated the versatility of colloidal crystal templates to selectively design different types of novel porous metallic nanostructures and their promising applications. Despite rapid advances in this area from the late 1990s, the macroporous metal nanostructures with long-range ordered lattices and their applications are still in an early stage of technical development. A number of challenges remain before these materials will find viable practical applications. First, the diversity of the template materials is limited to only silica and polymers including PMMA and PS. In this regard, it is necessary to develop new strategies for producing monodisperse colloidal particles with different materials or different shapes. This may lead to the creation of a series of distinctive properties. Some work has recently started to address this issue by exploring biological templates for synthesizing such colloidal particles and investigating their feasibility as building blocks for the formation of colloidal crystals.[38] Second, the fabrication of colloidal crystals with superior quality and advanced features has been met with limited success so far. Much effort including patterning of solid template-directed or aqueous droplet template-directed crystallization methods has been presented in this field. However, their feasibility as templates in creating long-range ordered macroporous metal nanostrutures has still not been explored.[39] Third, as discussed above, although various methods have already been successfully applied to fabricate highly ordered macroporous metal nanostrutures, one of primary challenges is how to achieve control over the infiltration of the desired composite metals into the interstitial voids of the templates that often determines the quality and the structures of the resultant materials and hence their properties.

Besides resolving the above-mentioned questions, future work in this field is likely to continue to focus on the exploitation of potential applications of these materials.[40] We believe that the rapidly growing interest in macroporous metal nanostrutures will certainly fuel the excitement and stimulate research in this field.

Note Added after ASAP. This paper was posted to the web on January 25, 2008 with a typographical error in the Conspectus. The revised version was posted on January 30, 2008.

BIOGRAPHICAL INFORMATION

Lehui Lu received his B.S. degree and Ph.D. degree in chemistry from Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, in 2000 and 2003, respectively, under the direction of Professor Hongjie Zhang and Professor Shiquan Xi. He joined the faculty of the State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, in 2007 as a full professor.

Alexander Eychmüller studied Physics receiving his Ph.D. at the University of Göttingen, Germany, and the Max-Planck-Institute for Biophysical Chemistry in 1987 working under the supervision of Dr. K.-H. Grellmann and Prof. A. Weller. A postdoctoral stay at the University of California, Los Angeles, with Prof. M. A. El-Sayed was followed by an appointment as a researcher at the Hahn-Meitner-Institute Berlin in the department of Prof. A. Henglein. He moved to the University of Hamburg with Prof. H. Weller, habilitated in 1999, and was appointed full professor at the TU Dresden in 2005.

FOOTNOTES

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