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### Introduction

Bimetallic core-shell nanoparticles (NPs) have attracted tremendous attention in recent years owing to their unique and novel optical, electrical and catalytic properties.<sup>1-9</sup> Recently, more and more studies focus on the catalysis of bimetallic core-shell NPs because the catalytic activity of such structured NPs can be greatly influenced by their size, structure and compositions.<sup>10-13</sup> Up to now, different methods have been developed for fabricating well-dispersed bimetallic NPs.<sup>14-16</sup> A typical route of synthesizing bimetallic core-shell NPs is by reducing a second metal onto the presynthesized cores. Although such a method can effectively control the size and shape of the NPs, the problem of aggregation has plagued

## Fabrication of thermally stable and active bimetallic Au–Ag nanoparticles stabilized on inner wall of mesoporous silica shell<sup>†</sup>

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A general method has been developed for the fabrication of highly dispersed and thermally stable bimetallic Au–Ag nanoparticles (NPs) stabilized on the inner wall of a mesoporous silica shell. In our approach, gold particles were formed in the first step on carbon spheres decorated with  $Sn^{2+}$  cations. Upon Ag<sup>+</sup> adsorption and reduction by L-ascorbic acid in the second step, specific nanoparticles with a gold–silver alloy core and a silver nanoshell have been formed. Important evidence of the core–shell configurations of the bimetallic Au–Ag nanoparticles were clearly characterized by UV-vis, TEM and HAADF-STEM observations combined with elemental mapping and line scans. The mesoporous silica outer shell was obtained through the hydrolysis and condensation of the precursors tetraethoxysilane (TEOS) in a basic condition and cetyltrimethylammonium bromide (CTAB) as a structure-directing agent. On this basis, the nanoreactors were fabricated after calcination, which further serves as a nanoreactor for the reduction of *p*-nitrophenol. Furthermore, such particles have been found to be thermally stable and their sizes remain substantially unchanged even upon calcination in air at 500 °C and a reduction treatment in H<sub>2</sub>. Potentially, the method can be developed into a general approach to synthesize other highly dispersed and thermally stable bimetallic nanoparticles stabilized on the inner wall of a mesoporous silica shell.

us, especially when using a thermal treatment for the removing the protective agents.

Monodispersed mesoporous hollow spheres should be an wonderful candidate to solve such a problem.<sup>17-19</sup> For instance, when functional noble-metal nanoparticles are located into a hollow silica shell, these composite spheres can not only effectively isolate noble metal NPs and protect them against aggregation, but also allow the diffusion of small molecules in and out of the reactors.<sup>20-26</sup> So far, the fabrication of monodispersed mesoporous hollow spheres can be broadly divided into two categories: template-free and templating approaches.<sup>27-29</sup> Although the process of the first method is simple, templating approaches offer important advantages, including narrow size-distribution products with well-defined structural features. However, there are, nevertheless, inherent drawbacks in the template removal process. The multiple metal particles encapsulated in the hollow spheres tend to sinter and grow into larger particles after calcination, especially in the cases where they are subjected to a thermal treatment for the removal of a surfactant or template due to heat- and atmosphere-induced sintering and restructuring. To prevent or reduce sintering, many attempts have been made, including confining gold particles in the nanopores of a mesoporous support and so on.<sup>30-32</sup> Generally, aminated organic/

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<sup>&</sup>lt;sup>b</sup>Graduate University of the Chinese Academy of Sciences, Beijing, 100049, China †Electronic supplementary information (ESI) available: The TEM of Au–Ag@SiO<sub>2</sub> after the reduction treatment by H<sub>2</sub>; calculating the mean diameters of the (Au– Ag)/C@mSiO<sub>2</sub> composite microspheres; the reaction almost does not occur before adding catalysts; the TEM of the Au@mSiO<sub>2</sub> composite microspheres and the distribution of the pore size. See DOI: 10.1039/c3dt51546j

In this work, we have successfully used a successive twostep reduction approach to prepare (Au-Ag)/C composite spheres in which Au-Ag bimetallic NPs are well-anchored on the carbon surfaces. On this basis, a nanoreactor composed of a mesoporous silica shell and bimetallic NPs residing in the silica shell was fabricated. The nanoreactor framework with metal NPs act as a core anchored on the inner wall and the mesoporous silica acts as a shell to not only stabilize the metal particles, but also allow the diffusion of small molecules in and out of the reactors. A synthesized route is illustrated in Scheme 1. Firstly, monodisperse CNs with a specific particle size were prepared as the support and Au NPs were further loaded onto the surfaces of the CNs. Then, the CNs decorated with Au NPs were dispersed in water and a certain amount of PVP and L-ascorbic acid were responsible for the creation of the Au-Ag bimetallic heterostructures supported on the carbon spheres. After the addition of a AgNO<sub>3</sub> solution, the (Au-Ag)/C composite NPs were obtained. Herein, the CNs not only provide a platform for loading metal nanoparticles but also serve as a sacrificial hard template for the fabrication of a nanoreactor with a yolk-shell structure. Secondly, the mesoporous silica outer shell is obtained through the hydrolysis and condensation of the precursors tetraethoxysilane (TEOS) in a basic condition and cetyltrimethylammonium bromide (CTAB) as a structure-directing agent. Finally, a simple extension of this process yields (Au-Ag)@mSilica yolk-shell nanostructures via calcination in air at 550 °C for 4 h.

### **Experimental methods**

#### Materials

Hexadecyl trimethyl ammonium bromide (CTAB) and tetraethyl orthosilicate (TEOS) were purchased from Sigma-Aldrich. Glucose, stannous, gold chloride, silver nitrate and vitamin C were purchased from Sinopharm Chemical Reagent Co., Ltd.



#### Synthesis of the carbon nanoparticles (CNs)

Glucose (4.5 g) was dissolved in 50 ml to form a clear solution and then transferred into a Teflon-sealed autoclave. The autoclave was maintained at 180 °C for 4 h.<sup>33</sup> The precipitation was isolated by centrifugation, cleaned by four cycles of centrifugation–washing–redispersion in water and in ethanol and finally oven-dried at 60 °C for further use.

# Synthesis of the bimetallic core-shell nanoparticles on the surfaces of the CNs

Synthesis of the Au/C nanoparticles (NPs). In a typical process, 0.1 g of carbon NPs dispersed in 50 ml of distilled water was added to a three-necked flask and 0.1 g of SnCl<sub>2</sub> dissolved in 20 ml of a 0.02 M HCl solution was added for sensitization. The mixture was supersonicated for 15 min, aged for 3 h and subjected to three centrifugation–water wash–redispersion cycles and dispersed in 50 ml of distilled water. Then, a solution of HAuCl<sub>4</sub> (2.9 mM, 5 ml) was added into the solution and further stirred for 1 h. The final products was subjected to five centrifugation–water wash–redispersion cycles and oven-dried at 60 °C overnight.

Synthesis of the (Au–Ag)/C NPs. The Au/C composite NPs obtained from the last step were first dispersed in a solution containing 50 ml of  $H_2O$ , 10 ml of PVP ( $K_{30}$ , 0.05 g) and 20 ml of L-ascorbic acid under stirring. Then, 10 ml of AgNO<sub>3</sub> was injected into the above-mentioned mixture using a pipette. The molar concentration of L-ascorbic acid and AgNO<sub>3</sub> in the final solution was 1.76 mM and 0.21 mM, respectively. The final products were subjected to two centrifugation–water wash–redispersion cycles and dried at 60 °C for 12 h.

Synthesis of the (Au–Ag)@mesoporous  $SiO_2$  nanoreactor. The obtained (Au–Ag)/C NPs were dispersed in a solution containing 100 ml of distilled water, 60 ml of ethanol and 1.45 ml of an ammonia aqueous solution and then 0.3 g of CTAB dispersed in 15 ml of ethanol was added to the solution with vigorous stirring for 30 min. Afterward, 0.3 ml of TEOS was added to the solution drop by drop and further stirred for 6 h.<sup>34</sup> The products were separated by five centrifugation–water–ethanol wash–redispersion cycles. Finally, calcination was carried out in air at 550 °C with a heating rate of 5 °C min<sup>-1</sup> and maintained at that temperature for 4 h to eventually remove the CTAB and carbon template.

# Details for the catalytic reaction of the reduction of *p*-nitrophenol (4-NP)

The reduction of 4-NP by NaBH<sub>4</sub> was chosen as a model reaction to test the catalytic activity of the catalysts. Typically, the reaction proceeded under room temperature conditions. To a mixture of 184 mg of NaBH<sub>4</sub> dispersed in 2.3 ml of H<sub>2</sub>O, 16.7 ml of 0.18 mmol L<sup>-1</sup> 4-NP and 10 ml of distilled water were added. Then, a certain amount of the catalyst (Au-Ag)-(@mSiO<sub>2</sub> or Ag(@mSiO<sub>2</sub> microspheres were added into the mixture under stirring. The mixture was kept stirring and we took 2 ml of the mixture by pipette every 5 min. The samples were analyzed immediately on an analyticjena specord 50 UV-visible spectrometer. The concentration change of *p*-nitrophenol was determined by the absorbance at its maximum peak. In the presence of the catalysts, the absorption of *p*-nitrophenol at 400 nm decreases along with a concomitant increase of the ~300 nm peak of *p*-aminophenol. The absorption spectra of the solution were measured in the range of 250–550 nm.

#### Characterization

Structural and morphological investigations of the samples were performed by a JSM-6701F scanning electron microscope (SEM) and transmission electron microscope (TEM, Tecnai-G2-F30). A Lambda 750 ultraviolet and visible (UV-vis) spectrophotometer was employed for the analysis of the 4-NP reduction and to investigate in detail the structural evolution during each step of the preparation. X-ray diffraction using Cu–K $\alpha$  radiation (XRD, Panalytical X'Pert Pro) and Brunauer–Emmett–Teller (BET, ASAP 2020M) was employed for the analysis of the mesoporous structure.

### **Results and discussion**

As shown in Fig. 1a, Au NPs were well-anchored onto the surfaces of carbon spheres after the purification and collection of the synthesized Au/C NPs processes. Actually, carbon/metal composite particles can also be used for the catalytic reaction. However, due to stability and reusability considerations, carbon/metal composite particles are not suitable because the negatively charged Au NPs are absorbed onto the surface of the carbon spheres through electrostatic attraction. We speculated that the mechanism of depositing bimetallic NPs onto the surfaces of carbon spheres can be summarized in two successive steps. Firstly, the negatively charged AuCl<sub>4</sub><sup>-</sup> ions were strongly adsorbed on the positively charged Sn<sup>2+</sup> cations absorbed on the surface of the carbon spheres. Then, the Sn<sup>2+</sup> cations served as a strong reductant for the reduction of local  $AuCl_4^-$  (Scheme 2). Secondly, the negatively charged Au NPs were absorbed on the surface of the carbon spheres through electrostatic attraction. Au NPs with an average size of 8 nm (Fig. 1c) were synthesized and no agglomeration could be observed (Fig. 1b). Following that, Ag<sup>+</sup> cations were allowed to adsorb preferentially on the negatively charged gold particle surface via electrostatic attractions and metallic bonding.35,36 Following the reduction by L-ascorbic acid, a silver nanoshell was produced on the gold core. The Au-Ag structured bimetallic NPs were well-anchored to the surface of the carbon spheres



Fig. 1 The low and high magnification TEM image of the (a, b) Au/C NPs and (c, d) (Au–Ag)/C NPs and their corresponding size distribution (c, f).

(Fig. 1d). The NPs increased slightly and a wide distribution of particle diameters was observed from the histogram, but aggregation barely occur (Fig. 1e). The mean size of the particles was 15 nm and the largest diameter was about 20 nm. Both investigations revealed that the products were well-dispersed as individual spherical nanoparticles immobilized on carbon surfaces. Taking into account the presence of a hydroxymethyl group on the surface of the carbon sphere, we have to recognize that trace monometallic Ag particles could arguably exist in our method, but, observed from our results, bimetallic particles are predominant because of strong bimetallic interactions and a very low concentration of  $Ag^+$  cations.<sup>33,37</sup>

As shown in Fig. 2a, the surfactant-templating process results in a CTAB/SiO<sub>2</sub> mesophase coated on the (Au-Ag)/Ccomposite NPs. This shows that the average size of the spheres were about 450 nm. In order to avoid the collapse of the shell during the process of calcination, we believe that a relatively thick shell is more suitable. Fig. 2b shows a silica shell with a thickness was about 120 nm. As can be seen in Fig. 2c, the synthesized  $(Au-Ag)/C@SiO_2$  composite microspheres were visualized by STEM imaging. This technique enables high-contrast imaging of high-*Z* elements (such as Au or Ag) against the lower-*Z* background (such as SiO<sub>2</sub>). Fig. 2d is a high



Scheme 2 The mechanism of depositing Au NPs onto the surfaces of the carbon spheres.



**Fig. 2** The low and high magnification TEM (a, b) and STEM image (c, d) of the (Au–Ag)/C@SiO<sub>2</sub> NPs.



Fig. 3 (a) TEM image (a) and STEM image (b) of the hollow (Au–Ag)@mSiO<sub>2</sub> NPs; the morphology after the reduction treatment by  $H_2$  (c); a series of UV-vis spectra during each step of the preparation.

magnification of the STEM imaging of the synthesized nanocomposite NPs. The contrast clearly shows that the  $(Au-Ag)/C@SiO_2$  composite microspheres were successfully obtained through the hydrolysis and condensation of the precursor tetraethyl orthosilicate (TEOS).

We fabricated hollow  $(Au-Ag)@mSiO_2$  composite microspheres after calcination at 550 °C for 4 h to remove the carbon core and surfactant, containing Au-Ag bimetallic NPs anchored onto the inner wall. As shown in Fig. 3a, even with a high temperature treatment, the size distribution of the metal nanoparticles did not show an obvious change. The majority of particle diameters are less than 25 nm, observed from the

inset. The STEM image of the hollow (Au–Ag)@mSiO<sub>2</sub> NPs looks like a bale of cotton (Fig. 3b), which can further demonstrate their hollow structures. Compared with the thickness of the silica shell shown in Fig. 2 and 3, we found that the shell thickness drastically reduced. This phenomenon was caused by shrinkage of the silica shell during the process of calcination. Fig. S1<sup>†</sup> shows the TGA curves of (Au–Ag)/C@SiO<sub>2</sub> and that the residual mass of the microspheres after calcination was about 52%, which presents the mass of Au–Ag@mSiO<sub>2</sub>.

A series of UV-vis spectra were observed and analyzed to investigate in detail the structural evolution during each step of the preparation. As shown in Fig. 3d, when Sn<sup>2+</sup> was adsorbed on the carbon spheres surfaces, the UV-vis spectrum of the sample at this stage shows a very broad peak centered at 436 nm. When the AuCl<sup>-</sup> ions adsorbed on the carbon sphere surfaces were reduced by Sn<sup>2+</sup> cations, uniform gold particles were produced. The UV-vis spectrum of this sample at this stage shows a peak centered at 572 nm. The characteristic of the surface plasma resonance (SPR) of gold nanoparticles changed from about 525 nm to after 572 nm, as a result of the modulation effect of the carbon spheres. Subsequently, Ag<sup>+</sup> cations were predominantly adsorbed on the Au NPs. Following the reduction by L-ascorbic acid, a silver nanoshell was produced on the gold core. The silver atoms in the nanoshell still remain as a pure silver phase and are in close contact with gold surface. They will diffuse into the gold core to form a gold-silver alloy phase due to the stronger bimetallic bonding.<sup>38,39</sup> Thus, there are two distinct SPR peaks, 541 nm and 450 nm, respectively. One has a blue shift of 31 nm compared to the C/Au SPR peak, which can be assigned to the SPR of the Au-Ag alloy phase. The other is centered at 450 nm and is characteristic of C/Ag. After the formation of the silica shell, a calcination treatment was carried out to remove the carbon spheres. The adsorption peak of Au@SiO2 was 526 nm, while the peak of Au-Ag@SiO<sub>2</sub> should show a blue-shift phenomenon after the formation of the Ag nanoshell.<sup>35</sup> However, the Au-Ag@SiO<sub>2</sub> shows a peak centered at 528 nm, indicating a small amount of aggregation of the Au-Ag nanoparticles during the calcination process. The disappearance of the SPR band at 450 nm is most likely due to the oxidation of silver by air to form silver oxide, which is transparent to the incident light. It is well known that a high temperature will induce, in most cases,<sup>40</sup> severe sintering of nanoparticles for thermodynamic reasons. However, in our case, a small amount of particles appear to reunite but serious aggregation was successfully avoided (observed from Fig. 3a and 3b). We attribute the reasons to a synergistic effect of the chemical bonding interaction and the large specific surface area of the mesoporous silica shell as well as the limiting effect of the Ag shell.<sup>22,41,42</sup> After the reduction treatment by H<sub>2</sub> (Fig. 3c), because the silver oxide is reduced to metallic silver, which drives more silver atoms to be alloyed with gold, the SPR band of the sample had a blue-shift from 528 nm to 521 nm. Satisfactorily, the vast majority of particle sizes remain essentially unchanged even through a series of harsh treatments.



Fig. 4 EDS elemental mapping of the Au–Ag NPs (a); STEM-EDS line-scan across a single Au–Ag NPs (b) and the corresponding EDS spectra (c).

In order to provide support for the structural characteristics of the bimetallic metal NPs anchored on the mesoporous silica shell, elemental mapping by EDS analysis was carried out to provide proof of the core/shell geometry of the nanoparticles. The elemental mapping (Fig. 4a) confirms the presence of a core-shell structure and the Ag content is also rich in the core region. We also employed the corresponding EDS spectra shown in Fig. 4c, but it was unable to provide definitive evidence for structural characteristics of the metal particles. The STEM-EDS line-scan EDS spectra across the Au-Ag NPs was carried out to further provide independent proof of the core/ shell geometry of the nanoparticles. Fig. 4b displays an STEM-EDS line scan across a single core-shell structured particle. This result reflects the higher atomic number of Au in the center of the particle and the higher atomic number of Ag in the outer shell. While Fig. 4b does appear to show enrichment of Ag along the edge of the bimetallic particles, it obviously shows a significant amount of Ag in the central region, which suggests the particle has more of an Au-Ag alloy character. All the results are consistent with the results of the UV-vis spectra that Au and Ag are homogeneously mixed in the core region. So, the presynthesized core-shell structured bimetallic particle consists of a Au-Ag alloy acting as a core and Ag acting as a shell.

The uniform and nonaggregated nature of the composite microspheres can be more easily observed in scanning electron microscopy (SEM) images, as shown in Fig. 5a and b. The histogram analysis shows that the  $(Au-Ag)/C@SiO_2$  and (Au-Ag). @mSiO\_2 NPs are about 450 nm and 320 nm, respectively (shown in the insets). These results are generally consistent with the result of the TEM images. The diameters of the composite microspheres were estimated by calculating the mean diameters of the  $(Au-Ag)/C@mSiO_2$  and  $(Au-Ag)@mSiO_2$  NPs by measuring at least 100 particles from the SEM images, as shown in Fig. S2.<sup>†</sup> In our experiment, the absolute majority of the particles were trapped inside the mesoporous silica shell, while very few particles were on the outlayer of the SiO\_2 (shown in Fig. 5c<sup>†</sup>). We infer that some broken microspheres



Fig. 5 SEM images of the (a)  $(Au-Ag)/C@SiO_2$  and (b)  $(Au-Ag)@mSiO_2$  NPs and their corresponding histogram analysis (insets). (c) TEM image of some particles on the external surface of the silica shell; (d) TEM image of some broken microspheres.

meant their metal nanoparticles dispersed into solution, causing the metal particles to be adsorbed on the external surface of the mesoporous silica during calcination (shown in Fig. 5d).

The mesoporous structure can not only stabilize the bimetallic NPs but also allow the diffusion of small molecules in and out of the reactors. Fig. 6a shows the mesoporous nature of the silica wall. Fig. 6b shows the nitrogen adsorption–desorption isotherm of the composite microspheres with a narrow hysteresis loop, both of which indicate the presence of mesopores. Fig. 6c shows the BJH pore size distribution, showing a sharp peak at 3.2 nm. The small-angle XRD pattern depicted in Fig. 6d shows a broad peak at 2.4°, indicating a worm-like mesopore with a uniform pore size. The BET surface area of the composite is 1167 m<sup>2</sup> g<sup>-1</sup>, similar to normal mesoporous silica.

Heterogeneous catalysis is one of the most important applications of bimetallic NPs.<sup>10,43-46</sup> It is well-known that the

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Fig. 6 (a) TEM of the mesoporous silica shell; (b) nitrogen adsorption-desorption isotherms and (c) pore size distribution of the (Au-Ag)@mSiO<sub>2</sub> composite micro-spheres; small-angle XRD pattern of the composite nanoreactor (d).



**Fig. 7** UV-vis spectra showing the gradual reduction of 4-NP over (a) no catalysts, (b) (Ag–Au)@mSiO<sub>2</sub> nanoreactors, (c) concentration changes of 4-NP as a function of reaction time by using different concentrations of Au–Ag@SiO<sub>2</sub> as a catalyst, (d) reusability of the hollow (Au–Ag)@mSiO<sub>2</sub> and bare Au nanoparticles as catalysts, respectively.

reduction of *p*-nitrophenol by NaBH<sub>4</sub> almost does not proceed in the absence of catalysts but proceeds rapidly with catalysts.<sup>47,48</sup> As shown in Fig. 7, the reaction barely occurs (Fig. 7a) but the reaction rate was significantly improved by adding catalysts (Fig. 7b). In the presence of catalysts, the absorption of *p*-nitrophenol at 400 nm decreases along with a concomitant increase of the  $\sim$ 300 nm peak of *p*-aminophenol. Although the outermost Ag shells were oxidized by air to form

silver oxide, they still exhibit good catalytic properties in the reduction of *p*-nitrophenol by NaBH<sub>4</sub>. The BET surface area and BJH pore size distribution of the Au–Ag@SiO<sub>2</sub> catalysts is 1167 m<sup>2</sup> g<sup>-1</sup> and 3.8 nm. Fig. 7c presents the effect of the Au–Ag@SiO<sub>2</sub> concentration on the reduction of 4-NP. With the increase in the amount of the catalyst, the catalytic rate becomes faster. Furthermore, the nanoreactors can be easily recovered from the reaction solution by centrifugation and show excellent reusability, an important characteristic of such a nanoreactor. Compared to the (Au–Ag)@SiO<sub>2</sub> composite microspheres, the conversion of 4-NP by bare Au nanoparticles decreased quickly because of the irreversible aggregation (shown in Fig. 7d).

### Conclusion

In summary, a reliable method for the fabrication of Au–Ag nanoparticles stabilized on the inner wall of a mesoporous silica shell has been demonstrated. This approach effectively prevents the agglomeration of the particles. The existence of mesopores on the silica shell made the interior of the Au–Ag $@SiO_2$  composite microspheres an ideal nanoreactor for heterogeneous catalytic reactions. In addition, these catalysts could be easily separated from the reaction solution and exhibit good reusability. Furthermore, the vast majority of the particle sizes remain essentially unchanged even through a series of harsh treatments. We believe that the process is versatile since it not only allows for independent adjusting of the diameter of the bimetallic core/shell NPs, but can also be applied to other bimetallic and alloy NPs.

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