

# Synergistic Catalysis of Au@Ag Core–Shell Nanoparticles Stabilized on Metal–Organic Framework

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**S** Supporting Information

**ABSTRACT:** For the first time, this work presents Au@Ag core–shell nanoparticles (NPs) immobilized on a metal–organic framework (MOF) by a sequential deposition–reduction method. The small-size Au@Ag NPs reveal the restriction effects of the pore/surface structure in the MOF. The modulation of the Au/Ag ratio can tune the composition and a reversed Au/Ag deposition sequence changes the structure of Au–Ag NPs, while a posttreatment process transforms the core–shell NPs to a AuAg alloy. Catalytic studies show a strong bimetallic synergistic effect of core–shell structured Au@Ag NPs, which have much higher catalytic activities than alloy and monometallic NPs.

Bimetallic core–shell nanoparticles (NPs) have attracted growing attention owing to their unique properties and great potential, which are different from those of monometallic counterparts and alloys.<sup>1</sup> Heterogeneous catalysis is one of the most important applications of bimetallic core–shell NPs; the catalytic reaction takes place only on the shell of the NPs whereas the core metal can markedly affect the performance of the whole NPs. Therefore, even slight changes in the structures, sizes, or/and chemical compositions of bimetallic core–shell NPs can influence their physicochemical properties.<sup>1d,2,3</sup> In general, core–shell NPs are prepared by simultaneous or successive reduction of metallic precursors. In the successive two-step reduction approach, it is fairly difficult to obtain the core–shell NPs on the sub-10 nm scale, especially in the absence of a stabilizer/surfactant.<sup>3b</sup> To the best of our knowledge, no attempt has yet been made to use porous materials (such as zeolite, mesoporous SiO<sub>2</sub>, etc.) to restrict the size of core–shell NPs to several nanometers. Metal–organic frameworks (MOFs), as a new class of porous materials, have predesignable pore structures and promising multifunctionalities.<sup>4</sup> Over the past decade, research efforts mostly aimed at preparing new MOF structures and studying their applications in gas storage and separation.<sup>5</sup> Given the similarity to zeolites, depositing metal NPs to MOFs could afford solid catalysts. It is expected that the crystalline porous structures of MOFs limit the migration and aggregation of metal NPs. So far, there have been some examples concerning monometallic NPs/MOF and only one report of MOF supported bimetallic alloy NPs with full characterizations since the pioneering work by Fischer and co-workers in 2005,<sup>6</sup> whereas no

core–shell NPs supported on MOFs have been studied. Herein, for the first time, Au–Ag core–shell NPs, representing one type of the most studied bimetallic core–shell particles,<sup>1c,e,h,7</sup> were stabilized on a representative MOF (ZIF-8). The ZIF-8 framework (Zn(MeIM)<sub>2</sub>, MeIM = 2-methylimidazole) holds an intersecting 3D structure, high thermal and chemical stabilities, and large pore size and surface area, which are desirable for depositing metal NPs.<sup>8</sup> With the limitation effect of the pore/surface structure of ZIF-8, Au@Ag NPs were successfully restricted to 2–6 nm without the help of a surfactant by a sequential deposition–reduction approach. The resultant Au and Ag exhibit remarkable synergistic catalytic activity, which can be tuned by systematically changing the composition or/and structure of the core–shell NPs.

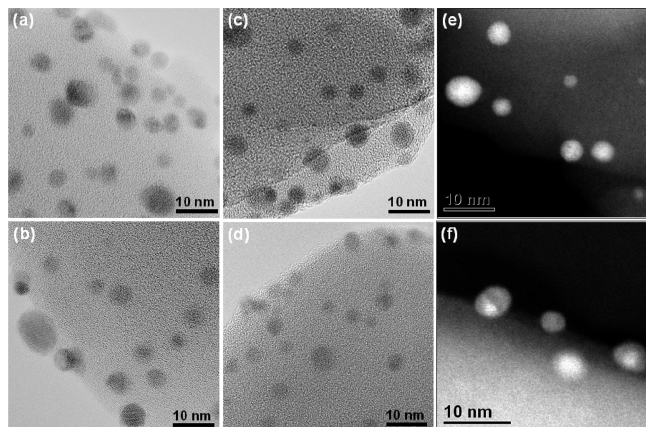
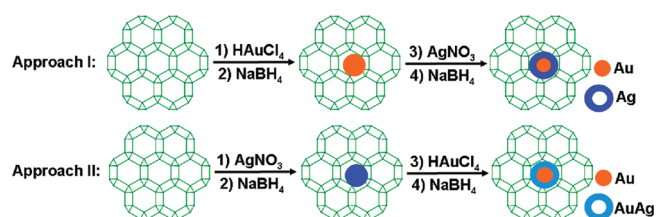
The desolvated ZIF-8 was sequentially immersed in aqueous solutions of Au and Ag precursors, with respective reduction and drying via approach I to yield Au@Ag core–shell NPs, simplified as I<sub>20</sub>, I<sub>21</sub>, I<sub>22</sub>, I<sub>23</sub>, and I<sub>24</sub> (I<sub>ab</sub>; a and b represent the weight percentages of Au and Ag to ZIF-8, respectively). The reversed deposition sequence for Ag and Au via approach II yielded Au@AuAg NPs, simplified as II<sub>02</sub>, II<sub>12</sub>, II<sub>22</sub>, and II<sub>42</sub> (II<sub>ab</sub>; a and b have the same meanings as above, Scheme 1).<sup>9</sup>

Very weak diffractions were detected for Au or/and Ag NP species from powder XRD patterns for all these samples,<sup>9</sup> indicating the formation of small Au/Ag NPs, which was further demonstrated by TEM and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) observations. As shown in Figure 1a–d, the particles of different samples have similar sizes and Au/Ag NPs are almost 2–6 nm with few aggregates, revealing that the porous surface structure of ZIF-8 may offer steric restriction to confine and prevent the growth of Au/Ag NPs although the particles are larger than pore sizes of ZIF-8, which is in accordance with the reported metal NPs/MOF.<sup>6,9</sup> Although the core–shell structure could not be observed from TEM images, a brighter core coated by a darker shell in each particle is quite clear in HAADF-STEM images (Figure 1e, f). The corresponding EDS results of both line scan and point analyses unambiguously demonstrate the Au-rich core and the Ag-rich shell.<sup>9</sup> The Au@Ag core–shell structure is formulated when Au and Ag were deposited in sequence (for I<sub>22</sub>, Figure 1c, e). Surprisingly, the deposition in a reverse order also produced NPs with a similar composition (for II<sub>22</sub>, Figure 1d, f). This can be attributed to a galvanic replacement reaction<sup>1f,h</sup> caused by the difference in reduction potentials of

**Received:** November 3, 2010

**Published:** January 7, 2011

## Scheme 1. Schematic Illustration for the Preparation Methods

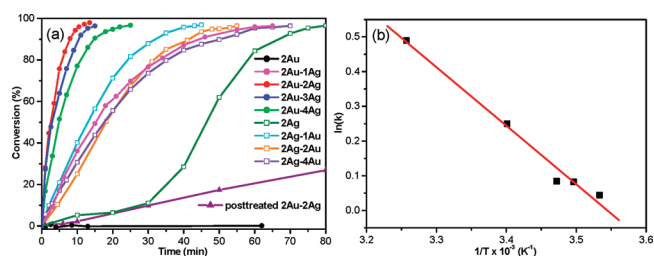


**Figure 1.** Representative TEM images for (a) 2%Au/ZIF-8 ( $\text{I}_{20}$ ), (b) 2%Ag/ZIF-8 ( $\text{II}_{02}$ ), (c) 2%Au@2%Ag/ZIF-8 ( $\text{I}_{22}$ ), and (d) 2%Ag-2%Au/ZIF-8 ( $\text{II}_{22}$ ) and HAADF-STEM images for (e)  $\text{I}_{22}$  and (f)  $\text{II}_{22}$ .

the two soluble metal salts ( $E^\circ_{\text{Ag}^+/\text{Ag}} = +0.80$  eV vs SHE;  $E^\circ_{\text{Au}^{3+}/\text{Au}} = +0.93$  eV vs SHE). Silver NPs were dissolved to reduce  $\text{Au}^{3+}$  to  $\text{Au}^0$  as a new core, followed by the coreduction of  $\text{Ag}^+$  and remnant  $\text{Au}^{3+}$  as a shell with  $\text{NaBH}_4$  to afford Au@AuAg core-shell NPs.<sup>9</sup> X-ray photoelectron spectroscopy (XPS) investigations also support the nanostructures with a Au-rich core and Ag-rich shell for both  $\text{I}_{22}$  and  $\text{II}_{22}$  samples.<sup>9</sup> The  $\text{N}_2$  physisorption measurements exhibit a slight decrease in surface area,<sup>9</sup> indicating some pores are blocked/occupied after depositing Au/Ag NPs.

Because of dielectric confinement, both Au and Ag NPs show a pronounced surface plasmon resonance (SPR) effect, giving optical properties remarkably different from those of their bulk counterparts. We observed that SPR features of Au–Ag core-shell NPs were significantly modulated by different Au/Ag contents and preparation sequences. The absorption peaks are dominated by the shell compositions and well tuned by the core (Au).<sup>9</sup>

Bimetallic Au and Ag NPs supported on ZIF-8 were tested for the catalytic reduction of 4-nitrophenol (4-NPh) by  $\text{NaBH}_4$  in water. It is well-known that the reaction does not proceed without catalysts but proceeds rapidly in the presence of metallic surfaces.<sup>10</sup> The reduction kinetics were monitored by UV–vis absorption spectroscopy of the reaction mixture after the addition of the catalyst.<sup>9</sup> The absorption of 4-NPh at 400 nm decreases along with a concomitant increase of the  $\sim 300$  nm peak of 4-aminophenol. As shown in Figure 2a, the reaction almost does not occur over a Au ( $\text{I}_{20}$ ) catalyst and proceeds slowly with “induction period” over a Ag ( $\text{II}_{02}$ ) catalyst.<sup>9</sup> The catalytic activity was significantly improved by applying Au–Ag core-shell catalysts.



**Figure 2.** (a) Catalytic conversion of 4-NPh over ZIF-8 stabilized catalysts: 2Au ( $\text{I}_{20}$ ), 2Au-1Ag ( $\text{I}_{21}$ ), 2Au-2Ag ( $\text{I}_{22}$ ), 2Au-3Ag ( $\text{I}_{23}$ ), 2Au-4Ag ( $\text{I}_{24}$ ), 2Ag ( $\text{II}_{02}$ ), 2Ag-1Au ( $\text{II}_{12}$ ), 2Ag-2Au ( $\text{II}_{22}$ ), 2Ag-4Au ( $\text{II}_{42}$ ), and posttreated  $\text{I}_{22}$ . For the detailed denotations, see Table S1 in the Supporting Information. (b) Arrhenius plots of the rate constants of the reduction of 4-NPh over  $\text{I}_{22}$ .

Since the concentration of  $\text{BH}_4^-$  added in the system is much higher in comparison with that of 4-NPh, it is reasonably assumed that the concentration of  $\text{BH}_4^-$  remains constant during the reaction. In this context, pseudo-first-order kinetics could be used to evaluate the kinetic reaction rate of the current catalytic reaction. As expected, a linear correlation of  $\ln(A_t/A_0)$  versus time ( $A_t$  and  $A_0$  represent the absorbance at the intervals and the initial stage of 4-nitrophenolate ion, respectively) is obtained.<sup>9</sup>

Among all these catalysts,  $\text{I}_{22}$  has the highest activity with a rate constant estimated to be  $4.97 \times 10^{-3} \text{ s}^{-1}$ , which is superior to that of most Au- and Ag-based catalysts under ambient conditions.<sup>10a–d</sup> Moreover, the catalyst also showed outstanding recyclable performance, revealing the stability of the catalyst,<sup>10e</sup> which was also confirmed by the TEM/HAADF-STEM observations after catalysis.<sup>9</sup> Unexpectedly, the activity of  $\text{I}_{22}$  greatly decreased after being subjected to oxidation and reduction treatments at elevated temperatures due to the formation of a AuAg alloy (basically 3–8 nm) closely coated by a thin Zn/N/O/C complex shell. The structure was characterized by TEM, HAADF-STEM observations combined with EELS and EDS analyses, and XPS investigations.<sup>9</sup> The fact indicates that alloyed AuAg NPs coated by a Zn complex shell have much lower activities than those of Au@Ag core-shell NPs. From the Arrhenius plots of the reaction rate constants over the  $\text{I}_{22}$  catalyst obtained in the range of 283–307 K (Figure 2b), the apparent activation energy ( $E_a$ ) is calculated to be 14 kJ/mol, which is much lower than those reported for Au- or Ag-based catalysts<sup>10c,g</sup> and further illuminates the synergistic catalytic effect of Au and Ag species. It is proposed that the prominent catalytic activity of Au@Ag core-shell NPs might be ascribed to the modification of the electronic structure in a core-shell NP,<sup>1e,9,11</sup> which is superior to that in an alloy or monometallic NP for the reduction of 4-NPh.

In summary, for the first time, core-shell structured bimetallic NPs were stabilized on a porous MOF by a facile successive deposition–reduction method. The bimetallic Au@Ag NPs synergistically improve the catalytic activity compared to their monometallic and alloy NPs. The present encouraging findings might open up a new avenue in the development of high-performance bimetallic core-shell nanostructured catalysts by using porous MOFs as supports. With the merits of large surface area, tunable size and shape of pores as well as functional group-modifiable walls of pores in MOFs,<sup>6c</sup> deposition of bimetallic NPs with special microstructures on MOFs will provide novel catalysts for heterogeneous catalysis.

## ■ ASSOCIATED CONTENT

**S Supporting Information.** Full experimental details and characterization data. These materials are available free of charge via the Internet at <http://pubs.acs.org>.

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## ■ ACKNOWLEDGMENT

The authors are thankful to the reviewers for valuable suggestions and to AIST and JST for financial support.

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