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One-Pot Synthesis of Oleylamine Coated AuAg Alloy NPs and Their Catalysis for CO Oxidation

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AuAg alloy nanoparticles (NPs) have stimulated increasing interest because of their unique optical,[1] electronic,[2] and catalytic[3] properties. One feature of these NPs is the tunability of surface plasmon resonance (SPR) frequency by the composition of the alloy, from 520 nm (for Au) to 400 nm (for Ag).[4] It has been also reported that AuAg alloy NPs show enhanced catalytic activity for CO oxidation compared to either Au or Ag NPs, due likely to a synergistic effect.[5] Previous reports have shown that AuAg NPs can be synthesized by laser ablation,[6] phase-transfer,[7] digestive ripening,[1a] co-reduction of Au and Ag salts in aqueous solution,[4] or a galvanic replacement reaction.[8] However, synthesis of monodiserpse AuAg alloy NPs with composition control is still a challenge, and most of the approaches reported previously rely on strong ligands like thiol for NP stabilization,[9] limiting their potentials for catalytic applications.

Here we report a one-pot synthesis of monodisperse AuAg alloy NPs by simultaneous reduction of gold and silver salts in an organic solution. Typically, 2 mmol of $AgNO_3$ was dissolved in 20 mL of oleylamine. The solution was slowly heated to 100 °C under nitrogen flow. A $HAuCl_4$ solution (0.2 mmol $HAuCl_4$ in 5 mL of octadecene with 1 mL of oleylamine) was injected into the hot solution. The solution temperature was then kept at 120 °C for 0.5 h before cooling to room temperature. The Au/Ag ratio was measured by energy-dispersive spectroscopy (EDX) to be 0.82/0.18. By changing the precursor ratio and growth time, the composition can be continuously tuned from Au-rich to Ag-rich. For example, with 2 mmol of $AgNO_3$, 0.2 mmol of $HAuCl_4$, and a growth time of 1 h (at 120 °C), $Au_{0.60}Ag_{0.40}$ NPs were obtained. Ag-rich NPs were syntehsized by further increasing

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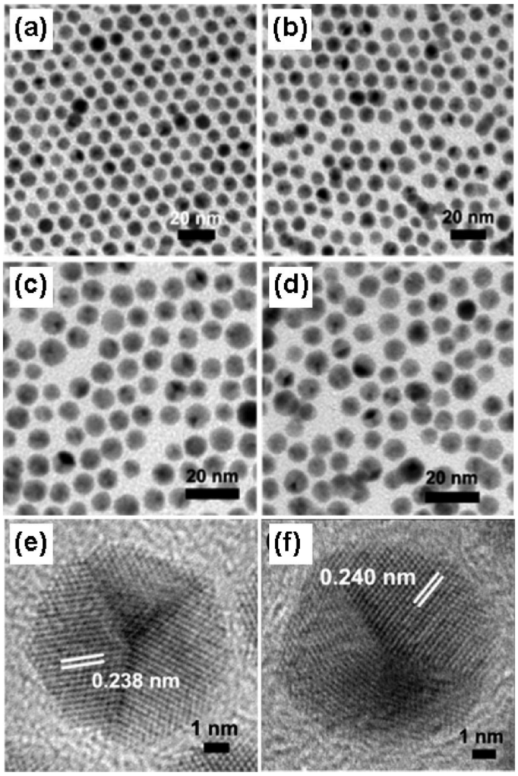

Figure 1. Representative TEM images of Au_xAg_{1-x} alloy NPs from the one-pot synthesis: (a) $Au_{0.82}Ag_{0.18}$, (b) $Au_{0.60}Ag_{0.40}$, (c) $Au_{0.52}Ag_{0.48}$, and (d) $Au_{0.39}Ag_{0.61}$ and HRTEM images of (e) $Au_{0.60}Ag_{0.40}$ and (f) $Au_{0.52}Ag_{0.48}$ NPs. The sizes of the NPs are measured to be 8 nm in (a) and (b) and 9 nm in (c) and (d), respectively.

the amount of silver precursor. Four millimoles of $AgNO_3$ reacted with 0.2 mmol of $HAuCl_4$ for 1 h led to $Au_{0.52}Ag_{0.48}$ NPs, while for 2 h gave $Au_{0.39}Ag_{0.61}$ NPs.

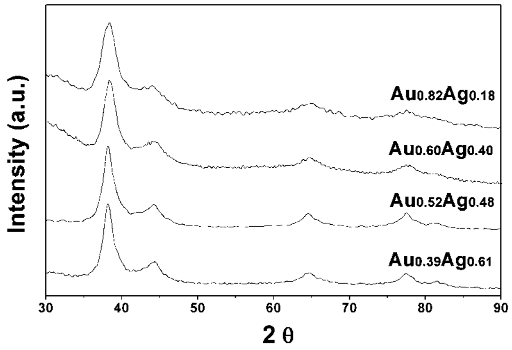

Figure 2. XRD patterns of Au_xAg_{1-x} alloy NPs.

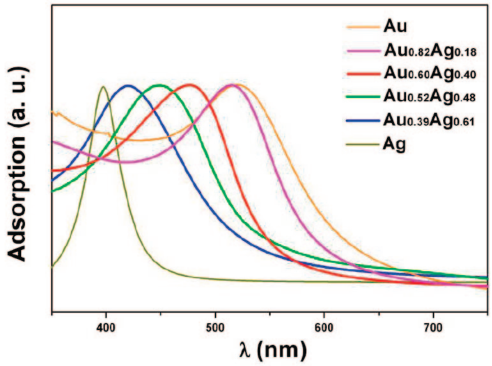

Figure 3. UV−vis spectra of Au_xAg_{1-x} alloy NPs. Spectra for Au, Ag NPs of similar size (∼8 nm) are also presented for comparison.

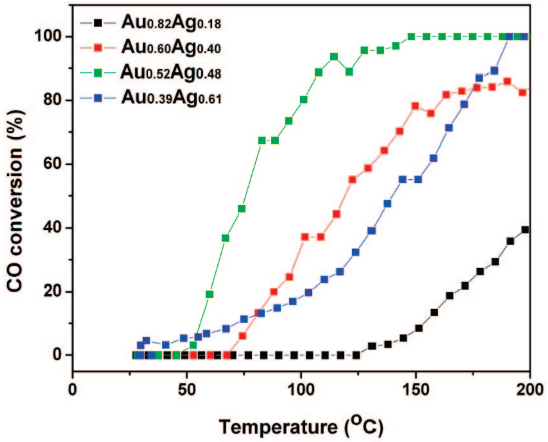

Figure 4. CO oxidation conversion (light-off) curves of Au_xAg_{1-x} NPs supported on SiO_2 and calcinated at 500 °C in 8% O_2/Ar for 1 h.

Figure 1 shows the TEM images for AuAg alloy NPs with various compositions. The NPs are monodisperse with size measured to be 8 nm for $Au_{0.82}Ag_{0.18}$ (Figure 1a) and $Au_{0.60}Ag_{0.40}$ (Figure 1b) or 9 nm for $Au_{0.52}Ag_{0.48}$ (Figure 1c) and $Au_{0.39}Ag_{0.61}$ (Figure 1d). The slightly bigger size of NPs in the latter two cases can be ascribed to the higher concentration of precursor or longer growth time, as mentioned above. High resolution TEM (HRTEM) studies of the NPs (Figure 1e,f) of the AuAg alloy NPs reveal that each NP tends to adopt the icosahedral morphology with multiple-twinned structures. The interplanar distance measured from the adjacent lattice fringes is 0.24 nm, corresponding to (111) planes of the face-centered cubic (fcc) Au or Ag. This multitwinned icosahedral structure is frequently observed in fcc metallic NPs at small sizes.[10] The maximization of {111} planes in icosahedron by forming twinned planes minimizes surface energy and compensate the extra strain energy generated by the twinned defects.[11] The crystal structure of the alloy NPs can be further characterized by XRD. Figure 2 shows XRD patterns of a series of Au_xAg_{1-x} NPs, which are consistent with fcc Au (or Ag). The crystal grain size estimated from XRD peak width is smaller than that measured from TEM images, indicating polycrystal nature of the as-synthesized NPs. This is consistent with the multitwinned structure of NPs observed in HRTEM (Figure 1e,f). Note that, due to the close lattice constants of Au (4.08 Å) and Ag (4.09 Å), HRTEM images and XRD patterns show no obvious difference for the four examined samples. However, such alloy NPs of different compositions have distinguished optical properties and can be characterized by their SPR peak shift in the UV−Vis spectra.

Figure 3 shows the UV−vis spectra of the as-synthesized AuAg alloy NPs. For comparison, spectra for Au, Ag NPs of similar size (∼8 nm) are also presented. The $Au_{0.82}Ag_{0.18}$ NPs have a SPR peak at 515 nm, close to the peak for Au NPs at this size. As the ratio of Ag to Au increases, the SPR peak blue-shifts toward that of Ag NPs. For $Au_{0.60}Ag_{0.40}$ NPs,

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the peak is at 476 nm. The peak shifts to 451 nm for $Au_{0.52}Ag_{0.48}$ and 430 nm for $Au_{0.39}Ag_{0.61}$ NPs. These observations indicate that the SPR of the AuAg alloy can be readily tuned by Au, Ag composition. The results further confirm the NPs we obtained are the AuAg alloy, not the core/shell structured Ag/Au, Au/Ag, or the mixture of Au and Ag NPs.[1a,2c]

The synthesis of the AuAg alloy NPs requires the right reaction temperature, 120 °C. In a solution of octadecene with oleylamine as the reductant/surfactant, Au NPs are synthesized by reducing $HAuCl_4$ at 65 °C.[12] Ag NPs can be made in a similar organic phase reaction with $AgNO_3$ as the precursor, oleylamine as both reducing agent and surfactant at 180 °C.[13] We noticed in our synthesis that neither too low a temperature (65 °C) nor too high a temperature (180 °C) was suitable for the AuAg alloy formation − usually only Au NPs or a mixture of Au, Ag NPs were obtained. We applied an intermediate temperature between these two extreme synthetic conditions and found that reaction at 120 °C was ideal for the alloy formation. At this temperature, $AgNO_3$ starts to be reduced, but it is still slower than the reduction of $HAuCl_4$. To balance the two reduction/growth processes, we used a much larger amount of Ag precursor than Au (e.g., $AgNO_3/HAuCl_4 = 20/1$) for the alloy synthesis. The higher concentration of Ag salt in the reaction mixture can compensate its slower reduction and lead to a comparative nucleation/growth speed with Au for alloy formation.

The AuAg alloy NPs obtained here can be applied as active catalyst, as the surfactant oleylamine binds weakly to either Au or Ag and can be readily removed. To examine the catalytic activity of the alloy NPs for CO oxidation we deposited the as-synthesized alloy NPs (in hexane) on fumed SiO_2 (Cabsil), dried the sample under vacuum at 70 °C for 10 h, and then calcined it at 500 °C in 8% O_2/Ar for 1 h. The catalytic activity for CO oxidation was examined by following an approach we reported previously.[14] TEM images of the catalyst before and after calcination (Supporting Information, Figure S1 and S2) show that most nanoparticles preserved their size after treatment, though certain sintering cannot be excluded. Figure 4 shows the light-off curves for the four alloy NPs. We can see that for all the alloy NPs tested, the $Au_{0.52}Ag_{0.48}$ shows the highest activity, achieving 100% conversion at 150 °C and 50% at 75 °C. Silica is known to be an inert support for Au catalyst in CO oxidation,[15] with the exception of a few particular cases.[16] Au/SiO_2 catalysts prepared by colloidal deposition are usually inactive up to 300 °C.[17] Our observations here confirm the previous findings by Mou et al. that the catalytic activity of Au for CO oxidation can be enhanced by alloying with Ag.[5a] The AuAg alloy NPs used in the study of Mou et al. were prepared by co-synthesis of NPs and oxide support. Though enhanced CO oxidation activity was observed for AuAg alloy NPs in their case, particle sizes, morphologies, and alloy compositions are still less controlled. Our new alloy nanoparticle catalytic system unequivocally indicates the dependence of Au catlytic activities on silver contents.

In summary, we have reported a one-pot synthesis of monodisperse AuAg alloy NPs with composition control. As a weak surfactant, oleylamine is easily removed, leaving AuAg NPs that are catalytically active for CO oxidation. The study on composition dependent CO oxidation reveals that the alloy NPs with a Au/Ag ratio close to 1/1 have the highest actvity. Their tunable optical and catalytic properties shown here indicate that these alloy NPs have great potential as optical probes for bioimaging and as active catalyst for chemical reactions.

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Supporting Information Available: TEM images of the AuAg/SiO_2 catalyst before and after calcination (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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