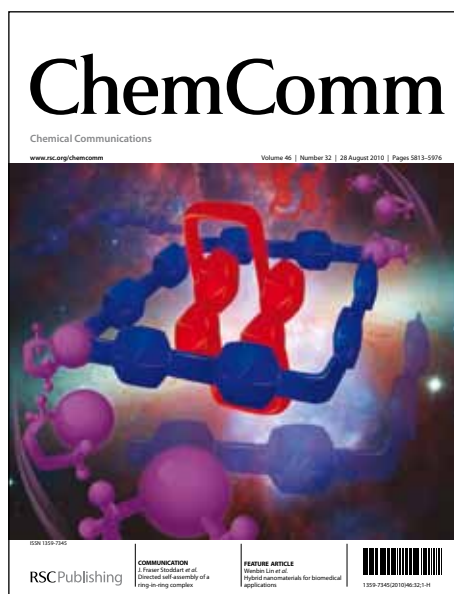


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ARTICLE TYPE

Stabilizing Gold Clusters by Heterostructured Transition-Metal Oxide-Mesoporous Silica Supports for Enhanced Catalytic Activities for CO Oxidation

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A strategy for stabilizing ultrasmall gold clusters under thermal treatment has been developed. The essence of this methodology lies in construction of heterostructured transition-metal oxide-mesoporous silica supports. The supported clusters have been demonstrated to be sintering resistant and highly active for catalytic CO oxidation.

Recently, gold nanoparticles have attracted increasing interest in the field of catalysis¹ in part due to their high activity in reactions such as CO oxidation,² propylene epoxidation,³ and others. Like other noble metal nanoparticles, gold can easily aggregate into large particles during reactions conducted at high temperature, resulting in a loss of catalytic activity. There are many strategies to prevent this sintering of metal nanoparticles, such as modification of metal-nanoparticle compositions,⁴ metal-support interfaces,⁵ and support nanostructures.⁶ However, in the cases reported above, the metal particle size is always larger than 2 nm. Few studies demonstrated the capability of stabilizing metal clusters with the sizes smaller than 2 nm.⁷

The synthesis of thiolate-protected ultrasmall gold clusters has been well studied since the initial report of a phase-transfer agent-mediated two-phase synthesis by Brust and Schffrin in 1994.⁸ Recently, various synthesis approaches to highly monodispersed Au_n(SR)_m clusters such as (n,m)=(25, 18), (38, 24) (144, 60) have been further developed.⁹ These monodispersed clusters display distinct optical and electronic properties compared to their larger counterpart (i.e., plasmonic nanoparticles > 2 nm).¹⁰ Their catalytic performance in epoxidation of styrene or selective oxidation of cyclohexane have also been reported.^{11b,c} In these papers, the thiolate groups surrounding the gold clusters were removed by ozone in a vacuum oven or calcined in vacuo.¹¹ Unfortunately, thermal treatment in atmosphere tends to result in highly aggregated particles with large sizes. For most supported catalysts, thermal treatment is required not only for removing organic groups (allowing reactants access to the catalyst active sites) but also for forming the metal-support interface that can significantly enhance the overall catalytic activity. Accordingly, it is important to develop a better

methodology for stabilizing ultrasmall gold clusters on supports that will be resilient against thermally induced sintering.

Herein, we report that gold clusters (Au₂₅, Au₁₄₄), after removal of the protecting thiolate ligands by thermal treatment, can be stabilized by heterostructured mesoporous supports. The essence of this strategy lies in use of the heterostructured binary oxide supports (M_xO_y-mSiO₂) synthesized through a combination of a transition-metal oxide and an ordered mesoporous silica. The size of the clusters is maintained after removing the thiolate ligands by thermal treatment in air, making this method superior to in-vacuo treatment. The small gold clusters supported on these heterostructured mesoporous supports were then used as active catalysts for CO oxidation.

Among different sized Au nanoclusters, Au₁₄₄(SR)₆₀ is of particular interest because it lies in between smaller clusters (e.g., Au₂₅(SR)₁₈) and larger fcc crystalline gold nanoparticles.¹² Monodispersed Au₁₄₄(SR)₆₀ clusters with SC₂H₄Ph as a capping ligand were synthesized under ambient conditions according to a previous report (synthesis details in ESI).^{9c} The UV-Vis spectrum of the product is shown in Fig. 1a. It exhibits two prominent absorption bands at 517 and 700 nm, which match well with those of Au₁₄₄(SC₂H₄Ph)₆₀ clusters.^{9c,13} The hetero-structured CuO-mSiO₂ support was synthesized using copper nitrate as the precursor that was adsorbed into the pores of mesoporous silica(EP-FDU-12)¹⁴ and decomposed at 350°C in air (Fig. 1c black line). The nanoparticle coating of CuO was highly uniform on EP-FDU-12 (EDAX elemental imaging of Cu and Si in Fig.2a). This material was denoted as CuO-EP-FDU-12. Monodispersed Au₁₄₄ clusters can be readily absorbed into the pores of CuO-EP-FDU-12 (synthesis details in ESI) in toluene because of the high surface area and large pore entrance of the EP-FDU-12. For comparison, EP-FDU-12 without CuO was also used as a support for Au₁₄₄ clusters (denoted as Au₁₄₄-EP-FDU-12). There is a large broad gold peak (2θ=38.1°) before calcination of 1.6% Au₁₄₄-EP-FDU-12 (Fig.1b black line), indicating that the Au₁₄₄ clusters have a very small particle size.

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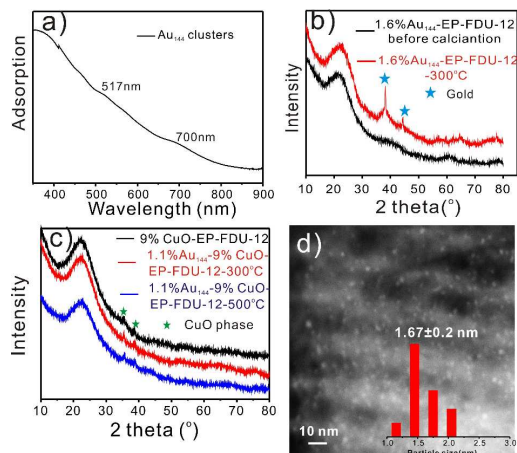


Fig.1 a) UV-vis spectrum of Au₁₄₄ gold clusters in toluene; b) XRD patterns of 1.6% Au₁₄₄ clusters supported on EP-FDU-12 before and after calcination; c) XRD patterns of 1.1% Au₁₄₄ clusters supported on CuO-EP-FDU-12 at different calcination temperature; d) STEM image of 1.1% Au₁₄₄ gold clusters supported on 9% CuO-EP-FDU-12 after calcination at 300°C.

As can be seen from Fig. 1c, there is no significant change associated with the gold peaks in the X-ray diffraction (XRD) pattern after calcination when the gold clusters are supported on 9% CuO-EP-FDU-12. In a sharp contrast, the gold clusters supported on the pure mSiO₂ (EP-FDU-12) readily aggregate into large particles (~14.2 nm) after calcination at 300°C in air (Fig. 1b red line). These observations clearly demonstrate that the gold clusters can be effectively stabilized on our heterostructured M_xO_y-mSiO₂ support after removal of the protecting thiolate group through thermal treatment. Z-contrast Scanning Transmission Electron Microscopy (STEM) further supports that gold clusters loaded on heterostructured CuO-EP-FDU-12 display sintering resistant properties. As observed from Fig. 1d, the small particle size of the Au₁₄₄ clusters remains after calcination at 300°C. The gold clusters are smaller than 2 nm (1.67 ± 0.2 nm). The observed size of Au₁₄₄ clusters through STEM imaging is consistent with their size in liquid phase that reported in the literature (1.7 nm).^{13,15} There is no significant S residue from the EDX analysis (Fig.S1). The desorption temperature of the thiolate groups for supported gold clusters lies between 200-250°C, according to the previous reports.^{13,16} No increase in the particle size of gold clusters on 9% CuO-EP-FDU-12 was observed after calcination in air at 300°C by XRD and STEM. A detailed energy dispersive X-ray (EDX) element mapping measurement of Au₁₄₄-CuO-EP-FDU-12 at a resolution of 20 nm shows a coexistence of Au, Cu, Si signals throughout the support (Fig.2a). This observation indicated the high dispersion of the CuO nanophase and the formation of the heterostructure of Au₁₄₄-CuO-EP-FDU-12.

To demonstrate the generality of our strategy to stabilize Au clusters via heterostructured supports, other transition metal oxides were also used to make heterostructures on mesoporous silica. Another support material, denoted as Co₃O₄-EP-FDU-12, was obtained through a similar procedure to that used to prepare CuO-EP-FDU-12. A calcination temperature of 500°C was employed to convert an impregnated cobalt salt into Co₃O₄ (see Fig. S2). In addition

to Au₁₄₄, Au₂₅ clusters^{9a} (UV-Vis spectrum Fig S3) were also included in our study. Similar observations were also made with the latter system. 2% Au₂₅ clusters supported on the pure EP-FDU-12 readily aggregate into large particles (~3 nm) after calcination at 300°C in air (XRD pattern Fig.S4). No sharp gold diffraction peaks were observed in the XRD patterns before and after calcination of 2% Au₂₅ clusters supported on Co₃O₄-EP-FDU-12, indicating the small size of Au₂₅ clusters. Both XRD and STEM (Fig.S2,S5) investigations demonstrate that gold clusters supported on Co₃O₄-EP-FDU-12 acquired sintering-resistant capabilities similar to those on CuO-EP-FDU-12.

There are two mechanisms associated with metal particle sintering in heterogeneous catalytic systems: Ostwald ripening and particle migration. A recent first principle calculation proposed a model for Au/IrO₂/TiO₂, in which IrO₂ islands sit on top of TiO₂ surface, and Au particles sit on top of IrO₂ islands,¹⁷ so that the migration of gold to an adjacent gold particle on another IrO₂ island is hindered by the large energy barrier across the TiO₂ surface.¹⁸ This large energy barrier roots in the difference between the metal-support interactions for IrO₂ and TiO₂. The larger the difference in metal-support interactions for these two oxides the greater the energy barrier for metal particle sintering. Therefore, the key to the development of a sintering-resistant support is to build the large heterogeneity contrast for metal-support interactions on support interfaces.

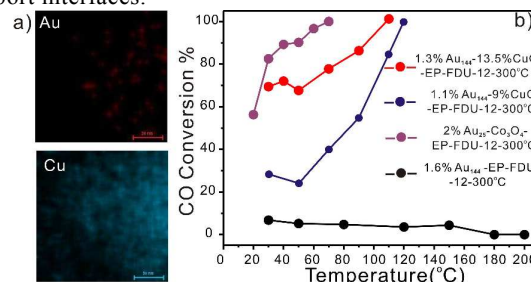


Fig.2 a) Elements mapping of Au clusters on CuO-EP-FDU-12; b) Light-off curves of the oxidation of CO as a function of temperature over supported gold clusters catalysts.

It is well known that silica has a much weaker metal-support interaction with noble metals than transition-metal oxides. Accordingly, the deposition of transition metal oxides (e.g., CuO, Co₃O₄) on mesoporous silica is a rational strategy toward sintering-resistant supports through transition metal oxide-silica heterostructures. Transition metal oxides have a strong interaction with silica and can be isolated on the pore surface of mSiO₂ to form “spacers” to hinder the movement of metal particles, hence avoiding particle sintering.^{5,19}

In our study, when the CuO content of CuO-EP-FDU-12 is as high as 13.5%, there are two distinct CuO-EP peaks in the XRD pattern (Fig.S6). Gold clusters on this heterostructured support can be stabilized at small particle size under condition of 300°C in air (XRD and STEM image Fig.S8,S9). However, under calcination at 400°C in air, gold clusters sinter into a large size (an obvious gold peak in XRD pattern Fig.S10 and a size distribution of 2.5 ± 0.6 nm from TEM Fig.S11). When the CuO content of CuO-EP-FDU-12 decreases to 9% or 4.5%, there are only very small CuO peaks visible in the

corresponding XRD pattern (Fig.1c and Fig.S6), implying that the CuO nanophase is more isolated on the pore surface of mesoporous silica. Interestingly, the sizes of gold clusters did not increase much in this case even after being calcined at 500°C (XRD pattern in Figure 1c and STEM studies in Fig.S12). Clearly, the sintering-resistant capability of a specific heterostructured mesoporous support can be fine tuned through the loading concentration of the corresponding transition-metal oxide.

To demonstrate the effect of mesopores on the sintering behavior, we also used commercial nonporous silica (Cab-O-Sil) as the control, whose surface was modified by CuO(13.5% and 9%). Because of the lower dispersion CuO on this nonporous support, the CuO particle size is significantly larger than that in CuO(13.5%,9%) -EP-FDU-12, which shows sharp CuO peaks in the corresponding XRD pattern (Fig.S13,S15). Furthermore, Au₁₄₄ clusters supported on the 13.5% and 9%CuO-Cab-O-Sil supports have a broad distribution of particle sizes (3.72 ± 1.89 nm and 3.58 ± 2.23 nm, respectively) after calcination at 300°C in air (Fig.S14,S16). This indicates that ordered mesoporous silica has the confinement effect on the particle size of metal oxides compared to the commercial nonporous Cab-O-Sil, further improving the stability of gold clusters.

The supported small gold clusters stabilized after calcination at 300°C in air have been used as a catalyst for CO oxidation. Figure 2b shows the conversion light-off curves of the supported gold clusters for CO oxidation. The gold clusters supported on both CuO-EP-FDU-12 and Co₃O₄-EP-FDU-12 are active for CO oxidation at low temperature. However, the gold clusters supported on pure EP-FDU-12 show no activity below 200°C (Fig. 2b black line). This lack of the catalytic activity can be attributed to the large particle size of the sintered gold clusters and the inability of SiO₂ to form effective catalytic interfaces with gold.^{4c} When EP-FDU-12 was modified by cobalt oxide, the resultant Co₃O₄-EP-FDU-12 itself showed activity for CO oxidation starting at 110°C and with a total conversion at 170°C (Fig.S17). When 2%Au₂₅ clusters were supported on Co₃O₄-EP-FDU-12, greatly enhanced activity in CO oxidation was observed, with 56% CO conversion even at 20°C and total conversion at 70°C (Fig. 2b purple line). It is noted that 1.6% gold clusters supported on EP-FDU-12 without removal of the thiolate groups show no activity for CO oxidation in spite of the small particle size (<2 nm). This inactivity is because of the covering of active sites by the thiol groups.^{4c}

In summary, we have demonstrated that gold clusters, after removal of the protecting ligands via thermal treatment, can be effectively stabilized on a heterostructured mesoporous support. A higher dispersion of a transition-metal oxide nanophase (eg. CuO, Co₃O₄) on mesoporous silica led to a greater stabilizing interaction with gold clusters than pure silica. The heterostructure-supported gold clusters can preserve their smaller size without sintering even under thermal treatment up to 500°C in air. This hetero-structured mesoporous support for stabilizing gold clusters opens doors for application of the recently developed ultrasmall noble metal clusters in catalysis.

Notes and references

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