Nanoengineering of Aggregation-Free and Thermally-Stable Gold Nanoparticles in Mesoporous Frameworks

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Experimental Details

Synthesis of gold nanoparticles (AuNPs)

For AuNPs with the diameter of 9 nm (AuNP-9), AuNP-9 was synthesized using a seed-mediated growth method.\(^1\)\(^,\)\(^2\) In a typical synthesis, a 100 mL aqueous solution containing of HAuCl\(_4\)·3H\(_2\)O (4.9 mg) and sodium citrate (3.7 mg) were first mixed in a conical flask. Then, 0.1 M of freshly prepared, ice-cold NaBH\(_4\) (1.5 mL) was quickly injected in to above solution under stirring. The solution was further stirred for 3-4 hrs. The as-made AuNPs has an average size of 4 nm (AuNP-4). The AuNP-4 was used as seeds to grow AuNP-9. The growth solution was prepared by adding HAuCl\(_4\) (44.3 mg) and CTAB (3.0 g) to water (90 mL), followed by the addition of 0.1 M of ascorbic acid (20 mL). Under strong stirring, 50 mL of as-made AuNP-4 seed solution was added to the above growth solution. The mixture was stirred for 30 min and then incubated overnight at 29 °C. The average size of obtained AuNPs is ~9 nm. AuNP-14, AuNP-20 and AuNP-30 were prepared using the sodium citrate reduction method.\(^1\)\(^,\)\(^3\) For AuNP-14, 100 mg of HAuCl\(_4\)·3H\(_2\)O was first dissolved in 1 L of water and heated to boiling under stirring. 30 mL of sodium citrate solution (1 wt%) was quickly added. The reaction mixture was then refluxed for 30 min. The average size of obtained AuNPs is ~14 nm. For AuNP-20 and AuNP-30, 10 mg of HAuCl\(_4\) was dissolved in 500 mL of water and heated to boiling under stirring. To this solution, 3 mL of sodium citrate solution (1 wt%) was quickly injected. The reaction mixture was then refluxed for 30 min. The solution was then cooled down to 85 °C. Another 3 mL of sodium citrate (1 wt%) solution was quickly injected into the solution, followed by the injection of 1 mL of HAuCl\(_4\) solution (1 wt%). By repeating this step three times/seven times every 15 min, AuNP-20/AuNP-30 could be produced accordingly.

Synthesis of PEO-SH: A 50 mL flask was charged with 3 mmol of monofunctionalized PEO\(_{45}\)-OH (6 g), 4.5 mmol of 3-mercaptopropionic acid (477 mg), 4.5 mmol of N,N’-dicyclohexylcarbodiimide (937 mg) and 0.75 mmol of 4-(dimethylamino)pyridine (91.5 mg) and 30 mL of anhydrous dichloromethane. The reaction mixture was then stirred under nitrogen at 0 °C for 40 h. After the reaction, the reaction mixture was passed through a silica gel to remove salts and precipitated in cold ethyl ether for three times. The final PEO-SH was dried under vacuum for 24 h and stored under nitrogen for use. The thiol-terminal group was confirmed by proton NMR spectra (-SH, 1.6 ppm) in CDCl\(_3\).\(^4\)

Synthesis of SBA-AuNP: In a typical synthesis, 5 g of P-123 was first dissolved into 159.5 g of deionized water. 31.3 g of concentrated HCl (26.5 mL) was added to the above solution under stirring at 35 °C. After stirring for 1 h, 10.4 g of TEOS and the predetermined amounts of AuNP-PEO were successively added dropwise. The mixture was further stirred for another 24 h at 35 °C, and subsequently hydrothermally-treated for an additional 24 h at 80
°C. The as-made samples were filtered and washed three times with water and ethanol. The powder was then collected and dried at 60 °C. To remove the polymer surfactants and PEO-SH, as-made AuNP/P-123/SBA-15 hybrids were calcined at 500 °C for 4 h with a ramp rate of 1 °C min⁻¹ to yield SBA-AuNP.

**Synthesis of resol precursor:** 0.61 g of phenol (6.5 mmol) was mixed with 0.13 g of NaOH solution (20 wt%, 0.65 mmol). After stirring for 30 min, 1.05 g of formalin (37 wt%, 13 mmol) was added dropwise, and stirred at 70 °C for an additional 1 h. After cooling down to room temperature, the pH of the solution was tuned to 7 using HCl solution. Then, water was removed with a rotary evaporator. The product was re-dissolved in ethanol at a concentration of 100 mg/mL for storage.

**Thermal stability of AuNP-4 and AuNP-14 physically adsorbed within mSiO₂:** 100 mg of the calcined mSiO₂ (KIT-6) was added into a 10 mL as-made aqueous solution of AuNP-4 (the concentration of AuNP-4 is 25 μg/mL) or AuNP-14 (0.1 mg/L). After stirring for 4 h at room temperature, the solution was then filtered and washed three times with water to obtain physically absorbed AuNPs within mSiO₂. To evaluate the thermal stability of as-made mSiO₂/AuNP, the sample was annealed at 500 °C under air for 4 hrs.

**Supporting References**

Figure S1. Supporting TEM images of mSiO₂-AuNP(14)-1% at different magnifications.
Figure S2. Structural characterizations of as-made \( m\text{SiO}_2\)-AuNP(14). (a) low-angle, (b) wide-angle XRD patterns, and (c, d) TEM images of as-made \( m\text{SiO}_2\)-AuNP(14). The inset in (d) is a picture of as-made \( m\text{SiO}_2\)-AuNP(14). The weak intensity of the XRD pattern and the low contrast in TEM images of AuNPs are due to the presence of polymer templates.

Figure S3. (a) Thermogravimetric analysis of as-made \( m\text{SiO}_2\)-AuNP(14)-1\% and (b) FT-IR spectra of as-made and calcined \( m\text{SiO}_2\)-AuNP(14)-1\%. Thermogravimetric analysis of as-made \( m\text{SiO}_2\)-Au14-1\% showed that the polymer templates were thermally degraded above 300 °C. FT-IR peaks of as-made \( m\text{SiO}_2\)-Au14-1\% at 1350-1500 cm\(^{-1}\) and 2850-3000 cm\(^{-1}\) corresponding to the C-H bending and stretching vibration of P-123, disappeared after calcination, indicating the complete removal of polymer templates. Both results confirm the removal of polymer templates after calcination at 500 °C for 2 h.
Figure S4. Structural characterizations of pure mesoporous KIT-6. (a,b) TEM images, (c) low-angle and (d) wide-angle XRD patterns, (e) N\textsubscript{2} sorption isotherms and (f) corresponded pore size distribution curve of pure KIT-6.
Figure S5. Structural characterizations of SBA-AuNP(14)-0.5%. (a, b) TEM images, (c) low-angle and (d) wide-angle XRD patterns of SBA-AuNP(14)-0.5% with a 2-D hexagonal \textit{p6mm} mesostructure. The inset in (a) is the digital photo of SBA-AuNP(14)-0.5%.
Figure S6. Evaluation of the colloidal stability of pre-synthesized citrate-capped AuNPs and AuNP-PEO. (a,b) UV-vis spectra of AuNPs with citrate ligands when increasing concentration of NaCl (a) and HCl (b); and (c,d) UV-vis spectra of AuNP-PEO in the increasing concentration of NaCl (c) and HCl (d).

Figure S7. (a) TEM image and (b) low-angle XRD pattern of the calcined $m$SiO$_2$-AuNP using AuNP-citrate as Au sources directly.
Figure S8. Supporting TEM images of $m$SiO$_2$-AuNP(14)-1% obtained by annealing at 500 °C for 48 h.
Figure S9. Evaluation of the thermal stability of mSiO$_2$-AuNP(14)-1% at elevated temperatures. (a-e) TEM images of mSiO$_2$-AuNP(14)-1% calcined at 400 ºC (a), 600 ºC (b), 700 ºC (c), 800 ºC (d) and 900 ºC (e). (f) UV-vis spectra of mSiO$_2$-AuNP(14)-1% annealed at 600 ºC, 800 ºC and 900 ºC. (g) Size distributions of mSiO$_2$-AuNP(14)-1% % calcined at 400 ºC, 600 ºC, 700 ºC, 800 ºC and 900 ºC. The annealing time is 1 h for all samples.
Figure S10. The schematic illustration of 2-D “nanoconfinement” effect of AuNPs within mesoporous supports. With annealing under high temperature, catalytically active AuNPs would migrate along mesoporous channels, and aggregate/fuse into the larger particles outside the mesopores, due to the weaker binding immobilization between NPs and mesoporous supports.

Figure S11. TEM images of AuNP-4 physically adsorbed within mSiO$_2$ (mSiO$_2$/AuNP(4)) before (a, b) and after (c, d) calcination at 500 °C for 2 h.
Figure S12. TEM images of AuNP-14 physically adsorbed on mSiO₂ (mSiO₂/AuNP(14)) before (a, b) and after (c, d) calcination at 500 °C for 2 h. Because the size of AuNP-14 is obviously larger than the pore size of mesoporous frameworks, AuNP-14 can only be physically adsorbed on the surface of mSiO₂. The absence of confinement effect of mesoporous framework cannot confine AuNPs to fuse into the larger ones during the high-temperature calcination.

Figure S13. XRD patterns of the samples shown in Figure 4. The gradual disappear of (220) reflection indicated the less ordered mesoporous structures in high content and large size of AuNPs.
Figure S14. (a, b) TEM images and (c) XRD pattern of the $m\text{SiO}_2$-AuNP(30)-1%. When loading size of pre-synthesized AuNPs is 30 nm, the periodicity and ordering of the mesoporous silica framework as well as the distribution of AuNPs are partially disrupted, mostly because of the large micelle size mismatch between AuNP-PEO and Pluronic P-123.

Figure S15. Wide-angle XRD patterns of $m\text{TiO}_2$-AuNP(14)-1% (black line), $m\text{Al}_2\text{O}_3$-AuNP(14)-1% (red line) and $m\text{ZrO}_2$-AuNP(14)-1% (green line) shown in Figure 5. XRD patterns indicated that $m\text{TiO}_2$ composes of anatase titania nanocrystals, while $m\text{ZrO}_2$ and $m\text{Al}_2\text{O}_3$ are completely amorphous.\textsuperscript{6}
Figure S16. Structural characterizations of $m$SiO$_2$-AuNP(14)-1% after CO oxidation for 130 h at 375 °C. (a,b) TEM images, (c) small-angle and (d) wide-angle XRD patterns of the $m$SiO$_2$-AuNP(14)-1% after CO oxidation for 130 h. The XRD pattern and TEM image of $m$SiO$_2$-AuNP(14)-1% after CO oxidation for 130 h clearly indicate that, i) periodically ordered mesoporous support, which was retained without collapse; ii) well-dispersed AuNPs, where AuNPs were aggregation-free and homogenously embedded in the mesoporous support; iii) uniform size of AuNPs of ~14 nm from both TEM and XRD, suggesting AuNPs supported in mesoporous framework were thermally stable without fusion or leaching.
Table S1. Catalytic performances of benzyl alcohol oxidation reactions using mesoporous material supported Au or Au-Pd bimetallic catalysts.

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<th>Time (h)</th>
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