Mesoporous Silica/Nanoparticle Composites Prepared by 3-D Replication of Highly Filled Block Copolymer Templates – Supplementary Information

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Introduction:

Composite materials of functional nanoparticles, specifically gold nanoparticles, with silica as the host matrix have attracted interest for use in catalysis[32], sensors[33] and optoelectronic devices[34]. Previous research efforts have incorporated gold nanoparticles into the pores of mesoporous silica by the in-situ reduction of gold precursors through thermal, chemical and photo reduction methods. Others have investigated the surface modification of mesoporous silica with functional groups, i.e. amines, to attract pre-synthesized gold nanoparticles to the mesoporous silica surface[35] as well as building the sol-gel network of the silica matrix around pre-synthesized gold nanoparticles[36,37]. Another approach focused on the transport properties of pre-synthesized gold nanoparticles within the mesoporous silica and then deposited the gold nanoparticles by adding an anti-solvent[38]. While these previous research efforts have successfully incorporated gold nanomaterials, either in-situ or pre-synthesized, the gold nanoparticles were incorporated within the pore of the mesoporous silica, which would hinder the transport of materials through the mesoporous silica, and/or lacked the presence of a true mesoporous structure, which are useful for applications such as catalysis and sensors.

Experimental:

Gold Nanoparticle Synthesis: Para-mercaptophenol functionalized gold nanoparticles were synthesized according to a modified Brust method[39]. In a standard synthesis, hydrogen tetrachloroaurate trihydrate (300 mg, 0.762 mmol) and para-mercaptophenol (690 mg, 5.468 mmol) were dissolved in chilled methanol (300 mL). Acetic acid (10 mL) was then added as one portion to avoid deprotonation of the para-mercaptophenol. A freshly made 0.4 mol/L solution of sodium borohydride was prepared and 90 mL was added as one portion to the solution carefully and under strong stirring. The solution was allowed to stir under ambient conditions for 3 hours. The solution was dried under a continuous stream of nitrogen (N_2) overnight to remove the solvent. Ethyl ether was then added to the nanoparticles which were then centrifuged at 10000 rpm for 20 minutes three separate times. An identical centrifuge step was performed with de-ionized water. Around ~ 400 mg of gold nanoparticles decorated with para-mercaptophenol were obtained.

Results and Discussion:

Error! Reference source not found. illustrates how the desired mesoporous silica doped with pre-synthesized NPs was produced. The process begins by spin-coating a solution of NPs with Pluronic® F127 and para-toluene sulfonic acid (PTSA), which is a strong organic acid used to promote the hydrolysis and condensation of the silica network, to create a 400 – 500 nm thin films. The solutions consisted of 10 wt. % solids (Pluronic® F127, pre-synthesized NPs and PTSA) and 90 wt. % co-solvent of 50:50 ethanol:de-ionized water for the case of Au NPs. Concentration of the pre-synthesized NPs ranged from 5 wt. % to 25 wt. % with respect to Pluronic® F127 while the concentration of the PTSA was held constant at 15 wt. % with respect to all solid materials. The solutions were stirred at room temperature for 15 minutes to ensure the components were sufficiently mixed. The solutions were then directly spin-coated in an air environment, through a 0.2 μm poly(tetrafluoroethylene) (PTFE) filter, on a cleaned silicon wafer for 30 seconds at 3000 rpm for the case of AU NPs. The thin films showed no signs of crystallization, de-wetting or macro-phase separation.

To template the mesoporous silica around the pre-synthesized NPs, the thin film samples were exposed to a humidified solution of $scCO_2$ containing the silicon alkoxide precursor of tetraethyl orthosilicate (TEOS) at 60 °C and 125 bar for 14 hours in the case of Au NPs.

Mesoporous silica samples containing pre-synthesized Au NPs of 5 wt. % and 25 wt. %, with respect to the Pluronic® F127 template, were created. XRD was used to evaluate the structure of the mesoporous silica/NP composites and the data is provided in Figure S2.

A high-resolution TEM (HRTEM) is provided in Figure S4 to show the crystallinity of the gold nanoparticles. To further confirm the presence of the gold nanoparticles within the mesoporous silica, X-ray diffraction (XRD) was collected and is shown in Figure S5. From the XRD results, the presence of the characteristic gold crystalline peaks further confirm the presence of the gold in the mesoporous silica thin film. As the concentration of the gold nanoparticles increases, the intensity of the gold crystalline peaks increases as well. Another observation from the XRD was the narrowing of the crystalline peaks from two circumstances; exposure to elevated temperatures and incorporation of more gold nanoparticles. This observation may be explained through the growth of the gold nanoparticles at elevated temperatures (sintering or Ostwald ripening) and/or closer proximities of nanoparticles to themselves at increased concentrations (migration and coalescence). For the system investigated in this report, both Ostwald ripening and coalescence may be occurring simultaneously at the higher loading of gold nanoparticles[40]. To monitor the growth of the gold nanoparticles within the mesoporous silica thin film, UV-Vis spectra were collected and shown in Figure S6. Due to the size of the nanoparticles being ~ 2 nm, the typical surface plasmon resonance (SPR) or plasmon absorbance, typically between 500 nm and 550 nm, depending on size and shape of the gold nanoparticle, was not present[41] and will maintain a brown color while in solution or thin film. If the ~ 2 nm gold nanoparticles were to become larger than 3 nm, the plasmon absorbance would be detected. From the UV-Vis spectra, the gold nanoparticles kept an average size of ~ 2 nm before generation of the silica network via $scCO_2$ processing due to the lack of a plasmon absorbance in the 500 nm to 550 nm range. However, at an elevated temperature of 60 °C during the $scCO_2$ infusion processing step, the gold nanoparticles have grown to be larger than 3 nm due to the presence of the plasmon absorbance in the 535 nm to 540 nm range. The plasmon resonance of the gold nanoparticles greater than 3 nm was still present after thermal degradation at 400 °C. To avoid pre-mature gold nanoparticle growth, the $scCO_2$ processing temperature was reduced to 40 °C and the UV-Vis spectra was compared in Figure S7 to the $scCO_2$ processing temperature of 60 °C. By reducing the $scCO_2$ processing temperature by 20 °C, the gold nanoparticles maintained a size less than 3 nm. However, even by reducing the $scCO_2$ processing temperature to 40 °C, the gold nanoparticles continued to grow to a size greater than 3 nm after thermal degradation at 400 °C, as shown in Figure S10. Other efforts were used to reduce the growth of the gold nanoparticles at elevated temperatures such as reduction of the thermal degradation temperature to 200 °C in air, which will thermally degrade the Pluronic® template[25] as well as the ligands present on the gold nanoparticles, shown in Figure S11, as well as increasing the degree of silica condensation through additional processing steps prior to thermal degradation such as exposure to ammonium hydroxide (NH_4OH) vapor, hydrothermal conditions and 254 nm UV-irradiation, Figure S12. Even with the additional efforts to reduce the gold nanoparticle growth, the gold nanoparticles were able to grow to a size greater than 3 nm, as shown by the UV-Vis results.

Low-angle X-ray diffraction (LAXRD) was used to evaluate the long-range order of the mesoporous silica doped with gold nanoparticles, which is shown in Figure S9. From the LAXRD data, the domain spacing, of both mesoporous silica samples containing pre-synthesized gold nanoparticles, remains constant at ~ 13.2 nm for the infused samples while the domain spacing for the calcined samples reduced to ~ 10.9 nm, which corresponded to a contraction, or shrinkage, of the mesopore by ~ 18 %. Also from the LAXRD data, the long-range order of the mesopore for the silica incorporated with 5 wt. % gold nanoparticles was significant while upon the addition of 25 wt. % pre-synthesized gold nanoparticles, the long-range order of the mesopore was severally compromised, however, still present.

Conclusions:

Within this report, we have presented a method for attaining functional nanoparticles (Au and FePt) within the walls of mesoporous silica. The nanoparticle used here was that of ~ 2 nm gold nanoparticles decorated with para-mercaptophenol ligands to selectively hydrogen bond to the hydrophilic segment of Pluronic® F127. To generate the silica to encapsulate the nanoparticles within the walls of the mesopores, a three-dimensional replication technique utilizing block copolymer phase separation, phase selective chemistries and $scCO_2$ infusion processing was used. The nanoparticles were confirmed to primarily reside within the walls of the mesoporous silica by electron microscopy, which would allow the mesopore to be free of obstruction for transport of materials. At a gold nanoparticle loading of 25 wt. %, with respect to the Pluronic® template and a reduced $scCO_2$ processing temperature of 40 °C, the gold nanoparticles were found to not grow significantly larger than 3 nm in diameter, which was characterized by UV-Vis spectroscopy. Through the combination of characterization techniques reported here to characterize the mesoporous silica doped with pre-synthesized gold nanoparticles, it appears that this type of material would be useful for applications that require access to gold nanoparticles that are hosted within the walls of mesoporous silica such as catalyst substrates and sensors.

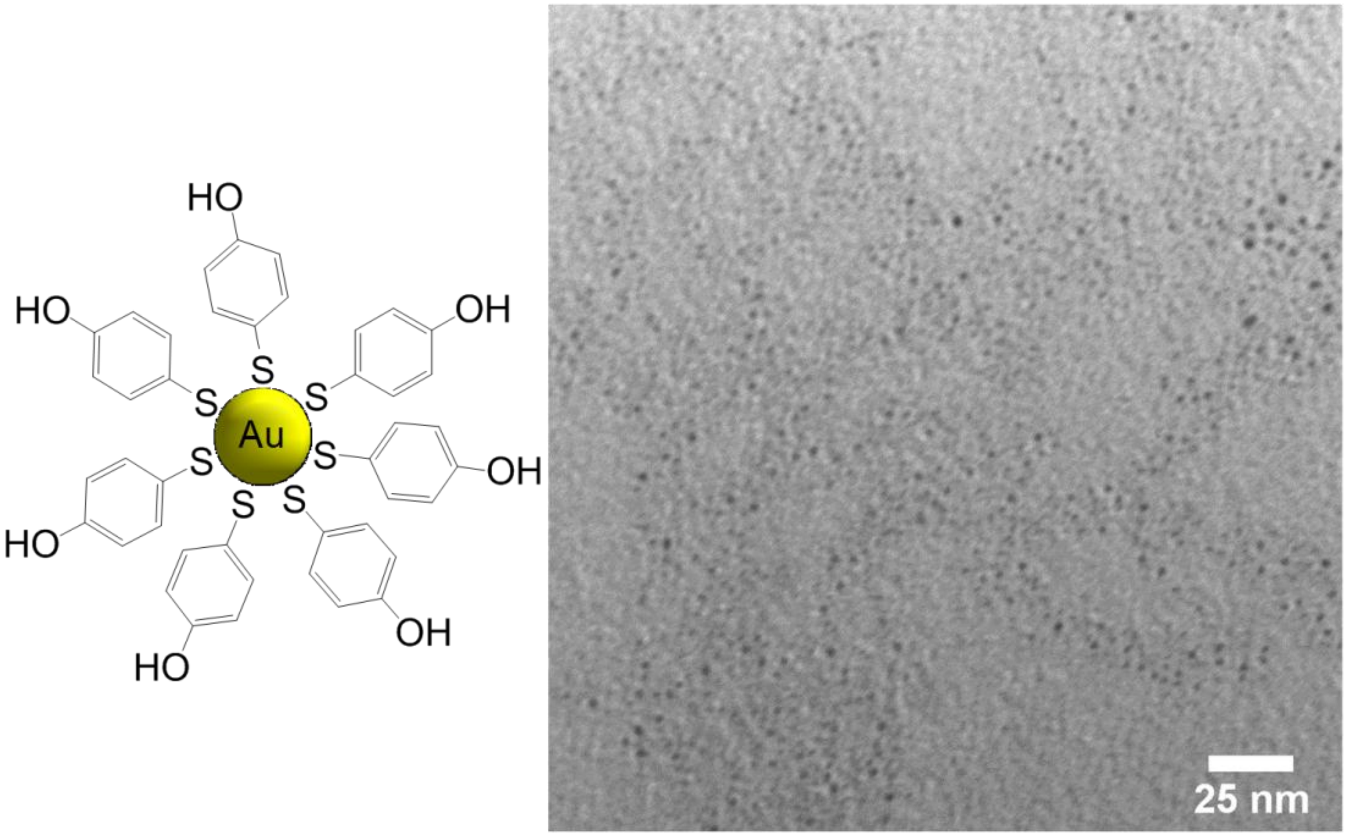

Figure S1. Cartoon depicting the gold nanoparticle decorated with para-mercaptophenol ligands (left). TEM image of the as synthesized gold nanoparticles functionalized with para-mercaptophenol ligands (right).

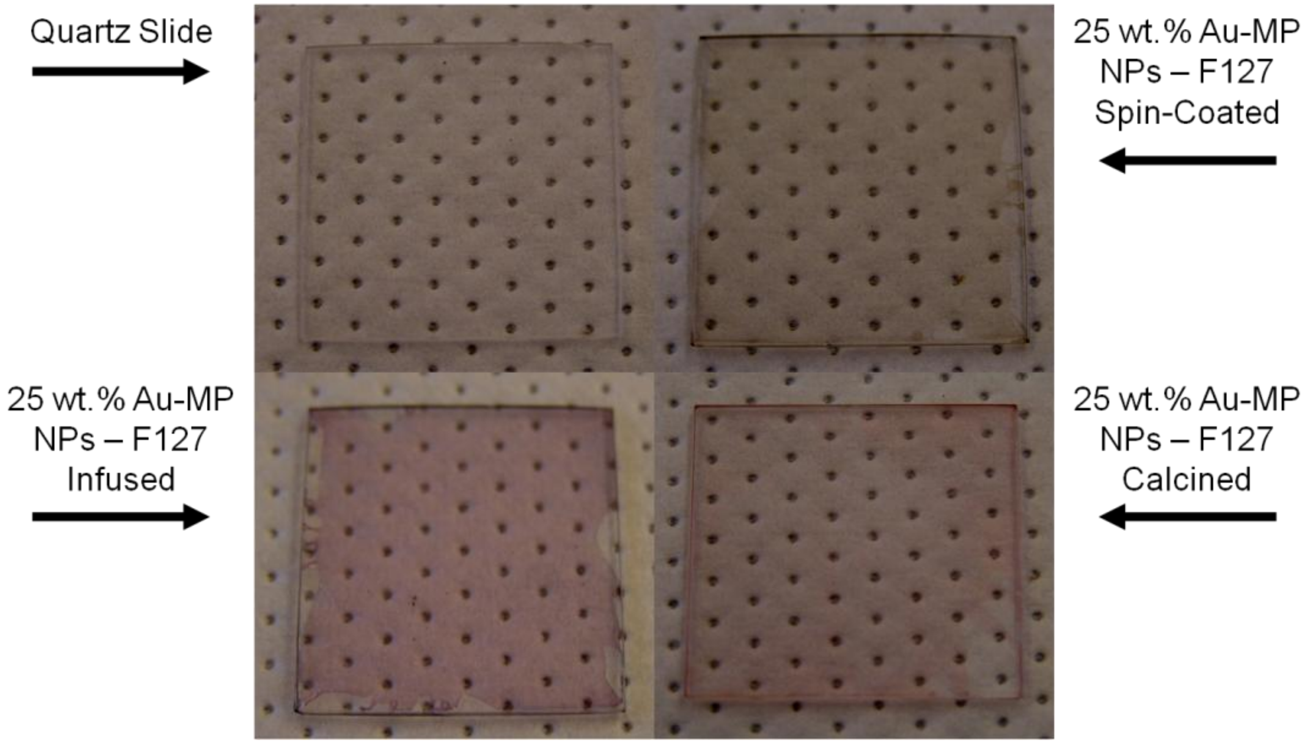

Figure S2. Photo of each processing step for Pluronic® F127 doped with 25 wt. % gold nanoparticles decorated with para-mercaptophenol ligands. The terms of infused and calcined refer to the presence of organic materials (infused) and to the presence of no organic material (calcined). $scCO_2$ infusion processing was performed at 60 °C for 14 hours while the thermal degradation was performed at 400 °C for 6 hours.

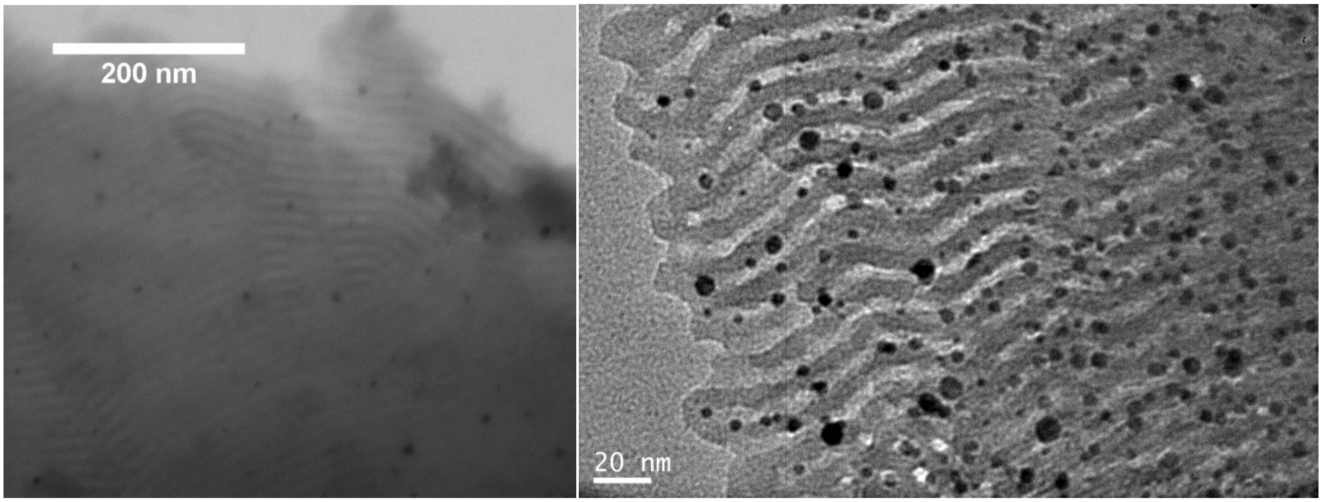

Figure S3. Scanning transmission electron microscopy (STEM) image of mesoporous silica created from Pluronic® F127 containing 5 wt. % pre-synthesized gold nanoparticles (left) and transmission electron microscopy (TEM) image of mesoporous silica created from Pluronic® F127 containing 25 wt. % pre-synthesized gold nanoparticles (right).

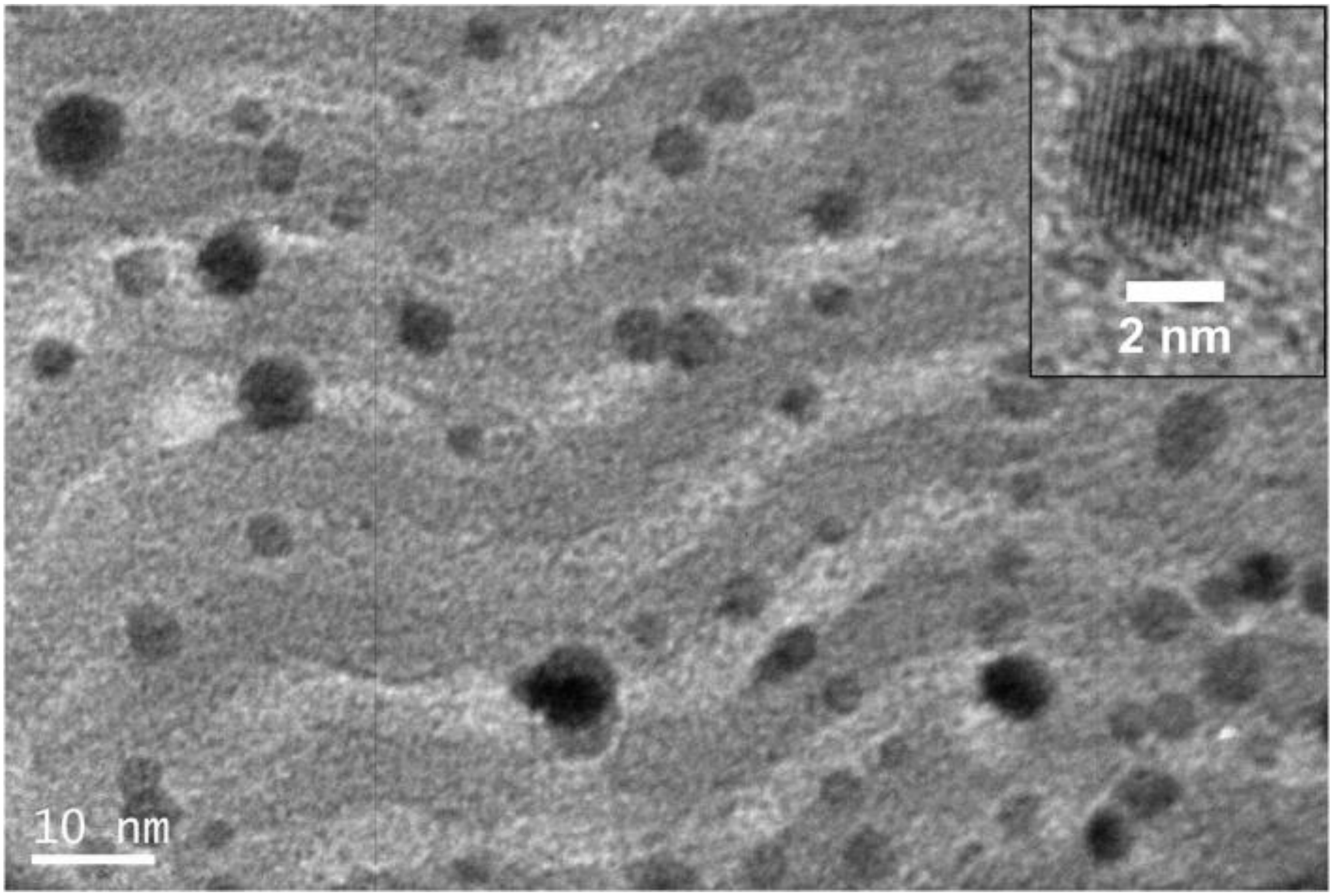

Figure S4. High-resolution TEM (HRTEM) of the mesoporous silica doped with pre-synthesized gold nanoparticles. Insert: HRTEM of an individual gold nanoparticle.

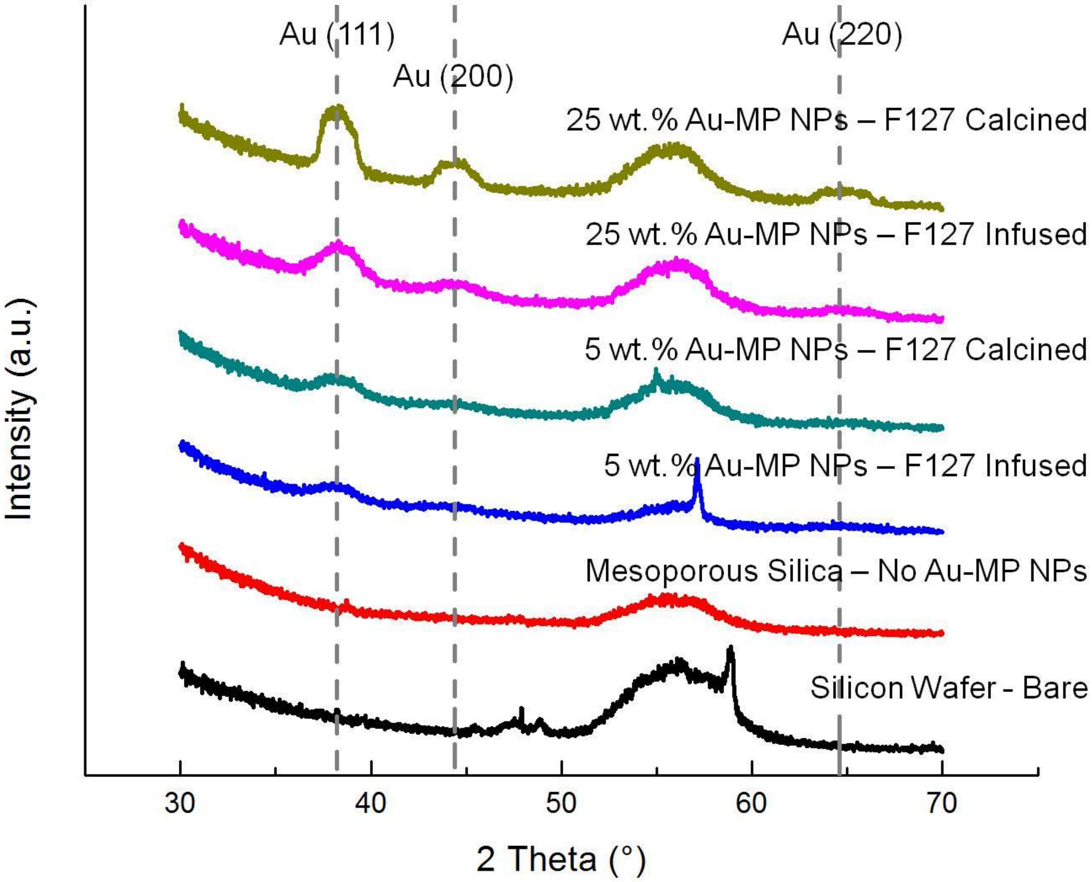

Figure S5. X-ray diffraction (XRD) of mesoporous silica doped with pre-synthesized gold nanoparticles. Weight percents of gold nanoparticles is with respect to Pluronic® F127. The terms of infused and calcined refer to the presence of organic materials (infused) and to the presence of no organic material (calcined).

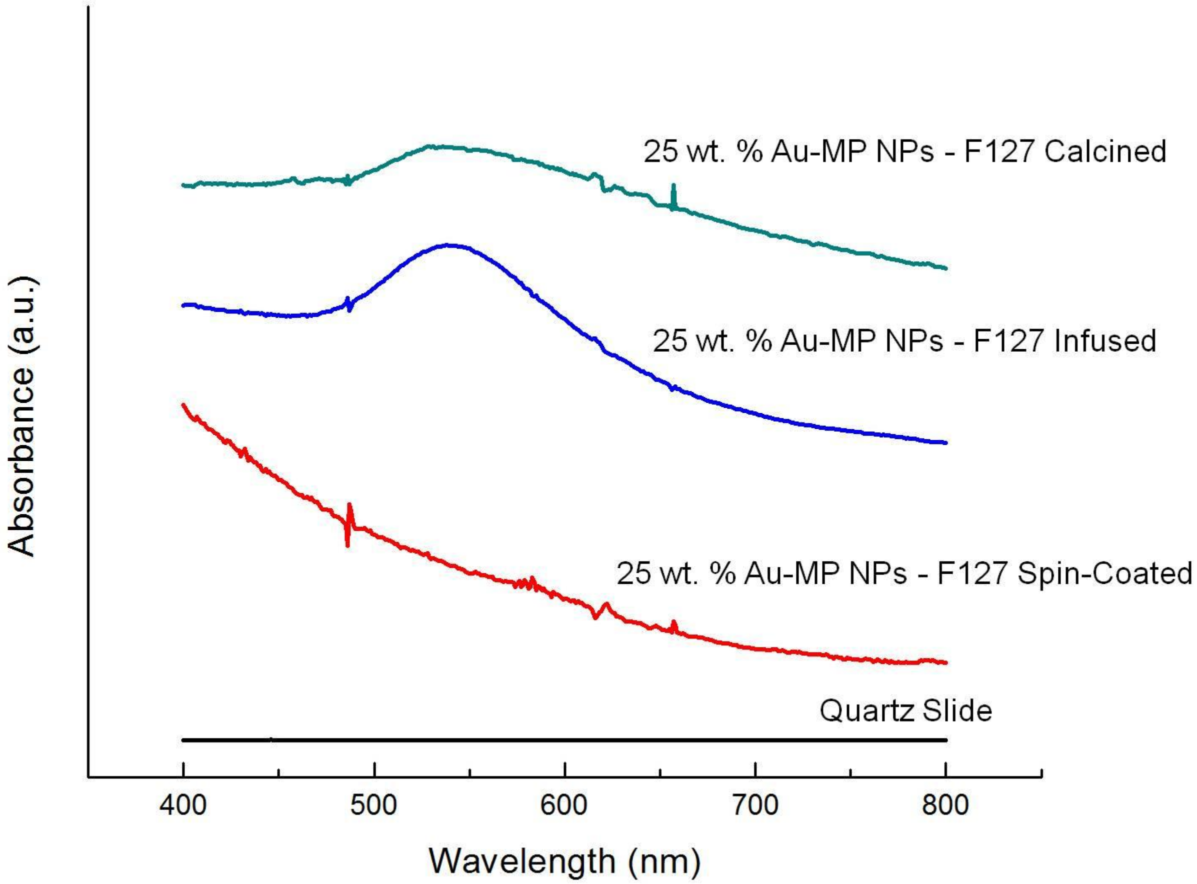

Figure S6. UV-Vis spectra acquired during the fabrication of mesoporous silica doped with pre-synthesized gold nanoparticles. The $scCO_2$ processing temperature was 60 °C. The terms of infused and calcined refer to the presence of organic materials (infused) and to the presence of no organic material (calcined).

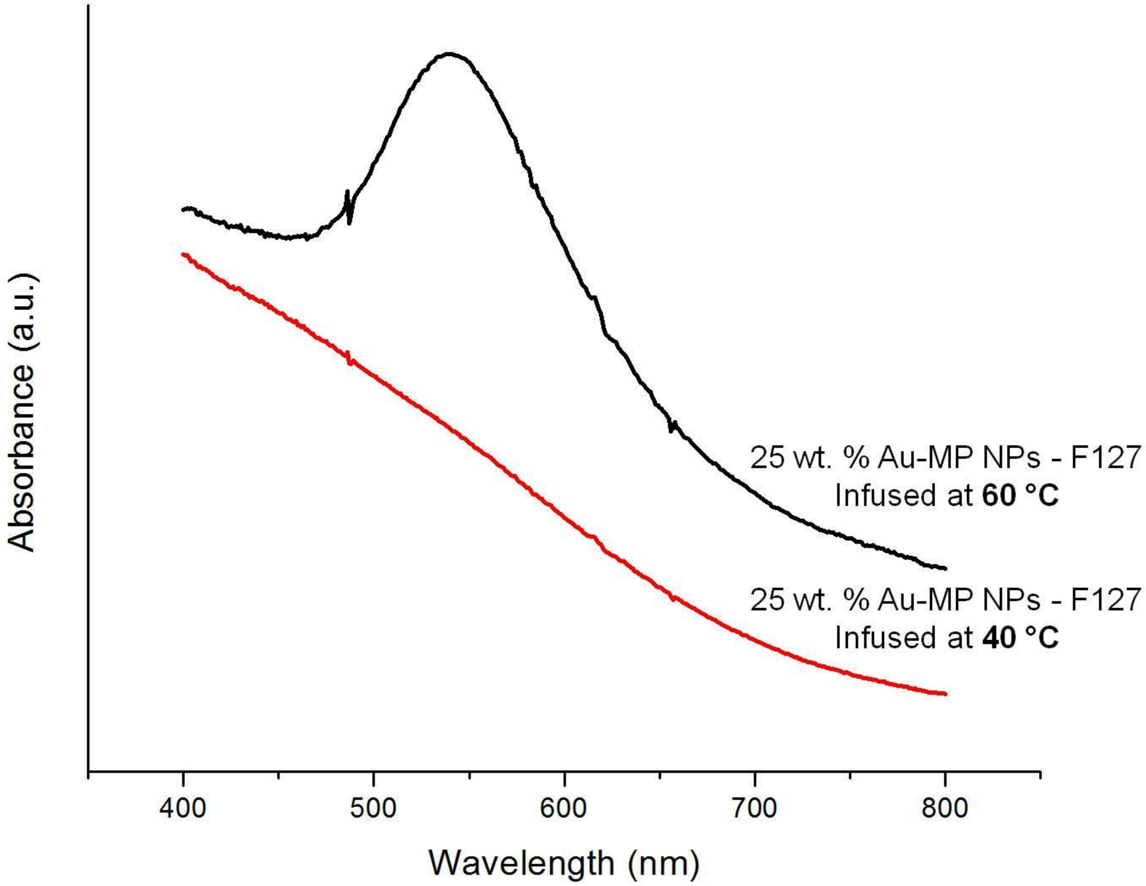

Figure S7. Comparison of plasmon absorbance for various $scCO_2$ processing temperatures.

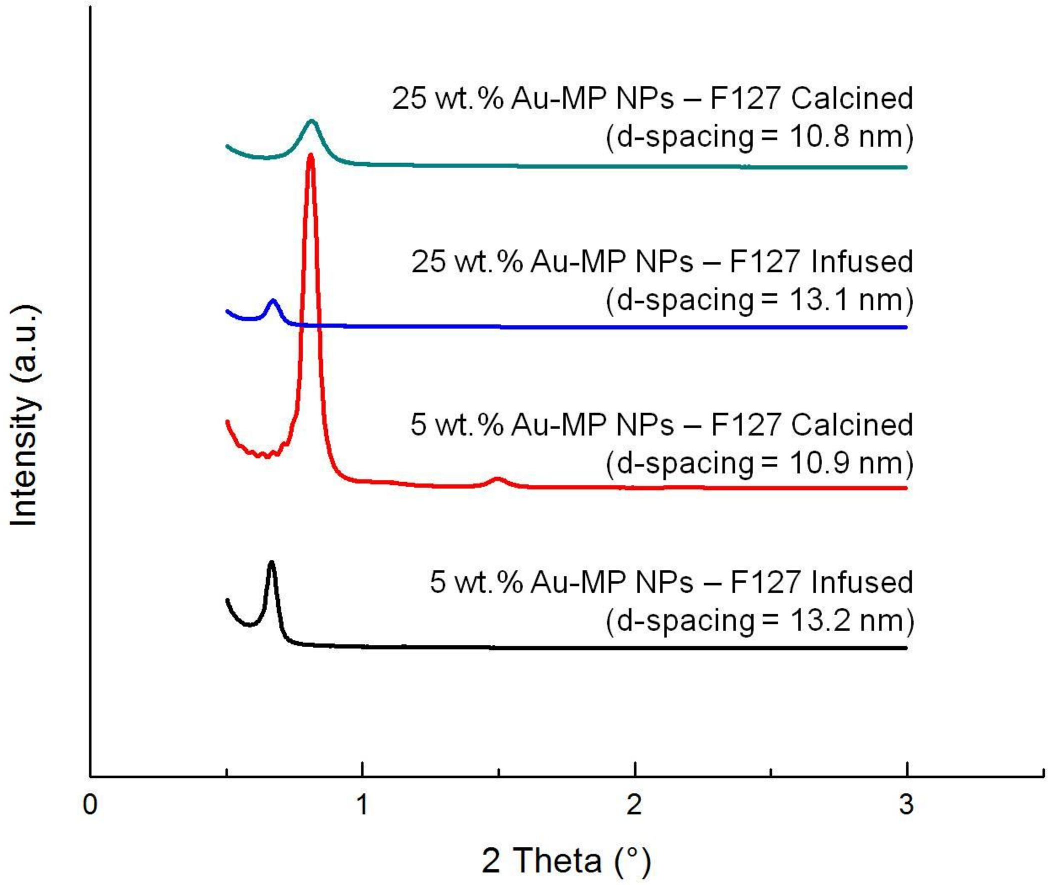

Figure S9. Low-angle X-ray diffraction (LAXRD) for mesoporous silica containing pre-synthesized gold nanoparticles. Weight percents of gold nanoparticles is with respect to Pluronic® F127. The terms of infused and calcined refer to the presence of organic materials (infused) and to the presence of no organic material (calcined).

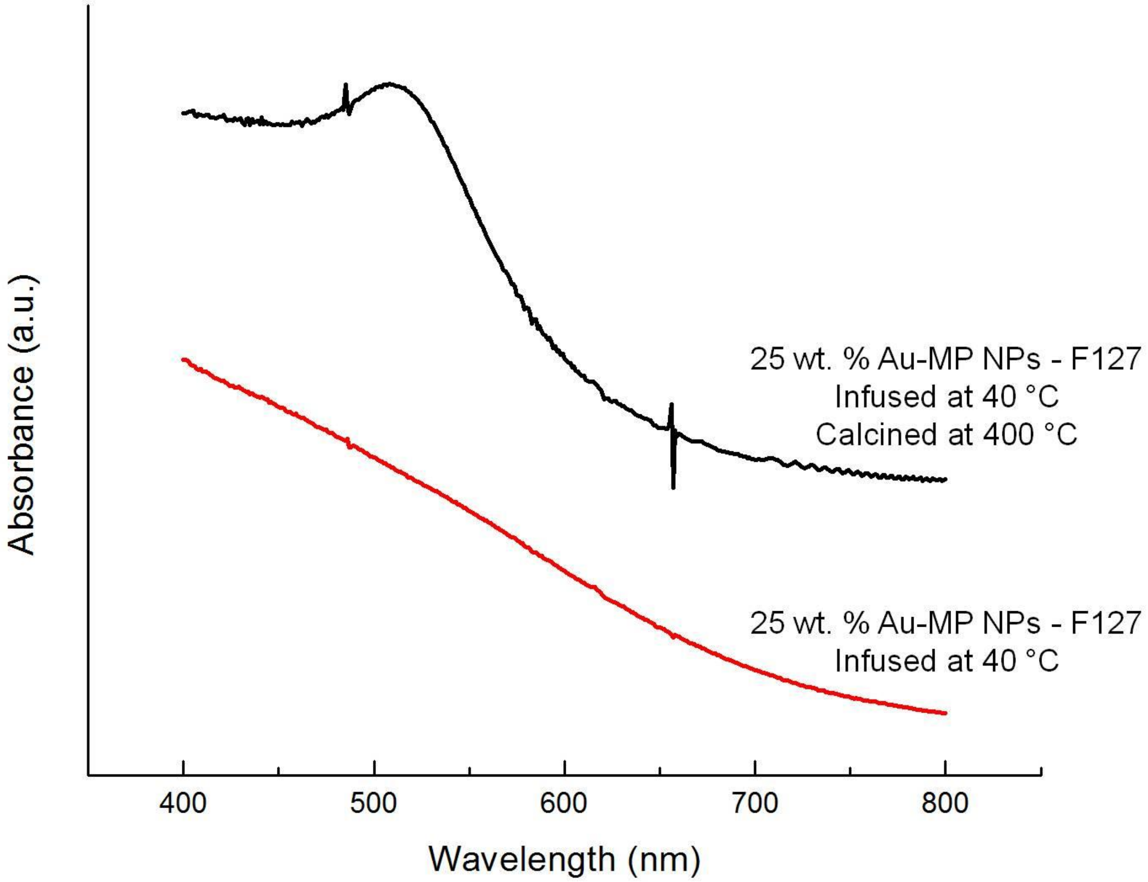

Figure S10. Comparison of plasmon absorbance for Pluronic® F127 doped with 25 wt. % gold nanoparticles decorated with para-mercaptophenol ligands processed at a scCO2 processing temperature of 40 °C and subsequent thermal degradation at 400 °C for 6 hours in air.

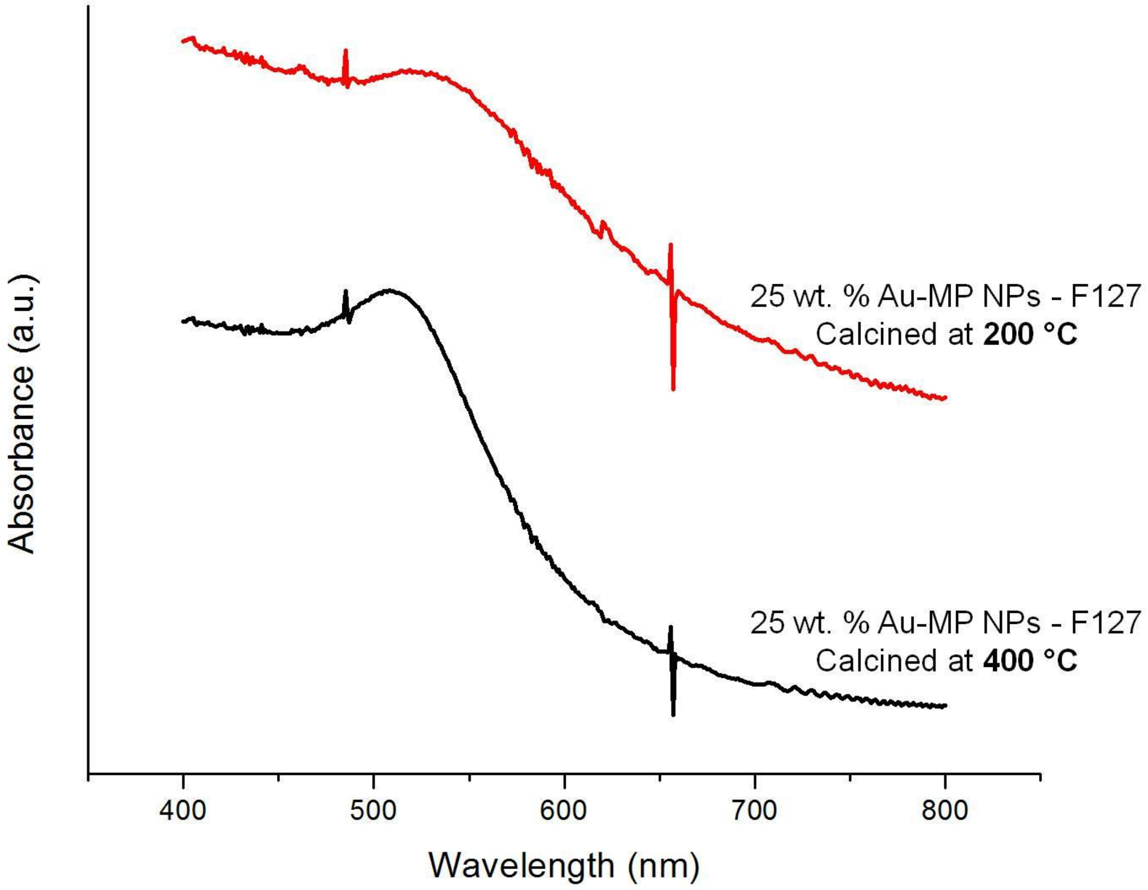

Figure S11. Comparison of plasmon absorbance for various thermal degradation temperatures.

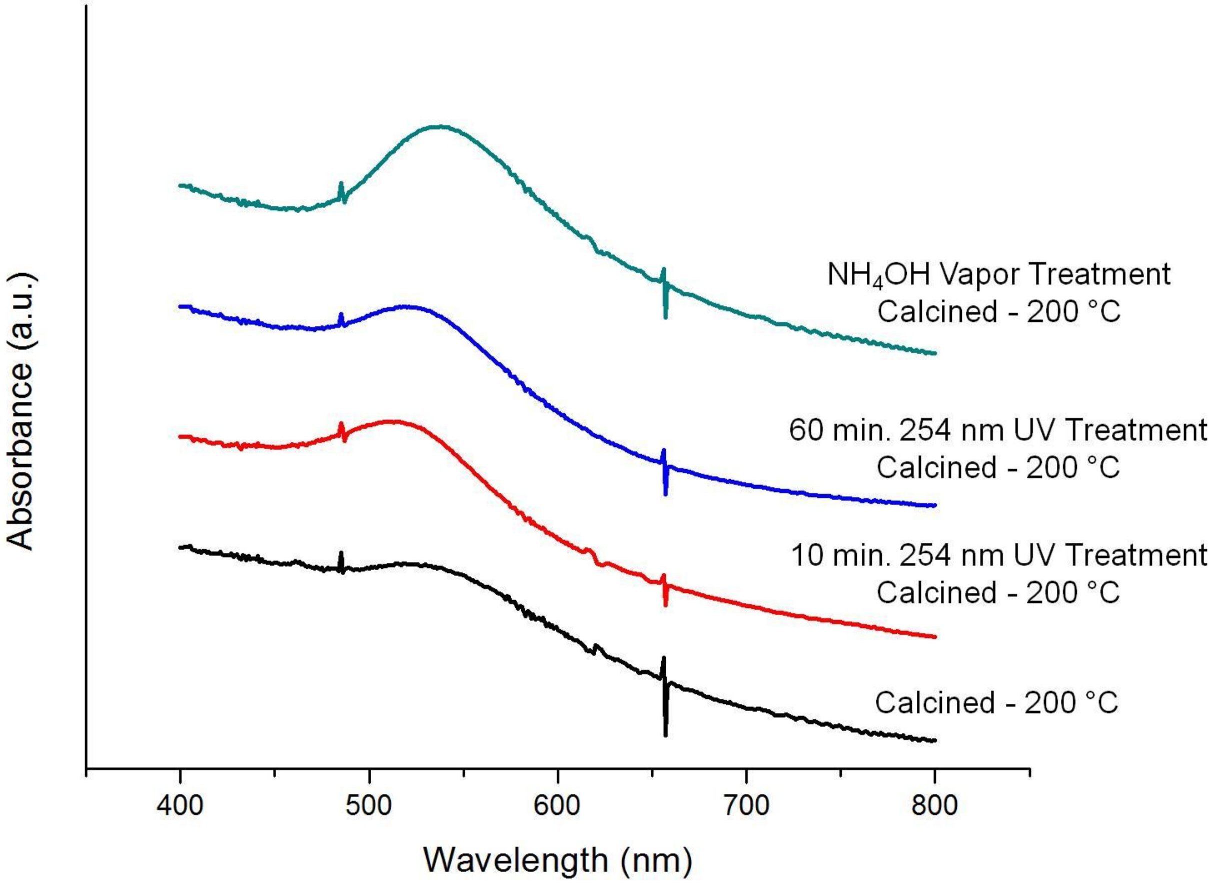

Figure S12. Comparison of plasmon absorbance for various processing steps to further condense the silica network prior to thermal degradation.

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