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Synthesis and Characterization of Hierarchical Porous Gold Materials

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Chemistry of Materials

Disclaimer

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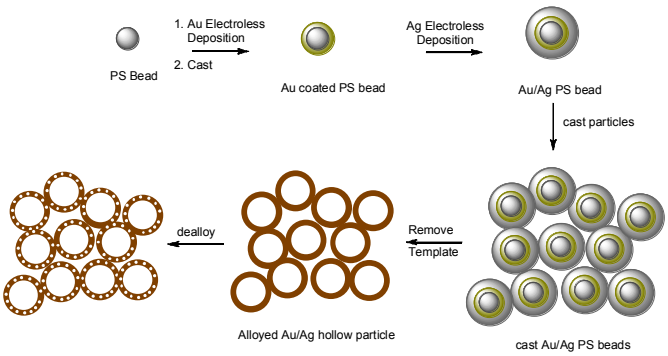
Introduction

Metallic porous materials are of great interest for electronic, catalytic, and sensor applications.[1] Templating and dealloying are two approaches to incorporate and control porosity within metals. Templating mainly uses sacraficial inorganic or organic materials to generate pore sizes ranging from 2 nm – 1 μm.[2] The dealloying process is a method that uses corrosion to selectively remove the least noble element(s) within an alloy which results in a nanoporous material of the more noble element.[3] For example, immersion of a $Ag_{70}Au_{30}$ (atom %) bulk alloy in nitric acid selectively removes the silver atoms leaving behind a nanoporous gold structure.

Materials with multimodal porosity, or hierarchical porous materials, are of interest because larger pores in the structure facilitate mass transport while smaller pores increase the surface area. Although porous noble metal materials have been used extensively in catalytic, electrochemical, and purification processes,[4] synthetic methods to prepare hierarchical porous noble metal materials are lacking despite significant progress in preparing multimodal porous ceramics and metal oxides.[5] We reasoned that combining templating and dealloying techniques would allow entry into multimodal porous noble metal materials. In this communication, we report the first synthesis of ultra-low density gold monoliths with multimodal pore structure.

To prepare hierarchical porous gold materials, our strategy was to prepare templated hollow silver/gold (Ag/Au) shells that could subsequently be dealloyed (Scheme 1). We



Scheme 1. Synthesis of hollow Au/Ag alloy particles

adopted a core-shell approach to prepare the hollow Ag/Au shells since synthetic routes to prepare gold coated silica[6] and polystyrene[7] (PS) core-shell particles are well developed. PS beads (10 μm and 1 μm) were chosen as templates since they are readily available and can be easily removed at elevated temperatures. In order to study the physical properties of individual particles, current synthetic procedures for gold coated core-shell particles have been optimized for preparing limited quantities of material at high dilution and therefore are inadequate for the preparation of macroscopic porous materials. Synthesis of gold coated particles at higher concentrations leads to particle aggregation which in turn interferes with the particle casting process. To minimize particle aggregation at higher particle concentrations, we experimented with polymer stabilizers

[1] (a) Stein, A. *Adv. Mater*. **2003**, *15*, 763. (b) Schüth, F. *Chem. Mater*. **2001**, *13*, 3184. (c) Sanchez, C.; Lebeau, B.; Chaput, F.; Boilot, J. P. *Adv. Mater*. **2003**, *15*, 1969. (d) Bond, G. C.; Thompson, D. T. *Catal. Rev. Sci. Eng*. **1999**, *41*, 319. (e) van Noort, D.; Mandenius, C. F. *Biosens. Bioelectron*. **1999**, *15*, 203.

[2]) (a) Yang, H.; Shi, Q.; Tian, B.; Lu, Q.; Gao, F.; Xie, S.; Fan, J.; Yu, C.; Tu, B.; Zhao, B. *J. Am. Chem. Soc*. **2003**, *125*, 4724. (b) Soler-Illia, G. J. D. A.; Sanchez, C.; Lebeau, B.; Patarin, J. *Chem. Rev*. **2002**, *102*, 4093 and references therein. (c) Zhao, D.; Huo, Q.; Feng, J.; Chmelka, B. F.; Stucky, G. D. *Science* **1998**, *279*, 548. (d) Xia, Y.; Gates, B.; Yin, Y.; Lu, Y. *Adv. Mater*. **2000**, 12, 693. (e) Kulinowski, K. M.; Jiang, P.; Vaswani, H.; Colvin, V. L. *Adv. Mater*. **2000**, *12*, 833. (f) Jiang, P.; Bertone, J. F.; Hwang, K. S.; Colvin, V. L. *Chem Mater.*, **1999**, *11*, 2132. (g) Yan, H.; Blanford, C. F.; Holland, B. T.; Parent, M.; Smyrl, W. H.; Stein, A. *Adv. Mater*. **1999**, *11*, 1003. (h) Velev, O. D.; Tessier, P. M.; Lenhoff, A. M.; Kaler, E. W. *Nature* **1999**, *401*, 548. Walsh, D.; Arcelli, L.; Ikoma, T.; Tanaka, J.; Mann, S. *Nat. Mater*. **2003**, *2,* 386.

[3] (a) Erlebacher, J.; Aziz, M. J.; Karma, A.; Dimitrov, N.; Sieradzki, K. *Nature* **2001**, *410*, 450. (b) Ding, Y,; Erlebacher, J. *J. Am. Chem. Soc*. **2003**, *125*, 7772. (c) Newman, R. C.; Sieradzki, K. *Science*, **1994**, *263*, 1708.

[4] (a) Bond, G. C.; Thompson, D. T. *Gold Bull*. **2000**, *33*, 41. (b) Bond, G. C.; Thompson, D. T. *Catal. Rev. Sci. Eng*. **1999**, *41*, 319. (c) Burke, L. D.; Nuget, P. F. *Electrochim. Acta* **1997**, *42*, 399. (d) Padilla, A. P; Rodriguez, J. A.; Saitua, H. A. *Desalination* **1997**, *114*, 203.

[5] (a) Kuang, D.; Brezesinski, T.; Smarsly, B. *J. Am. Chem. Soc*. **2004**, *126*, 1053. (b) Vasiliev, P. O.; Shen, Z.; Hodgkins, R. P.; Bergstrom, L. *Chem. Mater*. **2006**, 18, 4933 (c)Wang, H.; Huang, L.; Wang, Z., Mitra, A.; Yan, Y. *Chem. Comm*. **2001**, 1364. (d) Smatt, J. H.; Weidenthaler, C.; Rosenholm, J. B.; Linden, M. *Chem. Mater*. **2006**, *18*, 1443.

[6] (a) Pham, T.; Jackson, J. B.; Halas, N. J.; Lee, T. R. *Langmuir* **2002**, *18* 4915. (b) Westcott, S. L.; Oldenburg, S. J.; Lee, T. R.; Halas, N. J. *Langmuir* **1998**, *14*, 5396. (c) Graf, C.; van Blaaderen, A. *Langmuir* **2002**, *18*, 524. (d) Caruso, F.; Spasova, M.; Salgaueirino-Maceira, V.; Liz-Marzan, L. M. *Adv. Mater.* **2001**, *13*, 1090. (e) Caruso F.; Caruso, R. A.; Möhwald, H. *Science* **1998**, *282*, 1111. (e) Liang, Z.; Susha, A.; Caruso, F. *Chem. Mater*. **2003**, *15*, 3176. (f) Grabar, K. C.; Smith, P. C.; Musick, M. D.; Davis, J. A.; Walter, D. G.; Jackson, M. A., Guthrie, A. P. Natan, M. J. *J. Am. Chem. Soc*. **1996**, *118*, 1148. (g) Grabar, K. C.; Allison, K. J.; Baker, B. E.; Bright, R. M.; Brown, K. R.; Freeman, R. G.; Fox, A. P.; Keating, C. D.; Musick, M. D.; Natan, M. J. *Langmuir*, **1996**, *12*, 2353. (h) Park, S. W.; Park, M. Y.; Han, P. K.; Lee, S. W. *Bull. Korean. Chem. Soc*. **2006**, *27*, 1341.

[7] (a) Shchukin, D. G.; Caruso, R. A. *Chem. Comm*. **2003**, 1478. (b) Shi, W.; Sahoo, Y.; Swihart, M. T.; Prasad, P. N.; *Langmuir* **2005**, *21*, 1610. (c) Ji, T.; Lirtsman, V.; Avny, Y.; Davidov, D. *Adv. Mater*. **2001**, *13*, 1253. (d) Khan, M. A.; Perruchot, C.; Armes, S. P.; Randall, D. P. *J. Mater. Chem*. **2001**, *11*, 2363.

during gold depostion.[8] Electroless gold deposition on PS beads, in the presence of the stabilizer polyvinylpyrrolidinone (PVP), proceeded smoothly with little apparent particle aggregation.[9] Once the electroless gold deposition is complete, the PS beads are isolated, redispersed in distilled water, and then cast to create a PS-gold monolith. The casting procedure is analogous to slip-casting of ceramic[10] and metal[11] particles in which a suspension of PS/Au particles is placed in a plaster of paris mold and allowed to settle. The plaster of paris is a deposition surface for the particles and slowly removes water from the suspension to create a dry monolith. SEM images of cast PS/Au beads are shown in Figure 1. The relative polydispersity of the particles, high suspension concentration (≈ 10 wt%), and high rate of sedimentation result in randomly packed PS/Au spheres[12] with void spaces between individual particles. Unlike previous examples of

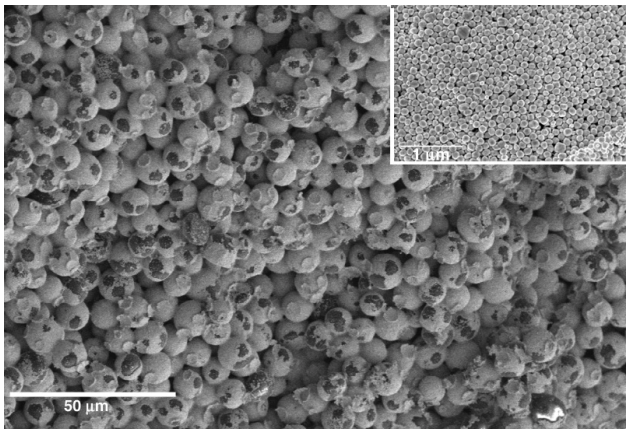


Figure 1. SEM micrograph of filter-cast gold coated PS spheres (9.6 µm diameter) fracture surface. The darker interior is the PS core which is exposed due to surface fracture while the lighter exterior surface is the gold surface coating. Inset shows higher magnification of the gold surface.

gold deposition on silica and PS particles, the gold coating is not a conformal film but is comprised of discrete gold particles, 100 – 150 nm in size (see inset). The PVP stabilizer likely favors growth of individual gold particles while inhibiting gold film formation.[13]

Ag/Au PS core shell particles were prepared by electroless deposition of silver on PS/Au spheres, Scheme 1. The sequence of metal deposition is important since depositing gold on silver may result in competing Ag^{o}/Au^{3+} galvanic and electroless deposition reduction reactions.[14] The gold:silver ratio can be adjusted by varying the gold and silver mole ratios during plating conditions, however, in the present work, we have focused on preparing $Ag_{0.85}Au_{0.15}$ and $Ag_{0.7}Au_{0.3}$ alloys.[15] Casting the Ag/Au PS beads and heating the monolith in an inert atmosphere at 400 ^{o}C removes the PS template and alloys the Ag/Au layers. Ag/Au alloy times were estimated using Fick's second law of diffusion.[16] Preparation of Ag/Au alloys is facile due to matching crystalline structures, nearly identical lattice constants[17a] and high diffusion rates of silver and gold atoms at elevated temperature.[17b]

Large cylindrical $Ag_{0.85}Au_{0.15}$ monoliths were readily synthesized with measured densities of 0.8 g/cc.[18] Little dimensional change in the monolith was observed after heat treatment but 23% mass loss was observed. The monolith structure, shown in Figure 2, is composed of hollow homogenous $Ag_{0.85}Au_{0.15}$ shells, roughly 10 µm in diameter, confirmed by Energy-Dispersive X-ray Analysis (EDAX).[19]

[8] To prepare the PS beads (10 µm or 1 µm) for gold deposition, PS beads were soaked in a gold sol to deposit gold nanoparticles (AuNP) on the PS surface to provide a surface for further gold deposition. The amount of deposited AuNP was modest and was estimated by measuring the gold sol Surface Plasmon Resonance (SPR) absorbance before and after PS bead treatment.Concentrations were measured by comparing the supernatant absorbance to a standard curve of AuNP of known concentrations For the 10 µm and 1 µm PS beads used in this study, we estimate that 1.2 mg gold/g styrene and 1.5 mg gold/g styrene were seeded on the PS beads, respectively.

[9] (a) Brown, K. R.; Walter, D. G.; Natan, M. J. *Chem. Mater*. **2000**, *12*, 306. (b) Brown, K. R.; Natan, M. J. *Langmuir*, **1998**, *14*, 726.

[10] Callister, W. D. *Materials Science and Engineering: An Introduction*; John Wiley & Sons, Inc.: New York, 2003; 6th ed.

[11] Hayes, J. R.; Nyce, G. W.; Kuntz, J. D.; Satcher, J. H.; Hamza, A. V. manuscript in preparation.

[12] Sedimentation of monodispersed colloidal spheres has been used to make ordered 3D crystalline thin films see: (a) D. H. Everett, *Basic Principles of Colloid Science*, Royal Society of Chemistry, London **1988**. (b) J. V. Sanders, *Nature* **1964**, *204*, 1151.

[13] Robust cylindrical gold monoliths (diameter = 4.5 mm, height = 2.6 mm) with a relative density of 9%, 1.7 g/cc, were prepared by heating the PS-gold monolith to 400 ^{o}C under an inert atmosphere. Under these conditions, the PS template is removed and AuNPs are sintered together to form a smooth hollow gold shell. The monolith structure was composed of hollow gold shells with void space between packed shells, as determined by SEM analysis. Although the PS templates were 9.6 µm in diameter, the resultant hollow gold shells were 5 µm in diameter and 200 nm thick indicating significant shrinkage during bakeout. See supporting information.

[14] (a) Sun, Y., Xia, Y. *J. Am. Chem. Soc*. **2004**, *126*, 389. (b) Sun, Y., Mayers, B., Xia, Y. *Nano. Lett*. **2002**, *2*, 481.

[15] For literature on colloidal Au/Ag alloys see: (a) Morris, R. H.; Collins, L. F.; J. Chem. Phys. 1964, 41, 3357. (b) Link, S.; Wang, Z. L.; El-Sayed, M. A. *J. Phys. Chem. B* **1999**, *103*, 3529 (c) Papavassiliou, G. C. *Prog. Solid State Chem.* **1980**, *12*, 185. (d) Henglein, F.; Henglein, A.; Mulvaney, P. Ber. *Bunsen-Ges. Phys. Chem.* **1994**, *98*, 180. (e) Shibata, T.; Bunker, B. A.; Zhang, Z.; Meisel, D.; Vardeman, C. F.; II; Gezelter, J. D.; *J. Am. Chem. Soc.* **2002**, *124*, 11989.

[16] Fick's second law can be used to estimate times required for complete alloying. Fick's Second Law for an interdiffusing interface with mutually soluble components is: $C(x,t) = 0.5 + 0.5erf(x/(2(Dt)^{1/2}))$. See Porter, D. A.; Easterling, K. E. Phase transformations in metals and alloys, 2nd ed.; Chapman & Hall, London 1992. The interdiffusion coefficient D used was 10^{-19} m^2/s.

[17] (a) Gold and silver are both face centered cubic with lattice contants of 4.0786 and 4.0862 Å respectively. (b) Dick, K.; Dhanasekaran, T.; Zhang, Z.; Meisel, D. *J. Am. Chem. Soc.* **2002**, *124*, 2312.

[18] Typical cylinder dimensions are 0.45 cm in diameter by 0.8 cm – 1 cm in height. Calculated full density of 85:15 (atom %) silver:gold alloy is 11.8 g/cc.

[19] Monoliths comprised of hollow 1 µm Ag/Au (70:30 atom %) shells were also synthesized. Typical monolith dimensions are 0.35 cm in diameter by 1.07 cm in height. Density of these monoliths were estimated at 1 g/cc. See supporting information.

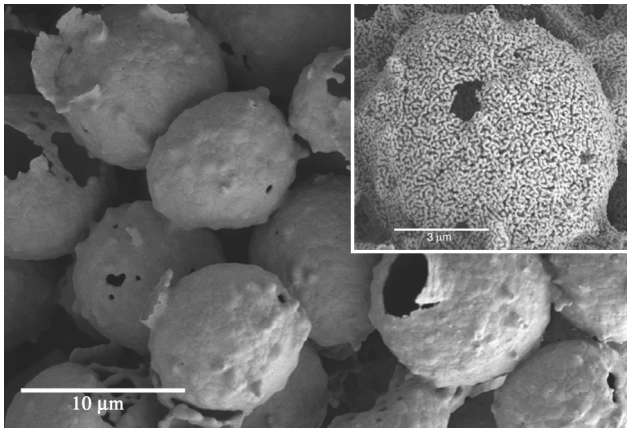


Figure 2. Fracture surface of a monolith containing hollow $Ag_{0.85}Au_{0.15}$ shells before dealloying. Inset showing surface of gold shell after dealloying.

The diameter of the shells roughly corresponds to the size of the PS bead template, indicating negligable shrinkage upon template removal. Holes in the shell walls are presumably due to the release of organic volatiles during bakeout. A $Ag_{0.85}Au_{0.15}$ monolith placed in conc. nitric acid, to selectively remove the silver, resulted in a violent reaction with significant bubble formation that cracked the monolith. Introducing a dilute nitric acid solution which was slowly increased in concentration until conc. nitric acid was the final etching solution was found to be more successful. After etching, monoliths were washed several times in distilled water to remove residual nitric acid and then placed in acetone. Once the water was completely exchanged with acetone, the monoliths were dried by supercritical CO_2 extraction (Tc = 31.1 ^{o}C, Pc = 7.4 Mpa).[20] Cylindrical gold monoliths (diameter = 4.5 mm, height = 8 mm – 1 cm) were isolated with measured densities as low as 0.28 g/cc or 1.5 % relative density. SEM images of a dealloyed shell is shown in Figure 2 (see inset). Dealloyed shell dimensions are roughly 9.6 µm in diameter and 200 nm thick, similar to non dealloyed silver/gold shell dimensions suggesting little volume change during the dealloying/drying steps. The dealloyed gold nanostructure on the shell surface is similar to previous reports with ligament spacings of 10 – 100 nm[3a] with no evidence of silver found in the EDAX spectrum. The gold foam surface area of 1.48 m^2/g, as determined by BET surface analysis, is comparable to previously reported values for dealloyed Au porous materials.[3a] Interestingly, the mole fraction of gold in the $Ag_{0.85}Au_{0.15}$ hollow shells is below the 3-D site percolation threshold for bulk alloys and dealloying is not predicted to form a stable bicontinuous gold structure.[21] Many factors may account for the stable dealloyed $Ag_{0.85}Au_{0.15}$ shells e.g., alloy preparation, length scale, geometry, etching conditions, and further investigations to understand this result are ongoing.

We have synthesized hierarchical porous gold foam monoliths by dealloying cast hollow Ag/Au shells. Large ultra-low density gold monoliths were synthesized by slipcasting, templating, and dealloying techinques and we are currently investigating the generality of this approach to prepare other hierarchical metallic porous materials. Monolithic catalysts are of interest as alternatives to traditional powder/slurry systems is increasing due to catalyst reusability and minimization of environmental waste.[22] The catalytic oxidation activity as well as the mechanical strength properties of these materials are currently under investigation.

Acknowledgment. This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Lab under Contract W-7405-Eng-48. The authors would like to thank Jim Ferreira for SEM analysis.

Supporting Information Available. Synthesis of metal coated PS beads and casting process. Additional SEM images of prepared foams with EDAX spectra.

[20] Monoliths dried from water or organic solvents at ambient temperature were more susceptible to cracking and densification.

[21] Vukmirovic, M. B.; Dimitrov, N.; Sieradski, K. *J. Electro. Chem. Soc.* **2002**, *149*, B428.

[22] (a) Boger, T.; Zieverink, M. M. P.; Kreutzer, M. T.; Kaptejn, F.; Moulijn, J. A.; Addiego, W. P. *Ind. Eng. Chem. Res*. **2004**, *43*, 2337. (b) Irandoust, S.; Andersson, B. *Catal. Rev.-Sci. Eng*. **1988**, *30*, 314. (c) Kapteijn, F.; Nijhuis, T. A.; Heiszwolf, J. J.; Moulijn, J. A. *Catal. Today* **2001**, *66*, 133. (d) Cybulski, A.; Moulijn, J. A. *Catal. Rev.-Sci. Eng.* **1994**, *36*, 179.

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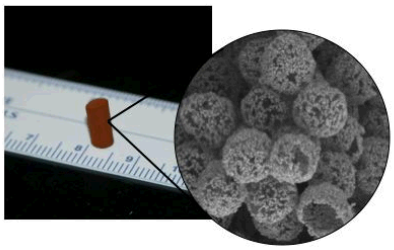
Synthesis and Characterization of Hierarchical Porous Gold Materials

A method to prepare hierarchical porous gold monoliths was developed. Cast hollow Au/Ag spheres, templated by polystyrene beads, were dealloyed to prepare hollow nanoporous shells. Robust gold monoliths with 2% relative density were readily achieved.



Supporting Information

Synthesis and Characterization of Hierarchical Porous Gold Materials

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Materials. Polystyrene beads (10 μm) were purchased from Duke Scientific (Palo Alto, CA). Polystyrene beads (1 μm) were synthesized using literature methods.[i] Gold and gold/DMAP nanoparticles were synthesized according to literature procedures.[ii] A modified procedure of that used by Natan et al. was used for electroless gold deposition in which polyvinylpyrrolidinone was added as stabilizer.[iii]

Synthesis of gold coated 10 μm polysytrene microparticles. 0.75 mL aliquot of a 10% soln of PS/DVB beads was stirred in a 10 mL portion of a gold colloid for 24h. The particles were then

isolated by centrifugation and washed with distilled water. The pink colored beads were redispersed in 80 mL of distilled water. Polyvinylpyrrolidinone (1.0 g, 0.1 mmol) and hydroxylamine hydrochloride (200 mg, 2.87 mmol) were added to the PS/DVB suspension. Under vigorous stirring, tetrachloroauric acid (135 mg, 0.397 mmol) was added to the suspension. The suspension gradually turned from a bright yellow to a golden brown color within 30 min. After 2h, the PS/DVB beads were isolated by centrifugation and washed with distilled water.

Synthesis of gold/silver coated 10 µm polysytrene microparticles. Gold coated polystyrene microparticles (vide supra) were suspended in 80 mL distilled water. Silver nitrate (380 mg, 2.23 mmol) and polyvinylpyrrolidinone (1.0 g, 0.01 mol) and conc. NH_4OH (2 mL) were added to the reaction mixture. Glucose (1.28 g, 7.1 mmol) was dissolved in 10 ml of distilled water and then added to the gold coated polystyrene reaction mixture. The reaction was stirred for 12 h at room temperature. The particles were then isolated by centrifugation and washed with distilled water.

Synthesis of gold coated 1 µm polystryene microparticles. Placed 1 mL of a x.xx % solution of 1µm polystyrene beads in 2 mL of gold/DMAP nanoparticles for 4 days. The particles were then isolated by centrifugation and washed with distilled water. The pink colored beads were redispersed in 80 mL of distilled water. Polyvinylpyrrolidinone (1.0 g, 0.1mol) and hydroxylamine hydrochloride (100 mg, 1.43 mmol) were added to the PS/DVB suspension. Under vigorous stirring, tetrachloroauric acid (100 mg, 0.29 mmol) was added to the suspension. The suspension gradually turned from a bright yellow to a golden brown color within 30 min. After 2h, the PS/DVB beads were isolated by centrifugation and washed with distilled water.

Synthesis of gold/silver coated 1 µm polysytrene microparticles. Gold coated polystyrene microparticles (vide supra) were suspended in 80 mL distilled water. Silver nitrate (285 mg, 1.69 mmol) and polyvinylpyrrolidinone (1.0 g, 0.01 mol) and conc. NH_4OH (2 mL) were added to the reaction mixture. Glucose (1.0 g, 5.5 mmol) was dissolved in 10 ml of distilled water and then added to the gold coated polystyrene reaction mixture. The reaction was stirred for 12 h at room temperature. The particles were then isolated by centrifugation and washed with distilled water.

Synthesis of gold/silver monoliths. Gold/Silver coated polystyrene microparticles (1 or 10 µm) were suspended in 1-2 mL of distilled water. The suspension was poured into a Teflon tube that had been placed in a plaster of paris mould. The plaster of paris slowly wicks away the water, leaving a cylindrical monolith of metal coated polystyrene beads deposited on the surface. After the water was completely removed from the suspension, the monolith was dried at 50 ^{o}C for 12 h. The monolith was then carefully removed from the Teflon tube. To remove the polystyrene core, the monolith was heat treated to 400 ^{o}C for 12 h (5 ^{o}C/ min ramp) under an N_2 atmosphere. Minimal reduction in monolith volume was observed after heat treatment.

Synthesis of dealloyed gold monoliths. Gold/Silver monoliths, templated with either 1 or 10 µm polystyrene microparticles, were placed into an acetone bath and allowed to soak overnight. Water was gradually introduced over the course of several days until the water composition was 100%. A 2 mL aliquot of a 3.55 M nitric acid solution was introduced into the gold/silver monolith. Over the course of several hours the monolith started to turn a dark brown color. After 24 h the monolith was dark brown color. The etching solution was removed and 2 mL of a 7.9 M solution added to the monolith and allowed to soak. After 12h this etching solution was removed and a 2 mL solution of 11.8 M nitric acid was added. After 8 h, the etching solution was removed and concentrated nitric acid was added to the monolith and allowed to soak for an additional 12 h. The concentrated nitric acid was removed and the monolith was soaked in distilled water to remove residual nitric acid. The water was then exchanged with acetone, preparatory to the supercritical drying step. The monolith was then dried with supercritical CO_2.

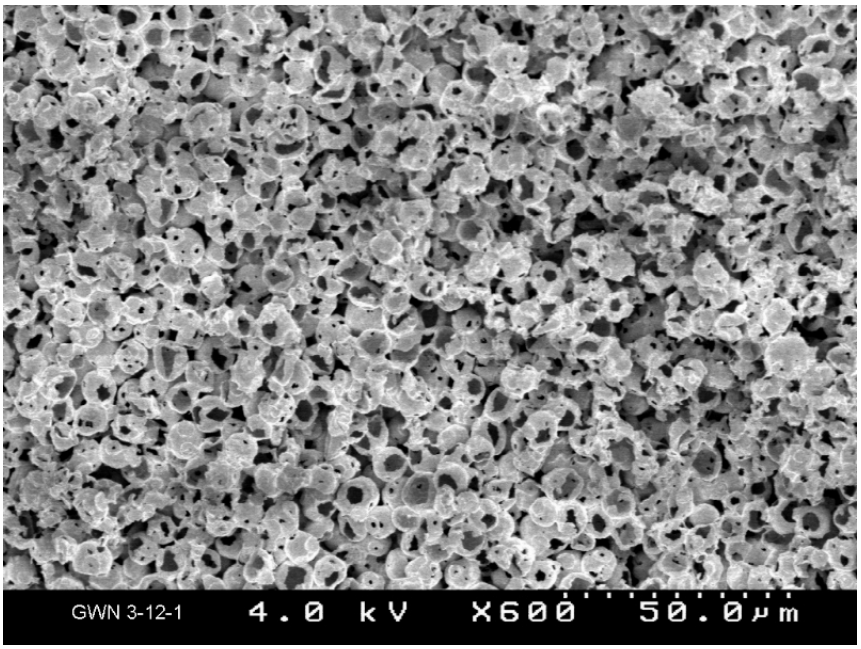


Figure 1. SEM image of monolith fracture surface containing PS templated gold shells.

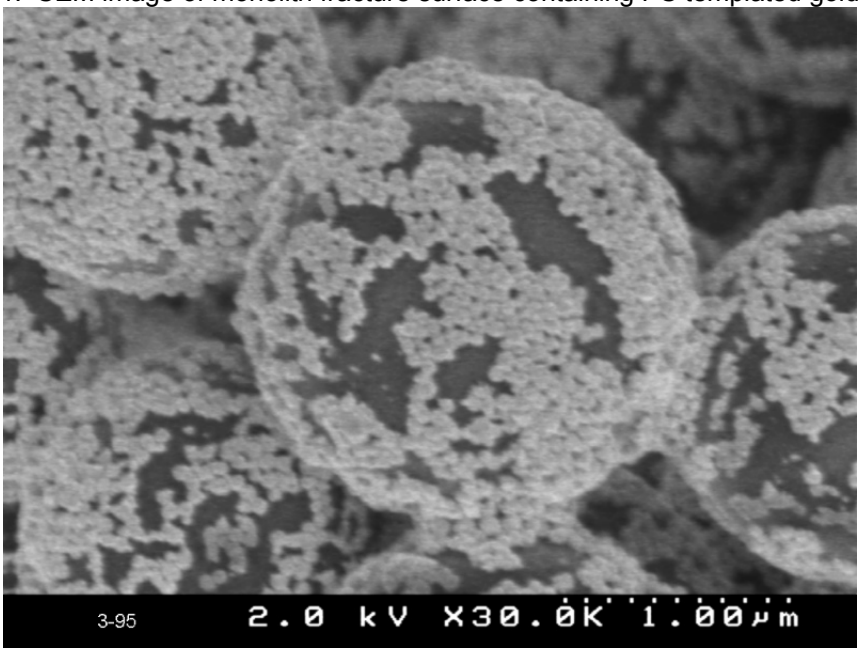


Figure 2. SEM image of gold deposited on 1 μm PS bead

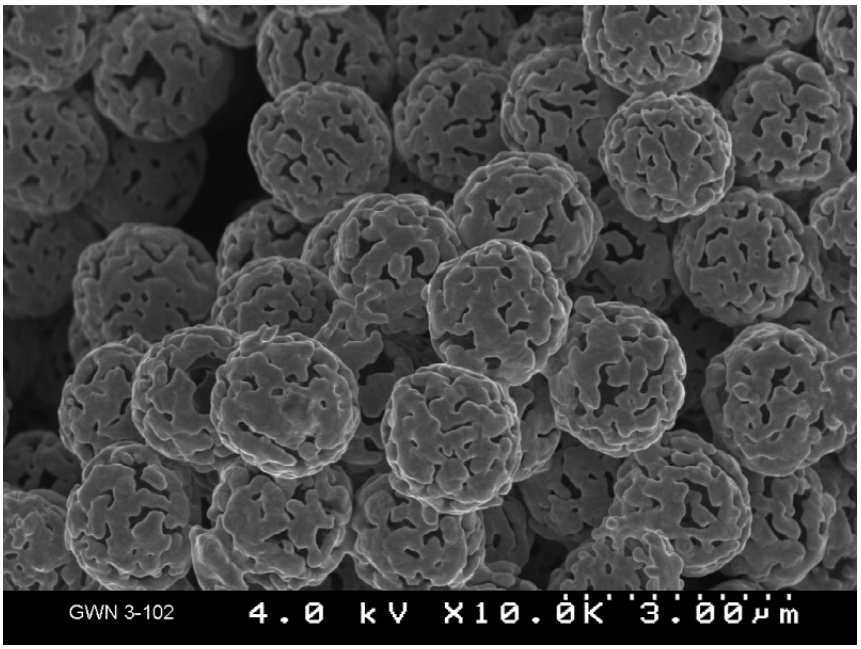


Figure 3. SEM image of monolith fracture surface containing 1 μm $Ag_{0.7}Au_{0.3}$ alloy hollow spheres.

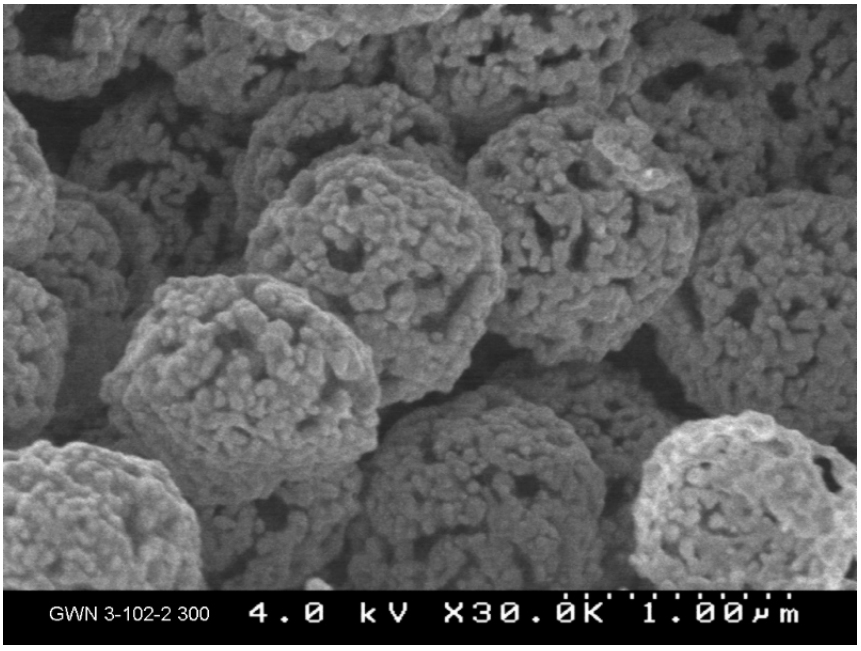


Figure 4. SEM image of monolith fracture surface containing 1 μm dealloyed Au hollow spheres post 300 ^{o}C anneal.

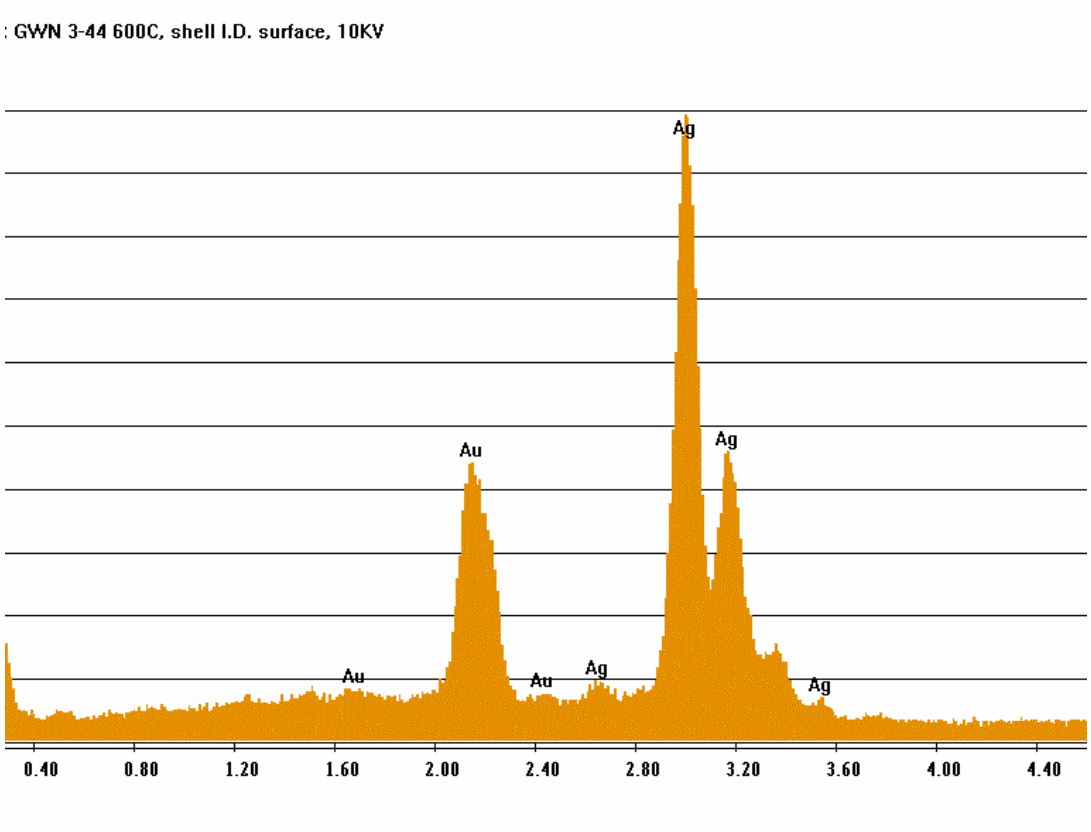


Figure 5. EDAX spectrum of hollow $Ag_{0.85}Au_{0.15}$ alloy shells

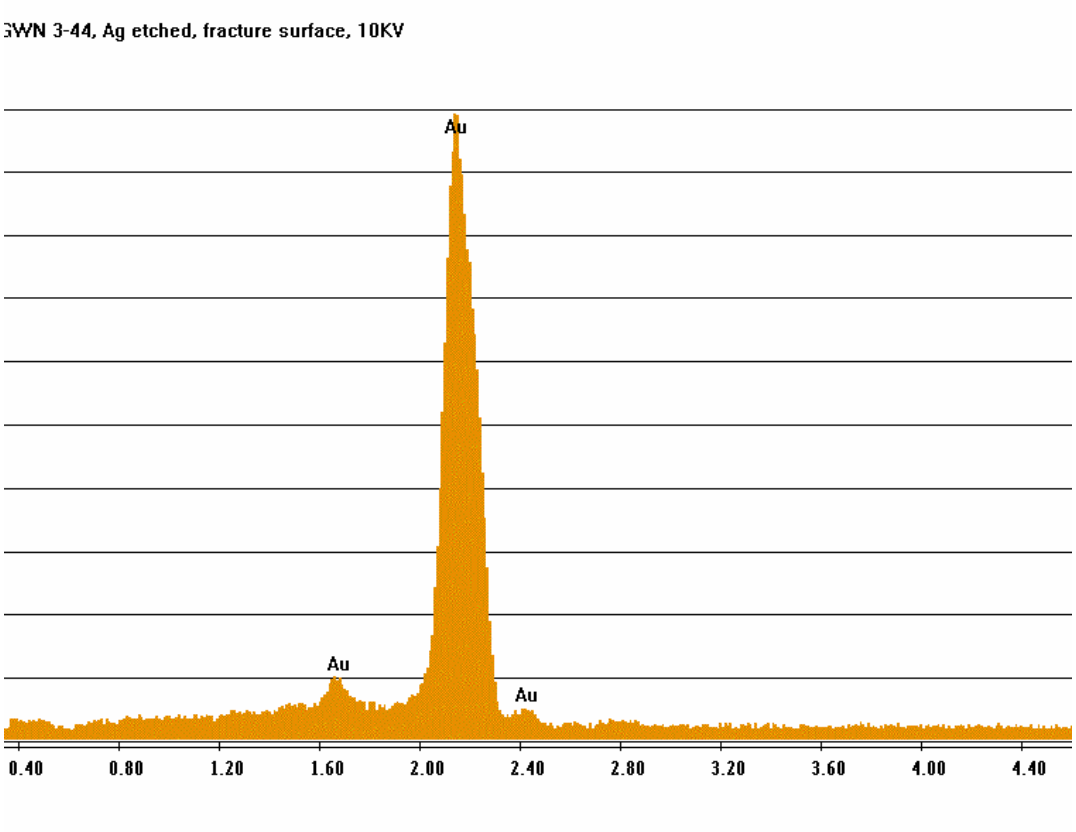
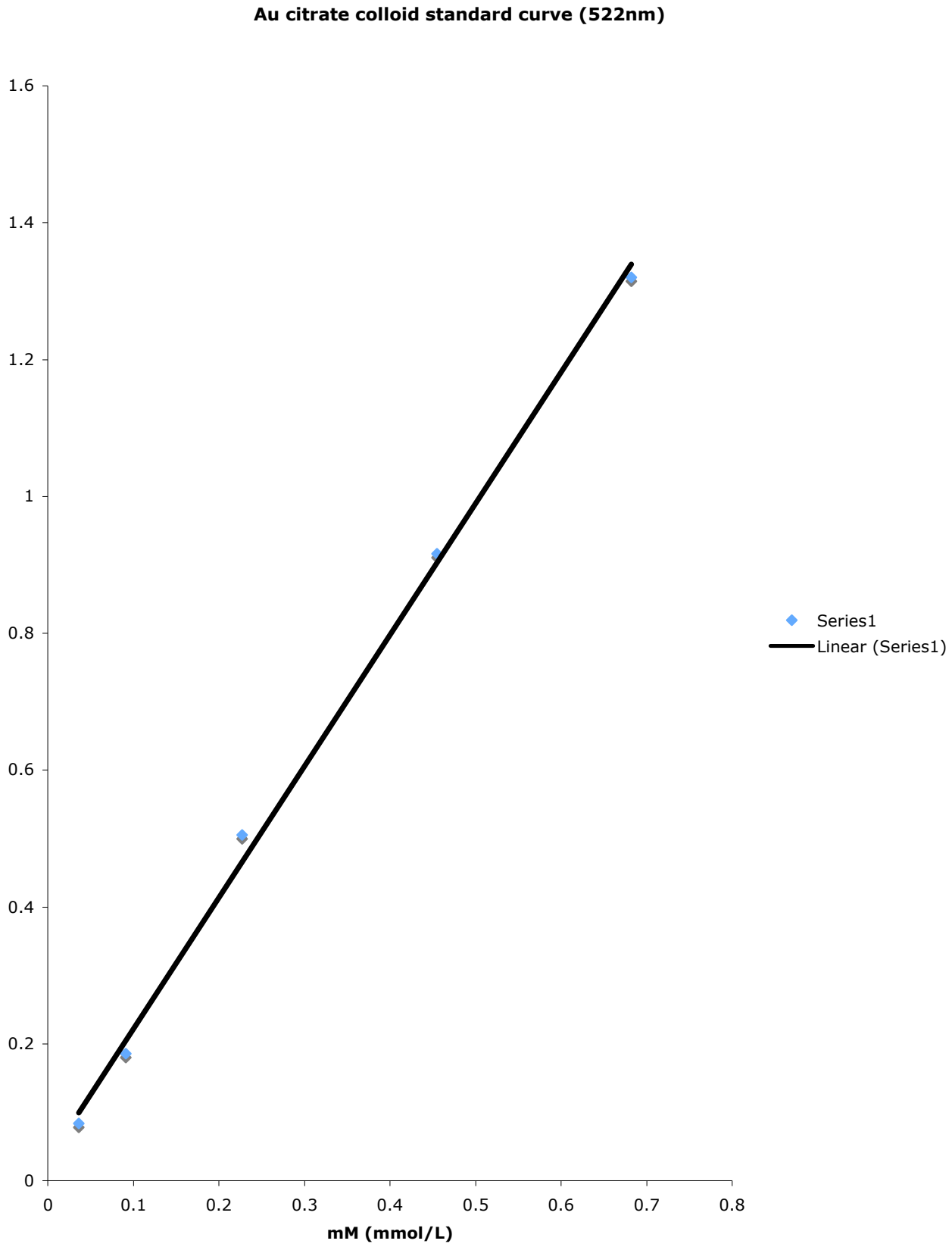


Figure 6. EDAX spectrum of dealloyed hollow Au nanoporous shells


Au citrate colloid standard curve (522nm)
1.6
1.4
1.2
1
0.8
0.6
0.4
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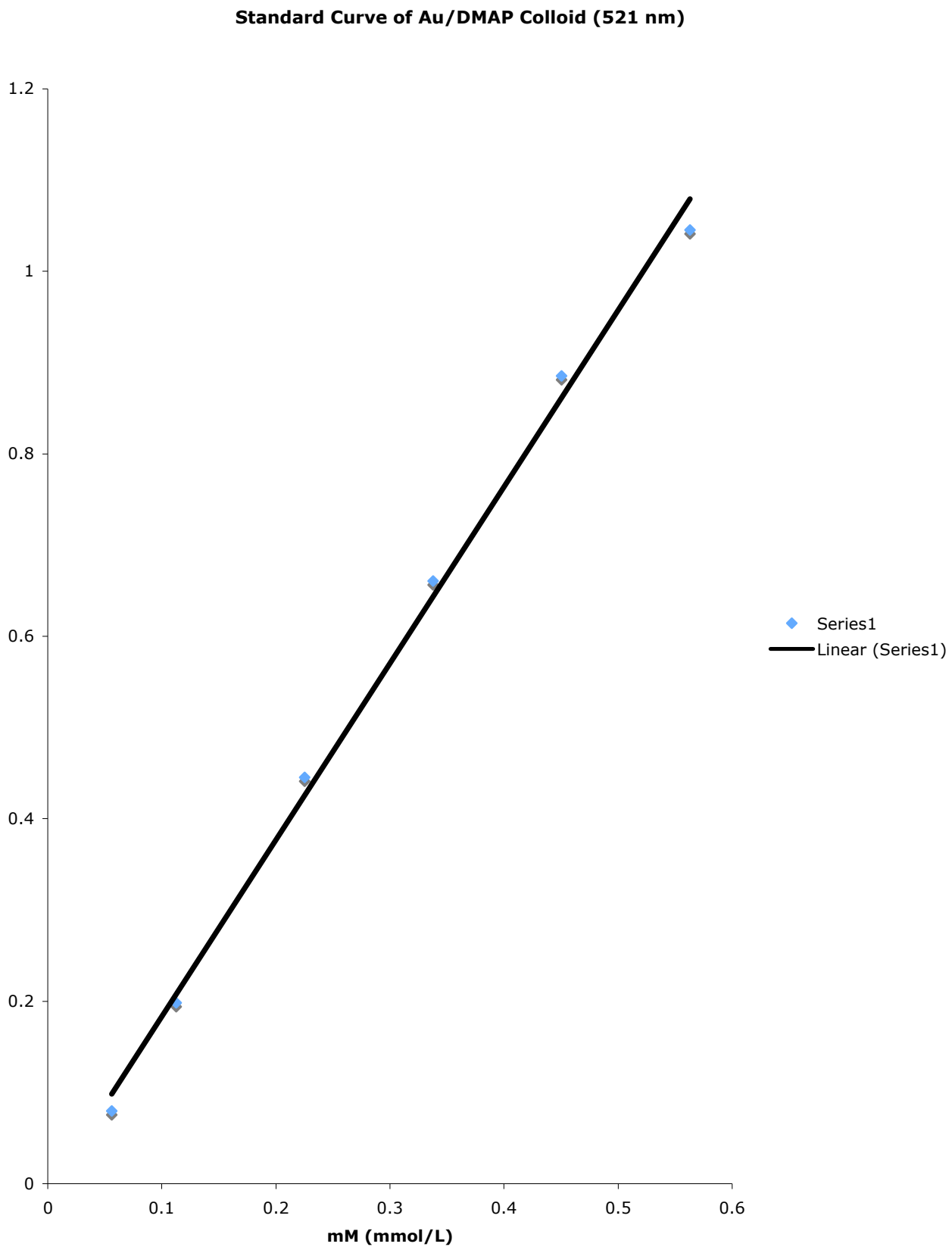
mM (mmol/L)
Series1
Linear (Series1)


Standard Curve of Au/DMAP Colloid (521 nm)
1.2
1
0.8
0.6
0.4
0.2
0
0
0.1
0.2
0.3
0.4
0.5
0.6
mM (mmol/L)
Series1
Linear (Series1)

[i] Khan, M. A.; Perruchot, C.; Armes, S. P., Randall, D. P. *J. Mater. Chem.* **2001**, *11*, 2363.
[ii] (a) Turkevich, J.; Stevenson, P. C.; Hillier, J. *Discuss. Faraday Soc*., **1951**, *11*, 55., (b) Gittins, D. I.; Caruso, F. *Angew. Chem. Int. Ed*. **2001**, *40*, 3001.
[iii] Brown, K. R.; Walter, D. G.; Natan, M. J. *Chem. Mater*. **2000**, *12*, 306.