Abstract

Reducing AgNO_3 by glucose at basic pH coated the surface of silica spheres with a high density of hemispherical silver nanoparticles (average diameter 3.2 ± 1 nm). A much lower silver concentration than is standard favored heterogeneous nucleation of silver on the silica surface at the expense of homogeneous nucleation in solution. The slow growth rate of the nuclei promoted the formation of discrete silver particles rather than a continuous shell. Based on scanning electron microscopy and transmission electron microscopy, the surface coverage of silver seed particles was as high as 25% at 10 °C without prior functionalization of the silica. The particles were composed of metallic silver based on x-ray photoelectron spectroscopy. There was a sharp increase in the silver surface coverage and decrease in the particle size when the temperature was raised from 5 °C to 10 °C and the amount of silica was decreased from 0.2 to 0.025 V/V%. The size was controlled by the diffusion barrier through the ion shell surrounding the silica spheres and by maintaining reaction conditions where the particles on the surface compete for silver.

Coating nonfunctionalized silica spheres with a high density of discrete silver nanoparticles

Stephen Purdy

*Department of Materials Science and Engineering
University of Arizona, Tucson, Arizona 85721, USA*

Anthony J. Muscat*

*Department of Chemical and Environmental Engineering
University of Arizona, Tucson, Arizona 85721, USA*

Keywords: colloids, nanoparticle, nucleation, Tollens reagent, diammine silver, surface coverage, core-shell
2010 MSC: 00-01, 99-00

Introduction

Core-shell nanoparticles with a variety of compositions have been studied extensively because of the potential to combine the advantageous properties of two or more materials (Senapati et al., 2014). In particular, much interest
5 has been placed on the coating of dielectric particles with metal nanoparticles (Jiang and Liu, 2003; Jackson and Halas, 2001; Brito-Silva et al., 2013; Peterson et al., 2007). The resulting properties of these composite materials depend largely on their structure (Preston and Signorell, 2009; Tzounis et al., 2014; Pan et al., 2014). For example, the surface plasmon resonance of silver-coated silica
10 particles changes from a single peak to multiple peaks or a single broad peak depending on the connectivity among the silver nanoparticles making up the shell (Peterson et al., 2007; Preston and Signorell, 2009). Similarly, the antimi-

*Corresponding author

Email address: muscat@email.arizona.edu (Anthony J. Muscat)

URL: <http://muscat.chee.arizona.edu/> (Anthony J. Muscat), +1-520-626-6580 (Anthony J. Muscat)

crobial activity of silver particles in the shell depends on their size (Markova et al., 2012; Kedziora et al., 2012). Since properties depend on the morphology
15 of the material in the shell, synthesis methods are needed that exert control over the shell material.

Synthesis methods for core-shell silica-silver nanoparticles can be broken down into two broad categories: seeded growth and direct reduction. With seeded growth the silica core is usually functionalized (Jackson and Halas, 2001; Kim et al., 2008; Choma et al., 2011), most commonly with either metal ions
20 such as tin (Choma et al., 2012) or an alkoxysilane terminated by either an amine (Kim et al., 2008; Choma et al., 2011; Brinson et al., 2008) or a thiol group (Heuck and Staufer, 2011). The metal nanoparticles are synthesized separately from the silica spheres, and added after the core particle is functionalized. Often
25 the synthesis of the metal nanoparticles includes a ligand or capping agent that makes the interaction between the particle and the silica surface more energetically favorable. Functionalization of the silica particle changes its zeta potential (Goodwin et al., 1990). Under the right conditions, the silica and the metal nanoparticle interact more strongly and adhere to one another. The seed
30 layer doesn't necessarily have to be composed of the same metal as the final coating. In several instances, gold is used as the seed layer, and the final silver shell is grown over the gold seeds by the reduction of a silver salt to metallic silver (Jackson and Halas, 2001; Choma et al., 2012; Dementeva et al., 2012). This method forms bimetallic coatings that have useful properties (Kim et al.,
35 2008; Zhang et al., 2007).

With direct reduction no seeding step is used. Instead, the metal precursors are reduced at the surface and deposit on the spheres (Zhang et al., 2004), eliminating the need to synthesize the seed particles separately. Similar to the seeded growth method, the surface of the core particles is often functionalized
40 to achieve high surface coverages (Kobayashi et al., 2001; Lee et al., 2006; Zhang et al., 2012). For direct reduction to work, the surfaces of the core particles and precursor ions must be oppositely charged. Otherwise electrostatic repulsion will make the formation of nuclei on the core surface energetically unfavorable.

Two of the most common chemistries used are the reduction of silver nitrate by
 45 polyvinylpyrrolidone (PVP) (Lee et al., 2006) and the reduction of diammine
 silver ($[\text{Ag}(\text{NH}_3)_2]^+$) by formaldehyde or glucose (Peterson et al., 2007; Pan
 et al., 2014; Homan et al., 2010). In the latter method the Tollens' reagent
 $[\text{Ag}(\text{NH}_3)_2]^+$ is formed by the complexation of silver ions with ammonia. The
 complex reacts with aldehydes and alpha hydroxy ketones yielding metallic sil-
 50 ver, ammonia, and carboxylic acids.

One drawback of direct reduction is the sparse seed layer that usually forms,
 which alters the morphology of the final coating. The low nucleation density is
 the result of either poor attraction between the silver salt and the silica surface
 or the competition between nucleation and growth. A good understanding of the
 55 chemistry and kinetics of seed layer formation is important because it determines
 whether particles in the final coating remain disconnected or connect and form
 a porous shell. In this study we show that a dense layer of nanometer-size
 silver nanoparticles deposit onto much larger silica particles without separately
 functionalizing or seeding the surface.

60 **Materials and Methods**

Materials

Tetraethoxysilane (TEOS) (Sigma: 86578), A.C.S. grade NH_4OH (Sigma:
 221228), A.C.S. grade AgNO_3 (Sigma: 209139), and A.C.S. grade D-(+)-glucose
 (Sigma: G5767) were purchased from Sigma Aldrich and used without further
 65 purification. 30% H_2O_2 , 96% H_2SO_4 , and A.C.S grade ethanol were purchased
 from ESP chemicals. 18.2 M Ω -cm DI water was used in all processes.

Silica Particle Synthesis

Silica particles were synthesized using a modified version of the Stöber
 method (Stöber et al., 1968; Bogush et al., 1988). Briefly, a room temperature
 70 solution of water and ammonium hydroxide in ethanol was added to a solution
 of TEOS in ethanol in a round bottom flask under stirring. The final volume of

the solution was 111 mL, and was 0.3 M in TEOS, 1 M in NH_4OH , and 8 M in H_2O . The flask was sealed with a ground glass stopper to prevent evaporation of ammonia during the reaction. After 2 h the resulting particles were centrifuged
75 (4000 RPM, 20 min) and washed 3 times with DI water. The washed particles were dispersed in DI water by sonicating for 10 min. The particle diameter was approximately 500 nm.

Silver Coating

Silica particles were coated with silver by modifying the procedure described
80 in reference (Peterson et al., 2007). We used a much lower silver concentration at similar ammonia and glucose concentrations and increased both the temperature and reaction time to favor nucleation over particle growth. Coating was performed in a capped plastic Erlenmeyer flask (250 mL). The reactions were carried out below room temperature by partially submerging the flask in a bath
85 of ice water. First, silica particles suspended in water were added to a glucose solution under moderate stirring and cooled to the desired reaction temperature, which was typically 10 °C. A second solution of AgNO_3 and NH_4OH was added to the mixture of silica particles and glucose to initiate the reaction. Unless otherwise noted, the final solution concentrations were 2 mM AgNO_3 , 33 mM
90 glucose, and 63 mM NH_4OH , with a silica concentration of 0.025 V/V% and a total volume of 50 mL. The reaction was stopped by placing the vessel in an ice bath. The coated particles were separated from the supernatant by centrifugation in a refrigerated centrifuge (Hermle Z400K) pre-set to 0 °C at 4000 RPM for 20 min. Washing and centrifugation were repeated 3 times with DI water.
95 Finally, particles were redispersed in ethanol and stored in a refrigerator.

Characterization

UV-Vis spectra were collected on a Jasco V670 UV-Vis spectrometer. Samples for UV-Vis experiments were dispersed in ethanol and pipetted into a polymethylmethacrylate (PMMA) cuvette. Scanning electron microscopy (SEM)

100 was performed on a Hitachi S-4800 field emission SEM at an accelerating voltage of 20 kV and a probe current of 10-12 μ A. Samples for SEM were prepared by dip coating a 200 mesh copper TEM grid with the particle dispersion. Particle sizes were measured from the images using ImageJ. Transmission electron microscopy (TEM) was performed on a Hitachi H8100 at an accelerating voltage of 200 kV. Samples for TEM were drop cast on a lacey carbon TEM grid
105 and dried over night. Surface analysis was performed by x-ray photoelectron spectroscopy (XPS) equipped with a non-monochromatic Al K α x-ray (1486.6 eV) source and a double-pass cylindrical mirror analyzer (Physical Electronics 549). Spectra were acquired at a constant pass energy of 50 eV. All peaks were
110 referenced to the C 1s binding energy at 284.5 eV. Samples for XPS analysis were prepared by drop casting particles dispersed in ethanol on a piece of silicon wafer that was 1 cm by 2 cm in size. Substrates for XPS analysis were degreased and cleaned with a 3:1 V/V% mixture of sulfuric acid and hydrogen peroxide (piranha) before use. Samples for XPS were outgassed over night in ultrahigh
115 vacuum before transfer to the XPS chamber for analysis.

Results

Figure 1a shows the typical morphology observed on the surface of a silica sphere. The silver nanoparticles appear as light patches in the SEM image. The particles cover much of the surface and are evenly distributed with few
120 agglomerates. The particles are discrete and do not form a continuous layer, evidenced by the charging in the SEM image. Figure 1b shows the edge of a silica sphere imaged by TEM. Fringes from a larger silver particle are visible at the far left of the image. Smaller silver particles appear as darker regions on the inner section of the sphere due to Z-contrast. The sphere is coated with a thin layer
125 of amorphous material that grew outwards the longer the electron beam focused on a single area. At 200 kV accelerating voltage, any organic material present in the sample degrades to amorphous carbon. The source of the organic material is most likely adsorbed solvent or incompletely hydrolyzed TEOS present in the

Figure 1: Typical results of the silver coating procedure at 10 °C, 2 mM AgNO₃, 63 mM NH₄OH, 33 mM glucose, and 0.025 V/V% silica. Using a low molarity of silver nitrate leads to a high surface coverage of small silver particles 3.2±1 nm in size. All scale bars are 25 nm in length. a) SEM of silica particle surface, b) TEM image of coated silica particle, c) histogram of silver particles from two SEM images, and d) Ag 3d XPS spectrum.

Stöber sphere. Figure 1c shows a histogram of silver particle sizes after a 120 min coating reaction measured from SEM images at ×800k magnification. The sizes of 224 particles were measured from two separate synthesis batches. The average particle size is 3.2±1 nm. A small number of particles larger than 6 nm were also present. Figure 1d shows the Ag 3d XPS spectrum of a silicon wafer containing the silica spheres, confirming the presence of metallic silver on the sphere surface. The two peaks are located at 368.2 and 374.2 eV and assigned to the Ag 3d_{5/2} and Ag3d_{3/2} states of metallic silver.

Figure 2: SEM images of silica particles coated at 10 °C, 2 mM AgNO₃, 63 mM NH₄OH, 33 mM glucose, and 0.025 V/V% silica; a) bare silica, b) 30 min, c) 60 min, d) 120 min. Scale bars are all 50 nm in length.

Scanning Electron Microscopy

Figure 2 shows how the coating morphology changes with reaction time at 10 °C. Samples were imaged before coating (bare silica spheres Figure 2a) and after 30 min (Figure 2b), 60 min (Figure 2c), and 120 min (Figure 2d). At $\times 150k$ magnification (not shown), it is difficult to resolve individual particles, but the surface texture of the coated spheres looks markedly different from the uncoated sphere. At $\times 400k$ magnification in Figure 2, individual silver particles are resolved as diffuse light areas. Because the silica particles are insulating and the silver particles are not close enough together to form a conductive path, a significant amount of charging is evident in the images. An accurate surface coverage is difficult to quantify from the SEM images because the silver nanoparticles do not have discrete boundaries at any magnification, and at around 3 nm in size, the particles are close to the resolution limit of the microscope. However, a rough estimate can be made based on the average particle size and the number of particles in a given area. For the 30 min sample, the average particle size was 3.9 ± 0.8 nm (108 particles measured), and the surface coverage was estimated to be 10%. For the 60 min sample, the average particle size was 3.1 ± 0.8 nm (160 particles measured), and the surface coverage was estimated to be 11.5%. For the 120 min sample, the average particle size was 3.2 ± 1 nm (224 particles measured), and the surface coverage was estimated to be 25%. This is close to, but somewhat higher than the value obtained when the size of each individual particle is used to estimate the percentage of the surface covered with silver.

Figure 3 shows the changes that occur in the morphology for different coating times when the reaction is carried out at 5 °C instead of at 10 °C. Samples were made for reactions lasting 30 min (Figure 3a), 60 min (Figure 3b), and 120 min (Figure 3c). For all times at 5 °C the surface coverage of silver on the silica particles is poor and the silver particles are larger than those present when the reaction temperature is 10 °C (compare Figure 2). The silver particles do not appear to change in size when the reaction time is lengthened. Instead the number of silver particles present increases with increasing time. Particles are located almost exclusively on the surface of the silica spheres, and not on the

Figure 3: SEM images of synthesis run at 5 °C and 2 mM AgNO_3 , 63 mM NH_4OH , 33 mM glucose, and 0.025 V/V% silica at reaction times of a) 30 min, b) 60 min c) 120 min. Scale bars are 200 nm in length.

substrate despite three centrifugation and washing cycles prior to preparing the sample for SEM. The few silver particles that were present on the copper SEM
170 substrate are similar in size to the particles present on the silica particle. For the 30 min reaction many spheres had few or no observable silver particles at $\times 100k$ magnification. From the few particles observed (14 particles at $\times 150k$ magnification) the average diameter was 11.5 ± 2.9 nm. The change in surface texture typical of the presence of many small silver particles was not present
175 either. Rather the sphere surface was smooth and featureless, bearing more resemblance to the surface texture of the control sample (Figure 2a). For the 60 min sample, the average particle size was 11.6 ± 2.9 nm (99 particles at $\times 150k$ magnification). In this sample, the number of particles is higher, but the size and standard deviation are almost identical to the 30 min sample. For the 120
180 min sample, the average particle size is 10.1 ± 2.8 nm (172 particles measured at $\times 150k$ magnification).

Figure 4 shows the surface coverage when the amount of silica particles is varied. All samples were run with the same size silica particles (approximately 500 nm) for two hours at 10°C . The molarities used in the coating process were
185 2 mM AgNO_3 , 63 mM NH_4OH , and 33 mM glucose. Samples were made at 0.025 V/V% (Figure 4a), 0.05 V/V% (Figure 4b), 0.1 V/V% (Figure 4c), and 0.2 V/V% silica (Figure 4d). These values correspond to an increase in surface area from the 0.025 V/V% by a factor of 2, 4, and 8 for the 0.05, 0.1 and 0.2 V/V% samples respectively. At 0.025 V/V%, the average particle size was
190 3.2 ± 1 nm, with a surface coverage of approximately 25%. Increasing the silica concentration to 0.05 V/V% caused the surface coverage to drop to 9% with an average particle size of 3.7 ± 1 nm. The surface coverage at 0.1 V/V% was less than 1%, and at 0.2 V/V% the surface coverage was 0%.

X-ray Photoelectron Spectroscopy

195 Figure 5 shows the high resolution XPS spectra of the silver coated silica particles. The O 1s spectrum has a peak centered at 532.8 eV and a shoulder at 530.2 eV. We assign these peaks to O-Si and O-Ag respectively. O-Ag bonds

Figure 4: SEM images of synthesis results at 10 °C and 2 mM AgNO_3 , 63 mM NH_4OH , 33 mM glucose at reaction times of 120 min and silica V/V% of a) 0.025, b) 0.05, c) 0.1, d) 0.2.

in metallic silver have a binding energy between 528 and 533 eV depending on the configuration (Waterhouse et al., 2004). The Ag 3d spectrum has two peaks centered at 368.2 eV and 374.2 eV that correspond to the $3d_{5/2}$ and $3d_{3/2}$ states of metallic silver (Moulder et al., 1995). The Si 2p spectrum has two peaks centered at 96.7 eV and 103.2 eV. The peak at 103.2 eV corresponds to SiO_2 in the Stöber spheres and on any exposed parts of the silicon wafer. The peak at 96.7 eV corresponds to Si, but is shifted to lower binding energy by over 2 eV from where it typically appears at 99.3 eV. The large shift is indicative of inhomogeneous charging in this sample. The silicon substrate develops a different surface potential than the silica particles when irradiated by the x-ray source (Kelly, 2003) because the two are not in electrical contact. Thus there are two charging corrections, one for the particles and another for the silicon substrate. We charge corrected for the particles which explains the good agreement between the binding energies of peaks due to the coated particles and values typically found in the literature as well as the low value for the peak resulting from the substrate. Similar phenomenon can be seen in reference (Sohn, 2013).

Discussion

The presence of silver after the coating reaction is confirmed by the high resolution Ag 3d and O 1s XPS spectra. The chemical state of the silver is metallic based on the binding energy of the Ag $3d_{5/2}$ state. The binding energy of this state for metallic silver is in the narrow range from 368.1-368.3 eV, while this peak in silver oxides is shifted to lower binding energies from 367.4-368.0 eV (Moulder et al., 1995). Because the silver present is metallic, the Ag-O peak is indicative of oxygen in a solid solution with silver or a surface oxygen species. At a binding energy of 530.2 eV, our result agrees most closely with oxygen dissolved in the bulk of metallic silver, which has a binding energy between 530.3-530.6 eV (Bao et al., 1996; Waterhouse et al., 2004).

The formation of a dense seed layer by the direct reduction method requires

Figure 5: High resolution XPS spectra of silver coated Stöber spheres at 10 °C 2 mM AgNO₃, 63 mM NH₄OH, 33 mM glucose, and 0.025 V/V% silica. Red circles: raw data. Grey line: peak fit. Black line: component peaks of fit.

both heterogeneous nucleation and fast nucleation compared to particle growth because the two are in competition for precursors. It is unlikely that under the conditions tested in this study that homogeneous nucleation occurs or that silver nucleates homogeneously and then attaches to the sphere surface. If homogeneous nucleation occurred then we would expect particle agglomeration on the surface, but a relatively monodispersed seed layer was observed by SEM even when nucleation was slowed by lowering the temperature to 5 °C. Homogeneously nucleated silver particles must have precipitated during centrifugation along with the coated silica particles. If this is the case, any homogeneously nucleated silver particles would have been seen in SEM and TEM images as silver particles on the substrate. If any homogeneously nucleated silver particles remained in the supernatant in even a small concentration, it would have been colored, but in all experiments, the supernatant was clear and colorless. Furthermore, the silver particles were not removed by sonication between centrifugation and washing cycles because few silver particles were found on the copper grid in all of the SEM images taken. The silver was strongly attached to the silica even though the surface was not functionalized and no post synthesis annealing was applied. The TEM micrograph in Figure 1b shows the profile of one very large silver particle on the silica surface. The particle is hemispherical in shape with a distinct flat interface between the silver particle and the silica surface, suggesting that the particle nucleated on the silica surface, rather than sticking to the surface after forming in solution.

At an NH_4OH concentration of 63 mM, the pH of the coating solution is around 11. At this pH, the silica surface is negatively charged (Goodwin et al., 1990). The partial negative charge from the surface hydroxyl groups on the silica surface attracts the diammine silver ions in solution to the surface. When a reducing agent is present, the diammine silver ion is reduced to metallic silver on or close to the silica surface. With a negatively charged surface, it is unlikely that metallic nanoparticles, which are also negatively charged in solution (Alvarez-Puebla et al., 2005), would stick to the surface due to electrostatic repulsion. Functionalizing the silica surface to create an amine terminated surface instead

of a hydroxyl terminated surface changes the zeta potential of the surface enough that nanoparticles in solution can stick to the surface at low to neutral pH (Park et al., 2006). This change in zeta potential explains why most synthesis methods that use a seeding technique usually functionalize the surface first. This makes the interaction between silica and the seed nanoparticles more energetically favorable which allows for a dense seed layer. As shown in Figure 2d many small silver particles nucleated on the silica surface by maintaining a high pH and slowing the rate of silver reduction. The rate was slowed by reducing the concentrations of AgNO_3 and glucose and lowering the temperature of the coating reaction below room temperature.

The effect of temperature is seen in Figures 2 and 3. The surface coverage is higher and the particles are smaller at 10°C than at 5°C . The change in surface coverage is due to the increased energy barrier to nuclei formation at lower temperature. This energy barrier controls the critical nucleus size, and as the critical nucleus size increases, the nucleation rate decreases (Rempel et al., 2009). Since there are more nuclei present at 10°C than at 5°C and the availability of precursors and reducing agent is the same, the particles are smaller.

The availability of nucleation sites also plays a role in surface coverage. The number of suitable nucleation sites is directly related to the available surface area. If the silver nanoparticles nucleate evenly across all available surface area, it would follow that an increase in equivalent nucleation sites would cause the particles to be more spread out. This is demonstrated in Figure 4a (0.025 V/V% silica) and Figure 4b (0.050 V/V% silica). The distance between particles grows as the silica concentration is reduced because there are more nucleation sites available. The coverage of silver particles on the surface is reduced as a consequence. Both the average particle size and standard deviation do not change dramatically in the 0.025% and 0.05% silica concentrations. From this we conclude that not all nucleation sites have been filled. If growth and nucleation compete for available precursors, one would expect that if all the sites were filled, the surface coverage would reach a maximum and the particles that are

present would start to grow to a larger size. In the region of silica V/V% tested,
290 this was not the case.

The concentration of AgNO_3 and glucose changes the rate of chemical reduction of the diammine silver ion to metallic silver which in turn alters the morphology of the final coating (Brinson et al., 2008). When the solution becomes supersaturated with metallic silver (which occurs at very low concentrations),
295 nuclei of metallic silver form. If this reaction rate is too fast, supersaturation can reach a level that homogeneous nucleation is energetically favorable (Rempel et al., 2009). This is seen when the reaction is carried out at higher AgNO_3 concentrations or higher temperatures (Jiang and Liu, 2003). A slow reduction rate allows for the formation of many nuclei on the silica surface that then compete for silver. This competition, along with the diffusion barrier through the
300 ion cloud around the silica particles, leads to the formation of many small silver particles.

Conclusions

In this paper we demonstrate that a dense layer of small (3.2 ± 1 nm) hemispherical silver particles can be grown on the surface of much larger silica
305 spheres without a separate functionalization step. Low concentrations of Tollens' reagent ($[\text{Ag}(\text{NH}_3)_2]^+$) and glucose and low temperature caused silver to nucleate on the silica surface not in the bulk solution and slowed the particle growth rate promoting good surface coverage. The highest surface coverage of discrete nanoparticles was achieved at 10°C and a silica concentration of 0.025
310 V/V%. Increasing the amount of silica present during the seeding reaction caused the surface coverage to drop. Lowering the temperature of the reaction from 10°C to 5°C decreased the surface coverage of silver and increased the particle size. The nanoparticles contained metallic silver as shown by the Ag
315 $3d_{5/2}$ XPS state at 368.2 eV. The size and coverage of the silver nanoparticles depend on the temperature, reactant concentrations, and available surface area of silica.

Peterson *et al.* used a higher silver concentration at similar ammonia and glucose concentrations and lower temperatures and reaction times than we used
320 because their objective was to promote particle growth and form a continuous metal shell (Peterson et al., 2007). This method was also used by Homan *et al.* on amine modified silica with varying diammine silver concentrations which changed the silver particle size and surface coverage (Homan et al., 2010). Kobayashi *et al.* used alternating washes in tin and silver ions to grow a coating
325 of metallic silver by the oxidation of Sn^{2+} to Sn^{4+} (Kobayashi et al., 2001). Pan *et al.* similarly used tin ions adsorbed on silica to grow 10 nm seeds which were then used to grow a full shell by reduction of Tollens' reagent with glucose (Pan et al., 2014). Jiang *et al.* found that higher AgNO_3 concentrations or temperatures favored homogeneous nucleation (Jiang and Liu, 2003).

330 The surface coverage of the seed layer could influence the morphology of a shell grown from it. The morphology of the shell material can have an effect on the optical, electronic, and antimicrobial properties of the core shell particle, making control of the seed layer an important part of tuning these properties. Furthermore, small metal nanoparticles have shown catalytic activity that is
335 very different from their bulk counterparts (Lopez et al., 2004). This, along with interactions between a metal catalyst and the substrate on which it is bound, makes core-shell nanoparticles an ideal system to test the combined effects of both particle size and substrate-catalyst interactions at the nanoscale.

Acknowledgments

340 The authors thank Pablo Mancheno for his help with collection and analysis of XPS data. The authors also thank Lance Hubbard for his assistance collecting SEM images and for useful conversations about electrostatics in colloidal systems.

References

- 345 R. A. Alvarez-Puebla, E. Arceo, P. J. G. Goulet, J. J. Garrido, and R. F. Aroca.
Role of nanoparticle surface charge in surface-enhanced Raman scattering. *J.*
Phys. Chem. B, 109(9):3787–3792, 2005. doi: 10.1021/jp045015o.
- X. Bao, M. Muhler, Th. Schedel-Niedrig, and R. Schlögl. Interaction of oxygen
with silver at high temperature and atmospheric pressure: A spectroscopic
350 and structural analysis of a strongly bound surface species. *Phys. Rev. B*, 54:
2249–2262, 1996. doi: 10.1103/PhysRevB.54.2249.
- G.H. Bogush, M.A. Tracy, and C.F. Zukoski IV. Preparation of monodisperse
silica particles: Control of size and mass fraction. *J. Non-Cryst. Solids*, 104
(1):95 – 106, 1988. doi: 10.1016/0022-3093(88)90187-1.
- 355 B. E. Brinson, J. B. Lassiter, C. S. Levin, R. Bardhan, N. Mirin, and N. J.
Halas. Nanoshells made easy: Improving Au layer growth on nanoparticle
surfaces. *Langmuir*, 24(24):14166–14171, 2008. doi: 10.1021/la802049p.
- A. M. Brito-Silva, R. G. Sobral-Filho, R. Barbosa-Silva, C. B. de Araújo,
A. Galembeck, and A. G. Brolo. Improved synthesis of gold and silver
360 nanoshells. *Langmuir*, 29(13):4366–4372, 2013. doi: 10.1021/la3050626.
- J. Choma, A. Dziura, D. Jamiłoa, P. Nyga, and M. Jaroniec. Preparation and
properties of silica-gold core-shell particles. *Colloids Surf., A*, 373(1-3):167 –
171, 2011. doi: 10.1016/j.colsurfa.2010.10.046.
- J. Choma, D. Jamiłoa, J. Ludwinowicz, and M. Jaroniec. Deposition of silver
365 nanoparticles on silica spheres and rods. *Colloids Surf., A*, 411(0):74 – 79,
2012. doi: <http://dx.doi.org/10.1016/j.colsurfa.2012.07.004>.
- O.V. Dementeva, M.A. Filippenko, K.E. Groman, and V.M. Rudoy. New mul-
tifunctional nanoparticles with mesoporous cores and silver shells. *Colloid J.*,
74(4):440–444, 2012. doi: 10.1134/S1061933X12040059.

- 370 J.W. Goodwin, R.S. Harbron, and P.A. Reynolds. Functionalization of colloidal
silica and silica surfaces via silylation reactions. *Colloid. Polym. Sci.*, 268(8):
766–777, 1990. doi: 10.1007/BF01411109.
- F.C.A. Heuck and U. Staufer. Electroless deposition and structuring of silver
electrodes in closed microfluidic capillaries. *J. Microelectromech. Syst.*, 20(2):
375 451–459, 2011. doi: 10.1109/JMEMS.2011.2105254.
- K. Homan, J. Shah, S. Gomez, H. Gensler, A. Karpouk, L. Brannon-Peppas,
and S. Emelianov. Silver nanosystems for photoacoustic imaging and image-
guided therapy. *J. Biomed. Opt.*, 15(2):021316–021316–9, 2010. doi: 10.1117/
1.3365937.
- 380 J. B. Jackson and N. J. Halas. Silver nanoshells: Variations in morphologies
and optical properties. *J. Phys. Chem. B*, 105(14):2743–2746, 2001. doi:
10.1021/jp003868k.
- Z. Jiang and C. Liu. Seed-mediated growth technique for the preparation of a
silver nanoshell on a silica sphere. *J. Phys. Chem. B*, 107(45):12411–12415,
385 2003. doi: 10.1021/jp035060g.
- A. Kedziora, W. Strek, L. Kepinski, G. Bugla-Ploskonska, and
W. Doroszkiewicz. Synthesis and antibacterial activity of novel tita-
nium dioxide doped with silver. *J. Sol-Gel Sci. Technol.*, 62(1):79–86, 2012.
doi: 10.1007/s10971-012-2688-8.
- 390 M. A. Kelly. Analyzing insulators with XPS and AES. In D. Briggs and
J. T. Grant, editors, *Surface Analysis by Auger and X-ray Photoelectron Spec-*
troscopy, pages 191–210. IMPublications, Charlton, 2003.
- J. Kim, W. W. Bryan, and T. Randall Lee. Preparation, characterization, and
optical properties of gold, silver, and gold-silver alloy nanoshells having silica
395 cores. *Langmuir*, 24(19):11147–11152, 2008. doi: 10.1021/la8016497.

- Y. Kobayashi, V. Salgueiriño-Maceira, and L. M. Liz-Marzán. Deposition of silver nanoparticles on silica spheres by pretreatment steps in electroless plating. *Chem. Mater.*, 13(5):1630–1633, 2001. doi: 10.1021/cm001240g.
- J. Lee, D. Kim, Y. Jun, and S. Oh. Preparation of silica-silver heterogeneous nanocomposite particles by one-pot preparation strategy using polyol process: Size-controlled immobilization of silver nanoparticles. *Mater. Res. Bull.*, 41(8):1407 – 1416, 2006. doi: j.materresbull.2006.02.010.
- N. Lopez, T.V.W Janssens, B.S Clausen, Y. Xu, M. Mavrikakis, T. Bligaard, and J. K. Nørskov. On the origin of the catalytic activity of gold nanoparticles for low-temperature CO oxidation. *J. Catal.*, 223(1):232 – 235, 2004. doi: 10.1016/j.jcat.2004.01.001.
- Z. Markova, K. Siskova, J. Filip, K. Safarova, R. Prucek, A. Panacek, M. Kolar, and R. Zboril. Chitosan-based synthesis of magnetically-driven nanocomposites with biogenic magnetite core, controlled silver size, and high antimicrobial activity. *Green Chem.*, 14:2550–2558, 2012. doi: 10.1039/C2GC35545K.
- J. F. Moulder, W. F. Stickle, P. E. Sobol, and K. D. Bomben. *Handbook of X-ray Photoelectron Spectroscopy*. Physical Electronics Inc., Eden Prairie, MN, 1995.
- K. Pan, Y. Liang, Y. Pu, Y. Hsu, J. Yeh, and H. C. Shih. Studies on the photocatalysis of core-shelled SiO₂-Ag nanospheres by controlled surface plasmon resonance under visible light. *Appl. Surf. Sci.*, 311(0):399 – 404, 2014. doi: 10.1016/j.apsusc.2014.05.074.
- S. Park, M. Park, P. Han, and S. Lee. The effect of pH-adjusted gold colloids on the formation of gold clusters over APTMS-coated silica cores. *Bull. Korean Chem. Soc.*, 27:1341–1345, 2006. doi: 10.5012/bkcs.2006.27.9.1341.
- M. S.M. Peterson, J. Bouwman, A. Chen, and M. Deutsch. Inorganic metalodielectric materials fabricated using two single-step methods based on

- the Tollens process. *J. Colloid Interface Sci.*, 306(1):41 – 49, 2007. doi: 10.1016/j.jcis.2006.10.013.
- 425 T. C. Preston and R. Signorell. Growth and optical properties of gold nanoshells prior to the formation of a continuous metallic layer. *ACS Nano*, 3(11):3696–3706, 2009. doi: 10.1021/nn900883d.
- J.Y. Rempel, M.G. Bawendi, and K.F. Jensen. Insights into the kinetics of semiconductor nanocrystal nucleation and growth. *J. Am. Chem. Soc.*, 131
430 (12):4479–4489, 2009. doi: 10.1021/ja809156t.
- S. Senapati, S. K. Srivastava, S. B. Singh, and A. R. Kulkarni. SERS active ag encapsulated Fe@SiO₂ nanorods in electromagnetic wave absorption and crystal violet detection. *Environ. Res.*, 135(0):95–104, 2014. doi: 10.1016/j.envres.2014.08.026.
- 435 Y. Sohn. SiO₂ nanospheres modified by Ag nanoparticles: Surface charging and CO oxidation activity. *J. Mol. Catal. A: Chem.*, 379(0):59 – 67, 2013. doi: 10.1016/j.molcata.2013.07.015.
- W. Stöber, A. Fink, and E. Bohn. Controlled growth of monodisperse silica spheres in the micron size range. *J. Colloid Interface Sci.*, 26(1):62 – 69,
440 1968. doi: 10.1016/0021-9797(68)90272-5.
- L. Tzounis, R. Contreras-Caceres, L. Schellkopf, D. Jehnichen, D. Fischer, C. Cai, P. Uhlmann, and M. Stamm. Controlled growth of Ag nanoparticles decorated onto the surface of SiO₂ spheres: A nanohybrid system with combined SERS and catalytic properties. *RSC Adv.*, 4:17846–17855, 2014.
445 doi: 10.1039/C4RA00121D.
- G. I. N. Waterhouse, G. A. Bowmaker, and J. B. Metson. Mechanism and active sites for the partial oxidation of methanol to formaldehyde over an electrolytic silver catalyst. *Appl. Catal. A-Gen.*, 265(1):85 – 101, 2004. doi: 10.1016/j.apcata.2004.01.016.

450 J. Zhang, J. Liu, S. Wang, P. Zhan, Z. Wang, and N. Ming. Facile methods to coat polystyrene and silica colloids with metal. *Adv. Funct. Mater.*, 14(11): 1089–1096, 2004. doi: 10.1002/adfm.200400119.

J. Zhang, H. Liu, Z. Wang, and N. Ming. Preparation and optical properties of silica@Ag-Cu alloy core-shell composite colloids. *J. Solid State Chem.*, 180
455 (4):1291 – 1297, 2007. doi: 10.1016/j.jssc.2007.01.035.

S. Zhang, F. Ren, W. Wu, J. Zhou, L. Sun, X. Xiao, and C. Jiang. Modified in situ and self-catalytic growth method for fabrication of Ag-coated nanocomposites with tailorable optical properties. *J. Nanopart. Res.*, 14(9), 2012. doi: 10.1007/s11051-012-1105-0.