

Toward a Thermally Robust Operando Surface-Enhanced Raman Spectroscopy Substrate

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The work presented here describes the first steps toward designing a thermally robust surface-enhanced Raman spectroscopy (SERS) substrate with the potential to conduct in situ monitoring of catalytic reactions. Nanosphere lithography (NSL) fabricated SERS substrates were coated with thin (0.2–1.0 nm) films of atomic layer deposited (ALD) Al₂O₃. The thermal stability of these substrates was examined at various temperatures (100–500 °C) and over time (up to 6 h) in nitrogen. The results showed that ALD Al₂O₃ coated nanoparticles maintained their original geometry significantly better than the bare Ag nanoparticles. While experiments showed that thicker ALD Al₂O₃ coatings resulted in the most stable nanoparticle structure, ALD Al₂O₃ coatings as thin as 0.2 nm resulted in thermally robust nanostructures as well. Additionally, the ALD Al₂O₃ coated nanoparticles were heated under propane to mimic reaction conditions. These experiments showed that while the nanoparticle geometries were not as stable under reducing atmosphere conditions, they were much more stable than uncoated nanoparticles and therefore have the potential to be used for SERS monitoring of reactions conducted at elevated temperatures.

Introduction

Heterogeneous catalysis plays a large role in the chemical industry since many products are fabricated by this process. The ability to monitor the surface chemistry during a catalytic reaction is important for improving current and developing new catalytic processes. In situ spectroscopic techniques have provided important fundamental information in regards to surface species and catalyst structure.^{1–3} Unfortunately, these experiments are often conducted under a controlled environment that does not mimic industrial temperature and pressure conditions. As a result, the data that are collected may not be comparable to the catalytic process in question. Operando spectroscopy is a method where spectroscopic data can be collected in situ under temperatures and pressures employed in industrial catalytic reactions.^{3,4} Therefore, the information found in operando spectroscopy experiments can provide valuable insight toward understanding industrial catalytic processes.

Nanosphere lithography (NSL) fabricated nanoparticles have been successfully utilized as surface-enhanced Raman spectroscopy (SERS) substrates.^{5–7} The signature optical property of these nanoparticles is the localized surface plasmon resonance (LSPR). The LSPR phenomenon occurs when light interacts with particles that are much smaller (~10–200 nm) than the incident wavelength.^{8,9} The resulting effect is that the electric field E near the particle surface is enhanced where $|E|^2$ can be 100–10 000 times larger than the incident field.⁸ This enhancement of the electromagnetic field makes these materials excellent SERS substrates.^{5–7} It is well-known that the SERS effect significantly enhances the Raman scattering signal when the Raman-active molecule is spatially confined within the elec-

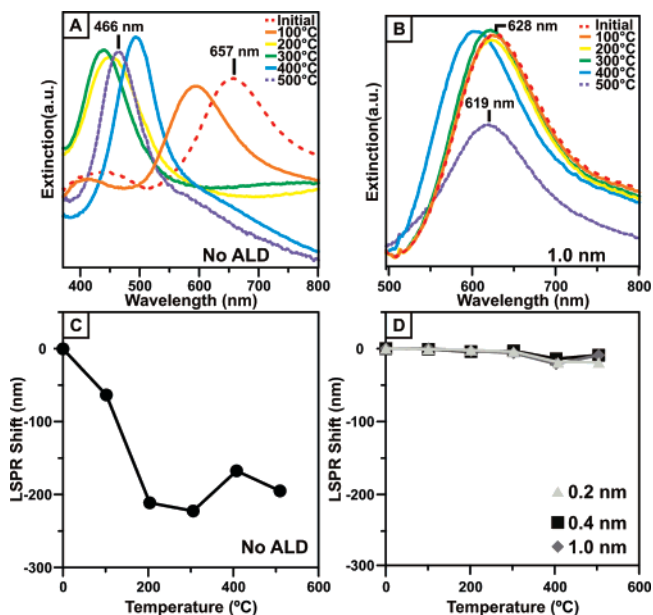


Figure 1. LSPR spectroscopy of bare Ag nanoparticles (A) and Ag nanoparticles coated with 1.0 nm ALD Al₂O₃ (B) heated at various temperatures. (C) Plot of LSPR shift vs temperature of bare Ag nanoparticles heated at various temperatures. (D) Plot of LSPR shift vs temperature of Ag nanoparticles coated with 0.2 nm (▲), 0.4 nm (■), and 1.0 nm (◆) ALD Al₂O₃ heated at various temperatures. All samples were heated at each temperature for 1 h under 1 Torr N₂.

tronic fields generated upon excitation of the LSPR of the nanostructured noble metal surface.¹⁰ The SERS signals of ensemble-averaged molecules demonstrate enhancements up to 8 orders of magnitude over normal Raman signals.^{6,11} Because NSL fabricated nanoparticles are excellent SERS substrates, they have the potential to be used to conduct in situ studies of model catalytic reactions. Because SERS is an extremely sensitive

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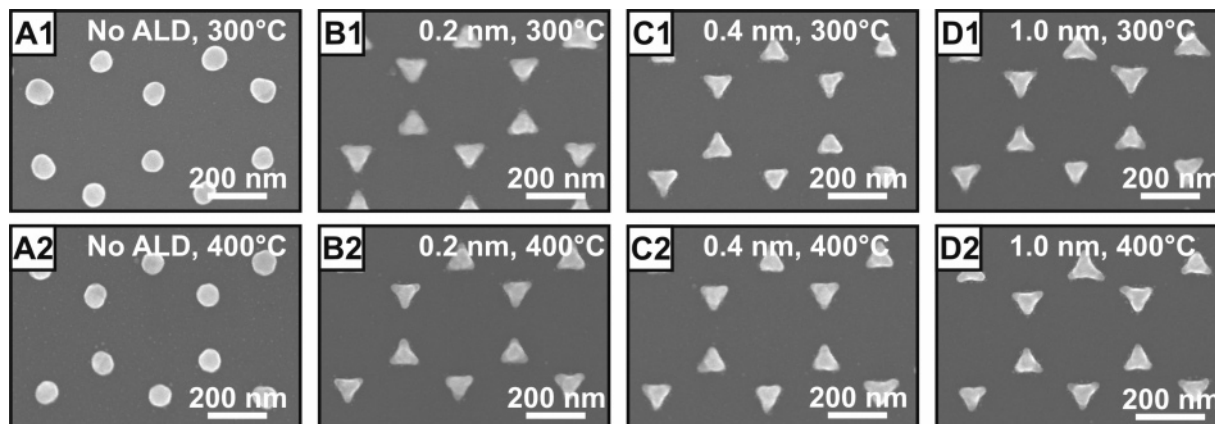


Figure 2. SEM images of bare Ag nanoparticles (A1 and A2) and Ag nanoparticles coated with 0.2 nm (B1 and B2), 0.4 nm (C1 and C2), and 1.0 nm (D1 and D2) ALD Al_2O_3 heated at 300 °C (A1, B1, C1, and D1) and 400 °C (A2, B2, C2, and D2). All samples were heated at each temperature for 1 h under 1 Torr N_2 .

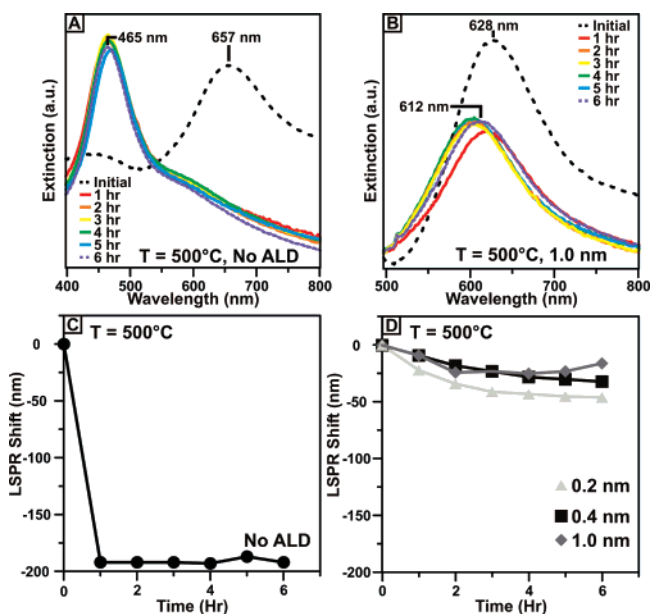


Figure 3. LSPR spectroscopy of bare Ag nanoparticles (A) and Ag nanoparticles coated with 1.0 nm ALD Al_2O_3 (B) heated at 500 °C over time. (C) Plot of LSPR shift of bare Ag nanoparticles heated at 500 °C over time. (D) Plot of LSPR shift of Ag nanoparticles coated with 0.2 nm (▲), 0.4 nm (■), and 1.0 nm (◆) ALD Al_2O_3 heated at 500 °C over time. All samples were heated under 1 Torr N_2 .

technique, operando SERS would allow for the study of catalytic surfaces that are normally difficult or impossible to characterize with normal Raman spectroscopy. Additionally, because SERS will only detect molecules on or near the noble metal surface, this technique would allow for the selective monitoring of just the surface bound species. Unfortunately, at elevated temperatures (300 °C),¹² these nanoparticles anneal and form hemispheres, which have been found to have significantly smaller enhancement factors than tetrahedrons.⁸ Therefore, any reaction that requires high temperatures, such as many catalytic processes, could not be studied with these nanoparticle substrates. Alternatively, if the nanoparticles could be designed to be thermally robust as well as maintain their optical properties, they would have a great potential to be used for operando SERS studies.

The work presented herein demonstrates the initial steps toward designing a thermally robust SERS sensor for conducting operando SERS experiments. Atomic layer deposition (ALD) has been utilized to fabricate thermally robust SERS substrates

that also have the potential to be a support for model catalytic reactions. ALD is a fabrication method that produces highly uniform and controlled thin films. Precursor gases are alternately pulsed through the reactor and purged away, resulting in a self-limiting growth process that constructs a film one monolayer at a time.¹³ Highly uniform monolayers of Al_2O_3 can be deposited with ~ 1 Å thickness resolution.¹⁴ Since Al_2O_3 is often used as a catalyst support, these substrates could be used to synthesize catalysts and monitor a variety of catalytic reactions.

LSPR spectroscopy and scanning electron microscopy (SEM) were used to compare the stability of bare Ag nanoparticles and Ag nanoparticles coated with 0.2, 0.4, and 1.0 nm ALD Al_2O_3 heated to various temperatures (50, 100, 200, 300, 400, and 500 °C) in N_2 and maintained at these elevated temperatures over time (up to 6 h). It was necessary to use thin coatings (1.0 nm or less) so that the SERS enhancement, which decays exponentially from the nanoparticle surface, would be preserved.⁵ The results of this work found that even after coating the Ag nanoparticles with only 0.2 nm ALD Al_2O_3 , the Ag nanoparticle arrays exhibit a substantially increased thermal stability, in comparison with bare Ag nanoparticles, at temperatures of at least 500 °C for several hours. Because these nanoparticles would ideally be used to conduct operando SERS experiments, they would be exposed to reactive compounds at elevated temperatures. Therefore, experiments were carried out with ALD Al_2O_3 coated Ag nanoparticles heated at various temperatures under propane to determine their stability under more reducing reaction conditions. At low temperatures (less than 200 °C), the ALD Al_2O_3 coated nanoparticle geometry is extremely stable. However, at higher temperatures (200 °C and above), the structure of the ALD Al_2O_3 coated nanoparticles is affected more by the propane environment than by N_2 . Therefore, it is believed that the atmospheric conditions have a significant effect on the nanoparticle stability at elevated temperatures. Overall, the geometry of the ALD Al_2O_3 coated nanoparticles was significantly more thermally stable than bare Ag nanoparticles, and therefore, they show a great potential to be used for operando SERS experiments.

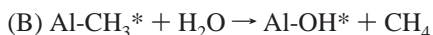
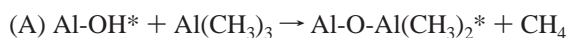
Experimental Procedures

Materials. Ag (99.99%) was purchased from D. F. Goldsmith (Evanston, IL). Borosilicate glass substrates, No. 2 Fisherbrand 18 mm circular coverslips, were acquired from Fisher Scientific (Pittsburgh, PA), and P-doped Si (111) was obtained from Wacker Siltronic (Portland, OR). Hexanes, methanol, H_2SO_4 , H_2O_2 , and NH_4OH were purchased from Fischer Scientific

(Fairlawn, VA). Surfactant-free carboxyl-terminated polystyrene nanospheres with 390 nm (± 19.5 nm) diameters were received in a suspension of water from Duke Scientific (Palo Alto, CA). Absolute ethanol was acquired from Pharmco (Brookfield, CT). Millipore cartridges (Marlborough, MA) were used to purify water to a resistivity of 18 M Ω cm $^{-1}$. Al $_2$ O $_3$ films were fabricated by ALD utilizing trimethylaluminum (TMA) purchased from Sigma Aldrich (Milwaukee, WI) and deionized water.

Nanosphere Lithography. NSL was used to fabricate monodispersed, surface-confined Ag nanoparticles.¹⁵ Glass and Si (111) substrates were cleaned in a piranha etch solution (3:1 H $_2$ SO $_4$ /H $_2$ O $_2$, 30%) for 30 min at 80 °C. After being rinsed with water, the substrates were sonicated for 60 min in 5:1:1 H $_2$ O/H $_2$ O $_2$ /NH $_4$ OH to create a hydrophilic surface on the substrate to facilitate self-assembly of the nanosphere masks. Finally, the substrates were rinsed and stored in water for future use. 2-D self-assembled monolayer masks of nanospheres were fabricated by drop-coating approximately 2.5 μ L of undiluted nanosphere solution (10% solid) on the pretreated substrates. The nanospheres were allowed to dry in ambient conditions. A total of 50 nm Ag was deposited by electron beam (e-beam) deposition in a Kurt J. Lesker Axxis e-beam deposition system (Pittsburgh, PA) with a base pressure of 10 $^{-6}$ Torr. The mass thickness and deposition rate (1 Å/s) were monitored using a Sigma Instruments 6 MHz gold plated QCM (Fort Collins, Colorado). After Ag deposition, the nanosphere masks were removed by sonication in absolute ethanol for 3 min.

ALD. Al $_2$ O $_3$ films were fabricated on the Ag nanoparticles by ALD. The reactor utilized in these experiments was similar to one described in previous publications.¹⁶ TMA and deionized H $_2$ O vapors were alternately pulsed through the reaction chamber utilizing ultrahigh purity (99.999%) N $_2$ as the carrier gas at a mass flow rate of 360 sccm and a pressure of 1 Torr using a growth temperature of 50 °C. Al $_2$ O $_3$ ALD proceeds on a hydroxylated surface according to the following eqs.¹⁴



The asterisks signify the surface species. One complete AB cycle is 42 s: (1) TMA reactant exposure time = 1 s, (2) N $_2$ purge following TMA exposure time = 10 s, (3) H $_2$ O reactant exposure time = 1 s, and (4) N $_2$ purge following H $_2$ O exposure time = 30 s. Long purge times are necessary at low temperatures to prevent chemical vapor deposition (CVD) of Al $_2$ O $_3$.¹⁷

Thermal Annealing. Thermal studies were conducted inside the ALD reaction chamber under 1 Torr N $_2$ or 10 Torr propane.

UV-vis Extinction Spectroscopy. LSPR extinction measurements of the Ag nanoparticle arrays were obtained using a variable angle spectroscopic ellipsometer (VASE) M-2000V from J. A. Wollam Co. operated in transmission mode.

SEM. SEM images of bare and ALD Al $_2$ O $_3$ coated NSL nanoparticles on Si (111) were observed with a Hitachi S-4700-II SEM with a field emission gun electron source. Images were collected using an accelerating voltage of 10.0 kV.

Results and Discussion

Thermal Stability under Nitrogen at Various Temperatures. The LSPR spectrum of metal nanoparticles is extremely sensitive to nanoparticle shape and size.^{10,18} Therefore, geometry changes of the nanoparticle structure due to thermal annealing can be detected by monitoring their LSPR spectrum. For

instance, a blue shift of the peak value of the LSPR spectrum (λ_{max}) will be observed if the Ag triangular nanoparticle changes shape as a result of annealing.^{10,18} Previous work has shown that bare Ag triangular nanoparticles that have been annealed at 300 °C for 1 h form hemispheres with $\lambda_{\text{max}} = \sim 450$ nm.¹² Figure 1 examines the shift of the LSPR spectrum of both bare Ag nanoparticles and Ag nanoparticles coated with 0.2, 0.4, and 1.0 nm ALD Al $_2$ O $_3$ before and after heating for 1 h at different temperatures (100, 200, 300, 400, and 500 °C). After heating the bare Ag nanoparticles for 1 h at 100 °C, a 62 nm blue shift in the LSPR spectrum occurs, indicating that a structure change due to temperature had already occurred (Figure 1A). Upon annealing the bare Ag nanoparticles at 200 °C for 1 h, an overall shift of 206 nm was observed, suggesting that the nanoparticles have become hemispherical. Alternatively, only a 9 nm blue shift of the LSPR spectrum is observed after heating Ag triangular nanoparticles coated with 1.0 nm ALD Al $_2$ O $_3$ at 500 °C for 1 h, indicating that the nanoparticles retained their original triangular shape.

A plot of LSPR shift versus temperature can be seen for bare Ag nanoparticles (Figure 1C) as well as Ag nanoparticles coated with 0.2 nm (\blacktriangle), 0.4 nm (\blacksquare), and 1.0 nm (\blacklozenge) of ALD Al $_2$ O $_3$ (Figure 1D). While the bare Ag nanoparticles already show a large negative LSPR shift (62 nm) after exposure to 100 °C, the LSPR of the nanoparticles coated with as little as 0.2 nm ALD Al $_2$ O $_3$ show significantly less negative shifting (21 nm) even after heating for 1 h at 500 °C. Ag nanoparticles with the thickest (1.0 nm) ALD Al $_2$ O $_3$ coatings have the smallest LSPR shifts after heating, indicating that thicker coatings protect the nanoparticle better.

Using SEM, the shape of the bare and ALD Al $_2$ O $_3$ coated Ag nanoparticles can be determined after thermal treatment. Figure 2 depicts SEM images of bare Ag nanoparticles (A1 and A2) and Ag nanoparticles coated with 0.2 nm (B1 and B2), 0.4 nm (C1 and C2), and 1.0 nm (D1 and D2) ALD Al $_2$ O $_3$ after heating for 1 h at 300 and 400 °C. The bare Ag nanoparticles formed hemispheres after thermal annealing at 300 and 400 °C (Figure 2A1,A2), which correlates well with the observed LSPR values measured after annealing at these temperatures. The SEM images show that while the ALD Al $_2$ O $_3$ coated nanoparticles retain their triangular shape, the heating does slightly affect their shape. A decrease of the perpendicular bisector (a straight line passing through the midpoint of a side and being perpendicular to that side) is seen after heating the ALD Al $_2$ O $_3$ coated nanoparticles at 300 °C for 1 h. An additional reduction of the perpendicular bisector is observed after annealing at 400 °C for 1 h. Overall, the geometry change is small, and therefore, these nanoparticles appear to be suitable for use at elevated temperatures with little structural change. While the LSPR spectra indicated that thicker ALD Al $_2$ O $_3$ coatings maintained the nanoparticle geometry the best, very little difference in nanoparticle geometry was observed by SEM.

Thermal Stability under Nitrogen at 500 °C versus Time. Thermal stability over time was examined for bare and ALD Al $_2$ O $_3$ coated Ag nanoparticles. Figure 3 depicts LSPR spectra of bare Ag nanoparticles (Figure 3A) and Ag nanoparticles coated with 1.0 nm ALD Al $_2$ O $_3$ (Figure 3B) taken at 1 h intervals over 6 h while heating at 500 °C under N $_2$. The LSPR shift versus time for both bare Ag nanoparticles (Figure 3C) and Ag nanoparticles coated with 0.2 nm (\blacktriangle), 0.4 nm (\blacksquare), and 1.0 nm (\blacklozenge) ALD Al $_2$ O $_3$ (Figure 3D) was plotted. As expected, the bare Ag nanoparticles experienced a dramatic LSPR shift from 657 to 465 nm in just 1 h, suggesting that the triangular nanoparticles had become hemispheres. The LSPR spectra

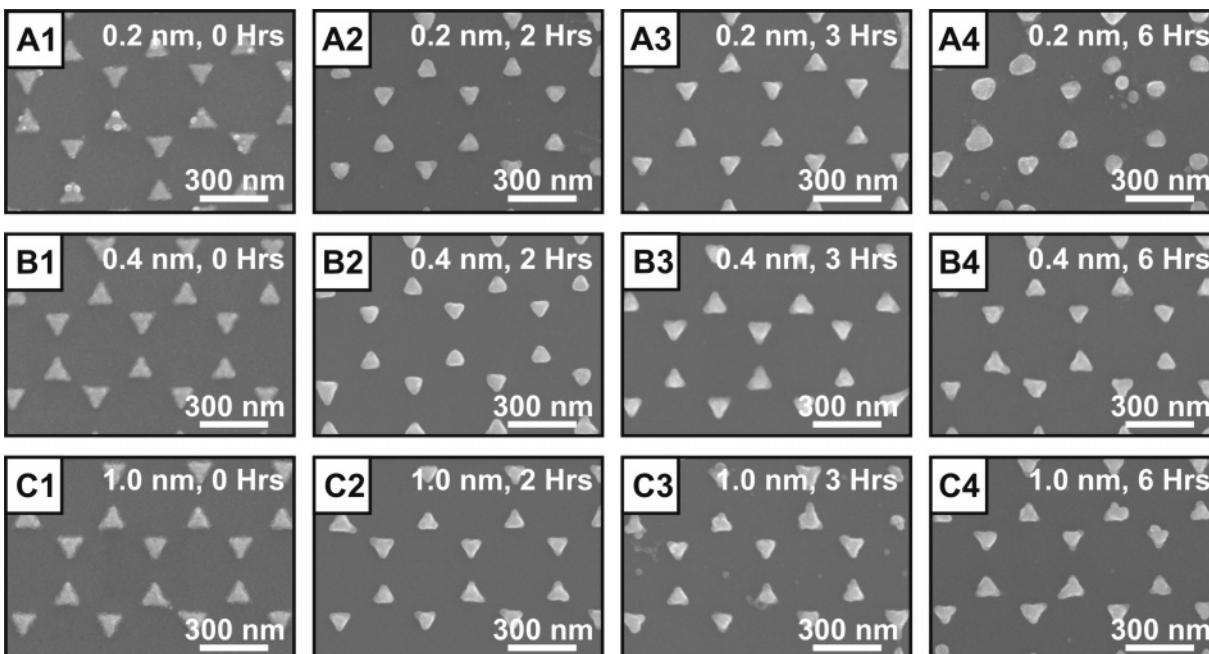


Figure 4. SEM images of Ag nanoparticles coated with 0.2 nm (A1–A4), 0.4 nm (B1–B4), and 1.0 nm (C1–C4) ALD Al_2O_3 heated at 500 °C for 0, 2, 3, and 6 h. All samples were heated under 1 Torr N_2 .

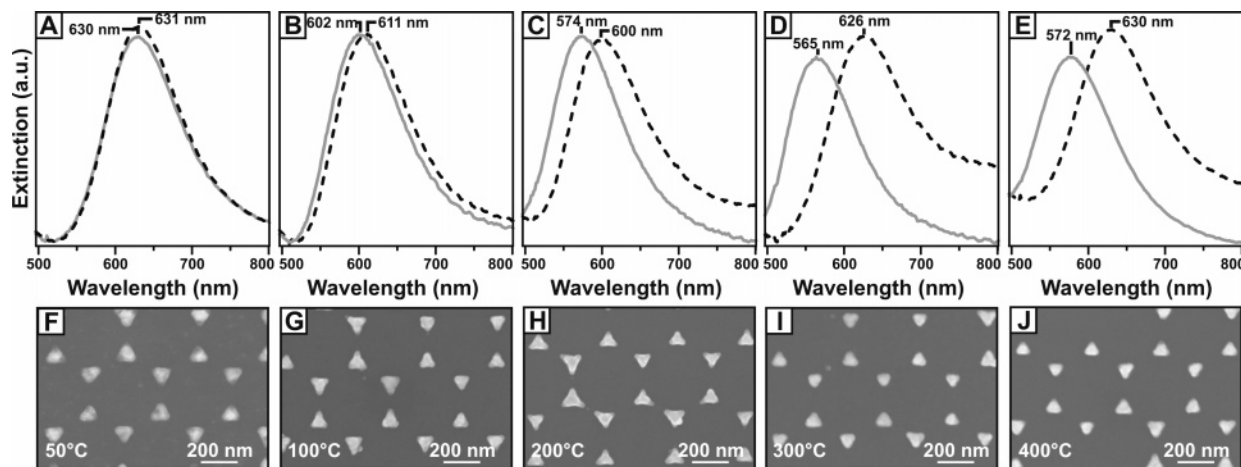


Figure 5. LSPR spectra of Ag nanoparticles coated with 1.0 nm ALD Al_2O_3 heated for 30 min at 50 °C (A), 100 °C (B), 200 °C (C), 300 °C (D), and 400 °C (E) under 10 Torr of propane. The initial LSPR λ_{max} is depicted by a black dashed line, and the LSPR λ_{max} after thermal annealing is depicted by a solid gray line. Each plot is paired with a corresponding SEM image taken after heating at 50 °C (F), 100 °C (G), 200 °C (H), 300 °C (I), and 400 °C (J).

remained constant for the subsequent hours, which correlates with the idea that a hemisphere should be the most geometrically stable structure for these nanoparticles. In contrast, the nanoparticles coated with 1.0 nm ALD Al_2O_3 exhibited an overall LSPR blue shift of just 16 nm after 6 h, suggesting very little change in shape. While the nanoparticles coated with 0.2 nm (Figure 3D) had a larger overall shift of 24 nm, this value still indicates that the triangular shape was well-maintained even after heating at 500 °C for 6 h. Overall, it was observed that the thickest ALD Al_2O_3 coating (1.0 nm) resulted in the most stable nanoparticle structure.

SEM images were taken of Ag nanoparticles coated with 0.2, 0.4, and 1.0 nm ALD Al_2O_3 heated at 500 °C after 0, 2, 3, and 6 h (Figure 4). After 2 h, an average reduction of ~ 14 nm of the nanoparticles' perpendicular bisectors was seen. After 6 h, a significant difference in nanoparticle shape and monodispersity was observed. The geometry of the Ag nanoparticles coated with 0.2 nm ALD Al_2O_3 had significantly changed (Figure 4A4)

but was still significantly more retained than the geometry of bare Ag nanoparticles after thermal annealing. A further average reduction of ~ 3 nm was found for the Ag nanoparticles coated with 0.4 and 1.0 nm ALD Al_2O_3 .

Thermal Stability under Propane. The experiments described previously demonstrate that ALD Al_2O_3 coated Ag nanoparticles are thermally stable under a relatively inert N_2 environment. However, to serve as operando SERS substrates for monitoring catalytic reactions, the Ag nanoparticles need to be stable in the presence of both reactants and products. To examine the suitability of these sensors for monitoring the reaction of alkanes, Ag nanoparticles coated with 1.0 nm ALD Al_2O_3 were heated at various temperatures for 30 min under 10 Torr propane. While the temperatures employed for the catalytic conversion of propane to propylene are typically higher than those used in this study, conversion of propane on highly active supported nanocrystalline oxides has been reported at temperatures as low as room temperature.¹⁹ Figure 5 shows

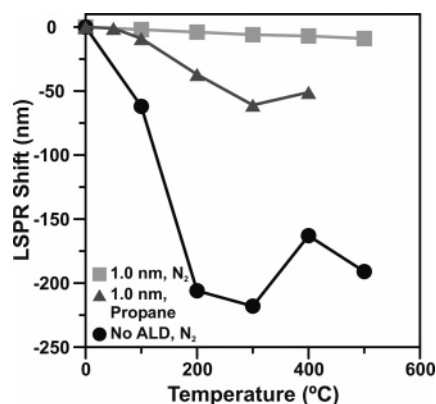


Figure 6. Plot of LSPR shift vs temperature for Ag nanoparticles coated with 1.0 nm ALD Al₂O₃ heated under 1 Torr N₂ (■) or 10 Torr propane (▲) and bare nanoparticles heated under 1 Torr N₂ (●).

LSPR spectra collected before and after heating at 50 °C (A), 100 °C (B), 200 °C (C), 300 °C (D), and 400 °C (E). Blue shifts of 1 and 9 nm are seen for the nanoparticles heated at 50 and 100 °C, respectively, implying minimal structural change. Interestingly, a larger blue shift of 36 nm was observed for the nanoparticles heated at 200 °C, suggesting a larger change in nanoparticle geometry in comparison to ALD Al₂O₃ coated nanoparticles that were heated under N₂. Finally, blue shifts of 61 and 58 nm were observed for nanoparticles annealed at 300 and 400 °C, respectively. These results signify that as the temperature is increased, larger structural changes occur. Furthermore, these experiments demonstrate that reactive compounds such as propane modify the nanoparticle structure at elevated temperatures more than N₂.

SEM images of the ALD Al₂O₃ coated nanoparticles after heating under propane are shown in Figure 5F–J. The nanoparticle perpendicular bisector decreased an average of 0.6 nm for the nanoparticles heated at 50 °C, showing that minimal structural change occurs when exposing the nanoparticles to propane at low temperatures. This result correlates well with the fact that only a 1 nm blue shift of the LSPR occurred after annealing. Additionally, little structural change (3.4 nm reduction of the perpendicular bisector) was seen for the nanoparticles heated at 100 °C. An average reduction in the perpendicular bisector of 6.9, 9.6, and 9.6 nm was seen for the nanoparticles heated at 200, 300, and 400 °C, respectively. The SEM images support the results found in the LSPR spectra, which indicate that larger geometry changes occur at higher temperatures.

While there are large structural changes in nanoparticle geometry when heating at high temperatures under propane, the changes are still much less significant than those observed for bare nanoparticles. Figure 6 depicts a plot of LSPR shift versus temperature for Ag nanoparticles coated with 1.0 nm ALD Al₂O₃ heated under N₂ (■) and propane (▲) as well as bare Ag nanoparticles heated under N₂ (●). The plot shows that the ALD Al₂O₃ coated nanoparticles heated under N₂ maintained their shape the most. ALD Al₂O₃ coated nanoparticles maintained their geometry at low temperatures under propane. Although the nanoparticles were not as stable as under N₂, they still maintained their structure by comparison to bare Ag nanoparticles. These results indicate that the thermally stable ALD Al₂O₃ coated nanoparticles show a potential to serve as effective operando SERS substrates. Additional measurements will determine if the ALD Al₂O₃ coated Ag nanoparticles still yield adequate SERS enhancement following heating in propane. It

is possible that thicker ALD Al₂O₃ coatings, or perhaps coatings of different ALD thin film materials, will provide better protection to the Ag nanoparticles under the reactive environment.

Conclusion

This work has shown that ALD Al₂O₃ coated Ag NSL fabricated nanoparticles can maintain their shape at high temperatures over time and therefore have the potential to be used as operando SERS substrates. Experiments were carried out to determine both the stability of bare Ag nanoparticles and the stability of Ag nanoparticles coated with various thicknesses (0.2, 0.4, and 1.0 nm) of ALD Al₂O₃ at several temperatures (100, 200, 300, 400, and 500 °C) and over long periods of time (up to 6 h). The results showed that ALD Al₂O₃ coated nanoparticles maintained their original geometry significantly better than the bare Ag nanoparticles. While experiments showed that thicker ALD Al₂O₃ coatings resulted in the most stable nanoparticle structure, ALD Al₂O₃ coatings as thin as 0.2 nm resulted in thermally robust nanostructures as well. LSPR spectra indicated that all the ALD Al₂O₃ coated nanoparticles maintained their shape well at temperatures of at least 500 °C. Nanoparticles with the thickest ALD Al₂O₃ coating (1.0 nm) showed the least structural change. While the nanoparticles coated with the most ALD Al₂O₃ (1.0 nm) maintained their geometry better at 500 °C for longer periods of time, the nanoparticles with thinner coatings of ALD Al₂O₃ still performed at a level where they could be used as successful SERS substrates at elevated temperatures over several hours. Finally, ALD Al₂O₃ coated Ag nanoparticles were heated at various temperatures under propane to mimic more realistic reaction conditions. These experiments showed that while the nanoparticle geometry was not as stable as under N₂, they were much more stable than uncoated nanoparticles. This work provides the first steps toward developing SERS substrates that can be used to perform operando SERS studies.

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