

Fabrication of Stabilized Gold Nanoparticle Oligomers for Surface-Enhanced Spectroscopies

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Cite This: *ACS Omega* 2021, 6, 31818–31821

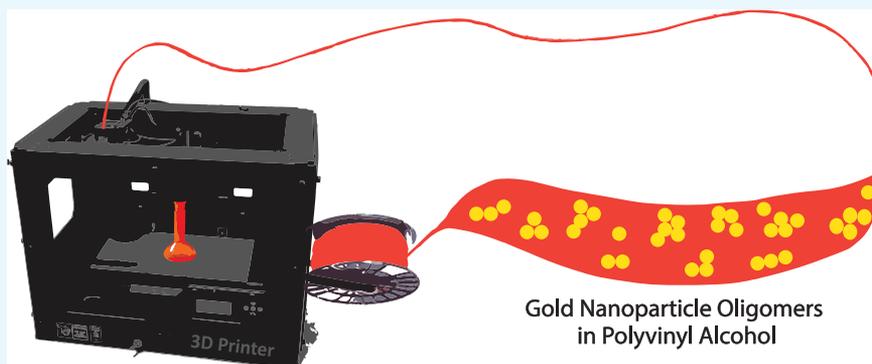


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ABSTRACT: Various time-resolved spectroscopies that take advantage of surface-enhancement have been developed. Only the most robust substrates can withstand the high-intensity laser pulses used by time-resolved methods. We present a simple and reliable stabilization procedure that uses polyvinyl alcohol for the formation of robust gold nanoparticle oligomers that can withstand different hydration and temperature levels. This procedure can be used to produce oligomers with varying and reproducible plasmon resonance conditions. Results show that gold nanoparticle oligomers stabilized in this way are sufficiently sturdy to be used in 3D printing, opening the door for easy production and integration of plasmonic substrates.

■ INTRODUCTION

Coinage metal nanoparticles can be used to amplify the electric field by as much as 2 orders of magnitude. This enhancement is localized at nanoparticle surface sites, and it can be used to enhance the signal of many spectroscopies,^{1,2} especially Raman scattering spectroscopies. Surface enhancement can result in enhancement factors as large as 8 orders of magnitude, making the spectroscopic detection of single molecules possible.³ Consequently, a wide variety of plasmonic substrates have been developed.⁴

The development of coherent Raman spectroscopies, such as femtosecond stimulated Raman spectroscopy (FSRS), can be used to study molecular structures on the timescale of molecular motions.^{5,6} Although many plasmonic substrates have been shown to be efficacious for surface-enhanced Raman scattering (SERS), only one substrate geometry consisting of stabilized Au nanoparticle oligomers has been shown to be effective for FSRS.^{7,8} The large power densities accessed by femtosecond laser pulses require the use of stabilized Au nanoparticle oligomers that can be constantly transported through the focal spot, where multiple high-intensity laser pulses overlap.^{7,8} Oligomers in solution can be stirred quickly, limiting their exposure to laser pulses.

Diverse methods for the formation of gold nanoparticle oligomers have been published.^{9–16} Some of the methods developed include DNA-mediated aggregation,⁹ light-triggered assembly of amphiphilic gold nanoparticles,¹¹ heterogeneous nucleation and growth of bimetallic nanoparticles,¹² and nanoparticle film formation at the oil–water interface.¹³ This work presents a new straightforward synthetic route for the production of stabilized Au nanoparticle oligomers. The oligomer stabilization method presented herein is fast and effective, and it allows for the formation of stabilized oligomers in solution. A big benefit of forming oligomers in this way is that the reporter molecule of interest is used to aggregate the gold monomers, thus ending up at the hotspot.

Stabilized Au nanoparticle oligomers can be further integrated into transparent materials with desirable mechanical properties. Polyvinyl alcohol (PVA) is a nontoxic water-soluble

Received: August 18, 2021

Accepted: November 3, 2021

Published: November 16, 2021



polymer commonly employed in the medical industry and 3D printing industry. For 3D printing, PVA is used as a support material that can be dissolved and removed by water. The protocol presented herein can be used for the formation of tunable, long-lasting, highly enhancing substrates that can be customized to contain an array of different reporter molecules.

RESULTS AND DISCUSSION

The extinction spectra reveal two main features, a peak due to the localized surface plasmon resonance (LSPR) of gold monomers and a peak due to the LSPR of nanoparticle oligomers. As monomers aggregate to form larger and larger oligomers, the monomer peak decreases in intensity, while the oligomer peak increases in intensity. The oligomer peak redshifts since oligomers become larger and also broadens because of increasing size distribution. Figure 1 shows the

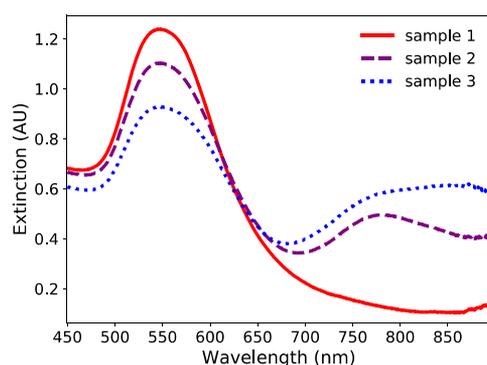


Figure 1. LSPR spectra of stabilized gold nanoparticle oligomers. Each sample was stabilized at various aggregation states.

LSPR spectra of several samples stabilized with the PVA solution. All samples were produced from the same gold monomer colloidal solution, showing that different aggregation levels can be achieved, depending on the time elapsed and on how much BPE solution is added.

The LSPR spectra were acquired continuously and saved between each stepwise addition of the BPE adsorbate solution. Desired plasmon resonance characteristics can be obtained by tracking nanoparticle aggregation in real time. Essentially, stabilizing PVA solution can be added when the desired aggregation level is achieved, thus halting aggregation and producing a sample with the chosen LSPR. Figure 2 shows the stabilizing effect of PVA on aggregating samples. Further addition of BPE solution, after stabilization with PVA, does not increase the aggregation state any further, leading to a flattening of the curve at the desired LSPR. The data for Figure 2 was acquired by tracking the peak wavelength of oligomer LSPR after subtracting the monomer peak, resulting in slightly different maxima than those observed in Figure 1. The aggregate peak starts forming after the addition of 40 μL of BPE solution. Sample 1 is not shown in Figure 2 because an oligomer peak never formed since PVA was added first. Controlling the aggregation level is of utmost importance since enhancement factors depend chiefly on the spectral overlap of substrates. Furthermore, line shapes can also depend quite dramatically on spectral overlap, as previously seen for FRSRs.⁸

The aggregation rate increases significantly after the addition of 80 μL of BPE solution. As time goes on, the aggregation state increases and oligomers become larger. Sample 4 was

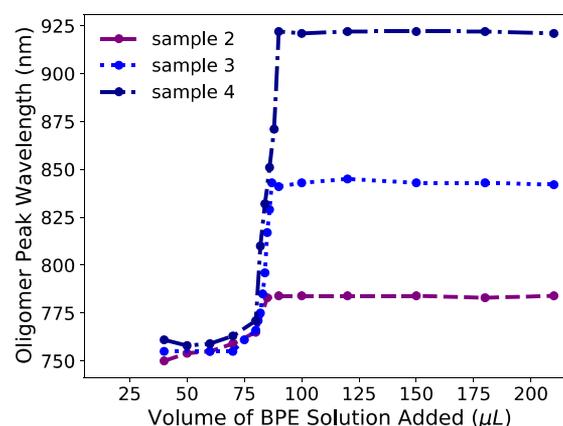


Figure 2. Oligomer LSPR wavelength maxima tracked throughout the aggregation of several samples versus the volume of BPE solution added.

allowed a longer time interval to aggregate before stabilization with PVA, thus resulting in oligomers with the most red-shifted oligomer LSPR peak. Sample 2, however, was stabilized quickly after the addition of the eighth 10 μL aliquot of BPE solution. Further addition of BPE solution aliquots after stabilization with PVA did not further increase the aggregation state and thus oligomer size.

PVA stabilization produces robust oligomers. Figure 3a shows the LSPR spectra of a gold nanoparticle oligomer

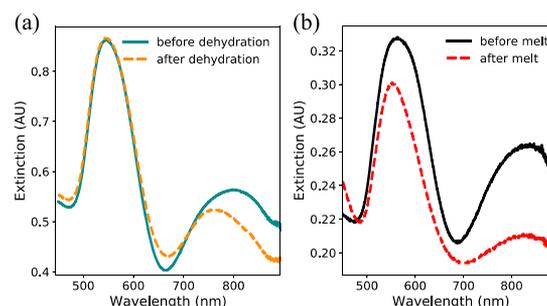


Figure 3. LSPR spectra for two gold nanoparticle oligomer samples. Panel (a) shows the spectra of stabilized oligomers before and after a dehydration/rehydration cycle. Panel (b) shows the spectra of stabilized oligomers encased in solid PVA (fully dehydrated) before and after melting the PVA.

sample before and after dehydration. Spectra were collected after the substrate was made and stabilized with PVA and after it was dehydrated/rehydrated with water. While the oligomer peak persists, it is blue-shifted by 40 nm, indicating the loss of larger aggregates. This could be due to fragmentation or curling of larger aggregates. However, the great majority of oligomers persist. Figure 3b shows LSPR spectra of a fully dehydrated gold oligomer sample in PVA, before and after melting at around 210 $^{\circ}\text{C}$. This high temperature is used by 3D printers to melt and deposit PVA. This polymer is used as a nontoxic support for complex prints that can be easily dissolved in water and removed by the user once the print is complete. These spectra show that the aggregation state of gold nanoparticles did not change upon heating at this temperature, making it possible to incorporate gold nanoparticle oligomers into 3D prints.

Figure 4a compares the SERS spectra obtained from oligomers stabilized with PVP, according to a previously

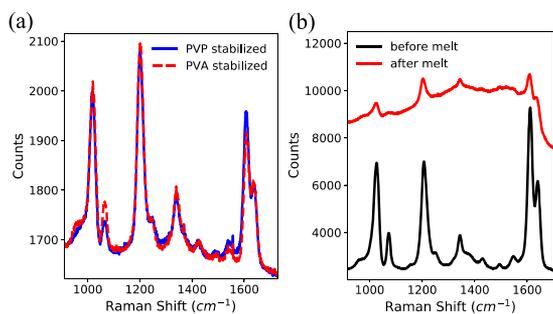


Figure 4. SERS spectra of stabilized gold nanoparticle oligomers. Panel (a) compares the spectra from PVA-stabilized oligomers with spectra from PVP-stabilized oligomers. Panel (b) compares spectra from before and after melting the PVA substrate containing oligomers.

published method,^{8,17} and oligomers stabilized with PVA. Surface enhancements are comparable, and it is interesting to note that the spectral signatures of PVA or PVP were not observed in SERS spectra. Stabilization in this manner produces oligomers that mainly produce SERS signal of the reporter molecule, in this case BPE, free of spectral contributions from the stabilizing polymer. Since BPE is used to aggregate the gold nanoparticles, it is expected that BPE molecules are contained at the hotspot. The addition of PVA encases already formed oligomers but does not access the hotspot closely. This type of oligomer has been shown to yield SERS enhancement factors of a few times 10^8 power.¹⁸

PVA is desirable over PVP since dehydration of PVA samples results in a material that is flexible, smooth, and clear. Dehydration of PVP samples results in a material that is either sticky or brittle, depending on ambient humidity. For these reasons, PVA can be used to make robust samples that are stable under various ambient conditions. Figure 4b compares the SERS signal obtained before and after melting a PVA sample containing gold oligomers. The BPE SERS signal after melting is still clearly distinguishable despite a large background that convolutes the spectrum. These results indicate that PVA-stabilized oligomers can be integrated into 3D printed materials as Raman tags.

CONCLUSIONS

We have demonstrated that a new synthetic route for the formation of gold nanoparticle oligomers can be used to stop aggregation and to stabilize oligomers. The aggregation state can be closely controlled, allowing for the formation of substrates with desired plasmonic characteristics. Oligomers formed this way are stable in dehydration/rehydration and heating/cooling cycles, resulting in a material with desirable mechanic properties. Stability to high-temperature heating/cooling cycles suggests compatibility of oligomer substrates with thermoplastic filament printers, making it possible to 3D print plasmonic substrates. These materials can be used as SERS nanotags with selected Raman reporter molecules or as substrates for time-resolved surface-enhanced spectroscopies.

METHODS

Gold nanoparticle oligomers were assembled from 90 nm gold monomers prepared with the standard citrate reduction method.¹⁹ Very briefly, 50 mL of a 0.01% wt/wt HAuCl₄ in

Milli-Q water solution was brought to boil under reflux. Once boiling, the solution was stirred and 0.24 mL of 1% wt/wt Na₃-citrate solution was added.¹⁸ After half an hour, the heating mantle was turned off and the solution was allowed to cool. The extinction spectra of the resulting solutions were obtained with a double-beam Shimadzu UV-2401PC spectrophotometer. The localized surface plasmon resonance (LSPR) spectra were acquired throughout the aggregation procedure in real time with a Pasco PS2600 spectrophotometer. Aggregation of 2 mL of gold monomer solution was induced by the addition of dilute aqueous *trans*-1,2-bis(4-pyridyl)ethylene (BPE) solution. The dilute BPE solution was obtained by the 200 times dilution of room-temperature saturated BPE solution in Milli-Q water. A saturated solution was used for making the dilute BPE solution because of the BPE's very low solubility in water. Multiple 10 μ L aliquots of BPE solution were added with mixing.

For all samples, gold nanoparticle aggregation was halted with the addition of 0.2 mL of 10% wt/wt PVA solution in water. The dehydration sample was dehydrated in a vacuum desiccator and rehydrated in Milli-Q water with sonication. The sample for the melting experiment was produced by the extra addition of 0.5 mL of the PVA solution, after the sample was initially stabilized. The resulting solution was applied to a microscope coverslip and dehydrated in a desiccator. The sample was placed on a preheated hotplate and quickly removed once melted. Note that if water is present in any amount, the sample will bubble when placed on the hotplate, losing its smooth glass-like surface. Lastly, one sample was stabilized by the addition of 0.2 mL of 5% 40 kDa polyvinylpyrrolidone (PVP) solution in ethanol⁸ instead of the PVA solution.

All reagents were purchased from Sigma-Aldrich and used without further purification, with the exception of PVA, which was purchased as a roll for 3D printing from Ultimaker. The SERS spectra were collected using a grazing incidence geometry setup on a Nikon TE300 inverted microscope. Excitation was carried out with a 785 nm SLM Series Mini Boxx Laser from Necsel, and the spectra were collected with an Andor iDUS DU416A-LDC-DD camera mounted to an Andor Kymera 328i spectrograph.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. R.G. carried out aggregation studies, while T.G.-D. developed procedures for working with PVA. M.G.

synthesized gold nanoparticles. B.N. was responsible for experiment design and SERS spectra acquisition.

Funding

This work was supported in part by NSF MRI Grant EAR 2018776 at Sonoma State University. We thank the Research, Scholarships, and Creative Activities Program (RSCAP), the School of Science and Technology, the Koret Foundation, and the Summer High School Internship Program (SHIP) at Sonoma State University for financial support.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We are grateful to SICPA for their instrument donation. Many thanks go to Professor Jon Fukuto for helpful discussions and for sharing instrumentation.

ABBREVIATIONS

PVA, polyvinyl alcohol; PVP, polyvinylpyrrolidone; SERS, surface-enhanced Raman scattering; FSRS, femtosecond stimulated Raman spectroscopy; BPE, 1,2-bis(4-pyridyl)-ethylene

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