LA-UR-10-03773

Approved for public release;
distribution is unlimited.

Title: SERS-Active Nanoparticle Aggregate Technology for Tags and Seals

Author(s): Leif O. Brown, Velma M. Montoya, George J. Havrilla, and Stephen K. Doorn

Intended for: INMM 51st Annual Meeting Proceedings

Los Alamos
NATIONAL LABORATORY
EST. 1943

SERS-Active Nanoparticle Aggregate Technology for Tags and Seals

Leif O. Brown, Velma Montoya, George J. Havrilla, and Stephen K. Doorn

Los Alamos National Laboratory, Los Alamos, NM 87545

Abstract

In this paper, we describe our efforts to create a modern tagging and sealing technology for international safeguards application. Our passive tagging methods are based on SANAs (SERS-Active Nanoparticle Aggregates; SERS: Surface Enhanced Raman Scattering). These SANAs offer robust spectral barcoding capability in an inexpensive tag / seal, with the possibility of rapid in-field verification that requires no human input. At INMM 2009, we introduced SANAs, and showed approaches to integrating our technology with tags under development at Sandia National Laboratories (SNL). Here, we will focus on recent LANL development work, as well as adding additional dimensionality to the barcoding technique.

Introduction

The field of international safeguards employs a broad array of tags, seals, and tamper-indicating devices to assist with identification, tracking, and verification of components and materials. These devices each have unique strengths suited to specific applications, and span a range of technologies from passive metal cup seals and adhesive seals to active, remotely monitored fiber optic seals. Regardless of the technology employed, essential characteristics center around security, environmental and temporal stability, ease of use, and the ability to provide confidence to all parties. Here, we present a new inexpensive tagging technology that will deliver these attributes, while forming the basis of either a new seal, or as a secure layer added to many existing devices.

Our approach uses the Surface Enhanced Raman Scattering (SERS) response from SANAs (SERS-Active Nanoparticle Aggregates, Figure 1) to provide a unique identifier or signature for tagging applications. SANAs are formed[1,2] from gold or silver nanoparticles in the 40 – 80 nm size range. A chemical dye is installed on the nanoparticle surface, and the nanoparticles are then aggregated into ensembles of ~100 to 500 nm diameter, prior to being coated with silica. The silica shell protects the finished SANA from environmental or chemical attack, while changing the dye provides each SANA with a unique signature for the tagging application. Typical dyes may include the classes of materials used as textile dyes, food colorings, pH dyes, etc...

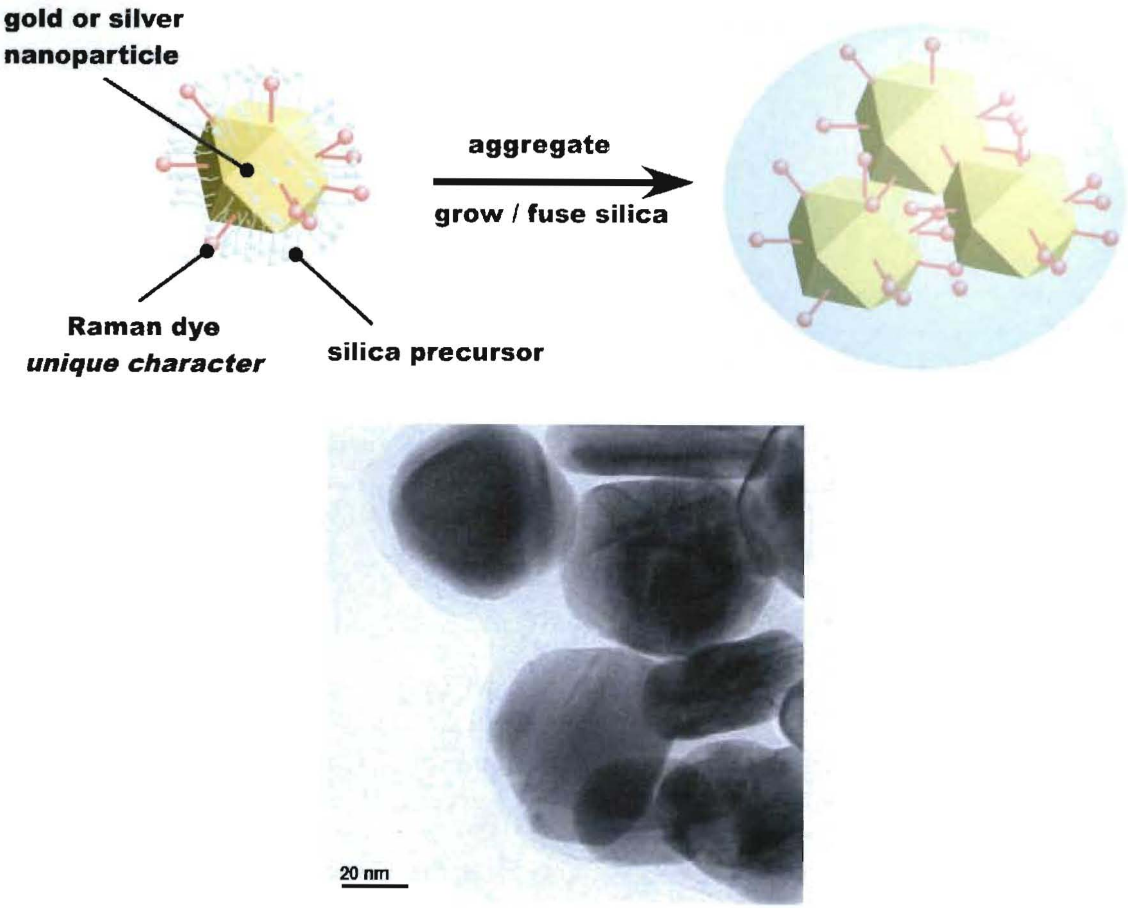

Figure 1. SERS-Active Nanoparticle Aggregates (SANAs). Top: General preparation method. Bottom: TEM of part of a silica-coated silver SANA. The metal cores appear dark in this image, while the haloes result from the silica coating.

Once completed, the SANA can be physically dispersed or embedded in seal materials, or the silica shell can be chemically functionalized in order to surface mount the SANA to certain materials, notably metals.

As described previously, the chemical dye gives the SANA a unique signature (Figure 2) that can be read using simple Raman instrumentation with laser excitation. On a simplest level, the spectrum can be reduced to a set of peak frequencies to give a 'chemical barcode'. More sophisticated analysis can involve relative peak heights, widths, and background contributions to give a more detailed signature often reveals differences between SANAs prepared with the same dye. The signature library will be very extensive: not only are there many unique chemical dyes to choose from, but dyes can be mixed in different ratios on SANAs to give identifiable combination signatures.

A key advantage to using SERS is that signals are amplified (within the SANA structure) to an intensity competitive with fluorescence. Consequently, power requirements for the excitation laser are low (<< 10 mW), allowing for the use of handheld, portable Raman instrumentation. A field inspector could then conceivably carry in a briefcase the necessary hardware for in-field verification. This hardware might consist of a subnotebook computer, with a laser pointer and CCD detector coupled to an objective aperture via fiber optic. The intense signal also raises tag security by lowering the material requirements – SANAs can be employed in very dilute concentrations, creating a significant obstacle to extraction of sufficient material for detailed analysis.

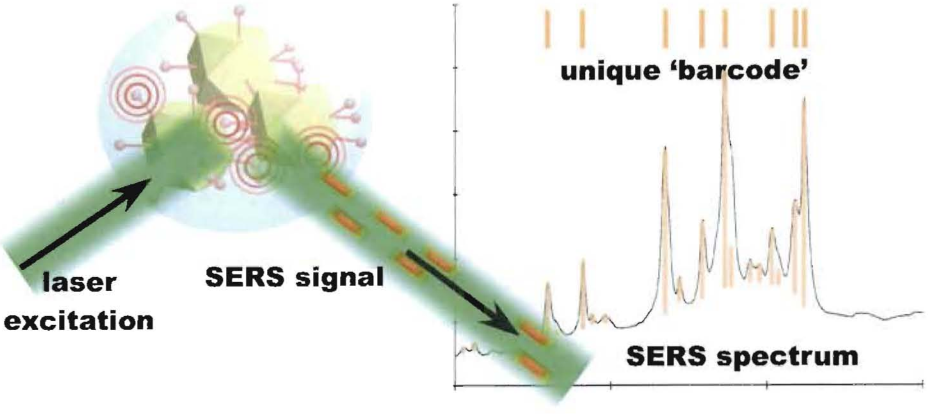

Figure 2. SANAs are read by laser to provide a spectroscopic barcode.

The high ratio of signal to laser power opens up other avenues of application. Using a more powerful laser and focused optics, an inspector could perform stand-off detection and verification of SANA-based seals.[3] Alternatively, a more detailed analysis could be performed using more sophisticated hardware at a centralized testing laboratory if required by the verification party.

SANA-based tags incorporate the fundamental advantages of most passive tagging and sealing technologies. The system will be inexpensive due to low material costs for the tags, and shared verification hardware. No on-site power sources or infrastructure will be required. No RF, WiFi, or other networking technologies will be required. Owners of sensitive facilities who are wary of active seals and their potential for intelligence gathering may find seals based on SANA tags to be more palatable.

Below, we describe our ongoing SANA development work. We briefly describe methods of spectral filtering, uses of different dye classes to expand the signature library, preliminary results on environmental testing and incorporation into matrix materials (including RPT), and initial work on 2D barcoding.

Spectral Filtering

Since acquisition of the SERS spectrum from a SANA is intended to provide a tag signature, it is important to consider how the raw data might be transformed into an identifiable signature. Much of the data we provide here will be in the processed form. An example of the processing used to create signatures can be seen in Figure 3. Essentially, the algorithm performs a peak find and assigns all points that are not within the found peaks to a background. That background is then interpolated, and subtracted from the raw data. Based on a noise analysis of the raw data, the algorithm then selects prominent features from the subtracted data, and performs peak fitting to produce the final signature. Currently, the background subtraction and noise analysis are fairly aggressive, which results in loss or merging of some minor peaks, but retention of the major features of the spectrum. In a verification scenario, one might imagine performing an initial identification using the major features, and then specifically searching for minor features based on information held in the verification library.

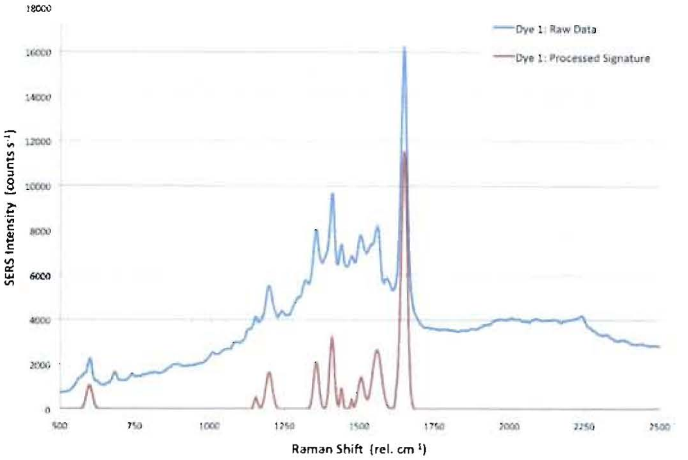

Figure 3. Raw data and processed signature for a SANA containing 'Dye 1'.

Signature Library Expansion

Most of the chemical dyes employed until recently in our SANAs have been of the chromophoric kind associated with fluorescent dyes, textile dyes, etc... The initial reason for using these dyes is that they give the best SERS enhancements, i.e., the strongest signals. However, recent improvements in our ability to make SANAs with inherently strong signals[4] mean that we no longer need the brightest dyes available. We are thus exploring the use of non-chromophoric 'dyes' containing aromatic entities and functional binding groups such as mercaptans and amines. The aromatic portion of the molecule provides sufficient chemical enhancement to induce a SERS response, while the binding group creates a covalent bond to the metal surface of the SANA, for a cleaner system than with chromophoric dyes attracted to the surface by electrostatic interactions.

There are two reasons to pursue dyes of this class. First is simple expansion of the available library. The second is to address and circumvent previously expressed concerns that chromophoric dyes may be subject to photobleaching during extended deployment of the tags.

An example of a SANA signature obtained from a member of this class, 4-mercaptobenzoic acid, is shown in Figure 4. Advantages of this dye class include cleaner backgrounds and better defined peaks. Use of the non-chromophoric dyes has required some adjustments in our preparation technique, but we anticipate inclusion of many more members of this class as we move forward.

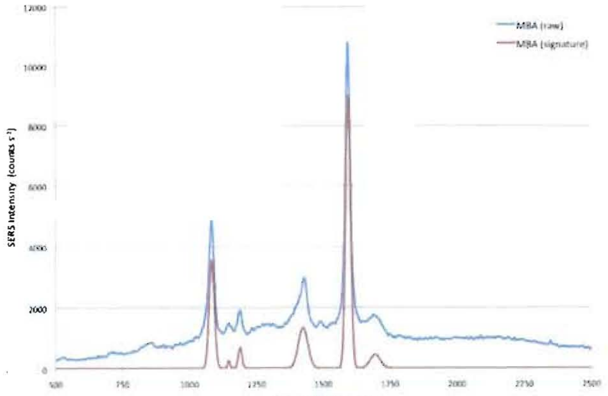

Figure 4. SANA signature obtained from a non-chromophoric dye, 4-mercaptobenzoic acid, excited at 532 nm, 3.4 mW.

Preliminary Environmental Testing

Uncoated silver and gold nanoparticles are known to suffer structural degradation over long periods, or during adverse environmental exposure. For this reason, SANAs receive a silica (or glass) coating of a thickness variable from a few nanometers to hundreds of nanometers as necessary. There is strong precedent for the vastly improved stability of glass-coated metal particles, both in our own work developing materials for solution-based flow cytometry, and published results from others dating back to the early 1990s.[5]

In Figure 5, we show results that relate to the environmental stability of our own materials. These studies are ongoing and have only recently begun, thus the results are very preliminary and limited in scope.

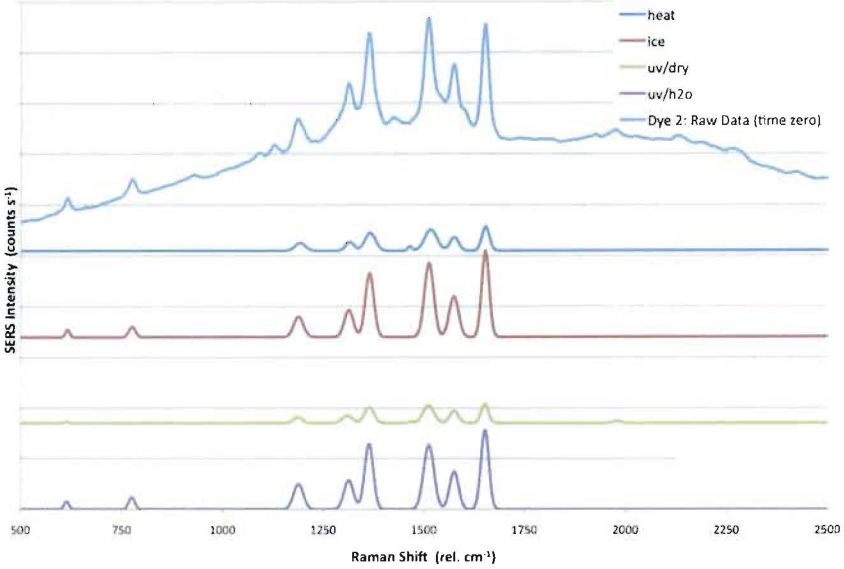

Figure 5. Sample SERS spectra / signatures of SANA containing 'Dye 2', excited at 532 nm with 3.4 mW. Top trace: Original solution at time zero. Remaining traces at 168 hours (one week). The ice trace was recorded while frozen. The remaining traces were recorded after reconstitution into water. Vertical grid lines spaced at 10,000 counts s^{-1}.

The raw data from the original aqueous solution is shown at top. The remainder were taken after subjecting the SANAs to 168 hours of heating at 90°C in dry state (dark blue) , freezing at -20°C in solution (red), exposure to 7 days of direct sunlight in the dry state (green), 7 days of sunlight in solution (purple).

Qualitatively, all samples survived. In all cases except the frozen sample, SANAs precipitated or formed a film. An attempt was made to reconstitute original solution strengths from each sample, but in most cases it was hard to redissolve all of the material – this accounts for most, if not all of the intensity discrepancies between the time zero sample and the one-week samples. Additional work will be required to perform testing that avoids this issue.

Incorporation into Matrix Materials

The results from the previous section encouraged us to begin testing the SANAs in a range of solid matrices. At time of writing, three matrices have been tested: commercial nail polish, commercial epoxy glue, and Reflective Particle Tag (RPT) resin from Sandia National Laboratories.

Nail polish provides an easy matrix to work with as it can be rapidly mixed with SANAs in well-controlled volumes, and contributes a weak background spectrum. Films were prepared on glass slides using varying amounts of SANAs in similar amounts of nail polish (Figure 6).

Figure 6. Films prepared from SANAs in commercial nail polish. Left: Blank (no SANA), and two dyes after preparation. Right: After heating at 90°C for 24 hours.

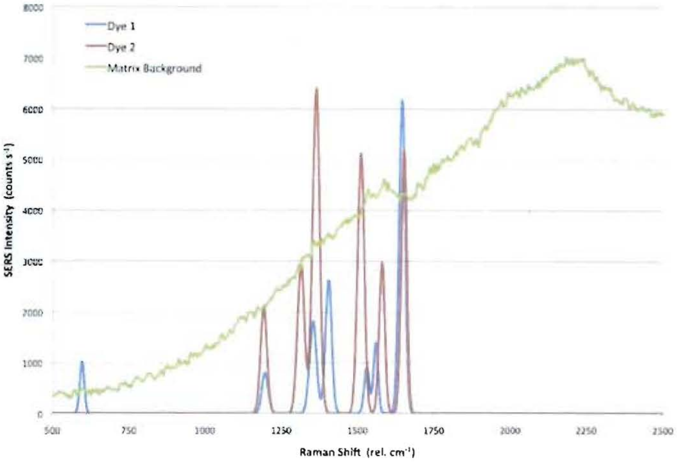

Figure 7. Signatures from SANAs containing 'dye 1' and 'dye 2' in nail polish, excited at 532 nm with 3.4 mW. Also shown, on the same vertical scale: raw background spectrum from nail polish.

SANA signatures were easily and cleanly resolved in the solid state (Figure 7). They remained so over the course of a week at normal room temperatures. However, the nail polish was found to decompose upon extended exposure to heat (see Figure 6, right) with or without SANAs embedded. Additionally, the matrix appears to cause a loss of signal upon rapidly repeated interrogation (a property not observed in thin films of pure SANAs) – although the signal fully recovers if left unexcited for several hours. Since the nail polish is of commercial origin, there may be unknown additives contributing to this effect.

Epoxy was chosen for the second matrix, also a commercial product. SANAs were mixed into the epoxy, which was then spread onto glass slides before it hardened. Again, good quality signatures were obtained upon Raman interrogation (Figure 8), but with considerably less fade than nail polish.

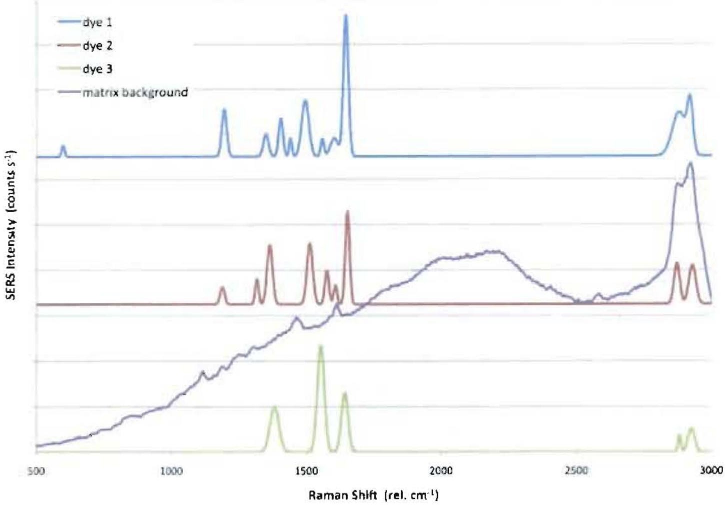

Figure 8. Signatures obtained from SANAs dispersed in epoxy resin (532 nm excitation, 3.4 mW) using three different dyes. The raw background from the epoxy matrix is also shown using the same vertical scale (2000 counts s^{-1} per grid line).

Epoxy has a stronger and more variable background than nail polish. In particular, it changes according to the conditions to which it is subjected (Figure 9, left). At room temperature, complete curing does not appear to occur even after one week (lack of curing is indicated by the peaks close to 3000 rel. cm^{-1}), and the SANA spectra remain visible during this time. After 24 hours of heating at 90°C, the epoxy background spectrum loses the characteristics of being uncured, and the resin itself gains a crystalline appearance. After prolonged exposure to heat or sunlight, the background becomes much stronger, indicative of fluorescence, to the point where the SERS spectra from the SANAs can no longer be observed (Figure 9, right). The immediate concern is that the light / heat exposure may have destroyed the SANAs. However, if the SERS spectrum is obtained using 633 nm excitation (instead of the standard 532 nm), the epoxy background is weakened just enough to be able to observe the SANA signatures. This suggests that the SANAs have survived.

This result is important as we move forward. Ideally, we will avoid the problems of matrix-generated fluorescence by choosing a different resin. However, we also have the option of decreasing (or avoiding) fluorescence by choosing a different excitation wavelength. In this particular case, 633 nm is a poor match for the SANAs because they are based on silver cores which have a better energy overlap with green excitation (hence the weak signal at 633 nm). By choosing SANAs with gold cores, we can achieve stronger signals at 633 nm (or even 785 nm) while potentially avoiding fluorescence from some matrices.

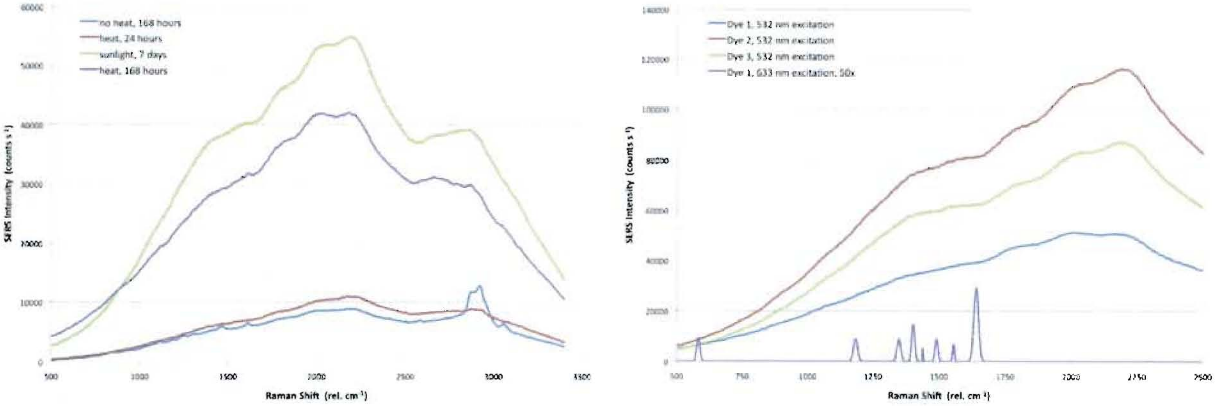

Figure 9. Left: Raw blank epoxy (no SANAs) SERS spectra unheated, heated at 90°C, and exposed to sunlight. Right: Raw SERS spectra from SANAs in epoxy after 168 hours of heat at 90°C. All spectra from 532 nm excitation, 3.4 mW, except lower right: 633 nm excitation, 1.6 mW.

Integration with Reflective Particle Tag (RPT) resin

A third choice for resin material is the Reflective Particle Tag (RPT) resin used at Sandia National Laboratories. SANA and RPT technologies are highly complementary. The verification needs of a combined RPT / SANA tag are easily encompassed in the same hardware, while affording two secure signature mechanisms based on widely differing technology. The resistance to counterfeiting is taken to a new level with the two signatures, while the traceability of tampered tags is greatly improved. For example, RPT offers excellent tamper resistance through the disruption of the optical reflection properties, yet the tampered, non-verified tag can (in this application) still be traced through the retained SERS signature from the SANA component of the resin.

In an informal collaboration with Peter Merkle at Sandia, we are investigating incorporation of SANAs into RPT. We have injected SANAs into RPT resin prior to hardening the hybrid material between two glass slides (Figure 10).

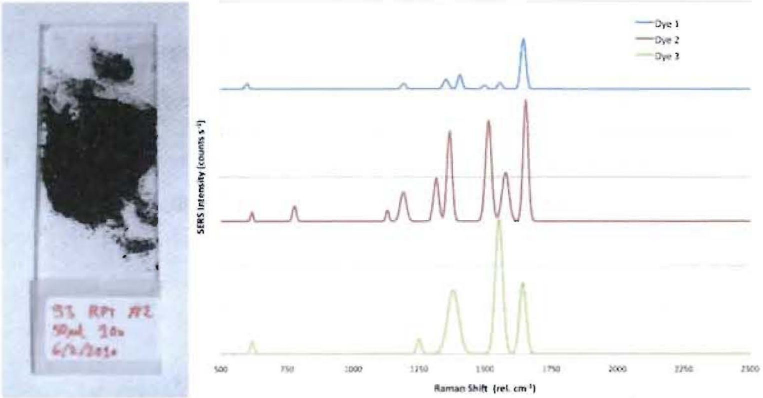

Figure 10. Left: SANAs incorporated into RPT resin. Right: Strong signatures obtained using 532 nm excitation, 3.4 mW. Vertical scale: 2000 counts s^{-1} per grid line.

We continue to observe strong SERS signatures, suggesting that the additional RPT components are not blocking either the laser excitation, or the resultant SERS emission.

2D Barcoding

As an alternative strategy to producing more complex barcodes, we are investigating expansion into two dimensions spatially. George Havrilla and Velma Montoya at LANL have a unique capability for performing 2D spatial patterning using a deposition device known as TIPS – Thermal Inkjet Picofluidic System. This device, based on thermal inkjet technology, is capable of delivering 1 to 300 pL of solution onto a variety of substrates. We are in the early stages of investigating 2D patterning of SANAs using this system.

Thusfar, we have proven the ability to deposit SANAs out of solution onto a substrate in a controlled pattern (Figure 11). The SANAs can then be detected by MXRF.

white light image **MXRF elemental image**

unaggregated SANAs
300 picoliter drops
est. 0.3 nanogram per drop

not visible in white light image

Figure 11. Early test of 2D deposition of SANAs as a precursor to 2D barcodes. Detection by MXRF. Background noise is introduced by the low sample mass.

In the near future we intend to detect these patterns using a Raman microscope – this will provide a 2D SANA barcode in which each point could be from a different SANA.

Summary

In this presentation we have outlined a next generation tagging method based on spectral barcoding using SERS. The new tagging technology is intended to lead to seals that will be highly secure, tamper evident, traceable (even when tampered with), passive, low cost, and verifiable in-field. We have shown that expansion from chromophoric dyes, to non-chromophoric species is viable. We have demonstrated that the SANA materials are resistant over at least short terms to heat, cold, and ultraviolet radiation, and we continue to measure these properties over increasing timescales. SANAs have been incorporated into plastic resins with strong resultant signatures that are not blocked by the resin material at room temperature. It has become apparent that selection of the resin is key – nail polish proved unstable with heat, and epoxy became fluorescent (blocking SERS) with extended heat and / or ultraviolet exposure. While the problems with epoxy can be circumvented by switching to gold-based SANAs and a different SERS excitation wavelength, we will continue to test different resins for use with the silver-based SANAs. We have also shown that SANAs remain viable when incorporated into RPT resin – this has important implications for developing SANA-based seals that are strongly tamper-resistant. Finally, we have performed initial experiments aimed at producing 2D barcodes through spatial deposition.

References

[1] Brown, L. O.; Doorn, S. K. *Langmuir* **2008**, *24*, 2178–2185.

[2] Brown, L. O.; Doorn, S. K. *Langmuir* **2008**, *24*, 2277–2280.

[3] Brown, L. O.; Doorn, S. K.; Lewis, C. Unpublished results.

[4] Goddard, G.; Brown, L. O.; Habbersett, R.; Brady, C. I.; Martin, J. C.; Graves, S. W.; Freyer, J. P.; Doorn, S. K. *Journal of the American Chemical Society* **2010**, *132*, 6081–6090.

[5] (a) Liz-Marzán, L. M.; Giersig, M.; Mulvaney, P. *Langmuir* **1996**, *12*, 4329–4335. (b) Tunc, I.; Suzer, S.; Correa-Duarte, M. A.; Liz-Marzán, L. M. *Journal of Physical Chemistry B* **2005**, *109*, 7597–7600.

Acknowledgments

This work is supported by the United States National Nuclear Security Administration's Office of Dismantlement and Transparency – Next Generation Safeguards Initiative (NGSI).