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SERS-Active Nanoparticles as a Barcoding Technology for Tags and Seals

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Abstract

In this paper, we present our work to modernize tagging and sealing technologies for international safeguards applications. Our work combines technologies developed at both Los Alamos National Laboratory (LANL), and Sandia National Laboratories (SNL), to offer a passive tag and seal system that can be applied and verified in field, with minimal training for on-site personnel, along with a low per-seal cost. Here, we focus primarily on LANL technology: the use of Surface Enhanced Raman Scattering (SERS) as an inexpensive verification tool. Our nanoparticles offer unique SERS responses, which we can then use to incorporate robust barcoding into tag materials. We describe this technology in more detail, offer preliminary results, and outline integration with SNL developments.

Introduction

Tags and seals form a group of technologies central to the international safeguards effort. Current tags and seals employ a wide range of methodologies in an attempt to ensure that materials of interest can be identified, tracked, and sealed. The ability to verify that materials have not been diverted is of major concern in the current nonproliferation climate. Prevention of diversion places high demands on tag and seal security – resistance to spoofing, coupled with definitive tamper resistance is key. These needs must be balanced against the demanding environments in which international inspectors must operate. Any new tag and seal technology must be able to meet today's security challenges without significantly burdening the inspectors of facility owners in terms of facility access requirements, or infrastructure needs.

Here, we present a new technology – SERS-Active Nanoparticle Aggregates (SANAs) – which we are employing in a joint Los Alamos–Sandia effort to meet modern tag and seal requirements. In our collaboration with Sandia, SANAs will be introduced into Reflective Particle Tag (RPT) technology to create a next generation tag and seal technology. In this presentation we will focus on SANAs.

Core Technology

SERS-Active Nanoparticle Aggregates (SANAs, Figure 1) are constructed from gold or silver nanoparticles in the 40 – 80 nm size range. (It should be noted that gold or silver is required to provide the signal enhancement inherent to the SERS technique.) A chemical 'dye' is attached to the nanoparticle surface, and the nanoparticles are aggregated into ensembles of ~100 to 500 nm diameter. The chemical dye provides individual identifying information to the aggregate, which is finally coated in a glass layer to provide environmental stability.

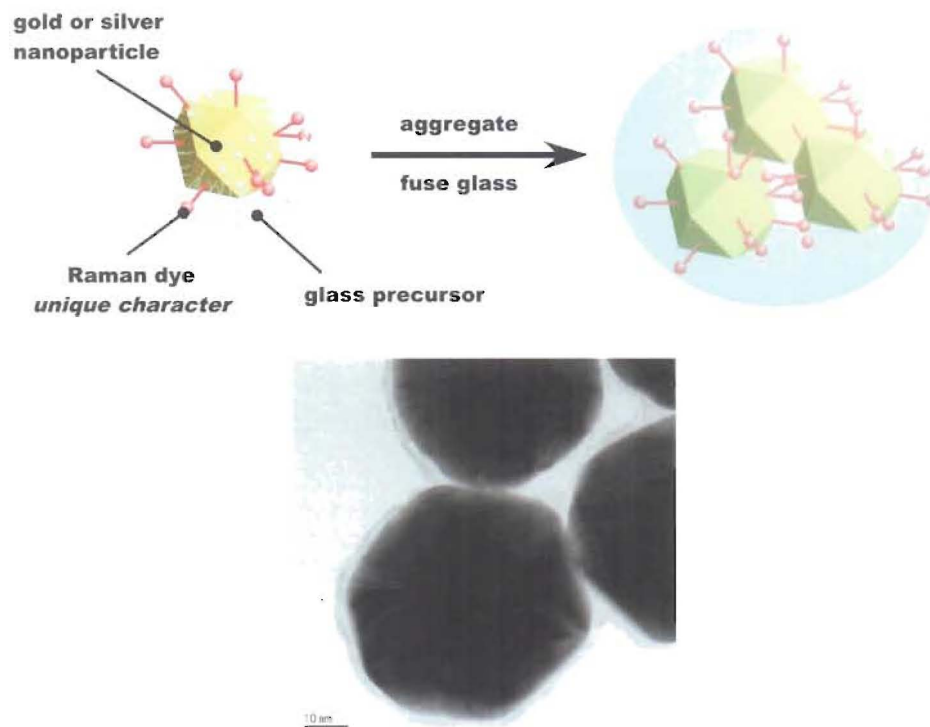


Figure 1. SERS-Active Nanoparticle Aggregates (SANAs). Top: General preparation method. Bottom: TEM of a silica-coated silver SANA. Silica coating in this case is several nanometers thick, a practical minimum for environmental stability and processing.

The completed SANA can be physically embedded in, or chemically surface-mounted to tag or seal materials. In either configuration, SANAs provide a chemical barcode, readable using detection hardware that can be easily contained in handheld form. Upon excitation by laser (Figure 2), a SANA returns a spectroscopic signal unique to the dye, or combination of dyes, adsorbed on the SANA metal surface. Depending on the end application, the signal can be reduced to a simple barcode, or examined in complex detail to provide a high security signature that is cost prohibitive to replicate.

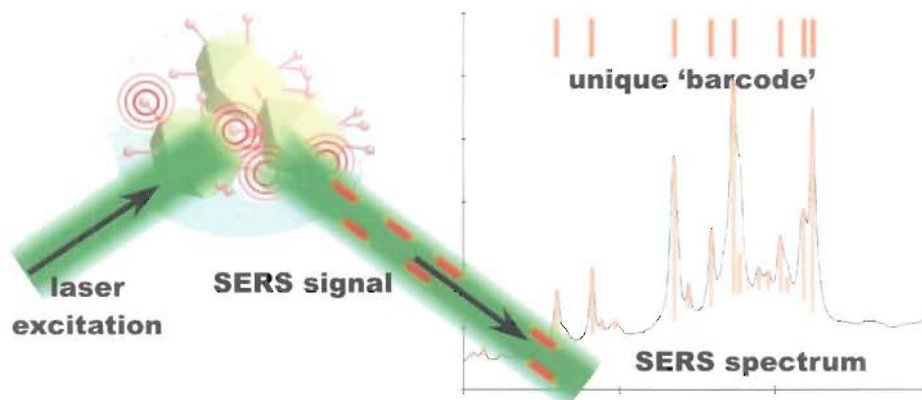


Figure 2. SANAs are read by laser to provide a spectroscopic barcode.

Technology Advantages

Tag and seal technology based on SANAs offers several advantages, as compared to currently deployed tagging methods:

Signature Library. The SERS signature can be extensively varied (see below) to provide a library of unique tag signatures limited mostly by the choice and precision of verification algorithm.

High Security. The SERS signature of a SANA-based seal will be cost prohibitive to replicate. This is in part due to the minimal use of SANA material, and the corresponding difficulty in extracting that material from the seal matrix for analysis. Difficulty in counterfeiting also derives from the method in which unique signatures will be generated – see discussion below.

In-field Verification. Unlike many existing tagging technologies, SANAs will be in-field verifiable using handheld instrumentation. For example, a basic verification system can be constructed using a subnotebook computer, with a laser pointer and CCD detector coupled to an objective aperture via fiber optic. It is anticipated that removal of the tag will be unnecessary over the lifetime during which an item must be tagged or sealed.

Passive Technology. Importantly, SANAs are a passive technology with no facility infrastructure requirements – the power source needed for verification will be carried with the portable instrumentation.

Minimal Human Input. Inspectors will be required (in most cases) merely to visually locate the tag, and target the SANA-containing material with the handheld verifier. The computer will then acquire the necessary data for automated verification. For initial placement of the tag, SANAs will be applied as part of the RPT resin, resulting in minimal facility intrusion.

Low Cost. The highly sensitive SERS technique, when coupled with the highly evolved state of our SANAs, allows us to use minimal quantities of precious metal per seal. Initial work by others produced silica-coated and dye-tagged metal particles that were readily detectable using cheap laboratory spectrometers. However, our use of these materials in flow cytometry required much brighter SERS signals that could be detected in short transit times on the microsecond timescale. Since the tag / seal application has no such stringent temporal requirements, we can now use several orders of magnitude less metal material, while also opting for a cheap excitation source such as a laser pointer. Currently, we estimate the material cost of SANAs to be < 1 cent per 300 cc of RPT resin.

Superior Environmental / Temporal Stability. Uncoated silver and gold nanoparticles are known to suffer structural degradation over long periods, or during adverse environmental exposure. For this reason, SANAs will 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.

Barcoding

As depicted in Figure 2, the SERS spectrum of a SANA-containing material can be reduced to barcodes of varying complexity. A simple barcode (top) contains only the

locations of significant peaks in the spectrum. With another level of information (bottom), the relative intensities of the peaks are encoded. Increasingly sophisticated algorithms can incorporate more of the spectral features in a form easily verified in the field.

To date we have performed fairly simple testing for barcoding SANAs. In Figure 3 we show a test barcode map produced from a series of SANAs with different dyes attached. The barcodes incorporate relative intensity information as shown by the color. The spectra were sliced into frequency bands, and the variance of each band was ranked across the entire dye library. Band 0 contains the most variance, and band 32 the least (note that band numbers are not correlated to actual spectral frequency). Bands after number 32 were discarded from the data as being relatively insignificant to this particular dye library.

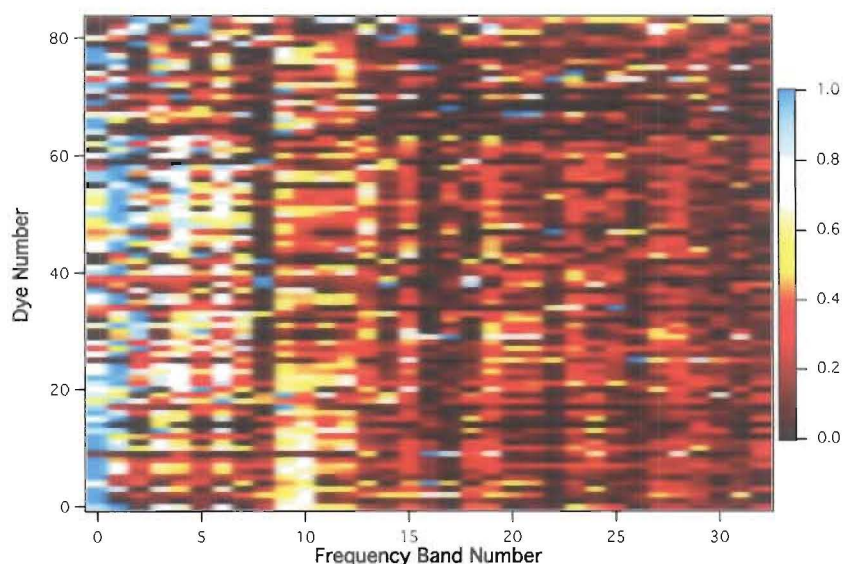


Figure 3. An example barcode map for a series of dyes. See text for explanation.

Using this barcoding approach, we can attempt to identify SANAs against the library. We find that identifying one of the actual SANAs used to create the library is almost always successful, as would be expected. However, when a *newly prepared* SANA is tested using a *dye contained in the library*, results are mixed. Even when identified successfully, the fit is usually poor. This is a very good result as it shows that the SERS spectrum is very sensitive to the ‘lot number’ of the SANA – it should be noted that for a deployed seal, the exact SANA signature will exist in the verification library. This variability in successive batches is described more below.

Signature Library and Security

The SERS signature derived from a SANA is determined by the Raman ‘dye’ attached to the metal surface during SANA preparation. We use the term ‘dye’ from a historical perspective – many of the chemicals we have employed have been colored or fluorescent materials. However, neither color nor fluorescence, are required properties.

For example, many colorless, non-fluorescent aromatic organic molecules make excellent SERS dyes due to significant electronic interaction with excited metal surfaces.

Much of our early work relied on direct attachment of the dye to the metal surface. While convenient for processing, this limited us to chemical dyes that had a very strong interaction with precious metals – mostly those that could link through a formal chemical bond. More recently, we modified our preparation techniques to eliminate this necessity, thus broadening our possible signatures to include those that have only a weak attraction to metal.

The apparent weakness in this approach is the possibility that the identity of the chemical dye could be determined, leading to the direct preparation of a counterfeit batch of SANAs. In practice, there are several inherent factors that work to neutralize this threat, as outlined below. In addition, there are several techniques we can employ to further frustrate this avenue of attack.

Identifying a Dye Contained within a SANA. The SERS spectrum contains information related to the types of chemical bond in the dye. It is an incomplete picture, as it offers only very partial information detailing the connectivity of those bonds. However, some dyes are very well known in SERS, and could thus be readily identified by someone with the right knowledge or experience. In some cases, enough information is present in the SERS spectrum to narrow the possibilities to a range that could be tested by trial and error. In remaining situations, the would be counterfeiter would likely have to physically remove the SANA from the seal material in order to obtain a wide enough range of analytical data to positively identify the dye. Given the minute amount of material employed in a seal, and the relatively low sensitivity of most analytical techniques, exact identification of a non-obvious dye will remain highly challenging.

Batch to Batch Variability. As described above, significant differences are usually observed in two different batches of a SANA containing the same dye. The causes are numerous. For example, SERS is highly sensitive to the orientation of the dye to the metal surface. The results include differing relative intensities of spectral peaks, and non-uniform background information. In some cases, certain peaks may be entirely absent from some batches. Surface orientation of a weakly attracted dye depends on many factors, including dye concentration, solution pH, and impurities and counter ions present. *Even when a dye is positively identified, obtaining the exact same spectral signature is improbable* if sufficient information is encoded in the verification algorithm.

Multiple Dyes. One of the simplest techniques we can utilize to frustrate counterfeiters is to simply include more than one dye in the mix. The resultant SERS signature will then depend on the identities of the contained dyes, their relative concentrations, their binding affinities, any influences they have upon each other, and the factors that cause the batch to batch variability described above. *Incorporation of multiple dyes into a single SANA will result in a highly secure tag that is cost prohibitive to replicate.*

Integration with RPT

Increasing tag security even further, we will integrate SANAs with Sandia's RPT technology. The two 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.

Summary

In this presentation we have outlined a next generation tagging method based on two independent secure technologies – spectral barcoding using SERS, and optical mapping using RPT. The combined tag will be highly secure, tamper evident, traceable (even when tampered with), passive, low cost, and in-field verifiable.

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