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(54) Title: SERS-ACTIVE PARTICLES OR SUBSTANCES AND USES THEREOF

(57) Abstract: A particle comprising a surface enhanced spectroscopy (SES)-enhancing antenna, a SES-active reporter molecule and an encapsulant surrounding the SES-active reporter and antenna combination. The particle also includes a security feature in addition to the SES activity provided by the reporter and antenna. Also disclosed are methods of fabricating, using and monitoring the quality of SES-active particles.

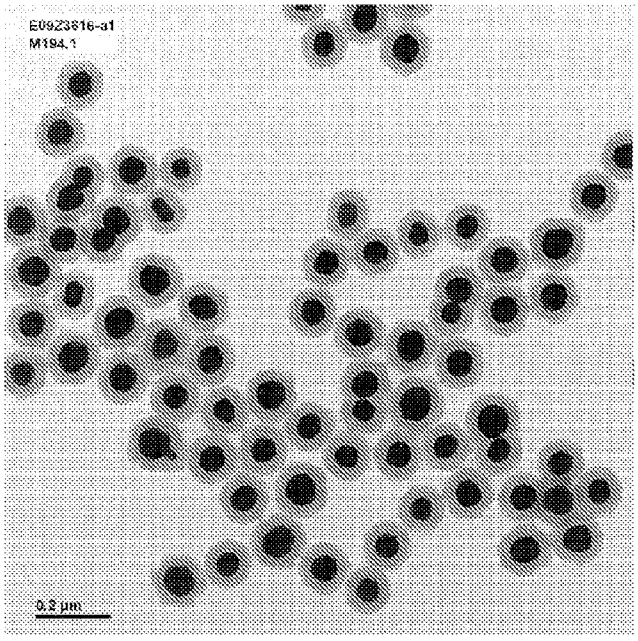


Fig 5

WO 2010/138914 A1

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SERS-ACTIVE PARTICLES OR SUBSTANCES AND USES THEREOF

TECHNICAL FIELD

[0001] The disclosed embodiments relate to surface enhanced spectroscopy active nanoparticles. More specifically, the disclosed particles and methods relate to particles and methods useful in industrial security.

BACKGROUND

[0002] Certain spectroscopy techniques feature the enhancement of a spectroscopic signal through electromagnetic interaction at a surface. Representative surface enhanced spectroscopic (SES) techniques include, but are not limited to surface enhanced Raman spectroscopy (SERS) and surface enhanced resonance Raman spectroscopy (SERRS). In SERS or SERRS, a metal or other enhancing surface will couple electromagnetically to incident electromagnetic radiation and create a locally amplified electromagnetic field that leads to 10^2- to 10^9-fold or greater increases in the Raman scattering of a SERS active molecule situated on or near the enhancing surface. The output in a SERS experiment is the fingerprint-like Raman spectrum of the SERS active molecule.

[0003] SERS and other SES techniques can be implemented with particles such as nanoparticles. For example, gold is a SERS enhancing surface, and gold colloid may be suspended in a mixture to provide for enhanced Raman spectrum detection. SERS may also be performed with more complex SERS-active nanoparticles, for example SERS nanotags, as described in US Patents No. 6,514,767, No. 6,861,263, No. 7,443,489 and elsewhere. In a SERS nanotag, a reporter molecule is adsorbed to a SERS-active surface, and both the SERS-active surface and the reporter are encapsulated, typically with silica or another relatively impervious material. One advantage of a silica or glass coating is that it prevents the adsorbed molecule from diffusing away. The coating or shell also prevents other molecules from adsorbing to the enhancing surface or particle core. This configuration imparts a level of robustness and environmental insensitivity to the particles that is, for many applications, a desirable feature.

[0004] A conventional SERS nanotag might have a single reporter and thus is configured to deliver a single type or value of identifying information. While quite useful, a tag having a single reporter and returning a single type of security information may not be as

sophisticated a taggant as is desired for industrial security purposes. The embodiments disclosed herein are directed toward overcoming one or more of the problems discussed above.

SUMMARY

[0005] One embodiment disclosed herein is a particle comprising a surface enhanced spectroscopy (SES)-enhancing antenna, a SES-active reporter molecule and an encapsulant surrounding the SES-active reporter and antenna combination. The particle also includes a security feature in addition to the SES activity provided by the reporter and antenna. The security feature may be but is not limited to a fluorescent signature, a magnetic property, a color, a radio frequency signature, a luminescence property, a neutron scattering signature, a microwave signature a mass spectral signature or similar identifying characteristic. Alternatively, the security feature may be additional SES activity for example, SERS activity at multiple excitation frequencies provided by multiple reporters which can be combined to form a code. The security feature may be associated with any portion of the particle including but not limited to the antenna, reporter, encapsulant, or any supplemental layer or structure.

[0006] A method of identifying an object is also disclosed, the method comprising associating a particle as described herein with an object and obtaining identifying information from the particle. The identifying information obtained may be supplemental to, in addition to or in combination with the SES spectrum provided by the antenna and reporter combination.

[0007] An alternative embodiment is a method of fabricating an SES-active particle comprising providing an SES-enhancing antenna and associating an SES-active reporter wherein the association. Optionally the reporter and antenna may be encapsulated. Some or all of the various fabrication steps do not occur in a solution.

[0008] An alternative embodiment is a method of fabricating an SES-active particle comprising providing an SES-enhancing antenna, associating an SES-active reporter with the SES-enhancing antenna and monitoring an SES signal obtained from the antenna and reporter combination as the reporter is associated with the antenna. In addition, the SES-active particle may be encapsulated. The quality of the SES particle and the progress of various synthesis steps may be monitored during fabrication.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] Fig. 1 is a plot of the SERS output of a reporter and antenna combination versus time, as the reporter is being associated with the antenna material.

[0010] Fig. 2 is a plot of the UV-visible absorbance of an SES-active particle obtained for particle synthesis quality control.

[0011] Fig. 3 is a plot of the IR absorbance of a SES-active particle obtained for particle synthesis quality control.

[0012] Fig. 4 is a plot of the SERS response of an SES-active particle compared to a known SERS response obtained for particle synthesis quality control.

[0013] Fig. 5 is a TEM image of a batch of SES-active particles obtained for particle synthesis quality control.

[0014] Fig. 6 is a SEM image of a batch of SES-active particle obtained for particle synthesis quality control.

[0015] Fig. 7 is a dynamic light scattering (DLS) plot used as a measure of particle size obtained for particle synthesis quality control.

DESCRIPTION

[0016] Unless otherwise indicated, all numbers expressing quantities of ingredients, dimensions, reaction conditions and so forth used in the specification and claims are to be understood as being modified in all instances by the term "about".

[0017] In this application and the claims, the use of the singular includes the plural unless specifically stated otherwise. In addition, use of "or" means "and/or" unless stated otherwise. Moreover, the use of the term "including", as well as other forms, such as "includes" and "included", is not limiting. Also, terms such as "element" or "component" encompass both elements and components comprising one unit and elements and components that comprise more than one unit unless specifically stated otherwise.

[0018] In general, taggants are materials, substances, molecules, ions, polymers, nanoparticles, microparticles, or other matter, incorporated into, onto or otherwise associated with objects for the purposes of identification or quantitation. More specifically, taggants are used in activities and products including but not limited to detection, analysis, and/or quantification measurements related to brand security, brand protection, trademark protection, product security, product identification, brand diversion, barcoding, grey market remediation, friend-or-foe analysis, product life cycle analysis, counterfeiting, anti-

counterfeiting, forensic analysis of authenticity, authentication, biometrics, object tracking, chain-of-custody analysis, product tampering, anti-smuggling, smuggling detection, supply-chain tracking, product tracking, lost revenue recovery, product serialization, serialized authentication, freshness tracking, sell-by date tracking, use-by date tracking, and standoff detection/identification.

[0019] Taggants can be added to all forms of matter, including but not limited to solids, liquids, gases, gels, foams, semi-solids, glasses, plasmas, liquid crystals, amorphous and magnetically-ordered solids, superconductors, superfluids, Bose-Einstein condensates, and supersolids.

[0020] Many known methods of detecting taggants utilize one of several spectroscopic techniques, for example a surface-enhanced spectroscopy (SES) techniques such as SERS or SERRS. Broadly speaking, suitable materials fall in two categories: nano-/microscale and macroscopic. For example, certain sizes and shapes of Ag and Au nanoparticles, and aggregates thereof, are known to support SERS. Likewise, a large variety of macroscopic SERS substrates have been described in the literature, including electrodes, evaporated films, Langmuir-Blodgett films, 2-dimensional planar arrays, and so forth.

[0021] Known prior art tagging methods which utilize SERS-active tags typically include a reporter molecule or dye with known SERS-active characteristics. For example, a known SERS-active chemical can be added as a dye to mark fuel and a subsequent SERS spectrum obtained when the SERS-active dye is associated with a SERS-active metal particle or substrate. Only a limited number of SERS active chemicals are known.

[0022] Many of the embodiments disclosed herein feature the use of a surface-enhanced spectroscopy (SES) active taggant. The most widely studied have been surface-enhanced Raman scattering and surface-enhanced fluorescence (SEF). But a variety of other surface enhanced phenomena have been observed including surface-enhanced hyper Raman scattering (SEHRS), surface-enhanced hyper Raman resonance scattering (SEHRRS), surface-enhanced Rayleigh scattering, surface-enhanced second harmonic generation (SHG), surface-enhanced infrared absorption reflectance (SEIRA), and surface-enhanced laser desorption ionization (SELDI). These are part of a wider field known as plasmon enhancement or plasmon-enhanced spectroscopy, which in addition to the phenomena mentioned above includes surface plasmon enhanced emission (such as SPASERS – surface plasmon amplification of spontaneous emission of radiation), plasmon enhanced diffraction, and plasmon enhanced optical transmission. Plasmon enhancement is also a method to

increase the efficiency of solar cells. As used throughout this disclosure SES includes the above listed and any related or similar spectroscopic technique.

[0023] Many of the examples herein are described with respect to SERS. It must be noted however that the methods, compositions and particles disclosed herein are equally applicable to SERRS, SEHRS, SEF, SEHRRS, SHG, SEIRA, SPASERS, or other surface enhanced or plasmon enhanced SES technique.

[0024] As noted above, one type of known SERS-active nanoparticle is a SERS nanotag, as described in US Patents No. 6,514,767, No. 6,861,263, No. 7,443,489 and elsewhere. All matters disclosed in US Patents No. 6,514,767, No. 6,861,263 and No. 7,443,489 are incorporated herein in their entirety for all matters disclosed therein. In a conventional SERS nanotag composition, a reporter molecule is adsorbed to a SERS-active surface, and both the SERS-active surface and the reporter are encapsulated, typically with silica or a glass. One advantage of a silica coating is that it prevents the adsorbed molecule from diffusing away, and also prevents other molecules from adsorbing to the surface. This imparts a level of robustness and environmental insensitivity to the SERS nanotag particles that is, for many applications, a desirable feature.

[0025] Surface enhanced Raman scattering (SERS)-active particles are useful in a variety of applications. One interesting application is anti-counterfeiting, and more specifically to verify the authenticity, source, age, and/or distribution path of banknotes, tax stamps, banderols, passports, identification cards, driver's licenses, work permits, fiduciary documents, stock and bond certificates, and other valuable documents that contain ink. Likewise, SERS-active particles can be used for similar purposes to mark or tag a variety of other materials that contain print or lettering composed of ink or lacquer, including but not limited to software, machine parts such as airplane parts or automobile parts, instrumentation, pharmaceutical and diagnostic products, medical devices, luxury goods, fast-moving consumer goods, CD's, DVD's and other electronic storage components, and so forth. Moreover, any ink- or lacquer-containing packaging for any type of product is a viable location for introduction of SERS-active particles for anti-counterfeiting, or authentication purposes. Additional closely related applications for SERS-active particles include: brand security, brand protection, trademark protection, product security, product identification, brand diversion, barcoding, grey market remediation, friend-or-foe analysis, product life cycle analysis, counterfeiting, forensic analysis of authenticity, biometrics, document tracking, chain-of-custody analysis, product tampering, anti-smuggling, smuggling detection, supply-chain tracking, product tracking, lost revenue recovery, product serialization,

serialized authentication, freshness tracking, sell-by date tracking, use-by date tracking, object tracking, standoff detection, and/or standoff identification. In addition, SERS-active particles can be used for combinations of these applications, including but not limited to a combination of authentication and sell-by-date tracking. Collectively, these applications are referred to as Industrial Security.

[0026] Certain SERS-active particles that are useful for these applications have at least three functional and useful properties. A first property is the ability to couple with electromagnetic radiation and provide electromagnetic enhancement. This first property is provided by an antenna. As used herein an "antenna" is the means to couple in or couple out electromagnetic radiation to or from the particle. The antenna also provides the electromagnetic enhancement responsible for some of or the entire SERS phenomenon. Typically the antenna is a metal particle, often but not always a particle core or particle shell. Depending upon the excitation wavelengths used, the antenna can also be a semiconductor particle.

[0027] A second functional property of a SERS particle useful as a taggant is the generation of a unique and distinguishable SERS spectral fingerprint upon optical interrogation. The molecule or species that gives rise to this fingerprint spectrum is referred to herein as the reporter or reporter molecule. The reporter must typically be in very close proximity or bound to the antenna to experience heightened electromagnetic fields or to be involved in chemical processes or effects that give rise to SERS.

[0028] Another functional property of a SERS particle suitable for tagging a material is that the reporter to antenna interface be protected. Protection is often, but not always provided by an encapsulant. In most cases, useful SERS-active particle will have at least three distinct structural components or elements, with one component providing each functionality. For example, a metal nanoparticle can serve as an antenna, an adsorbed organic molecule can serve as a reporter, and a silica shell can serves as the encapsulant. In some cases however, a particular species or element can provide multiple roles. For example, the encapsulant can also be the reporter, with certain functional groups of the encapsulant providing a fingerprint like Raman spectrum, while the same or other functional groups serve a barrier/protective function. Likewise, the antenna itself can serve as an encapsulant, for example, when the former is a solid, hollow particle and the reporters are located inside the particle. Alternatively, the particle could serve both as an antenna and as a reporter via its phonon or lattice vibrations. Each of the functional elements described above are discussed in detail below.

I. Antenna

[0029] The antenna can comprise one particle, or even part of one particle, for example a bi-hemispherical particle, where each hemisphere comprises a different composition and only one composition is SERS-active. The antenna can also comprise two particles, where the particles are in contact (i.e. a spacing of zero along some axis), or not in contact. It can also comprise three or more particles, where there is any allowing spacing and/or angle between each pair of particles. Larger aggregates or collections of particles are also useful, even those between 3 and 100 particles, especially at longer excitation wavelengths.

[0030] Each particle or particles in a SERS-active antenna can have a variety of sizes, shapes, geometries, and compositions. For example, the antenna might comprise a single Au particle that is a solid, 90-nm diameter cube. Alternatively it might comprise two particles, one Au and one Ag, one of which is solid, one of which is hollow, one of which is 20 nm and one of which is 400 nm, one of which is a pyramid-shaped particle, and one of which is an octahedron. Generally speaking, SERS experiments can be carried out at all wavelengths between 200 nm and 10 microns. Recently published uv SERS data suggests that the lower range might even approach excitation wavelengths even deeper in the uv, e.g. 150 nm. At excitation wavelengths less than 400 nm, new materials become candidates for antennas, including but not limited to Al. To cover this range of wavelengths, a particle or particles that comprise an antenna might be as small as 5 nm or perhaps even smaller, e.g. 1-2 nm, or as large as 50 microns. The antenna might exhibit a regular or irregular shape. It may be a particle, a core, and a shell, where the shell is metal and the core is silica, or another material. The composition may include any material (including but not limited metal, alloys, semiconductors, semi-metals, metal oxides, metal sulfides, metal nitrides, forms of carbon) or combination of materials that either (a) exhibits a surface plasmon band or bands between 200 nm and 10 microns or (b) can be demonstrated to support enhanced Raman scattering.

[0031] The antenna may have any number of other properties relevant to its use in industrial security, including but not limited to high or low density, high or low porosity, high or low conductivity, high or low dispersability, high or low mechanical stability, high or low elasticity, high or low coercivity, intense or no color, high or low chemical stability, high or low melting point, high or low resistance to change in shape, high or low tendency to scatter light, high or low stickiness to surfaces, high or low mass, high or low volume, and high or low reflectivity.

[0032] The antenna can be made by a single technique or by a combination of techniques. When the antenna comprises two or more particles, different methods may be used for each particle. Methods for manufacture of the particle or particles that comprise an antenna include those operating in the gas phase, in solution, in the solid state, or melts. Indeed, any of the myriad approaches described in literature to make nanoparticles or microparticles are candidates for synthesis of SERS-active substances. Examples of methods that can be used to make SERS-active particles include but is not limited to solution synthesis from pre-cursors, laser ablation, gas phase growth (e.g. chemical vapor deposition), flame pyrolysis, spray pyrolysis, grinding, milling, electro deposition, galvanic replacement, evaporation, nano-imprinting and staining, lithography, nanosphere lithography, atomic layer deposition, solution phase precipitation, explosion, combustion, melting, and annealing.

II. Reporter

[0033] SERS from single molecules has been reported, so the reporter could comprise a single molecule. Alternatively, it could comprise two or more molecules. The molecules could be the same, or they could be different. In other embodiments, many molecules could server as reporter. For example, between 100-1000 molecules per particle could comprise the reporter. Alternatively, between 100,000 and 1,000,000, or between 1,000,000 and 10 million molecules could comprise the reporter. While the majority of SERS comes from molecules adsorbed to the antenna, molecules near the antenna also experience enhanced electromagnetic fields. Depending on the size of the antenna and the excitation wavelength, this enhanced field could extend for up to 500 layers or molecules, depending on molecular size and orientation. For example, 100 layers of stacked graphene is roughly only 20 nm in thickness, well within range to experience the enhanced field from a 150-nm diameter antenna particle.

[0034] While reporters are typically molecules, either organic or containing a metal ion, they can also be solid-sate materials, polymers, ionic liquids, or supramolecular assemblies. Any molecule, material, substance, or combinations thereof that possess a distinct Raman spectrum or scatters light inelastically can serve the function of reporter.

[0035] The reporter may have any number of other properties relevant to its use in industrial security, including but not limited to high or low solubility in aqueous or non-aqueous solvents, high or low molecular weight, high or low ionization potential, high or low absorbance, high or low conductivity, high or low mechanical stability, high or low redox potential, high or low tendency to self-associate, high or low binding constants to surfaces,

high or low amounts of non-carbon/oxygen/nitrogen/sulfur elements (including but not limited to P, Tc, Ru, Hf, Cd, Hg, and Se), high or low optical activity (e.g. chirality), high or low dipole moment, high or low polarizability, high or low octane numbers, high or low cetane numbers, high or low flammability, high or low stability toward combustion, high or low thermal stability, high or low stability under ultraviolet light, high or low reactivity toward acid, high or low reactivity toward base, high or low reactivity towards any other substance, high or low melting point, high or low boiling point, high or low flash point, high or low freezing point, high or low purity, high or low tendency to isomerize, high or low conformational stability, and high or low tendency to self-associate.

[0036] The reporter may also exhibit an emission spectrum (fluorescent, luminescent). It may detectable by any other means, including but not limited to mass spectrometry, electrochemistry, infrared, NMR, EPR, Mossbauer spectroscopy, EXAFS, EELS, SIMS, and AFM, and may exhibit one or more unique signatures when interrogated by other means.

[0037] The structure of a reporter to be used for an industrial security application can be determined by any number of spectroscopic or spectrometric methods, including but not limited to mass spectrometry, Raman spectroscopy, infrared spectroscopy, nuclear magnetic resonance spectroscopy, nuclear quadrupole resonance spectroscopy, and electron paramagnetic resonance spectroscopy.

[0038] All methods used in chemical, biochemical, solid state, inorganic, organic, polymer, and materials synthesis are appropriate for fabrication of reporters. Specifically, a reporter can be assembled from two or more pieces, or it could be prepared by removing a piece, component, or part of a larger substance. The reporter can be made in zero steps, i.e. already occurring and available either commercially, or existing in any laboratory anywhere, or existing in Nature (including but not limited to substances in air, water, earth, stone, soil, lava etc.)], or in one step, or in multiple steps. The reporter can be a known substance, or one not previously reported.

[0039] Reporters can contain elements in their natural abundance, or can contain elements in non-natural abundances, or combinations with certain elements in their natural abundance and others in non-natural abundances. Reporters can contain stable or unstable isotopes. When unstable, the isotopes might decay over seconds, minutes, hours, days, weeks, months, years, decades, or centuries. Analysis of the spectrum that makes use of an unstable reporter can provide the age of object to which the reporter is associated.

[0040] Reporters can contain features that make analysis by means other than Raman spectroscopy difficult. For example, they can be designed to ionize poorly for mass spectrometry, or contain elements that confound analysis. Likewise, reporters can contain functionality (for example, free radicals) that interfere with conventional NMR analysis. Likewise, a reporter can contain functional groups designed to self-destruct upon conditions required to analyze their structure.

[0041] Reporters can be designed to be seen easily or with difficulty in a given medium. For example, they can be designed to have a Raman spectral feature or features not present in ink, making them easy to see in ink samples. Likewise, they can contain a feature or features similar or identical to those present in ink, making them difficult to see. The same is true for any other type of matrix into which anti-counterfeiting or industrial security technologies may be incorporated, including but not limited to paper, lacquer, glue, pills, excipients, active pharmaceutical ingredients, metals, polymers, solvents, fuels, oil, bio-fuels, foods, beverages, spirits, clothing, thread, labels, luxury goods, and machine parts. Thus, the Raman spectra of reporters can be obscured to any desired degree in any medium.

[0042] Reporters can be designed to exhibit desired spectral features, such as two bands of equal or nearly equal intensity in a given region of the spectrum. Alternatively, a reporter can be designed to have 3, or 4, or 5 bands of given ratios in different regions of the spectrum. In another embodiment, reporters can be designed to provide intense spectra in certain regions of the spectrum, and no features in other regions of the spectrum. Reporters can be designed to yield very simple spectra (for example, azide), or very complex spectra (for example, dyes).

[0043] A reporter may be associated with one type of antenna or with several. Likewise, each antenna could be associated with one or more reporters. An example of the former is where the reporter pyridine is bound to particles with 60-nm, 80-nm, and 100-nm diameters; an example of the latter is where pyridine, mecaptoethanol, and mercaptosulfonic acid are all bound to a 60-nm diameter particle. Combinations of these two scenarios are also possible.

[0044] The reporter or reporters can be introduced via the vapor phase, via the liquid phase, or in the solid state. Alternatively, it/they can be introduced using multiple phases at once. The reporter or reporters may be introduced all at once, or in several steps. Each step may involve different conditions, including but not limited to the phase (gas, liquid, solid), temperature, pressure, ionic strength, mixing rate, reaction time, reagent concentrations, solvents, manual or automated processes. Each step can occur separately or simultaneously.

The reporter can be introduced before antenna formation, during antenna formation or after antenna formation. Likewise, the reporter can be introduced before, during or after encapsulation.

[0045] Reporters can comprise mixtures of Raman-active and Raman-inactive species. Alternatively, reporters can be mixtures of strong and weak Raman scatterers. For example, a reporter could comprise a mixture of pyridine and 1-octanol, where the former gives a strong Raman signal and the latter a weak signal due to differences in polarizability. In another embodiment, reporters that adsorb to surfaces of antennas may be used with substances that do not adsorb strongly to the antenna and/or give very weak Raman spectra, but control reporter coverage, orientation, or surface mobility. For example, 2-mercaptoethanol, a fairly weak Raman scatter that does not adsorb particularly strongly to Au surfaces, might be used with the stronger adsorbing and more polarizable 4-mercapopyridine to control the amount adsorbed and surface orientation of the latter substance.

[0046] It certain cases it may be advantageous to keep the identity of the reporter secret during manufacture of SERS-active materials for industrial security applications. This can be accomplished by using a convergent synthesis and a double blind, where each of two groups make one piece of a reporter but do not know what the other group is making. A third group may be responsible for stitching the two pieces together, without knowing the identity of either. For example, Group A makes an activated carboxylate. Group B makes an activated amine. Group C mixes the molecules together to yield the desired reporter. This can be extended to any number of pieces or steps required to assemble the desired reporter.

[0047] Secrecy can be further enhanced if the mixing is done with automated equipment. For example, Group A supplies activated carboxylates A1, A2, and A3, and Group B supplies amines B1, B2, and B3. Group C loads the six substances into a robot that is controlled by Group D. Alternatively, the robot is linked directly to a database, whereby the combination is chosen at random and stored. This principle is not limited to activated carboxylate-amine, but rather is applicable to any combination of reactive precursors. Likewise, components X and Y can be designed to generate different materials in response to stimuli Z1, Z2, and Z3. Then group A provides either X1, X2, or X3, Group B provides either Y1, Y2, or Y3 and Group C provides either stimulus Z1, Z2, or Z3. The resulting material is not known to any group. An example of this would be a series of metals (e.g. Fe, Ru, Os) and chalcogenides (e.g. O, S, Se), that combine in different stoichiometries at high, medium, or low temperatures. In addition, all instrumentation and/or manufacturing tools including software and hardware used in production of the reporter can be designed to mask

the identity of the reporter (or a reporter component or pre-cursor) and any characteristic, e.g. the Raman spectrum which is produced by the reporter.

III. Encapsulant

[0048] An encapsulant can comprise one or more materials. It can be a solid, a semi-solid, a polymer, a glass, a particle or collection or particles, or any other material. It might comprise one layer, two layers, three layers, or many layers. The layers could be spatially distinct or completely interpenetrated. The encapsulant might surround the antenna and the reporter, or just the antenna, or just the reporter, or part of the antenna, or part of the reporter, or any combination thereof. The encapsulant might be in contact with the antenna or reporter, or it could be separated by a gas, a liquid, or a solid, or any mixture thereof.

[0049] The encapsulant can be introduced after the reporter/antenna junction is formed, or it can be introduced as the junction is formed, or it can be introduced before the junction is formed. For example, the encapsulant can be added to the antenna, and a reporter later introduced. Alternatively, the reporter can be incorporated into the encapsulant, and the antenna later introduced.

[0050] The encapsulant or encapsulants can be introduced via the vapor or gas phase, via the liquid phase, or in the solid state. Alternatively, the encapsulant or encapsulants can be introduced using multiple phases at once. The encapsulant or encapsulants may be introduced all at once, or in several stages.

[0051] The encapsulant can be complete as introduced, or it may require assembly, or formation, or growth on the particle. For example, silica encapsulants may be grown using one or more precursors that contain single Si atoms. Likewise, the encapsulant might be formed by scission of certain functional groups or moieties once attached to the antenna. The encapsulant may be formed via a batch process or via a continuous process.

[0052] The encapsulant may be bound covalently or non-covalently to the reporter or to the antenna, or to both, or to part of the antenna, or to part or some of the reporter, or any combinations thereof. The association of the encapsulant with an antenna/reporter may be due to steric considerations, for example the combination may be viewed by analogy as a ship in a bottle, with the antenna as the ship, the reporter as sailors on the ship, and the encapsulant as the bottle. Alternatively, the association of the encapsulant with the antenna/reporter may result solely from low solubility of the encapsulant in the medium (e.g. teflon in aqueous solution).

[0053] Addition of the encapsulant can result in increased or decreased spacing between two or more antenna components, or no change in spacing, and any combination thereof. Likewise, addition of the encapsulant can result in an increased number of reporters experiencing enhanced electric fields, or a decreased number, or no change in the number experiencing enhanced electric fields, or any combination thereof. Addition of the encapsulant can result in both changes in the spacing or two or more particles and in the positioning of one or more reporter molecules relative to the electromagnetic field.

[0054] Encapsulation can occur in one or more steps. Each step may involve different conditions, including but not limited to the phase (gas, liquid, solid), temperature, pressure, ionic strength, mixing rate, reaction time, reagent concentrations, solvents, manual or automated processes. Each step can occur separately or simultaneously.

[0055] The encapsulant or encapsulants can confer control over a variety of properties in the resulting particles, or alternatively such properties can be introduced via addition of a supplemental material (before, after, or during introduction of the encapsulant.) For example, consider porosity. The encapsulant can be structured to provide high or low porosity. Alternatively, introduction (or removal) of gas bubbles during the encapsulation step could yield similar effects upon porosity. Examples of properties of SERS-active particles that can be controlled o modified by the encapsulant or other supplemental materials include but are not limited to porosity, hydrophilicity, hydrobicity, refractive index, thermochromism, photochromism, wavelength selectivity, density, permeability, charge, state of aggregation, surface tension, surface charge, encapsulant conformality to antenna shape, toxicity, vapor pressure, solubility, opacity, chemical stability, physical stability, mechanical stability, chemical reactivity or inertness (via chemical functional groups), conductivity, elemental composition, melting temperature, glassing temperature, melting point, overall size, overall shape, zeta potential, and flammability.

[0056] In one example, a thermochromic ink may be incorporated into the encapsulant after an initial encapsulant coating is applied, but prior to an additional, thicker layer of encapsulant. In this manner, the resulting particles have both SERS activity and thermochromic properties. Using the appropriate commercially available inks, it is possible to develop a material that either turns off or turns on as a function of temperature. For example, if heating converts the thermochromic material to a color that absorbs the laser excitation photons, or the inelastically scattered photons, heating will render the SERS active particles effectively "spectroscopically silent". Likewise, if a thermochromic ink blocks laser excitation at a lower temperature, and upon heating changes to a color that is transparent to

the laser excitation or the inelastic Raman photons, heating will effectively "turn on" the SERS-active particles.

IV. Post-manufacture processes

[0057] A number of processes can be carried out on particles once synthesis is complete. These include but are not limited to exposure to heat, cold, high pressure, low pressure, different solvents than those used in synthesis, drying, RF energy, microwave energy, and ultrasound. Additionally, the particles can be subjected to any of the following processes, including but not limited to grinding, milling, sonication, centrifugation, exposure to high pH substances, exposure to low pH substances, acid treatment, treatment with base, separation by chromatography, field flow fractionation, or other means, combustion, sintering, laser irradiation at one or more wavelengths, uv or visible light exposure, evaporation, filtration, ultra-filtration, distillation, osmosis, wetting, and drying. The processes carried out on particles once synthesis is complete can occur in the gas phase, in the liquid phase, or in the solid phase. More than one process might be used after synthesis is complete, and more than one phase might be used.

[0058] Secure manufacture of the particles requires that waste particles or waste byproducts of manufacture be collected and/or destroyed. The waste by-products include waste solvents for any of the previously described steps that contain any amount of the antenna, reporter, encapsulant, particle, finished particle or combinations thereof that must be secured. For example, particles may be separated from a liquid so that only the particles are destroyed. The liquid could then be disposed of or reused.

[0059] There are a number of ways to destroy particles and other organic materials in waste or other processing solutions. Acid treatment can be used to destroy Au or other materials. CO_2 combustion or burning can be used to destroy particles. Other removal processes including but not limited to using solvents, partitioning (liquid or solid), clays or other materials may be useful.

[0060] Components of the waste can be recovered. After reclamation of the secure components water or other solvents can be purified for re-use. Waste metals or other precious materials can be recovered for re-use.

[0061] The equipment used to make, synthesize, purify, mix, process, separate or otherwise manipulate antennae, reporters, encapsulants, particles, and any combination of antennae, reporters, encapsulants and/or particles may periodically require cleaning. This can occur by disassembly of the equipment and cleaning of individual components, followed by

re-assembly, or by cleaning of the intact equipment. The cleaning may involve a variety of substances, including but not limited to detergents, acids, bases, surfactants, etchants, oxidants, reductants, free radicals, scavengers, organic solvents, aqueous solvents, air, O_2, ozone, N_2, Ar, and pressurized gases. Cleaning may involve combinations of materials, used sequentially or simultaneously.

[0062] Alternatively, one or more types of equipment or apparatus used to make, synthesize, purify, mix, process, separate or otherwise manipulate antennae, reporters, encapsulants, particles, and any combination of antennae, reporters, encapsulants and/or particles may be sterilized and re-used, especially if the article is susceptible to bacterial contamination. For example, the parts of pumps not exposed to solutions can be sterilized to remove the threat of introduction of bacteria.

[0063] Alternatively, one or more types of equipment or apparatus used to make, synthesize, purify, mix, process, separate or otherwise manipulate antennae, reporters, encapsulants, particles, and any combination of antennae, reporters, encapsulants and/or particles may be disposable. Disposability can eliminate the need for cleaning of any article use during the manufacture of SERS-active particles that might otherwise be re-used. For example, centrifugation tubes used to concentrate particles can be disposed of, provided residual material has been removed. Likewise, pipette tips used to dispense known quantities of reagents can be disposed of, provided residual material has been removed. The use of disposable elements to eliminate cleaning steps can be applied to all aspects of preparation, processing, or purification of SERS-active particles, including to synthesis of the antenna, the reporter, the encapsulant, or combinations thereof.

V. Process Monitoring and Characterization

[0064] The formation of antennas, reporters, encapsulants and SERS-active particles can be monitored in situ or ex situ by a number of means. Likewise, the resulting antennas, reporters, encapsulants and SERS-active particles can be characterized after production or processing. For example, the yield and/or purity of a synthesized reporter can be characterized by thin layer chromatography or nuclear magnetic resonance. Alternatively, the formation of an antenna such as colloidal gold can be monitored by measuring the UV-vis-near IR absorbance spectrum. In another example, the development of SERS activity when reporter and antenna are brought together in solution can be monitored in real time using time-resolved Raman spectroscopy. In another embodiment, the conformality of the encapsulant to an antenna core can be measured by SEM or TEM.

[0065] A large variety of measurement tools can be used for in situ or ex situ process monitoring or materials characterization. These include but are not limited to NMR, NQR, Mossbauer spectroscopy, small angle x-ray scattering, EXAFS, EPR, Raman spectroscopy, infrared spectroscopy, Auger, XPS, SIMS, static light scattering, dynamic light scattering, TEM, SEM, AFM, STM, neutron scattering, x-ray diffraction, mass spectrometry, x-ray crystallography, uv-vis-near IR extinction, fluorescence, luminescence, phosphorescence, microwave spectroscopy, and zeta potential measurements.

[0066] The following example is a short description of the manufacturing of SERS-active particles, having a Au-antenna, a selected reporter and a silica encapsulant with examples of in-situ process monitoring and characterization or quality control measurements. The representative manufacturing volume for particles with a Au-core diameter of 60nm is 1 liter. Several different reporters could be used for this product, as described above. An in-situ SERS-monitoring system is used for the evaluation of each reporter. The monitoring system consists of a Raman spectrometer (a Manufacturing Process Spectrometer, MPS), a syringe pump for the addition of reporter and a peristaltic pump to circulate the colloid solution between a 1L-beaker and a flow-quartz cuvette. SERS spectra are acquired with the MPS every 3 seconds during the addition of the reporter. Fig. 1 shows as an example of the aggregation curve 100 of a selected reporter. As shown on Fig. 1, plots of SERS intensity vs. time (or ml of added reporter) show 3 distinctive regions: a first linear section of the curve 102 followed by a sharp increase of the slope of the curve 104, indicating the onset of extensive aggregation, and a third section 106 where the SERS intensity decreases due to excessive aggregation. By using the described or a similar monitoring system it is possible to determine the optimal reporter concentration ensuring desired brightness and level of aggregation of the product.

[0067] This or a similar monitoring system may also be used during the first step of particle synthesis as described in detail below by stopping reporter addition when the desired SERS intensity is reached. Tag synthesis as described below consists of a number of steps and typically takes three days for completion.

EXAMPLES

[0068] The following example is provided for illustrative purposes only and is not intended to limit the scope of the invention.

Example 1: Synthesis of a selected SERS active particle

[0069] One type of SERS active particle may be synthesized as follows. A reporter, 3-aminopropyltrimethoxysilane (APTMS) is added to a solution containing Au colloid. After the addition of APTMS and with the use of the process monitoring equipment as described above, the reporter molecule is added until a desired Raman signal is obtained. The signal being monitored will typically increase to a maximum level as shown in Fig. 1.

[0070] Subsequently a thin layer of silica is grown around the Au colloid and associated reporter molecules which have adsorbed to the Au surface. Na-silicate is used to allow slow glass polymerization. After formation of the initial glass shell, a mixture containing Tetraethoxysilane (TEOS), ethanol and ammonia is added to increase glass shell thickness. If a thiolated surface is desired a mixture containing 95%TEOS to 5% Mercaptopropyltrimethoxysilane (MPTMS) may be used instead of 100% TEOS. Centrifugation is then used to remove any ethanol, free silica, and unreacted materials. Particles may then be resuspended in 18 MegaOhm water.

[0071] Quality control measurements that are used to verify good synthesis results include but are not limited to: Optical extinction measurements carried out between 180 nm and 1700 nm. Critical parameters include the wavelength of maximum extinction, full width at half maximum of peak, and optical density. Representative results of optical extinction measurements are illustrated in Fig. 2 and Fig. 3 and discussed in detail below. Raman spectra collected using 633 nm, 785 nm, and 1064 nm excitation. Representative results of Raman spectra measurements are illustrated in Fig. 4 and discussed in detail below. Transmission Electron Microscopy carried out at 10k magnification. Automated image analysis of at least 10 images may be used to provide measurements of glass shell thickness, degree of aggregation, and the relative quantity of free silica particles. A representative TEM image is included in Fig. 5 and discussed in detail below. Scanning electron microscopy carried out at 100k and 30k magnification. A representative SEM image is included in Fig. 6 and discussed in detail below. Dynamic Light Scattering (DLS) analysis used as a measure of particle size. A representative DLS plot is included in Fig. 7 and discussed in detail below.

[0072] Quality control data is summarized in Table 1 for 20 batches of thiolated SERS tags prepared as described above. Selected characterization measurements are also illustrated on Figs. 2 through 7 for a representative batch of tags.

Table 1. Characterization Data Summary of 20 batches: SERS-420, thiolated

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Batch#	Core dia (nm)	OD	λ_{max} (nm)	FWHM (nm)	SERS (785nm)	pyridine (988 cm-1)	SERS/Py	SERS/OD /Py	glass thickness (nm)	# particles reviewed	% mono mers	% total aggr.	% trimers + more	% free glass
M160.1	57.38	1.229	545	86	341	709	0.48	0.39	36.4	887	93.8	6.2	7.6	2.0
M160.2	57.38	1.209	544	88	334	709	0.47	0.39	35.2	794	94.4	5.6	14.3	1.5
M160.3	57.38	1.214	544	86	328	709	0.46	0.38	33.6	940	94.8	5.2	16.9	1.9
M160.4	57.38	1.236	545	86	392	709	0.55	0.45	37.6	796	94.4	5.6	29.8	2.0
M160.5	57.38	1.247	544	88	376	709	0.53	0.43	36.3	987	95.3	4.7	15.7	1.2
M160.6	57.38	1.284	544	88	380	709	0.54	0.42	35.8	961	94.2	5.8	17.6	1.4
M160.7	57.38	1.261	545	86	371	709	0.52	0.41	31.9	991	94.2	5.8	20.7	1.7
M164.2	60.62	1.277	546	94	280	684	0.41	0.32	36.2	582	93.5	6.5	12.8	4.3
M164.3	60.62	1.262	546	90	302	669	0.45	0.36	35.5	931	93.3	6.7	10.7	3
M164.4	60.62	1.232	547	92	298	657	0.45	0.37	35.8	542	93.7	6.3	16.3	2.3
M164.5	60.62	1.265	547	96	315	699	0.45	0.36	27.6	1095	94.5	5.5	10	2.3
M164.6	60.62	1.246	546	94	322	699	0.46	0.37	29.9	1072	94.8	5.2	16.9	2.8
M164.7	60.62	1.230	546	94	272	699	0.39	0.32	29.6	1024	94.2	5.8	22.4	2
M164.8	60.62	1.261	546	92	323	683	0.47	0.38	37	490	96.9	3.1	13.6	4.5
M164.9	60.62	1.292	546	94	314	683	0.46	0.36	38.4	399	94.8	5.2	7.1	2.4
M164.10	60.62	1.212	546	94	294	683	0.43	0.36	35	914	97	3	2.9	4.5
M164.11	60.62	1.246	546	92	305	683	0.45	0.36	34.4	487	96.8	3.1	5	4.8
M164.12	60.62	1.214	546	90	315	669	0.47	0.39	35.6	887	95.6	4.4	15.2	3.6
M164.13	60.62	1.263	546	90	285	669	0.43	0.34	34.7	687	95.8	4.2	13.9	2.8
M164.15	60.62	1.218	546	90	309	669	0.46	0.38	32.9	512	96.1	3.9	3.7	4.6

[0073] The quality control data of Table 1 more specifically includes the following:

- Column #2: the diameter of the Au-core (antenna).
- Columns #3, #4 and #5: parameters of the UV-vis spectrum; OD is the Optical Density (Absorbance); λ_{max} is the wavelength at the max absorbance and FWHM (Full Width Half Max) is the wavelength at half of the max absorbance. This data is graphically represented in Figs. 2 and 3.
- Column #6: SERS intensity of the batch at 785nm excitation. This data is graphically represented as plot 402 on Fig. 4.
- Column #7: SERS intensity of the Pyridine reference at 785nm excitation. This data is graphically represented as plot 404 on Fig. 4.
- Columns #8 and #9: calculated ratios SERS max of batch/SERS max of Pyridine and SERS max of batch/SERS max of pyridine/Optical density (OD) respectively.
- Columns #10, #12 through #15 are parameters calculated by evaluation of TEM images.
- Column #11: the number of particles (biotags) used for the evaluation.
- Columns #12, #13 and #14: percentage of monomers (single particles), % total aggregation and % aggregates (trimers and higher).
- Column #15: free glass (silica spheres without Au-core) is formed during the glass growth process and later removed during the clean steps.

VI. Use of SERS-active Particles

[0074] SERS particles can be stored at high concentrations of as much as 100% by weight after manufacture or at concentrations of as little as 0.001% by weight or any weight percentage in between. Particles can be stored in water and also in hydrocarbon based solvents, or in combinations of solvents, including but not limited to those that form one or two or more phases. The SERS particles can be dried and stored as powders. Drying can be performed by evaporation of volatile solvents for freeze drying, vacuum drying, lyophilization or heating to evaporate solvent and any other drying methods. The SERS particles can be stored in solvents that contain no other materials, or can be stored in solvents that contain other materials. For example, the particles could be stored in a solution that contains fluorescent molecules or particles, or in a solvent that contains other materials used for anti-counterfeiting or industrial security applications. Alternatively, the particles can be stored in an ink or varnish, or in a security ink or security varnish, and such materials can contain one or more additional industrial security or anti-counterfeiting technologies.

[0075] SERS particles can be concentrated by centrifugation, gravity, magnetic concentration steps, field flow fractionation, filtration, any form of chromatography, electrophoresis, osmosis, osmosis, reverse osmosis, .precipitation, or by any means known to those skilled in the art of concentrating nanoparticles or microparticles.

[0076] SERS particles can be stored in light or in complete darkness, or in any level of light in between. The SERS particles can be stored with a controlled climate of temperature, pressure or humidity, or in a variable climate of temperature, pressure, or humidity.

[0077] SERS particles can be mixed with agitation, shaking, sound waves, microwaves, RF energy, magnetic mixing, thermal conduction or thermal convection.

[0078] SERS particles can be made to be buoyant or to sink in a selected liquid. The SERS particles can then be re-suspended. SERS particles can be made hydrophobic by coating them with lipids, polymers or other materials. They can be encapsulated with emulsifiers. They can be attached to a material covalently or via charge or other forces. SERS particles can be made with linking molecules attached to the surface which are then used to add a second coating.

[0079] In one embodiment, the SERS particles may be introduced into inks and overcoat varnishes or other print media by concentrating them into an appropriate vehicle. The vehicle may be water based or hydrocarbon based or could be a mixture of solvents or

liquids. Typical vehicles are linseed oil and derivatives thereof, soy oil and derivatives thereof, mineral oils and derivatives thereof, phenolics and derivatives thereof, vegetable oils and derivatives thereof, glycerophthalic compounds and derivatives thereof and high molecular weight additives and derivatives thereof.

[0080] The vehicle is only one of many components of an ink, varnish or other print medium. There are also pigments, fillers, additives, binders, drying agents etc. There also can be one or more other overt or covert security materials within the vehicle or within the ink or varnish. In other embodiments, the SERS particles are mixed into any and all of these materials or the SERS particles can be the materials themselves or be bound to the materials. In this manner the ink itself is made from the SERS particles.

[0081] In one embodiment, the SERS particles are added at any step before, during or after the ink is made. The SERS particles can be added as a solid, as a liquid, or incorporated into a solid or liquid. The SERS particles can be rolled in or mixed in with various mixing tools including but not limited to helical mixers. The mixing can be in line, continuous or batch. The ink itself can be built out of the SERS particles. The SERS particles can be part of the pigment, filler binder, vehicle or any other component in the ink or printing materials.

[0082] In one embodiment, the SERS particles are added to any printing or stamping medium at concentrations of less than 50% weight/weight (w/w), or less than 5.0% w/w or less than 0.5% w/w, or at less than 0.1% w/w in the final medium. In other embodiments, the particles are present at lower concentrations, including but not limited to 0.01% w /w, or 0.001% w/w, or even 0.0001% w/w. The SERS particles may be added to the vehicle at 10% w/w, accordingly the particle concentration when the vehicle is added to the final medium is less than 10% w/w.

[0083] In one embodiment, the SERS particle tagged printing media are printed onto the secure document using all printing methods including but not limited to offset, flexo, gravure, intaglio, letterpress, ink jet, and silk screen. Multiple printing methods may be used for the SERS particles in or on the same document or object. The inks used can be one or more colors, including but not limited to black, white, off-white, red, blue, green, yellow, orange, pink, purple, magenta, indigo, violet, gray, brown, beige, or burgundy.

[0084] In one embodiment the print medium, ink or varnish, is transparent in the operating wavelength range of the SERS particles, from 633 nm to 2000 nm. In other embodiments, the transparency range can be from 150 nm to 5000 nm. In yet other embodiments, the print medium is transparent at wavelengths longer than 1064 nm.

[0085] In other embodiments, the SERS particles may be made into a dry powder before addition into an ink or a polymer film.

[0086] In other embodiments, the SERS particles may be sprayed over a substrate such as a metal film or other material. The substrate could comprise another security feature, such as a metallic foil, or thread, or optically variable device. In yet additional embodiments, the substrate can provide additional enhancement for SERS by coupling optically or electronically to the SERS particle. For example, the SERS particles can be deposited on a waveguide to increase the efficiency of scattering, or onto a SERS-active metal to increase enhancement factors. The SERS particles can be sprayed as a particle aerosol or in solvent. The solvent may be water or a hydrocarbon based solvent.

[0087] In other embodiments, the SERS particles may be embedded into polymer films. Polymer films embedded or coated with SERS particles can be part of a multilayer structure that includes a metal foil layer and other printed of stamped layers.

[0088] SERS particles can be used with or embedded inside any visual feature created with a crystalline array, diffraction grating, photonics band gap grating, optical waveguide, plasmonic waveguide or similar visual feature.

[0089] SERS particles can be used with a variety of other types of tagging materials. Alternatively, other tagging materials or light scattering processes can be combined within each SERS particle. The types of materials and detection methods include but are not limited to: Radioactivity, fluorescence, phosphorescence, magnetism, luminescence, up and down conversion, x-ray fluorescence, x-ray scattering, and neutron scattering. The materials can be RF responsive, microwave responsive, or thermally responsive.

[0090] The printed SERS particles can be combined with other features on a document. The SERS particles can be manipulated during printing, for example by diffusion, magnetism (i.e. aligning the SERS particles with magnetic field direction to control orientation & location), static charging or similar processes. Orienting the SERS particles can exploit polarized excitation to maximize SERS anisotropy.

[0091] SERS particles can be added at other steps in the production of the document. They can be sprayed on after production. The document can be dip coated by the taggants.

[0092] SERS particles can be applied into the substrate paper by using all of the same methods plus printing and spraying.

[0093] In one embodiment, during printing the media with the SERS particles are removed and cleaned from the machine. The printed SERS particles can are then disposed of

in a secure manner. Reuse and disposal methods are similar to those described for tag production. The SERS particles can be extracted from the ink or varnish.

[0094] In one embodiment, the addition of the SERS particle tagged material in the final item is inspected with process monitoring equipment. Multiple SERS particles can be used for individual items for serialization and each item can be detected while being made and verified.

[0095] All of the aforementioned tag addition techniques can be a continuous, i.e. web method or discrete i.e. batch or sheet method process.

[0096] SERS particles can have multiple functions. For example, the particles may have an antenna, reporter and encapsulant for SERS, and attached to the encapsulant layer is an additional layer with a specific property such as a fluorescent signature between 400 and 600 nm. Alternatively, this additional layer could confer to the particles magnetic properties, or a particular color, or a particular mass spectral signature.

[0097] Also disclosed is a method of tagging and identifying an object. The tagging method comprises providing a SES active particle as described above and associating the particle with a material or object of interest. The method of tagging may further include obtaining a SES spectrum and other identification information from the particle in association with the material of interest and thereby identifying the marked object or substance. supplemental identification information can be associated with the tag or the object, as described herein.

[0098] The small, robust, non-toxic, and easily-attachable nature of the particles disclosed herein allows their use for tagging virtually any desired object. The tagged object can be made of solid, liquid, or gas phase material or any combination of phases. The material can be a discrete solid object, such as a container, pill, or piece of jewelry, or a continuous or granular material, such as paint, ink, fuel, or extended piece of, e.g., textile, paper, or plastic, in which case the particles are typically distributed throughout the material.

[0099] Examples of specific materials or objects that can be tagged with the particles disclosed herein, or into which the particles can be incorporated include, but are not limited to:

- Packaging, including adhesives, paper, plastics, labels, and seals
- Agrochemicals, seeds, and crops
- Artwork
- Computer chips
- Cosmetics and perfumes

- Compact disks (CDs), digital video disks (DVDs), and videotapes
- Documents, money, and other paper products (e.g., labels, passports, stock certificates)
- Inks, paints, varnishes, lacquers, overcoats, topcoats, and dyes
- Electronic devices
- Explosives and weapons
- Food and beverages, tobacco
- Textiles, clothing, footwear, designer products, and apparel labels
- Polymers
- Insects, birds, reptiles, and mammals
- Powders
- Luxury goods
- Other anti-counterfeiting substances or materials, such as holograms, optically variable devices, color-shifting inks, threads, and optically-active particles
- Hazardous waste
- Movie props and memorabilia, sports memorabilia and apparel
- Manufacturing parts, automobile parts, aircraft parts, truck parts
- Petroleum, fuel, lubricants, gasoline, crude oil, diesel fuel, fuel additive packages, crude oil
- Pharmaceuticals, prescription drugs, over-the-counter medicines, and vaccines

[00100] The particles disclosed herein can be associated with the material in any way that maintains their association, at least until the particles are read. Depending upon the material to be tagged, the particles can be incorporated during production or associated with a finished product. Because they are so small, the particles are unlikely to have a detrimental effect on either the manufacturing process or the finished product. The particles can be associated with or attached to the material via any chemical or physical means that does not inherently interfere with particle functionality. For example, particles can be mixed with and distributed throughout a liquid-based substance such as paint, oil, or ink and then applied to a surface. They can be wound within fibers of a textile, paper, or other fibrous or woven product, or trapped between layers of a multi-layer label. The particles can be incorporated during production of a polymeric or slurried material and bound during polymerization or drying of the material. Additionally, the surfaces of the particles can be chemically derivatized with functional groups of any desired characteristic, for covalent or non-covalent attachment to the material. When the particles are applied to a finished product, they can be applied manually by, e.g., a pipette, or automatically by a pipette, spray nozzle, or the like.

Particles can be applied in solution in a suitable solvent (e.g., ethanol), which then evaporates.

[00101] The particles disclosed herein have a number of inherent properties that are advantageous for tagging, tracking and identifying applications. They offer a very large number of possible codes. For example, if a panel of particles is constructed with 20 distinguishable Raman spectra, and an object is labeled with two particles, there are 20*19/2 = 190 different codes. If the number of particles per object is increased to 5, there are 15,504 possible codes. Ten particles per object yields 1.1 x 10^6 different codes. A more sophisticated monochromator increases the number of distinguishable spectra to, e.g., 50, greatly increasing the number of possible codes. Alternatively, different amounts of particles can be used to generate an exponentially-increased number of possible codes. For example, with just four different particle types (N=4), present at three different intensity levels (e.g. High, Medium, Low) (L=3), chosen three at a time (P =3), can generate 58 different codes. With N=10, P=3, L =1, the number of codes is 175. With N=50, P=5, L=4, over a billion codes are possible.

[00102] In some embodiments, the particles may be applied to a document or other item in an ink or other marking material. Inks include, but are not limited to flexographic ink, lithographic ink, silkscreen ink, gravure ink, bleeding ink, coin reactive ink, erasable ink, pen reactive ink, heat reactive ink, visible infrared ink, optically variable ink, and penetrating ink. photochromic ink, solvent/chemical reactive ink, thermochromic ink, and water fugitive ink. A particle may also be applied in electrophotographic and ink jet printing machines and other systems including offset lithography, letterpress, gravure, heliogravure, xerography, photography, silk-screening systems, systems for imagewise deposition of discrete quantities of a marking material on a substrate surface, such as paint, chemical, and film deposition systems; and systems for integration of colorant materials in an exposed surface of a fibrous substrate, such as textile printing systems.

[00103] It should be noted that additional security features may be included or utilized along with the disclosed tags for a particular item or documents. One such additional security feature may be a separate security ink, such as bleeding ink, coin reactive ink, erasable ink, pen reactive ink, heat reactive ink, visible infrared ink, optically variable ink, penetrating ink. photochromic ink, solvent/chemical reactive ink, thermochromic ink or water fugitive ink. The tags may be applied as part of the ink, or in a separate step. Other non-ink based security features which may be utilized in addition to the disclosed tags for document or item marking include the use of an ascending serial number (horizontal and/or vertical format), bar code

and numerals, colored fibers, embedded security thread, face-back optical registration design (transparent register), foil imprints, holograms, latent impressions, micro printing, optical variable devices (OVD), planchettes, raised marks, segmented security threads, and watermarks.

[00104] The disclosed particles may be applied by coating an image, including but not limited to a hologram image, made with toner or ink compositions known in the art, as with an overcoat varnish, or a starch overcoat.

[00105] In the case of documents with other security features, such as those including polymer threads or metal foils, the particles may be applied to additional feature, such as the thread or the foil. Single tags may be considered to represent a bit of data that may be changeable according to the methods described herein. Thus groups of distinguishable particles disclosed herein may be applied to constitute an "alphabet" and combined as words or encoded information, which may be selectively variable, or variable over time.

[00106] The particles disclosed herein can be identified using a conventional spectrometer, for example a Raman spectrometer. In fact, one benefit of using SERS particles is the versatility of excitation sources and detection instrumentation that can be employed for Raman spectroscopy. Visible or near-IR lasers of varying sizes and configurations can be used to generate Raman spectra. Portable, handheld, and briefcase-sized instruments are commonplace. At the same time, more sophisticated monochromators with greater spectral resolving power allow an increase in the number of unique taggants that can be employed within a given spectral region. For example, the capability to distinguish between two Raman peaks whose maxima differ by only 3 cm^{-1} is routine.

[00107] Typically, if a suitable waveguide (e.g., optical fiber) is provided for transmitting light to and from the object, the excitation source and detector can be physically remote from the object being verified. This allows the disclosed particles to be used in locations in which it is difficult to place conventional light sources or detectors. The nature of Raman scattering and laser-based monochromatic excitation is such that it is not necessary to place the excitation source in close proximity to the Raman-active species. Moreover, the particles disclosed herein are amenable for use with all known forms of Raman spectrometers, including some more recent implementations, including spatially offset Raman, Raman absorption spectrometers, instruments to measure Raman optical activity, and so forth.

[00108] Another characteristic of the disclosed particles is that the measurement of their spectra does not need to be strictly confined to "line of sight" detection, as with, e.g.,

fluorescent tags. Thus their spectrum can be acquired without removing the particles from the tagged object, provided that the material is partially transparent to both the excitation wavelength and the Raman photon. For example, water has negligible Raman activity and does not absorb visible radiation, allowing the particles disclosed herein in water to be detected. The particles can also be detected when embedded in, e.g., clear plastic, paper, or certain inks.

[00109] The disclosed particles also allow for quantitative verification, because the signal intensity is an approximately linear function of the number of analyte molecules. For standardized particles (uniform analyte distribution), the measured signal intensity reflects the number or density of particles. If the particles are added at a known concentration, the measured signal intensity can be used to detect undesired dilution of liquid or granular materials.

[00110]

VII. Detecting SERS Particles:

[00111] In one embodiment, SERS particles in tagged items are detected with an instrument capable of measuring inelastically scattered light and determining the identity of the SERS particles and by extension the tagged item. In one embodiment, the instrument requires an excitation source that illuminates the tagged item. The inelastically scattered light from the SERS particles is collected. The spectrum of scattered light is analyzed and the identity of the particles, and hence the item, is determined. The reader may be a Raman Spectrometer. The instrument to collect and analyze the Raman spectrum (the reader) can be as small as 1 cubic millimeter and as large as 1000 cubic meters.

[00112] The light source used to excite the particles may be a monochromatic light from a laser operating in the solid state, in gas or in liquid. The laser can be continuous or pulsed. A continuous laser can have powers from 01. femtowatt up to 1 megawatt. A pulsed laser can have similar total power with pulses as short as less than 1 femtosecond, and with a pulse repetition rate up to 1 terahertz. Alternatively, multiple light sources can be used. In one embodiement, two separate excitation wavelengths (e.g. 720 nm and 785 nm) are used to compensate for detectors that have low photon-to-electron conversion efficiencies in certain spectral regions, using one excitation wavelength to cover a certain portion of the Raman shift window (e.g. 100 – 1800 cm^{-1}), and the second to cover another (e.g. 1801-3600 cm^{-1}).

[00113] In addition to lasers, the light can come from an electroluminescent material such as a light emitting diode. Alternatively, the excitation light can come from an

incandescent or fluorescent light source. In all embodiments the excitation wavelength range can be from 100 nm to 100 microns. The excitation light can be spectrally filtered with discrete filters or spatially dispersing elements.

[00114] In one embodiment, the monochromatic light spectral width is less than 0.5 nm. In other embodiments, the spectral width is from 0.01 nm bandwidth to 100 nm bandwidth. The excitation and collected light may be steered to and from the item under interrogation with lenses, mirrors, light pipes, gratings, waveguides, optical fiber or any other component. All optical and mechanical elements can, but need not be, integrated into a single platform.

[00115] In one embodiment the excitation source and collection system are connected to the sample delivery optics with light pipes or optical fibers. In other embodiments, discrete optical elements connect the excitation source and detection element. The discrete optics include lenses, mirrors or other waveguides. In other embodiments the excitation source, the collection spectrometer or all items are made using micro-manufacturing techniques such as LIGA, molding, etching, MEMS, NEMS, lithography, photolithography, or other monolithic methods. The illuminated spot from the excitation source may be larger than 100 microns in diameter. In other embodiments, the illuminated spot may be as small as 100 square nanometers and as large as 1 square meter.

[00116] In one embodiment the collected light is analyzed by a spectrometer. The spectrometer uses a grating to disperse the collected light onto an area array detector, preferably a Charge Coupled Device (CCD). The CCD divides the spectrum into bins, with each bin corresponding to a given wavelength range. The number of bins used can range from 1 bin to many thousands of bins. In one embodiment, the number of bins is more than 20.

[00117] The optics of the spectrometer typically has a specific spectral resolution. For example, the resolution may be less than 10 nm or between 1 nm to 4 nm. In other embodiments, the resolution is from 0.01 nm to 5000 nm. The selected resolution can be 0.01 cm^{-1} to 40000 cm^{-1} expressed as wave numbers.

[00118] In one embodiment, the method of optically separating light into bins uses any form of light dispersion with a prism, grating or any spatially dispersing element. In other embodiments, a digital micro mirror array is used to spatially disperse light. Other tunable spectral filters are used including acousto-optic tunable filters, electro-optics tunable filters, liquid crystal tunable filters. Any form of scanning spectral analysis can be used as well such as Fourier Transform correlation spectroscopy. In another embodiment, a single detection

element or an array of detection elements may is used. The spectrum is analyzed with discrete optical filters or with the other aforementioned spectral filtering methods

[00119] In one embodiment, the detector element is a CCD or photodiode array made from silicon, InGAs, or any other semiconductor. Recently, detectors made from organic materials (e.g. conducting polymers) and from carbon-based composites have been described. In other embodiments, the detection element is any element that converts electromagnetic energy, i.e. photons into electrons or other electrical energy or thermal energy or sound energy.

[00120] The converted electrical energy is analyzed by an electrical circuit. The circuit will typically, if required convert the analog signal from the detector to a digital signal that is stored in or analyzed by a computer. The digital signal can be analyzed to determine the presence of the tag. The digital signal can be a discrete signal level or a stream of signal levels corresponding to a spectrum. In other embodiments, the circuit can use analog logic elements to determine the signal level of the tag and whether the item is tagged or not.

[00121] In one embodiment, the acquired spectrum is analyzed by a computer to determine the presence of the SERS particles after accounting for the presence of other materials contributing to the spectrum, i.e other inks, materials soiling etc. For example, the SERS particles with a commercially available Raman Spectrometer, such as the Delta Nu Reporter. The Raman spectrometer may be controlled by a small computer in a phone or other personal data assistant. The small computer may communicate with the Raman Spectrometer over a wireless connection, either blue tooth or wi-fi or other wireless protocol. In this embodiment, the small computer may receive the acquired spectrum from the Raman Spectrometer, analyzes the spectrum and identifies the item.

[00122] In another embodiment the reader system is part of another machine. The reader uses a signal from the machine to start detection of the tag and perform classification all in real time. The machine contains a central processor that identifies the tagged item and makes a decision on the item whether it is real or not and or whether the tag is correct. The machine can be one used in the processing, issuing, sorting, counting, screening, tracking, or authentication of banknotes or currency, or for any other industrial security application, and where the tagged items could be pills, bullets, items of clothing, machine parts, software, food, beverages, or any other item to which SERS particles are applied.

[00123] In other embodiments, the machine is a currency or stamp or document printing press or inkjet printer or digital printer or any other type of printing instrumentation

where the reader is used for process monitoring. In other embodiments, the machine is part of a final packaging or labeling line where the taggants are checked as a final step.

[00124] In addition to Raman spectral analysis, the instrumentation or reader can perform other functions. For example, the instrument can measure both elastic and inelastic light scattering. Alternatively, the instrument can acquire an optical image of an item as well as a spectral signature. Likewise, the instrument can measure a fluorescence spectrum in one spectral window and a Raman spectrum in another spectral window.

[00125] The spectrum can be analyzed for spectral peaks, widths, heights, and positions, numbers of peaks, ratios of peaks, or combinations thereof. The spectrum can be analyzed by any number of mathematical methods, including but not limited to wavelet analysis, principal component analysis, linear and non-linear regression, or combinations thereof. In addition Fourier transform, Laplace transforms, Hildebrand transforms, Hadamard transforms or any other mathematical method, i.e. first to higher order derivatives, first or higher order integrals or any other analysis, can be used to manipulate the spectral information. All of the above methods can be used to remove any interfering or extraneous or unwanted signals, including but not limited to (a) standard interferences, including but not limited to daylight, impurities, paper, ink, thread, fiber, metal, liquids, solids, solvents, moisture, (b) use-related signals, including that from dirt, stains (e.g. coffee, beer, skin fluids), dust, charcoal, trace drugs (e.g. cocaine), and (c) interfering optical signals, including but not limited to fluorescence, luminescence, absorbance, scattering, phosphorescence, and chemiluminescence.

[00126] In one embodiment SERS particles are used on their own or in combinations to make codes. Tag and their combinations are organized in a database which can be correlated to products, lot numbers or other attributes. Libraries of know tag spectra can be used to find the wanted tag spectra. Libraries can include all other compounds, spoofs or any other anticipated material. Backgrounds and other components can be separated using the same methods. Backgrounds and other contaminants can be modeled synthetically by using a polynomial or other mathematical function, rolling circle subtraction and spectral filtering

[00127] The database information can be stored on the detection device or stored on a remote computer. The remote computer could be part of a cellular phone or other mobile device that is linked to a single or multiple instruments. The remote computer could be a personal computer, laptop, or central computing cloud that communicates with a range of instruments, from 1 to 2 million, over the internet connection or other communication protocol. The instruments and computers can be linked through a wireless network

[00128] Multiple attributes of the SERS particles can be used to determine the identity of a marked item. These attributes include the amount of material and the quality of the spectrum, the amount of the material relative to another material, the spectra relative to other spectra.

[00129] The classification of a code or combination of SERS particles can be performed using statistical methods, such as Bayesian methods. These methods can be used to assign probabilities that the sample contains the code. In other methods a threshold is set for an attribute.

[00130] Various embodiments of the disclosure could also include permutations of the various elements recited in the claims as if each dependent claim was a multiple dependent claim incorporating the limitations of each of the preceding dependent claims as well as the independent claims. Such permutations are expressly within the scope of this disclosure.

[00131] While the embodiments disclosed herein have been particularly shown and described with reference to a number of examples, it would be understood by those skilled in the art that changes in the form and details may be made to the various embodiments disclosed herein without departing from the spirit and scope of the disclosure and that the various embodiments disclosed herein are not intended to act as limitations on the scope of the claims.

[00132] All references sited herein are incorporated in their entirety by reference for all matters disclosed therein.

CLAIMS

What is claimed is:

1. A particle comprising:
   a surface-enhanced spectroscopy (SES)-active antenna;
   a SES-active reporter molecule associated with said SES-enhancing antenna;
   a security feature in addition to SES-activity; and
   an encapsulant surrounding the SES-active reporter and antenna combination.

2. The particle of claim 1 wherein the security feature comprises at least one of a fluorescent signature, a magnetic property, a particle color, a radio frequency signature, a luminescent property, a neutron scattering signature, a microwave signature or a mass spectral signature.

3. The particle of claim 1 wherein the security feature comprises SERS activity at multiple excitation frequencies.

4. The particle of claim 1 wherein the security feature comprises a code based upon the spectrum obtained from a combination of two or more SERS-active materials.

5. The particle of claim 1 wherein the security feature comprises thermochromic ink.

6. The particle of claim 1 wherein the security feature is associated with the encapsulant.

7. The particle of claim 6 wherein the security feature comprises thermochromic ink.

8. The particle of claim 1 wherein the security feature is detectable by detecting at least one of radioactivity, fluorescence, phosphorescence, magnetism, luminescence, up and down conversion, x-ray fluorescence, x-ray scattering, neutron scattering, radio frequency response, microwave response, or thermal response.

9. The particle of claim 1 wherein the reporter comprises a mixture of a SES-active species and a SES-inactive species.

10. The particle of claim 1 wherein the reporter comprises a mixture of a strong Raman scattering species and a weak Raman scattering species.

11. The particle of claim 1 wherein the reporter comprises an unstable isotope which will decay over a period of time.

12. A method of identifying an object comprising:
obtaining a SES spectrum from a SES-active particle associated with the object; and
obtaining identifying information from a security feature associated with the SES-active particle.

13. The method of identifying an object of claim 12 wherein the security feature comprises at least one of a fluorescent signature, a magnetic property, a particle color, a radio frequency signature, a luminescent property, a neutron scattering signature, a microwave signature or a mass spectral signature.

14. The method of identifying an object of claim 12 wherein the identifying information is obtained from the security feature by detecting at least one of radioactivity, fluorescence, phosphorescence, magnetism, luminescence, up and down conversion, x-ray fluorescence, x-ray scattering, neutron scattering, radio frequency response, microwave response, or thermal response.

15. The method of identifying an object of claim 12 further comprising associating the particle with an enhancing substrate.

16. The method of identifying an object of claim 12 further comprising associating the particle with a waveguide.

17. The method of identifying an object of claim 12 further comprising obtaining identifying information from a second security feature associated with the object.

18. The method of identifying an object of claim 12 further comprising obtaining the SES spectrum and obtaining the identifying information from the security feature with a single dual-purpose reader.

19. A method of fabricating a SES-active particle comprising:

providing an SES-enhancing antenna; and

associating a SES-active reporter with the SES-enhancing antenna wherein said association step does not occur in a solution.

20. The method of fabricating a SES-active particle of claim 19 further comprising:

encapsulating the SES-active reporter and SES-enhancing antenna combination with an encapsulant wherein said encapsulation step does not occur in a solution.

21. The method of fabricating a SES-active particle of claim 20 wherein at least one of the steps of associating a SES-active reporter with the SES-enhancing antenna or encapsulating the SES-active reporter and SES-enhancing antenna combination with an encapsulant is caused to occur by at least one of laser ablation, gas phase growth, flame pyrolysis, spray pyrolysis, grinding, milling, electro deposition, galvanic replacement, evaporation, nano-imprinting, nano-staining, lithography, nanosphere lithography, atomic layer deposition, explosion, combustion, melting or annealing.

22. A method of fabricating a SES-active particle comprising:

providing an SES-enhancing antenna;

associating a SES-active reporter with the SES-enhancing antenna; and

monitoring a SES signal obtained from the antenna and SES reporter combination as the reporter is associated with the antenna.

23. The method of fabricating a SES-active particle of claim 22 further comprising:

encapsulating the SES-active reporter and SES-enhancing antenna combination with an encapsulant; and

monitoring a quality of the SES particle synthesis.

24. The method of claim 23 wherein the step of monitoring a quality of the SES-active particle comprises at least one of monitoring optical extinction, monitoring Raman spectra, analyzing a TEM image, analyzing SEM image or performing a dynamic light scattering analysis.

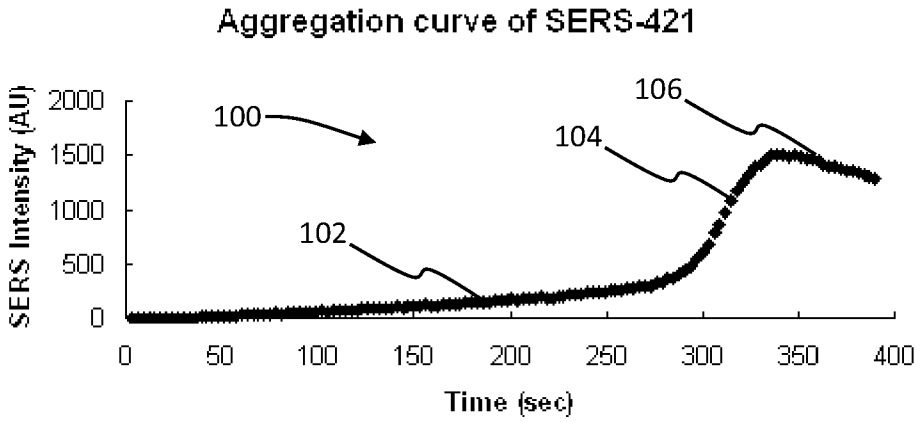

Aggregation curve of SERS-421
SERS Intensity (AU)
2000
1500
1000
500
0
100
102
104
106
0
50
100
150
200
250
300
350
400
Time (sec)

Fig 1

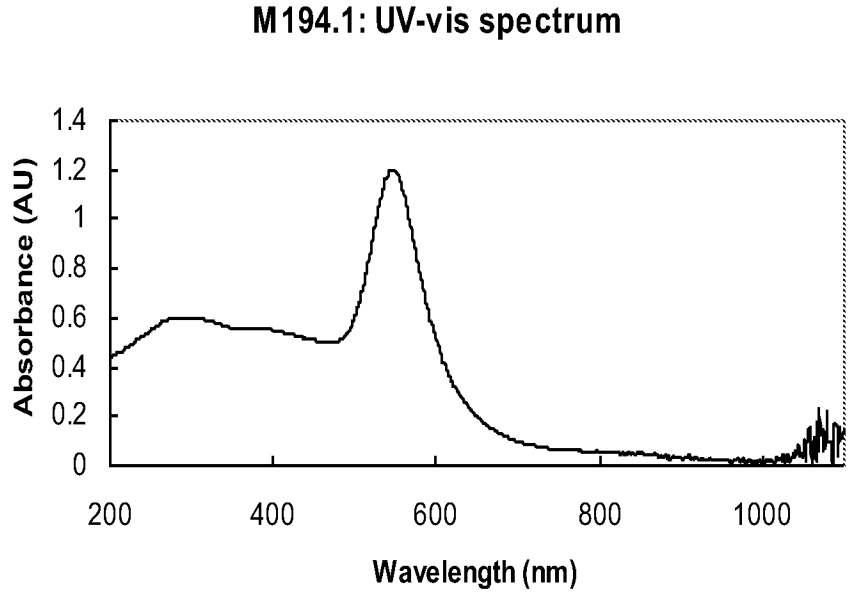

M194.1: UV-vis spectrum
Absorbance (AU)
1.4
1.2
1
0.8
0.6
0.4
0.2
0
200
400
600
800
1000
Wavelength (nm)

Fig 2

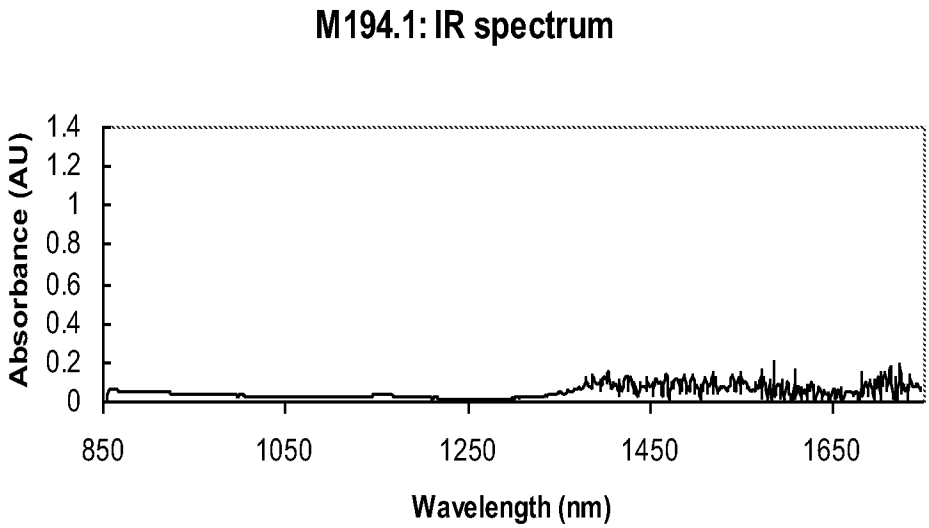

M194.1: IR spectrum
Absorbance (AU)
1.4
1.2
1
0.8
0.6
0.4
0.2
0
850
1050
1250
1450
1650
Wavelength (nm)

Fig 3

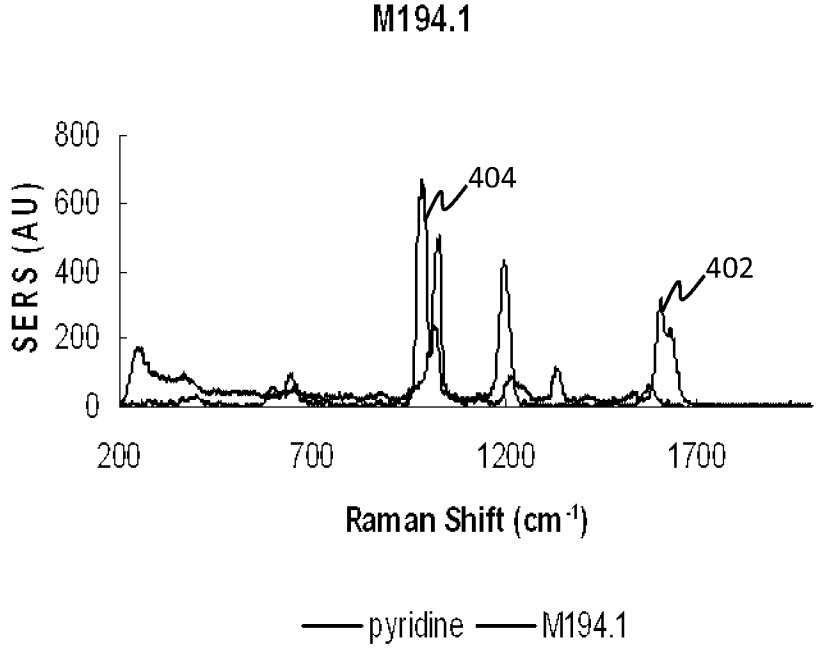

M194.1
SERS (AU)
800
600
400
200
0
404
402
200
700
1200
1700
Raman Shift (cm-1)
pyridine
M194.1

Fig 4

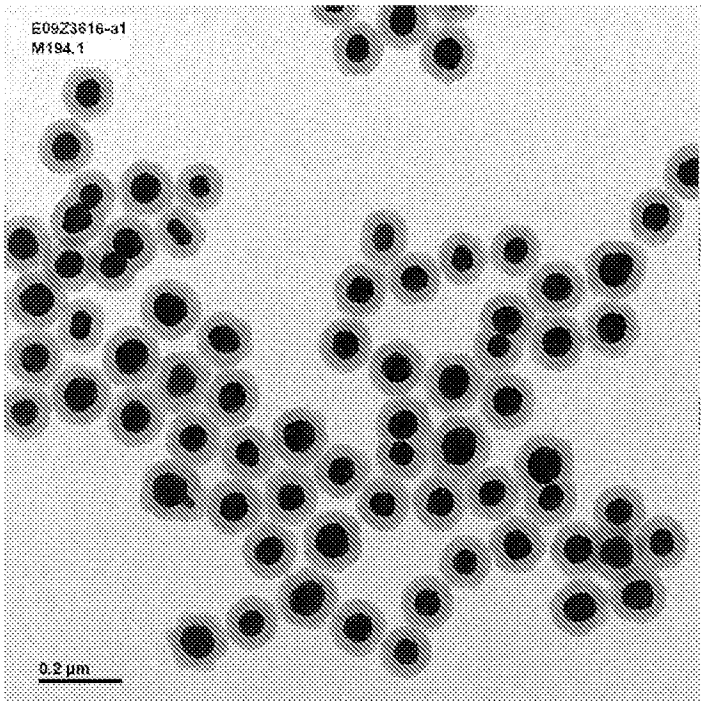


Fig 5

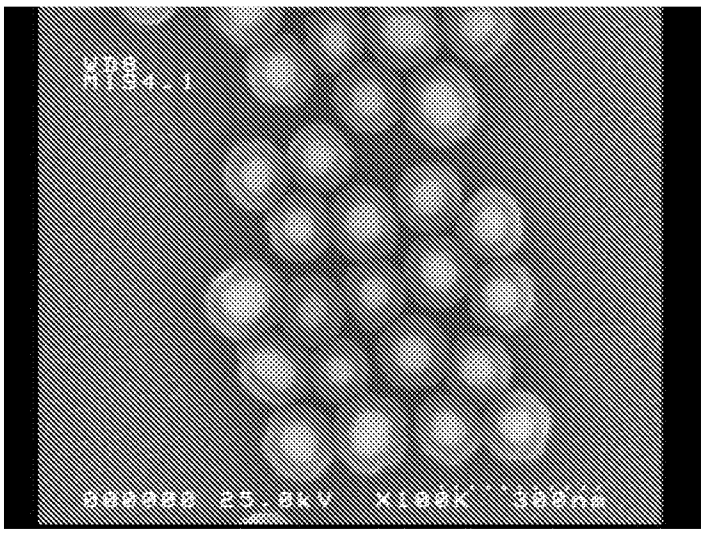


Fig 6

			Diam. (nm)	% Intensity	Width (nm)
Z-Average (d.nm):	155	**Peak 1:**	159	100.0	31.7
PdI:	0.059	**Peak 2:**	0.00	0.0	0.00
Intercept:	0.934	**Peak 3:**	0.00	0.0	0.00

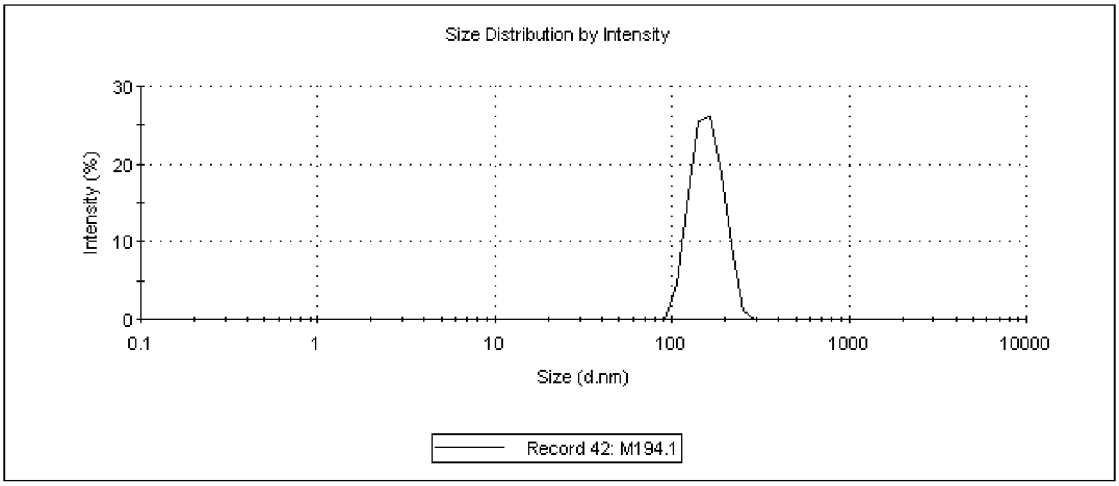


Fig 7

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2010/036728

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - G01N 33/00 (2010.01)
USPC - 252/408
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC(8) - G01N 33/00, 33/549; G01J 3/44; G06K 9/74 (2010.01)
USPC - 252/408; 356/71, 301; 435/6

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
MicroPatent, Freepatentsonline, Google, Google Patents, Science Direct

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 2006/0038979 A1 (NATAN et al) 23 February 2006 (23.02.2006) see entire document	12-15, 17, 18 --- 5-7, 16
X --- Y	US 2009/0121193 A1 (NATAN) 14 May 2009 (14.05.2009) see entire document	22-24 --- 1-11, 19-21
Y	US 2007/0247620 A1 (KOO) 25 October 2007 (25.10.2007) see entire document	1-11, 16, 19-21
A	US 6,506,342 B1 (FRANKEL) 14 January 2003 (14.01.2003) see entire document	1-24

☐ Further documents are listed in the continuation of Box C. ☐

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
15 July 2010	26 JUL 2010
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Blaine R. Copenheaver PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

Form PCT/ISA/210 (second sheet) (July 2009)