ELECTRIDE MEDIATED SURFACE ENHANCED RAMAN SCATTERING (SERS)

Applicant: United States of America as Represented by the Administrator of NASA, Washington, DC (US)

Inventor: Mark S. Anderson, La Crescenta, CA (US)

Assignee: The United States of America as Represented by the Administrator of the National Aeronautics and Space Administration, Washington, DC (US)

Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 171 days.

Appl. No.: 14/101,547
Filed: Dec. 10, 2013

Int. Cl.
GOIJ 3/44 (2006.01)
GOIN 21/65 (2006.01)
GOIN 21/01 (2006.01)
H01L 51/50 (2006.01)

U.S. Cl.
CPC ................. GOIN 21/658 (2013.01); GOIJ 3/44 (2013.01); GOIN 21/01 (2013.01); H01L 51/5012 (2013.01)

Field of Classification Search
USPC .......... 356/301; 435/6; 29, 39; 287.1, 287.2; 435/287.7, 283.1, 306.1; 252/519.1, 519.4, 252/62.2; 313/309, 486, 496

See application file for complete search history.

References Cited
U.S. PATENT DOCUMENTS
5,675,972 A * 10/1997 Edelson ................ F25B 21/00 313/310

OTHER PUBLICATIONS

ABSTRACT
An electride may provide surface enhanced Raman scattering (SERS). The electride, a compound where the electrons serve as anions, may be a ceramic electride, such as a conductive ceramic derived from mayenite, or an organic electride, for example. The textured electride surface or electride particles may strongly enhance the Raman scattering of organic or other Raman active analytes. This may also provide a sensitive method for monitoring the chemistry and electronic environment at the electride surface. The results are evidence of a new class of polariton (i.e., a surface electride-polariton resonance mechanism) that is analogous to the surface plasmon-polariton resonance that mediates conventional SERS.

19 Claims, 10 Drawing Sheets
References Cited

U.S. PATENT DOCUMENTS


OTHER PUBLICATIONS


* cited by examiner
FIG. 3

Absorbance

Nanometers

Electrode

Magnetite

300
FIG. 4

START

Synthesize Ceramic Electride Substrate

Chemically Reduce Mayenite Precursor

Store Ceramic Electride Substrate

Cleave Beads

Apply Analyte Coating

Perform SERS

END
1
ELECTRIDE MEDIATED SURFACE ENHANCED RAMAN SCATTERING (SERS)

ORIGIN OF THE INVENTION

Embodiments of the present invention described herein were made in the performance of work under NASA contract NAS7-03001 and are subject to the provisions of Public Law #96-517 (35 U.S.C. §202) in which the Contractor has elected not to retain title.

FIELD

The present invention generally pertains to surface enhanced Raman scattering (SERS), and more specifically, to electride mediated SERS.

BACKGROUND

The enhanced optical fields near the surface of illuminated nanostructures form the basis of sensitive analytical methods that include SERS, tip-enhanced Raman spectroscopy (TERS), and surface enhanced infrared absorption. These methods exploit a surface plasmon resonance condition of special metallic nanostructures.

Early SERS efforts were based on rough silver electrodes. This was extended to gold and other metal nanostructures that were engineered to optimize the surface plasmonic interactions. In addition to surface plasmon resonance, there are other polariton resonance conditions that yield enhanced electric fields near the surface of illuminated nanostructures. Surface phonon resonance also provides enhanced optical fields near the surface of illuminated dielectric particles and is used for surface enhanced infrared absorption spectroscopy. This is a part of a larger general effort to couple light into small device structures for photonic applications and for sensitive chemical analysis.

Conventional SERS applications use metal nanostructures. However, SERS applications that use electrides rather than metals may be beneficial.

SUMMARY

Certain embodiments of the present invention may be implemented and provide solutions to the problems and needs in the art that have not yet been fully solved by conventional SERS approaches. For instance, some embodiments texture the surface of an electride, such as a ceramic electride or an organic electride, to facilitate enhanced SERS.

In one embodiment of the present invention, an apparatus includes an electride substrate comprising a textured surface. The apparatus also includes an analyte coated over at least part of the textured surface of the electride substrate.

In another embodiment of the present invention, an apparatus includes an electride substrate comprising [CA24AJ28064J+4(4e-)]. The ceramic electride substrate has a roughened surface including cleaved beads. The apparatus also includes an analyte including trans-1,2-bis(4-pyridyl)ethylene (BPE). The analyte is coated over at least part of the roughened surface of the ceramic electride substrate.

In yet another embodiment of the present invention, a method includes cleaving beads of an electride substrate to produce textured areas. The method also includes coating the rough areas of the electride substrate with an analyte.

BRIEF DESCRIPTION OF THE DRAWINGS

In order that the advantages of certain embodiments of the invention will be readily understood, a more particular description of the invention briefly described above will be rendered by reference to specific embodiments that are illustrated in the appended drawings. While it should be understood that these drawings depict only typical embodiments of the invention and are not therefore to be considered to be limiting of its scope, the invention will be described and explained with additional specificity and detail through the use of the accompanying drawings, in which:

FIG. 1A is a graph illustrating counts versus Raman shift (cm⁻¹) for a ~1 nm BPE film on rough, textured regions of a fractured electride surface, according to an embodiment of the present invention.

FIG. 1B is a graph illustrating counts versus Raman shift (cm⁻¹) for a smooth area of the BPE film of FIG. 1A with no SERS activity, according to an embodiment of the present invention.

FIG. 1C is a graph illustrating counts versus Raman shift (cm⁻¹) for rough mayenite of the BPE film of FIG. 1A, according to an embodiment of the present invention.

FIG. 1D is a graph illustrating counts versus Raman shift (cm⁻¹) for a thick (10 µm) BPE reference film with no SERS, according to an embodiment of the present invention.

FIG. 2A is a graph illustrating counts versus Raman shift (cm⁻¹) for a top spectrum of SERS of a thin (1 nm) BPE film on an electride powder, according to an embodiment of the present invention.

FIG. 2B is a graph illustrating counts versus Raman shift (cm⁻¹) for SERS of BPE on plasma sputtered gold, according to an embodiment of the present invention.

FIG. 2C is a graph illustrating counts versus Raman shift (cm⁻¹) for a thick (10 µm) BPE reference film with no SERS, according to an embodiment of the present invention.

FIG. 3 is a graph illustrating visible reflectance spectra for an electride powder (top) and a partially reduced mayenite precursor (bottom), according to an embodiment of the present invention.

FIG. 4 is a flowchart illustrating a method for producing a textured ceramic electride, according to an embodiment of the present invention.

FIG. 5 is an image of an electride surface, according to an embodiment of the present invention.

DETAILED DESCRIPTION OF THE EMBODIMENTS

Some embodiments use a ceramic or organic electride to facilitate enhanced SERS. For instance, certain embodiments texture the surface of the electride, such as a mayenite-derived ceramic electride, to produce a rough electride surface and facilitate enhanced SERS. After the electride is synthesized, “beads” are produced. These beads are then cleaved. See image 500 of FIG. 5. When coated with a Raman active analyte, the rough areas of the electride have greatly enhanced Raman scattering. The rough areas act like nano-antennas and create an enhanced electric field. Such embodiments may provide a sensitive method for monitoring the chemistry and electronic environment at the electride surface.

Electrides are a class of ionic compounds where electrons are not localized on specific atoms or molecules, but occupy sites typically populated by anions. In electrides, the electrons are not completely delocalized as in metals and may be regarded as a crystalline form of solvated electrons. Elec-
Electrons occupying the anionic sites have unusual properties as a result of their small mass compared to typical anions. A surface “electride-plasmon” resonance forms the basis of electride-mediated SERS in some embodiments. This is distinct from the surface plasmon-polariton resonance mediating conventional SERS.

The electride substrate used in some embodiments may be a mayenite derived ceramic compound, \([\text{CA}24\text{A}128\text{O}64]^{4+}\) (4e—), that is thermally stable and relatively unreactive. The analyte may be trans-1,2-bis(4-pyridyl)ethylene (BPE) cast as a thin film on a roughened electrode surface or on the powdered electride. However, other suitable electrides and analytes may be used, as would be understood by one of ordinary skill in the art. BPE has been previously used to quantitatively compare SERS substrates and lacks resonant enhancement in the visible region. BPE was tested for SERS using 532 nm and 785 nm laser excitation frequencies. The surface enhanced Raman spectra of thin BPE films on the electride was compared to an unenhanced spectrum of a thick BPE film and the conventional SERS spectrum of BPE on a sputtered gold substrate.

The synthesis of the ceramic electride \([\text{CA}24\text{A}128\text{O}64]^{4+}\) in some embodiments uses a high temperature processing of the mayenite precursor \((\text{CaO})_{12}(\text{Al}_{2}\text{O}_{3})\), by sintering stoichiometric proportions of calcium carbonate and aluminum oxide at 1300°C-1400°C in oxygen. The mayenite precursor may then be chemically reduced to form the electride by heat cycling past its melting point (~1415°C) to 1600°C in a sealed, carbon containing vessel. The synthesized electride may be in the form of ~5 mm sized beads that may then be cleaved in half using a clean razor blade and tapping with a small mallet under nitrogen. See image 500 of FIG. 5, which shows an electride surface. This fracturing method produced areas that greatly vary in surface roughness. Smooth glassy areas are often adjacent to rough areas (within 10-20 µm). When coated simultaneously using 785 nm laser may be set at a 2 mW power level and the 785 nm excitation frequencies corresponds with the broad overlapping peaks seen in reflectance spectrum of the powder at 560 nm and 702 µm, respectively. Taken together, this provides evidence of a surface plasmon resonance at visible frequencies. The surface plasmon resonances should be shifted from the bulk plasma resonance depending on the size, shape, and aggregation of the surface features. The difference between the surface plasmon resonance of conventional SERS using metals and electride mediated SERS depends on the differences in the electronic structure of conductive electrides and metals. The electronic states in the mayenite-based electride were previously analyzed by optical reflectance spectra using the Drude-Lorentz model.

In summary, for electride precursors that are not fully reduced, the electrons are localized in the cags of F+ centers in CaO (F+ states). The electrons move by hopping as polarons, with conductive activation energy of 0.1 eV. The more fully reduced, higher conductivity electride has a higher density of F+ states forming more delocalized bands that overlap the conduction band with both localized and delocalized electrons. The electride has metallic conduction and a more Drude-type response that dominates with the electrons delocalized over the ceramic cage. The mayenite has a weak localization behavior and a small temperature dependence of electrical conductivity near
room temperature. This fully reduced form would be expected to be the most SERS active material.

Put in a more general context, surface plasmon-polaritons in certain metals mediate the electromagnetic contribution of conventional SERS. Polaritons are formed by the strong coupling of electromagnetic waves with an electric or magnetic dipole-carrying excitation and are considered a form of quasi-particle. SERS in some embodiments has been demonstrated using an electrode. The distinction between this surface electrode-polariton and a surface plasmon-polariton lies in the differences in the nature of the anionic electrons in an electrode and electrons in a metallic conductor.

In addition to the electromagnetic resonance enhancement underlying SERS, there is a chemical enhancement component that is attributed to a charge transfer from the analyte to the substrate. The chemical enhancement contribution to SERS...
The invention claimed is:

1. An apparatus to enhance a target analyte for detection via Raman scattering, comprising:
   a Raman spectroscopy system;
   a substrate comprising an electrode material having a textured surface, the substrate positioned to be interrogated by the Raman spectroscopy system; and
   the target analyte coated over at least part of the textured surface of the electrode substrate to enhance detection of the target analyte for Raman scattering.

2. The apparatus of claim 1, wherein the textured surface is formed from cleaving beads off the substrate.

3. The apparatus of claim 2, wherein the beads are cleaved using a clean razor blade and tapping with a small mallet under nitrogen.

4. The apparatus of claim 1, wherein the substrate comprises an organic electrode or a ceramic electrode.

5. The apparatus of claim 1, wherein the electrode comprises mayenite derived ceramic compound [Ca24Al28O64]+4(4e—).

6. The apparatus of claim 1, wherein the analyte comprises trans-1,2-bis(4-pyridyl)ethylene (BPE).

7. The apparatus of claim 1, wherein the analyte is cast as a thin film on the textured surface or on a powdered electrode.

8. The apparatus of claim 1, wherein the substrate is synthesized via high temperature processing of mayenite precursor (CaO)12(Al2O3), by sintering stoichiometric proportions of calcium carbonate and aluminum oxide at 1300°C to 1400°C in oxygen.

9. The apparatus of claim 8, wherein the mayenite precursor is chemically reduced to form the electrode substrate by heat cycling past its melting point to 1600°C in a sealed, carbon containing vessel.

10. The apparatus of claim 1, wherein the ceramic electrode substrate is synthesized via high temperature processing of mayenite precursor (CaO)12(Al2O3), by sintering stoichiometric proportions of calcium carbonate and aluminum oxide at 1300°C to 1400°C in oxygen.

11. The apparatus of claim 10, wherein the mayenite precursor is chemically reduced to form the ceramic electrode substrate by heat cycling past its melting point to 1600°C in a sealed, carbon containing vessel.

12. An apparatus comprising:
   a ceramic electrode substrate comprising [Ca24Al28O64]+4(4e—), the ceramic electrode substrate having a roughened surface comprising cleaved beads; and
   an analyte comprising trans-1,2-bis(4-pyridyl)ethylene (BPE), the analyte coated over at least part of the roughened surface of the ceramic electrode substrate.

13. The apparatus of claim 12, wherein the beads are cleaved using a clean razor blade and tapping with a small mallet under nitrogen.

14. The apparatus of claim 12, wherein the analyte is cast as a thin film on the roughened surface or on a powdered electrode.

15. A method to enhance Raman scattering in a Raman spectroscopy system, comprising:
   cleaving beads off a substrate comprising an electrode material to produce textured areas; and
   coating the textured areas of the substrate with an analyte; and,
   performing surface enhanced Raman spectroscopy (SERS) on the coated substrate.

16. The method of claim 15, wherein the SERS is performed using 532 nm and 785 nm excitation frequencies.

17. The method of claim 15, further comprising:
   synthesizing the substrate via high temperature processing of mayenite precursor (CaO)12(Al2O3), by sintering stoichiometric proportions of calcium carbonate and aluminum oxide at 1300°C to 1400°C in oxygen.

18. The method of claim 17, further comprising:
   chemically reducing the mayenite precursor to form the substrate by heat cycling past its melting point to 1600°C in a sealed, carbon containing vessel.

19. The method of claim 15, further comprising:
   storing the substrate under dry nitrogen.