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
(56) References Cited

U.S. PATENT DOCUMENTS


OTHER PUBLICATIONS


* cited by examiner
FIG. 2A
FIG. 3

Electrode

Manganese

Nanometers

Absorbance
FIG. 4

START

Synthesize Ceramic Electride Substrate

Chemically Reduce Mayenite Precursor

Store Ceramic Electride Substrate

Cleave Beads

Apply Analyte Coating

Perform SERS

END
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 electrodes 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 electrode, such as a ceramic electrode or an organic electrode, to facilitate enhanced SERS.

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

In another embodiment of the present invention, an apparatus includes a ceramic electrode substrate comprising [CA24A128O64]+(4e−). The ceramic electrode 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 electrode substrate.

In yet another embodiment of the present invention, a method includes cleaving beads of an electrode substrate to produce textured areas. The method also includes coating the rough areas of the electrode 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. IA 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. IB is a graph illustrating counts versus Raman shift (cm⁻¹) for a smooth area of the BPE film of FIG. IA with no SERS activity, according to an embodiment of the present invention.

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

FIG. ID 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. IE 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 electrode powder, according to an embodiment of the present invention.

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

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

FIG. IK is an image of an electrode surface, according to an embodiment of the present invention.

Detailed Description of the Embodiments

Some embodiments use a ceramic or organic electrode to facilitate enhanced SERS. For instance, certain embodiments texture the surface of the electrode, such as a mayenite-derived ceramic electrode, to produce a rough electrode surface and facilitate enhanced SERS. After the electrode 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 electrode 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 electrode 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-
The 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, [CA24A128064]⁺⁺⁻⁻, 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 powdery electrode. However, other suitable electrodes 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 electrode 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 [CA24A128064]⁺⁺⁻⁻ in some embodiments uses a high temperature processing of the mayenite precursor (CaO)₁₂(Al₂O₃)₈, by sintering stoichiometric proportions of calcium carbonate and aluminum oxide at 1300 °C-1400 °C. 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 electrode 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 with a test compound (e.g., trans-1,2-bis(4-pyridyl)ethylene (BPE) or generic analytes that are SERS active), these smooth and rough areas can be directly compared for SERS activity. The electride may be stored under dry nitrogen and the top surface may be cleaved away immediately before testing.

Raman spectroscopy may be performed with any suitable system, such as a Bruker Senterra (Bruker Optics, Billerica, Mass.) system equipped with 532 nm and 785 nm lasers. The samples may be interrogated using the 20x objective and the spectra may be acquired using 5 second integrating times with a test compound (e.g., trans-1,2-bis(4-pyridyl)ethylene (BPE) or generic analytes that are SERS active), these smooth and rough areas can be directly compared for SERS activity. The electride may be stored under dry nitrogen and the top surface may be cleaved away immediately before testing.

The visible spectra may be acquired using a Cary 5E spectrometer (Agilent, Santa Clara, Calif.), or any other suitable spectrometer. A white spectrally flat polystyrene substrate (PTFE) coated integrating sphere and a spectrally flat PTFE reference (Labsphere, North Sutton, N.H.) may be used. The sample particles may be dispersed on a PTFE substrate and the total hemispherical reflectance may be measured from 400 nm and 800 nm. The samples may be in the form of finely ground powders on a spectrally neutral, PTFE substrate to better reveal the surface modes. This dilution may be necessary to prevent optical saturation of the strongly absorbing, pure sample.

In graphs 100-130 of FIGS. 1A-D, BPE was used with 532 nm excitation. The SERS spectrum of a ~1 nm BPE film may be readily obtained on the rough, textured regions of the fractured electrode surface as shown in graph 100 of FIG. 1A. Smooth, evenly cleaved areas did not produce SERS activity. See graph 110 of FIG. 1B. In order to show that the enhanced signal is not due to the rough surface, the BPE analyte may be similarly deposited on a rough, partially reduced mayenite (see graph 120 of FIG. 1C). As shown in FIG. 1C, this did not produce a detectable Raman signal of BPE and the enhancement due to surface roughness alone can be ruled out. Using a thick (~10 µm), unenhanced BPE film on a mirror as a reference (see graph 130 of FIG. 1D), SERS enhancement can be bounded to be greater than 10⁴ for the 532 nm excitation. The SERS enhancement, based on theoretical and experimental work, occurs less than 25 nm from the substrate surface.

The electrode mediated SERS at 785 nm excitation is given in graphs 200-220 of FIGS. 2A-C. The electrode's SERS enhancement factor at 785 nm excitation is bounded to be greater than 10⁴. This is similar to the conventional SERS BPE spectrum from sputtered gold. As expected for SERS, both the electrode mediated SERS and sputtered gold mediated SERS spectra have somewhat different peak ratios from the unenhanced reference BPE.

In addition to SERS demonstrated in FIGS. 1A-D, and 2A-C, the electrode was examined by the visible reflectance to reveal surface plasmon resonances. This approach is also used for characterization of metallic SERS substrates. The spectra of partially reduced mayenite and the reduced electrode are compared in the 400 nm to 800 nm wavelength range (see graph 300 of FIG. 3). The visible reflectance spectra are shown for the electrode powder (top) and the partially reduced mayenite precursor (bottom). The electrode has additional peaks at 479 nm, 561 µm, 614 nm, and 702 nm. The surface modes of the fully reduced electrode are revealed in the visible wavelength range. The frequencies of these surface modes may be shifted somewhat depending on the size, shape, and aggregation of the particles.

The SERS activity of the electrode measured at 532 nm and 785 nm excitation frequencies corresponds with the broad overlapping peaks seen in reflectance spectrum of the powder at 560 nm and 702 nm, 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 electrode mediated SERS depends on the differences in the electronic structure of conductive electrides and metals. The electronic states in the mayenite-based electrode were previously analyzed by optical reflectance spectra using the Drude-Lorentz model.

In summary, for electrode precursors that are not fully reduced, the electrons are localized in the cages of F⁺ states (F⁺ states). The electrons move by hopping as polarons, with conductive activation energy of 0.1 eV. The more fully reduced, higher conductivity electrode has a higher density of F⁺ states forming more delocalized bands that overlap the cage conduction band with both localized and delocalized electrons. The electrode has metallic conductivity and a more Drude-type response that dominates with the electrons delocalized over the ceramic cage. The mayenite electrode has 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-excitation carrying 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 plasma-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 electride or a ceramic electride.

5. The apparatus of claim 1, wherein the electride comprises mayenite derived ceramic compound \([\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]+4(4e^-)\).

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 electride.

8. The apparatus of claim 1, wherein the substrate is synthesized via high temperature processing of mayenite precursor \((\text{CaO})_{12}(\text{Al}_2\text{O}_3)_2\), 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 \((\text{CaO})_{12}(\text{Al}_2\text{O}_3)_2\), 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 \([\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]+4(4e^-)\), 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 electride 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 \((\text{CaO})_{12}(\text{Al}_2\text{O}_3)_2\), 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.