(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau

(43) International Publication Date
03 January 2019 (03.01.2019)

WIPO | PCT

(10) International Publication Number
WO 2019/003247 A1

(51) International Patent Classification:
G01N 21/65 (2006.01)

(21) International Application Number:
PCT/IN2018/050422

(22) International Filing Date:
27 June 2018 (27.06.2018)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
201741023122 30 June 2017 (30.06.2017) IN

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA,

(54) Title: A TUNABLE SERS SUBSTRATE

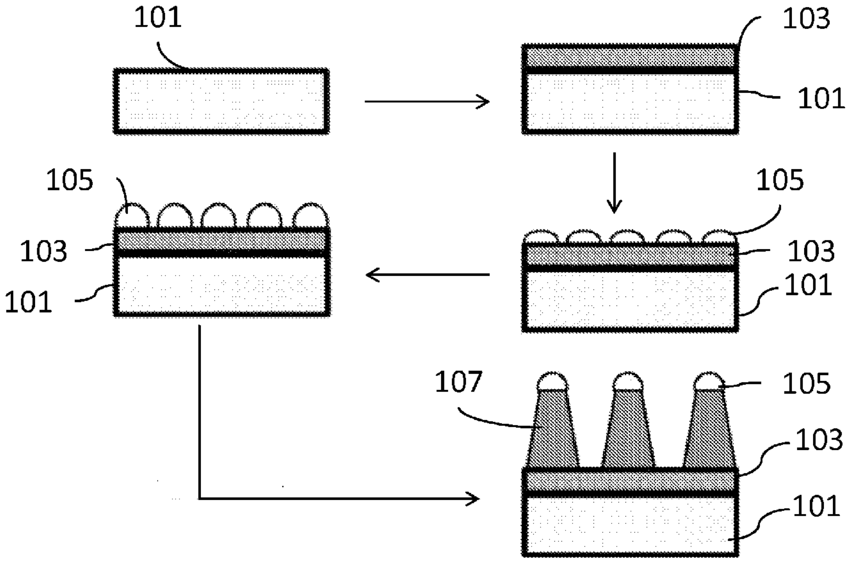

FIG. 1

(57) Abstract: The invention provides a method for obtaining a tunable SERS substrate. The method includes selecting a base. A layer of a dielectric is deposited on the base through plasma enhanced chemical vapor deposition. A first metal is selected as a catalyst for deposition on the dielectric layer. Nanowires are grown on the deposited metal layer. The nanowires formed are then introduced in a solution of a second metal for varying duration of time to obtain growth of nanostructures on the nanowires. The nanostructures grown on the nanowire yields a SERS substrate. The duration of contact of the nanowires with the metal solution determines the tunability of the SERS substrate formed.

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SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

A TUNABLE SERS SUBSTRATE

FIELD OF INVENTION

The invention generally relates to the field of physical chemistry and particularly to a method for obtaining a substrate for performing surface enhanced Raman spectroscopy.

BACKGROUND

Raman spectroscopy is a powerful technique which provides analyte specific spectra. However, the technique is inadequate in detecting analyte at low concentration. Surface Enhanced Raman Spectroscopy, generally referred to as SERS is a technique capable of obtaining Raman spectra of an analyte, by enhancing the signal more than 4 orders of magnitude, as compared to the normal Raman signal enabled detection of even single analyte molecule. The aforementioned effect is observed when the analyte is at close proximity to a metal nanostructure surface. When the incident electromagnetic wave interacts with the metal nanostructure, the free electrons on the metal collectively oscillate giving rise to localized surface plasmons resonance called as LSPR. LSPR results in intense electric field at the metal surface which in turn increases the weak Raman signal of the analyte by orders of magnitude.

SERS is performed either in a metal colloidal solution or on metal nanostructures fabricated on top of a base substrate which is termed as SERS substrate. A SERS substrate has the advantage of further integration with lab-on-a-chip systems for potential bio-sensor application. Guillot N.,et.al., Yue. W, et.al., and Das G, et.al., the details of which are incorporated herein by reference, have reported fabrication of SERS substrate using lithography. self-assembly of nanoparticles have been demonstrated by Yap FL, et al., and Lee, W, et al., the details of which are incorporated herein by reference. There have been numerous methods that have shown physical vapor deposition of metalson nanostructures. Controlled nanostructure fabrication with optimal precision and high enhancement factor is obtained by e-beam lithography. But, large area fabrication and cost is a major disadvantage in lithography. Orientation of structure requires specific placement of substrate with respect to the polarization of incident LASER to achieve high enhancement. Lin W.-C et al., Whitney, AV et al., and Hulteen JC et al., the details of which are incorporated herein by reference, have shown that self-assembly of polystyrene beads is subjected to several innovative fabrication process for large area substrates. but the process does not significantly reduce the cost. there are also methods known for obtaining nanostructures by large area fabrication processes possess high enhancement factors. However, the synthesis process includes multiple fabrication steps. One significant disadvantage of the aforementioned methods of formation of SERS substrate is that the substrate formed needs to be kept under controlled environment for obtaining accurate analysis. Hence, there is a need for a SERS substrate that is robust and can be adopted under normal conditions.

BRIEF DESCRIPTION OF DRAWINGS

So that the manner in which the recited features of the invention can be understood in detail, some of the embodiments are illustrated in the appended drawings. It is to be noted, however, that the appended drawings illustrate only typical embodiments of this invention and are therefore not to be considered limiting of its scope, for the invention may admit to other equally effective embodiments.

FIG.1 shows a schematic representation of the process for obtaining a tunable SERS substrate, according to an embodiment of the invention.

FIG.2 shows SEM photographs of various stages of formation of a tunable SERS substrate, according to an embodiment of the invention.

FIG.3 shows intensity graphs of standard molecules tested using the tunable SERS substrate.

FIG.4 shows SERS intensity peaks of molecules TNT, being detected using the SERS substrate obtained, according to an example of the invention.

SUMMARY OF THE INVENTION

One aspect of the invention provides a method for obtaining a tunable Sensitive and large area Surface Enhanced Raman Scattering, SERS, substrate. The method includes selecting a base. A layer of a dielectric is deposited on the base through plasma enhanced chemical vapor deposition. A first metal is selected as a catalyst for deposition on the dielectric layer. Nanowires are grown on the deposited metal layer. The nanowires can be formed to obtain various configurations. The nanowires formed are then introduced in a solution of a second metal for varying duration of time to obtain a growth of nanostructures on the nanowires. The nanostructures grown on the nanowire yields a SERS substrate. The duration of contact of the nanowires with the metal solution determines the tunability of the SERS substrate formed.

The substrate consists of dense vertical germanium nanowires grown by plasma enhanced chemical vapour deposition. Metals exhibiting plasmon resonance effect such as silver can be grown on the nanowires by galvanic displacement reaction. The reaction results in growth of nanostructures on the tip of the nanowires resulting in formation of hotspots. The hotspots are highly localized at the tips of the nanowire which aids in detection of analyte at low concentration. The sensitivity can be further improved by obtaining SERS signal versus reaction time during the displacement reaction. This enables to define accurate time for the reaction for a specific wavelength.

DETAILED DESCRIPTION OF THE INVENTION

Various embodiments of the invention provide a method for obtaining a tunable SERS substrate. The method includes selecting a base. A layer of a dielectric is deposited on the base through plasma enhanced chemical vapor deposition. A first metal is selected as a catalyst for deposition on the dielectric layer. Nanowires are grown on the deposited metal layer. The nanowires formed are then reacted with a solution of a second metal for varying duration of time to obtain a growth of nanostructures on the nanowires. The nanostructures grown on the nanowire yields a SERS substrate. The duration of contact of the nanowires with the metal solution determines the tunability of the SERS substrate by increasing the plasmon resonance formed. The method described briefly herein shall be described in detail as example of the invention.

FIG.1 shows a schematic representation of the process for obtaining a tunable SERS substrate, according to an embodiment of the invention. The method for obtaining a SERS substrate includes selecting a base 101. Examples of base include but are not limited to a glass, a plastic, a ceramic or a metal. In one example of the invention, silicon substrate is chosen as the base. A dielectric 103 is then chosen to be deposited over the base 101. Examples of dielectric include but are not limited to SiO_2, Si_3N_4,HfO_2, Al_2O_3, TiO_2 and dielectrics of other molecules that is capable or exhibiting similar dielectric properties as that of the above state dielectrics are chosen. In one example of the invention, SiO_2 is chosen as the dielectric and is deposited as a film of about 30nm thickness by plasma enhanced chemical vapour deposition technique.

The base 101 coated with the dielectric layer 103 is then deposited with a metal 105. Examples of metal chosen include but are not limted to gold, copper, silver and any metal capable of forming eutectic alloy with the semiconductor chosen for forming nanowires. In one example of the invention, gold is deposited on the base coated with the dielectric. The deposition of the gold is achieved through any of the known techniques of metal deposition. In one example of the invention, the gold is deposited by sputtering technique onto the base. Subsequent to formation of the dielectric layer 103, nanowires 107 of a semiconductor are grown. Examples of semiconductor include germanium or silicon. In one example of the invention, germanium is used as the semiconductor. Germanium in the form of GeH_4 is grown on the dielectric layer through plasma enhanced chemical vapour deposition technique. The nanowires 107 thus formed can be either as a single wire or multiple wires. Further, the nanowires can form either an island or a film.

The nanowires of germanium thus formed on the dielectric layer are then reacted with a salt solution of a metal to form nanostructures of the metal on the germanium nanowires. The reaction is achieved through galvanic displacement reaction on the substrate. A typical requirement for the process is to have a substrate with higher reduction potential with respect to the desired metal. In one embodiment of the invention, all metals with a redox potential lesser than germanium is chosen. In one example of the invention, silver is chosen in the form of silver nitrate, $AgNO_3$ for forming nanostructures on the germanium nanowires formed. Other examples of metal selected for growth of nanostructures include but are not limited to copper, gold, palladium, platinum, nickel and aluminium. The duration of reaction of the germanium nanowire with the silver nitrate determines the wavelength at which the intensity of substrate is maximum. The dependency of wavelength of response to the reaction time, enables tunability of the substrate towards a wide range of wavelength in the range from about 440 nm to about 830 nm. Further, the formation of nanostructures, as described herein above does not require special environment to achieve the same. Hence, the obtained SERS substrate is robust and has extended life without degradation of the properties of the substrate.

The substrate obtained in a manner as described herein above is then characterised . A physical characterisation is done using scanning electron microscope. FIG.2 shows SEM photographs of various stages of formation of a tunable SERS substrate, according to an embodiment of the invention. Fig.2(a) SEM image (top view) of PECVD grown germanium nanowire. The images show the density of nanowire grown on the substrate. Fig.2(b)SEM image (cross-sectional view) of PECVD grown germanium nanowire. The images show the vertical growth as well as the length of the nanowires. Fig.2(c) SEM image (top view) of germanium nanowire treated with silver nitrate for 10 minutes. The size of the silver nanostructures formed on the tip controls the location of the surface plasmon resonance there by tuning the substrate to a specifc wavelength. Fig.2(d)SEM image (cross-sectional view) of germanium nanowire treated with silver nitrate for 10 minutes. The image shows the extent of the silver nanostructures on the nanowires which is found to be localised on the tip of the nanowire due to surface tension of the nanowire substrates.

FIG.3 shows intensity graphs of standard molecules (4-Mercaptobenzoic Acid) tested using the tunable SERS substrate at 514 nm (FIG.3a) and at 785 nm (FIG.3b). Intensity contour plot from 50 various points are provided in FIG.3c and FIG.3d at 514 nm and 785 nm respectively for reproducibility. FIG.4 shows SERS intensity peaks of molecules TNT and Phenylalanine being detected using the SERS substrate obtained, according to an example of the invention.

The invention as described herein above, provides a method for fabrication of large area SERS substrate with scalable fabrication steps. The base substrate of germanium nanowires can be stored in a sealed container without degrading the structures. The metal nanostructures can be grown by immersing the nanowire in alkaline or acidic solution of the desired metal, at any desired instance of time, resulting in extended shelf life of the substrate. The extended shelf life of the substrate eliminates the need of additional expensive steps of deposition. The need based growth of nanostructures results in optimization of the reaction time. The optimal reaction time yields various size of the nanostructures for a specific wavelength laser. The varying size of the nanostructures represents high tunability. However, functionalization may increase the sensitivity towards a particular analyte by many folds. The substrate as obtained by the method described herein can be integrated into techniques known in the art for analyte detection resulting in increased sensitivity towards analyte detection. In one example, the SERS substrate as obtained, can be effectively integrated in a microfluidic device. The microfluidic device can be obtained by integrating the SERS substrate during the design and formation of the microfluidic device. The fabrication process step can provision for a raised chamber height in microfluidics thereby increasing the throughput of such device.

The foregoing description of the invention has been set merely to illustrate the invention and is not intended to be limiting. Since modifications of the disclosed embodiments incorporating the spirit and substance of the invention may occur to person skilled in the art, the invention should be construed to include everything within the scope of the appended claims and equivalents thereof.

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We Claim:

1. A method for obtaining a tunable SERS substrate, the method comprising:
    selecting a base;
    depositing a layer of a dielectric on the base;
    selecting a first metal as a catalyst for deposition on the dielectric layer;
    growing nanowires of a semiconductor through plasma enhanced chemical vapor deposition; and
    reacting the nanowires formed in a salt solution of a second metal for a varying duration of time to obtain a SERS substrate;

wherein the duration of reaction of the nanowires determines the wavelength tunability of the SERS substrate formed with respect to a specific wavelength matching the plasmon resonance of the metal.

2. The method of claim 1, wherein the base is selected from a list comprising of a glass, a plastic, a ceramic or a metal.
3. The method of claim 1, wherein the dielectric is selected from a list comprising of SiO_2, Si_3N_4, HfO_2, Al_2O_3,andTiO_2.
4. The method of claim 1, wherein the first metal is selected from a list comprising of gold, copper, silver and any metal forming an eutectic alloy or a mix with the semiconductor.
5. The method of claim 1, wherein the semiconductor is selected from either germanium or silicon.
6. The method of claim 1, wherein the nanowires is grown on the sites of deposition of the first metal.

7. The method of claim 1, wherein the nanowires grown can be grown either as an island or as a film.
8. The method of claim 1, wherein the salt solution of the second metal is selected from a list comprising of silver, gold, copper, nickel, aluminium platinum and palladium.
9. The method of claim 1, wherein the second metal selected is below the redox potential of the nanowires formed.
10. The method of claim 1, wherein the second metal is reduced and deposited on the nanowires through galvanic displacement reaction.
11. A tunable SERS substrate comprising of:

    a base;

    a layer of dielectric deposited on the base;

    a layer of a first metal formed on the deposited dielectric;

    at least two nanowires of a semiconductor formed on the first metal; and

    at least two nanostructures of a second metal grown on the nanowires.
12. The base of claim 11, wherein the base is selected from a list comprising of a glass, a plastic, a ceramic or a metal.
13. The substrate of claim 11, wherein the dielectric is selected from a list comprising of SiO_2, Si_3N_4, HfO_2, Al_2O_3, and TiO_2.
14. The substrate of claim 11, wherein the semiconductor is either germanium or silicon.

15. The substrate of claim 11, wherein the first metal is selected from a list comprising of gold, copper, silver and any metal forming eutectic alloy with the semiconductor.
16. The substrate of claim 11, wherein the nanowires is either a germanium nanowire or a silicon nanowire.
17. The substrate of claim 11, wherein the second metal is selected from a list comprising of silver, gold, copper, nickel, aluminium platinum and palladium.
18. The substrate of claim 11, wherein the tunability of the substrate is dependent on the frequency, the frequency in the range of about 440 nm to about 830 nm.

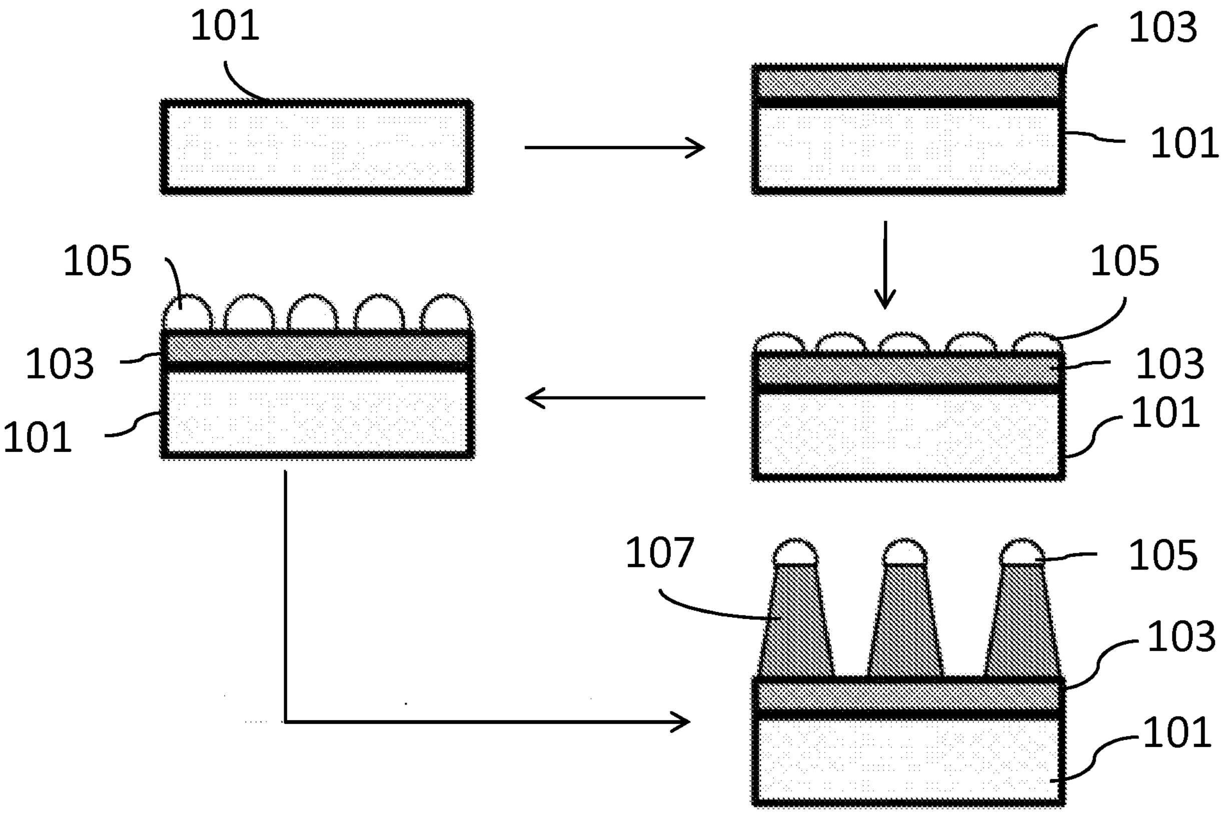

FIG. 1

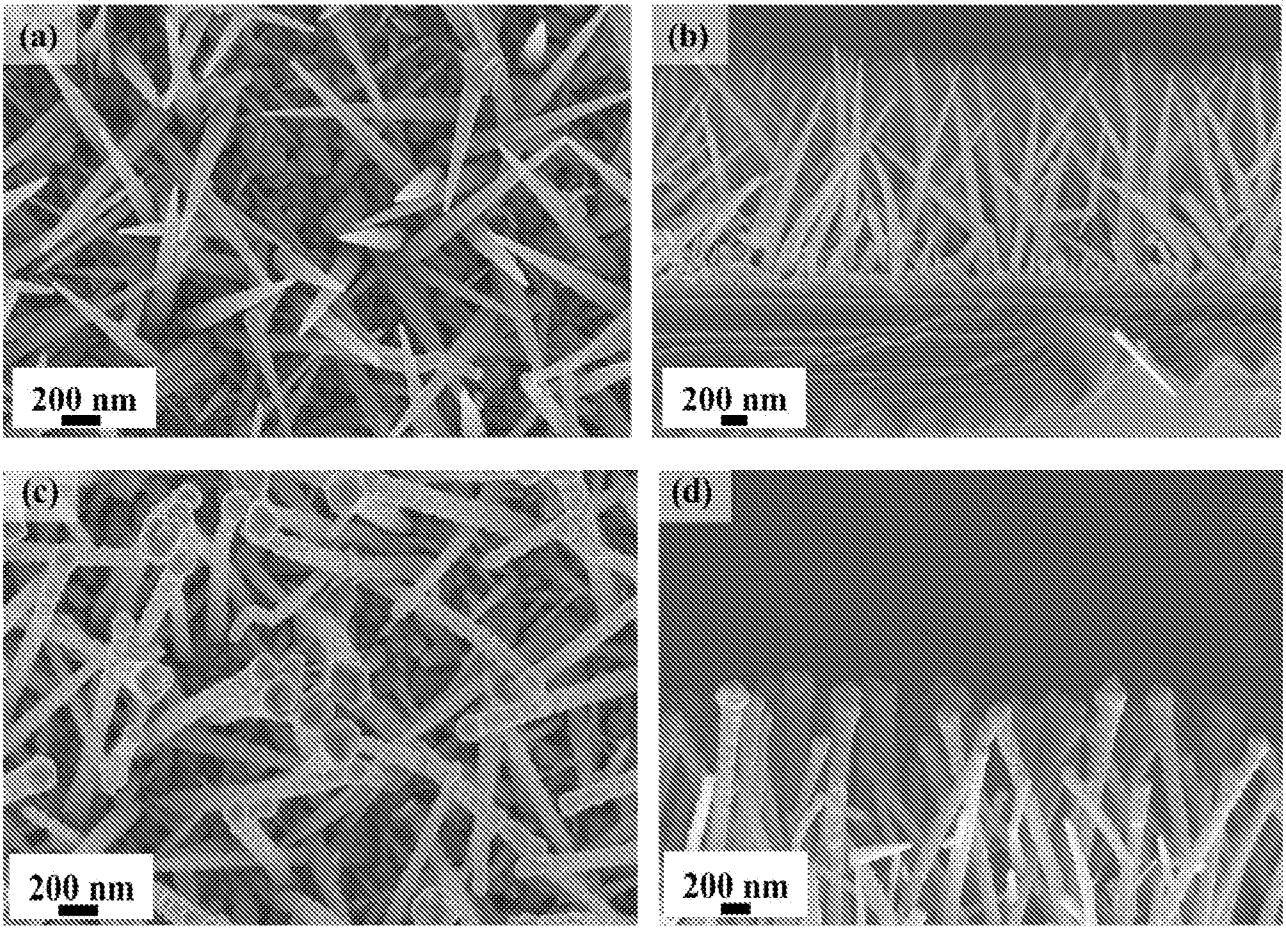

FIG. 2

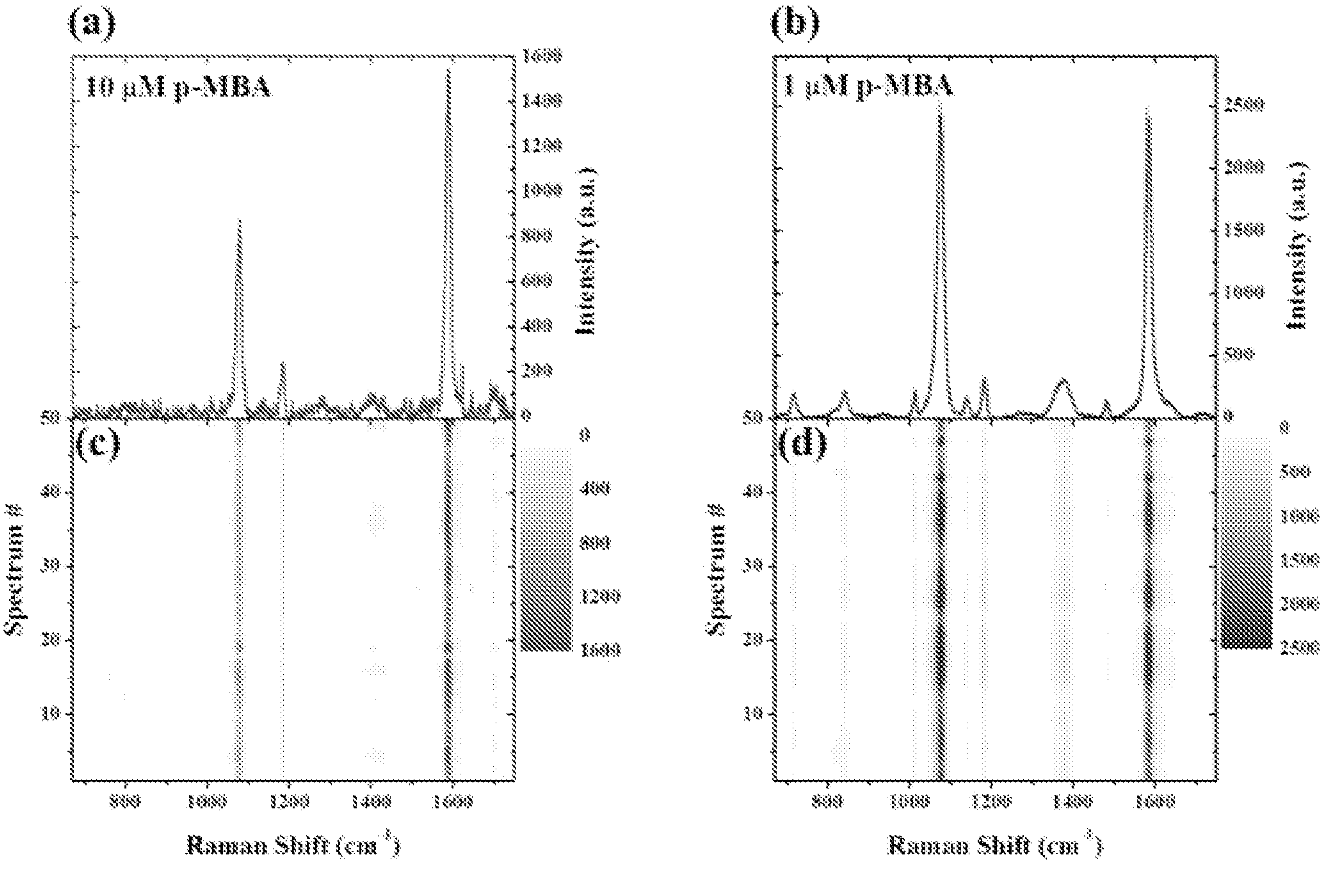
(a)
10 μM p-MBA
1600
1400
1200
1000
800
600
400
200
0
Intensity (a.u.)
(b)
1 μM p-MBA
2500
2000
1500
1000
500
0
Intensity (a.u.)
(c)
50
40
30
20
10
Spectrum #
0
400
800
1200
1600
800
1000
1200
1400
1600
Raman Shift (cm⁻¹)
(d)
50
40
30
20
10
Spectrum #
0
500
1000
1500
2000
2500
800
1000
1200
1400
1600
Raman Shift (cm⁻¹)

FIG. 3

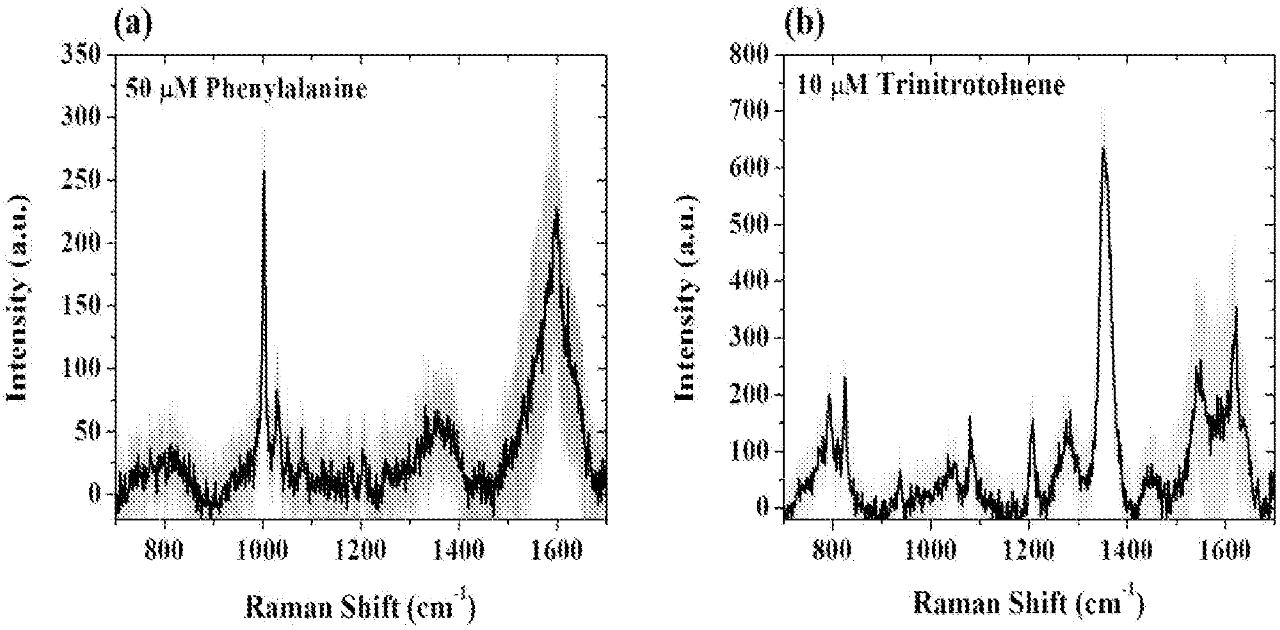
(a)
50 μM Phenylalanine
Intensity (a.u.)
350
300
250
200
150
100
50
0
800
1000
1200
1400
1600
Raman Shift (cm-1)
(b)
10 μM Trinitrotoluene
Intensity (a.u.)
800
700
600
500
400
300
200
100
0
800
1000
1200
1400
1600
Raman Shift (cm-1)

FIG. 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IN2018/050422

A. CLASSIFICATION OF SUBJECT MATTER
G01N21/65 Version=2018.01

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)

G01N

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)

TotalPatent One, IPO Internal Database

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	Nayak DR et al., "Impact of ultrathin dielectric spacers on SERS: energy transfer between polarized charges and plasmons", J. Mater. Chem. C, The Royal Society of Chemistry Publishing, DOI: 10.1039/C6TC05122G, vol. 5, pp 2123-2129, 03 February 2017 Experimental: Materials and Methods, Supplementary: Table S1	1-18
Y	Wang T et al., "The effect of dielectric constants on noble metal/semiconductor SERS enhancement: FDTD simulation and experiment validation of Ag/Ge and Ag/Si substrates", Scientific Reports, Nature Publishing, DOI: 10.1038/srep04052, vol. 4, pp 4052(1-7), 11 February 2014 Abstract, Page 6: Methods	1-18
Y	Peng M et al., "Reductive self-assembling of Ag nanoparticles on Germanium nanowires and their application in ultrasensitive surface-enhanced Raman spectroscopy", Chem. Mater., American Chemical Society Publishing, DOI: 10.1021/cm200186v, vol. 23, pp 3296-3301, 28 June	1-18

☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

*	Special categories of cited documents:
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"&"	document member of the same patent family

Date of the actual completion of the international search 04-10-2018	Date of mailing of the international search report 04-10-2018
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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	2011 Abstract	
Y	US 2014/0043605 A1 (NATIONAL TSING HUA UNIVERSITY [TW]), 13 February 2014 paragraph [0029]-[0033], claim 1	1-18

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/IN2018/050422

Citation	Pub.Date	Family	Pub.Date
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		TW I469917 B	21-01-2015
		US 9127984 B2	08-09-2015