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(71) Applicants:
- **Valstybinis moksliniu tyrimu institutas Fiziniu ir technologijos mokslu centras**
  10257 Vilnius (LT)
- **Vilnius University**
  01513 Vilnius (LT)

(72) Inventors:
- **Stankevicius, Evaldas**
  Vilnius (LT)
- **Petrikaite, Vita**
  Vilnius (LT)
- **Niaura, Gediminas**
  Vilnius (LT)
- **Sablinskas, Valdas**
  Vilnius (LT)
- **Ceponkus, Justinas**
  Vilnius (LT)
- **Matulaitiene, Ieva**
  Vilnius (LT)
- **Trusovas, Romualdas**
  Vilnius (LT)
- **Mikoliunaite, Lina**
  Vilnius (LT)
- **Talaikis, Martynas**
  Vilnius (LT)
- **Zdaniauskiene, Agne**
  Vilnius (LT)
- **Adomaviciute-Grabusove, Sonata**
  Vilnius (LT)

(74) Representative: **AAA Law**
A. Gostauto 40B
03163 Vilnius (LT)

(54) **LASER-BASED METHOD FOR FABRICATION OF MAGNETO-PLASMONIC NANOPARTICLES**

(57) The invention relates to a method for producing magneto-plasmonic particles by laser ablation. Two metallic samples are used in a liquid medium. First metallic sample being a thin metal film has magnetic or plasmonic properties, and second metallic sample accordingly has plasmonic or magnetic properties. When both metallic samples are thin metal films, they are deposited on ultra-thin glass substrates. In another case the first metallic sample is a thin metal film and the second sample is a bulk metal. When the samples are exposed to a laser beam, plasma is induced in the thin metallic coatings or thin metallic coating and surface layer of the bulk metal sample. As plasma expands from both metal samples mixes. The plasma then shrinks in the solution to form hybrid nanoparticles with magneto-plasmonic properties.

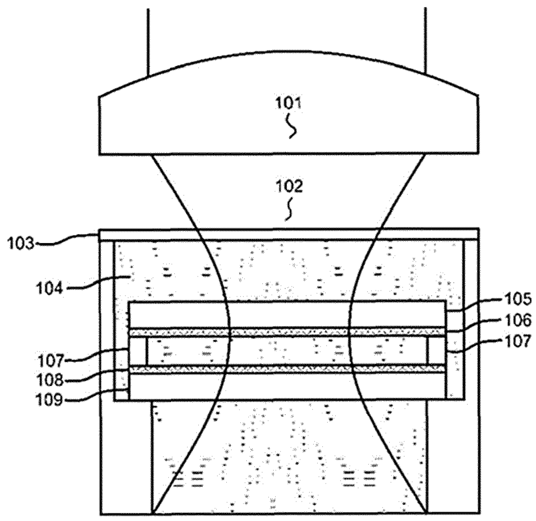

Fig. 1.

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B22F 2202/13

Description

TECHNICAL FIELD

[0001] The invention relates to a method of producing magneto-plasmonic particles by laser irradiation.

BACKGROUND ART

[0002] Magneto-plasmonic nanoparticles can be generated using chemical synthesis, microemulsion synthesis, sonochemical synthesis, physical vapor deposition and hybridization of pre-synthesized nanoparticles. Main disadvantages of known methods are toxicity of the chemical precursors, time-consuming of the process, low efficiency of large-scale production, high cost and impurity of production, expensive vacuum required equipment, etc. Our proposed laser-based method solves these problems: the laser-based process does not use toxic chemical precursors. High efficiency and purity of the production can be ensured using non-vacuum equipment with inexpensive laser systems.

[0003] The formation of magneto-plasmonic particles with laser irradiation often lacks flexibility by precisely controlling the formed nanoparticle composition, which may vary depending on the specific application.

[0004] US patent application No. US11/092,717 (publication No. US2006/0057384A1) describes how to coat gold nanoparticles with a magnetic shell using laser ablation. Gold and iron colloidal nanoparticles are mixed and then irradiated with a laser beam. Main disadvantage is that process comprises multiple steps for obtaining magneto plasmonic nanoparticles.

[0005] US patent No. US7,029,514 describes synthesis of core-shell nanoparticles using a chemical synthesis of nanoparticles from metal salts. Main disadvantage is that process comprises using chemical synthesis comprising use of chemical substances such as salts, resulting in bimetal nanoparticles with additives and necessity for additional cleaning process of the nanoparticle.

[0006] US patent application No. US14/312,824 (publication No. US2014/0322138A1) describes a method for producing a colloidal suspension using laser pulses and the variable electrical conductivity of the medium during the generation of nanoparticles. Main disadvantage is that the process requires adjusting increased number of particle production parameters.

[0007] US patent application No. US16/439,052 (publication No. US2019/0334180A1), hybrid nanoparticles are produced using laser ablation and galvanic replacement reaction. Main disadvantage of the process is necessity of increased number of nanoparticle production steps.

[0008] M. Muniz-Miranda, F. Muniz-Miranda, E. Giorgetti, Spectroscopic and microscopic analyses of Fe3O4/Au nanoparticles obtained by laser ablation in water, Nanomaterials 10 (2020) 132. DOI: 10.3390/nano10010132 discloses production of Fe3O4-Au magneto-plasmonic nanoparticles by laser ablation of iron and gold samples in two successive steps.

[0009] Further, V. Amendola, S. Scaramuzza, F. Carraro, E. Cattaruzza, Formation of alloy nanoparticles by laser ablation of Au/Fe multilayer films in liquid environment, J. Colloid Interface Sci. 489 (2017) 18-27. DOI: 10.1016/j.jcis.2016.10.023 discloses production of Fe-Au magneto-plasmonic nanoparticles by nanosecond laser (1064 nm) ablation of Au/Fe/glass coatings in ethanol and water. Here, two successive layers of metal films were laser ablated in ethanol and water.

[0010] C. Gellini, F.L. Deepak, M. Muniz-Miranda, S. Caporali, F. Muniz-Miranda, A. Pedone, C. Innocenti, C. Sangregorio, Magneto-plasmonic colloidal nanoparticles obtained by laser ablation of nickel and silver targets in water, J. Phys. Chem. C 121 (2017) 3597-3606. DOI: 10.1021/acs.jpcc.6b1 1628 discloses first laser ablation of bulk nickel target and second laser ablation stage comprising ablating the bulk silver target in an aqueous media.

[0011] The present invention is dedicated to overcoming of the above shortcomings and for producing further advantages over prior art.

BRIEF DESCRIPTION OF THE INVENTION

[0012] The invention relates to a method for producing magneto-plasmonic particles by laser ablation. The method uses two metallic samples each being a distinct metal sample one from another and simultaneously placed opposite each other in a liquid medium. First metallic sample, which is a thin metal film, has magnetic or plasmonic properties, and the other metallic sample accordingly has plasmonic or magnetic properties. When both metallic samples are thin metal films, they are deposited on ultra-thin glass substrates as coating. In another case the first metallic sample is a thin metal film, and the second sample is bulk metal.

[0013] The metallic samples are arranged in front of each other at a certain distance in the liquid medium. When the samples are exposed to a laser beam that is perpendicular to the surface plane of glass substrate of the thin metal film, plasma is induced in the thin metallic coatings. When bulk metal is used as the second metallic sample, plasma is induced on the surface layer of the bulk metal sample.

[0014] As plasma expands, in both cases, i.e., the thin meal films or thin metal film and layer of bulk metal, it mixes together. The plasma then shrinks in the solution to form hybrid nanoparticles with magneto-plasmonic properties.

[0015] Properties of the generated nanoparticles depend on distance between the coatings, thickness of the used coatings, focusing conditions of the laser beam, and energy and duration of the laser pulses. The produced magneto-plasmonic nanoparticles can be used in cancer diagnosis and treatment by using surface-enhanced Raman spectroscopy and other methods.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] Features of the invention believed to be novel and inventive are set forth with particularity in the appended claims. The invention itself, however, may be best understood by reference to the following detailed description of the invention, which describes exemplary embodiments, given in non-restrictive examples, of the invention, taken in conjunction with the accompanying drawings, in which:

Fig. 1 shows a scheme for generation of magneto-optical nanoparticles using laser ablation of two thin films facing each other according to the invention.

Fig. 2 shows a scheme for generation of magneto-optical nanoparticles using laser ablation of thin film on the top and bulk metal target on the bottom facing each other according to the invention.

Fig. 3 shows an example of magneto-plasmonic nanoparticles obtained by method according to the invention.

Fig. 4 shows magneto-plasmonic nanoparticles obtained by method according to the invention arranged using a magnet.

Fig. 5 shows Raman spectrum of 4-mercaptobenzoic acid at magneto-plasmonic nanoparticles obtained by method according to the invention. In Figure a and b show two different spots on the same sample.

[0017] Preferred embodiments of the invention will be described herein below with reference to the drawings. Each figure contains the same numbering for the same or equivalent element.

DETAILED DESCRIPTION OF THE INVENTION

[0018] It should be understood that numerous specific details are presented in order to provide a complete and comprehensible description of the invention embodiment. However, the person skilled in art will understand that the embodiment examples do not limit the application of the invention which can be implemented without these specific instructions. Well-known methods, procedures and components have not been described in detail for the embodiment to avoid misleading. Furthermore, this description should not be considered to be constraining the invention to given embodiment examples but only as one of possible implementations of the invention.

[0019] Method for generation of magneto-plasmonic nanoparticles using laser ablation of two metallic samples (106, 108, 108'), where the metallic samples are two thin metal films (106, 108) deposited on a transparent substrate (105, 109), or one thin metal film (106) deposited on a transparent substrate (105) and a bulk metal sample (108'). In all cases of the invention, first (106) and second (108, 108') metal targets differ in type of metal.

[0020] Each of the two thin metal films (106, 108) are deposited on a glass substrate (105, 109) and placed opposite each other in a liquid medium (104). First thin metal film (106) has magnetic properties, i.e. a magnetic response to magnetic fields, and the second thin metal film (108) has plasmonic properties, i.e. surface plasmon resonance, enhancement of electromagnetic field. The first thin metal film (106) can have plasmonic properties and the second thin metal film (108) accordingly will have magnetic properties. Distance between the thin metal films (106, 108) is controlled by varying thicknesses of spacers (107). The arranged substrates (105, 109) coated with metallic thin films (106, 108) are irradiated by a laser beam (102) focused using a lens (101) through a glass window in a cuvette (103). The composition of the generated nanoparticles is controlled by varying thicknesses of the thin metal film (106, 108), spacing between them, the laser beam (102) focusing conditions, laser beam (102) pulse energy, duration and scanning speed. All these parameters influence the temperature and dynamics of plasma from both targets (106, 108), leading to the different degree of plasma mixing and the formation of different kind of hybrid nanoparticles.

[0021] When thin metal films (106, 108) on ultrathin transparent substrates (105, 109) are used as the laser beam (102) targets, the top target, first thin metal film (106), is positioned so the substrate (105) faces the laser beam (102). The laser beam (102) passes the transparent substrate (105) and ablation of the first thin metal film (106) occurs. Afterwards, the laser beam (102) passes gap between the first thin metal film (106) and the second thin metal film (108) and starts ablation of the second thin metal film (108). The targets (106, 108) can be interchanged by placing the magnetic thin metal film on top as the first thin metal film (106) and the plasmonic thin metal film at the bottom as the second thin metal film (108) and vice versa. The first thin metal film (106) and the second thin metal film (108) may be interchanged at any point during the ablation process, for example in the middle of the ablation process.

[0022] Both thin films (106, 108) are placed in a liquid medium, such as water, acetone, isopropanol, etc. Both thin metal films (106, 108) are placed facing each other perpendicular to the laser beam (102) at a distance, for example of 1 to 500 μm, which can be adjusted using spacers (107) or a precise translation stage. The ablation process is performed by scanning a laser beam (102) or moving the whole setup with a stationary laser beam (102). In another case one thin metal film (106) on a transparent glass substrate (105) and a bulk metal sample are placed opposite each other in a liquid medium (104). First thin metal film (106) has magnetic properties, i.e. a magnetic response to magnetic fields, and the bulk metal sample (108') has plasmonic properties, i.e. surface plasmon resonance, enhancement of electromagnetic field. The first thin metal film (106) can have plasmonic properties and the bulk metal sample (108') accordingly will have magnetic properties. Distance between the thin metal film (106) and the bulk metal sample (108') is controlled by varying thicknesses of spacers (107). The arranged substrate (105) coated with thin metal film (106) and surface layer of the bulk metal sample (108') are irradiated by a laser beam (102) focused using a lens (101) through a glass window in a cuvette (103). The composition of the generated nanoparticles is controlled by varying thicknesses of the thin metal film (106), spacing between thin metal film (106) and the bulk metal sample (108'), the laser beam (102) focusing conditions, the laser beam (102) pulse energy, duration and scanning speed. All these parameters influence the temperature and dynamics of plasma from both targets (106, 108'), leading to the different degree of plasma mixing and the formation of different kinds of hybrid nanoparticles. When the first thin metal film (106) on an ultrathin transparent substrate (105) and bulk metal sample (108') are used as laser beam (102) targets, as shown in Fig. 2, the top target, the first thin metal film (106), is positioned so the substrate (105) faces the laser beam (102). When the laser beam (102) passes the transparent substrate (105) ablation of the first thin metal film (106) occurs. Afterwards, the laser beam (102) passes the gap between the first thin metal film (106) and the bulk metal sample (108') and starts ablating the second target which is the bulk metal sample (108'). The bottom target must be bulk and the top target only a thin metal film (106) on an ultrathin transparent substrate (105).

[0023] Both the first thin metal film (106) and the bulk metal sample (108') are placed in a liquid medium, such as water, acetone, isopropanol, etc. Both (106, 108') are placed facing each other perpendicular to the laser beam (102) at a distance, for example of 1 to 500 μm, which can be adjusted using spacers (107) or a precise translation stage.

[0024] In all embodiments of the invention plasma is induced in the thin metallic films (106, 108) or the thin metallic film (106) and the bulk metal sample (108') when the target (106, 108') are exposed to the laser beam (102). In both cases the targets (106, 108, 108') emit plasma at temperatures ranging from 1000 to 10000 K and expand during the process. Then, plasma in both cases from both targets (106, 108, 108') interacts together, the shockwave is created that travels through the plasma and mixes the ablated material from both targets (106, 108, 108'). Plasma cooling leads to the recombination of ions and electrons to form hybrid nanoparticles, which exhibit magneto-plasmonic properties in a solution. The obtained hybrid magneto-plasmonic nanoparticles can be applied in medicine, for example, in cancer diagnosis and treatment by using surface enhanced Raman spectroscopy and other methods.

[0025] According to a particular example of the invention, the ablation targets thin metallic films (106, 108) of thickness from 1 nm to 1 μm deposited on ultrathin, up to 150 μm, transparent substrate for applied laser radiation material substrate (105, 109) or targets a thin metal film (106) of thickness from 1 nm to 1 μm deposited on ultrathin, up to 150 μm, transparent substrate and the bulk metal target (108'). Each thin film (106, 108) comprises of one metal or a few different metals. For example, gold and silver films are deposited on separate areas of one substrate or mixed using periodic patterns through the surface for depositing on one substrate.

[0026] Although numerous characteristics and advantages together with structural details and features have been listed in the present description of the invention, the description is provided as an example fulfilment of the invention. Without departing from the principles of the invention, there may be changes in the details, especially in the form, size and layout, in accordance with most widely understood meanings of the concepts and definitions used in claims.

Claims

1. Laser-based method for fabrication of magneto-plasmonic nanoparticles comprises ablating two different metal samples in a liquid medium **characterized in that** the method comprises

providing two different metal samples (106, 108, 108') facing each other in a liquid medium (104) where first metal sample is a thin metal film (106) deposited on an ultrathin transparent substrate (105) and has magnetic properties or plasmonic properties and the second metal sample (108, 108') has respectively plasmonic properties or magnetic properties,

irradiating the metal samples (106, 108, 108') by a laser beam (102) focused using a lens (101) through a glass window in a cuvette (103) for obtaining plasma from both metal samples (106, 108, 108'),

where both metal samples (106, 108, 108') emit plasma at temperatures ranging from 1000 to 10000 K and expand during the process,

where plasma from both metal samples (106, 108, 108') interacts one with another creating a shockwave that travels through the plasma and mixes the ablated material from both metal samples (106, 108, 108').

cooling the plasma for recombining ions and electrons to form magneto-plasmonic nanoparticles.

2. Method according to claim 1, where the laser beam (102) is firstly focused on the first thin metal film (106) through the transparent substrate (105), being top target, afterwards, the laser beam (102) is passed through gap between the ultrathin transparent substrate (105) of the first thin metal film (106) and the second metal sample (108, 108') for focusing on the second metal sample (108, 108').

3. Method according to claim 1 or 2, where the second metal sample (108) is a thin metal film (108) deposited on an ultrathin transparent substrate (109).

4. Method according to claim 3, comprising control of distance between the first thin metal film (106) and the second thin metal film (108) by varying thicknesses of spacers (107).

5. Method according to claim 3 or 4, where the first thin metal film (106) and the second thin metal film (108) are interchanged at any point during the ablation process.

6. Method according to claim 1 or 2, where the second metal sample is a bulk metal sample (108').

7. Method according to claim 6, comprising control of distance between the first thin metal film (106) and the bulk metal sample (108') by varying thicknesses of spacers (107).

8. Method according to any one of claims 1 - 7, comprising control of laser beam (102) focusing conditions.

9. Method according to any one of claims 1 - 7, comprising control of laser beam (102) pulse energy and duration.

10. Method according to any one of claims 1 - 9, where the liquid medium (104) is selected from water, acetone, isopropanol.

11. Method according to any one of claims 1 - 10, where both metal samples (106, 108, 108') are positioned facing each other perpendicular to the laser beam (102) at a distance of 1 to 500 μm.

12. Method according to any one of claims 3-5, the thin metal films (106, 108) have thickness from 1 nm to 1 μm and are deposited on the substrate (105, 109) up to 150 μm thick.

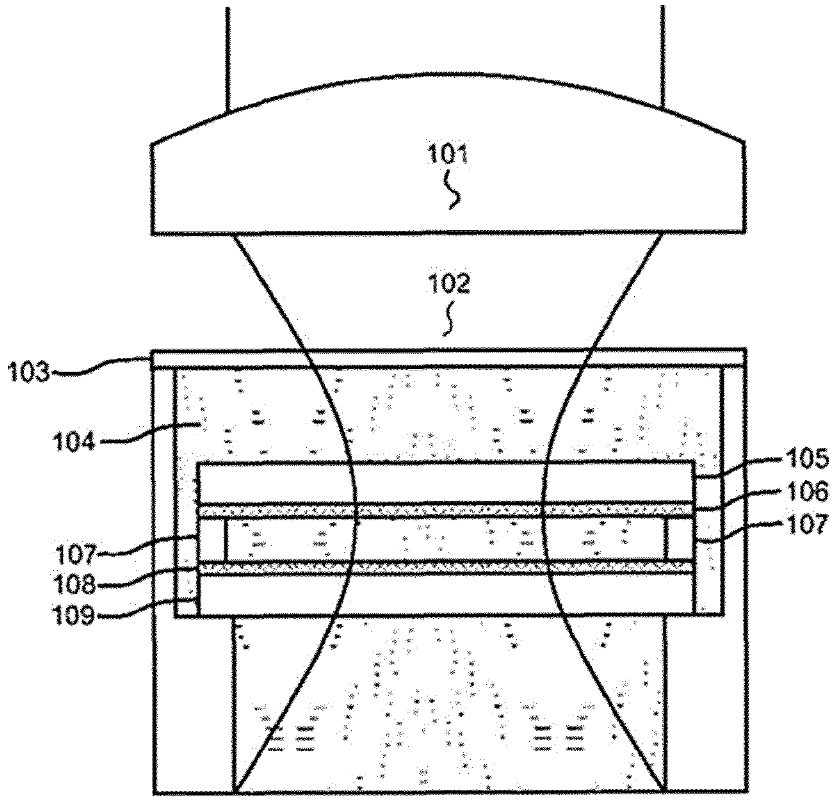
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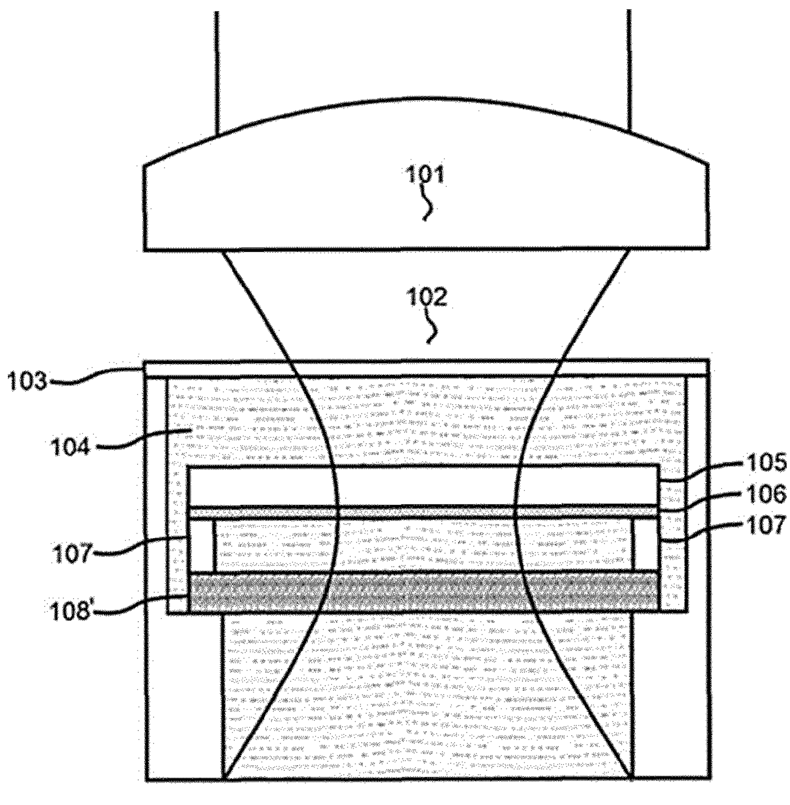
Fig. 1.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106
107
107
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Fig. 2

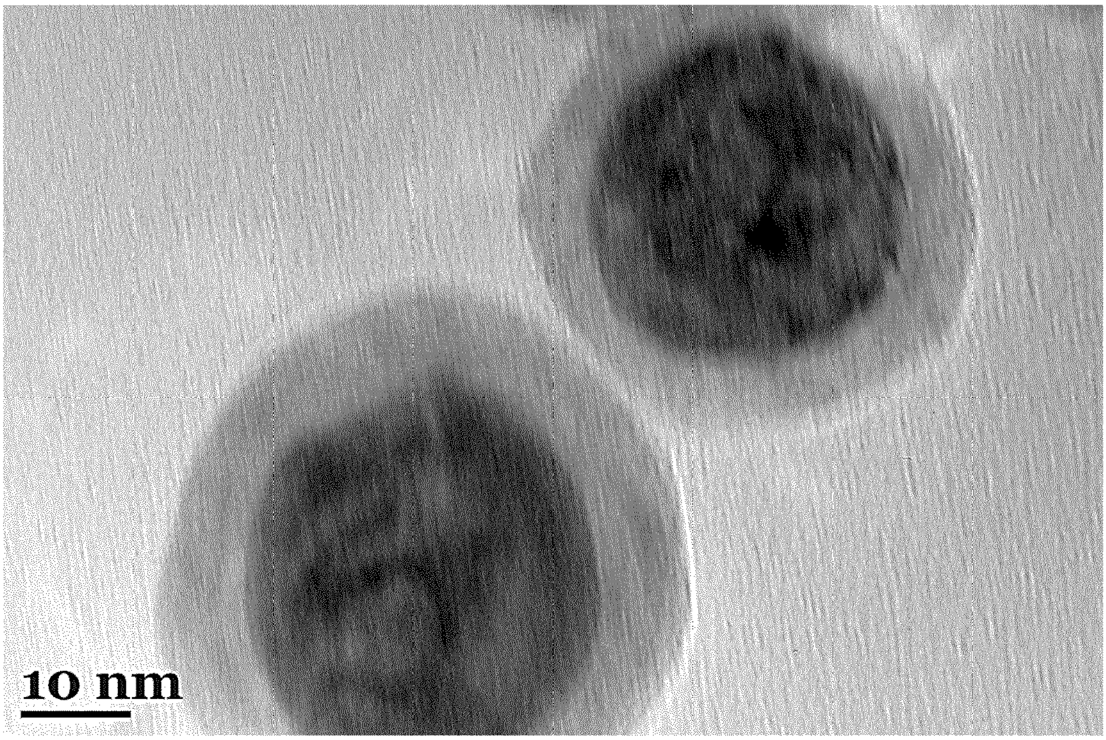

Fig. 3

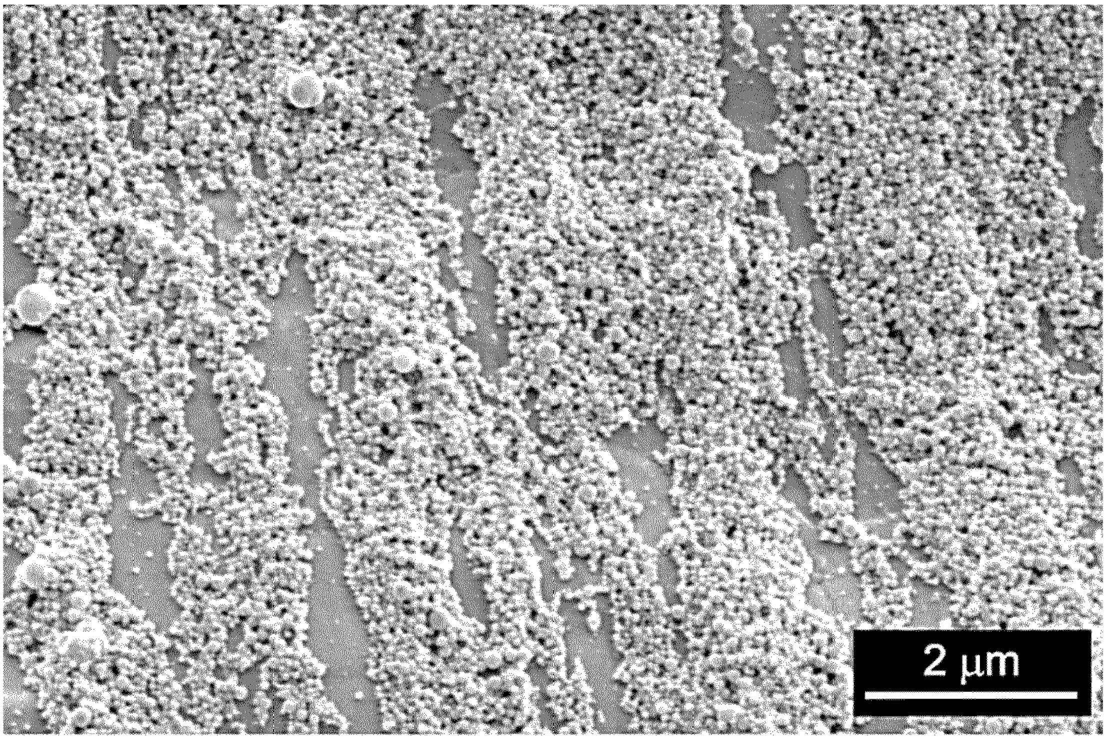

Fig. 4

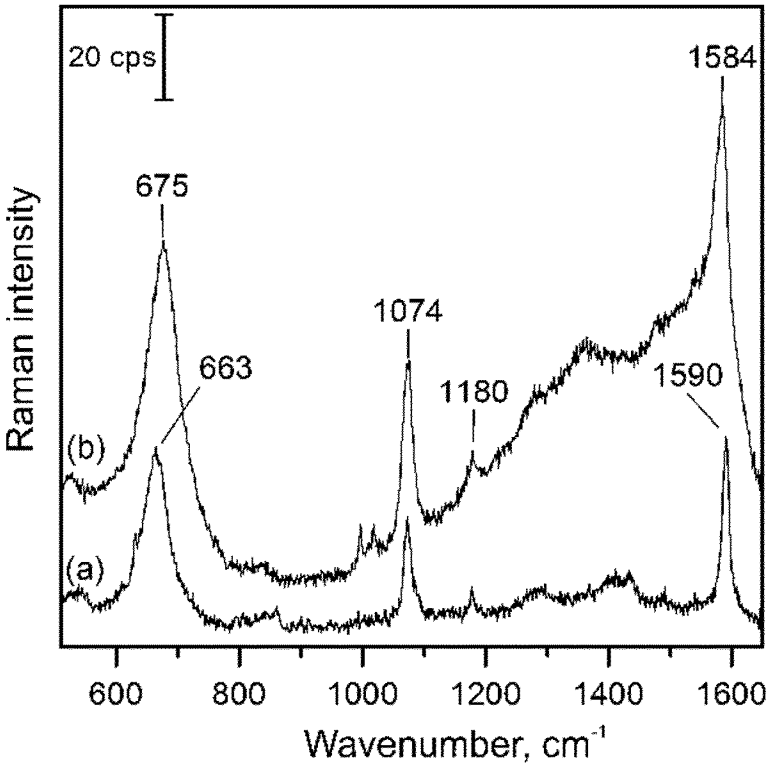
20 cps
1584
675
1074
663
1180
1590
(b)
(a)
Raman intensity
600
800
1000
1200
1400
1600
Wavenumber, cm-1

Fig. 5.

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EUROPEAN SEARCH REPORT

Application Number
EP 23 21 2167

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	SABLINSKAS VALDAS ET AL: "Magneto-plasmonic nanoparticles for SERS", PROCEEDINGS OF THE SPIE, SPIE, US, vol. 11797, 6 August 2021 (2021-08-06), pages 117972B-117972B, XP060145100, ISSN: 0277-786X, DOI: 10.1117/12.2597199 ISBN: 978-1-5106-5738-0 * figures 1, 2 * * 2. Methodology * * 3.1 Laser ablation synthesis of nanoparticles *	1-12	INV. B22F1/054 B22F9/14 B22F1/17 C22C1/04
X,D	AMENDOLA VINCENZO ET AL: "Formation of alloy nanoparticles by laser ablation of Au/Fe multilayer films in liquid environment", JOURNAL OF COLLOID AND INTERFACE SCIENCE, ACADEMIC PRESS,INC, US, vol. 489, 13 October 2016 (2016-10-13), pages 18-27, XP029857354, ISSN: 0021-9797, DOI: 10.1016/J.JCIS.2016.10.023 * table 1 * * figures 1, 4 * * 2. Materials and methods *	1-12	
A	WO 2023/198617 A2 (BASF SE [DE]) 19 October 2023 (2023-10-19) * example 1 *	1-12	

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TECHNICAL FIELDS SEARCHED (IPC)

B22F
C22C
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The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
The Hague	10 May 2024	Fodor, Anna

CATEGORY OF CITED DOCUMENTS

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EUROPEAN SEARCH REPORT

Application Number
EP 23 21 2167

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	SUBHAN ABDUL ET AL: "Pulsed Laser Synthesis of Bi-Metallic Nanoparticles for Biomedical Applications: A Review", 2022 ADVANCES IN SCIENCE AND ENGINEERING TECHNOLOGY INTERNATIONAL CONFERENCES (ASET), IEEE, 21 February 2022 (2022-02-21), pages 1-7, XP034103639, DOI: 10.1109/ASET53988.2022.9735057 [retrieved on 2022-03-14] * figure 1 * -----	1-12	
			TECHNICAL FIELDS SEARCHED (IPC)

The present search report has been drawn up for all claims

1

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The Hague	10 May 2024	Fodor, Anna

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10-05-2024

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2023198617 A2	19-10-2023	NONE	

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