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(54) **FUNCTIONALIZED SILK FIBROIN SECURITY MARKER**

(57) The invention relates to a functionalized silk fibroin security marker comprising one, two, three or more different security taggants selected from the group consisting of metallic particles, preferably metallic nanoparticles; magnetic particles, preferably magnetic nanoparticles; and peptide sequences, use of the inventive security marker within the substrate and/or on the surface of a security document, a functionalized security document comprising the inventive security marker as well as processes for manufacturing and authenticating the inventive functionalized silk fibroin security marker and inventive security document.

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Description

FIELD OF THE INVENTION

[0001] The invention relates to a functionalized silk fibroin security marker comprising one, two, three or more different security taggants selected from the group consisting of metallic particles, preferably metallic nanoparticles; magnetic particles, preferably magnetic nanoparticles; and peptide sequences, use of the inventive security marker within the substrate and/or on the surface of a security document, a functionalized security document comprising the inventive security marker as well as processes for manufacturing and authenticating the inventive functionalized silk fibroin security marker and inventive security document.

BACKGROUND

[0002] Silk is a natural product with 5000 years of consolidated worldwide manufacturing basically in the field of textile tissues and fibre with a great tradition and impact in dressing and fashion market. Natural silk produced by the silkworm (*bombix mori*) constitutes of two proteins, namely sericin and fibroin. The last one is the most abundant biopolymer and possesses the property of being totally bio-resorbable into living systems without any cytotoxicity effect and is called within the present application silk fibroin.

[0003] Silk is a natural product. The mechanical properties of silk have been historically recognized for a variety of applications from augmented strength in special tissues and fibres such as parachutes used in the Second World War. Silk is water soluble and can be structurally controlled and modified in order fine tune the water solubility properties. The sericin component of silk is thermo degradable and is removed with water treatment and recovered usually for cosmetic and drugs industries. Silk fibroin is the constituent most applied into the textile industry.

[0004] Further applications of silk started with assessing a water based process of reverse engineering allowing a silk-fibroin solution to be obtained from silk cocoons by David Kaplan.

[0005] WO 2015/114649 A1 (Council of scientific & industrial research) discloses a silk fibroin security fibre and process for the preparation thereof, wherein the silk fibroin security fibre is loaded with inorganic fluorescent chromophore and organic IR absorbing chromophore useful to combat counterfeiting.

[0006] There is, however, a continuing aim for providing novel security markers for securing security documents, in particular banknotes, to provide solutions against counterfeiting.

SUMMARY

[0007] The aforementioned aim is solved by means of the claimed inventive subject matter. Preferred embodiments thereof are described in the dependent claims as well as in the following description.

[0008] According to a first aspect of the present invention a functionalized silk fibroin security marker is provided, characterized in that the silk fibroin comprises one, two, three or more different security taggants selected from the group consisting of metallic particles, preferably metallic nanoparticles; magnetic particles, preferably magnetic nanoparticles; and peptide sequences.

[0009] According to a second aspect of the present invention a use of an inventive security marker is provided within the substrate and/or on the surface of a security document, preferably banknote.

[0010] According to a third aspect of the present invention a process for the manufacture of an inventive security marker is provided, characterized in that the process comprises or consists of the following steps:

a) providing a suitable amount of silk fibroin,

b) providing suitable amount of one, two, three or more different security taggants selected from the group consisting of metallic particles, preferably metallic nanoparticles; magnetic particles, preferably magnetic nanoparticles; and peptide sequences and

c) functionalizing the silk fibroin of step a) with the one, two, three or more different security taggants provided in step b).

[0011] According to a fourth aspect of the present invention a functionalized security document, preferably banknote, is provided, characterized in that the security document, preferably the banknote comprises one, two, three, four or more different inventively functionalized silk fibroin security markers.

[0012] According to a fifth aspect of the present invention a process of manufacturing an inventively functionalized security document, preferably banknote, is provided, characterized in that the process comprises and/or consists of the following steps:

a) applying the one, two, three, four or more different inventive security markers within at least part of the substrate of the inventive security document and/or

b) applying the one, two, three, four or more different inventive security markers at least on part of the surface of the inventive security document.

[0013] According to a sixth aspect of the present invention a process for authenticating the inventively functionalized security document, preferably banknote, is provided, characterized in that the authenticating process comprises or consists of authenticating the functionalized security document with one, two, three or more authenticating means selected from the group consisting of UV-VIS spectrometer, X-Ray Fluorescence Analyzer (XRF tool), magnetic sensor, ambient mass spectrometer (AMS), X-ray Absorption Near Edge Structures (XANES) detector, infrared (IR) spectrometer, Raman spectrometer, such as Surface Enhanced Raman Spectroscopy (SERS), refractometer, Localized Surface Plasmon Resonance (LSPR), Wide-Angle X-ray Scattering (WAXS), Small-Angle X-ray Scattering (SAXS), Fourier transform infrared (FT-IR) spectroscopy, Transmission Electron Microscopy (TEM), Scanning Electron Microscope (SEM) and Terahertz detection systems.

[0014] The aforementioned inventive embodiments can - as far as it is reasonable in view of a technical expert - comprise any possible combination of the preferred inventive embodiments, which are disclosed in the following and in particular in the dependent claims.

DETAILED DESCRIPTION OF AN EXAMPLE EMBODIMENT

[0015] The present inventors have identified a novel platform technology for applying one, two, three or more different security taggants selected from the group consisting of metallic particles, preferably metallic nanoparticles; magnetic particles, preferably magnetic nanoparticles; and peptide sequences to a security document, preferably banknote by providing the inventively functionalized silk fibroin security marker. In case one security taggant is inventively used, then the term "different" in "one, two, three or more different security taggants" does not apply. Furthermore, the silk fibroin without functionalization does not act as an inventive security marker and/or security taggant.

[0016] The inventive security marker can be provided in any suitable form. Inventive security documents, preferably banknotes may comprise one, two, three or more security markers in the same or in different forms selected from the group consisting of fibres, films, gels, sponges and solutions. Thus, the inventive security marker may be applied at least in part, e.g. locally, or throughout the inventive security document, preferably banknote. The inventive security markers may, thus, be applied within the security document substrate and/or on the surface of the surface of the security document. The inventive silk fibroin security marker may be comprised in the inventive security document, preferably banknote, in a concentration of up to 20 wt.-%, alternatively 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, or 19 wt.-% respectively based on the total weight of the security document, preferably banknote.

[0017] In the context of the present invention the term "silk fibroin" is used to define the silk fibroin protein or fragments thereof substantially devoid of sericin.

[0018] The inventive silk fibroin security marker is a natural and biocompatible constituent, as it acts as a renewably natural polymer source with excellent mechanical and/or optical properties in particular when substituting cellulose polymer in cellulose-based security documents. Furthermore, the inventive silk fibroin security marker can be easily combined with cellulose-based security documents, as silk fibroin and cellulose exhibit similar intermolecular bondings, in particular on the basis of hydrogen bonds and Van der Waals forces, and may interact sterically. Thus, silk fibroin provides manufacturing advantages over other, e.g., synthetic polymers alternatively used as carrier for security markers.

[0019] Generally, conventional silk fibroin is suitable for the first aspect of the present invention. As an example, suitable silk fibroin may be reverse engineered from silk obtained, *e.g.,* from the silkworm (*bombix mori*) by a) taking the produced silk containing cocoon and boiling for sericin degumming; b) isolating silk fibroin in LiBr; and c) dialyzing and using water-pure silk fibroin solution. A detailed silk fibroin extraction protocol is disclosed in D. N. Rockwood, R. C. Preda, T. Yücel, X. Wang, M. L. Lovett, D. L. Kaplan, Materials fabrication from Bombyx mori silk fibroin, Nat Protoc 2011, 6, 1612-1631 and incorporated herein in its entirety. Other silk sources, such as from silk spider, moth genera such as *Antheraea, Cricula, Samia* and *Gonometa,* etc. are also applicable for the present invention. In case the following description discloses the use of silk worms as a source for silk, then the other sources, such as silk spider may also be used in general. The use of silk worm may however be preferred with respect to the present invention.

[0020] The reengineered or commercially available silk fibroin may inventively be functionalized with one, two, three, four or more security taggants by mixing a suitable amount of aqueous silk fibroin solution with one, two, three, four or more security taggants. Preferably the one or more security taggants are present as a colloidal aqueous dispersion of respective metallic, magnetic or peptidic nanoparticles. More preferably, the colloidal aqueous dispersions of the respective one, two, three, four or more different security taggants are previously homogenized, e.g. by sonication (e.g., 10 minutes).

[0021] Alternatively, the inventive functionalized silk fibroin may be produced by feeding domesticated silk worms with a respective security taggant diet and/or by genetically modifying silk worms to produce the inventively functionalized silk fibroin. Methods for feeding domesticated silk worms or genetically modifying silk worms are disclosed in Natalia C. Tansil, Leng Duei Koh, and Ming-Yong Han "Functional Silk: Colored and Luminescent", Adv. Mater. 2012, 24, 1388-1397 and are incorporated herein in its entirety.

[0022] The resulting functionalized silk fibroin dispersion may inventively be further processed by use of several techniques such as spin coating, nano-imprinting, contact printing, ink-jet printing, or spray drying to form different substrates, such as films, gels, sponges, tubes and fibres. These substrates may inventively be incorporated within or onto the substrate of security documents, in particular banknotes. Detailed fabrication methods for forming different substrates, such as films, gels, sponges, tubes and fibres are disclosed, e.g., in

Rockwood *et al., ibid.* and incorporated herein in its entirety.

[0023] In a preferred embodiment of the first inventive aspect, the inventive security marker comprises two or more different taggants. The silk fibroin enables as carrier substrate the combination of two or more taggants (metallic (nano)particles, magnetic (nano)particles, and/or peptide sequences), which can otherwise not be combined into one moiety, e.g., by grafting of cellulose.

[0024] Such an inventive combination of different taggants may be preferred, as the characteristic properties, such as magnetic properties, plasmon bands of nobel metal nanoparticles, etc. of the separate taggants may be influenced due to the close proximity of the different taggants.

[0025] For example, by combining in particular magnetic and metallic nanoparticles as taggants in the inventive security marker, a shift of magnetic properties of the magnetic nanoparticles and/or a shift of plasmon bands of noble metallic nanoparticles can be determined due to the close proximity of the magnetic and metallic nanoparticles.

[0026] Alternatively, by combining nobel metallic nanoparticles and peptide sequences (also called amino acid tags) as taggants, a shift of enhanced Raman scattering may be determined due to adsorption of the amino acid tags onto the surface of the nobel metallic nanoparticles. Such an inventively multifunctionalized security marker may be locally applied in a security document, preferably banknote, and may provide a localized high concentration of two, three or more taggants. Such a localized high concentration of two, three or more taggants selected from the group consisting of metallic particles, preferably metallic nanoparticles; magnetic particles, preferably magnetic nanoparticles; and peptide sequences can - in contrast - not be provided by grafting onto cellulose during paper making.

[0027] According to a further preferred embodiment of the first inventive aspect, the one, two, three or more taggants are selected from the group consisting of metallic nanoparticles; magnetic nanoparticles; and small peptide sequences.

[0028] The metallic and/or magnetic nanoparticles (NPs) suitable for the first aspect of the present invention are generally characterized to have a dimension between 1 and 100 nanometers. Suitable metallic NPs for the present invention are in particular selected from the group of noble metal NPs due to their size and shape dependent unique optical properties, which arise from their surface plasmon resonances.

[0029] In general different concentrations of metallic (nano) particles can be used to tag the silk fibroin. According to a preferred embodiment the metallic particles, preferably metallic nanoparticles are incorporated into silk fibroin at higher concentrations , preferably at a weight of 0.1 to 10 wt.-%, alternatively 1, 2, 3, 4, 5, 6, 7, 8 or 9 wt.-% respectively based on the total weight of the silk fibroin used for the manufacture of the silk fibroin security marker.

[0030] Metallic particles, in particular metallic NPs can generally be authenticated optically by UV-VIS spectroscopy as well as by dynamic light scattering. In particular X-Ray Fluorescence Analyzer (XRF) tools (portable, benchtop or in-process sensors) can be used to verify the presence of noble metals, in particular nobel metal NPs. Furthermore, exposure of metallic particles, in particular metallic NPs to laser radiation in the area close to the plasmon absorption band can locally generate heat. The generated heat can be detected by a temperature gauge. Metallic NPs may in particular be authenticated by use of Localized Surface Plasmon Resonance (LSPR), Raman spectroscopies, such as Surface Enhanced Raman spectroscopy (SERS), UV-VIS spectrometry, and TeraHertz detection systems.

[0031] According to a preferred embodiment hydrotalcite-like compounds (HTlc) or layered double hydroxide (LDHs) compounds represented by the general formula "$[M(II)_{1-x}M(III)_x(OH_2)]^{x+}[A^{n-}{}_{x/n}]$ mH2O where M(II) is a divalent cation such as Mg, Ni, Zn, Cu, or Co, M(III) is a trivalent cation such as Al, Cr, Fe, or Ga and A is an anion of charge n" are not part of the inventive security taggants, in particular inventively used metallic (nanoparticles) as security taggants.

[0032] Suitable magnetic nanoparticles for the present invention are preferably selected from the group of ferrite nanoparticles or iron oxide (magnetite or maghemite) nanoparticles. Such inventive magnetic nanoparticles may optionally be coated with a shell, wherein the shell material is preferably selected from the from of silica, silicones, polymers, and inorganic or organic acids. Alternatively, the inventive magnetic nanoparticles may comprise a magnetic core coated with a shell material, wherein the core material is preferably selected from the group consisting of elementary magnetic metal, more preferably iron, cobalt, or nickel, and wherein the shell material is selected from the grop consisting of metal oxides or graphene.

[0033] In general different concentrations of magnetic (nano) particles can be used to tag the silk fibroin. According to a preferred embodiment the magnetic particles, preferably magnetic nanoparticles are incorporated into silk fibroin at higher concentrations, preferably at a weight 0.1 to 10 wt.-%, alternatively 1, 2, 3, 4, 5, 6, 7, 8 or 9 wt.-% respectively based on the total weight of the silk fibroin used for the manufacture of the silk fibroin security marker.

[0034] Magnetic particles, preferably magnetic NPs to be used in the present invention can generally be authenticated by measuring the magnetic moment per atom and the magnetic anisotropy of nanoparticles as well as the Curie (TC) or the Néel (TN) temperatures, and the coercivity field (HC). Furthermore, the magnetic particles, preferably magnetic nanoparticles may also be authenticated by UV-Vis spectrometer, Fluorescence detection methods, Fourier transform infrared (FT-IR) spectroscopy, Raman spectroscopies, such as Surface Enhanced Raman Spectroscopy (SERS), Transmission Electron Microscopy (TEM), Scanning Electron Microscope (SEM) and magnetometer, and TeraHertz detection systems.

[0035] Magnetic particles, preferably magnetic nanoparticles are advantageous as taggants for the inventive security marker, as they can be detected also at higher speeds, such as present in high speed sorting machines for banknotes.

[0036] Suitable peptide sequences (also called amino acid tags) to be used as inventive taggants can be in the range up to 100 amino acid units. Preferably, the peptide sequence used as inventive taggant comprises or consists of an amino acid sequence, which is not naturally existing in the security marker silk fibroin and/or the security document, preferably banknote. The primary amino acid structure of naturally occurring silk fibroin mainly consists of the recurrent amino acid sequence $(Gly\text{-}Ser\text{-}Gly\text{-}Ala\text{-}Gly\text{-}Ala)_n$, wherein Gly represents glycine, Ser represents serine, Ala represents alanine and n represents a naturally occurring number bigger than 1. In particular, the peptide sequence used as taggant (amino acid tag) uses primarily amino acids that have a low concentration in the naturally occurring silk fibroin. Such amino acids with low natural concentration are preferably selected from the group consisting of serine, arginine, histidine, lysine, aspartic acid, glutamic acid, threonine, asparagines, glutamine, cystein, selenocystein, proline, valine, isoleucine, leucine, methionine, phenylalanine, tyrosine, and tryphtophan. By increasing those amino acids, which are at naturally low content in the silk fibroin, the security marker may be authenticated by detection of the specific amino acids above the respective natural threshold. The concentration of the inventively used peptide sequences (amino acid tags) can be up to 5 wt.-%, alternatively 1, 2, 3, or 4 wt.-% respectively based on the total weight of the silk fibroin used for the manufacture of the silk fibroin security marker.

[0037] The peptide sequence as security taggant in the inventive security marker may be different for different security documents, in particular banknotes. In case of banknotes, the banknotes of different denominations may comprise security markers tagged with different peptide sequences. Alternatively, each banknote may comprise a unique peptide sequence tagged with an inventive security marker. Such inventive peptide sequence tagged security markers provide a chemical fingerprint for the respective security documents, in particular banknotes, and can be detected in particular by using Ambient Mass Spectrometry (AMS) and XANES (X-ray absorption near-edge structures). Ambient Mass Spectrometry (AMS) can be considered an attractive alternative for security document, preferably banknote inspection at the molecular level due to its ability to provide direct, fast and highly specific molecular signatures and chemical selective mages from printed surfaces. Two desorption/ionization techniques (DESI and EASI) furthermore may function as an instantaneous, reproducible, and non-destructive method for chemical analysis of peptide sequence tagged inventive security markers in security documents, in particular banknotes. Alternatively, inventive banknotes comprising inventive security markers with peptide sequences different from the sequences with natural low concentration in silk fibroin may also be authenticated by Wide-Angle X-ray Scattering (WAXS), and Small-Angle X-ray Scattering (SAXS).

[0038] Ambient mass spectroscopy (AMS) can be easily automated for high throughput analysis using devices similar to those already applied for banknote counting. Miniature mass spectrometers able to operate with ambient ionization techniques are also being made more compact and robust. Therefore, the use of such hand-portable and affordable instruments would allow on-site (in banks or markets for instance) and wide-spread application of this nearly instantaneous and unbiased chemical fingerprinting method for banknote analysis and chemical security items.

[0039] According to a further alternative or cumulative preferred embodiment the inventive security marker may comprise or consist of further one, two or more different security taggants selected from the group consisting of luminescent agents, such as UV fluorescent agents, phosphorescent agents, and electroluminescent agents, as well as IR absorbing agents. In case the inventive security document comprises one further security taggant, then the term "different" does not apply. This said, the present invention does not relate to a security marker, in particular security fibre exhibiting as security taggants only an (inorganic) UV fluorescent chromophore and an (organic) IR absorbing chromophore. In particular the security fibre disclosed in WO 2015/114649 A1 is not comprised in the present invention.

[0040] In accordance with the present invention, the metallic and/or magnetic nanoparticles or peptide sequence may be conjugated with a suitable luminescent, preferably UV fluorescent agent. However, such a conjugation with a luminescent, preferably US fluorescent agent is not essential for carrying out the present invention and thus, may also not be conducted.

[0041] In accordance with an alternative or cumulative preferred embodiment of the first aspect of the present invention, the form of the inventively functionalized silk fibroin security marker is selected from the group consisting of fibres, films, gels, sponges and solutions.

[0042] The preferred embodiments of the first inventive aspect can be combined with each other as far as it is reasonable in view of a technical expert.

[0043] In accordance with the use of the inventive security marker within the substrate and/or on the surface of a security document as the second aspect of the present invention, the preferred embodiments of the inventive security marker as the first aspect of the present invention also apply.

[0044] In accordance with the process for the manufacture of an inventive security marker as the third aspect of the present invention, the preferred embodiments of the inventive security marker as the first aspect of the present invention also apply.

[0045] In accordance with the inventive security document, preferably banknote, markers as fourth aspect of the present invention, the preferred embodiments of the inventive security marker as the first aspect of the present invention also apply.

[0046] According to a preferred embodiment, the inventive security document comprises one, two, three, four or more differently functionalized inventive silk fibroin security markers incorporated within at least part of the security document substrate and/or applied as a coating at least on part of the surface of the security document, preferably banknotes.

[0047] According to an alternatively or cumulatively preferred embodiment, the inventive security document comprises one, two, three, four or more different forms, in particular selected from the group consisting of fibres, films, gels, sponges and solutions, of the same or of differently functionalized inventive silk fibroin security markers.

[0048] In accordance with the inventive process of manufacturing an inventively functionalized security document, preferably banknote, as the fifth aspect of the present invention, the preferred embodiments of the inventive security marker as the first aspect of the present invention also apply.

[0049] According to inventive functionalizing process step a) a suitable amount of silk fibroin, preferably an aqueous solution of silk fibroin e.g., commercially available or reengineered is provided (see D. N. Rockwood, R. C. Preda, T. Yücel, X. Wang, M. L. Lovett, D. L. Kaplan, Materials fabrication from Bombyx mori silk fibroin, Nat Protoc 2011, 6, 1612-1631).

[0050] In step b) of the inventive functionalizing process a suitable amount of one, two, three, four or more different security taggants selected from the group consisting of metallic particles, preferably metallic nanoparticles; magnetic particles, preferably magnetic nanoparticles; and peptide sequences, preferably in form of a colloidal aqueous dispersion, is/are provided. Preferably, the colloidal aqueous dispersion of the respective one, two, three, four or more different security taggants are previously homogenized, e.g. sonicated in particular for 10 minutes.

[0051] In step c) of the inventive functionalizing process the silk fibroin, preferably the aqueous silk fibroin solution of step a) is mixed with the one, two, three, four or more different security taggants, wherein the different security taggants are preferably used in form of a colloidal aqueous dispersion, of step b). The mixing can be conducted in a vessel comprising the silk fibroin of step a) or in a vessel comprising the respective security taggants of step b) or in a further vessel. The mixing is preferably conducted at ambient room temperature. The final silk fibroin concentration of the functionalized silk fibroin dispersion ranges preferably from 1 to 50 wt./vol. %, preferably 2 to 10 wt./vol. %, more preferably 5 wt./vol.%. The respective final security taggant concentration in the functionalized silk fibroin dispersion ranges preferably from 0.1 to 10 wt./wt. %, preferably 0.5 to 5 wt./wt. %, more preferably 0.6 wt./wt. %, 1.2 wt./wt. %, 1.8 wt./wt.%, 2.4 wt./wt. %, 3.0 wt./wt. % or 3.6 wt./wt.%.

[0052] The inventively functionalized silk fibroin dispersion may be used to form a film, a tube, a sponge, a fiber, or micrsosphrere, which can be inventively applied as a security marker within the substrate and/or on the surface of a security document. Possible production methods of respective films, tubes, sponges, fibers or microspheres are disclosed in D. N. Rockwood, R. C. Preda, T. Yücel, X. Wang, M. L. Lovett, D. L. Kaplan, Materials fabrication from Bombyx mori silk fibroin, Nat Protoc 2011, 6, 1612-1631 and are incorporated herein in its entirety. Accordingly, a functionalized silk fibroin film may be produced by drop casting a suitable amount of the functionalized silk fibroin dispersion (e.g., 160 μL per drop) onto a suitable substrate, such as glass or polydimethylsiloxane (PDMS), drying the resulting film, preferably slow drying in particular for 4 hours preferably in a sterile environment. In case PDMS is used as substrate, the resulting functionalized silk fibroin film may be piled off to be used as a free-standing functionalized silk fibroin film.

[0053] In accordance with the inventive process for authenticating the functionalized inventive security document, preferably banknote, as the sixth aspect of the present invention the preferred embodiments of the inventive security marker as the first aspect of the present invention also apply.

Claims

1. Functionalized silk fibroin security marker, **characterized in that** the silk fibroin comprises one, two, three, four or more different security taggants selected from the group consisting of metallic particles, preferably metallic nanoparticles; magnetic particles, preferably magnetic nanoparticles; and peptide sequences.

2. Security marker according to claim 1, wherein at least two different security taggants are selected.

3. Security marker according to claim 1 or 2, wherein the security marker comprises or consists of further one, two, three or more different security taggants selected from the group consisting of luminescent agents and IR absorbing agents.

4. Security marker according to any one of claims 1 to 3, wherein the form of the functionalized silk fibroin security marker is selected from the group consisting of fibres, films, gels, sponges and solutions.

5. Use of a security marker according to any one of claims 1 to 4 within the substrate and/or on the sur-

face of a security document.

6. Process for the manufacture of a security marker according to any one of claims 1 to 4, **characterized in that** the process comprises or consists of the following steps:

a) providing suitable amount of silk fibroin,
b) providing suitable amount of one, two, three, four or more different security taggants selected from the group consisting of metallic particles, preferably metallic nanoparticles; magnetic particles, preferably magnetic nanoparticles; and peptide sequences and
c) functionalizing the silk fibroin of step a) with the one, two, three, four or more different security taggants provided in step b).

7. Functionalized security document, preferably banknote, **characterized in that** the security document, preferably the banknote, comprises one, two, three, four or more differently functionalized silk fibroin security markers according to any one of claims 1 to 4.

8. Security document according to claim 7, wherein the one, two, three, four or more different functionalized silk fibroin security markers are incorporated within at least part of the security document substrate and/or are applied as a coating at least on part of the surface of the security document.

9. Security document according to claim 7 or 8, wherein the security document comprises one, two, three, four or more different forms, preferably selected from the group consisting of fibres, films, gels, sponges and solutions, of the same or of differently functionalized inventive silk fibroin security markers.

10. Process of manufacturing a functionalized security document, preferably banknote according to any one of claims 7 to 9, **characterized in that** the process comprises and/or consists of the following steps:

a) applying the one, two, three, four or more different security markers of any one of claims 1 to 4 within at least part of the substrate of the security document and/or
b) applying the one, two, three, four or more different security markers of any one of claims 1 to 4 at least on part of the surface of the security document.

11. Process for authenticating the functionalized silk fibroin security marker according to any one of claims 1 to 4 or the functionalized security document, preferably banknote, according to any one of claims 7 to 9, **characterized in that** the authenticating process comprises or consists of authenticating the functionalized security marker or the functionalized security document with one, two, three or more authenticating means selected from the group consisting of UV-VIS spectrometer, X-Ray Fluorescence Analyzer (XRF tool), magnetic sensor, ambient mass spectrometer (AMS), X-ray Absorption Near Edge Structures (XANES) detector, infrared (IR) spectrometer, Raman spectrometer, such as Surface Enhanced Raman Spectroscopy (SERS), refractometer, Localized Surface Plasmon Resonance (LSPR), Wide-Angle X-ray Scattering (WAXS), Small-Angle X-ray Scattering (SAXS), Fourier transform infrared (FT-IR) spectroscopy, Transmission Electron Microscopy (TEM), Scanning Electron Microscope (SEM) and Terahertz detection systems.

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EUROPEAN SEARCH REPORT

Application Number
EP 17 18 5930

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	WO 2006/008163 A2 (UNIV MUENCHEN TECH [DE]; SCHEIBEL THOMAS [DE]; HUEMMERICH DANIEL [DE];) 26 January 2006 (2006-01-26)	1-4	INV. D01F1/10 D01F4/02 B42D25/369 B42D25/373
A	* claims 1-3,14,15,20-22,34-37,45 * * figures 2,5 * * page 42, lines 10-20 * * page 19, lines 15-25 *	5-11	
X	WO 2012/031282 A2 (TUFTS UNIVERSITY TRUSTEES OF TUFTS COLLEGE [US]; OMENETTO FIORENZO [US) 8 March 2012 (2012-03-08)	1-4	
A	* claims 1-18 * * paragraph [0084] *	5-11	
X	WO 2012/145594 A2 (TUFTS COLLEGE [US]; LO TIM JIA-CHING [US]; LEISK GARY G [US]; LI LEI [) 26 October 2012 (2012-10-26)	1,2,4	
A	* claims 1-30 *	3,5-11	
Y,D	WO 2015/114649 A1 (COUNCIL SCIENT IND RES [IN]) 6 August 2015 (2015-08-06) * the whole document *	1-11	TECHNICAL FIELDS SEARCHED (IPC)
Y	US 2011/291401 A1 (BERGSMANN MARTIN [AT] ET AL) 1 December 2011 (2011-12-01) * example 7 * * paragraph [0087] *	1-11	D01F B42D
Y	WO 2009/140266 A2 (UNIV CORNELL [US]; HERZ ERIK [US]; HENDRICK ERIN SUE [US]; FREY MARGAR) 19 November 2009 (2009-11-19) * claims 24,26,40 * * paragraphs [0004], [000186] *	1-11	
Y	WO 2015/006117 A1 (CELANESE ACETATE LLC [US]) 15 January 2015 (2015-01-15) * claims 1-15 * * paragraphs [0001] - [0003], [0025] *	1-11	

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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	27 November 2017	Verschuren, Jo

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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Application Number
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Place of search	Date of completion of the search	Examiner
The Hague	27 November 2017	Verschuren, Jo

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