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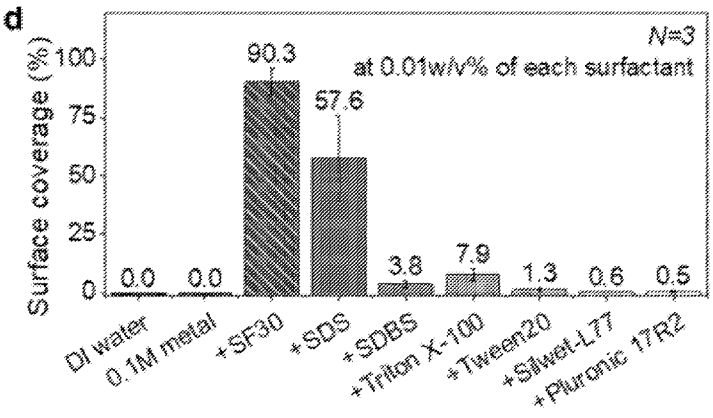

Fig. 2

(57) Abstract: The present disclosure provides methods, systems, and compositions where silk fibroin is used as a surfactant. Silk fibroin can have an unexpectedly large impact on surface energy at very low concentrations, while having a very small impact on the surface tension properties of the aqueous liquid itself. Silk fibroin showed exceptional capacity to enhance wetting of hard-to-wet surfaces, exceeding the performance of conventional surfactants. In cases where it is important for an aqueous industrial process to maintain surface tension while enhancing surface wetting, silk fibroin may provide enhanced wetting without significantly altering the surface tension of the aqueous solution.

WO 2025/137239 A1

SILK FIBROIN SURFACTANTS AND METHODS OF MAKING AND USING THE SAME

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims priority to and the benefit of U.S. Provisional Application No. 63/612,080, filed in the U.S. Patent and Trademark Office on Dec. 19, 2023. The foregoing patent application is incorporated herein by reference in its entirety for all purposes.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH

[0002] This invention was made with government support under N00014-19-1-2399 awarded by the Department of Defense. The government has certain rights in the invention.

BACKGROUND

[0003] At a rudimentary level of understanding of how surfactants function in industrial processes, surfactants immediately impact the surface tension and can improve surface wetting by changing the contact angle from a steeper contact angle to a lower angle, thereby allowing the liquid to spread out more on a surface. At a deeper level of understanding, surfactants can impact interactions at various interfaces and these impacts can operate by other mechanisms of action which do not necessarily result in an immediate change of surface tension. The surfactant can adjust surface energy of a substrate, which can thereby allow easier deposition of a material, for example. It can do all of this with or without changing surface tension.

[0004] A person having ordinary skill in the art of industrial processes that involve surface wetting (e.g., semiconductor processing, electronics processing, etc.) would have a rudimentary level of understanding of how surfactants work. As such, they would typically deploy surfactants for the purpose of adjusting surface tension. For these skilled artisans, if a surfactant does not have an immediate impact on contact angle, then such a surfactant would typically be termed "poor" performing or worse.

[0005] At a higher level of skill with a more sophisticated understanding of surface chemistry, it may be appreciated that surfactant performance is not limited to an ability to immediately adjust surface tension. In this context, there are a wide variety of aqueous processes that are presently sub-optimal by virtue of insufficient surface wetting. As one example, aqueous deposition of metal remains challenging on a wide variety of surfaces due to energetic mismatch between the surfaces and the aqueous environment.

[0006] A need exists for new and improved surfactants which are capable of overcoming one or more of the aforementioned shortcomings. In some cases, without wishing to be bound by any particular theory, there may be advantages to having the capability to improve surface wetting without immediately impacting surface tension.

SUMMARY

[0007] In one aspect, the present disclosure provides a method of using silk fibroin as a surfactant. The method includes wetting a first surface with an aqueous silk solution comprising silk fibroin in an amount by weight of between 0.001% and 0.10%. Depositing pure water onto the first surface produces a contact angle of greater than 90°. The wetting provides at least 75% surface coverage.

[0008] In another aspect, the present disclosure provides a method of depositing a layer of a predetermined solute from an aqueous solvent onto a predetermined surface. The predetermined solute is optionally a metal precursor. The method includes contacting the predetermined surface with an aqueous silk solution comprising the predetermined solute and silk fibroin in an amount by weight of between 0.001% and 0.10%. The predetermined solute is present in an amount sufficient for depositing onto the predetermined surface. The contacting thereby deposits the predetermined solute onto the predetermined surface.

[0009] In a further aspect, the present disclosure provides a method of improving an industrial process that does not previously utilize silk fibroin. The industrial process includes at least one aqueous solution that does not adequately wet a first surface. The method includes adding silk fibroin to the at least one aqueous solution in an amount by weight of between 0.001% and 0.10%. The at least one aqueous solution adequately wets the first surface upon addition of the silk fibroin.

[0010] In yet another aspect, the present disclosure provides a method of using silk fibroin as a surfactant. The method includes, within a single process that wets two different surfaces having different surface energies, using silk fibroin as a surfactant for wetting the two different surfaces having the different surface energies, wherein the wetting achieves at least 50% surface coverage on each of the two different surfaces.

[0011] In another aspect, the present disclosure provides a method of using silk fibroin as a surfactant. The method includes the following sequential steps: a) wetting a first surface with an aqueous silk solution including silk fibroin in an amount by weight of between 0.001% and 0.10%; b) drying the first surface; and c) removing residual silk fibroin from the dried first surface.

[0012] In a further aspect, the present disclosure provides a method of improving surface wetting. The method includes: a) measuring an immediate comparison contact angle and optionally a time-varying comparison contact angle for a comparison aqueous solution applied to a first surface; and b) applying an aqueous silk solution consisting essentially of the comparison aqueous solution and silk fibroin in an amount by weight of between 0.001% and 0.10%. An immediate contact angle of the aqueous silk solution is the same or greater than the comparison contact angle immediately following

applying. The time-varying contact angle of the aqueous silk solution is lower than the comparison contact angle after 1 minute or more following the applying.

[0013] In another aspect, the present disclosure provides a method of making a nanoscale silk coating. The method includes: spin coating an aqueous silk fibroin solution on a first surface to form a deposited silk film; and rinsing the deposited silk film with deionized water, thereby forming the nanoscale silk coating.

[0014] These and other systems, methods, objects, features, and advantages of the present disclosure will be apparent to those skilled in the art from the following detailed description of the preferred embodiment and the drawings.

[0015] References to items in the singular should be understood to include items in the plural, and vice versa, unless explicitly stated otherwise or clear from the text. Grammatical conjunctions are intended to express any and all disjunctive and conjunctive combinations of conjoined clauses, sentences, words, and the like, unless otherwise stated or clear from the context.

BRIEF DESCRIPTION OF THE FIGURES

[0016] The disclosure and the following detailed description of certain embodiments thereof may be understood by reference to the following figures:

[0017] Fig. 1A is a schematic diagram illustrating amphiphilicity of regenerated silk fibroin (SF) chain.

[0018] Fig. 1B is a schematic illustration of the improvement in surface coverage achieved by spin-coating a metal hydrate solution with increasing concentrations of SF.

[0019] Fig. 1C depicts surface coverage (%) of SF-added aqueous metal solution on (Fig. 1c) an untreated SiO_2 substrate as a function of concentration and boiling time (*i.e.*, molecular weight).

[0020] Fig. 1D depicts surface coverage (%) of a SF-added aqueous metal solution a hydrophobic treated SiO_2 substrate as a function of concentration and boiling time (*i.e.*, molecular weight).

[0021] Fig. 2A depicts time-dependent evolution of interfacial tension by SF in aqueous solution.

[0022] Fig. 2B depicts the time-dependent evolution of work of adhesion by SF in aqueous solution.

[0023] Fig. 2C depicts the initial contact angle and attained with SF with respect to other commercial and state-of-the-art surfactants.

[0024] Fig. 2D depicts the surface coverage attained with SF with respect to other commercial and state-of-the-art surfactants.

[0025] Fig. 3A is a schematic illustration of the self-segregation of the surfactant during the coating process.

[0026] Fig. 3B is an XPS depth profiling for chemical compositional analysis of a 25 nm thick In_2O_3 film with 0.3 w/v% silk at varying depth.

[0027] Fig. 3C is a N1s distribution in an In_2O_3 film with SF deposited on substrates with different free surface energies. Left: fluoro-octyl-trichloro-silane (FOTS)-treated SiO_2, middle: untreated SiO_2, right: plasma-treated SiO_2. The white dashed line indicates the interface with the SiO_2 substrate.

[0028] Fig. 3D depicts height (left) and deflection (right) AFM maps of the buried SF layer, obtained by selectively etching the metal oxide (scale bar: 1 μm). Left: FOTS-treated SiO_2; middle: untreated SiO_2; right: plasma-treated SiO_2.

[0029] Fig. 4A depicts the structure of a SiO_2-gated IGZO:SF-based field effect transistor (FET) (left). Transfer curves (center) of transistors fabricated with varying SF amounts and charge mobility (right) of transistors with varying SF amounts over different surface energy substrates.

[0030] Fig. 4B depicts the structure of an Al_2O_3:SF-based insulator (left) and its current density-electric field curves.

[0031] Fig. 4C depicts the structure of a $MAPbI_3$:SF-based perovskite (left). I-V characteristics of the fabricated $MAPbI_3$ film under white light illumination at different lateral voltages (center) and in time (right).

[0032] Fig. 4D depicts the structure of a NiO:SF-based photodetector (left) and its I-V characteristics under white light illumination (right). All devices are fabricated over hydrophobic-treated substrates.

[0033] Fig. 5 depicts comparative performances of SF and commercial surfactants. Surface coverage comparison between aqueous solutions containing silk surfactants and other commercial surfactants over the same hydrophobic substrates.

[0034] Fig. 6 depicts XPS depth profiling of C1s (top left), N1s (top right), O1s (bottom left), and Si2p (bottom right) of pure silk fibroin film to investigate how silk fibroin is distributed in the metal oxide film.

[0035] Fig. 7 depicts XPS N1s signal mapping in indium oxide films made of aqueous metal precursor with varying silk concentrations on substrates with different surface energies. Left: FOTS-treated SiO_2; middle: untreated SiO_2; right: plasma-treated SiO_2.

[0036] Fig. 8A depicts AFM micrographs of the solid SF aggregates formed at the interface.

[0037] Fig. 8B depicts the as received substrate for reference.

[0038] Fig. 9 depicts the adaptive adsorption behavior of silk surfactants.

[0039] Fig. 10 depicts the universality of silk surfactant-assisted wetting for various water-enabled nanodevices.

[0040] Fig. 11A depicts a multi-layer stacking process by sequential coating over universal substrates without surface treatment. The coated film can be transferred to the desired substrate through release technology.

[0041] Fig. 11B depicts device structure of an Al_2O_3-gated IGZO transistor prepared by sequential coating of each metal precursor.

[0042] Fig. 11C depicts a transfer curve of an Al_2O_3-gated IGZO transistor prepared by sequential coating of each metal precursor.

[0043] Fig. 11D depicts a transfer-printed halide perovskite ($MAPbI_3$) film over a transparent PET film.

[0044] Fig. 11E depicts the optical properties of a $MAPbI_3$ film.

DETAILED DESCRIPTION

[0045] Before the present disclosure is described in further detail, it is to be understood that the disclosure is not limited to the particular embodiments described. It is also understood that the terminology used herein is for the purpose of describing particular embodiments only, and is not intended to be limiting. The scope of the present disclosure will be limited only by the claims. As used herein, the singular forms "a", "an", and "the" include plural embodiments unless the context clearly dictates otherwise.

[0046] In this application, unless otherwise clear from context, (i) the term “a” may be understood to mean “at least one”; (ii) the term “or” may be understood to mean “and/or”; (iii) the terms “comprising” and “including” may be understood to encompass itemized components or steps whether presented by themselves or together with one or more additional components or steps; and (iv) the terms “about” and “approximately” are used as equivalents and may be understood to permit standard variation as would be understood by those of ordinary skill in the art; and (v) where ranges are provided, endpoints are included.

[0047] ***Approximately:*** as used herein, the term “approximately” or “about,” as applied to one or more values of interest, refers to a value that is similar to a stated reference value. In certain embodiments, the term “approximately” or “about” refers to a range of values that fall within 25%, 20%, 19%, 18%, 17%, 16%, 15%, 14%, 13%, 12%, 11%, 10%, 9%, 8%, 7%, 6%, 5%, 4%, 3%, 2%, 1%, or less in either direction (greater than or less than) of the stated reference value unless otherwise stated or otherwise evident from the context (except where such number would exceed 100% of a possible value).

[0048] ***Composition:*** as used herein, may be used to refer to a discrete physical entity that comprises one or more specified components. In general, unless otherwise specified, a composition may be of any form – e.g., gas, gel, liquid, solid, etc. In some embodiments, "composition" may refer to a combination of two or more entities for use in a single embodiment or as part of the same article. It is not required in all embodiments that the combination of entities result in physical admixture, that is, combination as separate co-entities of each of the components of the composition is possible; however many practitioners in the field may find it advantageous to prepare a composition that is an admixture of two or more of the ingredients in a pharmaceutically acceptable carrier, diluent, or excipient, making it possible to administer the component ingredients of the combination at the same time.

[0049] ***Improve, increase,*** **or** ***reduce:*** as used herein or grammatical equivalents thereof, indicate values that are relative to a baseline measurement, such as a measurement in a similar composition made according to previously known methods.

[0050] ***Substantially:*** as used herein, the term "substantially" refers to the qualitative condition of exhibiting total or near-total extent or degree of a characteristic or property of interest. One of ordinary skill in the biological arts will understand that biological and chemical phenomena rarely, if ever, go to completion and/or proceed to completeness or achieve or avoid an absolute result. The term "substantially" is therefore used herein to capture the potential lack of completeness inherent in many biological and chemical phenomena.

[0051] It should be apparent to those skilled in the art that many additional modifications beside those already described are possible without departing from the inventive concepts. In interpreting this disclosure, all terms should be interpreted in the broadest possible manner consistent with the context. Variations of the term "comprising" should be interpreted as referring to elements, components, or steps in a non-exclusive manner, so the referenced elements, components, or steps may be combined with other elements, components, or steps that are not expressly referenced. Embodiments referenced as "comprising" certain elements are also contemplated as "consisting essentially of" and "consisting of" those elements. When two or more ranges for a particular value are recited, this disclosure contemplates all combinations of the upper and lower bounds of those ranges that are not explicitly recited. For example, recitation of a value of between 1 and 10 or between 2 and 9 also contemplates a value of between 1 and 9 or between 2 and 10.

[0052] As used herein, "silk fibroin" refers to silk fibroin protein whether produced by silkworm, spider, or other insect, or otherwise generated (Lucas et al., Adv. Protein Chem., 13: 107-242 (1958)). Any type of silk fibroin can be used in different embodiments described herein. Silk fibroin

produced by silkworms, such as Bombyx mori, is the most common and represents an earth-friendly, renewable resource. For instance, silk fibroin used in a silk film may be attained by extracting sericin from the cocoons of B. mori. Organic silkworm cocoons are also commercially available. There are many different silks, however, including spider silk (e.g., obtained from Nephila clavipes), transgenic silks, genetically engineered silks, such as silks from bacteria, yeast, mammalian cells, transgenic animals, or transgenic plants, and variants thereof, that can be used. See, e.g., WO 97/08315 and U.S. Pat. No. 5,245,012, each of which is incorporated herein by reference in their entireties.

[0053] The present disclosure provides a variety of methods which are believed to be separate and distinct inventions, but which have some degree of overlap with one another by virtue of sharing one or more common features. Unless the context clearly dictates otherwise, a feature that is described with respect to one method is applicable to any of the methods described herein. For example, if a silk fibroin concentration is disclosed for a method of using silk fibroin as a surfactant, then that silk fibroin concentration is also applicable to a disclosed method of depositing a layer of predetermined solute from an aqueous solvent onto a predetermined surface.

[0054] The present disclosure provides a method of using silk fibroin as a surfactant.

[0055] In one aspect, the method of using silk fibroin as a surfactant includes wetting a first surface with an aqueous silk solution comprising silk fibroin in an amount by weight of between 0.001% and 0.10%. The first surface is hydrophobic. Depositing pure water onto the first surface produces a contact angle of greater than 90°. The wetting provides at least 75% surface coverage, as measured using the methods described herein.

[0056] In one aspect, the method of using silk fibroin as a surfactant includes, within a single process that wets two different surfaces having different surface energies, using silk fibroin as a surfactant for wetting the two different surfaces having the different surface energies, wherein the wetting achieves at last 50% surface coverage on each of the two different surfaces.

[0057] In one aspect, the method of using silk fibroin as a surfactant includes the following sequential steps: a) wetting a first surface with an aqueous silk solution comprising silk fibroin in an amount by weight of between 0.001% and 0.10%; b) drying the first surface; and c) removing residual silk fibroin from the dried first surface. Without wishing to be bound by any particular theory, it is believed that silk fibroin may be uniquely capable of functioning as a surfactant while also being readily isolated from the system following its use as a surfactant.

[0058] Removing residual silk fibroin from a dried surface (e.g., the dried first surface) can involve rinsing, optionally with deionized water. The specific means of removing residual silk fibroin from the dried surface is not intended to be limiting.

[0059] Wetting can be measured in a variety of ways, as can be appreciated by a skilled artisan. In one case, wetting is determined by an ability to deposit a solute onto a surface. Greater ability to deposit the solute represents a higher degree of wetting. In some cases, the ability to deposit metal onto a surface correlates with a degree of wetting. In some cases, surface coverage of deposition of a solute as a percentage value can be used to define a degree of wetting as used herein. In some specific examples, the method of determining surface coverage includes: acquiring a digital image of a surface (e.g., a spin-coated surface, or a surface coated via dip-coating, spray coating, screen printing, or roll-to-roll processing), where a coated nanofilm and substrate have visible color contrast, from a top perspective (e.g., using a DSLR camera setup); converting the original images into a threshold mask image using image analysis software (e.g., ImageJ software); and surface coverage was quantitatively measured.

[0060] In some cases, the wetting described herein provides at least 75% surface coverage. In some cases, the wetting described herein provides at least 80% surface coverage. In some cases, the wetting described herein provides at least 85% surface coverage. In some cases, the wetting described herein provides at least 90% surface coverage.

[0061] The present disclosure provides a method of depositing a layer of a predetermined solute from an aqueous solvent onto a predetermined surface. In some cases, the predetermined solute can optionally be a metal precursor. The method includes contacting the predetermined surface with an aqueous silk solution comprising the predetermined solute and silk fibroin in an amount by weight of between 0.001% and 0.10%. The predetermined solute is present in the aqueous silk solution in an amount sufficient for depositing onto the predetermined surface (e.g., above a minimal threshold). The contacting thereby deposits the predetermined solute onto the predetermined surface. The layer can have one or more of the properties described herein with respect to a nanoscale silk coating (e.g., thickness, uniformity of thickness, water uptake). Once deposited, the layer can be further processed as would be appreciated by a skilled artisan (e.g., patterning).

[0062] The first surface and/or the predetermined surface can be a metal surface, a semiconductor surface, a polymeric surface, or the like. Examples of suitable metal surfaces include, but are not limited to, gold, silver, platinum, alloys thereof, and the like. Examples of suitable semiconductor surfaces include, but are not limited to, silicon, type III-V semiconductors, such as GaAs or GaN, type II-VI semiconductors, such as CdSe, CdS, CdTe, ZnSe, ZnS, or ZnTe, and the like. Examples of

suitable polymeric surfaces include but are not limited to elastomeric surfaces (e.g., PDMS), thin polymeric films (e.g., PET films), and the like.

[0063] The specific surface is not intended to be limited. The scope of materials covered by the disclosure includes materials having the surface energy properties that a skilled artisan would recognize as appropriate for the present disclosure (e.g., surface energy that causes a contact angle of greater than 90° with pure water).

[0064] In some cases, the surface is a portion of a semiconductor device. Semiconductor devices typically include a substrate, an electrode layer, and a semiconductor layer. The electrode layer and semiconductor layer are each on the substrate. The first surface can be located on the electrode layer and/or the semiconductor layer.

[0065] The present disclosure provides a method of improving an industrial process that does not previously utilize silk fibroin. The industrial process includes at least one aqueous solution that does not adequately wet a first surface. The method includes adding silk fibroin to the at least one aqueous solution in an amount by weight of between 0.001% and 0.10%. The adding adequately wets the first surface upon addition of the silk fibroin. One exemplary industrial process that does not currently use silk fibroin and which would benefit from the use of silk fibroin as a surfactant as described herein is industrial semiconductor manufacturing. Other exemplary industrial processes include, but are not limited to, industrial painting and/or paint manufacturing, industrial coating and/or coating manufacturing, industrial adhesives and/or adhesive manufacturing, industrial film manufacturing by solution processing, and the like.

[0066] The present disclosure provides a method of improving surface wetting. The method includes: a) measuring an immediate comparison contact angle and optionally a time-varying comparison contact angle for a comparison aqueous solution applied to a first surface; and b) applying an aqueous silk solution consisting essentially of or consisting of the comparison aqueous solution and silk fibroin in an amount by weight of between 0.001% and 0.10%. The immediate contact angle of the aqueous silk solution is the same or greater than the comparison contact angle immediately following applying. The time-varying contact angle of the aqueous silk solution is lower than the comparison contact angle after 1 minute or more following the applying.

[0067] While the time-varying contact angle of the aqueous silk solution is lower than the comparison contact angle to a given degree (e.g. some defined percent lower or some defined percent greater change over time), the surface tension of the aqueous silk solution is not altered to the same degree. If the contact angle changes by a given amount, the surface tension changes by only 50% as

much, 25% as much, or even 10% as much. In some cases, the surface tension is not measurably altered, while the contact angle is changed.

[0068] The present disclosure provides a method of making a nanoscale silk coating. The method includes: spin coating an aqueous silk fibroin solution on a first surface to form a deposited silk film; and rinsing the deposited silk film with deionized water, thereby forming the nanoscale silk coating. The method can also include spin coating a protective layer on the nanoscale silk coating. The protective layer can be polymethyl methacrylate (PMMA). The method can also include spin coating a photoresist on the protective layer and developing the photoresist.

[0069] The methods described herein can include patterning of a deposited silk film or any deposited layers (e.g., protecting layer). Patterning can include etching. Patterning can include O_2 plasma treatment.

[0070] When a silk film or nanoscale silk coating is deposited, either as a permanent part of a device or structure or as a sacrificial layer, the silk film or nanoscale silk coating can be further treated with and/or immersed in an organic solvent. The organic solvent can be selected from the group consisting of methanol, ethanol, acetone, glacial acetic acid (and perhaps other acidic solvents), and combinations thereof.

[0071] A deposited silk film or nanoscale silk coating can have a thickness that is tailored for a given use and is unexpectedly uniform. The deposited silk film or nanoscale silk coating can have a thickness of at most 300 nm, at most 200 nm, at most 100 nm, at most 50 nm, at most 10 nm, or at most 5 nm. The deposited silk film or nanoscale silk coating can have a thickness of at least 3 nm, at least 5 nm, at least 10 nm, at least 50 nm, at least 100 nm, or at least 200 nm. The deposited silk film or nanoscale silk coating has a thickness that varies by less than plus or minus 25%, less than plus or minus 20%, less than plus or minus 15%, or less than plus or minus 10% across the entire nanoscale silk coating. The deposited silk film or nanoscale silk coating can have a free water uptake of at least 12%wt, at least 10%wt, at least 8%wt, or at least 6%wt.

[0072] In cases where patterning is utilized, a deposited and patterned silk film or a patterned nanoscale silk coating can have lateral resolution of at most 5 μm, at most 4 μm, at most 3 μm, at most 2 μm, or at most 1 μm.

[0073] The aqueous silk solution for use in any of the methods described herein can include silk fibroin in an amount by weight of between 0.001% and 0.10%. In some cases, the concentration could extend slightly higher and include a range of between 0.001% and 0.20%. In some cases, the aqueous silk solution includes silk fibroin in an amount by weight of at least 0.001%, at least 0.005%, at least 0.01%, at least 0.02%, at least 0.03%, at least 0.04%, at least 0.05%, at least 0.06%,

at least 0.07%, or at least 0.09%. In some cases, the aqueous silk solution includes silk fibroin in an amount by weight of at most 0.10%, at most 0.09%, at most 0.08%, at most 0.075%, at most 0.07%, at most 0.06%, at most 0.05%, at most 0.04%, at most 0.03%, or at most 0.02%, or at most 0.01%. Applicant discovered that an unexpectedly small amount of silk fibroin can have an unexpectedly large impact on one or more advantageous properties (e.g., ability to deposit metal on a given surface). In some cases, the aqueous silk solution may include silk fibroin in an amount by weight of between 0.01% and 0.10%. In some cases, the aqueous silk solution may include silk fibroin in an amount by weight of between 0.001% and 0.01%. In some cases, the aqueous silk solution may include silk fibroin in an amount by weight of between 0.05% and 0.10%. In some cases, the aqueous silk solution may include silk fibroin in an amount by weight of between 0.001% and 0.05%. In some cases, the aqueous silk solution may include silk fibroin in an amount by weight of between 0.01% and 0.05%.

[0074] The aqueous silk solution can, and in the case of some of the disclosed methods (i.e., the method of depositing a solute) does, include one or more non-silk, non-water components, such as electrolytes, solutes, and the like. Specifically, the aqueous silk solution can, and in the case of some methods does, include a precursor that is intended to be deposited on the first surface. The precursor can be a metal precursor or a semiconductor precursor. A skilled artisan will recognize that some aqueous deposition processes are presently hindered by an inability to wet certain surfaces and the disclosed methods may be applicable to those aqueous deposition processes and certain surfaces.

[0075] The aqueous silk solution can include additives that are functional or non-functional, with various practical limits as would be appreciated by a skilled artisan. In some cases, the aqueous silk solution can include one or more bioreactive elements. Examples of bioreactive elements include, but are not limited to, enzymes (e.g., horseradish peroxidase), antibiotics (e.g., Doxorubicin, Ciprofloxacin, etc.), proteins (e.g., BPT-2 or P24 protein), or the like. If the method is being utilized within a specific process, then the nature of that underlying process may significantly impact the nature of the additives. For instance, if a method is utilized in a metal deposition process, then additives that are reactive with metal precursors would be excluded, though they may be contemplated in other embodiments.

[0076] One particularly unexpected achievement gained by the methods disclosed herein is the provision of a surfactant that has only a modest impact on the time-varying surface tension of a solution itself while simultaneously having a significant impact on one or more of a time-varying contact angle, a wetting capability, and/or a surface coverage performance.

[0077] In some cases, the use of silk fibroin as described herein can cause an impressive change in contact angle and surface tension after 1 minute, 2 minutes, 3 minutes, 4 minutes, 5 minutes, 6 minutes, 7 minutes, 8 minutes, 9 minutes, or 10 minutes. Such change decouples the surface tension from the contact angle in a fashion that is not achieved by other surfactants. Silk fibroin has a unique combination of a small impact on surface tension and a large impact on contact angle. In other words, traditional surfactants appear to function by fundamentally altering the properties of water, such that the surface tension changes (e.g., interface with air) and the contact angle changes (e.g., interface with a surface), while the silk fibroin surfactant appears to function by minimally altering the properties of water, such that the surface tension is minimally altered, while impacting the contact angle by virtue of the surfactant's impact at the surface. This observation exposes a major advantage of the disclosed methods: because the mechanism of action is limited to the water-surface interface, and because such an interface represents a very small fraction of area/volume of a liquid covering a surface, the amount of silk fibroin surfactant can be incredibly small when compared to the amount of traditional surfactant that is required. While traditional surfactants typically remain in solution and continue altering the material properties of water throughout the bulk of the water as they function, the hypothesized mechanism of action of the silk fibroin surfactant requires only so much silk fibroin surfactant as is needed to sufficiently alter the surface energy (i.e., molecules from throughout the volume of water can be aggregated at the surface, thus depleting their concentration in the water, which has minimal impact on water's bulk material properties). The use of less material lowers costs and also simply imposes fewer observed and potential changes in aqueous solutions which might impact their function. Silk fibroin surfactants may allow larger area surfaces to be wetted during industrial processes, while minimally impacting the chemical nature of the aqueous solutions used in those processes.

[0078] The disclosure presents a novel and promising approach for controlling interfacial energy in the solution processing field by utilizing SF, an amphiphilic biopolymer. The disclosure demonstrates that SF exhibits superior interfacial energy control efficiency compared to commercial surfactants, enabling effective aqueous solution processing over universal surfaces. In the context of wetting, SF can interact favorably with non-polar surfaces through adsorption and act as intermolecular bridges between solid-liquid interfaces. This behavior improves surface coverage of aqueous solutions on hydrophobic substrates even at very low concentrations (0.01 w/v%) of SF. The fibroin heavy chains, which are composed of internal hydrophobic blocks and hydrophilic regions at the chain ends, can adsorb on hydrophobic substrates, lying flat along the surface, resulting in self-segregation and forming high-purity metal oxide films on the substrate. The efficacy of this approach

is demonstrated through the fabrication of transistors, capacitors, and photodetectors using various aqueous metal precursors containing 0.01 wt% silk, which were spin-coated onto hydrophobic substrates. The prepared devices can be successfully transferred to flexible substrates or released to become self-standing devices using a simple approach. The unique adsorption of SF provides a promising alternative to traditional surfactants for aqueous solution processing over universal substrates. It opens up opportunities to integrate natural materials and technologies while providing excellent practicality, environmental sustainability, and stability.

[0079] The control of solid-liquid interfacial energy has been studied extensively due to its importance in various fields, including surface science, materials science, and engineering fields like solution processing. Solution processing refers to the use of liquid solutions to deposit, pattern, and process materials. This technique is attractive due to its low cost, ease of operation, and potential for large-area processing. To achieve high-quality films and patterns, it is essential to optimize the interfacial energy between the solid substrate and liquid solution.

[0080] In recent years, the demand for aqueous solution processing techniques has been increasing recently. Water is abundant and less environmentally harmful than most organic solvents used in traditional manufacturing methods, and it can also be used as a recyclable and renewable energy source. In addition, water has already been used for a long time as a common solvent in various industrial fields and has been evaluated for performance and stability. Despite the advantages of using water as a solvent, there are still limitations to its application. The main limitation is the difficulty in achieving good wetting on certain substrates, which can limit the versatility of the process. To overcome this limitation, various surface treatment techniques could be utilized, such as physical and chemical surface treatments or the addition of surfactants to the solution.

[0081] However, these methods have their own drawbacks, such as technical difficulties, high cost, or environmental concerns. For example, surface treatment methods can damage the substrates or underlaid films in case of multilayered structure fabrication. Surfactant molecules may remain within the fabricated structures, which deteriorate the material properties. Also, acid/base chemicals for surface treatment and some commercial surfactants require special caution due to adverse health and environmental effects. Therefore, there is a need for efficient, versatile, and sustainable methods that can overcome these limitations and enable the use of water-based solutions in a wider range of applications.

[0082] Natural amphiphiles, which can act as an interfacial bridge through adsorption, are well known for their robust and universal adhesion. SF extracted from *Bombyx Mori* cocoon is an excellent candidate for a natural surfactant. The heavy chains of SF are amphiphilic, consisting of

large terminal hydrophilic parts and internal hydrophobic blocks. Also, they mainly consist of four amino acids: Glycine (Gly), Alanine (Ala), Serine (Ser), and Tyrosine (Tyr) that account for about 92% of total fibroin. Gly and Ala have aliphatic side chains making them hydrophobic. On the contrary, Ser and Tyr show hydrophilic properties due to the hydroxyl group in their chemical structure. Despite the fact that this amphiphilic biopolymer can facilitate intermolecular interactions by regulating the interfacial energy, there is a lack of research acknowledging silk as a natural surfactant and exploring the integration of biological materials into modern technology.

[0083] Natural amphiphile fibroins can play a universal interfacial bridge enabling aqueous solutions to overcome the wetting limitation. The unique polarity distribution of the heavy chains in silk enables efficient control of the interfacial energy at the molecular level. This finding suggests that silk-aqueous solution mixture can effectively interact with universal surfaces. Quantitative comparison was performed to assess the efficacy of SF surfactant in improving surface coverage relative to commercial products at equivalent concentrations, demonstrating its superior performance. The adsorption of SF at the wetting interface is attributed to molecular interactions between fibroin and the surface. Macroscopic surface coverage is determined by the molecular weight of silk and its concentration in aqueous solution. The hydrophobic block of fibroin demonstrates favorable adsorption on non-polar surfaces, resulting in the creation of a self-separated adsorption layer. This layer has a flat topology along the surface and is localized at the interface, making it ideal for forming high-purity metal oxide films on hydrophobic substrates. As a demonstration of universality and efficacy, electronic and photonic devices are fabricated by coating diverse aqueous solution-based metal precursors onto hydrophobic substrates. The resultant devices show comparable performances to those fabricated using a conventional vacuum processing method. Furthermore, as-coated film devices are transferred to flexible substrates or delaminated to be free-standing devices, demonstrating the expandability of this technology.

[0084] This disclosure proposes the use of an amphiphilic biopolymer, specifically silk fibroin extracted from *Bombyx Mori* cocoon, as a superior surfactant candidate to address current problems in the aqueous solution-processing field in an efficient, universal, inexpensive, and sustainable manner. Silk fibroin exhibits superior wetting enhancement compared to commercial surfactants. For instance, a trace amount of silk fibroin (0.01w/v%) can wet an aqueous metal precursor over hydrophobic substrates, resulting in greater than 90% surface coverage, whereas conventional surfactants exhibit less than 70% surface coverage.

[0085] The superior wetting performance of silk fibroin is attributed to its efficient interfacial energy control ability. The unique polarity distribution and long chain structure of silk fibroin's

heavy chain enable it to have excellent adsorption capability on most substrates and act as an intermolecular bridge for adhesion between the substrate and the aqueous solution. By measuring the surface tension of the liquid over time and the contact angle between the substrate and the solution, it was confirmed that silk has excellent interfacial energy control ability according to Young's equation.

[0086] This adsorption behavior is independent of the substrate's surface-free energy and does not require any separate surface treatment. Regarding a non-pretreated substrate, an even much lower concentration of silk fibroin (0.005 w/v%) is sufficient to wet aqueous solutions, whereas the pure aqueous metal solution results in partial wetting over the same substrate.

[0087] Moreover, this technology is applicable to any water-soluble precursor solution. In this disclosure, more than nine water-based metal precursor solutions were successfully coated on hydrophobic substrates. The coated films showed performance comparable to vacuum-processed devices as electronic or photonic devices.

[0088] Finally, functional films coated on substrates with low surface energy can be transferred onto other transparent and flexible polymer substrates using transfer printing techniques or can be delaminated as self-standing functional thin films.

[0089] Taken together, this disclosure suggests the potential of silk fibroin as an effective, universal, renewable, and sustainable surfactant candidate.

[0090] The present disclosure provides a novel solution to the physical limitation of aqueous solution wetting by demonstrating the superior efficiency, versatility, and sustainability of using silk fibroin as a surfactant. Compared to other commercial surfactants, silk fibroin requires a lower mass-to-volume ratio (w/v%) to achieve over 90% surface wetting results in aqueous solutions. In addition, silk fibroin can be applied to coat any water-based precursor over any substrate without the need for additional pre-treatment steps and regardless of the substrate's surface energy. Furthermore, silk fibroin is an FDA-approved natural protein, ensuring the sustainability of the technique. Overall, the present invention provides a highly efficient, versatile, and sustainable solution to the problem of aqueous solution wetting by utilizing silk fibroin as a superior surfactant.

[0091] Solution processing is a flexible method for producing a variety of materials by using solutions or suspensions of chemical precursors. Aqueous solution processing is a type of solution processing that uses water-based solvents instead of organic solvents, which can reduce health hazards and environmental impact. However, achieving uniform coating and film thickness can be challenging due to wettability issues caused by the high surface tension of water. To address this issue, researchers are exploring different surface treatments and modifications to enhance substrate

wettability and improve aqueous solution adhesion. However, current methods have limitations, such as damaging substrates, surfactant residues, and the use of hazardous chemicals. Therefore, more efficient, versatile, and sustainable methods are needed to overcome these limitations and enable the use of water-based solutions in a wider range of applications.

[0092] Broadly, this disclosure describes an efficient surfactant that provides excellent wetting properties at a low mass-to-volume ratio, resulting in a small amount of residual surfactant molecules within the formed film. This allows the coated film to exhibit properties that closely resemble those of the pure material. No additional pre-treatment processes are required. By eliminating a process step, cost savings are achieved and concerns about potential substrate or pre-laid film damage from plasma or strong acid/alkali treatment are avoided. Additionally, there are no additional environmental treatment costs. Products such as hexamethyldisilazane (HDMS) and Omnicoat, which are utilized to enhance wetting on substrates prior to conventional solution processes, require separate purification processes for disposal. However, this technology utilizes silk, an environmentally friendly and biodegradable material, as a surfactant, avoiding such concerns.

[0093] Water, the most life-essential and versatile solvent, has significant potential in bridging biological systems and the field of nanotechnology. However, challenges aroused by the high surface tension of water in achieving universal wetting at bio-nano interfaces require innovative solutions that go beyond conventional surface treatments or wetting agents. The unexplored potential of the silk fibroin chain's amphiphilic nature is reported, rooted in its unique primary sequences, as a regulator of aqueous wetting interfaces. Even in minute quantities (at 0.01 w/v%), silk fibroin significantly enhances surface coverage and outperforms commercial surfactants in precisely controlling interface energy between water-based solution-hydrophobic surfaces. This effect is ascribed to the adaptive adsorption of silk surfactants onto substrates with diverse surface energy, facilitating intermolecular interactions between unlikely pairs of materials. Using silk surfactants, nine different types of water-enabled nanodevices are successfully fabricated, spanning from semiconductor to photovoltaic cells, with performance on par with vacuum processes over water-repellent surfaces without using any surface pre-treatments. This natural surfactant can facilitate and revolutionize the development of the next generation of bio-nano interfaces.

[0094] Water is undoubtedly the most valuable and essential substance for living organisms and modern industry. Primarily, it acts as an indispensable component for biosystems and serves as a solvent for various biological substances such as proteins and nucleic acids, making it a crucial material in biotechnology. From the nanotechnology perspective, water plays a significant role as a solvent that can dissolve a wide range of polar and ionic substances and disperse various

nanomaterials, therefore possessing a significant potential to promote the convergence of state-of-the-art nanotechnology and biology. However, when it comes to the formation of bio-nano interfaces, pure water, due to its particularly high surface tension (approximately 72 mN/m at room temperature), exhibits suboptimal wetting capabilities except for some specific conditions, such as high surface energy or high polarity. Various attempts have been made to form the desired level of wetting between highly cohesive liquid and low energy surface, involving the direct or indirect modification of liquid surface tension or solid surface energy, such as adding surfactants, using organic co-solvents, surface energy modification, and nanopatterning. While these practices effectively enhance the degree of wettability, they also raise concerns, including the potential negative impact on the composition and morphology of the affected solution or surface. Additionally, in the context of developing next-generation bio-nano interfaces, these approaches may not be practical for use with biological substances and can contribute to increased costs and environmental issues. Therefore, enabling the universal wetting of water-based nanotechnology demands practical and sustainable strategies to regulate the interfacial energies that depart from traditional approaches.

[0095] Silk fibroin (SF), extracted from the *Bombyx mori* cocoon, has been extensively studied as a versatile biopolymer in bio and nanoscience, owing to its distinctive characteristics—biocompatibility, ease of functionalization and an unparalleled ability to be shaped and structured at the nanoscopic levels. The heavy chain of this versatile biopolymer comprises large hydrophilic blocks at both N- and C-terminal ends, with predominant inner hydrophobic moieties bound by hydrophilic segments, giving it the characteristics of a complex multiblock-copolymer structure. At the molecular level, 97% of this heavy chain is composed of non-polar or polar amino acids, such as Glycine, Alanine, Serine, Tyrosine, Valine, Threonine, and Glutamic acid. This composition not only explains the amphipathic nature of the heavy chain, but also can serve as the basis for meticulous intermolecular interactions between unlikely pairings of materials. Despite the widely recognized amphiphilic nature of this biopolymer, the impact of SF on the aqueous wetting interface regulation for universal wetting in water-enabled nanotechnology has not been fundamentally assessed.

[0096] This disclosure investigates the potential of SF for tuning the interfacial energy landscape between water-based solutions and water-repellent surfaces. The ability of SF to mediate the interactions between these unlike pairs arises from its intrinsic amphiphilic traits of the heavy chain. To demonstrate its ability to control the aqueous wetting interface and practicality in water-enabled nanodevice fabrication, silk surfactants-added water solution are spread over a hydrophobic-functionalized surface and fabricate nano (opto)electronic devices. Even small amounts (less than

0.01 w/v%) of SF at aqueous wetting interface are superior in improving macroscopic wetting results and controlling interfacial energy at the intermolecular level. Through several atomic-scale surface analyses, the physical distribution of silk surfactants in the formed metal-oxide thin films are traced and its adaptive adsorption mechanism is revealed. Combining these observations with existing polymer adsorption theories, propose the adaptive wetting enhancement mechanism of silk surfactants to aqueous wetting interfaces is proposed. Finally, the fabrication of assorted water-enabled nano electronic and photonic devices on hard-to-wet substrates is demonstrated without any loss in device performance due to the presence of the natural surfactant.

[0097] In one aspect, a method of using silk fibroin as a surfactant may include wetting a first surface with an aqueous silk solution comprising silk fibroin in an amount by weight of between 0.001% and 0.10%, wherein depositing pure water onto the first surface produces a contact angle of greater than 90°, and wherein the wetting provides at least 75% surface coverage. The wetting may also provide at least 80%, at least 85%, or at least 90% surface coverage.

[0098] In another aspect, a method of depositing a layer of a predetermined solute from an aqueous solvent onto a predetermined surface, wherein the predetermined solute is optionally a metal precursor, includes contacting the predetermined surface with an aqueous silk solution comprising the predetermined solute and silk fibroin in an amount by weight of between 0.001% and 0.10%, wherein the predetermined solute is present in an amount sufficient for depositing onto the predetermined surface, the contacting thereby depositing the predetermined solute onto the predetermined surface. The predetermined solute may be the metal precursor. The predetermined solute may be deposited onto the predetermined surface with at least 75%, at least 80%, at least 85%, or at least 90% surface coverage.

[0099] In another aspect, a method of improving an industrial process that does not previously utilize silk fibroin, the industrial process including at least one aqueous solution that does not adequately wet a first surface, may comprise adding silk fibroin to the at least one aqueous solution in an amount by weight of between 0.001% and 0.10%, wherein the at least one aqueous solution adequately wets the first surface upon addition of the silk fibroin. The industrial process may be a semiconductor device manufacturing process.

[0100] In another aspect, a method of using silk fibroin as a surfactant includes using silk fibroin as a surfactant for wetting the two different surfaces having different surface energies within a single process that wets two different surfaces having different surface energies, wherein the wetting achieves at least 50% surface coverage on each of the two different surfaces. A first of the two different surfaces may be a metal or semiconductor surface.

[0101] In one aspect, a method of using silk fibroin as a surfactant includes the following sequential steps: a) wetting a first surface with an aqueous silk solution comprising silk fibroin in an amount by weight of between 0.001% and 0.10%; b) drying the first surface; and c) removing residual silk fibroin solution from the dried first surface. Removing the residual silk fibroin may comprise rinsing the dried first surface, optionally with deionized water.

[0102] In another aspect, a method of improving surface wetting includes the following steps: a) measuring an immediate comparison contact angle and optionally a time-varying comparison contact angle for a comparison aqueous solution applied to a first surface; and b) applying an aqueous silk solution consisting essentially of the comparison aqueous solution and silk fibroin in an amount by weight of between 0.001% and 0.10%, wherein an immediate contact angle of the aqueous silk solution is the same or greater than the comparison contact angle immediately following applying, wherein the time-varying contact angle of the aqueous silk solution is lower than the comparison contact angle after 1 minute or more following the applying.

[0103] In one aspect, a method of making a nanoscale silk coating includes spin coating an aqueous silk fibroin solution on a first surface to form a deposited silk film and rinsing the deposited silk film with deionized water, thereby forming the nanoscale silk coating. The method may further comprise spin coating a protective layer on the nanoscale silk coating. The protective layer may be polymethyl methacrylate (PMMA). The method may further comprise spin coating a photoresist on the protective layer and developing the photoresist. The method may further comprise patterning the deposited silk film and/or the protecting layer. The patterning may be achieved via O_2 plasma treatment. The method may further comprise immersing the nanoscale silk coating in a polar organic solvent. The polar organic solvent may be selected from the group consisting of methanol, ethanol, acetone, and combinations thereof.

[0104] The nanoscale silk coating may have a thickness of at most 300 nm, at most 200 nm, at most 100 nm, at most 50 nm, at most 10 nm, or at most 5 nm. The nanoscale silk coating may have a thickness of at least 3 nm, at least 5 nm, at least 10 nm, at least 50 nm, at least 100 nm, or at least 200 nm. The nanoscale silk coating may have a thickness that varies by less than plus or minus 25%, less than plus or minus 20%, less than plus or minus 15%, or less than plus or minus 10% across the entire nanoscale silk coating. The nanoscale silk coating may exhibit a lateral resolution of at most 5 μm, at most 4 μm, at most 3 μm, at most 2 μm, or at most 1 μm. The nanoscale silk coating may exhibit a free water uptake of at least 12%wt, at least 10%wt, at least 8%wt, or at least 6%wt.

[0105] The first surface may be a portion of a semiconductor device comprising a substrate, an electrode layer, and a semiconductor layer each on the substrate, wherein the first surface is located

at least one of the electrode layer and the semiconductor layer. The nanoscale silk coating may have at least one bioreactive element. The silk fibroin may be present in the aqueous silk fibroin solution in an amount by weight of between 0.001% and 0.10% or between 0.01% and 0.05%, including but not limited to, at least 0.001%, at least 0.01%, at least 0.02%, at least 0.03%, at least 0.04%, at least 0.05%, at least 0.06%, at least 0.07%, or at least 0.09%, and at most 0.10%, at most 0.09%, at most 0.08%, at most 0.07%, at most 0.06%, at most 0.05%, at most 0.04%, at most 0.03%, or at most 0.02%. The aqueous silk fibroin solution may further comprise at least one bioreactive element.

[0106] The disclosure emphasizes the surfactant capabilities of silk fibroin. Such emphasis is not intended to limit its teachings to silk fibroin and may be extended under certain circumstances to encompass other entities that a skilled artisan would recognize as having sufficient similarity to silk fibroin to achieve similar performance.

[0107] While the disclosure has been disclosed in connection with the preferred embodiments shown and described in detail, various modifications and improvements thereon will become readily apparent to those skilled in the art. Accordingly, the spirit and scope of the present disclosure is not to be limited by the foregoing examples, but is to be understood in the broadest sense allowable by law.

[0108] Unless otherwise specified or indicated by context, the terms "a", "an", and "the" mean "one or more." For example, "a molecule" should be interpreted to mean "one or more molecules."

[0109] As used herein, "about", "approximately," "substantially," and "significantly" will be understood by persons of ordinary skill in the art and will vary to some extent on the context in which they are used. If there are uses of the term which are not clear to persons of ordinary skill in the art given the context in which it is used, "about" and "approximately" will mean plus or minus $\leq$10% of the particular term and "substantially" and "significantly" will mean plus or minus >10% of the particular term.

[0110] As used herein, the terms "include" and "including" have the same meaning as the terms "comprise" and "comprising." The terms "comprise" and "comprising" should be interpreted as being "open" transitional terms that permit the inclusion of additional components further to those components recited in the claims. The terms "consist" and "consisting of" should be interpreted as being "closed" transitional terms that do not permit the inclusion of additional components other than the components recited in the claims. The term "consisting essentially of" should be interpreted to be partially closed and allowing the inclusion only of additional components that do not fundamentally alter the nature of the claimed subject matter.

[0111] All methods described herein can be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by context. The use of any and all examples, or exemplary language (e.g., "such as") provided herein, is intended merely to better illuminate the invention and does not pose a limitation on the scope of the invention unless otherwise claimed. No language in the specification should be construed as indicating any non-claimed element as essential to the practice of the invention.

[0112] All references, including publications, patent applications, and patents, cited herein are hereby incorporated by reference to the same extent as if each reference were individually and specifically indicated to be incorporated by reference and were set forth in its entirety herein.

[0113] Preferred aspects of this invention are described herein, including the best mode known to the inventors for carrying out the invention. Variations of those preferred aspects may become apparent to those of ordinary skill in the art upon reading the foregoing description. The inventors expect a person having ordinary skill in the art to employ such variations as appropriate, and the inventors intend for the invention to be practiced otherwise than as specifically described herein. Accordingly, this invention includes all modifications and equivalents of the subject matter recited in the claims appended hereto as permitted by applicable law. Moreover, any combination of the above-described elements in all possible variations thereof is encompassed by the invention unless otherwise indicated herein or otherwise clearly contradicted by context.

[0114] While the invention has been illustrated and described in detail in the foregoing drawings and description, the same is to be considered as illustrative and not restrictive in character, it being understood that only illustrative embodiments thereof have been shown and described and that all changes and modifications that come within the spirit of the invention are desired to be protected. For example, any of the features or functions of any of the embodiments disclosed herein may be incorporated into any of the other embodiments disclosed herein.

[0115] The following examples illustrate some embodiments and aspects of the invention. It will be apparent to those skilled in the relevant art that various modifications, additions, substitutions, and the like can be performed without altering the spirit or scope of the invention, and such modifications and variations are encompassed within the scope of the invention as defined in the claims which follow. The following examples do not in any way limit the invention.

[0116] EXAMPLES

[0117] Example 1. Adaptive Natural Surfactant for Universal Wetting of Water-enabled Nanotechnology

[0118] Silk fibroin as a natural surfactant

[0119] The silk fibroin (SF) chain regenerated from the silkworm cocoon possesses a complex multiblock-copolymer structure composed of various amino acids, exhibiting amphiphilic traits as shown in Fig. 1A. Thanks to these characteristics, similar to how synthetic surfactants function, the presence of SF in a water-based solution can alter the thermodynamic energy state of the system at its bulk or boundary. Fig. 1B illustrates the experimentally observed effect of adding SF on the wettability of water solutions spin-coated over a hydrophobic substrate. Within the extremely small concentration range, as the concentration of the biopolymer increases, the liquid mixture achieves progressively better surface coverage, transitioning from (i) nonwetting to (ii) dewetting, (iii) partial wetting, and finally to (iv) complete wetting.

[0120] A quantitative assessment of macroscopic wetting improvement outcomes was conducted, considering the impact of the biopolymer's molecular weight—controlled by degumming time—and its concentration in the aqueous solution. This assessment was carried out by depositing the SF-added aqueous metal precursor solutions on substrates with different surface energy. Fig. 1C maps the wetting coverage outcomes on an untreated substrate, and Fig. 1D shows the results for a hydrophobic substrate. The hydrophobic surface was obtained by functionalizing a SiO_2/Si wafer with a silane-based self-assembled monolayer (fluoro-octyl-trichloro-silane, FOTS). SF chains boiled for less than 30 minutes typically consist of long-chain fibroin (LCF), while fibroin boiled for more than 30 minutes is called short-chain fibroin (SCF), with approximate molecular weights of 460-150 kDa and 150-50 kDa, respectively. It's noteworthy that aqueous solutions containing at least 0.003 w/v% of LCF can coat more than 90% of the surface area over untreated bare SiO_2/Si substrates. This coverage is independent of boiling time (*i.e.*, chain length) below the 30-minute threshold but improved linearly with concentration. As the chain length becomes shorter with boiling times over 30 minutes, higher silk concentrations are needed to cover more than 90% of the surface. The different effectiveness of LCF and SCF in aiding good wetting formation becomes more apparent when considering hydrophobic FOTS-treated substrates. The spin-coating coverage is almost independent of fibroin's chain length in the LCF range, readily achieving 90% coverage with 0.01 w/v% of SF, but it is highly dependent on the fibroin concentration in the mixture. When SCF is considered, a concentration of more than 0.02 w/v% of SCFs is needed to thoroughly coat the substrate.

[0121] Efficient interfacial energy control using silk surfactants

[0122] From a thermodynamic perspective, wetting is the phenomenon in which a liquid spreads across a solid surface, aiming to minimize free energy and establish a stable state with balanced interfacial tensions between the liquid, gas, and solid phases. Wetting between a liquid and a solid

can be quantitatively evaluated through interfacial energy or the work of adhesion between the two phases, represented by Young's equation and the work of adhesion equation, respectively. To characterize the aqueous wetting enhancement by silk surfactants, we evaluated the changes in surface tension and contact angle of SF-containing solution on hydrophobic substrates (Fig. 5). In a comparative assessment with deionized water (DIW) and pure 0.1 M indium metal precursor solution, the silk surfactant-added solution showed similar surface tension changes over time with the control group. However, the contact angle exhibited a more significant change compared to the control group. These results indicate silk surfactants at the minute level affect the interfacial energy rather than the surface energy of the solution. Through this analysis, the changes in interfacial energy and work of adhesion between aqueous solution and a non-polar surface are represented in Fig. 2A and Fig. 2B, respectively. The wetting discussed here is non-reactive, meaning no chemical reactions or absorption occurs. Therefore, it can be assumed that there is no change in the chemical composition of the solid substrate during the wetting, and consequently, no change in the substrate's surface free energy. Under these assumptions, Fig. 2A shows a significant reduction in the interfacial energy between the silk-containing solution and the solid surface. Additionally, Fig. 2B explains that silk surfactants increase the interfacial adhesion between the two contact phases.

[0123] The surface energy control ability of silk surfactants surpasses that of commercial surfactants. This property is attributed to the nature of silk chains, composed of assorted amino acids and a complex multiblock-copolymer structure, thereby effectively mediating various molecular-level interaction scenarios. A comparison was made by mixing four commercial surfactants and two block-copolymer types of surfactants in aqueous solutions with the same mass-to-volume ratio as SF. The results of contact angles and surface coverage on hydrophobic substrates were then compared. Unlike silk, commercial surfactants effectively lowered the surface tension of the solution, forming low initial contact angles with hydrophobic substrates (Fig. 2C). Despite this effective reduction in surface tension, the direct control over interfacial energy is lower than that of silk. As shown in Fig. 2D, the solution containing natural surfactant shows over 90% surface coverage on the hydrophobic substrate, while solutions containing commercial synthetic surfactants exhibit partial or dewetting results over the same substrate (see Fig. 5).

[0124] Adaptive adsorption of silk surfactants at film-substrate interface

[0125] Fig. 3 unveils the intricate adsorption mechanism of SF on surfaces with varying energy profiles. As depicted in Fig. 3A, it was postulated that SF's exceptional efficiency in wetting hydrophobic surfaces stems from its complex adsorption behavior. The hydrophobic internal blocks of SF's heavy chain form robust connections with the non-polar surface, while the hydrophilic sites

on SF engage in favorable interactions with aqueous solutions. To corroborate the hypothesis regarding SF's adsorption behavior, SF-containing indium precursor was coated onto three sets of interfaces with contrasting surface energies: bare, plasma-treated, and FOTS-treated SiO_2 substrates. Subsequently, X-ray photoelectron spectroscopy (XPS) depth profiling and atomic force microscopy (AFM) was employed to meticulously analyze the surface chemical composition and physical morphology of these films.

[0126] XPS depth profiling on a 25 nm-thick SF film provided a reference for the binding energy of electrons emitted from the amine groups of the protein as shown in Fig. 6, confirming that SF emits a strong nitrogen (N1s) signal at 400 eV. This reference was then used to investigate the physical distribution of silk within metal oxide films formed from solutions containing silk surfactants. Interestingly, even in metal oxide films coated with a 0.3 M indium precursor solution containing up to 0.1 w/v% silk surfactants, we failed to detect nitrogen signals. This is likely due to the low mass ratio of silk, which is approximately lower than 1.1%, within the coated indium oxide film. This finding indicates that concentrations of silk below 0.01 w/v% in aqueous solutions fall into an extremely minute category, challenging to detect and analyze with conventional atomic surface analysis equipment, though it is enough to regulate the aqueous wetting interface. Noticeable protein-related peaks (*i.e.*, carbon and nitrogen) emerged at the film-substrate interface when the surfactant concentration was increased above 0.3 w/v%, as shown in Fig 3B. The N1s signal was tracked in metal oxide films deposited on various surface energy substrates and found that it consistently appears primarily near the film-substrate interface. However, the intensity of these protein signals differs depending on the substrates as shown in Fig. 3C and Fig. 7. This difference implies slight variations in the adsorption efficiency of silk surfactants based on surface energy profiles. The hydrophobic segments of silk chains engage in stronger intermolecular interactions with non-polar, low-surface energy substrates. On the other hand, on highly polar surfaces, SF chains are also adsorbed at the interface, but their physical distribution is not limited to the interface but expanded throughout the film.

[0127] Referring to Fig. 7, all test samples underwent coating with 0.3 M indium precursor solutions to produce 25 nm-thick films, with the interface demarcated by a white dot line. It becomes evident that the film coated with a 0.3 M indium precursor containing 0.1 w/v% silk exhibits no discernible amine signal. Notably, the silk-to-indium weight ratio in this solution is approximately 1.1%. However, as the silk content in the solution increases, a noticeable augmentation in the intensity of the amine signal is observed. Examining the solutions containing 0.3 w/v% and 1.0 w/v% silk (silk-to-indium weight ratios for 3.3% and 13.1%, respectively), intensive signals emerge

near the interface. On non-polar surfaces, silk demonstrates an intensive distribution near the interface, evident through a strong N1s signal in the vicinity of the interface. However, on bare or polar surfaces, silk is still detectable at the interface, but it tends to exhibit a more uniform distribution within the film. These results underpin the adaptive adsorption behavior of silk surfactants depending on the surface energy profile.

[0128] To investigate the physical morphology of the SF adsorption layer, AFM was employed for further analysis. Indium oxide films coated on substrates were selectively etched using a diluted hydrochloric acid solution to expose the wetting interface. Fig. 3D and Fig. 8 illustrate the AFM height and deflection signal profiles of the revealed surface. Similar to the XPS analysis results, no noticeable features were found at low silk concentrations, but distinct surface topologies emerged with increased silk surfactant concentrations in the coating solution. On hydrophobic substrates, the observed surface structure exhibited a flat-lying shape, a common morphology when hydrophobic part-dominant surfactant molecules are adsorbed onto non-polar surfaces. For plasma-treated substrates, sparse island-shaped aggregates remained on the substrate with an average thickness of approximately 17 nm. An atomic force spectroscopy analysis (Fig. 6) was then conducted to ascertain the authenticity of the observed AFM surface structures. The results confirmed that the surface features observed in the AFM analysis were indeed attributed to the adsorbed SF on the substrate.

[0129] These observations match well with the pre-reported theories, like surfactant spreading mechanism and polymer adsorption theory. The former describes how surfactant molecules adsorb at the solid-liquid interface during dynamic spreading. The latter suggests that the adsorption behavior of polymer surfactants can be influenced by the contact surface's energy and polarity. Based on these observations and existing theory, an adaptive adsorption-assisted wetting enhancement mechanism by silk surfactants is proposed, as illustrated in Fig. 9. This adaptability of the surfactant enables the ubiquitous and rapid formation of high-quality metal oxide thin films on a wide range of surfaces, without the need for a complex optimization of the deposition parameters to ensure acceptable wettability and surface coverage.

[0130] Referring to Fig. 6, 25 nm-thick silk film is coated on 300 nm wet thermal oxide substrate. To get rid of adventitious carbon layer, ion bombardment is conducted for 30 s before XPS depth profiling. Strong carbon (C1s) and nitrogen (N1s) signals are detected from the top surface till the interface. Oxygen signal (O1s) is detected from the top surface to the end of the etch. On the other hand, silicon (Si2p) signal is only detected after the interface. These XPS results are used as a reference to investigate how silk fibroin is distributed in the metal oxide film.

[0131] Referring to Fig. 8, these images were achieved by selectively etching the metal oxide in an acid bath, thus exposing the buried interface of SF with substrates of different surface energies, at increasing SF concentrations. As the surface energy increases (left to right), the morphologies of SF aggregates change from a flat-lying shape to a vertically grown island shape. These results also support the adaptive adsorbing of silk surfactant at the interface.

[0132] Referring to Fig. 9, the adsorption behavior of silk surfactant exhibits a notable dependence on the surface energy status. On non-polar surfaces, the hydrophobic segments of the silk chain adsorb to the substrate, agglomerating flat along the surface. In contrast, on polar surfaces, the hydrophilic terminal ends of the silk chain are more inclined to interact with the surface compared to its hydrophobic segments. This interaction leads to the formation of vertically agglomerated structures.

[0133] Pioneering water-enabled nanotechnologies with silk surfactant

[0134] Fig. 4 showcases nanodevices, including semiconductors and photovoltaic cells, formed by spreading a water solution over a water-repellent surface and highlights their characteristics. It is known that surfactant molecules, when used to solution-process devices, could remain within the coated active material, potentially compromising the performance of the devices. Therefore, the impact of silk surfactants on the performance of fabricated water-enabled nanodevices was investigated. Our results indicate that the presence of silk surfactants within the active layers is minimal. The electronic inertness and self-separated distribution of the natural surfactant in the metal oxides collectively preserve the functionality of the electronic materials while ensuring excellent film quality.

[0135] Fig. 4A demonstrates that the presence of small quantities of SF in the indium gallium zinc oxide (IGZO) transistor channel does not significantly alter the transfer characteristic curves of the device up to a concentration of 0.03 w/v% of SF in the precursor solution. The thin-film transistors maintain mobilities in the 1-10 cm^2/Vs range, with a notable drop observed only above the 0.1 w/v% level of silk. It is worth noting that a lower concentration of 0.01 w/v% is sufficient to achieve optimal surface coverage on low-energy substrates where conventional aqueous precursor solutions cannot be deposited. When transistors are fabricated on highly hydrophobic FOTS-treated surfaces, the charge mobilities remain at ~1 cm^2/Vs even at low SF concentrations, with only a nominal decrease compared to reference levels obtained with pristine IGZO on a hydrophilic substrate. Conceivably, the gradual degradation of the transport properties with SF concentration is primarily ascribable to the disruption of the metal oxide microstructure, as the silk-to-metal oxide ratio increases. Another possible contribution to the extracted mobility drop is that SF tends to vertically

segregate at the low energy interfaces, thus introducing a nanometric insulating interface that may partially reduce the capacitive coupling of the semiconductor with the bottom-gate electrode. Nonetheless, besides the impact on the charge carrier mobility, we also note that the presence of SF within the IGZO film does not introduce non-idealities in the transfer curves of the transistors, such as hysteresis or worse subthreshold swing, as SF is known to present an excellent dielectric interface for semiconductors.

[0136] This technology can be applied to coat dielectric materials, as demonstrated in Fig. 4B. The Al_2O_3 film exhibits a leakage current of approximately 10^{-7} A/cm^2 before breakdown occurs. The inset shows that the capacitance of the film remains constant at approximately 250 nF/cm^2 over a frequency range of 1 kHz to 100 kHz. The calculated dielectric constant of the film is about 6.9, indicating that a good gate dielectric layer can be fabricated using a silk-added metal precursor. Moreover, as shown in Fig. 4C and Fig. 4D, $MAPbI_3$-based and NiO-based optoelectronic films were coated onto hydrophobic n-type silicon substrates using this technique. Under illumination from a LED light source with a maximum output of 150 mW/cm^2, both films exhibited photocurrent generation. The $MAPbI_3$ films demonstrated typical photoconductive behavior, generating higher photocurrent under increased irradiation. In contrast, the NiO films coated over n-type substrates exhibited photodiode behavior. While Fig. 4 demonstrates the effectiveness of this technique for 4 representative devices, its applicability extends to a broader range of water-soluble materials and advanced solution-processed fabrication methods, as illustrated in Fig. 10 and Fig. 11, respectively.

[0137] Referring to Fig. 10, the wetting mechanism proposed in this study can be applied to almost any aqueous metal precursor solution. As examples, the digital images show the coating results on a hydrophobic substrate after adding 0.01 w/v% of silk fibroin to a total of 9 different metal precursor aqueous solutions.

[0138] Referring to Fig. 11, (a) this technology can be applied to multi-layer stacking by sequential coating over universal substrates without surface treatment, and the coated film can be transferred to the desired substrate through release technology. For examples, (b, c) device structure and transfer curve of an Al2O3-gated IGZO transistor prepared by sequential coating of each metal precursor. (d, e) Transfer-printed halide perovskite (MAPbI3) film over a transparent PET film and its optical properties.

[0139] EQUIVALENTS AND SCOPE

[0140] The recitation of a listing of elements in any definition of a variable herein includes definitions of that variable as any single element or combinations (or subcombinations) of listed elements. The recitation of an embodiment herein includes that embodiment as any single

embodiment or in combination with any other embodiments or portions thereof. Those skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, many equivalents to the specific embodiments of the invention described herein. The scope of the present invention is not intended to be limited to the above Description, but rather is as set forth in the following claims:

CLAIMS

What is claimed is:

1. A method of using silk fibroin as a surfactant, the method comprising:

wetting a first surface with an aqueous silk solution comprising silk fibroin in an amount by weight of between 0.001% and 0.10%, wherein depositing pure water onto the first surface produces a contact angle of greater than 90°,

wherein the wetting provides at least 75% surface coverage.

2. The method of claim 1, wherein the wetting provides at least 80%, at least 85%, or at least 90% surface coverage.

3. A method of depositing a layer of a predetermined solute from an aqueous solvent onto a predetermined surface, wherein the predetermined solute is optionally a metal precursor, the method comprising:

contacting the predetermined surface with an aqueous silk solution comprising the predetermined solute and silk fibroin in an amount by weight of between 0.001% and 0.10%, wherein the predetermined solute is present in an amount sufficient for depositing onto the predetermined surface, the contacting thereby depositing the predetermined solute onto the predetermined surface.

4. The method of claim 3, wherein the predetermined solute is the metal precursor.

5. The method of any one of claims 3 to the immediately preceding claim, wherein the predetermined solute is deposited onto the predetermined surface with at least 75%, at least 80%, at least 85%, or at least 90% surface coverage.

6. A method of improving an industrial process that does not previously utilize silk fibroin, the industrial process comprising at least one aqueous solution that does not adequately wet a first surface, the method comprising:

a) adding silk fibroin to the at least one aqueous solution in an amount by weight of between 0.001% and 0.10%, wherein the at least one aqueous solution adequately wets the first surface upon addition of the silk fibroin.

7. The method of the immediately preceding claim, wherein the industrial process is a semiconductor device manufacturing process.

8. A method of using silk fibroin as a surfactant, the method comprising:

within a single process that wets two different surfaces having different surface energies, using silk fibroin as a surfactant for wetting the two different surfaces having the different surface energies, wherein the wetting achieves at least 50% surface coverage on each of the two different surfaces.

9. The method of the immediately preceding claim, wherein a first of the two different surfaces is a metal or semiconductor surface.

10. A method of using silk fibroin as a surfactant, the method comprising the following sequential steps:

a) wetting a first surface with an aqueous silk solution comprising silk fibroin in an amount by weight of between 0.001% and 0.10%;

b) drying the first surface; and

c) removing residual silk fibroin from the dried first surface.

11. The method of the immediately preceding claim, wherein removing residual silk fibroin comprises rinsing the dried first surface, optionally with deionized water.

12. A method of improving surface wetting, the method comprising:

a) measuring an immediate comparison contact angle and optionally a time-varying comparison contact angle for a comparison aqueous solution applied to a first surface; and

b) applying an aqueous silk solution consisting essentially of the comparison aqueous solution and silk fibroin in an amount by weight of between 0.001% and 0.10%, wherein an immediate contact angle of the aqueous silk solution is the same or greater than the comparison contact angle immediately following applying, wherein the time-varying contact angle of the aqueous silk solution is lower than the comparison contact angle after 1 minute or more following the applying.

13. A method of making a nanoscale silk coating, the method comprising:

spin coating an aqueous silk fibroin solution on a first surface to form a deposited silk film; and

rinsing the deposited silk film with deionized water, thereby forming the nanoscale silk coating.

14. The method of the immediately preceding claim, the method further comprising spin coating a protective layer on the nanoscale silk coating.

15. The method of the immediately preceding claim, wherein the protective layer is polymethyl methacrylate (PMMA).

16. The method of either of the two immediately preceding claims, the method further comprising spin coating a photoresist on the protective layer and developing the photoresist.

17. The method of the immediately preceding claim, the method further comprising patterning the deposited silk film and/or the protecting layer.

18. The method of the immediately preceding claim, wherein the patterning is achieved via O_2 plasma treatment.

19. The method of the immediately preceding claim, the method further comprising immersing the nanoscale silk coating in a polar organic solvent.

20. The method of the immediately preceding claim, wherein the polar organic solvent is selected from the group consisting of methanol, ethanol, acetone, and combinations thereof.

21. The method of any one of claims 13 to the immediately preceding claim, wherein the nanoscale silk coating has a thickness of at most 300 nm, at most 200 nm, at most 100 nm, at most 50 nm, at most 10 nm, or at most 5 nm.

22. The method of any one of claims 13 to the immediately preceding claim, wherein the nanoscale silk coating has a thickness of at least 3 nm, at least 5 nm, at least 10 nm, at least 50 nm, at least 100 nm, or at least 200 nm.

23. The method of any one of claims 13 to the immediately preceding claim, wherein the nanoscale silk coating has a thickness that varies by less than plus or minus 25%, less than plus or minus 20%, less than plus or minus 15%, or less than plus or minus 10% across the entire nanoscale silk coating.

24. The method of any one of claims 13 to the immediately preceding claim, wherein the nanoscale silk coating exhibits a lateral resolution of at most 5 μm, at most 4 μm, at most 3 μm, at most 2 μm, or at most 1 μm.

25. The method of any one of claims 13 to the immediately preceding claim, wherein the nanoscale silk coating exhibits a free water uptake of at least 12%wt, at least 10%wt, at least 8%wt, or at least 6%wt.

26. The method of any one of claims 13 to the immediately preceding claim, wherein the first surface is a portion of a semiconductor device comprising:

a substrate; and

an electrode layer and a semiconductor layer, each on the substrate,

wherein the first surface is located on at least one of the electrode layer or the semiconductor layer.

27. The method of any one of claims 13 to the immediately preceding claim, wherein the nanoscale silk coating has at least one bioreactive element contained therein.

28. The method of the immediately preceding claim, wherein the aqueous silk solution comprises at least one bioreactive element.

29. The method of any one of the preceding claims, wherein the silk fibroin is present in the aqueous silk fibroin solution in an amount by weight of between 0.001% and 0.10% or between 0.01% and 0.05%, including but not limited to, at least 0.001%, at least 0.01%, at least 0.02%, at least 0.03%, at least 0.04%, at least 0.05%, at least 0.06%, at least 0.07%, or at least 0.09%, and at most 0.10%, at most 0.09%, at most 0.08%, at most 0.07%, at most 0.06%, at most 0.05%, at most 0.04%, at most 0.03%, or at most 0.02%.

30. The method of any one of the preceding claims, wherein the aqueous silk fibroin solution further comprises at least one bioreactive element.

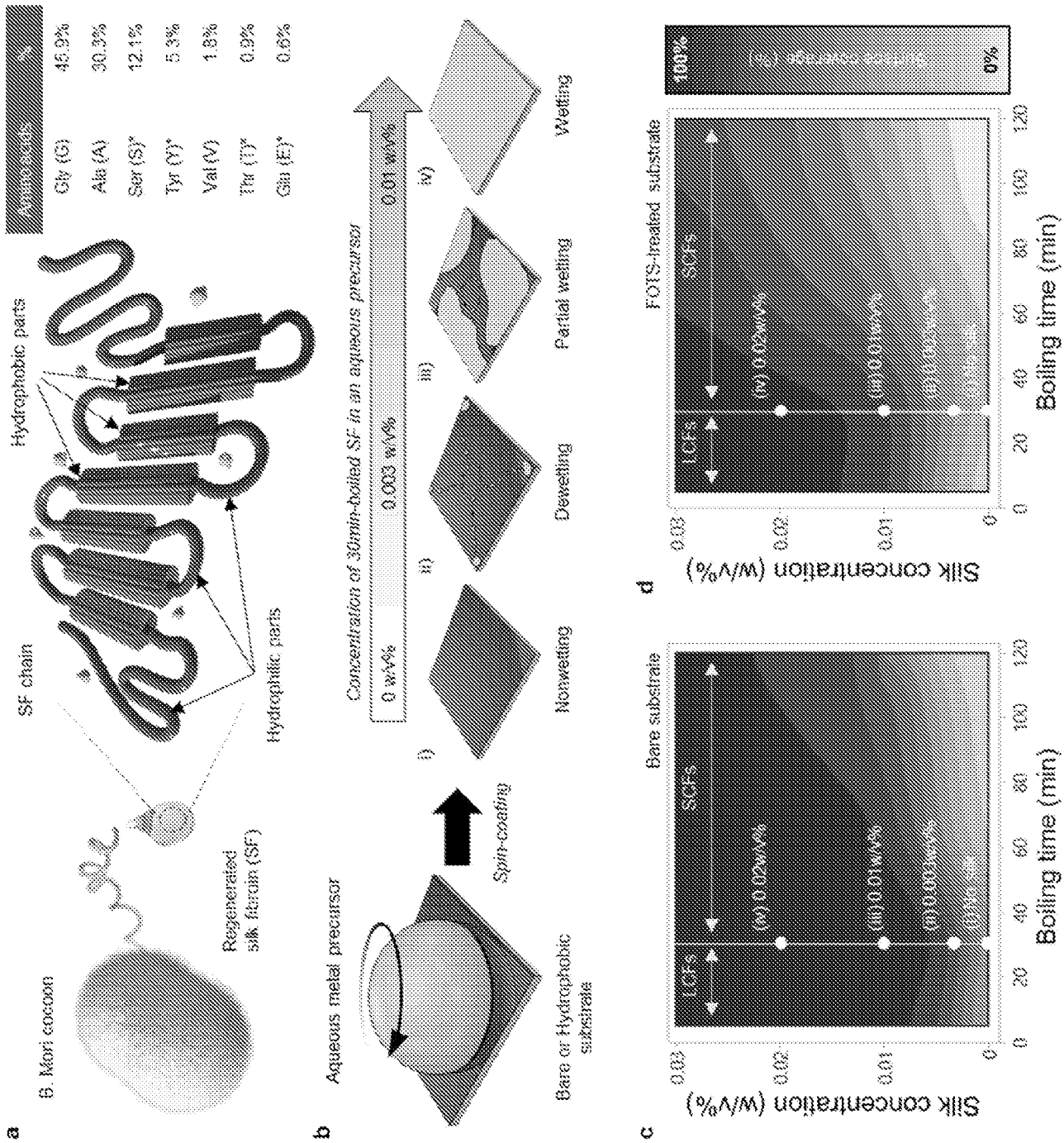
a
B. Mori cocoon
Regenerated silk fibroin (SF)
SF chain
Hydrophobic parts
Hydrophilic parts
Amino acids %
Gly (G) 45.9%
Ala (A) 30.3%
Ser (S)* 12.1%
Tyr (Y)* 5.3%
Val (V) 1.8%
Thr (T)* 0.9%
Glu (E)* 0.6%
b
Aqueous metal precursor
Bare or Hydrophobic substrate
Spin-coating
Concentration of 30min-boiled SF in an aqueous precursor
0 w/v%
0.003 w/v%
0.01 w/v%
i)
ii)
iii)
iv)
Nonwetting
Dewetting
Partial wetting
Wetting
c
Bare substrate
LCFs
SCFs
Silk concentration (w/v%)
Boiling time (min)
d
FOTS-treated substrate
100%
0%
Silk concentration (w/v%)
Boiling time (min)

Fig. 1

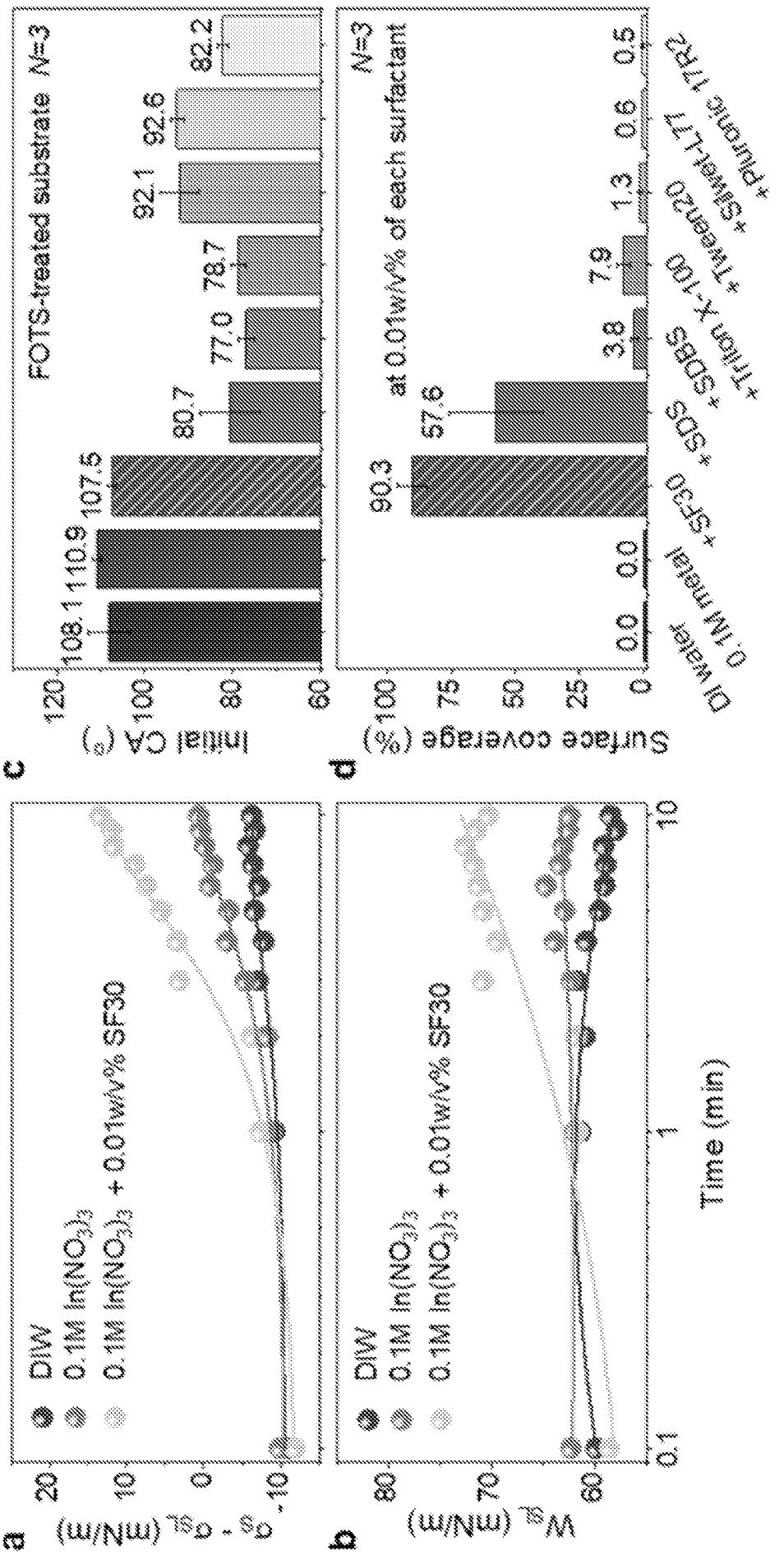
a
$\sigma_S - \sigma_{SL}$ (mN/m)
DIW
0.1M In(NO3)3
0.1M In(NO3)3 + 0.01w/v% SF30
b
W_{SL} (mN/m)
Time (min)
c
Initial CA (°)
FOTS-treated substrate N=3
108.1
110.9
107.5
80.7
77.0
78.7
92.1
92.6
82.2
d
Surface coverage (%)
N=3
at 0.01w/v% of each surfactant
0.0
0.0
90.3
57.6
3.8
7.9
1.3
0.6
0.5
DI water
0.1M metal
+SF30
+SDS
+SDBS
+Triton X-100
+Tween20
+SilWet-L77
+Pluronic 17R2

Fig. 2

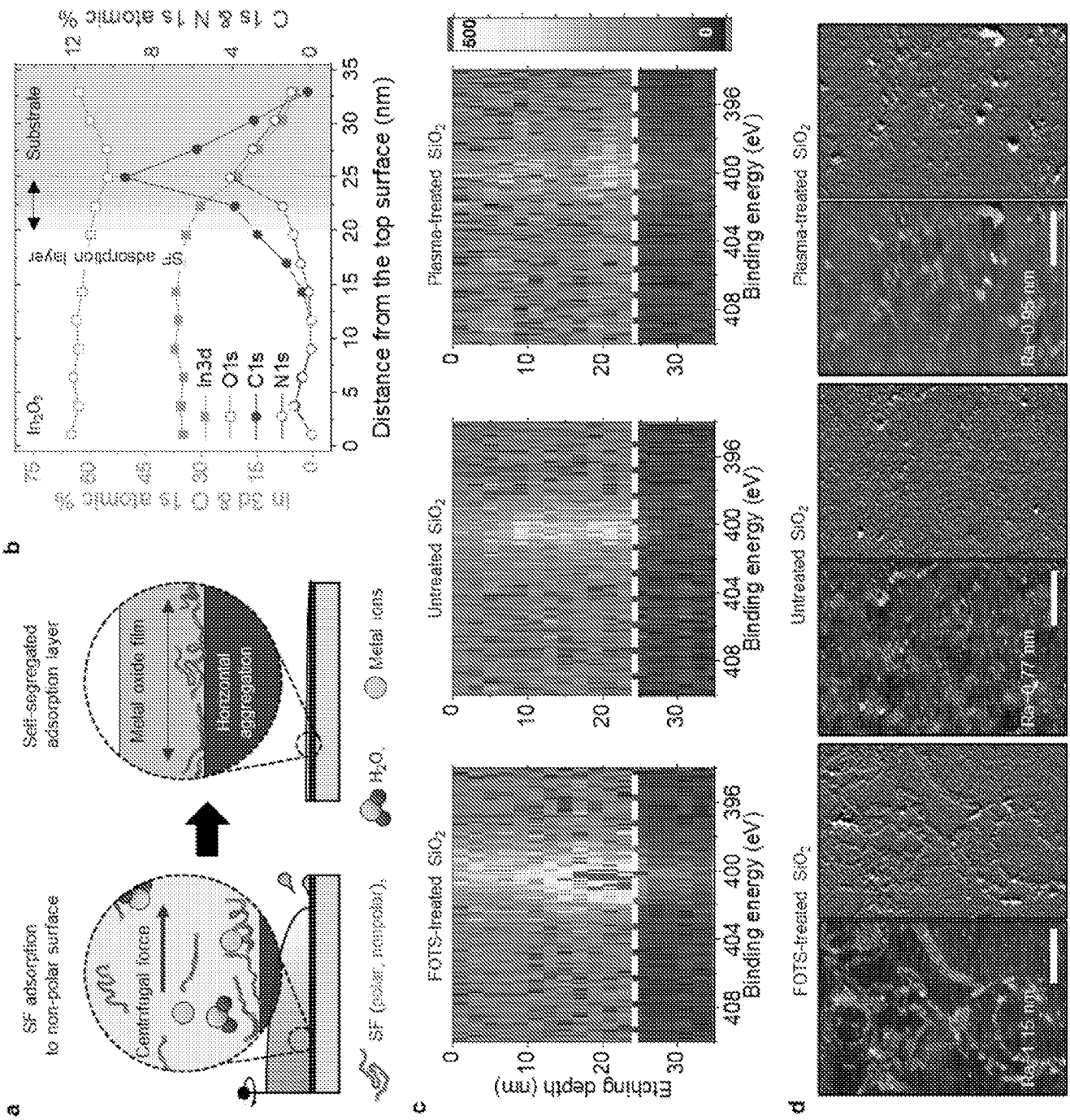
a
SF adsorption to non-polar surface
Centrifugal force
Self-segregated adsorption layer
Metal oxide film
Horizontal segregation
SF (polar, nonpolar),
H_2O
Metal ions
b
In 3d & O 1s atomic %
C 1s & N 1s atomic %
In_2O_3
Substrate
SF adsorption layer
In3d
O1s
C1s
N1s
Distance from the top surface (nm)
c
FOTS-treated SiO_2
Untreated SiO_2
Plasma-treated SiO_2
Etching depth (nm)
Binding energy (eV)
d
FOTS-treated SiO_2
Untreated SiO_2
Plasma-treated SiO_2
Ra=1.15 nm
Ra=0.77 nm
Ra=0.52 nm

Fig. 3

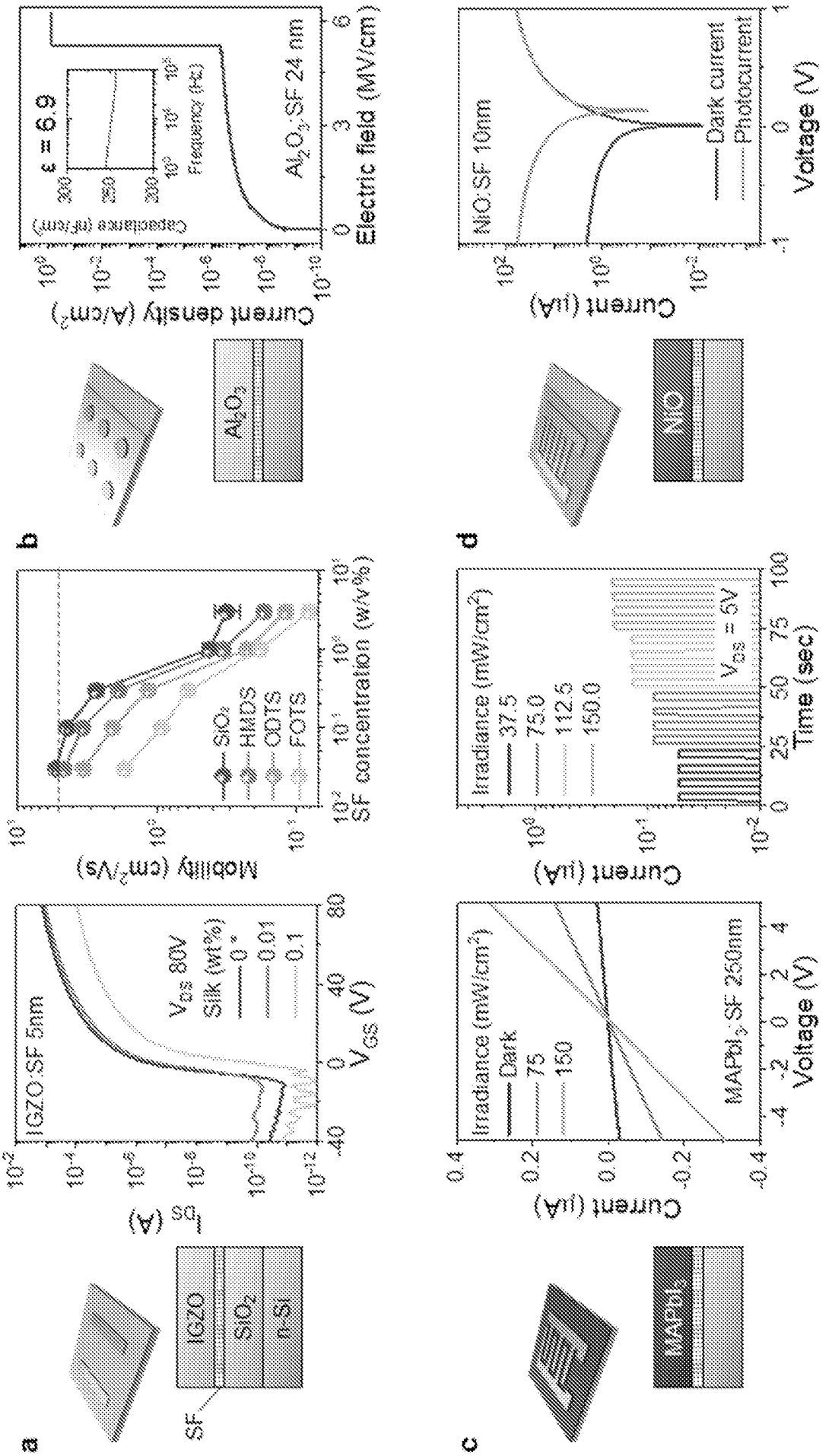
a
IGZO
SiO2
n-Si
SF
IGZO:SF 5nm
Vds 80V
Silk (wt%)
0
0.01
0.1
IDS (A)
VGS (V)
b
Al2O3
Current density (A/cm2)
Capacitance (nF/cm2)
ε = 6.9
Frequency (Hz)
Al2O3:SF 24 nm
Electric field (MV/cm)
Mobility (cm2/Vs)
SiO2
HMDS
ODTS
FOTS
SF concentration (w/v%)
c
MAPbI
Irradiance (mW/cm2)
Dark
75
150
MAPbI3:SF 250nm
Current (μA)
Voltage (V)
d
NiO
NiO:SF 10nm
Current (μA)
Dark current
Photocurrent
Voltage (V)
Irradiance (mW/cm2)
37.5
75.0
112.5
150.0
Vds = 5V
Current (μA)
Time (sec)

Fig. 4

Biopolymer
Anionic surfactant
Nonionic surfactant
Block-copolymer surfactant
SF30
SDS
SDBS
TritonX100
Tween20
Silwet L-77
Pluronic 17R2

Fig. 5

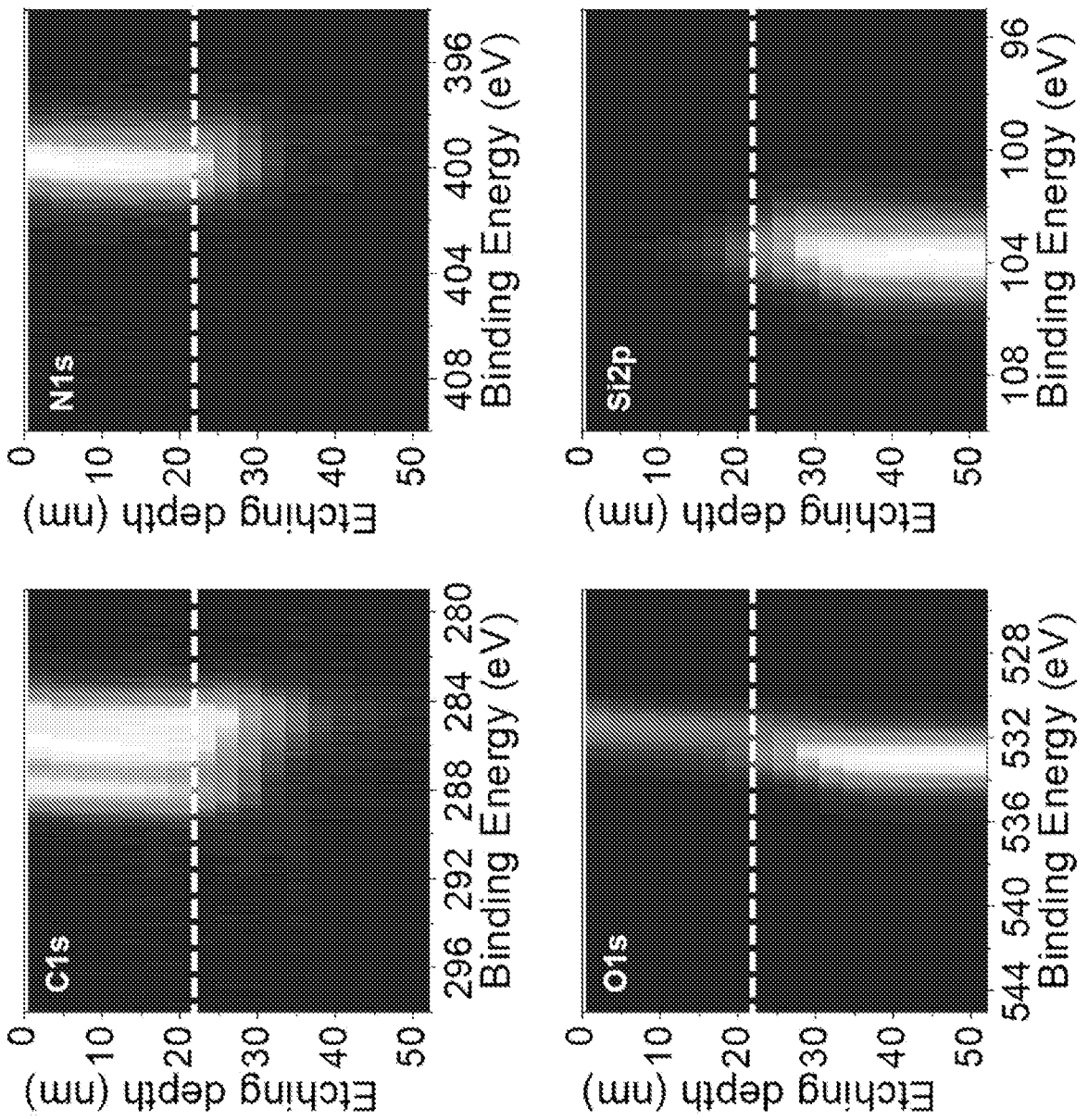
C1s
N1s
O1s
Si2p
Etching depth (nm)
0
10
20
30
40
50
296 292 288 284 280
408 404 400 396
544 540 536 532 528
108 104 100 96
Binding Energy (eV)

Fig. 6

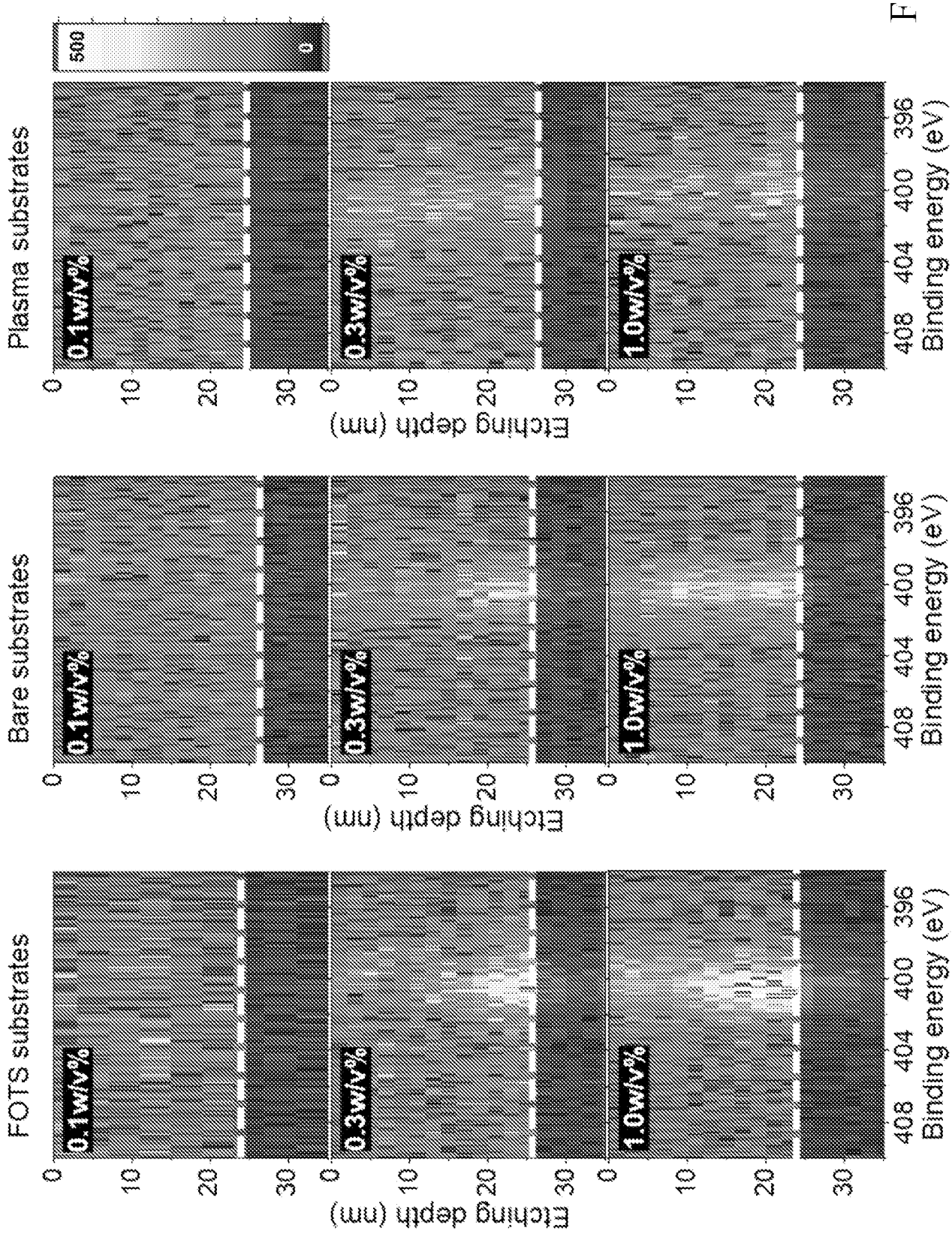
FOTS substrates
Bare substrates
Plasma substrates
0.1w/v%
0.3w/v%
1.0w/v%
Etching depth (nm)
Binding energy (eV)
500
0

Fig. 7

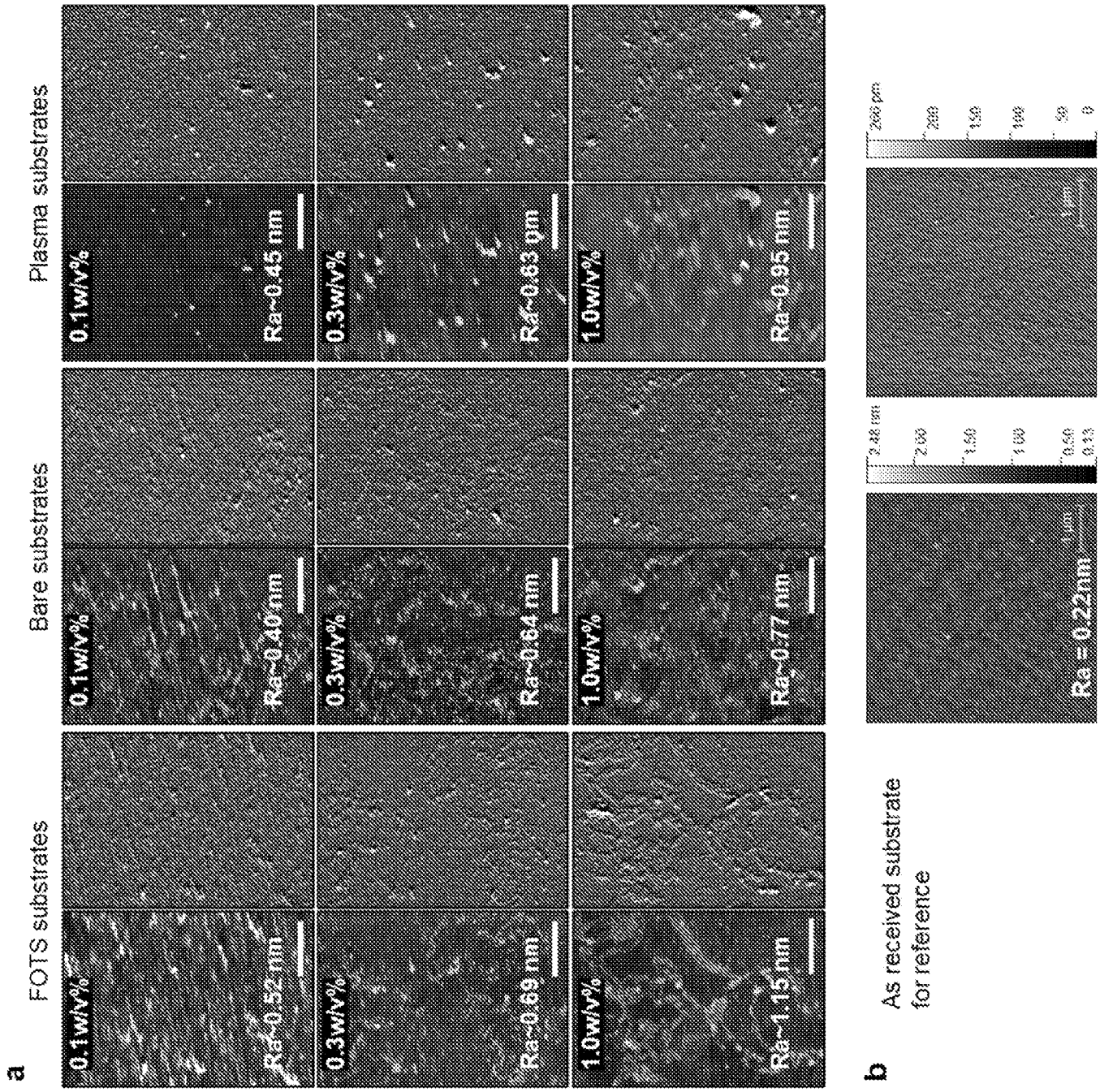
a
FOTS substrates
Bare substrates
Plasma substrates
0.1w/v%
Ra~0.52 nm
Ra~0.40 nm
Ra~0.45 nm
0.3w/v%
Ra~0.89 nm
Ra~0.84 nm
Ra~0.83 nm
1.0w/v%
Ra~1.15 nm
Ra~0.77 nm
Ra~0.95 nm
b
As received substrate for reference
Ra = 0.22nm

Fig. 8

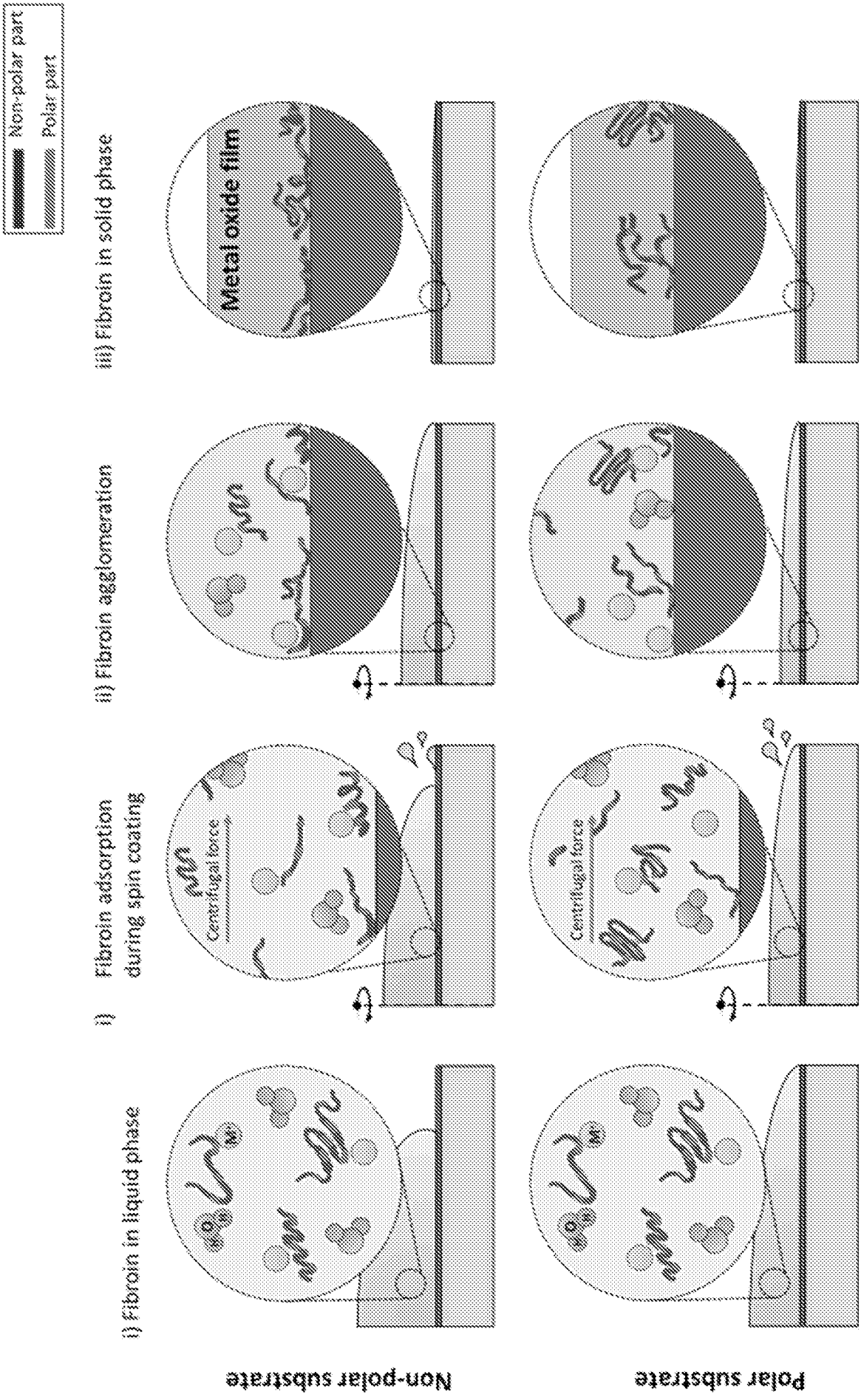
Non-polar part
Polar part
i) Fibroin in liquid phase
ii) Fibroin adsorption during spin coating
iii) Fibroin agglomeration
iiii) Fibroin in solid phase
Centrifugal force
Metal oxide film
Non-polar substrate
Polar substrate

Fig. 9

Characteristics	Precursors
Insulating	Al, Zr
Semiconducting	In, Ga, Zn
Conducting	In & Sn
Metallic	Pd
Transporting	Ni, Cu
High refractive index	Zr
Perovskite	Cs, Pb

Fig. 10

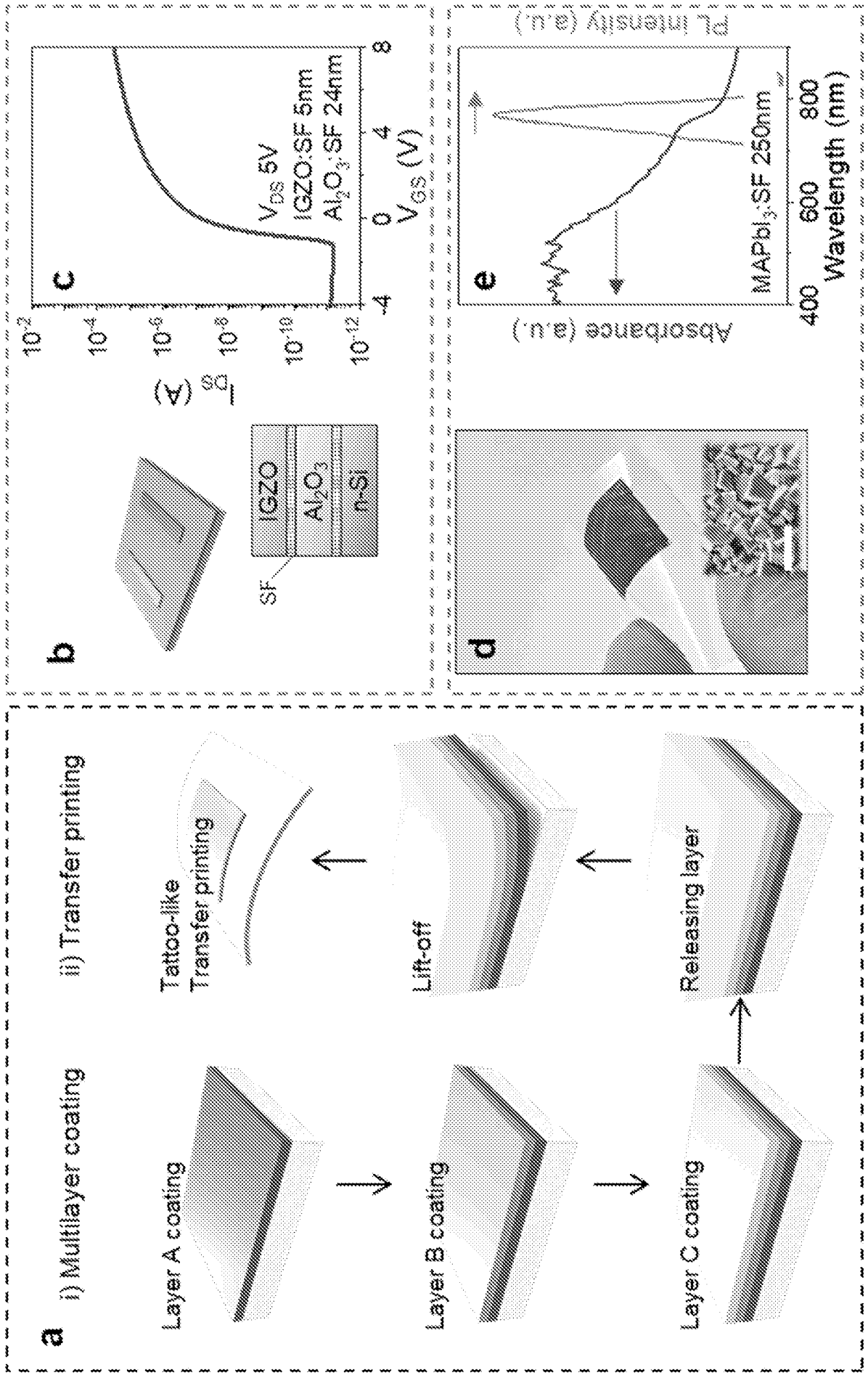
a
i) Multilayer coating
ii) Transfer printing
Layer A coating
Layer B coating
Layer C coating
Releasing layer
Lift-off
Tattoo-like
Transfer printing
b
IGZO
Al_2O_3
n-Si
SF
c
V_{DS} 5V
IGZO:SF 5nm
Al_2O_3:SF 24nm
I_{DS} (A)
V_{GS} (V)
d
e
$MAPbI_3$:SF 250nm
Absorbance (a.u.)
PL Intensity (a.u.)
Wavelength (nm)

Fig. 11

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2024/060977

A. CLASSIFICATION OF SUBJECT MATTER

IPC: ***A61K 38/17*** (2025.01); ***C11D 1/00*** (2025.01); ***C09D 189/00*** (2025.01); *C08J 3/07* (2025.01)

CPC: ***A61K 38/1767; C11D 1/00; C09D 189/00;*** *C08J 3/07*

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)

See Search History Document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

See Search History Document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

See Search History Document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2023/0123989 A1 (TRUSTEES OF TUFTS COLLEGE) 20 April 2023 (20.04.2023) entire document	1-2
A	US 2023/0151168 A1 (Zhejiang Lab) 18 May 2023 (18.05.2023) entire document	1-2
A	US 2022/0331493 A1 (ZHA et al.) 20 October 2022 (20.10.2022) entire document	1-2
X	Valisalmi et al., "Highly Hydrophobic Films of Engineered Silk Proteins by a Simple Deposition Method", 16 March 2023, Langmuir.; 39(12):4370-4381. doi: 10.1021/acs.langmuir.2c03442. PMID: 36926896; PMCID: PMC10061925. abstract, pg 4371 col 1 para 3, pg 4731 col 2 para 3, pg 4377 col 1 para 3, pg 4377 col 2 para 2	1-2
P,X	Kim, "Role of Silk Fibroin for Regulating Wetting Interfaces in High-Resolution Aqueous Nanofilm Fabrication", February 2024, Tufts University ProQuest Dissertations and Theses. entire document	1-2

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

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"D" document cited by the applicant in the international application
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
06 February 2025 (06.02.2025)	**23 April 2025 (23.04.2025)**

Name and mailing address of the ISA/US	Authorized officer
COMMISSIONER FOR PATENTS **MAIL STOP PCT, ATTN: ISA/US** **P.O. Box 1450** **Alexandria, VA 22313-1450** **UNITED STATES OF AMERICA**	**KARI RODRIQUEZ**
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2024/060977

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	Kim et al. "Silk fibroin as a surfactant for water-based nanofabrication", 29 July 2024, Nat. Nanotechnol. 19, 1514–1520 (2024). https://doi.org/10.1038/s41565-024-01720-3 entire document	1-2

INTERNATIONAL SEARCH REPORT

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Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☑ Claims Nos.: **21-30**
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1.

Group I: Claims 1-2, directed to a method of using silk fibroin as a surfactant, the method comprising depositing pure water onto the first surface produces a contact angle of greater than 90°.

Group II: Claims 3-5, directed to a method of depositing a layer of a predetermined solute from an aqueous solvent onto a predetermined surface.

Group III: Claims 6-7, directed to a method of improving an industrial process that does not previously utilize silk fibroin.

Group IV: Claims 8-9, directed to a method of using silk fibroin as a surfactant, the method comprising using silk fibroin as a surfactant for wetting the two different surfaces having the different surface energies.

Group V: Claims 10-11, directed to a method of using silk fibroin as a surfactant, the method comprising drying the first surface, and removing residual silk fibroin from the dried first surface.

Group VI: Claims 12, directed to a method of improving surface wetting comprising measuring an immediate comparison contact angle and optionally a time-varying comparison contact angle for a comparison aqueous solution applied to a first surface.

Group VII: Claims 13-20, directed to a method of making a nanoscale silk coating comprising spin coating an aqueous silk fibroin solution.

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Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☑ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.: **1-2**

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.