

**PATENT APPLICATION FILED UNDER THE PATENT COOPERATION TREATY
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FOR

Roll-to-roll fabrication of nanostructured film

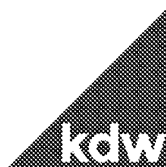
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ROLL-TO-ROLL FABRICATION OF NANOSTRUCTURED FILM

RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Patent Application No. 63/542,430, filed October 4, 2023, the content of which is incorporated herein in its entirety.

GOVERNMENT RIGHTS

[0002] This invention was made with United States government support under 1916110 awarded by the National Science Foundation (NSF). The U S government has certain rights in the invention.

BACKGROUND OF THE INVENTION

[0003] Nanostructures have shown great promise in a variety of applications in energy transport, conversion, and storage, opto-electronics, nano-electronics, photonics, sensing, biotechnology, and medicine. A series of fabrication methods based on lithography, physical vapor deposition, chemical vapor deposition, chemical synthesis, electrochemical deposition, etc. have been developed to control the shape, size distribution, and surface chemistry of nanostructures. However, most of the methods are either costly or non-scalable. Roll-to-roll fabrication is a film-based scalable fabrication method that is a highly favorable approach for industry, while so far, the roll-to-roll technology for nanostructure fabrication is mainly based on nanoimprinting and lithography.

[0004] Therefore, a low-cost and highly controllable roll-to-roll templated deposition method for fabricating nanostructured films remains needed.

SUMMARY OF THE INVENTION

[0005] One aspect of the present application is to provide a method for fabricating a nanostructured film, comprising:

preparing a first ion-conductive layer formed of a first porous scaffold or polymer gel containing first electrolytes,

creating a stacked structure comprising a conductive substrate, a first porous template disposed on the substrate, the first ion-conductive layer disposed on the template, and a first metal anode disposed on the first ion-conductive layer;

providing a first plurality of rollers on the first metal anode;

applying pressure to the stacked structure via the first plurality of rollers so that the first porous template conforms and stays attached to the substrate;

applying a first galvanic potential between the first metal anode and the conductive substrate;

growing a first nanostructure from the substrate into the first porous template by first electrochemical deposition so that the substrate and the first porous template are bonded together; and

removing the first porous template by chemical dissolution or chemical etching to obtain the nanostructured film.

[0006] This method may further comprise providing a conveyor belt beneath the substrate.

[0007] In accordance with a preferred embodiment, the nanostructure deposition may be conducted on both sides of the substrate. In that case, the method may further comprise preparing a second ion-conductive layer formed of a second porous scaffold or polymer gel containing second electrolytes. The stacked structure may further comprise, in sequence, a second porous template disposed beneath the substrate, the second ion-conductive layer disposed underneath the second porous template, and a second metal anode. The method may further comprise:

providing a second plurality of rollers underneath the second metal anode;
applying pressure to the stacked structure via the second plurality of rollers so the second porous template conforms and stays attached to the substrate,
applying a second galvanic potential between the second metal anode and the substrate;
growing a second nanostructure from the substrate into the second porous template by second electrochemical deposition so that the substrate and the second porous template are bonded together; and
removing the second porous template to obtain the nanostructured film by chemical dissolution or chemical etching.

[0008] The first and/or second porous scaffolds may be made of a material selected from the group consisting of membrane, filter film, porous polymer films, foam, fabric, paper, sponge, and the first and/or second polymer gel may be selected from the group consisting of hydrogel and other polymer gels, such as organogels and amphiphilic gels.

[0009] Based on another aspect of the present application, tube rollers comprising radially, tubes, electrolytes, and anodes may replace the rollers, electrolytes, and anodes discussed above. In that case, the method for fabricating a nanostructured film may comprise:

preparing a first plurality of ion-conductive tube rollers, with each of the first plurality of ion-conductive tube rollers comprising, in sequence, radially from outside to inside, a first porous tube containing first electrolytes, and a first anode;
forming a stacked structure comprising a conductive substrate and a first porous template disposed on the substrate,
placing the first plurality of ion-conductive tube rollers on the stacked structure,

applying pressure to the stacked structure via the first plurality of ion-conductive tube rollers so that the first porous template conforms and stays attached to the substrate;

growing a first nanostructure from the substrate into the first porous template by first electrochemical deposition so that the substrate and the first porous template are bonded together;

applying a first galvanic potential between the first anode and the substrate; and

removing the first porous template to obtain the nanostructured film by chemical dissolution or chemical etching.

[00010] As a preferred embodiment, the method may further comprise a step of providing a conveyor belt beneath the substrate.

[00011] In accordance with a preferred embodiment, the nanostructure deposition may be conducted on both sides of the substrate. In that case, the method may further comprise:

preparing a second plurality of ion-conductive tube rollers, with each of the second plurality of ion-conductive tube rollers comprising, in sequence, radially from outside to inside, a second porous tube, second electrolytes, and a second anode;

placing the second plurality of ion-conductive tube rollers underneath the stacked structure,

applying pressure to the stacked structure via the second plurality of ion-conductive tube rollers so that the second porous template conforms and stays attached to the substrate;

growing a second nanostructure from the substrate into the second porous template by second electrochemical deposition so that the substrate and the second porous template are bonded together;

applying a second galvanic potential between the second anode and the substrate;
and

removing the second porous template to obtain the nanostructured film by
chemical dissolution or chemical etching.

[00012] As a preferred embodiment, at least one of the inner surface and outer surface of the first and/or second porous tubes is further covered with an ion-conductive layer comprising electrolytes with a better deformability for a better contact with the first and/or second anodes and/ or the first and/or second porous templates than the first and/or second porous tubes.

[00013] The first anode may be a cylindrical rod.

[00014] A further aspect of the present application is a multi-layer product comprising:

- a conductive substrate,
- a first porous template disposed on the substrate,
- a first ion-conductive layer disposed on the template, with the first ion-conductive layer being formed of a first porous scaffold or a polymer gel containing first electrolytes;
- a first metal anode disposed on the first ion-conductive layer; and
- a first plurality of rollers on the first metal anode.

[00015] As a preferred embodiment, the product may further comprise a conveyor belt beneath the substrate.

[00016] As another preferred embodiment, the product may further comprise:

- a second porous template disposed beneath the substrate,
- a second ion-conductive layer disposed underneath the second porous template,

with the second ion-conductive layer being formed of a second porous scaffold or polymer gel containing second electrolytes

a second metal anode, and

a second plurality of rollers underneath the second metal anode.

[00017] Yet another aspect of the present application is a multi-layer product comprising:

a conductive substrate;

a first porous template disposed on the substrate; and

a first plurality of ion-conductive tube rollers on the first porous template, wherein each of the first plurality of ion-conductive tube rollers comprises, in sequence, radially from outside to inside, a first porous tube containing first electrolytes, and a first anode.

[00018] The multi-layer product may further comprise a conveyor belt beneath the substrate.

[00019] The multi-layer product may further comprise:

a second porous template disposed underneath the conductive substrate;

a second plurality of ion-conductive tube rollers underneath the second porous template, with each of the second plurality of ion-conductive tube rollers comprising, in sequence, radially from outside to inside, a second porous tube, second electrolytes, and a second anode.

BRIEF DESCRIPTION OF THE DRAWINGS

[00020] Figure 1 schematically shows the stacked anode (101), ion-conductive layer containing electrolyte (102), template layer (103), conductive substrate (104) transported between rollers (105) and conveyor belt (106) based on an embodiment of this application.

[00021] Figure 2 schematically shows the stacked sandwich structure consisting of anode (201), ion-conductive layer containing electrolyte (202), template layer (203) and

conductive substrate (204) transported between two sets of rollers (205) based on another embodiment of this application.

[0001] Figure 3 schematically shows the template layer (301) and conductive substrate (302) transported (moved or delivered) between the roller assembly and the conveyor belt (305) based on yet another embodiment of this application. The roller assembly consists of the anode (303) and the ion-conductive tube roller containing electrolyte (304).

[0002] Figure 4 schematically shows the template (401) and conductive substrate (402) transported between the roller assembly and the conveyor belt (406) based on a further embodiment of this application. The roller assembly consists of the ion-conductive tube roller containing electrolyte (403) wrapped by a soft ion-conductive layer containing electrolyte (404) on both inner and outer sides, with the anode (405) in the middle.

[0003] Figure 5 schematically shows the porous template (501) and conductive substrate (502) transported between two sets of roller assemblies based on another embodiment of this application. The roller assembly consists of the ion-conductive tube roller containing electrolyte (503) wrapped by a soft ion-conductive layer containing electrolyte (504) on both inner and outer sides, with the anode (505) in the middle.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0004] As used herein, the term “about” when immediately preceding a numerical value means a range of plus or minus 10% of that value, for example, “about 50” means 45 to 55, “about 25,000” means 22,500 to 27,500, etc., unless the context of the disclosure indicates otherwise, or is inconsistent with such an interpretation.

[0005] As used herein, the singular forms “a,” “an,” and “the” include plural references unless the context clearly dictates otherwise. Unless defined otherwise, all technical and scientific terms used herein have the same meanings as commonly understood by one of

ordinary skill in the art. Nothing in this disclosure is to be construed as an admission that the embodiments described in this disclosure are not entitled to antedate such disclosure by virtue of prior invention. As used in this document, the term “comprising” means “including, but not limited to.”

[0006] While various compositions, methods, and devices are described in terms of "comprising" various components or steps (interpreted as meaning "including, but not limited to"), the compositions, methods, and devices may also "consist essentially of" or "consist of" the various components and steps, and such terminology should be interpreted as defining essentially closed-member groups.

[0007] With respect to the use of substantially any plural and/or singular terms herein, those having skill in the art may translate from the plural to the singular and/or from the singular to the plural as is appropriate to the context and/or application. The various singular/plural permutations may be expressly set forth herein for sake of clarity.

[0008] It will be understood by those within the art that, in general, terms used herein, and especially in the appended claims (for example, bodies of the appended claims) are generally intended as “open” terms (for example, the term “including” should be interpreted as “including but not limited to,” the term “having” should be interpreted as “having at least,” the term “includes” should be interpreted as “includes but is not limited to,” etc.). It will be further understood by those skilled in the art that if a specific number of an introduced claim recitation is intended, such an intent will be explicitly recited in the claim, and in the absence of such recitation no such intent is present. For example, as an aid to understanding, the following appended claims may contain usage of the introductory phrases “at least one” and “one or more” to introduce claim recitations. However, the use of such phrases should not be construed to imply that the introduction of a claim recitation by the indefinite articles “a” or “an” limits any particular claim containing such introduced claim recitation to

embodiments containing only one such recitation, even when the same claim includes the introductory phrases "one or more" or "at least one" and indefinite articles such as "a" or "an" (for example, "a" and/or "an" should be interpreted to mean "at least one" or "one or more"); the same holds true for the use of definite articles used to introduce claim recitations. In addition, even if a specific number of an introduced claim recitation is explicitly recited, those skilled in the art will recognize that such recitation should be interpreted to mean at least the recited number (for example, the bare recitation of "two recitations," without other modifiers, means at least two recitations, or two or more recitations). Furthermore, in those instances where a convention analogous to "at least one of A, B, and C, etc." is used, in general such a construction is intended in the sense one having skill in the art would understand the convention (for example, "a system having at least one of A, B, and C" would include but not be limited to systems that have A alone, B alone, C alone, A and B together, A and C together, B and C together, and/or A, B, and C together, etc.). In those instances where a convention analogous to "at least one of A, B, or C, etc." is used, in general such a construction is intended in the sense one having skill in the art would understand the convention (for example, "a system having at least one of A, B, or C" would include but not be limited to systems that have A alone, B alone, C alone, A and B together, A and C together, B and C together, and/or A, B, and C together, etc.). It will be further understood by those within the art that virtually any disjunctive word and/or phrase presenting two or more alternative terms, whether in the description, claims, or drawings, should be understood to contemplate the possibilities of including one of the terms, either of the terms, or both terms. For example, the phrase "A or B" will be understood to include the possibilities of "A" or "B" or "A and B."

[0009] In addition, where features or aspects of the disclosure are described in terms of Markush groups, those skilled in the art will recognize that the disclosure is also thereby described in terms of any individual member or subgroup of members of the Markush group.

[0010] As will be understood by one skilled in the art, for any and all purposes, such as in terms of providing a written description, all ranges disclosed herein also encompass any and all possible subranges and combinations of subranges thereof. Any listed range may be easily recognized as sufficiently describing and enabling the same range being broken down into at least equal halves, thirds, quarters, fifths, tenths, etc. As a non-limiting example, each range discussed herein may be readily broken down into a lower third, middle third and upper third, etc. As will also be understood by one skilled in the art all language such as “up to,” “at least,” and the like include the number recited and refer to ranges which may be subsequently broken down into subranges as discussed above. Finally, as will be understood by one skilled in the art, a range includes each individual member. Thus, for example, a group having 1-3 cells refers to groups having 1, 2, or 3 cells. Similarly, a group having 1-5 cells refers to groups having 1, 2, 3, 4, or 5 cells, and so forth.

[0011] This disclosure is not limited to the particular systems, devices and methods described, as these may vary. The terminology used in the description is for the purpose of describing the particular versions or embodiments only and is not intended to limit the scope.

[0012] In this application, we developed a roll-to-roll templated deposition method that is low-cost and highly controllable for fabricating nanostructured films. Two different approaches are developed.

[0013] Based on the first approach, stacked layers will be placed between a plurality of rollers (preferably 2-100, more preferably 5-20 rollers) and a conveyor belt (*see* Figure 1) or between two groups of rollers (*see* Figure 2) (preferably 2-100 pairs, more preferably 5-20 pairs of rollers) on opposite sides of the stacked layers and continuously transported

(moved or delivered). The stacking from top to bottom comprises an anode, an ion-conductive layer containing electrolytes, a template layer, and a cathode substrate layer. A pressure is applied to the stacked layers by the rollers and/or the conveyor belt, to cause the template to conform and stay attached to the target surface. The pressure is controlled by adjusting the pre-set distance between the rollers or between the rollers and the conveyor belt. A soft and deformable material is preferred for roller contact, which provides wider adjustability for the applied pressure. The material may be rubber, polymer, silicone, foam, sponge, etc. A galvanic potential is applied between the anode and substrate, to allow electrochemical deposition of the nanostructures on the substrate.

[00014] The electrodeposition happens at the roller-compressed region and the region between the rollers, where the stacked layers remain tightly contacted. The deformability of the roller under pressure, and the size and number of the plurality of rollers, and the gap distance between the nearby rollers from the same group determine the size of the region for the electrodeposition of the nanostructures on the substrate. After electrodeposition, nanostructures are formed inside the template, and the template and the substrate are tightly bonded to each other.

[00015] The electrodeposited nanostructures on the substrate can be grown to a desired size solely through the above-described process, or through a two-step growing process. Specifically, for the two-step growing process, the template and substrate may be bonded through the above-described process and then separated from the stacking and delivered to an electrochemical bath, with a metal anode disposed in parallel with the bonded template and substrate to continue growing the nanostructure to a desired size.

[00016] The template is then removed to release the nanostructure. The removal process may involve chemical dissolution or chemical etching. For example, when a track-etched

polycarbonate membrane is used as a template, it can be dissolved by organic solvents like dichloromethane, chloroform, etc.

[00017] The ion-conductive layer may be a porous scaffold containing electrolyte, for example, membrane, filter film, porous polymer films, foam, fabric, paper, sponge, etc., where the electrolyte is filled/infiltrated/contained inside the porous and the scaffold layer plus electrolyte is conductive to ions. The ion-conductive layer may also be formed of hydrogels or other polymer gels capable of containing the electrolyte and conductive to ions. The gel used for the ion-conductive layer may be a network of polymer chains capable of absorbing and retaining a sufficient amount of aqueous or organic solvents while maintaining their structure.

[00018] The material of the to-be-deposited nanostructures may be a metal, such as copper, nickel, silver, gold, brass, cadmium, chromium, and iron, and a semiconductor, such as ZnS, ZnO, ZnSe, CdMnTe, CdS, ZnTe, GaSe, InSe, CdSe, CuInGaSe₂, CdTe, CuInSe₂, and Ni(OH)₂ that can be electrochemically deposited. The material of the anode and electrolyte correspond accordingly. For example, when the to-be-deposited nanostructure is formed of Ni, the anode is preferably Ni, and the electrolyte is preferably nickel sulfate, nickel chloride, nickel sulfamate, nickel ammonium sulfate, etc.

[00019] The deposited nanostructure may be controlled by varying the electrodeposition current, voltage, and duration. The voltage and current may be varied based on the material that will be electrochemically deposited. Generally, the voltage varies from 0 ~ 1.2 V, and the current varies from 0 ~ 300 mA/cm². The duration depends on how fast the stacked layers pass through the deposition area before being separated, or in other words, how long the stack remains tightly contacted.

[00020] The template film may be a commercially available item, including but not limited to various types of track-etched polymer films such as track-etched polycarbonate (TEPC),

track-etched polyester (TEPET), track-etched polyimide (TEPI), track-etched polypropylene (TEPP), track-etched polystyrene (TEPS), etc., and porous membranes or polymer films such as aluminum oxide membranes, silver membranes, cellulose acetate membranes, ceramic membranes, glass fiber membranes, mixed cellulose ester (MCE) membrane, Nylon membranes, polyacrylonitrile membranes, polycarbonate membranes, polyether sulfone membranes, polyester membranes, polyethylene membranes, polypropylene membranes, PTFE membranes, PVDF membranes, etc., and other porous templates, such as anodic aluminum oxides and porous silicon layers.

[00021] The substrate is either conductive or coated with a conductive top layer. The conductive layer or coating may be formed of an electrically conductive metal, including, but not limited to, Ag, Au, Pt, Cu, Al, Fe, Zn, Ni, Co, Ru, bronze, brass, Pb, stainless steel, etc., or a conductive polymer, including, but not limited to, PEDOT:PSS, PH1000, and Poly(3-hexylthiophene) (P3HT), or a semiconductor with acceptable resistivity, including but not limited to Si, doped-Si, silicon nitride, indium doped tin oxide, and fluorine-doped tin oxide, and other conductive material, such as graphene, carbon nanotube, and carbon fiber.

[00022] For the second approach, instead of a normal roller, a stiff ion-conductive tube containing electrolyte serves as both the roller and the ion-conductive layer between the anode and template (*see* Figure 3). A cylindrical rod serves as the anode. The inner and outer surfaces of the tube may further be covered by a soft ion-conductive layer mentioned in the 1st approach to achieve a soft contact between the tube roller and the anode rod, and between the tube roller and the template layer (*see* Figure 4). In this second approach, the stacked layer passing through the rollers is simplified to contain a porous template and the substrate film. A template-substrate-template stack may also be used to pass through groups of rollers (preferably 2-100 pairs of rollers, more preferably 5-20 pairs of rollers) to

concurrently achieve the nanostructure deposition on both sides of the substrate (*see* Figure 5).

[00023] Ion-conductive tube roller may be formed of a porous tube that is hydrophilic to the electrolyte, for example, a porous polymer tube made of polyethylene, PTFE, or PVDF, or a porous metal tube formed of a metal material that does not react with the electrolyte, including but not limited to, copper, nickel, stainless steel, titanium, aluminum, platinum, silver, gold, iron, lead, cobalt, and other metals and alloys.

[00024] Except for the ion-conductive layer, all other materials may be the same as discussed above in connection with the first approach discussed above.

[00025] In both the first and second approaches, the obtained nanostructure is grown from the substrate into the template so that the two layers are tightly bonded together. If the nanostructure growth has not finished, then the substrate with the template may be transferred to a standard electroplating bath for continuous growth. When the desired height is achieved, the nanostructure may be released from the porous template by dissolving/removing the template. The continued growth and template dissolving/removing steps may also be realized by the roll-to-roll process.

[00026] Figure 1 schematically shows stacked anode (101), ion-conductive layer containing electrolyte (102), template layer (103), and conductive substrate (104) transported between rollers (105) and conveyor belt (106) based on the first approach discussed above.

[00027] Figure 2 schematically shows a stacked sandwich structure comprising anode (201), ion-conductive layer containing electrolyte (202), template layer (203), and conductive substrate (204) transported between two sets of rollers (205) based on the first approach described above. The nanostructure grows on both sides of the substrate.

[00028] Figure 3 schematically shows template layer (301) and conductive substrate (302) transported between the roller assembly and the conveyor belt (305). The roller assembly

consists of the anode (303) and the ion-conductive tube roller containing electrolyte (304) based on the second approach discussed above.

[00029] Figure 4 schematically shows template (401) and conductive substrate (402) transported between the roller assembly and the conveyor belt (406). The roller assembly consists of the ion-conductive tube roller containing electrolyte (403) wrapped by soft ion-conductive layer containing electrolyte (404) on both inner and outer sides, with the anode (405) in the middle based on the second approach discussed above.

[00030] Figure 5 schematically shows porous template (501) and conductive substrate (502) transported between two sets of roller assemblies. The roller assembly comprises the ion-conductive tube roller containing electrolyte (503) wrapped by a soft ion-conductive layer containing electrolyte (504) on both inner and outer sides, with the anode (505) in the middle based on the second approach discussed above. The nanostructure grows on both sides of the substrate.

[00031] Based on the embodiments of the instant invention, the overall fabrication speed has been greatly increased, and the deposition area has largely improved (e.g., longitudinally from 7mm to 66mm). The benefit comes not just from the roller-compressed area but also from the areas between the rollers. After the compression from the roller area, the layers are tightly attached to each other, and nanowires may keep growing into the template.

CLAIMS

We claim:

1. A method for fabricating a nanostructured film, comprising:
 - preparing a first ion-conductive layer formed of a first porous scaffold or a polymer gel containing first electrolytes,
 - creating a stacked structure comprising a conductive substrate, a first porous template disposed on the substrate, the first ion-conductive layer disposed on the template, and a first metal anode disposed on the first ion-conductive layer;
 - providing a first plurality of rollers on the first metal anode;
 - applying pressure to the stacked structure via the first plurality of rollers so that the first porous template conforms and stays attached to the substrate;
 - applying a first galvanic potential between the first metal anode and the conductive substrate;
 - growing a first nanostructure from the substrate into the first porous template by first electrochemical deposition so that the substrate and the first porous template are bonded together; and
 - removing the first porous template by chemical dissolution or chemical etching to obtain the nanostructured film.
2. The method of claim 1, wherein the method further comprises a step of providing a conveyor belt beneath the substrate.
3. The method of claim 1 wherein the method further comprises preparing a second ion-conductive layer formed of a second porous scaffold or

polymer gel containing second electrolytes, wherein the stacked structure further comprises, in sequence, a second porous template disposed beneath the substrate, the second ion-conductive layer disposed underneath the second porous template, and a second metal anode, and the method further comprises:

providing a second plurality of rollers underneath the second metal anode;

applying pressure to the stacked structure via the second plurality of rollers so that the second porous template conforms and stays attached to the substrate,

applying a second galvanic potential between the second metal anode and the substrate;

growing a second nanostructure from the substrate into the second porous template by second electrochemical deposition so that the substrate and the second porous template are bonded together; and

removing the second porous template to obtain the nanostructured film by chemical dissolution or chemical etching.

4. The method of claim 1 wherein the first porous scaffold is made of a material selected from the group consisting of membrane, filter film, porous polymer films, foam, fabric, paper, and sponge, and the first polymer gel is selected from the group consisting of hydrogels, organogels, and amphiphilic gels.

5. A method for fabricating a nanostructured film comprising:

preparing a first plurality of ion-conductive tube rollers, wherein each of the first plurality of ion-conductive tube rollers comprises, in

sequence, radially from outside to inside, a first porous tube containing first electrolytes, and a first anode;

forming a stacked structure comprising a conductive substrate and a first porous template disposed on the substrate,

placing the first plurality of ion-conductive tube rollers on the stacked structure,

applying pressure to the stacked structure via the first plurality of ion-conductive tube rollers so that the first porous template conforms and stays attached to the substrate;

growing a first nanostructure from the substrate into the first porous template by first electrochemical deposition so that the substrate and the first porous template are bonded together;

applying a first galvanic potential between the first anode and the substrate; and

removing the first porous template to obtain the nanostructured film by chemical dissolution or chemical etching.

6. The method of claim 5, wherein the method further comprises providing a conveyor belt beneath the substrate.
7. The method of claim 5 wherein the stacked structure further comprises a second porous template disposed underneath the substrate, and the method further comprises:

preparing a second plurality of ion-conductive tube rollers, wherein each of the second plurality of ion-conductive tube rollers comprises, in sequence, radially from outside to inside, a second porous tube, second electrolytes, and a second anode;

placing the second plurality of ion-conductive tube rollers underneath the stacked structure

applying pressure to the stacked structure via the second plurality of ion-conductive tube rollers so that the second porous template conforms and stays attached to the substrate;

growing a second nanostructure from the substrate into the second porous template by second electrochemical deposition so that the substrate and the second porous template are bonded together;

applying a second galvanic potential between the second anode and the substrate; and

removing the second porous template to obtain the nanostructured film by chemical dissolution or chemical etching.

8. The method of claim 5 wherein the first porous tube has a first inner surface and a first outer surface, and wherein at least one of the first inner surface and the first outer surface is further covered with a third ion-conductive layer comprising third electrolytes with a better deformability for a better contact with the first anode and/ or the first porous template than the first porous tube.
9. The method of claim 7 wherein the second porous tube has a second inner surface and a second outer surface, and wherein at least one of the second inner surface and the second outer surface is further covered with a fourth ion-conductive layer comprising fourth electrolytes with better deformability for better contact with the second anode and/or the second porous template than the second porous tube.
10. The method of claim 5 wherein the first anode is a cylindrical rod.

11. The method of claim 5 wherein the first porous tube is formed of a hydrophilic material selected from the group consisting of polyethylene, PTFE, PVDF, and a metal that does not react with the first electrolytes.
12. The method of claim 11 wherein the metal is selected from the group consisting of copper, nickel, stainless steel, titanium, aluminum, platinum, silver, gold, iron, lead, cobalt, and other metals and alloys.
13. A multi-layer product comprising:
 - a conductive substrate,
 - a first porous template disposed on the substrate,
 - a first ion-conductive layer disposed on the template, wherein the first ion-conductive layer is formed of a first porous scaffold or a polymer gel containing first electrolytes;
 - a first metal anode disposed on the first ion-conductive layer;
 - and
 - a first plurality of rollers on the first metal anode.
14. The multi-layer product of claim 13 further comprising a conveyor belt beneath the substrate.
15. The multi-layer product of claim 13 further comprising:
 - a second porous template disposed beneath the substrate;
 - a second ion-conductive layer disposed underneath the second porous template, wherein the second ion-conductive layer is formed of a second porous scaffold or polymer gel containing second electrolytes;
 - a second metal anode; and
 - a second plurality of rollers underneath the second metal anode.
16. A multi-layer product comprising:

a conductive substrate;

a first porous template disposed on the substrate; and

a first plurality of ion-conductive tube rollers on the first porous template, wherein each of the first plurality of ion-conductive tube rollers comprises, in sequence, radially from outside to inside, a first porous tube containing first electrolytes, and a first anode.

17. The multi-layer product of claim 16 further comprising a conveyor belt beneath the substrate.

18. The multi-layer product of claim 16 further comprising:

a second porous template disposed underneath the conductive substrate;

a second plurality of ion-conductive tube rollers underneath the second porous template, wherein each of the second plurality of ion-conductive tube rollers comprises, in sequence, radially from outside to inside, a second porous tube, second electrolytes, and a second anode.

19. The method of any of the preceding claims, wherein the first nanostructure and second nanostructure are made of a metal selected from the group consisting of copper, nickel, silver, gold, brass, cadmium, chromium, and iron.

20. The method of any of the preceding claims, wherein the first nanostructure and second nanostructure are made of a semiconductor selected from the group consisting of ZnS, ZnO, ZnSe, CdMnTe, CdS, ZnTe, GaSe, InSe, CdSe, CuInGaSe₂, CdTe, CuInSe₂, and Ni(OH)₂.

21. The method of any of the preceding claims, wherein the first electrochemical deposition and the second electrochemical deposition are controlled by adjusting electrodeposition current, voltage, and duration.
22. The method of any of the preceding claims, wherein the first porous template and the second porous template are made of a material selected from the group consisting of track-etched polycarbonate (TEPC), track-etched polyester (TEPET), track-etched polyimide (TEPI), track-etched polypropylene (TEPP), track-etched polystyrene (TEPS), aluminum oxide membranes, silver membranes, cellulose acetate membranes, ceramic membranes, glass fiber membranes, mixed cellulose ester membrane, Nylon membranes, polyacrylonitrile membranes, polycarbonate membranes, polyethersulfone membranes, polyester membranes, polyethylene membranes, and polypropylene membranes, PTFE membranes, PVDF membranes, anodic aluminum oxides, porous silicon layers.
23. The method of any of the preceding claims, wherein the substrate is either conductive or coated with a conductive top layer.
24. The method of any of the preceding claims, wherein the process comprises transferring the substrate bonded with the first porous template and/or the second porous template, to an electroplating bath comprising a third metal anode and/or a fourth metal anode for continuous growth.
25. The method of claim 24 further comprising a step of separating the substrate bonded with the first porous template and/or the second porous

template from the stacked structure when the stacked structure comprises the first ion-conductive layer and/or the second ion-conductive layer.

26. The method of any of the preceding claims, wherein the substrate acts as a cathode during the growth of the first and second nanostructures.