[0006] In addition, current extrusion-based printing methods are limited to resolutions of 200–1000 μm due to the nozzle size, posing a limitation for an affordable 3D printing method for biomaterial or electronics applications requiring high resolution printing. While the more costly AM methods such as inkjet printing, stereolithography (SLA) and two photon 3D printing (TPP) allow for 10-50 μm, ~1 μm and less than 100 nm resolution respectively, the printable materials are limited by the printing mechanism and are often proprietary to the manufacturer of the machine. Moreover, they can have reduced structural properties due to the vertical layering of the material and lack of functionality, constraining the application and quality of the printed structures. Accordingly, there is a need to develop new AM methods that are able to produce structures in high resolution that do not suffer from the limitations of the previous AM methods in the art.

[0007] Further, there are difficulties in printing pure conductors in a range of 3D geometries, while maintaining high conductivity of the printed material using AM methods known in the art. There are currently many dimensional constraints on the production of conductive polymer structures (e.g. the polymers themselves are unsuitable for direct processing as they are typically insoluble, making manufacture of complex shapes and characterisation of the polymers themselves difficult). Independent of the method of formation, there are currently several challenges in utilizing conductive polymers (CP) for miniaturized devices: (1) lack of a manufacturing method that enables a high degree of control over the deposited microstructure in all three dimensions; (2) characterization of the manufactured devices is often complex; (3) deposition speed is too slow.

[0008] Some of the methods that have been attempted for micro-/nano-scale fabrication using CPs are: (a) conventional cleanroom lithography; (b) atomic force microscope (AFM) dip-pen nanolithography; (c) AFM scratch lithography; (d) cantilever-based electrochemical deposition; (e) integrated microfluidic systems; (f) scanning electrochemical microscope (SECM); (g) electrohydrodynamic jet printing; (h) inkjet printing; and (i) electropolymerization. All of the above mentioned fabrication methods have their benefits and limitations, however most of them either require a high upfront investment, are lacking in their control of the fabricated structure, or lack in resolution of the printed structure. Accordingly, there is a need to develop new AM methods that enable precise dimensional control for printing highly conductive polymer structures for, e.g., microelectronics applications.

[0009] It is an aim of the present invention to at least partially satisfy at least one of the above needs.

Summary

[00010] The inventors of the present disclosure have surprising found that by using localized electrodeposition resulting from an applied oxidation or reduction potential between an

electrode and a substrate within a container of dissolved electro-depositable material, they have been able to create three dimensional structures in a controlled manner.

[00011] In particular, by measuring the current between the electrode and substrate during the deposition process, they have surprising found that the method may enable the ability to monitor and control deposition processes *in situ*, thereby allowing precise monitoring of reactions at electro-depositable material concentrations as low as 10^{-3} to 10^{-5} M, and enabling control of printing parameters in real time using data from the monitoring. Further, the method may be suitable for forming structures made from a variety of materials, including conductive and insulating polymers, semiconductors and metals. The method may also be suitable for producing structures comprising more than one type of material, i.e. multi-material printing.

[00012] According to a first example of the disclosure there is provided a method for forming a multidimensional structure, the method comprising the following steps:

providing an electrode and a substrate in a fluid,

wherein the fluid comprises:

an electrolyte, and

a precursor agent dispersed therein;

applying an electric potential difference between the substrate and the electrode to reduce or oxidise the precursor agent, thereby depositing a solid material;

measuring current between the substrate and the electrode; and

moving the electrode within the fluid to form a multidimensional structure of the solid material.

[00012a] In one aspect, the present disclosure refers to a method for forming a multidimensional structure, the method comprising the following steps:

providing an electrode having an exposed area or tip to be contacted with a fluid and a substrate,

contacting a fluid with the exposed area or tip of the electrode and the substrate, wherein the surface area of the electrode in contact with the fluid is from 10^{-9} m^2 to 10^{-4} m^2 and the fluid comprises an electrolyte, and a precursor agent dispersed therein;

applying an electric potential difference between the substrate and the electrode to reduce or oxidise the precursor agent, thereby depositing a solid material; and

moving the electrode along an x, y, and z axis to form a multidimensional structure of the solid material.

[00013] The following options may be used in conjunction with the first example, either individually or in any suitable combination.

[00014] The current between the substrate and the electrode may be measured at a plurality of time points. In certain examples, the time points are from about 100 μs to about 1 second apart.

[00015] In certain examples, the current between the substrate and the electrode is measured as a function of time.

[00016] The method may further comprise varying one or more of the electrical potential difference between the substrate and the electrode, and the position of the electrode when the current is above, below, or at a predetermined value. In certain examples, the method comprises increasing the electric potential difference between the substrate and the electrode, and/or decreasing the distance between the electrode and the substrate or multidimensional structure, when the current is below the predetermined value.

[00017] The method may comprise adjusting the electrical potential from a first voltage to a second voltage. In certain examples the method comprises cycling the electrical potential between the first voltage and second voltage. The cycling may comprise varying the electrical potential difference from the first voltage to the second voltage and back to the first voltage, wherein the absolute average rate of change in electric potential difference when varying the electric potential difference from the first voltage to the second voltage is substantially the same as when varying the electric potential difference from the second voltage back to the first voltage.

[00018] In certain examples, the cycling does not comprise voltage pulses.

[00019] The time for one cycle from the first voltage to the second voltage and back to the first voltage may be 100 μs or more.

[00020] The precursor agent may be selected from the group consisting of metal salts and monomeric materials.

[00021] The concentration of the precursor agent in the fluid may be from about 10^{-5} M to about 1.5 M.

[00022] The fluid may be in a container, and the electrode and substrate may be within the fluid in the container.

[00023] The fluid may comprise an organic solvent. The organic solvent may be acetonitrile.

[00024] In certain examples, the fluid does not comprise water.

[00025] The solid material may be selected from the group consisting of vinyl polymers, conjugated polymers, metals, and combinations thereof.

[00026] In certain examples, the solid material is selected from the group consisting of polypyrrole, poly(3,4-ethylenedioxythiophene), polythiophene, polyaniline, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS), polypyrrole:dopamine copolymer, polyvinylimidazole, and copper.

[00027] The precursor agent may be selected from the group consisting of metal ion salts, metal ion complexes, ionic liquids, vinyl monomers, and monomers of conjugated polymers.

[00028] In certain examples the precursor agent is selected from the group consisting of aniline, pyrrole, thiophene, 3,4-ethylenedioxythiophene, vinylimidazole, and copper salts.

[00029] The electrolyte may comprise tetrabutylammonium hexafluorophosphate (TBAHFP).

[00030] In certain examples, the fluid is a first fluid, and the method further comprises:

replacing the first fluid with a second fluid, wherein the second fluid comprises:

an electrolyte, and

a precursor agent dispersed therein, wherein the precursor agent of the second fluid is different to the precursor agent of the first fluid; and

applying an electrical potential difference between the electrode and the substrate to reduce or oxidise the precursor agent of the second fluid, thereby depositing a second solid material.

[00031] In certain examples, the fluid comprises a first precursor agent and a second precursor agent, and the method comprises:

applying a first electrical potential difference between the electrode and the substrate to reduce or oxidise the first precursor agent, thereby depositing a first solid material; and

applying a second electrical potential difference between the electrode and the substrate to reduce or oxidise the second precursor agent, thereby depositing a second solid material.

[00032] In certain examples, the first precursor agent is EDOT, the first solid material is PEDOT, the second precursor agent is vinylimidazole, and the second solid material is polyvinylimidazole.

[00033] The electrode may be a microelectrode or nanoelectrode. The surface area of the electrode may be from about 10^{-9} m^2 to about 10^{-4} m^2.

[00034] The electrode may comprise platinum, carbon, or gold.

[00035] The substrate may comprise indium tin oxide (ITO), silicon, aluminium, steel, gold, or a combination thereof.

[00036] The multidimensional structure may be a three-dimensional structure. It may be electrically conductive. In certain examples it may be a composite structure.

[00037] In certain examples there is provided a method for forming a multidimensional structure, the method comprising the following steps:

providing an electrode and a substrate in a fluid,

wherein the fluid comprises:

TBAHFP, and

pyrrole in acetonitrile;

applying an electric potential difference between the substrate and the electrode to oxidise the pyrrole, thereby depositing polypyrrole;

measuring current between the substrate and the electrode; and

moving the electrode within the fluid to form a multidimensional structure of the polypyrrole;

wherein the current between the substrate and the electrode is measured as a function of time; and the method further comprises increasing the electric potential difference between the substrate and the electrode, and/or decreasing a distance between the electrode and the substrate or multidimensional structure, when the current is below a predetermined value.

[00038] In certain examples there is provided a method for forming a multidimensional structure, the method comprising the following steps:

providing an electrode and a substrate in a fluid,

wherein the fluid comprises:

TBAHFP, and

EDOT in acetonitrile;

applying an electric potential difference between the substrate and the electrode to oxidise the EDOT, thereby depositing PEDOT;

measuring current between the substrate and the electrode; and

moving the electrode within the fluid to form a multidimensional structure of the PEDOT;

wherein the current between the substrate and the electrode is measured as a function of time; and the method further comprises increasing the electric potential difference between the substrate and the electrode, and/or decreasing a distance between the electrode and the substrate or multidimensional structure, when the current is below a predetermined value.

[00039] In certain examples there is provided a method for forming a multidimensional structure, the method comprising the following steps:

providing an electrode and a substrate in a fluid,

wherein the fluid comprises:

TBAHFP, and

thiophene in acetonitrile;

applying an electric potential difference between the substrate and the electrode to oxidise the thiophene, thereby depositing polythiophene;

measuring current between the substrate and the electrode; and

moving the electrode within the fluid to form a multidimensional structure of the polythiophene;

wherein the current between the substrate and the electrode is measured as a function of time; and the method further comprises increasing the electric potential difference between the substrate and the electrode, and/or decreasing a distance between the electrode and the substrate or multidimensional structure, when the current is below a predetermined value.

[00040] In certain examples there is provided a method for forming a multidimensional structure, the method comprising the following steps:

providing an electrode and a substrate in a fluid,

wherein the fluid comprises:

TBAHFP, and

aniline in acetonitrile;

applying an electric potential difference between the substrate and the electrode to oxidise the aniline, thereby depositing polyaniline;

measuring current between the substrate and the electrode; and

moving the electrode within the fluid to form a multidimensional structure of the polyaniline;

wherein the current between the substrate and the electrode is measured as a function of time; and the method further comprises increasing the electric potential difference between the substrate and the electrode, and/or decreasing a distance between the electrode and the substrate or multidimensional structure, when the current is below a predetermined value.

[00041] In certain examples there is provided a method for forming a multidimensional structure, the method comprising the following steps:

providing an electrode and a substrate in a fluid,

wherein the fluid comprises:

TBAHFP, and

vinylimidazole in acetonitrile;

applying an electric potential difference between the substrate and the electrode to oxidise the vinylimidazole, thereby depositing polyvinylimidazole;

measuring current between the substrate and the electrode; and

moving the electrode within the fluid to form a multidimensional structure of the polyvinylimidazole;

wherein the current between the substrate and the electrode is measured as a function of time; and the method further comprises increasing the electric potential difference between the

substrate and the electrode, and/or decreasing a distance between the electrode and the substrate or multidimensional structure, when the current is below a predetermined value.

[00042] In certain examples there is provided a method for forming a multidimensional structure, the method comprising the following steps:

providing an electrode and a substrate in a fluid,

wherein the fluid comprises:

TBAHFP,

EDOT, and

vinylimidazole in acetonitrile;

applying a first electric potential difference between the substrate and the electrode to oxidise the EDOT, thereby depositing PEDOT;

applying a second electrical potential difference between the substrate and the electrode to oxidise the vinylimidazole, thereby depositing polyvinylimidazole;

measuring current between the substrate and the electrode; and

moving the electrode within the fluid to form a multidimensional structure of the PEDOT and polyvinylimidazole;

wherein the current between the substrate and the electrode is measured as a function of time; and the method further comprises increasing the electric potential difference between the substrate and the electrode, and/or decreasing a distance between the electrode and the substrate or multidimensional structure, when the current is below a predetermined value.

[00043] In certain examples there is provided a method for forming a multidimensional structure, the method comprising the following steps:

providing an electrode and a substrate in a fluid,

wherein the fluid comprises:

TBAHFP, and

Cu^{2+} in acetonitrile;

applying an electric potential difference between the substrate and the electrode to reduce the Cu^{2+}, thereby depositing copper;

measuring current between the substrate and the electrode; and

moving the electrode within the fluid to form a multidimensional structure of the copper;

wherein the current between the substrate and the electrode is measured as a function of time; and the method further comprises increasing the electric potential difference between the

substrate and the electrode, and/or decreasing a distance between the electrode and the substrate or multidimensional structure, when the current is below a predetermined value.

[00044] In certain examplse there is provided a method for forming a multidimensional structure, the method comprising the following steps:

providing an electrode and a substrate in a fluid,

wherein the fluid comprises:

TBAHFP,

EDOT, and

Cu^{2+};

applying a first electric potential difference between the substrate and the electrode to oxidise the EDOT, thereby depositing PEDOT;

applying a second electrical potential difference between the substrate and the electrode to reduce the Cu^{2+}, thereby depositing copper;

measuring current between the substrate and the electrode; and

moving the electrode within the fluid to form a multidimensional structure of the PEDOT and copper;

wherein the current between the substrate and the electrode is measured as a function of time; and the method further comprises increasing the electric potential difference between the substrate and the electrode, and/or decreasing a distance between the electrode and the substrate or multidimensional structure, when the current is below a predetermined value.

[00045] In a second example there is provided a device for producing a multidimensional structure, said device comprising:

an electrode;

a container for holding a fluid;

one or more motors for moving the electrode within the container;

a substrate within the container; and

a potentiostat for applying an electric potential difference between the substrate and the electrode and for measuring current between the substrate and the electrode, which allows for the *in situ* monitoring of the printing process.

[00045a] In another aspect, the present disclosure refers to a device for producing a multidimensional structure, said device comprising:

an electrode having an exposed area or tip to be contacted with a fluid and being configured to be moveable along an x, y and z axis;

a substrate;

one or more motors for moving the electrode to contact the exposed area or tip of the electrode and the substrate with the fluid such that the surface area of the electrode in contact with the fluid is from 10^{-9} m^2 to 10^{-4} m^2; and

a potentiostat for applying an electric potential difference between the substrate and the electrode and for measuring current between the substrate and the electrode.

[00046] The following options may be used in conjunction with the second example, either individually or in any suitable combination.

[00047] The device may further comprise a reference electrode in electrical connection to the potentiostat.

[00048] The device may further comprise a quartz crystal microbalance (QCM) for measuring the mass of the multidimensional structure.

[00049] In certain examples, the device comprises three motors.

[00050] In certain examples, the device is a 3D printer.

[00051] The device according to the second example may be used in the method according to the first example. The method according to the first example may use the device according to the first example.

[00052] In a third example there is provided a multidimensional structure which is formed using the method of the first example.

[00053] The following options may be used in conjunction with the third example, either individually or in any suitable combination.

[00054] The multidimensional structure may be a three-dimensional structure. It may be electrically conductive. In certain examples it may be a composite structure.

[00055] The device according to the second example may be used to produce the multidimensional structure according to the third example. The multidimensional structure according to the third example may be produced using the device according to the second example.

[00056] In a fourth example there is provided a printer when used to print a multidimensional structure according to the method of the example.

[00057] The following options may be used in conjunction with the fourth example, either individually or in any suitable combination.

[00058] The printer may be a 3D printer.

[00059] The printer according to the fourth example may be the device according to the second example. The device according to the second example may be the printer according to the fourth example.

Brief Description of Drawings

[00060] **FIGURE 1:** Images of electrodes used for the example printing methods: (A) a nanoelectrode; (B) a microelectrode.

[00061] **FIGURE 2:** Depiction of an example multidimensional printer device.

[00062] **FIGURE 3:** Depiction of an example printing process.

[00063] **FIGURE 4:** A schematic diagram of an example device for printing a multidimensional structure. Figure 4(A) shows the entire device in a top-down view. Figures 4(B) and 4(C) show expanded regions of the device in perspective and front elevation views, respectively.

CLAIMS

1. A method for forming a multidimensional structure, the method comprising the following steps:

providing an electrode having an exposed area or tip to be contacted with a fluid and a substrate,

contacting a fluid with the exposed area or tip of the electrode and the substrate, wherein the surface area of the electrode in contact with the fluid is from 10^{-9} m^2 to 10^{-4} m^2 and the fluid comprises an electrolyte, and a precursor agent dispersed therein;

applying an electric potential difference between the substrate and the electrode to reduce or oxidise the precursor agent, thereby depositing a solid material; and

moving the electrode along an x, y, and z axis to form a multidimensional structure of the solid material.

2. The method of claim 1, wherein the current between the substrate and the electrode is measured at a plurality of time points.

3. The method of claim 2, wherein the time points are from 100 μs to 1 second apart.

4. The method of any one of claims 1 to 3, wherein the current between the substrate and the electrode is measured as a function of time.

5. The method of any one of claims 1 to 4, further comprising varying one or more of the electrical potential difference between the substrate and the electrode, and the position of the electrode when the current is above, below, or at a predetermined value.

6. The method of claim 5, comprising increasing the electric potential difference between the substrate and the electrode, and/or decreasing a distance between the electrode and the substrate or multidimensional structure, when the current is below the predetermined value.

7. The method of any one of claims 1 to 6, further comprising adjusting the electrical potential from a first voltage to a second voltage.

8. The method of any one of claims 1 to 7, wherein the precursor agent is selected from the group consisting of metal salts, vinyl monomers, and monomers of conjugated polymers.

9. The method of any one of claims 1 to 8, wherein the concentration of the precursor agent in the fluid is from 10^{-5} M to 1.5 M.

10. The method of anyone of claims 1 to 9, wherein the fluid is in a container, and the electrode and substrate are within the fluid in the container.

11. The method of any one of claims 1 to 10, wherein the fluid comprises an organic solvent.

12. The method of any one of claims 1 to 11, wherein the fluid does not comprise water.

13. The method of any one of claims 1 to 12, wherein the solid material is selected from the group consisting of vinyl polymers, conjugated polymers, metals, and combinations thereof.

14. The method of any one of claims 1 to 13, wherein the precursor agent is selected from the group consisting of metal ion salts, metal ion complexes, ionic liquids, vinyl monomers, and monomers of conjugated polymers.

15. The method of any one of claims 1 to 14, wherein the fluid is a first fluid, and the method further comprises:

replacing the first fluid with a second fluid, wherein the second fluid comprises:

an electrolyte, and

a precursor agent dispersed therein, wherein the precursor agent of the second fluid is different to the precursor agent of the first fluid; and

applying an electrical potential difference between the electrode and the substrate to reduce or oxidise the precursor agent of the second fluid, thereby depositing a second solid material.

16. The method of any one of claims 1 to 14, wherein the fluid comprises a first precursor agent and a second precursor agent, and the method comprises:

applying a first electrical potential difference between the electrode and the substrate to reduce or oxidise the first precursor agent, thereby depositing a first solid material; and

applying a second electrical potential difference between the electrode and the substrate to reduce or oxidise the second precursor agent, thereby depositing a second solid material.

17. A device for producing a multidimensional structure, said device comprising:

an electrode having an exposed area or tip to be contacted with a fluid and being configured to be moveable along an x, y and z axis;

a substrate;

one or more motors for moving the electrode to contact the exposed area or tip of the electrode and the substrate with the fluid such that the surface area of the electrode in contact with the fluid is from 10^{-9} m^2 to 10^{-4} m^2; and

a potentiostat for applying an electric potential difference between the substrate and the electrode and for measuring current between the substrate and the electrode.

18. The device of claim 17, further comprising a reference electrode in electrical connection to the potentiostat.

19. The device of claim 17 or 18, further comprising a quartz crystal microbalance (QCM) for measuring the mass of the multidimensional structure.

20. The device of any one of claims 17 to 19, which is a 3D printer.