MATERIALS AND METHODS OF MANUFACTURE

[0001] The invention relates to materials and methods of manufacture of materials. In particular, the invention relates to an array suitable for use as a catalyst and methods of making an array. The invention further relates to a catalyst, and a method of forming a catalyst. In particular, the catalyst is part of an array structure.

BACKGROUND

[0002] Catalysts are used to increase the rate of reactions or decrease the energy required to initiate or drive a reaction. They are commercially particularly useful for large scale commodity reactions, such as hydrogenation, dehydrogenation, reforming and oxidation reactions.

[0003] Precious metals such as platinum (Pt) and palladium (Pd) are traditionally used as high performance catalysts. However, due to their high cost and scarcity, significant effort has been made to develop substitutes or alternatives. Recent focus in catalysis has been on enhancing the catalytic performance by combining them with other less precious materials (for example, see W. Yu, et al. Review of Pt-Based Bimetallic Catalysis: From Model Surfaces to Supported Catalysts, *Chem. Rev*. 2012, 112, 5780−5817).

[0004] WO2018106128 (Manufacturing Systems Limited) has shown that catalytic activity of platinum can be enhanced by changing from a flat electrode to one with surface structures that have the platinum applied to them.

BRIEF SUMMARY

[0004a] In one aspect, there is provided an array comprising:

a support substrate;

surface structures protruding from a surface of the support substrate formed from or coated with a first material;

a second material deposited on at least some of the surface structures such that the second material is in contact with the first material; and

wherein the first material, the second material or the first and second material is conducting or semiconducting;

wherein the first and second material at least partially form a composite.

[0004b] In another aspect, there is provided a method of forming an array, the method comprising:

applying a current between a first electrode and a second electrode in a conductive fluid;

the first electrode comprising:

a support substrate;

surface structures protruding from a surface of the support substrate formed from or coated with a first material; and

a second material deposited on at least some of the surface structures in contact with the first material;

wherein:

the first material, the second material or the first and second material is conducting or semiconducting;

the current density applied is sufficient to form a composite at least the interface of the first and second material.

[0004c] In another aspect, there is provided a method of carrying out a reaction, the method comprising bringing the array of the above or the array formed by the method of the above into contact with at least one reactive species, wherein the array acts as a catalyst.

[0004c] In another aspect, there is provided a method of carrying out an electrochemical reaction, the method comprising applying a current between the electrocatalyst array of the above, or an electrocatalyst array formed by the method of the above and a counter electrode in a conductive fluid.

SUMMARY OF INVENTION

[0005] In a **first aspect**, there is provided an array comprising:

a support substrate;

surface structures protruding from a surface of the support substrate formed from or coated with a first material;

a second material deposited on at least some of the surface structures such that the second material is in contact with the first material; and

wherein the first material, the second material or the first and second material is conducting or semiconducting;

wherein the first and second material at least partially form a composite.

[0006] In some embodiments the composite is an electrolytic reaction product of the first material and the second material.

CLAIMS

1. An array comprising:

a support substrate;

surface structures protruding from a surface of the support substrate formed from or coated with a first material;

a second material deposited on at least some of the surface structures such that the second material is in contact with the first material; and

wherein the first material, the second material or the first and second material is conducting or semiconducting;

wherein the first and second material at least partially form a composite.

2. A method of forming an array, the method comprising:

applying a current between a first electrode and a second electrode in a conductive fluid;

the first electrode comprising:

a support substrate;

surface structures protruding from a surface of the support substrate formed from or coated with a first material; and

a second material deposited on at least some of the surface structures in contact with the first material;

wherein:

the first material, the second material or the first and second material is conducting or semiconducting;

the current density applied is sufficient to form a composite at least the interface of the first and second material.

~~2~~3. The array of claim~~s~~ 1 or the method of claim 2, wherein the composite is an electrolytic reaction product of the first material and the second material.

~~3~~4. The array of claim ~~2~~ 3, wherein the electrolytic reaction product is prepared by applying a current of sufficient density to the array to cause a reaction between the first material and the second material.

~~4~~5. The array of any one of claims 1, 3 or ~~to 3~~ 4 wherein the composite exhibits a modified electronic structure compared to the first and second materials, or the method of claim 2 or 3, wherein the composite exhibits a modified electronic structure compared to a mixture of the first and second materials prior to the composite being formed.

~~5~~6. The array or method of claim ~~4~~5, wherein the modified electronic structure is exhibited by observing a change in the linear sweep voltammetry between an array comprising the first and second materials and the array further comprising the composite.

~~6~~7. The array or method of claim ~~5~~6, wherein the change in linear sweep voltammetry comprises a shift of an oxidation or reduction to a more positive or negative voltage.

~~7~~8. The array or method of any one of claims ~~4~~5 to ~~6~~7, wherein the modified electronic structure is exhibited by observing a change in energy-dispersive x-ray spectroscopy of the array comprising the first and second materials and the array further comprising the composite.

~~8~~9. The array or method of any one of claims ~~4~~5 to ~~6~~7, wherein the composite is formed at edges and/or apices of the surface structures.

~~9~~10. The array of any one of claims 1 to 9 or the method of any one of claims 2, 3 or 5 ~~1~~ to ~~8~~9 wherein the composite is selected from an intermetallic compound, a polymer-metal composite, organic-inorganic composite, an alloy, a multi-metallic compound; preferably the composite is a metal-element alloy (for example carbon, sulfur, or silicon combined with metal), or a metal-metal alloy.

~~10~~11. The array of any one of claims 1 to 10 or the method of any one of claims 2, 3 or 5 ~~1~~ to ~~9~~10, wherein the first material is a metal.

~~11~~12. The array of any one of claims 1 to 11 or the method of any one of claims 2, 3 or 5 ~~of any one of claims 1~~ to ~~10~~ 11, wherein the second material is selected from a polymer, an organic compound, an inorganic compound, a metal.

~~12~~13. The array of any one of claims 1 to 12 or the method of any one of claims 2, 3 or 5 ~~of any one of claims 1~~ to ~~11~~ 12, wherein the second material is selected from an s-block element (group 1 and 2 of the periodic table), a p-block element (group 13, 14, 15, 16 or 17 of the periodic table) a d block metal (a transition metal), preferably the second material is selected from an alkali metal (group 1), an alkaline earth metal, a transition metal, a metalloid, preferably the second material is a metal.

~~13~~14. The array of any one of claims 1 to 13 or the method of any one of claims 2, 3 or 5 ~~of any one of claims 1~~ to ~~12~~ 13, wherein the first material is selected from Ni, Ti, V, Cr, Fe, Co, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Mo, Tc, Ru, Ro, Pd, Ag, Cd, In, Sb, Sn, Cs, Ba, La, Ce, PR, Nd, W, Os, Ir, Au, Pb, Bi, Ra, U, Pt, and Au.

~~14~~15. The array of any one of claims 1 to 14 or the method of any one of claims 2, 3 or 5 ~~of any one of claims 1~~ to ~~13~~ 14, wherein the second material is different to the first metal and is selected from Ni, Ti, V, Cr, Fe, Co, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Mo, Tc, Ru, Ro, Pd, Ag, Cd, In, Sb, Sn, Cs, Ba, La, Ce, PR, Nd, W, Os, Ir, Au, Pb, Bi, Ra, U, Pt, and Au.

~~15~~16. The array of any one of claims 1 to 15 or the method of any one of claims 2, 3 or 5 ~~of any one of claims 1~~ to ~~14~~ 15, wherein the first material is selected from Ni, Cu, Zn, Co, Al, Ti, and the second material is selected from Pt, Co, Au, Ni, Ag, Ti, Cr, Cu, Mg, Mn, Fe, Zn.

17. The array of any one of claims 1 to 16 or the method of any one of claims 2, 3 or 5 to 16, wherein the first and/or second material is a metal and is in the form of one or more of an oxide, a hydride, a halide, hydroxide, a salt, a carbide, an organometallic complex, a complex, an alloy, a cluster.

~~16~~18. The array of any one of claims 1 to 17 or the method of any one of claims 2, 3 or 5 ~~of any one of claims 1~~ to ~~15~~ 17, wherein second material forms a layer on the first material, or the second material forms an intermittent layer on the first material.

~~17~~19. The array of any one of claims 1 to 18 or the method of any one of claims 2, 3 or 5 ~~of any one of claims 1~~ to ~~16~~ 18, wherein the second material is deposited on at least some of the surface structures such that it is imbedded or incorporated into the first material.

~~18~~20. The array of any one of claims 1 to 19 or the method of any one of claims 2, 3 or 5 ~~of any one of claims 1~~ to ~~17~~ 19, wherein the thickness of the second material layer or intermittent layer is greater than 0 nm but less than about 1000nm.

~~19~~21. The array of any one of claims 1 to 20 or the method of any one of claims 2, 3 or 5 ~~of any one of claims 1~~ to ~~18~~ 20, wherein the second material is deposited at the edges and/or apices of the surface structure.

~~20~~22. The array of any one of claims 1 to 21 or the method of any one of claims 2, 3 or 5 ~~of any one of claims 1~~ to ~~19~~ 21, wherein the second material is deposited on less than about 100% to about 0.0000001% of the surface when viewed from above or the second material is deposited on less than about 50% of the surface area.

~~21~~23. The array of any one of claims 1 to 22 or the method of any one of claims 2, 3 or 5 ~~of any one of claims 1~~ to ~~20~~ 22, wherein one or more further material(s) that is different to the first and/or second materials and is deposited on at least some of the surface structures.

~~22~~24. The array or method of claim ~~21~~23, wherein further material(s) is/are in contact with at least one of the first material, the second material or one or more of the other further material(s).

~~23~~25. The array or method of claims ~~21~~23 or ~~22~~24, wherein the one or more further material(s) is selected from a polymer, an organic compound, an inorganic compound, a metal.

~~24~~26. The array or method of any one of claims ~~21~~ 23 to ~~23~~ 25, wherein there is between one and fifty further material(s).

~~25~~27. The array of any one of claims 1 to 26 or the method of any one of claims 2, 3 or 5 ~~of any one of claims 1~~ to ~~22~~ 26, wherein the surface structures are integral with the support substrate.

~~26~~28. The array of any one of claims 1 to 27 or the method of any one of claims 2, 3 or 5 ~~of any one of claims 1~~ to ~~25~~ 27, wherein the support substrate and the surface structures are formed from the first material.

~~27~~29. The array of any one of claims 1 to 28 or the method of any one of claims 2, 3 or 5 ~~of any one of claims 1~~ to ~~26~~ 28, wherein the surface structures form a uniform, discontinuous array on the surface structure.

~~28~~30. The array of any one of claims 1 to 29 or the method of any one of claims 2, 3 or 5 ~~of any one of claims 1~~ to ~~27~~ 29, wherein the surface structures are uniformly sized.

~~29~~31. The array of any one of claims 1 to 30 or the method of any one of claims 2, 3 or 5 ~~of any one of claims 1~~ to ~~28~~ 30, wherein the surface structure(s) comprises of a distal end portion, said distal end portion being spaced most from the surface from which said surface structure(s) extend, said distal end portion being of a sharp or peak or spike or apex or tip or ridge form.

~~30~~32. The array of any one of claims 1 to 31 or the method of any one of claims 2, 3 or 5 ~~of any one of claims 1~~ to ~~29~~ 31, wherein a top or distal end of the surface structure is of a substantially similar or reduced width compared to a bottom or proximal end of the surface structure, wherein distal and proximal are in relation to a surface of a support substrate to which the surface structures are associated or protruding from.

~~31~~33. The array of any one of claims 1 to 32 or the method of any one of claims 2, 3 or 5 ~~of any one of claims 1~~ to ~~30~~ 32, wherein the width of the surface structure where it joins the support substrate is between about 5nm to about 5000µm.

~~32~~34. The array of any one of claims 1 to 33 or the method of any one of claims 2, 3 or 5 ~~of any one of claims 1~~ to ~~31~~ 33, wherein the height of the surface structure is between about 5nm to about 5000µm.

~~33~~35. The array of any one of claims 1 to 34 or the method of any one of claims 2, 3 or 5 ~~of any one of claims 1~~ to ~~32~~ 34, wherein the array is a catalyst.

~~34. A method of forming an array, the method comprising:~~

~~applying a current between a first electrode and a second electrode in a conductive fluid;~~

~~the first electrode comprising:~~

~~a support substrate;~~

~~surface structures protruding from a surface of the support substrate formed from or coated with a first material; and~~

~~a second material deposited on at least some of the surface structures in contact with the first material;~~

~~wherein:~~

~~the first material, the second material or the first and second material is conducting or semiconducting;~~

~~the current density applied is sufficient to form a composite at least the interface of the first and second material.~~

~~35. The method of claim 34 wherein the composite is an electrolytic reaction product of the first material and the second material.~~

~~36. The method of claim 34 or 35 wherein the composite the composite exhibits a modified electronic structure compared to a mixture of the first and second materials prior to the composite being formed.~~

~~37. The method of any one of claims 34 to 36 wherein the modified electronic structure is exhibited by observing a change in the linear sweep voltammetry of the array.~~

~~38. The method of any one of claims 34 to 37 wherein the change in linear sweep voltammetry of the array comprises a shift of an oxidation or reduction to a more positive or negative voltage.~~

~~39. The method of any one of claims 34 to 38 wherein the modified electronic structure is exhibited by a change in energy-dispersive x-ray spectroscopy of the array.~~

~~40. The method of any one of claims 34 to 39 wherein the composite or alloy or intermetallic compound is preferentially formed at edges and/or apices of the surface structures.~~

~~41. The method of any one of claims 34 to 40 wherein the composite material is selected from an intermetallic compound, a polymer-metal composite, organic-inorganic composite, an alloy, a multi-metallic compound preferably the composite is a metal-element alloy (for example carbon, sulfur, or silicon combined with metal), a metal-metal alloy.~~

~~42. The method of any one of claims 34 to 41 wherein the first material is a metal.~~

~~43. The method of any one of claims 34 to 42 wherein the second material is selected from a polymer, an organic compound, an inorganic compound, a metal.~~

~~44. The method of any one of claims 34 to 43 wherein the second material is selected form an s-block element (group 1 and 2 of the periodic table), a p-block element (group 13, 14, 15, 16 or 17 of the periodic table) a d block metal (a transition metal), preferably the second material is selected from an alkali metal (group 1), an alkaline earth metal, a transition metal, a metalloid, preferably the second material is a metal.~~

~~45. The method of any one of claims 34 to 44 wherein the first material is selected from Ni, Ti, V, Cr, Fe, Co, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Mo, Tc, Ru, Ro, Pd, Ag, Cd, In, Sb, Sn, Cs, Ba, La, Ce, PR, Nd, W, Os, Ir, Au, Pb, Bi, Ra, U, Pt, and Au.~~

~~46. The method of any one of claims 34 to 45 wherein the second material is different to the first material and is selected from Ni, Ti, V, Cr, Fe, Co, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Mo, Tc, Ru, Ro, Pd, Ag, Cd, In, Sb, Sn, Cs, Ba, La, Ce, PR, Nd, W, Os, Ir, Au, Pb, Bi, Ra, U, Pt, and Au.~~

~~47. The method of any one of claims 34 to 46 wherein the first material is selected from Ni, Cu, Zn, Co, Al, Ti, and the second material is selected from Pt, Co, Au, Ni, Ag, Ti, Cr, Cu, Mg, Mn, Fe, Zn.~~

~~48. The method of any one of claims 34 to 47 wherein the first and/or second material is a metal and is in the form of one or more of an oxide, a hydride, a halide, hydroxide, a salt, a carbide, an organometallic complex, a complex, an alloy, a cluster.~~

~~49. The method of any one of claims 34 to 48 wherein second material forms a layer on the first material, or the second material forms an intermittent layer on the first material.~~

~~50. The method of any one of claims 34 to 49 wherein the second material is deposited on at least some of the surface structures such that it is imbedded or incorporated into the first material.~~

~~51. The method of any one of claims 34 to 50 wherein the thickness of the second material layer or intermittent layer is greater than 0 nm but less than about 1000nm.~~

~~52. The method of any one of claims 34 to 51 wherein the second material is deposited at the edges and/or apices of the surface structure.~~

~~53. The method of any one of claims 34 to 52 wherein the second material is deposited on less than about 100% to about 0.0000001% of the surface when viewed from above or the second material is deposited on less than about 50% of the surface area.~~

~~54. The method of any one of claims 34 to 53 wherein one or more further material(s) that is different to the first and/or second materials and is deposited on at least some of the surface structures.~~

~~55. The method of any one of claims 34 to 54 wherein further material(s) is/are in contact with at least one of the first material, the second material or one or more of the other further material(s).~~

~~56. The method of any one of claims 34 to 55 wherein the one or more further material(s) is selected from a polymer, an organic compound, an inorganic compound, a metal.~~

~~57. The method of any one of claims 34 to 56 wherein there is between one and fifty further material(s).~~

~~58. The method of any one of claims 34 to 57 wherein the surface structures are integral with the support substrate.~~

~~59. The method of any one of claims 34 to 58 wherein the support substrate and the surface structures are formed from the first material.~~

~~60. The method of any one of claims 34 to 59 wherein the surface structures form a uniform, discontinuous array on the surface structure.~~

~~61. The method of any one of claims 34 to 59 wherein the surface structures are uniformly sized.~~

~~62. The method of any one of claims 34 to 61 wherein the surface structure(s) comprises of a distal end portion, said distal end portion being spaced most from the surface from which said surface structure(s) extend, said distal end portion being of a sharp or peak or spike or apex or tip or ridge form.~~

~~63. The method of any one of claims 34 to 62 wherein a top or distal end of the surface structure is of a substantially similar or reduced width compared to a bottom or proximal end of the surface structure, wherein distal and proximal are in relation to a surface of a support substrate to which the surface structures are associated or protruding from.~~

~~64. The method of any one of claims 34 to 63 wherein the width of the surface structure where it joins the support substrate is between about 5nm to about 5000μm.~~

~~65. The method of any one of claims 34 to 64 wherein the height of the surface structure is between about 5nm to about 5000μm.~~

~~66~~36. The method of any one of claims ~~34~~ 2, 3 or 5 to ~~65~~35, wherein the conductive fluid comprises the second metal and the second metal is deposited on at least some of the surface structures electrochemically when the current is applied.

~~67~~37. The method of any one of claims ~~34~~ 2, 3 or 5 to ~~66~~ 36, wherein the conductive fluid comprises the second metal and the second metal is deposited at the edges and/or apices electrochemically when the current is applied.

~~68~~38. The method of any one of claims ~~34~~ 2, 3 or 5 to ~~67~~37, wherein a~~the~~ potential difference established between the first electrode and the second electrode is between about -20V and +20V, preferably between about -10V and +10V, preferably between about -5V and +5V, preferably between about -1V and +1V, or the potential difference established between the first electrode and the second electrode is between about +/-20V and +/-0.5V, preferably between about +/-10V and +/-0.5V, preferably between +/-7V and +/-0.5V, preferably between +/-6V and +/-1V.

~~69~~39. The method of any one of claims ~~34~~ 2, 3 or 5 to ~~68~~ 38, wherein the current applied between the first electrode and second electrode is an average of about 0.1 to about 500A/cm^2 across the first electrode and/or the second electrode; or about 0.1 to about 50A/cm^2; or about 0.1 to about 20A/cm^2; or about 0.2 to about 20 A/cm^2; or about 0.2 to about 15 A/cm^2; or about 0.5 to about 500A/cm^2; or about 0.5 to about 50A/cm^2; or about 0.5 to about 20A/cm^2; or about 0.5 to about 10 A/cm^2; or about 0.5 to about 8 A/cm^2; or about 0.5 to about 5 A/cm^2; or about 0.5 to about 4 A/cm^2; or about 1 to about 4 A/cm^2, across the first electrode and/or the second electrode.

~~70~~40. The method of any one of claims ~~34~~ 2, 3 or 5 to ~~69~~ 39, wherein the current is applied for a time sufficient to form a composite, preferably the current is applied for about 1 second to about 1 week, or about 1 second to about 24 hours, or about 1 minute to about 24 hours, or about 5 minutes to about 24 hours, or about 10 minutes to about 24 hours, about 0.5 hours to about 24 hours, or about 1 hour to about 12 hours.

~~71~~41. The method of any one of claims ~~34~~ 2, 3 or 5 to ~~70~~ 40, wherein the conductive fluid comprises the one or more further material(s) and the one or more further material(s) is deposited on at least some of the surface structures electrochemically when the or a current is applied, preferably the current is the current that forms the composite or the current is prior to the current that forms the composite.

~~72~~42. The method of any one of claims ~~34~~ 2, 3 or 5 to ~~71~~ 41, wherein the conductive fluid comprises the one or more further material(s) and the one or more further material(s) is deposited at the edges and/or apices electrochemically when the current is applied.

~~73~~43. The method of any one of claims ~~34~~ 2, 3 or 5 to ~~72~~ 42, wherein the conductive fluid comprises water and/or an organic solvent.

~~74~~44. The method of any one of claims ~~34~~ 2, 3 or 5 to ~~73~~ 43, wherein the conductive fluid comprises an electrolyte.

~~75~~45. The method of any one of claims ~~34~~ 2, 3 or 5 to ~~74~~ 44, wherein the concentration of the electrolyte is about 0.05M to about 20M

~~76~~46. The method of any one of claims ~~34~~ 2, 3 or 5 to ~~75~~ 45, wherein the method further comprise the step of depositing, incorporating or embedding the one or more further material(s) in or onto the array following forming the composite, preferably the method further comprise the step of depositing, incorporating or embedding the one or more further material(s) in or onto the array by diffusion or ion implanting following forming the composite.

~~77~~47. A method of carrying out a reaction, the method comprising bringing the array of any one of claims 1 to ~~33~~35 or the array formed by the method of any one of claims ~~34~~ 2, 3 or 5 to ~~76~~ 46 into contact with at least one reactive species, wherein the array acts as a catalyst.

~~78~~48. A method of carrying out an electrochemical reaction, the method comprising applying a current between the electrocatalyst array of any one of claims 1 to ~~33~~ 35, or an electrocatalyst array formed by the method of any one of claims ~~34~~ 2, 3, or 5 to ~~76~~ 46 and a counter electrode in a conductive fluid.