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, wherein the surface structures comprise of a distal end portion, said distal end portion being spaced most from the surface from which said surface structures extend, said distal end portion being of a sharp or peak or spike or apex or tip or ridge form;

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 materials are 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, wherein the surface structures comprise of a distal end portion, said distal end portion being spaced most from the surface from which said surface structures extend, said distal end portion being of a sharp or peak or spike or apex or tip or ridge form; 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 materials are conducting or semiconducting;

the current density applied is sufficient to form a composite at least at the interface of the first material and the 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, wherein the surface structures comprise of a distal end portion, said distal end portion being spaced most from the surface from which said surface structures extend, said distal end portion being of a sharp or peak or spike or apex or tip or ridge form;

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 materials are conducting or semiconducting;

wherein the first and second materials 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, wherein the surface structures comprise of a distal end portion, said distal end portion being spaced most from the surface from which said surface structures extend, said distal end portion being of a sharp or peak or spike or apex or tip or ridge form; 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 materials are conducting or semiconducting;

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

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

4. The array of claim 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.

5. The array of any one of claims 1, 3 or 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.

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

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

8. The array or method of any one of claims 5 to 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.

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

10. The array of any one of claims 1 to 9 or the method of any one of claims 2, 3 or 5 to 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.

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

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

13. The array of any one of claims 1 to 12 or the method of any one of claims 2, 3 or 5 to 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.

14. The array of any one of claims 1 to 13 or the method of any one of claims 2, 3 or 5 to 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.

15. The array of any one of claims 1 to 14 or the method of any one of claims 2, 3 or 5 to 14, 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.

16. The array of any one of claims 1 to 15 or the method of any one of claims 2, 3 or 5 to 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.

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

19. The array of any one of claims 1 to 18 or the method of any one of claims 2, 3 or 5 to 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.

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

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

22. The array of any one of claims 1 to 21 or the method of any one of claims 2, 3 or 5 to 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.

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

24. The array or method of claim 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).

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

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

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

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

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

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

31. The array of any one of claims 1 to 30 or the method of any one of claims 2, 3 or 5 to 30, 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.

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

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

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

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

36. The method of any one of claims 2, 3 or 5 to 35, wherein the conductive fluid comprises the second material and the second material is deposited at the edges and/or apices of the surface structures electrochemically when the current is applied.

37. The method of any one of claims 2, 3 or 5 to 36, wherein a 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.

38. The method of any one of claims 2, 3 or 5 to 37, 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.

39. The method of any one of claims 2, 3 or 5 to 38, wherein the current is applied for a time sufficient to form the 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.

40. The method of any one of claims 2, 3 or 5 to 39, 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.

41. The method of any one of claims 2, 3 or 5 to 40, 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 of the surface structures electrochemically when the current is applied.

42. The method of any one of claims 2, 3 or 5 to 41, wherein the conductive fluid comprises water and/or an organic solvent.

43. The method of any one of claims 2, 3 or 5 to 42, wherein the conductive fluid comprises an electrolyte.

44. The method of any one of claims 2, 3 or 5 to 43, wherein a concentration of the electrolyte is about 0.05M to about 20M

45. The method of any one of claims 2, 3 or 5 to 44, 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.

46. A method of carrying out a reaction, the method comprising bringing the array of any one of claims 1 to 34 or the array formed by the method of any one of claims 2, 3 or 5 to 45 into contact with at least one reactive species, wherein the array acts as a catalyst.

47. 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 34, or an

electrocatalyst array formed by the method of any one of claims 2, 3, or 5 to 45 and a counter electrode in a conductive fluid.