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 electrocatalyst array comprising:

a support substrate;

a plurality of surface structures protruding from a surface of the support substrate formed from or coated with a first metal, 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 metal deposited on at least some of the plurality of surface structures such that the second metal is in contact with the first metal; and

wherein the first and second metals are conducting;

wherein the first and second metals at least partially form a composite, the composite formed as sub-structures on the plurality of surface structures, the composite

formed at a higher density at edges and/or apices of the distal end portion of the plurality of surface structures than on the remaining surfaces of the plurality surface structures, and wherein the composite exhibits a modified electronic structure compared to the first and second metals.

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

applying a current producing a current density of at least 0.1 A/cm^2 between a first electrode and a second electrode in a conductive fluid;

the first electrode comprising:

a support substrate;

a plurality of surface structures protruding from a surface of the support substrate formed from or coated with a first metal, 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 metal deposited on at least some of the plurality of surface structures in contact with the first metal;

wherein:

the first and second metals are conducting;

the current density is sufficient to form a composite of the first metal and the second metal, the composite formed as sub-structures on the plurality of surface structures, the composite formed at a higher density at edges and/or apices of the distal end portion of the plurality of surface structures than on the remaining surfaces of the plurality surface structures,

wherein the composite exhibits a modified electronic structure compared to the first and second metals prior to the composite being formed.

[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 electrocatalyst array comprising:

a support substrate;

a plurality of surface structures protruding from a surface of the support substrate formed from or coated with a first metal, 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 metal deposited on at least some of the plurality of surface structures such that the second metal is in contact with the first metal; and

wherein the first and second metals are conducting;

wherein the first and second metals at least partially form a composite, the composite formed as sub-structures on the plurality of surface structures, the composite formed at a higher density at edges and/or apices of the distal end portion of the plurality of surface structures than on the remaining surfaces of the plurality surface structures, and

wherein the composite exhibits a modified electronic structure compared to the first and second metals.

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

applying a current producing a current density of at least 0.1 A/cm^2 between a first electrode and a second electrode in a conductive fluid;

the first electrode comprising:

a support substrate;

a plurality of surface structures protruding from a surface of the support substrate formed from or coated with a first metal, 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 metal deposited on at least some of the plurality of surface structures in contact with the first metal;

wherein:

the first and second metals are conducting;

the current density is sufficient to form a composite of the first metal and the second metal, the composite formed as sub-structures on the plurality of surface structures, the composite formed at a higher density at edges and/or apices of the distal

end portion of the plurality of surface structures than on the remaining surfaces of the plurality surface structures,

wherein the composite exhibits a modified electronic structure compared to the first and second metals prior to the composite being formed.

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

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

5. The array of claim 4, wherein the current density is at least 0.1 A/cm^2.

6. The array or method of any one of claims 1 to 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 metals 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 6 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 metals and the array further comprising the composite.

9. The array of any one of claims 1 to 8 or the method of any one of claims 2, 3 or 6 to 8 wherein the composite is selected from an intermetallic compound, an alloy, or a multi-metallic compound.

10. The array of any one of claims 1 to 9 or the method of any one of claims 2, 3 or 6 to 9, wherein the second metal is selected from an s-block element (group 1 and 2 of the periodic table), a p-block element (group 13, 14, 15, or 16 of the periodic table) a d block metal (a transition metal), preferably the second metal is selected from an alkali metal (group 1), an alkaline earth metal, a transition metal.

11. The array of any one of claims 1 to 10 or the method of any one of claims 2, 3 or 6 to 10, wherein the first metal is selected from Ni, Ti, V, Cr, Fe, Co, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sb, Sn, Cs, Ba, La, Ce, Pr, Nd, W, Os, Ir, Au, Pb, Bi, Ra, U, Pt, and Au.

12. The array of any one of claims 1 to 11 or the method of any one of claims 2, 3 or 6 to 11, wherein the second metal 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, Rh, Pd, Ag, Cd, In, Sb, Sn, Cs, Ba, La, Ce, Pr, Nd, W, Os, Ir, Au, Pb, Bi, Ra, U, Pt, and Au.

13. The array of any one of claims 1 to 12 or the method of any one of claims 2, 3 or 6 to 12, wherein the first metal is selected from Ni, Cu, Zn, Co, Al, Ti, and the second metal is selected from Pt, Co, Au, Ni, Ag, Ti, Cr, Cu, Mg, Mn, Fe, Zn.

14. The array of any one of claims 1 to 13 or the method of any one of claims 2, 3 or 6 to 13, wherein the first and/or second metal 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.

15. The array of any one of claims 1 to 14 or the method of any one of claims 2, 3 or 6 to 14, wherein the second metal forms a layer on the first metal, or the second metal forms an intermittent layer on the first metal.

16. The array of any one of claims 1 to 15 or the method of any one of claims 2, 3 or 6 to 15, wherein the second metal is deposited on at least some of the plurality of surface structures such that it is imbedded or incorporated into the first metal.

17. The array of claim 16 or the method of claim 16, wherein a thickness of the second metal layer or intermittent layer is greater than 5 nm but less than 50nm, or greater than 5nm but less than 10nm.

18. The array of any one of claims 1 to 17 or the method of any one of claims 2, 3 or 6 to 17, wherein the second metal is deposited at the edges and/or apices of the surface structure.

19. The array of any one of claims 1 to 18 or the method of any one of claims 2, 3 or 6 to 18, wherein the second metal is deposited on less than 50% of the surface area when viewed from above.

20. The array of any one of claims 1 to 19 or the method of any one of claims 2, 3 or 6 to 19, wherein one or more further metal(s) that is different to the first and/or second metals is deposited on at least some of the plurality of surface structures.

21. The array or method of claim 20, wherein further metal(s) is/are in contact with at least one of the first metal, the second metal or one or more of the other further metal(s).

22. The array or method of any one of claims 20 or 21, wherein there is between one and fifty further metal(s).

23. The method of any one of claims 20 to 22, wherein the conductive fluid comprises the one or more further metal(s) and the one or more further metal(s) is deposited at the edges and/or apices of the plurality of surface structures electrochemically when the current is applied.

24. The method of any one of claims 20 to 23, wherein the method further comprise the step of depositing, incorporating or embedding the one or more further metal(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

metal(s) in or onto the array by diffusion or ion implanting following forming the composite.

25. The array of any one of claims 1 to 24 or the method of any one of claims 2, 3 or 6 to 24, wherein the plurality of surface structures are integral with the support substrate.

26. The array of any one of claims 1 to 25 or the method of any one of claims 2, 3 or 6 to 25, wherein the support substrate and the plurality of surface structures are formed from the first metal.

27. The array of any one of claims 1 to 26 or the method of any one of claims 2, 3 or 6 to 26, wherein the plurality of surface structures form a uniform, discontinuous array on 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 6 to 27, wherein the plurality of surface structures are uniformly sized.

29. The array of any one of claims 1 to 28 or the method of any one of claims 2, 3 or 6 to 28, 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 plurality of surface structures are associated or protruding from.

30. The array of any one of claims 1 to 29 or the method of any one of claims 2, 3 or 6 to 29, wherein a width of the surface structure where the surface structure joins the support substrate is between 5nm and 5000µm.

31. The array of any one of claims 1 to 30 or the method of any one of claims 2, 3 or 6 to 30, wherein a height of the surface structure is between 5nm and 5000µm.

32. The array of any one of claims 1 to 31 or the method of any one of claims 2, 3 or 6 to 31, wherein the array is a catalyst.

33. The method of any one of claims 2, 3 or 6 to 32, wherein the conductive fluid comprises the second metal and the second metal is deposited on at least some of the plurality of surface structures electrochemically when the current is applied.

34. The method of any one of claims 2, 3 or 6 to 33, wherein the conductive fluid comprises the second metal and the second metal is deposited at the edges and/or apices of the plurality of surface structures electrochemically when the current is applied.

35. The method of any one of claims 2, 3 or 6 to 34, wherein the conductive fluid comprises water and/or an organic solvent.

36. The method of any one of claims 2, 3 or 6 to 35, wherein the conductive fluid comprises an electrolyte.

37. The method of claim 36, wherein a concentration of the electrolyte is 0.05M to 20M.

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

39. The method of any one of claims 2, 3 or 6 to 38, wherein the current density is an average of 0.1 to 500A/cm^2 across the first electrode and/or the second electrode; or 0.1 to 50A/cm^2; or 0.1 to 20A/cm^2; or 0.2 to 20 A/cm^2; or 0.2 to 15 A/cm^2; or 0.5 to 500A/cm^2; or 0.5 to 50A/cm^2; or 0.5 to 20A/cm^2; or 0.5 to 10 A/cm^2; or 0.5 to 8 A/cm^2; or 0.5 to 5 A/cm^2; or 0.5 to 4 A/cm^2; or 1 to 4 A/cm^2, across the first electrode and/or the second electrode.

40. The method of any one of claims 2, 3 or 6 to 39, wherein the current is applied for a time sufficient to form the composite, preferably the current is applied for 1 second to 1 week, or 1 second to 24 hours, or 1 minute to 24 hours, or 5 minutes to 24 hours, or 10 minutes to 24 hours, 0.5 hours to 24 hours, or 1 hour to 12 hours.

41. The method of any one of claims 2, 3 or 6 to 40, wherein the conductive fluid comprises the one or more further metal(s) and the one or more further metal(s) is deposited on at least some of the plurality of 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.

42. A method of carrying out a reaction, the method comprising bringing the array of any one of claims 1 to 32 or the array formed by the method of any one of claims 2, 3 or 6 to 41 into contact with at least one reactive species, wherein the array acts as a catalyst.

43. 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 32, or an electrocatalyst array formed by the method of any one of claims 2, 3, or 6 to 41 and a counter electrode in a conductive fluid.