Claims

1. A method of forming a non-stoichiometric metal oxide nanoparticle agglomerate, comprising:

a) aerosolizing *via* a nozzle of a burner, a heated mixture comprising a combustible gas mixture having an oxygen-lean equivalence ratio (φ) and a volatile metal oxide precursor, where the combustible gas mixture is ignited at an outlet of the nozzle to provide a flame, such that the volatile metal oxide precursor is decomposed and undergoes rapid nucleation and coagulation to form non-stoichiometric metal oxide nanoparticles in the presence of the flame; and

b) depositing the non-stoichiometric metal oxide nanoparticles on a surface of a substrate positioned at a distance from the nozzle for a period of time for aggregation and oxidation of nanoparticles to form a non-stoichiometric metal oxide nanoparticle agglomerate on the surface of the substrate, wherein:

the oxygen-lean equivalence ratio (φ) of the combustible gas mixture is less than or equal to 1.5; and

a velocity of the combustible gas mixture at the nozzle of the burner is from 300 to 500 cm/s.

2. The method according to Claim 1, wherein the oxygen-lean equivalence ratio (φ) is from 1.05 to 1.5.

3. The method according to Claim 2, wherein the oxygen-lean equivalence ratio (φ) is from 1.1 to 1.4.

4. The method according to any one of the preceding claims, wherein the combustible gas mixture comprises an inert gas (e.g. argon), oxygen and one or both of hydrogen gas and a hydrocarbon gas (e.g. C_2H_4).

5. The method according to Claim 4, wherein the inert gas represents greater than 70 volume% of the combustible gas mixture, with oxygen and one or both of hydrogen gas and the hydrocarbon gas providing the balance.

6. The method according to Claim 5, wherein:
the inert gas provides from 75 to 79.9 volume% of the combustible gas mixture;
oxygen provides from 10 to 17 volume% of the combustible gas mixture; and

hydrogen gas and/or the hydrocarbon gas provide from 5 to 10.1 volume% of the combustible gas mixture.

7. The method according to Claim 6, wherein:
the inert gas provides from 78 to 79.75 volume% of the combustible gas mixture;
oxygen provides from 14.4 to 15 volume% of the combustible gas mixture; and
hydrogen gas and/or the hydrocarbon gas provide from 5.25 to 8 volume% of the combustible gas mixture.

8. The method according to any one of the preceding claims, wherein:
(a) the volatile metal oxide precursor is injected into the heated mixture at a flow rate of from 2 mL/h to 100 mL/h, such as from 3 mL/h to 50 mL/h, such as from 5 mL/h to 25 mL/h, such as from 10 mL/h to 20 mL/h; and/or
(b) the volatile metal oxide precursor has a concentration of from 100 to 1,500 ppm, such as from 250 to 900 ppm, in the combustible gas mixture.

9. The method according to any one of the preceding claims, wherein the flame has a temperature of from 1,500 to 2,500 K.

10. The method according to any one of the preceding claims wherein the substrate is a rotatable substrate, such that when rotated, the deposition of the non-stoichiometric metal oxide nanoparticle agglomerate occurs on only the portion of the substrate within an area under the flame at any given point of time.

11. The method according to Claim 10, wherein the rotatable substrate is rotated at a speed of from 0.1 rpm to 500 rpm, such as from 1 rpm to 300 rpm, or from 1 rpm to 100 rpm, such as 0.1 rpm, 1 rpm, 100 rpm or 300 rpm.

12. The method according to Claim 10 or Claim 11, wherein the deposited non-stoichiometric metal oxide nanoparticle agglomerate is substantially removed from the surface of the rotatable substrate by a collection means or apparatus, such that the deposited non-stoichiometric metal oxide nanoparticle agglomerate is continuously collected from the surface of the rotatable substrate with each rotation, optionally wherein the rotatable substrate is rotated at a speed of from 0.1 rpm to 20 rpm, such as from 0.2 rpm to less than or equal to 5 rpm, such as 1 rpm.

13. The method according to Claim 12, wherein the method is operated for a period of from 1 minute to infinity, such as from 5 minute to 1 month, such as from 15 minutes to 1 week, such as from 25 minutes to 1 hour.

14. The method according to Claim 10, wherein the deposited non-stoichiometric metal oxide nanoparticle agglomerate is deposited on the surface of the rotatable substrate over a period of time of from 1 second to 15 minutes, optionally wherein the rotatable substrate is rotated at a speed of from 100 rpm to 500 rpm, such as from 100 rpm to 300 rpm.

15. The method according to Claim 12 or Claim 13 or the method according to Claim 14, wherein the rotatable substrate is actively cooled after passing through the flame, optionally wherein the rotatable substrate is cooled by a plurality of nozzles of air, each delivering from 20 to 200 L/min, such as from 50 to 150 L/min, such as from 75 to 100 L/min.

16. The method according to any one of the preceding claims, wherein the distance between the nozzle of the burner and the substrate is from 5 to 25 mm, such as from 14 mm to 20 mm, such as greater than 14 mm to 15 mm.

17. The method according to any one of the preceding claims, wherein the substrate has a temperature of from 298 K to 800 K, such as from 350 K to 780K, such as from 400 K to 500 K, optionally wherein the temperature of the substrate is measured at a point outside of the flame.

18. The method according to any one of the preceding claims, wherein the volatile metal oxide precursor comprises a metal that is able to form a stable reducible oxide.

19. The method according to Claim 18, wherein the volatile metal oxide precursor comprises one or more metals selected from the group consisting of Ti, Ce, Co, Fe, Cu and W, optionally wherein the volatile metal oxide precursor comprises Ti.

20. The method according to any one of the preceding claims, wherein one or both of the following apply:

(a) the formed non-stoichiometric metal oxide nanoparticle agglomerate comprises oxygen vacancies, optionally wherein the oxygen vacancies are formed at grain boundaries; and

(b) the deposition in step (b) is carried out in an environment comprising oxygen.

21. The method according to any one of the preceding claims, wherein the deposition in step (b) is carried out in an environment comprising oxygen.

22. A device for the formation of a non-stoichiometric metal oxide nanoparticle agglomerate, the device comprising:

a burner comprising a nozzle and a feed intake adapted to accept a combustible gas mixture and a volatile metal oxide precursor;

a rotatable stagnation plate comprising a plate with a circular substrate holding region and a motor to rotate the rotatable stagnation plate; and

a collection means or apparatus, wherein:

the nozzle of the burner is adapted to be placed at a fixed position over a portion of the circular substrate holding region, such that in use the nozzle generates a flame that deposits a non-stoichiometric metal oxide nanoparticle agglomerate on a surface of a substrate situated within the circular substrate holding region while the stagnation plate is rotating; and

the collection means or apparatus is arranged to remove the non-stoichiometric metal oxide nanoparticle agglomerate from the surface of the substrate following its deposition.

23. The device according to claim 22, wherein the collection means or apparatus comprises:

a collector head comprising a scraper adapted to be placed in contact with the substrate so as to dislodge the non-stoichiometric metal oxide nanoparticle agglomerates deposited onto the surface of the substrate;

a blowing mechanism; and

a collection vessel, where the blowing mechanism is adapted to supply a gas to direct the dislodged non-stoichiometric metal oxide nanoparticle agglomerates into the collection vessel.

24. The device according to claim 22, wherein the collection means or apparatus comprises:

a collector head comprising:

a body portion;

a scraper extending from the body portion and adapted to be placed in contact with the substrate so as to dislodge the non-stoichiometric metal oxide nanoparticle agglomerates from the surface of the substrate;

a plurality of holes in the body portion;

a collection vessel; and

a vacuum system in fluid connection with the plurality of holes in the body portion and the collection vessel, such that, when in use, the vacuum system transports the dislodged non-stoichiometric metal oxide nanoparticle agglomerates from the substrate *via* the plurality of holes in the body portion and deposits them in the collection vessel, optionally wherein the collection means or apparatus further comprises a cyclone separator.

25. The device according to any one of Claims 22 to 24, wherein the device further comprises a plurality of jet nozzles to cool the rotatable stagnation plate by blowing a gas (e.g. dry air) onto a surface of the stagnation plate opposite to a surface in contact with a flame generated by the nozzle when in use.

26. A non-stoichiometric metal oxide nanoparticle agglomerate comprising a plurality of oxygen vacancies, wherein each nanoparticle has a size of 20 nm or less, such as from 5 to 20 nm, and has a disordered surface layer.

27. The non-stoichiometric metal oxide nanoparticle agglomerate according to Claim 26, wherein the disordered surface layer has a thickness of less than or equal to 1 nm.

28. The non-stoichiometric metal oxide nanoparticle agglomerate according to Claim 26 or Claim 27, wherein the metal is selected from one or more of the group consisting of Ti, Ce, Co, Fe, Cu and W, optionally wherein the metal is Ti.

29. The non-stoichiometric metal oxide nanoparticle agglomerate according to any one of Claims 26 to 28, wherein the non-stoichiometric metal oxide nanoparticle agglomerate is a blue non-stoichiometric titanium oxide nanoparticle agglomerate, where the titanium oxide nanoparticles in the agglomerate comprise a heterophase of rutile and anatase, optionally wherein the percentage of the rutile phase is from 65% to 85% and/or the nanoparticles further comprise a TiO_2-II phase.