

NON-STOICHIOMETRIC METAL OXIDES WITH TUNABLE OXYGEN VACANCIES

Field of Invention

- 5 Disclosed herein is a method of forming a non-stoichiometric metal oxide nanoparticle agglomerate by aerosolizing a heated mixture comprising a combustible gas mixture and a volatile metal oxide precursor. The metal may be Ti.

Background

- 10 The listing or discussion of a prior-published document in this specification should not necessarily be taken as an acknowledgement that the document is part of the state of the art or is common general knowledge.

- 15 Non-stoichiometric semiconductor materials have been identified as promising catalysts for efficient energy conversion and storage. Numerous defective semiconductors such as metal oxides (TiO_2 , ZnO , BiVO_4 , SrTiO_3 , etc.), metal sulphides (CdS , MoS_2 , ZnS , In_2S_3 , etc.) and nitride materials (C_3N_4 , Ta_3N_5 , etc.) have been explored and found to be active in the catalytic reactions. These materials are widely applied in the areas of solar-to-chemical energy
20 conversion involving photocatalytic water splitting, CO_2 reduction, N_2 fixation and dye-sensitized solar cells. The defect engineering is considered as an effective approach to modulate surface chemistry, electronic structure and charge transport.

- Based on the dimensionality of the defects, crystal defects may be spatially classified into four
25 types: 0D point defects (e.g., OV, doping), 1D line defects (e.g., dislocations), 2D planar defects (e.g., stacking faults, grain boundary) and 3D volume defects (e.g., crack, voids). These defects could alter the atom coordination environment and generate vacancy states which affect light absorption, charge separation and transfer, and thus catalytic or photocatalytic activity. An in-depth understanding of the defect nature by characterization is
30 essential for unveiling the fundamental structure-activity relationship.

- Numerous strategies have been explored to synthesize oxygen-deficient TiO_{2-x} , including hydrogen thermal treatment, high energy particle bombardment and heating TiO_2 under vacuum or oxygen depleted conditions. Although these methods have their own strengths, the
35 limitations include high-energy input, complex post-treatment and poor ability to adjust the defect state. A one-step synthesis method that allows tuning the location and abundance of OVs conveniently has not been reported so far.

Flame synthesis has the advantages of high throughput, low waste, simple operation and not requiring any post-treatment. The scalability and efficiency of flame synthesis makes it a robust fabrication method to produce functional nanostructured materials for various applications, such as dye sensitized solar cells, water treatment and toxic gas sensing.

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There is a therefore a need for improved materials and methods for making high-performance catalysts that address the problems mentioned above.

Summary of Invention

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Aspects and embodiments of the invention are disclosed in the following numbered clauses.

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

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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

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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:

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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.

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

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

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4. The method according to any one of the preceding clauses, 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. C₂H₄).
5. The method according to Clause 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 Clause 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 Clause 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 clauses, 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 clauses, wherein the flame has a temperature of from 1,500 to 2,500 K.
10. The method according to any one of the preceding clauses 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 Clause 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.
- 5 12. The method according to Clause 10 or Clause 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
10 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 Clause 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,
15 such as from 25 minutes to 1 hour.
14. The method according to Clause 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
20 rotated at a speed of from 100 rpm to 500 rpm, such as from 100 rpm to 300 rpm.
15. The method according to Clause 12 or Clause 13 or the method according to Clause 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
25 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 clauses, 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.
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17. The method according to any one of the preceding clauses, 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.
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18. The method according to any one of the preceding clauses, wherein the volatile metal oxide precursor comprises a metal that is able to form a stable reducible oxide.

19. The method according to Clause 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.
- 5 20. The method according to any one of the preceding clauses, wherein the formed non-stoichiometric metal oxide nanoparticle agglomerate comprises oxygen vacancies, optionally wherein the oxygen vacancies are formed at grain boundaries.
- 10 21. The method according to any one of the preceding clauses, 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:
- 15 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:
- 20 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
- 25 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 clause 22, wherein the collection means or apparatus
- 30 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
- 35 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 clause 22, wherein the collection means or apparatus comprises:
- a collector head comprising:
 - 5 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;
 - 10 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
 - 15 collection vessel, optionally wherein the collection means or apparatus further comprises a cyclone separator.
25. The device according to any one of Clauses 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 25 20 nm, and has a disordered surface layer.
27. The non-stoichiometric metal oxide nanoparticle agglomerate according to Clause 26, wherein the disordered surface layer has a thickness of less than or equal to 1 nm.
- 30 28. The non-stoichiometric metal oxide nanoparticle agglomerate according to Clause 26 or Clause 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.
- 35 29. The non-stoichiometric metal oxide nanoparticle agglomerate according to any one of Clauses 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 $\text{TiO}_{2-\text{II}}$ phase.

Drawings

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Certain embodiments of the present disclosure are described more fully hereinafter with reference to the accompanying drawings.

10 **Fig. 1** Illustration of FSRs synthesis process of $\text{TiO}_{2-\text{x}}$ (a) in the flame and (b) post flame undergoing thermal sintering and oxidation on hot glass substrate.

Fig. 2 XRD patterns of as-prepared $\text{TiO}_{2-\text{x}}$ samples obtained at different deposition time and commercial P25 TiO_2 .

15 **Fig. 3** (a) FESEM, (b) TEM and (c) HRTEM images of $\text{TiO}_{2-\text{x}}$ -6 min. HRTEM images of (d) $\text{TiO}_{2-\text{x}}$ -10 min, (e) $\text{TiO}_{2-\text{x}}$ -15 min and (f) $\text{TiO}_{2-\text{x}}$ -30 min.

20 **Fig. 4** (a) Structural model of a rutile TiO_2 viewed from $[1\bar{1}1]$ projection. The light grey and dark grey spheres represent Ti and O atoms, respectively. (b) Atomic-resolution aberration-corrected HAADF-STEM image of $\text{TiO}_{2-\text{x}}$ -15 min viewed from $[1\bar{1}1]$ projection. (c) and (d) are the close-up of the marked areas (dash line) in (b). (e) HAADF-STEM image of $\text{TiO}_{2-\text{x}}$ -30 min.

25 **Fig. 5** (a) Raman spectra (inset: enlarged spectra in the range of 110-200 cm^{-1} ; A: anatase, R: rutile) and (b) EPR spectra of flame-made $\text{TiO}_{2-\text{x}}$. XPS spectra of (c) Ti 2p and (d) O 1s.

Fig. 6 TEM image of $\text{TiO}_{2-\text{x}}$ -1 min with disordered cores and amorphous layers.

30 **Fig. 7** (a) UV-vis DRS spectra (inset: enlarged spectra in the range of 340-380 nm). (b) Bandgap analysis. (c) Transient photocurrent density of flame-made $\text{TiO}_{2-\text{x}}$ and P25 TiO_2 under 300 W xenon lamp ($\lambda \geq 400$ nm). (d) Time-resolved PL decay of $\text{TiO}_{2-\text{x}}$ samples with 0.1 wt% Pt loaded after the reaction.

Fig. 8 (a) H_2 evolved after 4 h of photoreaction (20 mg of TiO_2 , 0.1 wt% Pt, 25 vol% methanol, 300 W Xe lamp, ≥ 400 nm). (b) Stability test.

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Fig. 9 TEM image of (a) $\text{TiO}_{2-\text{x}}$ -6 min, (b) $\text{TiO}_{2-\text{x}}$ -10 min, (c) $\text{TiO}_{2-\text{x}}$ -15 min and (d) $\text{TiO}_{2-\text{x}}$ -30 min.

Fig. 10 Raman spectra of P25, anatase TiO₂ and rutile TiO₂.

Fig. 11 HAADF image of 0.1 wt% Pt loaded (a) TiO_{2-x}-6 min, (b) TiO_{2-x}-10 min, (c) TiO_{2-x}-15 min, (d) TiO_{2-x}-30 min, and (e) P25 after photocatalytic H₂ production.

Fig. 12 A flame reactor setup with a rotatable stagnation plate with interval particle collection (IPC).

Fig. 13 (A) Prototype 1 of the continuous particle collection (CPC) system. **(B)** Top view of Prototype 1 with key dimensions.

Fig. 14 Prototype 2 of the continuous particle collection (CPC) system.

Fig. 15 Top view of the CPC system, illustrating the average plate temperatures on different sections of the plate.

Fig. 16 (A) Photographs of powders collected with varying deposition time using IPC and CPC methods, from left to right: (a) CPC, 1 rpm (b) IPC, 1 rpm, 5 mins, (c) IPC, 1 rpm, 15 mins; (d) IPC, 1 rpm, 25 mins. **(B)** Powder XRD patterns with NiO (ca. 14%) mixed in as the internal standard. The intensities are scaled by the highest NiO peak to allow direct comparison between samples. **(C)** Ti 2p XPS spectra with Ti 2p_{3/2} peak set to 458.6 eV. The enlarged shoulder area is shown in the inset at 455-457 eV where Ti³⁺ 2p_{3/2} peak is expected (457 eV). **(D)** The fitted FWHM values for the Ti 2p_{3/2} peak. The peak broadening has been reported to correspond to the presence of defects/Ti³⁺. **(E)** Elemental analysis results.

Fig. 17 (A) Photographs of powders collected with varying rotation speed using IPC and CPC methods, from left to right: (a) CPC, 1 rpm, (b) IPC, 300 rpm, 15 mins, (c) IPC, 100 rpm, 15 mins, (d) IPC, 1 rpm, 15 mins. **(B)** Powder XRD patterns with NiO (ca. 14%) mixed in as the internal standard. The intensities are scaled by the highest NiO peak to allow direct comparison between samples. **(C)** Ti 2p XPS spectra with Ti 2p_{3/2} peak set to 458.6 eV. The enlarged shoulder area is shown in the inset at 455-457 eV where Ti³⁺ 2p_{3/2} peak is expected (457 eV). **(D)** The fitted FWHM values for the Ti 2p_{3/2} peak. The peak broadening has been reported to correspond to the presence of defects/Ti³⁺.

Fig. 18 (A) Photographs of powders collected with varying premixed gas equivalence ratio using CPC method, from left to right: (a) 1.20, (b) 1.10, (c) 1.05, (d) 1.00, (e) 0.90. **(B)** Powder

XRD patterns with NiO (ca. 14%) mixed in as the internal standard. The intensities are scaled by the highest NiO peak to allow direct comparison between samples.

Fig. 19 Effect of the particle layer build up on the stagnation temperature.

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Fig. 20 Comparison of the (A) median particle sizes and the (B) GSDs of the particle size distributions in the current (see Table 8) and previous work (J. Aerosol Sci. **133**, 96–112).

Fig. 21 (A) Photographs of powders collected with varying rotation speed using CPC methods, from left to right: (a) 1 rpm, (b) 0.5 rpm, (c) 0.3 rpm, (d) 0.2 rpm, (e) 0.1 rpm. The sample colors here are slightly different than those shown in other figures (for example for CPC 1 rpm) as the samples shown here were mixed with a mortar and pestle to homogenise and densify the powder after synthesis. **(B)** Powder XRD patterns. **(C)** Ti 2p XPS spectra with Ti 2p_{3/2} peak set to 458.6 eV. The enlarged shoulder area is shown in the inset at 455–457 eV where Ti³⁺ 2p_{3/2} peak is expected (457 eV). **(D)** The fitted FWHM values for the Ti 2p_{3/2} peak. The peak broadening has been reported to correspond to the presence of defects/Ti³⁺. The FWHM absolute values here are not directly comparable with the values in other figures as the XPS spectra in this figure were obtained later compared to the spectra in the other figures with an equipment maintenance service done in between. The FWHM values are therefore likely to be affected by the equipment service.

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Fig. 22 a) BET adsorption-desorption isotherms and b) pore size distributions of flame-made TiO_{2-x} and P25 TiO₂.

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Description

It has been surprisingly found that non-stoichiometric metal oxides may be fabricated by a one-step method as described herein. The method allows the defect content (e.g. oxygen vacancies) and location to be controlled by varying simple parameters, such as deposition time, while providing consistent particle sizes. In particular, it is found that a moderate level of defects may effectively promote charge separation, enhancing performances in catalytic, photocatalytic, or photoelectrochemical processes (such as photocatalytic activity of H₂ production).

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In a first aspect of the invention, there is provided a method of forming a non-stoichiometric metal oxide nanoparticle agglomerate, comprising:

- 5 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
- 10 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.

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In embodiments herein, the word “comprising” may be interpreted as requiring the features mentioned, but not limiting the presence of other features. Alternatively, the word “comprising” may also relate to the situation where only the components/features listed are intended to be present (e.g. the word “comprising” may be replaced by the phrases “consists of” or “consists essentially of”). It is explicitly contemplated that both the broader and narrower interpretations can be applied to all aspects and embodiments of the present invention. In other words, the word “comprising” and synonyms thereof may be replaced by the phrase “consisting of” or the phrase “consists essentially of” or synonyms thereof and *vice versa*.

25 The phrase, “consists essentially of” and its pseudonyms may be interpreted herein to refer to a material where minor impurities may be present. For example, the material may be greater than or equal to 90% pure, such as greater than 95% pure, such as greater than 97% pure, such as greater than 99% pure, such as greater than 99.9% pure, such as greater than 99.99% pure, such as greater than 99.999% pure, such as 100% pure.

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The equivalence ratio (ϕ) is defined as the ratio of the actual fuel/air (or other oxidiser) ratio to the stoichiometric fuel/air (or other oxidiser) ratio. Stoichiometric combustion occurs when all the oxygen is consumed in the reaction, and there is no molecular oxygen (O_2) in the products. If the equivalence ratio is equal to one, the combustion is stoichiometric. If it is < 1 , the combustion is fuel-lean with excess air, and if it is > 1 , the combustion is fuel-rich or oxygen-lean which results in an incomplete combustion. Hence, oxygen-lean equivalence ratio used herein refers to an equivalence ratio of more than 1.

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As noted above, the oxygen-lean equivalence ratio (ϕ) is less than or equal to 1.5. For example, the oxygen-lean equivalence ratio (ϕ) may be from 1.05 to 1.5. In more particular embodiments that may be mentioned herein, the oxygen-lean equivalence ratio (ϕ) may be from 1.1 to 1.4. Without wishing to be bound by theory, it is believed that the oxygen-lean equivalence ratio ($\phi > 1$) may allow the formation of blue non-stoichiometric titanium oxide nanoparticle agglomerates (or blue TiO_2), while avoiding production of a large amount of soot and carbon contaminants. The oxygen-lean equivalence ratio may also avoid formation of secondary flames which may increase temperature and promote the oxidation of blue TiO_2 ,

The combustible gas mixture may comprise any suitable combination of an inert gas (e.g. argon), oxygen and a combustible gas. For example, the combustible gas mixture may comprise an inert gas (e.g. argon), oxygen and one or both of hydrogen gas and a hydrocarbon gas (e.g. C_2H_4). Any suitable combination of gasses that provide the oxygen-lean equivalence ratios (ϕ) disclosed above may be used. In particular embodiments that may be mentioned herein, the inert gas may represent 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. More particularly, the inert gas may provide from 75 to 79.9 volume% of the combustible gas mixture, oxygen may provide 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. In further embodiments that may be mentioned herein, the inert gas may provide 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.

It is important that the combustible gas mixture velocity at the nozzle must be larger than the flame speed to stabilise the flame, thereby providing a stable flame for use in the process. This may be achieved by using a velocity for the combustible gas mixture at the nozzle of the burner of from 300 to 500 cm/s. Importantly, this velocity range may be used with a nozzle of any suitable dimension. An alternative way to look at the gas velocity is to consider the flow rate of the combustible gas mixture. For example, when the nozzle has a diameter of 1.4 cm (14 mm), the flow rate of the combustible gas mixture may be from 18 to 30 sL/minute (SLPM), which provided a velocity of from 300 to 500 cm/s. It will be appreciated that in order to maintain the same velocity range with a larger or smaller nozzle will result in an increase or decrease in the flow rate, respectively. The standard liter per minute (SLM or SLPM) is a unit of volumetric flow rate of a gas at standard conditions for temperature and pressure (STP; which is usually defined as a temperature of 273.15 K (0 °C) and an absolute pressure of

101.325 kPa (1 atm)). When used herein, the flow rate of the gas is measured before it is preheated and the MFCs were also calibrated at standard conditions (0 °C, 1 atm).

Any suitable volatile metal oxide precursor may be used, provided that the metal used is one that can provide a non-stoichiometric metal oxide. More particularly, the volatile metal oxide precursor may comprise a metal that is able to form a stable reducible oxide. Examples of suitable volatile metal oxide precursors include metal salts and metal composites with other metals. Suitable metals that may be mentioned as part of the volatile metal oxide precursors include, but are not limited to, Ti, Ce, Co, Fe, Cu, W, and combinations thereof. In particular embodiments that may be mentioned herein the metal in the volatile metal oxide precursor may be Ti. The volatile metal oxide precursors used herein may be solid or liquid and may have a boiling point or a sublimation point less than or equal to 350°C, such as from 120 to 300°C, such as from 150 to 250°C. Additionally or alternatively, the volatile metal oxide precursors may be a solid or liquid and have a significant vapour pressure at the temperature used for the gas supplied to the burner. For example, at a temperature of less than or equal to 350°C, such as from 120 to 300°C, such as from 150 to 250°C. The higher the vapour pressure of a precursor, the higher the loading rate that can be used in the system. As a general rule, the higher the vapour pressure of the precursor, the better. As an example, the vapour pressure of titanium (IV) isopropoxide at 150°C may be about 77 mmHg.

Examples of particular volatile metal oxide precursors that may be mentioned herein include, but are not limited to, titanium (IV) isopropoxide, titanium tetrachloride, WF_6 , and combinations thereof. In particular embodiments that may be mentioned herein, the volatile metal oxide precursors may be titanium (IV) isopropoxide and/or titanium tetrachloride (e.g. titanium (IV) isopropoxide).

Any suitable amount of the volatile metal oxide precursor may be used in the method disclosed herein. For example, the volatile metal oxide precursor may be 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. Additionally or alternatively, the volatile metal oxide precursor may have a concentration of from 100 to 1,500 ppm, such as from 250 to 900 ppm, in the combustible gas mixture. As will be appreciated, the latter by means of concentration will be unaffected by the size of the nozzle of the burner, while the former may be affected by this feature of the physical apparatus. For example, a 20 mL/h flow rate of titanium (IV) isopropoxide with a 28 sL/minute flowrate of the combustible gas mixture (using a 14 mm nozzle) corresponds to 900 ppm of titanium (IV) isopropoxide. Similarly, a 3 mL/h

flow rate of titanium (IV) isopropoxide with a 15 sL/ minute flowrate of the combustible gas mixture (using a 14 mm nozzle) corresponds to 250 ppm of titanium (IV) isopropoxide.

5 The flame used in the method may have any suitable temperature. For example, the temperature may have a temperature of from 1,500 to 2,500 K. These temperatures may relate to the theoretical adiabatic flame temperature that may be achieved based on the combustion gas mixture.

10 Any suitable substrate may be used in the process. For example, the substrate may be a rotatable substrate. This may refer to a planar disc or to a conveyor belt as the substrate. In the situation where the substrate is rotatable, it will be appreciated that only the portion of the substrate under the flame at any given point of time will be subject to the deposition of the non-stoichiometric metal oxide nanoparticle agglomerate. However, as the substrate rotates, this will allow for a "fresh" portion of substrate to be subjected to deposition. The rotation of
15 the rotatable substrate may be at any suitable speed. For example, the rotatable substrate may be rotated at a speed of from 0.1 rpm to 500 rpm, such as from 0.2 rpm to 350 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.

20 For the avoidance of doubt, it is explicitly contemplated that where a number of numerical ranges related to the same feature are cited herein, that the end points for each range are intended to be combined in any order to provide further contemplated (and implicitly disclosed) ranges.

25 Thus, there the rotatable substrate may be rotated at a speed of:
from 0.1 rpm to 1 rpm, from 0.1 rpm to 100 rpm, from 0.1 rpm to 300 rpm, from 0.1 rpm to 500 rpm;
from 1 rpm to 100 rpm, from 1 rpm to 300 rpm, from 1 rpm to 500 rpm;
from 100 rpm to 300 rpm, from 100 rpm to 500 rpm; and
30 from 300 rpm to 500 rpm.

As will be appreciated, if the rotatable substrate is in motion then, unless the method is stopped after one revolution (or cycle) or the substrate cleaned, part of the substrate where deposition has already taken place will undergo a further round of deposition. This may allow the build-
35 up of nanoparticles on the surface of the substrate over time. When such a method is used, the deposited non-stoichiometric metal oxide nanoparticle agglomerate may be deposited on the surface of the rotatable substrate over a period of time of from 1 second to 15 minutes.

The period of time selected for deposition of the nanoparticles (or deposition time) may allow for the formation of desired materials, such as blue TiO₂. The rotatable substrate in such methods may be rotated at a speed of from 100 rpm to 500 rpm, such as from 100 rpm to 300 rpm.

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In alternative embodiments, the deposited non-stoichiometric metal oxide nanoparticle agglomerate may be 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. The rotation used herein may be 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 from 1 rpm to less than or equal to 4.5 rpm, such as 1 rpm.

As will be appreciated, variations of the collection described above may be conducted. For example, the collection may be arranged to occur after a set amount of time and/or a set number of rotations.

When used herein, the term "substantially removed" may refer to the removal of greater than or equal to 95% (such as greater than or equal to 97%, such as greater than or equal to 98%, such as greater than or equal to 99%, such as greater than or equal to 99.5%, such as greater than or equal to 99.9%) of the deposited non-stoichiometric metal oxide nanoparticle agglomerate on the surface of a substrate.

When the method makes use of a rotatable substrate, it may be operated on a "continuous flow" basis. That is particularly the case when the deposited non-stoichiometric metal oxide nanoparticle agglomerate is continuously collected from the surface of the rotatable substrate with each rotation (or set number of rotations/amount of time). In such an arrangement, the method may be operated for a period of from 1 minute to infinity, such as from 5 minutes to 1 month, such as from 15 minutes to 1 week, such as from 25 minutes to 1 hour.

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One limitation on the extended operation of the method may be due to the apparatus used, which may deform or degrade over time. This may be solved by the use of, for example, two or more scrapers (see the description of suitable devices below), where when the first-deployed scraper has degraded and can no longer be used, the second scraper may be deployed in its place and the first-deployed scraper can then be replaced, thereby allowing it to replace the second-deployed scraper and thereby allow continuous collection over an extended period of time.

35

- When the method makes use of a rotatable substrate, the substrate may act to cool itself after passing through the flame by convection due to the rotation. Alternatively, the rotatable substrate may be actively cooled after passing through the flame. As will be appreciated, any
- 5 suitable number of nozzles with any suitable flow rate can be used. For example, a rotatable substrate may be 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. In particular embodiments that may be disclosed herein, the active cooling may be conducted using four nozzles each using a flow rate of 25 L/min of air onto the underside of the substrate. As will be appreciated, the
- 10 actual number of nozzles and flow rate used will depend on the size of the nozzle/flame and the substrate's composition/size. For example, a flow rate of from 20 to 200 L/min from each nozzle may be suitable for a 30 cm diameter plate in combination with a 1.4 cm diameter nozzle.
- 15 Any suitable size of nozzle can be used. The nozzle size used may be one in which a stable flame can be produced. Provided that it is possible to achieve a relatively uniform velocity at the nozzle of the burner for the combustible gas mixture of from 300 to 500 cm/s, there is no limit on the size of the nozzle size.
- 20 The nozzle of the burner may be placed at any suitable distance from the substrate in order to provide the deposition of the desired non-stoichiometric metal oxide nanoparticle agglomerate. For example, the distance between the nozzle of the burner and the substrate may be from 5 to 25 mm, such as from 14 mm to 20 mm, such as greater than 14 mm to 15 mm. Thus, the distance between the nozzle of the burner and the substrate may be:
- 25 from 5 to 14 mm, from 5 to 15 mm, from 5 to 20 mm, from 5 to 25 mm;
from 14 to 15 mm, from 14 to 20 mm, from 14 to 25 mm;
from 15 to 20 mm, from 15 to 25 mm; and
from 20 to 25 mm.
- 30 The distance of the nozzle of the burner from the substrate may affect the stability of the flame, but may not directly affect the properties of the resulting particles. As such, the skilled person will be able to determine an appropriate distance for any set-up through routine trial and error, as they will look for a stable flame for use in the method.
- 35 As will be appreciated, the substrate will be subjected to the flame and so it may have a temperature close to, or at, room temperature or it may have an elevated temperature (thereby requiring the use of active cooling). For example the substrate may have a temperature of

from 298 K to 800 K, such as from 350 K to 780K, such as from 400 K to 500 K. The temperature of the substrate may be measured at any suitable point of the substrate (e.g. within the flame or outside it). In particular embodiments, the temperature of the substrate may be measured at a point no longer under the flame (e.g. on a part of the substrate that has
5 been under the flame during the process).

As noted the method disclosed herein produces non-stoichiometric metal oxide nanoparticle agglomerates. The formed non-stoichiometric metal oxide nanoparticle agglomerates may comprise oxygen vacancies. In certain embodiments, the oxygen vacancies may be formed
10 at grain boundaries.

In the method disclosed herein, the deposition in step (b) may be carried out in an environment comprising oxygen. That is, the ambient environment on the side outside of the flame and the burner may be one that contains oxygen (e.g. the ambient environment may be air).
15

The flame produced in the method disclosed herein may be accompanied by a sheathe of an inert gas, such as argon or nitrogen. Further details of the sheathe gas may be obtained from the experimental section below, which may be adapted according to the nozzle, velocity and flame to be used in any particular embodiment in line with a person in the art's knowledge.
20

As will be appreciated, the method disclosed above may be achieved making use of a suitable device. Thus, in a further aspect of the invention, there is provided a device for the formation of a non-stoichiometric metal oxide nanoparticle agglomerate, the device **100** comprising:

a burner **110** comprising a nozzle **115** and a feed intake (not shown) adapted to accept
25 a combustible gas mixture and a volatile metal oxide precursor;

a rotatable stagnation plate **120** comprising a plate with a circular substrate holding region and a motor **125** to rotate the rotatable stagnation plate; and

a collection means or apparatus **130**, wherein:

the nozzle **115** of the burner is adapted to be placed at a fixed position over a
30 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
35 metal oxide nanoparticle agglomerate from the surface of the substrate following its deposition.

Examples of suitable devices are shown in Figures 13 and 14.

In Figure 13 (considering both of Figures 13A and B), there is disclosed a device **100** that has:

- a burner **110** comprising a nozzle **115** and a feed intake adapted to accept a combustible gas mixture and a volatile metal oxide precursor;
- a rotatable stagnation plate **120** comprising a plate with a circular substrate holding region and a motor **125** to rotate the rotatable stagnation plate; and
- a collection means or apparatus **130**, wherein:
 - the nozzle **115** 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 **104** that deposits a non-stoichiometric metal oxide nanoparticle agglomerate **144** on a surface **145** of a substrate **140** situated within the circular substrate holding region while the stagnation plate is rotating, where the collection means or apparatus **130** is formed from a collector head **131** comprising a scraper **132** adapted to be placed in contact with the substrate **140** so as to dislodge the non-stoichiometric metal oxide nanoparticle agglomerates **144** deposited onto the surface of the substrate **140**;
 - a blowing mechanism **133**; and
 - a collection vessel **134**, where the blowing mechanism is adapted to supply a gas to direct the dislodged non-stoichiometric metal oxide nanoparticle agglomerates into the collection vessel. As will be appreciated, the collection vessel may comprise an apparatus that helps to direct the dislodged non-stoichiometric metal oxide nanoparticle agglomerates into the collection vessel. This may be an apparatus that simply funnels the dislodged particles into the collection vessel, or it might simply be the side of the scraper. The blowing mechanism may comprise an air blowing machine and channels that direct the blown air across the substrate and scraper, thereby urging the dislodged non-stoichiometric metal oxide nanoparticle agglomerates into the collection vessel. As shown in Figure 13, the channels may simply be tubing **134a** that runs along an upper edge of the scraper that then has a U-bend to provide the desired directionality of the blown air/gas.

In Figure 14, there is disclosed a device **100** that has:

- a burner **110** comprising a nozzle **115** and a feed intake adapted to accept a combustible gas mixture and a volatile metal oxide precursor;
- a rotatable stagnation plate **120** comprising a plate with a circular substrate holding region and a motor **125** to rotate the rotatable stagnation plate; and
- a collection means or apparatus **130**, wherein:
 - the nozzle **115** 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 **104** that

deposits a non-stoichiometric metal oxide nanoparticle agglomerate **144** on a surface **145** of a substrate **140** situated within the circular substrate holding region while the stagnation plate is rotating, where the collection means or apparatus **130** is formed from a collector head **131** comprising:

- 5 a body portion **135**;
- a scraper **132** 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 **136** in the body portion;
- 10 a collection vessel **134**; 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
- 15 collection vessel. As shown in Figure 14, the collection means or apparatus may further comprise a cyclone separator **138a**.

In Figure 14, the vacuum system includes a number of vacuum pumps **138b** (e.g. one or two) to provide a suction effect that suck up the dislodged non-stoichiometric metal oxide nanoparticle agglomerates, which then pass through the holes **136** and associated tubing **138c** into a cyclone separator **138a** that is intended to separate the air from the dislodged non-stoichiometric metal oxide nanoparticle agglomerates, with the latter being deposited in the collection vessel **134**. As some of the dislodged non-stoichiometric metal oxide nanoparticle agglomerates may not be separated from the air through the cyclone separator, there may

20 also be a filter **138d** placed in front of the vacuum pumps **138b** to separate out and collect any non-stoichiometric metal oxide nanoparticle agglomerates that are not deposited into the collection vessel.

It will be appreciated that the devices described above may be adapted readily by anyone skilled in the field. For example, Equivalents of a rotatable plate may be used, such as a conveyor belt system. While the depicted devices only make use of a single scraper, the system may be designed with two or more scrapers. When there are more than one scraper two or more scrapers may be used in tandem (one in front of the other) to ensure that the non-stoichiometric metal oxide nanoparticle agglomerates are completely (or as close to this as possible) from the surface of the substrate. Additionally or alternatively, the use of one or more

30 scrapers may allow for a scraper to be replaced without having to stop production.

The devices described above may also be fitted with a plurality of jet nozzles **150** 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.

- 5 In yet a further aspect of the invention, there is also provided 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. As will be appreciated the oxygen vacancies occur within the nanoparticles and/or at grain boundaries within agglomerates. The particle size may be measured by
10 methods described in the examples below.

The disordered surface layer may have any suitable thickness. For example, the disordered surface layer may have a thickness of less than or equal to 1 nm.

- 15 As mentioned hereinbefore, any metal that can provide a non-stoichiometric metal oxide may form the metal in the non-stoichiometric metal oxide nanoparticle agglomerates disclosed herein. For example, the metal may be selected from one or more of the group consisting of Ti, Ce, Co, Fe, Cu and W, optionally wherein the metal is Ti.

- 20 In particular embodiments that may be mentioned herein, the non-stoichiometric metal oxide nanoparticle agglomerate may be 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 $\text{TiO}_{2-\text{II}}$ phase.

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Further aspects and embodiments of the invention are provided in the following non-limiting examples.

Examples

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Disclosed herein is the preparation of TiO_{2-x} nanoparticles for photocatalysis using a flame stabilized on a rotation surface (FSRS) method. In this method, a thin flame is stabilised above a convectively cooled substrate such that a steep temperature gradient is formed near the substrate. While the present example uses a FSRS method, other substrates may be used as
35 long as the surface of the substrate may be cooled sufficiently fast. It was found that particles formed in the flame were subject to a short residence time and a fast-cooling rate during the deposition, resulting in the formation of ultrafine nanoparticles with high monodispersity. The

growth of particles in high temperature and oxygen-deficient conditions in flame also leads to a high concentration of defects including oxygen vacancies (OVs) in the deposited particles. However, upon prolonged deposition, the particles on the rotatable substrate may further grow through the formation of grain boundaries (GBs) due to the thermal sintering and react with oxygen in the atmosphere to decrease the OV concentration. This may provide a convenient way to control the location and abundance of OVs by simply varying the deposition time.

Example 1. Fabrication of blue TiO_{2-x} nanoparticles with flame synthesis method

OV-containing blue TiO_{2-x} was prepared through a one-step flame stabilized on a rotating surface (FSRS) method shown in Fig. 1a.

In a typical procedure, a premixed gas consisting of 7.2% C_2H_4 , 14.4% O_2 and 78.4% Ar (an oxygen-lean mixture with mixture equivalence ratio, $\varphi = 1.5$, φ is defined as the ratio of the actual fuel/air ratio to the stoichiometric fuel/air ratio) was preheated to 150 °C with a total flow rate of 18 L/min (STP) (corresponding to an equivalent velocity of 304 cm/s). Titanium chloride (TiCl_4 , Aldrich, 99.9%) was injected into the heated gas mixture using a syringe pump at a flow rate of 3 mL/h. The premixed gas carrying vaporized TiCl_4 was then issued from an aerodynamic nozzle with an exit outlet of 1 cm in diameter and impinged on a rotating disk. The rotating disk (30.5 cm in diameter) was placed 1.5 cm below the nozzle outlet, and kept at a rotating speed of 300 rpm. Upon ignition, a flat laminar flame was formed and stabilized above the rotating disk. Inside the flame, TiCl_4 vapor rapidly reacted to form liquid-like TiO_2 droplets which subsequently formed the ultrafine TiO_{2-x} nanoparticles. The nanoparticles were deposited on the glass substrates placed in the slots on the rotating disk. Due to heat transfer from the flame, the temperature of the glass substrates gradually increased from room temperature to around 450 K within 15 min, as measured by an infrared thermometer from the bottom of the rotating disk. At the end of the process, the powder was scrapped off from the substrates and directly used for loading of the cocatalyst without further post-treatment. The samples were named as TiO_{2-x} -deposition time ($x = 6$ min, 10 min, 15 min or 30 min). The observed color of these samples varies from dark blue (6 min), to light blue (10 min), pale blue (15 min), and almost colorless (30 min).

Example 2. Physiochemical properties of blue TiO_{2-x}

XRD

Powder X-ray diffraction (XRD) patterns were acquired in Bruker D2 Phaser diffractometer with Cu K α ($\lambda=1.54184$ Å) radiation at 30 kV and 10 mA. The measurement of Brunauer–Emmett–Teller (BET) surface area was obtained in Quantachrome Autosorb-6 sorption system by N₂ adsorption and desorption at 77 K.

5

The phase composition of flame-made TiO_{2-x} was first analyzed by XRD. As shown in Fig. 2, the flame-made TiO_{2-x}, especially TiO_{2-x}-6 min, is much less crystalline than P25 TiO₂, suggesting there are defects and disorders in their structures. All TiO_{2-x} samples comprise dominant rutile phase and minor anatase phase. In addition, a small content of TiO₂-II phase is also present. The phase composition calculated based on the method of Rietveld refinement is shown in Table 1 below. All flame-made TiO_{2-x} has over 70% of rutile phase. For comparison, P25 TiO₂ is composed of around 80% anatase and 20% rutile. The XRD results indicate that the deposition time has no significant influence on the phase composition, although the color of the samples changes drastically from deep blue (6 min) to white (30 min), coupled with a slight increase in the crystallinity.

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Table 1. The specific surface area (SSA), phase composition and bandgap energy of flame-made TiO_{2-x} samples and P25.

Sample	SSA (m ² g ⁻¹) ¹⁾	Pore volume (cm ³ g ⁻¹)	Rutile content (%)	Anatase content (%)	TiO ₂ -II content (%) ^b	Bandgap energy (eV)
6 min	100.1	0.50	76.5	13.3	10.2	2.80
10 min	116.8	0.63	71.2	19.9	8.9	2.93
15 min	120.5	0.62	72.8	16.8	10.4	3.00
30 min	118.3	0.29	79.4	15.8	4.8	3.03
P25	50.0	0.19	19.8	80.2	0	3.20

^b Phase composition result with low accuracy was obtained due to the presence of amorphous phase in TiO_{2-x}.

20

Effect of deposition time on morphology

Field emission scanning electron microscopy (FESEM) was conducted on JEOL JSM 6701F microscope. Transmission electron microscope (TEM) images and high-angle annular dark-field (HAADF) images were obtained in JEOL JEM-2100F TEM/STEM and JEOL JEM-ARM200F/300F equipped with a Cs corrector.

25

Fig. 3 shows the morphology of flame-made TiO_{2-x} samples. In **Fig. 3a**, the FESEM image of TiO_{2-x} -6 min indicates that loosely aggregated nanoparticles were formed with particle sizes of around 10-20 nm. In the TEM image (**Fig. 3b**), the outlines of spherical nanoparticles can be easily observed, indicating that the sintering level between particles is minimal due to the short time on the substrate. The nanoparticles have crystalline cores and the surface/sub-surface displays amorphous and disordered layers. These features are further shown in the HRTEM image. As shown in **Fig. 3c**, disordered domains are clearly observed, especially on the particle surface. The core shows lattice fringes with interplanar spacings of 0.322 nm and 0.249 nm, which are attributed to (110) and (101) planes of rutile TiO_2 respectively. The disordered surface layer has a thickness of around 1 nm. Inside the flame, the vaporized TiCl_4 precursor rapidly reacts with O_2 and other radical species to form Ti-containing intermediate species which act as the precursor of TiO_2 nanoparticles. Due to the oxygen-lean condition of the flame (calculated equilibrium O_2 mole fraction is 5.83×10^{-5}), the intermediate species are likely to be oxygen deficient (Ti_xO_y , $y/x < 2$). The formed nanoparticles are therefore expected to contain a high concentration of oxygen vacancies. As the vacancies are introduced to the particles from the very early stages (instead of from reduction of stoichiometric TiO_2 at a later stage), the oxygen vacancies should be distributed throughout the particles, both in bulk and surface, as manifested in the sample with a short deposition time, TiO_{2-x} -1 min (**Fig. 6**). The TiO_{2-x} -1 min sample formed at such a short deposition time exhibits the most disordered structure with amorphous outer layers measured to be ≈ 2.1 nm.

As the deposition time increases, the OV in particles deposited on the substrates may react with the atmospheric O_2 given the temperature of the substrates. This results in a decrease in OV concentration, especially surface OVs, with increasing deposition time. With prolonged oxidation time, the crystallinity of the particles also improves. In **Fig. 3d**, for example, TiO_{2-x} -10 min exhibits lattice disorders in the bulk phase with a thinner amorphous layer present compared with TiO_{2-x} -6 min. Further increase in deposition time leads to the better crystalline core of TiO_{2-x} -15 min with less surface defects observed in **Fig. 3e**. **Fig. 3f** shows the HRTEM image of TiO_{2-x} -30 min, where much less lattice defects and almost no amorphous surface layer can be observed in TiO_{2-x} -30 min.

Based on the qualitative HRTEM observations of all samples, the reduction in the extent of both bulk and surface defects correlates well with the deposition time. While the measured substrate temperature was relatively low (450 K), the actual temperature of the upper layer of particles exposed to the flame is expected to be much higher given the calculated adiabatic flame temperature of 2376 K. The adiabatic flame temperature was calculated at constant enthalpy and pressure using the software package *kinetics*[®] with the USC-II chemical

mechanism for $\text{H}_2/\text{CO}/\text{C}_1\text{-C}_4$ by Wang et al (USC Mech Version II. High-Temperature Combustion Reaction Model of $\text{H}_2/\text{CO}/\text{C}_1\text{-C}_4$ Compounds). As a result, particles may further undergo thermal sintering after the deposition on the substrate, resulting in the formation of grain boundaries (GBs) between adjacent nanoparticles as observed in **Figs. 3c-f**. The GB appears to be more obvious in samples with longer deposition time due to the longer sintering.

As further revealed by the TEM images in **Fig. 9a-d**, the nanoparticles collected beyond 6 min deposition time lose the spherical shape and form aggregated structure. Consistent with the morphological features, the Brunauer–Emmett–Teller (BET) surface area of all flame-made TiO_{2-x} (100–120 $\text{m}^2 \text{g}^{-1}$) is much higher than that of P25 TiO_2 (50 $\text{m}^2 \text{g}^{-1}$) (**Table 1**). The reduction of the surface area of TiO_{2-x} -30 min compared to TiO_{2-x} -10 and 15 min is ascribed to the prolonged sintering and aggregation. All the TiO_2 samples exhibit the isotherm of Type H3 hysteresis, which have no limiting adsorption at high P/P_0 (**Figure 22a**). This type of isotherm originates from nonrigid aggregates of plate-like nanoparticles or numerous slit-shaped pores. This is consistent with the feature of our samples which consist of aggregated nanoparticles as shown in **Fig. 9**. Correspondingly, the measured pore size (**Figure 22b**), i.e., the interparticle distance, is very large and generally above 20 nm with an average pore size in a range of 43–48 nm for flame made TiO_{2-x} . However, the pore volume varies among different samples (**Table 1**). In particular, a significant decrease of the pore volume of TiO_{2-x} -30 min was observed which is caused by more severe sintering.

STEM analysis of TiO_{2-x} -15 min and TiO_{2-x} -30 min

Structural analysis of TiO_{2-x} -15 min was carried out by applying atomic-resolution aberration-corrected STEM which shows more details about the defects in the sample. The structural model of rutile TiO_2 projecting from $[\bar{1}\bar{1}1]$ direction is shown in **Fig. 4a**. This matches well with the observed STEM image of TiO_{2-x} -15 min (**Fig. 4b**). Here, the defects such as stepped surface and stacking faults can be easily observed. The edge, corner and step atoms represent low coordination sites which serve as active sites for anchoring of metal co-catalysts as well as the adsorption and activation of reactant species. In addition to the surface defects, a large area of bulk defects (disordered area) can be also observed in **Fig. 4b**, which reduces the crystallinity and impairs the well-ordered arrangement of atoms. The bulk defects across the nanocrystal induce stacking faults. Careful examination of the stacking sequence of lattice planes reveals that some planes of atoms are misplaced and shifted from the original regular position, as shown in **Figs. 4c, 4d**. The formation of stacking faults could be related to the sintering of the nanoparticles or the removal of the vacancies during the crystal growth. STEM

analysis of TiO_{2-x} -30 min shows that the nanocrystal displays well-ordered lattices without obvious bulk defects (Fig. 4e).

Chemical properties

5

Spectroscopic techniques including Raman, EPR and XPS were used to further investigate the chemical properties of flame-made TiO_{2-x} . Raman spectra were recorded on Renishaw InVia Raman Spectrometer with the excitation wavelength of 514.5 nm. X-ray photoelectron spectroscopy (XPS) was conducted in Kratos AXIS Ultra DLD spectrometer with binding energy calibrated by C 1s peak at 284.7 eV. Electron paramagnetic resonance (EPR) was conducted in a Bruker EMX-10/12 EPR spectrometer at 9.363 GHz.

Compared with the Raman spectra of pure anatase and rutile TiO_2 (Fig. 10), flame-made TiO_{2-x} exhibit mixed vibrational modes as they comprise both phases and much broader signals due to lower crystallinity as shown in Fig. 5a. The rutile phase exhibits two first-order vibrational modes: E_g (445 cm^{-1}) and A_{1g} (611 cm^{-1}) while the anatase phase displays E_g (144 cm^{-1}) vibrational mode. The anatase and rutile E_g modes ascribed to Ti-O vibration are shifted to higher and lower frequencies, respectively accompanied by a peak broadening effect at shorter deposition time of 6 and 10 min (inset in Fig. 5a). This proves higher abundance of OV's in both two phases for defective samples. The removal of one oxygen atom triggers the tendency of the three nearest-neighbor Ti atoms relaxing away from the oxygen vacancy to strengthen their bonds to other oxygen atoms. This outward relaxation induces disordered structures and shortens the length of the Ti-O bond locally, leading to the blue shift and broadening of anatase E_g signal. The rutile E_g mode is related to out-of-phase, librational movement of oxygen atoms along the c-axis. The red shift of this mode is believed to arise from the lattice distortion and c-axis motion of oxygen in rutile phase.

The existence of Ti^{3+} in blue TiO_{2-x} can be further confirmed by EPR. As shown in Fig. 5b, the broad signal with $g = 1.93$ signifies the surface exposed Ti^{3+} sites which is stronger at shorter deposition time. In particular, the strongest signal in TiO_{2-x} -6 min is consistent with its dark blue color (Fig. 1b), signifying that numerous Ti^{3+} defects are formed in the reductive flame environment. With prolonged contact time with air on the substrate above ambient temperature, Ti^{3+} is gradually oxidized to Ti^{4+} . Almost no signal was detected in TiO_{2-x} -30 min and P25.

XPS analysis was performed to study the surface and sub-surface chemical states of the samples. As shown in Fig. 5c, the two peaks at binding energy of 458.7 eV and 464.4 eV are attributed to Ti $2p_{3/2}$ and Ti $2p_{1/2}$ of Ti^{4+} , respectively. The existence of Ti^{3+} on the surface of

TiO_{2-x}-6 min and 15 min is evidenced by the shoulder peaks at 457.4 eV and 463.1 eV, assigned to Ti 2p_{3/2} and Ti 2p_{1/2} of Ti³⁺. Such signals were hardly found on the surface of TiO_{2-x}-30 min and P25. Correspondingly, OV_s are present on the surface to maintain the charge equilibrium. In the O 1s spectra (**Fig. 5d**), the main peak of O 1s at 529.9 eV is assigned to Ti-O lattice bond without nearby OV_s, while the shoulder peak at 531.8 eV belongs to O-atoms in the vicinity of an O-vacancy. The larger shoulder peak of TiO_{2-x}-6 min consistently indicates that more OV_s are present on its surface compared to other samples.

Summary

Based on the results above, the mechanism of formation of OV_s in TiO_{2-x} is proposed as shown in **Fig. 1b**. In the fuel-rich reductive flame, the nucleation and particle growth are accompanied by the formation of Ti³⁺ and OV_s. Within the short residence time of 6~7 milliseconds, TiO_{2-x} nanoparticles grow rapidly to around 10-20 nm. During this process, the defects originally located at outer layers are "migrated" to the core, resulting in a random distribution of OV_s in the entire particle. Upon deposition, the nanoparticles undergo thermal sintering and oxidation by atmospheric O₂. Eventually, after long exposure in the atmosphere (30 min), the quantity of OV_s decrease and the sample become colorless.

Example 3. Photophysical properties of blue TiO_{2-x}

The quantitative results of OV_s in blue TiO_{2-x} obtained in Example 2 would provide greater understanding of the correlations between the distribution of OV_s and their photophysical properties including bandgap energy, transient photocurrent density and charge carrier kinetics.

Bandgap energy

UV-visible diffuse reflectance spectra (UV-vis DRS) were collected in a UV-2450 spectrophotometer (Shimadzu).

As shown in **Fig. 7a**, compared to P25 TiO₂ with a bandgap energy of 3.2 eV, all flame-made TiO_{2-x} exhibit the absorption edge at longer wavelength due to the predominant rutile phase in these samples. Among flame-made TiO_{2-x}, TiO_{2-x}-6 min has the smallest bandgap energy of 2.8 eV. The remaining all have a bandgap energy of around 3.0 eV which is the bandgap energy of rutile phase (**Fig. 7b** and **Table 1**). Sample TiO_{2-x}-6 min also displays a large absorption tail in the visible light and NIR region. The obvious reduction of bandgap energy

and tail-up phenomenon in TiO_{2-x} -6 min against the other flame-made TiO_{2-x} indicates that the surface disorder (ca. 1 nm thick amorphous outer layer) plays an important role in these properties. On the other hand, bulk defects appear to have less influence as shown by samples TiO_{2-x} -10 min and 15 min which contain around the same or even more bulk defects than TiO_{2-x} -6 min.

Photocurrent density

The photoelectrochemical measurement was conducted in a three-electrode cell system controlled by a CHI 660E electrochemistry workstation with TiO_{2-x} coated on ITO (Sigma-Aldrich, L x W x thickness: 25 mm x 25 mm x 1.1 mm) as the working electrode, Pt as the counter electrode, and Ag/AgCl as the reference electrode. To obtain the catalyst ink, 5 mg of TiO_{2-x} (as prepared from Example 1) and 20 μL of Nafion solution (5 wt%) were added into 980 μL of ethanol solution to form a homogeneous ink by ultrasonication for 15 min. For preparation of the working electrode, 40 μL portion of such catalyst ink was deposited on the ITO conductive glass with an area of 0.196 cm^2 and dried at 40 $^{\circ}\text{C}$ for 2 h. A 300 W xenon lamp (Newport) with a cut-off filter ($\lambda \geq 400 \text{ nm}$) was used as the light source. The photocurrent was recorded in the 0.5 M Na_2SO_4 solution with an applied potential of 0.6 V versus Ag/AgCl.

Transient photocurrent density measurement results are shown in **Fig. 7c**. Although sample TiO_{2-x} -6 min has the smallest bandgap and largest absorption tail in visible light, its photocurrent density is the lowest among all flame-made TiO_{2-x} under visible light irradiation ($\lambda \geq 400 \text{ nm}$). The highest photocurrent density was obtained from TiO_{2-x} -15 min which is about 2.5 times higher than that from TiO_{2-x} -6 min. Such observations imply that TiO_{2-x} -15 min with moderate amount of OVs possesses the highest charge separation efficiency.

Charge carrier kinetics

To further study the charge carrier kinetics at the interface between TiO_{2-x} and Pt cocatalyst, time-resolved photoluminescence (PL) spectroscopy was performed with 0.1 wt% Pt loading after the photoreaction. The time-resolved photoluminescence (PL) spectra were collected in an Edinburgh Instruments FLS920 PL spectrometer with excitation at 375 nm.

By fitting the spectra using a biexponential decay function ($I(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2}$), the PL lifetimes were calculated through the relationship ($\tau_{average} = (A_1 \tau_1^2 + A_2 \tau_2^2) / (A_1 \tau_1 + A_2 \tau_2)$),⁴¹ containing the parameters of fast decay (τ_1), slow decay (τ_2) and their amplitudes (A_1 , A_2),

respectively. The fast decay process is related to the nonradiative quenching of the excited electrons transferring from TiO_{2-x} to Pt cocatalyst. The slow decay process is ascribed to the radiative recombination of electrons migrating back to the ground state.⁴² Hence, smaller fast decay (τ_1) for faster interfacial electron extraction and larger amplitude A_1 for higher contribution to the whole quenching process are desirable for the superior photocatalytic performance. As shown in **Fig. 7d** and **Table 2**, TiO_{2-x} -15 min exhibits the smallest τ_1 and the largest A_1 values, leading to the shortest average lifetime (τ_{average}), while P25 TiO_2 possesses the longest τ_{average} compared with the flame-made samples. This result demonstrates that the photoexcited electrons captured and accumulated at the GB OV's can efficiently transfer to the Pt cocatalyst for photo-reduction reaction. The presence of these interfacial defects is beneficial to minimizing the radiative coupling of electrons and holes.

Table 2 The fitted time constants and the respective weighting factors of time-transient PL decay spectra

Samples	A_1 (%)	τ_1 (ns)	A_2 (%)	τ_2 (ns)	τ_{average} (ns)
TiO_{2-x} -6 min	81.7	0.57	18.3	6.18	4.543728
TiO_{2-x} -10 min	85.3	0.52	14.7	5.93	4.105538
TiO_{2-x} -15 min	88.6	0.49	11.4	5.85	3.736552
TiO_{2-x} -30 min	80.1	0.56	19.9	5.96	4.478155
P25 TiO_2	77.2	0.68	22.8	7.69	6.07476

Example 4. Photocatalytic activity for H_2 evolution using flame-made TiO_{2-x}

The photocatalytic reaction was conducted in aqueous solutions with methanol serving as the sacrificial reagent under visible light irradiation ($\lambda \geq 400$ nm).

Photocatalytic measurement

The photocatalytic H_2 evolution measurement was carried out in a 300 mL top-irradiation Pyrex glass cell connected to a closed gas circulation and evacuation system. The reaction cell was maintained at 18 °C by the external cooling water circulation. A 300 W xenon lamp (Newport) with a cut-off filter ($\lambda \geq 400$ nm) was applied as the light source. In a typical experiment, 20 mg of TiO_{2-x} (prepared according to Example 1) was dispersed in 120 mL of aqueous methanol solution (25 vol%). Next, 0.1 wt% Pt was *in situ* photodeposited as the cocatalyst by adding 20 μL of 1 mg Pt/mL H_2PtCl_6 solution (Sigma-Aldrich). Before light irradiation, the reaction system was evacuated and purged with argon several times to remove the air and finally

refilled with argon to reach about 30 Torr. The H₂ evolved was analyzed by an online gas chromatograph (Agilent 6890N, thermal conductivity detector).

The stability test of TiO_{2-x}-15 min (0.1 wt% Pt loaded) was performed in three consecutive runs of 12 h each under the same condition. After each run, the photoreactor system was evacuated and purged with Ar several times to remove H₂ produced before the next run.

ICP measurement was conducted on Prodigy High Dispersion ICP. During the preparation, the photocatalyst loaded with Pt after the photoreaction was treated with H₂ (30 mL min⁻¹) at 300 °C for 4 h to reduce PtO_x species to Pt⁰. Then, 0.02 g of each sample after hydrogenation was dissolved in 2 mL aqua regia and filtrated to remove TiO₂. The concentration of Pt⁴⁺ in each solution was then analyzed by the ICP equipment

Results

As shown in **Fig. 8a**, with 0.1% Pt as the cocatalyst, all the flame-made TiO_{2-x} samples exhibit superior photocatalytic activity compared with P25 TiO₂. The trend in H₂ evolution activity is consistent with those in photocurrent density and PL decay results. TiO_{2-x}-15 min displays the highest activity with a H₂ evolution rate of 960 μmol h⁻¹ g⁻¹ which is around 12 times of that over P25 TiO₂. Among the flame-made TiO_{2-x} samples, since there is no significant variation in the surface area and phase composition (**Table 1**), the defect state should be the main contributing factor to the activity difference.

Consistently, TiO_{2-x}-6 min exhibits the lowest photoactivity. By comparing the activity of TiO_{2-x}-10, 15 and 30 min against their OV properties, it can be concluded that a moderate bulk OVs are desirable to achieve higher photocatalytic activities. Furthermore, it was found that the nanoparticles of Pt cocatalyst are preferentially deposited at or near the GBs (**Fig. 11**) due to higher electron concentrations at GBs. In addition, OVs at GBs should effectively anchor Pt species and facilitate the reduction of Pt⁶⁺ to Pt⁰. The average cluster size of Pt is the smallest, even with some single Pt atoms identified (**Table 3**). The percentage of Pt⁰ is found to be the highest in TiO_{2-x}-15 min (**Table 3**). Based on inductively coupled plasma (ICP) data (**Table 3**), the loading of Pt in TiO_{2-x}-15 min (0.076 wt%) is the highest among all samples. However, in combination with the Pt⁰% by XPS, the Pt⁰ loading in TiO_{2-x}-15 min is around 13% and 44% higher than that in TiO_{2-x}-10 min and TiO_{2-x}-30 min, respectively. In contrast, the loading of Pt⁰ in TiO_{2-x}-6 min and P25 TiO₂ is substantially lower. These results indicate that the OVs locked at GBs due to the thermal sintering of nanoparticles during the synthesis can facilitate

the anchoring and reduction of Pt species. The average Pt size was also found to be the smallest on TiO_{2-x}-15 min, even with some single Pt atoms identified.

Table 3. Pt loading based on ICP measurement, percentage of Pt species based on XPS analysis and Pt sizes based on TEM analysis on different TiO₂ samples after reaction.

	Pt loading [wt%] ^a Total ^b (Pt ⁰ ^c)	Pt ⁰ (%)	Pt ²⁺ (%)	Pt ⁴⁺ (%)	Pt average size (nm)
TiO _{2-x} -6 min 0.1% Pt	0.061% (0.027%)	43.8	56.2	0	1.75
TiO _{2-x} -10 min 0.1% Pt	0.072% (0.046%)	64.5	35.5	0	1.48
TiO _{2-x} -15 min 0.1% Pt	0.076% (0.052%)	68.4	31.6	0	1.30
TiO _{2-x} -30 min 0.1% Pt	0.071% (0.036%)	50.3	49.7	0	1.62
P25 0.1% Pt	0.060% (0.024%)	40.1	59.9	0	2.80

^a Theoretical loading based on the amount of Pt precursor is 0.1 wt%; ^b by IPC measurement;

^c total Pt% multiply by Pt⁰% from XPS results.

The activity of our best 0.1% Pt-TiO_{2-x} photocatalyst is comparable with those of some best OV-containing TiO₂ photocatalysts with 0.5-1% Pt (or Pd) reported so far under visible light irradiation (**Table 4**) In several previous works, it was proposed that less bulk defects and more surface defects are advantageous to the photocatalytic reaction. However, based on our current study, a balanced concentration of both surface and bulk defects together with the promotional effect of GB OVs improves the performance evidently.

Table 4. Summary of typical defective TiO₂ for photocatalytic H₂ generation.

	Photocatalyst	Weight of catalyst	Co-catalyst loading	Light source	Reactant solution	H ₂ production rate, μmol h ⁻¹ g ⁻¹ (μmol h ⁻¹)
Our work	Flame-made blue TiO _{2-x}	20 mg	0.1 wt% Pt	300 W Xe lamp, >400nm	25 % CH ₃ OH/H ₂ O	960 (19.2)

	Photocatalyst	Weight of catalyst	Co-catalyst loading	Light source	Reactant solution	H ₂ production rate, $\mu\text{mol h}^{-1} \text{g}^{-1}$ ($\mu\text{mol h}^{-1}$)
S1	Ti ³⁺ self-doped black TiO ₂ nanotubes	50 mg	0.5 wt% Pt	300 W Xe lamp, >420nm	20 % CH ₃ OH/H ₂ O	200 (10)
S2	Hydrogenated Blue Titania	100 mg	0.5 wt% Pt	300 W Xe lamp, >400nm	20 % CH ₃ OH/H ₂ O	66.7 (6.67)
S3	Sub-10 nm defective TiO ₂	100 mg	1 wt% Pt	200 W Xe lamp, >400nm	10 % CH ₃ OH/H ₂ O	932 (93.2)
S4	Black TiO ₂	25 mg	1 wt% Pt	400 W Xe lamp, >400nm	20 % CH ₃ OH/H ₂ O	440 (11)
S5	Hydrogenated TiO ₂	50 mg	0.43 mol% Pd (0.57 wt%)	300 W Xe lamp, >400nm	20 % CH ₃ OH/H ₂ O	130 (6.5)
S6	B/N doping red TiO ₂	100 mg	0.5 wt% Pt	300 W Xe lamp, >420nm	10 % CH ₃ OH/H ₂ O	6.9 (0.69)

S1. *ACS Sustain. Chem. Eng.* 5, 6894-6901 (2017).

S2. *ACS Catal.* 8, 1009-1017 (2018).

S3. *Nat. Commun.* 6, 5881 (2015).

S4. *Energy Environ. Sci.* 8, 3539-3544 (2015).

5 S5. *Energy Environ. Sci.* 9, 2410-2417 (2016).

S6. *Chem. Eur. J.* 25, 1787-1794 (2019).

The recycle test of TiO_{2-x}-15 min (0.1 wt% Pt loaded) indicates that the photocatalyst has good stability (**Fig. 8b**). After 3 runs of reaction with 12 h in each run, the activity only dropped 9.7% which is mainly due to the evaporation and consumption of the sacrificial agent in the reaction.

Example 5: Continuous particle collection (CPC) method and mechanisms for achieving collection

As mentioned above, particles may be formed by a FSRS method. In a typical setup as shown in Fig. 12, a rotatable stagnation plate 120 (100-300 rpm) is located at a fixed distance under a burner nozzle 115 (5-25 mm) of a burner 110. The plate 120 forces a flow divergence of the premixed gas issued from the burner nozzle 115 which results in a flat flame 104 being formed and stabilized above the stagnation plate 120. When a particle precursor is mixed into the premixed gas mixture, particles 144 are formed in the flame 104 and then deposited on the plate 120. It is suggested that the plate rotation convectively cools the deposited particles 144 and prevent further sintering during the deposition. Additional cooling may be provided by multiple jet nozzles 150 (dry air) placed under the plate as illustrated in Fig 12.

Typically, the deposition of these particles is done over a certain period (typically 10 to 60 minutes), after which the flame is extinguished, and deposited particles are collected from the stagnation plate. This approach may be termed interval particle collection (IPC) and has two main drawbacks.

1. Despite the convective cooling provided by the plate rotation, the deposition time may affect the properties of the deposited particles (e.g., crystal phases, defect concentrations, etc). In other words, the particle properties may be constrained by the synthesis yield. For example, the defect concentration of TiO₂ particles prepared using the IPC method decreases with increasing deposition time based on the observed sample coloration. This may be due to the gradual change of particle properties as they are periodically exposed to the flame during synthesis. Further, particles deposited usually form a porous layer on the plate surface. The porous layer of the oxide particles acts as a poor thermal conductor, creating a strong thermal gradient on the particle layer. This results in a gradual increase in the stagnation temperature as the particle layer builds up as illustrated in Fig. 19. This effect is easily amplified as a relatively long deposition time of 10-60 mins typically required to collect enough sample for typical applications (e.g., catalysis tests) or material characterizations (e.g., powder x-ray diffraction). While multiple runs can be performed to collect enough samples in an experiment, such method is heavily time and resource consuming due to the manual work required to scrape the samples periodically, as well as the required pretreatment period every time the flame is extinguished for the particle collection.
2. As a result of the effect of the deposition time and the evolving thermal gradient on the particle layer, it is reasonable to expect that the particle properties in a synthesis batch will be inhomogeneous. This may adversely affect the performance of the materials in the intended applications.

Prototypes 1 and 2 deploying the CPC method

The drawbacks of the IPC method may be addressed by a continuous particle collection (CPC) method. Two prototypes of the CPC method are shown in **Fig. 13** and **Fig. 14**.

The same collection mechanism is employed in both prototypes shown. A collector head **131** consisting of a scrapper **132** is fixed above the plate **120** and used to scrap and dislodge the particles **144** as the plate **120** is rotating during the synthesis. The scrapper **132** is made from a heat resistant material with lower hardness than the plate **120** (made of stainless steel) to prevent scratching the plate **120**. In this case, the scrapper **132** is made of two sheets of 0.25 mm Nomex™ polymer (heat resistant polymer) fixed perpendicular to the plate surface.

As particles **144** are dislodged by the scrapper, two different mechanisms may be employed to direct the particles to the final particle collector. In prototype 1 (**Fig. 13A and 13B**), a small flow of compressed dry air **133** (CDA, 3.5 lpm) through a 1/16" stainless steel tube **134a** was used to push the scrapped particles off the stagnation plate **120** and into a particle collector **134**. The particles in the collector **134** easily settle due to the gravity. In prototype 2 (**Fig. 14**), vacuum pumps **138b** were used to suck the particles through drilled holes or orifices **136** on a tube **138c** inside the collector head **131**. The particles were then separated using a cyclone separator **138a** and a filter **138d**. The main advantage of this approach is that the particles can be removed from the scrapper **132** by the suction more quickly (compared to using CDA blow **133** in prototype 1) to prevent a prolonged contact of particles with the hot stagnation plate **120**. However, the strong suction generated by the pumps created an aerosolized flow that is harder to separate and results in a reduced collection efficiency.

One difference between the IPC and CPC methods is the range of rotation speed attainable. Due to the contact between the scrapper and the rotatable plate, the CPC method involves a significantly higher off-axis load on the motor. As a result (with the current motor **125** used in the setup), the CPC is limited to a rotation speed of < 5 rpm, compared to up to 300 rpm for IPC.

Example 6: Effect of various parameters on particle properties

A series of experiments were conducted using the IPC and CPC prototype 1 methods (as described in Example 5) to demonstrate the effects of the deposition time and the plate rotation

speed on the particle properties. In addition, the effect of the flame equivalence ratio in the CPC method is investigated. The synthesis conditions are summarized in **Tables 5 and 6**.

Table 5. Constant parameters used in the experiments.

Nozzle diameter	14 mm
Nozzle-plate distance	10 mm
Precursor	TTIP, 99.7% (Sigma Aldrich)
Precursor injection rate	20 ml/h
Plate cooling	100 lpm of CDA from 4 nozzles (25 lpm per nozzle)
Premixed gas flowrate	28 slpm (see Table 6)
Sheath flowrate	20 slpm N ₂
Pretreatment*	10 mins, flame only
CDA flow rate (CPC prototype 1)	3.5 slpm

- 5 *Stable plate temperatures are achieved between 5-10 mins of flame ignition, depending on the flame conditions. Thus, all experiments were performed with 10-min flame-only pretreatment before precursor injection is started.

- 10 Based on the conditions in Table 6, the premixed gas velocity is 473 cm/s. This is based on a premixed gas flowrate of 28 slpm provided by a nozzle having a diameter of 14 mm (1.4 cm) and a nozzle temperature of 150 °C. It is noted that nozzles of different sizes may be used, provided that the premixed gas velocity at the nozzle is larger than the flame speed in order to stabilize the flame.

- 15 Also based on the conditions in Table 6, the precursor is injected into heated mixture at a flow rate of 900 ppm, which is calculated from the precursor injection rate and the premixed gas flow rate.

- 20 **Table 6.** Synthesis conditions varied in the experiments and the synthesis yields for each condition.

#	Gas mixture flowrates (slpm)	Equivalence ratio (ER)	Collection method, rot. speed, t_{dep}	Yield (mg/min)
1	22.12 Ar, 4.20 O ₂ , 1.68 C ₂ H ₄	1.20	IPC, 1 rpm, 5 mins	19.6
2	22.12 Ar, 4.20 O ₂ , 1.68 C ₂ H ₄	1.20	IPC, 1 rpm, 15 mins	19.1
3	22.12 Ar, 4.20 O ₂ , 1.68 C ₂ H ₄	1.20	IPC, 1 rpm, 25 mins	19.8
4	22.12 Ar, 4.20 O ₂ , 1.68 C ₂ H ₄	1.20	IPC, 100 rpm, 15 mins	18.7
5	22.12 Ar, 4.20 O ₂ , 1.68 C ₂ H ₄	1.20	IPC, 300 rpm, 15 mins	n/a
6	22.12 Ar, 4.20 O ₂ , 1.68 C ₂ H ₄	1.20	CPC, 0.1 rpm, 60 mins	18.5
7	22.12 Ar, 4.20 O ₂ , 1.68 C ₂ H ₄	1.20	CPC, 0.2 rpm, 42 mins	19.4
8	22.12 Ar, 4.20 O ₂ , 1.68 C ₂ H ₄	1.20	CPC, 0.3 rpm, 60 mins	20.8
9	22.12 Ar, 4.20 O ₂ , 1.68 C ₂ H ₄	1.20	CPC, 0.5 rpm, 60 mins	19.7
10	22.12 Ar, 4.20 O ₂ , 1.68 C ₂ H ₄	1.20	CPC, 1 rpm, 60 mins	18.5
11	22.12 Ar, 4.20 O ₂ , 1.68 C ₂ H ₄	1.20	CPC, 1 rpm, 50 mins	18.1
12	22.26 Ar, 4.20 O ₂ , 1.54 C ₂ H ₄	1.10	CPC, 1 rpm, 48 mins	15.5
13	22.33 Ar, 4.20 O ₂ , 1.47 C ₂ H ₄	1.05	CPC, 1 rpm, 47 mins	15.3
14	22.40 Ar, 4.20 O ₂ , 1.40 C ₂ H ₄	1.00	CPC, 1 rpm, 47 mins	15.8
15	22.54 Ar, 4.20 O ₂ , 1.26 C ₂ H ₄	0.90	CPC, 1 rpm, 49 mins	14.5

The flame with ER = 1.20 (#1-11) was chosen as the standard flame as the particles prepared exhibit a very strong coloration (dark blue) such that the changes due to the variations in the collection method can be clearly demonstrated. The average plate temperatures after pre-treatment period (about 10 mins) for the different flame conditions (without precursor) are summarized in **Table 7**.

Table 7. Average plate temperatures* at points denoted in the illustration on **Fig. 15**.

Flame ER, rot. speed	T ₁ (°C)	T ₂ (°C)	T ₃ (°C)	T ₄ (°C)
ER = 1.20, 300 rpm	504	166	128	122
ER = 1.20, 100 rpm	388	153	129	139
ER = 1.20, 1 rpm	363	153	108	121
ER = 1.10, 1 rpm	320	151	109	119
ER = 1.05, 1 rpm	309	143	105	115
ER = 1.00, 1 rpm	295	137	102	111
ER = 0.90, 1 rpm	241	131	92	101

*Measurements were done with K-type sheathed thermocouple wires (Omega, TJC36-CASS-020U-6) placed in contact with the top surface of the rotatable plate. No precursor is used as particle deposition on the thermocouples will impact the reading. At higher rotation speeds, friction between the thermocouples and the plate may result in elevated temperatures. At point 5 1, closest to the flame, the thermocouple is also directly heated by the hot gas from the flames so the readings may not reflect the actual plate temperature.

The prepared samples are subsequently characterized using digital photographs, powder x-ray diffraction and X-ray photoelectron spectroscopy. Powder X-ray diffraction (XRD) patterns 10 were recorded with a D8 Advance diffractometer (Bruker) with Cu Ka radiation (40 kV, 30 mA), 217.5 mm radius, 0.6 mm/0.3° divergence slit, and 2.5° Soller slit. The 2 θ scan range was 10–80° with a step size of 0.025 and 0.8 s per step. Zero-background silicon sample holders with 10mm x 0.2 mm cavity were used. X-ray photoelectron spectra (XPS) were recorded using a Kratos AXIS Ultra photoelectron spectrometer (Kratos Analytical) fitted with a monochromatic 15 Al Ka source (1486.71 eV, 5 mA, 15 kV). The photoelectrons were collected at an electron take-off angle of 90°. The binding energy shift was corrected by setting the Ti 2p_{3/2} binding energy to 458.6 eV (Biesinger *et al*, 2010).

Shorter deposition time favors formation of blue TiO₂

20 **Fig. 16** summarizes the results comparing the effect of varying the deposition time (for IPC) and continuous method (CPC). These results suggest that the dark blue coloration is only obtained with CPC method or IPC with a very short deposition time (5 min). As the blue coloration is linked to the defect centres in TiO₂ crystals (Breckenridge *et al*, 1953), it is likely 25 that the blue coloration gradually disappears when longer deposition times (IPC-15 min, IPC-25 min) are used. Without wishing to be bound by theory, the disappearance of the blue coloration with longer deposition times may be because of the oxidation and sintering processes during the continued exposure of the deposited particles to the flame. For example, the sintering is demonstrated by the sharper rutile peak at 2 θ = 27.4° as deposition time 30 increases (**Fig. 16B** and **16D**, XRD). The relative amount of defects/Ti³⁺ on the particle surface also decreases as a function of the deposition time as evidenced by the Ti 2p_{3/2} peak broadening in the XPS spectra in **Fig. 16C** and **16E**.

Plate rotation speed does not significantly affect particle coloration

35 **Fig. 17** shows the results of varying the rotating speed (for IPC) with CPC at 1 rpm speed used as reference. The effect of rotation speed is not very significant as shown by the particle

coloration (**Fig. 17A**) and the relative amount of defects/Ti³⁺ from the XPS spectra (**Fig. 17C**). This suggests that the plate rotation is not a very effective cooling mechanism (see Table 7).

Flame equivalent ratio (ER or ϕ) significantly affects crystal phase and particle coloration

5

The effect of the flame equivalence ratio (ER) is summarised in **Fig. 18** (CPC method). The results are consistent with our previous results, showing that the crystal phase composition is strongly dependent on the mixture equivalence ratio. The blue coloration also disappears as the equivalence ratio decreases (oxygen concentration increases).

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Based on the results above, without wishing to be bound by theory, it is believed there are two main requirements for the manufacturing of blue TiO₂. First, the fuel-to-oxidiser ratio (or flame equivalent ratio must be high enough. Specifically, the mixture equivalence ratio of the flame must be higher than approximately 1.1. Much higher equivalence ratio (above approximately 2.0), however, is not desirable as such flames tend to produce a large amount of soot/carbon contaminant. High equivalence ratios may lead to the formation of secondary flames as the excess fuel mixes with the surrounding air. In the absence of an additional cooling mechanism, the secondary flames may significantly increase the plate temperature and thus promote the oxidation of the blue TiO₂.

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Second, prolonged exposure of the deposited particles to a high temperature condition should be minimised as the blue TiO₂ is easily oxidised at this condition. This can be achieved by efficient cooling of the plate or using a short deposition time as defined in the detailed description (the exact cooling or deposition time required depends on the flame, precursor, precursor loading rate, collection mechanism, etc.).

25

Particle size measurements

The particle size measurements resulting from selected collection methods are provided in **Table 8**. These data are also compared with a previous work (J. Aerosol Sci. **133**, 96–112.) in **Fig. 20**, where the particles were collected *in situ* and immediately quenched so that the equivalent deposition time is close to zero (see the original work for more details).

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The results appear to show that the collection method or deposition time has very little impact on particle size. The results show that particle size is mainly controlled by precursor loading.

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Table 8. Measured particle sizes and distributions for selected samples

Collection method (sample #)	Total count	Median diameter (nm)	D_p	GSD	SD	Particle shape
IPC, 1 RPM, 5 mins (1)	1314	10.2		1.36	3.28	Spherical
IPC, 1 RPM, 25 mins (3)	1506	10.4		1.41	3.65	Slightly faceted
CPC, 1 RPM (10)	1047	10.2		1.37	3.28	Spherical
CPC, 0.1 RPM (6)	1225	10.6		1.39	3.56	Slightly faceted

Effect of rotation speed in CPC system

The effect of rotation speed in the CPC system is summarized in **Fig. 21**. The results show that the blue coloration gradually disappears as the rotation speed decreases (**Fig. 21a**). This is accompanied by a slight sharpening of the XRD peaks which correspond to higher crystallinity as the defects are oxidized (**Fig. 21b**). As the rotation speed decreases, there is a decrease in the defect concentration as reflected by a smaller Ti 2p_{3/2} full width half maximum (FWHM) in the XPS result (**Fig. 21c** and **Fig. 21d**).

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Comparative Example: Use of high oxygen-lean equivalence ratio

It was found that samples obtained at 20 min of deposition time with very high equivalence ratio (>2, i.e., very oxygen lean) were all colorless, in contrast to the blue TiO_{2-x} formed in the examples above. Although these comparative samples have some surface defects as detected by XPS and EPR, the performances of the optimum comparative sample in terms of photocurrent density and photocatalytic activity for hydrogen production from water were inferior to the optimum sample in the current examples, indicating that defects promote charge separation and transfer.

20

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 the formed non-stoichiometric metal oxide nanoparticle agglomerate comprises oxygen vacancies, optionally wherein the oxygen vacancies are formed at grain boundaries.
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.