

Micro-structured nanomaterial

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Technical field

The present invention relates to the preparation of metal oxide thin films. In an embodiment, the thin films have use as photodetectors. In other embodiments, the
10 films have use in gas sensors, opto-electronic and electrochemical devices.

Background

Nanomaterials comprised of self-assembled three-dimensional (3D) hierarchical
15 structures are finding applications in a wide range of applications including batteries, sensors, solar cells, photodetectors and functional coatings. In the last decades, self-assembled nanoparticle networks have emerged as multifunctional building blocks for a new generation of highly sensitive sensing technologies. When self-assembled as a porous structure, these nanoscale building blocks can
20 offer a dramatic increase in the surface-to-volume ratio in comparison to a bulk material and can provide superior sensitivity, beneficial quantum confinement, short electron-hole separation lengths and unique surface reaction sites. Despite these promising features, the integration of these 3D porous nanostructures into devices remains a challenge due to relatively poor carrier transport properties of
25 nanostructured materials.

In a nanoparticle network, carrier transport can be achieved by conventional electron or hole movement through contiguous semiconductor regions or by carrier hopping, from nanoparticle to nanoparticle, within the network, and in this way
30 carrier transport depends strongly upon the precise nature of the nanoparticle-nanoparticle (NP-NP) contact. Many self-assembled 3D nanostructures suffer from high contact resistance because the nanoparticles are only being held together by van der Waals, electrostatic, π - π , or hydrogen bonds. This high-contact resistances have a strong adverse effect on device sensitivity and overall

performance. Reduced dependence on carrier hopping, improved carrier transport and greatly enhanced device performance are likely to be realised if nanoparticles can be more effectively 'fused' together to form low-defect, covalently-bonded and atomically coherent interfaces.

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Zinc oxide (ZnO) is a metal oxide that is an important II-VI semiconductor. This is due to its excellent electrical properties i.e. high carrier concentration in magnitude of 10^{18} - 10^{20} and electron mobility around 100 - $260 \text{ cm}^2 \cdot \text{V}^{-1}$, high transparency, easy preparation, reasonably high chemical and mechanical stability and rich earth

10 abundance. ZnO is thus a prominent semiconductor for potential application in the areas of environmental gas sensing and monitoring, solar cells, ultraviolet (UV) radiation detection and calibration, catalysis, piezoelectric nanogenerators and optical communications.

15 In the field of UV detection, ZnO can enable the efficient detection of UV light and exhibits a high selectivity against the visible spectrum ($R_{\text{UV}}/R_{\text{vis}}$), making ZnO based materials an intrinsically solar-blind UV photodetector.

Nanostructured 3-Dimensional ZnO thin films are promising candidates for

20 wearable UV photodetectors on chips. Multiple methods for the preparation of 3D ZnO UV photodetection thin films exist, such as sol-gel, spin coating, electrospinning, spray pyrolysis (SP), flame spray pyrolysis (FSP), Radio-frequency Magnetron sputtering (RFMS), hydrothermal (HT), and chemical vapour deposition (CVD). The 3D thin films can be prepared by stacking formed 2D nanosheet or

25 nanoflowers; by creating arrays of 1D nanowires or nanorods, or by creating networks of 0D nanoparticles. Amongst the techniques described, FSP exhibits an ultra-rapid synthesis capacity to fabricate high crystalline quality metal oxide nanoparticle aerosols and super-structural ultraporous thin films.

30 Previously, Ultraporous Nanoparticle Network (UNN) ZnO photodetectors with 98% porosity have been fabricated by FSP. A record high photocurrent of 1.2 mA under $0.1 \text{ mW} \cdot \text{cm}^{-2}$ was reported. However, the UNN ZnO photodetector suffered prolonged response kinetics with over 250s and 150s for rise and decay times respectively. By introducing p-type NiO clusters to the surface of UNN n-type ZnO

nanoparticles, to thereby form 3D nanoscale heterojunctions (3DNH), the response kinetics were significantly improved (to 5s and 9s for rise and decay time respectively) due to high UV light absorption and a carrier migration length of a few nanometres between the p/n domains.

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Processes for improving the UV photodetection performance of metal oxide films such as UNN ZnO are desirable. Accordingly, the present invention is predicated on attempting to improve the UV photodetection performance of metal oxide films such as UNN ZnO, specifically in the term of high photocurrent, stable UV

10 detecting repeatability and fast photo-response kinetics. While UNN ZnO is used an exemplary metal oxide film the application is not so limited.

Summary of invention

15 In a first aspect there is provided a process for forming a nanostructured metal oxide micro-cluster, the process comprising the steps of:

obtaining a thin film of metal oxide attached to an underlying surface, the thin film having a peripheral edge;

20 adding a droplet of volatile solvent adjacent to the peripheral edge of the thin film;

allowing the droplet of volatile solvent to wet the thin film of metal oxide and subsequently evaporate, thereby allowing capillary force induced self-assembly to change the thin film structure.

25 It has been found, in embodiments, that thin films with a porosity of at least 95% can be produced by the present process with a unique dendrite-like microstructure on different substrates. When the metal oxide is ZnO, UV photodetectors deposited using the present process exhibit, in embodiments, high photocurrent responsivity and fast response kinetics when compared to ZnO thin films that are not subject to the process. These improvements are found without implementing complex
30 microstructure manipulation or adding functional additives to the thin film such as by loading the metal oxide with secondary materials or doping. A single droplet of a volatile solvent has been found to produce two unexpected effects:

The first is the formation of stump-like micro-clusters in the thin film. These new stump-like structures are thought to be formed by the capillary force of the volatile solvent. Without wishing to be bound by theory, it is thought that the introduction of the volatile solvent not only transforms the morphology of the metal oxide but also prompts the release of structural defects and allow the metal oxide nanoparticles to regrow via Ostwald ripening.

The second transformation effect occurs at the nanoscale where two metal oxide nanoparticles are nanowelded (nanojoined) into each other creating nanoparticle necking. This can be seen in the TEM images of the nanoparticles. In the conventional methods (reported in the literature), this necking usually only happens after thermal sintering of the metal oxide nanoparticles (nanofilms) in the furnace.

Thus, the structure that is changed in the thin film can be the nanostructure of the thin film and the microstructure of the thin film.

A preferred metal oxide for use in the present process is zinc oxide. Zinc oxide has been found to exhibit microscale transformation from Ultraporous Nanoparticle Networks (UNN) (sometimes referred to as dendritic like nanoclusters (DNCs) into stump-like nanojoined/microclusters (sometimes referred to as nano-micro cluster arrays NMCAs), which transformation is driven by the capillary force of the evaporating volatile solution. These morphological changes are accompanied by an increase in crystallinity, a decrease in the number of very small particles, and a significant improvement in the device characteristics. While zinc oxide is an exemplary and useful metal oxide to subject to the present process, similar exertion is applicable to other metal oxides such as tin oxide, titanium dioxide, and copper oxide etc.

Thus, in a second aspect there is provided a thin film of metal oxide having stump like micro-clusters of metal oxide distributed over a surface.

The underlying surface on which the thin film is formed can be any material that is inert and robust enough to support the film. The substrate having the surface can be silicon. The substrate can be glass. The substrate can comprise interdigitated

platinum electrodes (IDE) thereon so that the resultant thin film can be useable as a photodetector.

5 The thin film of metal oxide having a stump like clusters of metal oxide distributed over a surface can be formed by a method according to the first aspect. The process can comprise forming a thin film of metal oxide on a surface. Rather than forming the thin film of metal oxide, a substrate having the thin film pre-prepared thereon can be obtained. In this embodiment, the thin film may have been prepared by and obtained from a third party.

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In order to prepare the film, flame spray pyrolysis (FSP) can be used. A precursor containing metal atoms can be dissolved in a solvent to provide a total metal atom concentration in the range of from about $0.1 \text{ mol} \cdot \text{L}^{-1}$ to about $0.5 \text{ mol} \cdot \text{L}^{-1}$. In an embodiment, the total metal atom concentration is $0.3 \text{ mol} \cdot \text{L}^{-1}$. The prepared
15 solution of metal atoms in solvent can be supplied to a surface at a rate of about 2, 3, 5 or $7 \text{ mL} \cdot \text{min}^{-1}$ and dispersed into a fine spray. The fine spray can be ignited thereby creating a burner.

A water-cooled substrate holder can be placed at Xcm height above the burner
20 (HAB). The water cooling can keep the substrate temperature below about 150, 200, 220, 240 °C. Spraying can be undertaken for 20, 50, 100, 150 or 200s to result in a metal oxide thin film deposited on the surface of the substrate. The HAB may be about 8, 10, 12, 14, 16, 18, or 20 cm. In an embodiment the HAB may be 12 cm.

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Prior to wetting the thin film, it can be important to form a proper precursor thin film structure. A precursor thin film that can be modified by the present process is one which when subject to the process herein results in the stump-like nanojoined/microclusters. A precursor thin film should have dendrite like structures
30 when viewed under TEM. This may be caused by partial sintering of the primary nanoparticles due to high temperature. If the precursor thin film is formed improperly, instead of forming stump-like nano/micro-clusters, the non-dendrite structure of the nanofilms transforms into micro-islands instead of stump-like structure with some visible cracks. If the initial UNN structure (before dropping the

volatile solvent) is dendrite like, the stump-like structure after dropping volatile solvent is guaranteed regardless of metal oxide type.

5 The Xcm height above the burner can be key to the formation of the proper precursor thin film. These as-deposited nanoparticles are mechanically fragile since they are only held together by van der Waals forces and the height of the substrate above the burner (HAB) is thought to have a significant effect on the properties of layers. A shorter HAB is thought to increase the substrate temperature and enhance sintering of primary nanoparticles, this shortens the
10 deposition paths for the nanoparticles, which in turn produces a higher penetration depth for nanoparticles as the nanostructures form. Thus, layers with a shorter HAB can be more robust with slightly increased density.

15 The Xcm distance can be different depending on the type of metal oxide. The skilled person will be able to determine by trial and error based on the teachings herein what is the HAB for the given metal oxide film that results in a thin film with the proper morphology prior to wetting with the volatile solvent. In an embodiment in which the metal oxide is ZnO, the HAB is in the range of from about 9cm to about 14cm. In an embodiment, the HAB for formation of ZnO thin film is 12cm.
20 When HAB < 9 cm, the zinc oxides are severely aggregated resulting in the formation of denser/more stable/stronger films, thus, no obvious morphological changes are observed after the addition of volatile solvent. In contrast, when HAB $\geq$ 14 cm, the dendrite-like pattern disappears, and micro-islands are formed upon addition of volatile solvent. The micro-islands have visible cracks after capillary
25 force induced exertion.

The dendrite-like pattern in the precursor thin film prior to addition of volatile solvent is thought to be crucial to the formation of the resultant structure. The dendrite-like patterns in the properly formed thin film are thought to be the result of
30 nanoparticle self-assembly via Brownian Motion and nanoparticle diffusion, leading to the deposition of nanoparticles on the substrate. The nanoparticles are connected to each other by weak Van der Waals force with negligible interaction to neighbours, which makes them easy to move/tilt as a whole unit under capillary force to form the stump-like clusters.

Once formed, the precursor thin film is attached to the underlying surface. The attachment points can be chemical bonds. The chemical bonds can be covalent bonds. The thin film is not readily removable from the underlying surface simply by application of friction force. However, it should be understood that strong intentional rubbing optionally with addition of solvent may dislodge the film. The importance of the adherence of the film to the surface is that in some embodiments, thin films can be formed which are not proper for use in the method, and these improper thin films that lack dendrite like structures can be identified by their lack of cohesion with the underlying surface. These improper spongy thin films are not properly adhered to the underlying surface and can be readily dislodged by application of small forces such as a blast of pressurized air. Furthermore, the improper thin films have been shown to have a different thickness and morphology when compared to the films prepared according to the present invention.

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Some parameters for detecting the formation of the precursor thin film include:

- Film has dendrite-like structure
- Thin film is attached to the underlying substrate
- Thin film is porous with at least 50% film porosity
- Thin film has a film thickness > 200nm

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The thin film once formed and prior to exposure to the volatile solvent can be porous. The thin film can have a porosity of at least 85, 90, 95 or 98%. The thickness of the thin film can be in the range of from about 3 to about 25 micrometres such as about 16 to about 25 micrometres. The thin film comprises microstructures formed from nanoparticles. The average diameter of the nanoparticles can be in the range from about 12 to 30nm such as about 14 to about 16 nm. When the thin film is formed from ZnO and is prepared according to the description herein the average particle size of the ZnO can be about 15.54 nm.

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The thin film is prepared on the surface of the substrate so as to have a peripheral edge. This means that there is at least one part of the surface of the substrate that is not covered with thin film so that a boundary is formed between surface-with-

thin-film and surface-free-from-thin-film. This boundary is important, because the droplet of volatile solvent is added to the surface at a location where there is no thin film. There can be a boundary formed around the whole area of the thin film. There can be a boundary formed along one edge part of the thin film. The
5 boundary can be formed by obscuring that part of the surface of the substrate during deposition of the film, so that the film could not be deposited on that area.

At least one droplet of volatile solvent can be added next to the edge of the thin film. There can be one droplet. There can be more than one droplet. The volatile
10 solvent can have a temperature less than 100°C. The volatile solvent can be an alcohol. The alcohol can be methanol or ethanol. The volatile solvent can have a high boiling point. The solvent will still evaporate over time. The specific evaporation time will depend on factors such as temperature, air circulation, and the surface area of the drop. Suitable solvents could be DMF or toluene.

15 The droplet of volatile solvent can be placed adjacent to the peripheral edge of the thin film. This is preferred to the alternative of adding the droplet on top of the thin film. If the droplet is added on top of the thin film, there can be significant disruption of the underlying metal oxide structure.

20 Once the droplet is in place, the substrate can be tilted to allow the droplet to run over the thin film and thereby wet the surface area. However, the wetting can also be undertaken if the surface remains horizontal.

25 The droplet size to surface area of thin film can be about 1 μ L per 0.08, 0.1 or 1.1 cm² of thin film. Depending on the active area of the thin film, the droplet size applied to the thin film can be about 2 μ L to about 10 μ L. In an embodiment, the droplet size is 5 μ L. The droplet evaporates at ambient temperature and pressure. As it evaporates, capillary force induced self-assembly to changes the underlying
30 thin film nanostructure. When the metal oxide is ZnO, stump-like ZnO nano/microclusters can be formed by the capillary forces induced by the evaporating volatile solvent during and following its infiltration into the film matrix and the rapid evaporation process of it afterwards.

At least one application of volatile solvent can be made to the thin film. There can be one application. There can be more than one application.

5 The solvent can be left to penetrate the porous material via capillary action, and then given time to completely evaporate by being left in an ambient environment. The time in the ambient environment can be at least 30 mins, 1 or 2 hours.

10 The changed morphology post capillary force induced self-assembly, can result in a thin film that has about 8, 10, 12 or 15% decrease in film thickness. There can also be a slight decrease in film porosity compared to the same film prior to wetting with the volatile solvent. Furthermore, there can be a decrease in the number of metal oxide nanoparticles, but an increase in the average metal oxide particle size by about 10%. This decreased number but increased size is thought to demonstrate the Ostwald ripening process.

15 Optionally, the as-prepared sample of thin film metal oxide can be annealed. Whilst annealing can optimise the thin film structure, the thin film can be used in the next process step without annealing. If the film is annealed, it can be heated to a temperature of at least about 150, 200, 250 or 300 °C. The heating can be for a period of at least about 6, 10 or 12 hours at ambient pressure. It is thought that the annealing stabilises the nanoparticle size and may avoid resistive-sintering during the photo-detection measurements. The annealing step has been shown to have no effects on the film's stump like cluster morphology. However, the film's stump like cluster's crystallinity increased slightly.

25 The stump-like clusters can have an average height of at least about 12, 16, or 20 μm . The stump-like clusters can an average top diameter of at least about 16, 20 or 24 μm . The stump-like clusters can an average bottom diameter of at least about 20, 25 or 30 μm . The stump-like clusters can an average distance between stumps of at least about 8, 10, 12 μm . Each stump can be surrounded by at least about 5, 7, 9, 11 other stumps. There can be at least about 1 million stumps on every mm^2 of area.

When ZnO thin films are fabricated using a 0.3M Zinc precursor with HAB = 12cm

and spray time of 100s, followed by dropping 5 μL volatile solvent (preferably ethanol): the average height of stump is around 16 μm , average diameter is 20 μm at the top and 25 μm on the base resulting in approximate 10 μm gap between stumps. One stump is surrounded by about 5-7 others stumps, therefore, there are
5 about 1 million stumps on every mm^2 area.

In an embodiment, an additive can be added to the metal oxide nanostructure to further enhance conductivity. The additive can be a carbon-based additive. The additive can be graphene oxide. The additive can be carbon nanotubes. The
10 additive can be noble metals. The additive can be metal atoms. The additive can be added to the volatile solvent prior to the solvent being deposited next to the edge of the thin film. The additive is thought to disperse into the metal oxide thin film as the solvent evaporates.

15 While photodetectors are discussed therein, it should be understood that the thin films have potential application in other areas such as environmental gas sensing and monitoring, solar cells, ultraviolet (UV) radiation detection and calibration, catalysis, piezoelectric nanogenerators and optical communications.

20 The present invention provides a method in which the application of a single droplet of a solvent such as ethanol can induce significant changes in the morphological, structural, optical and electronic properties of metal oxide thin films. The inventors have found the surprising effect that a single droplet of a volatile solvent can be just as effective as some of the more conventional and more
25 expensive sintering techniques.

The changes observed are thought to be a result of capillary forces that are provided by the application of the volatile solvent. When first applied to the sample surface and in order to minimize surface tension, the solvent itself is drawn by
30 capillary action into the narrow gaps that exist between individual nanocluster dendrites. As the solvent evaporates, this surface tension, or capillary force, causes the tops of adjacent dendrites to coalesce. After this first transformation, and as the solvent continues to evaporate the solvent surface slowly descends to the base of the layers and the capillary forces applied close the base of the

nanoclusters (at the liquid-air interface), become sufficient to cause the bases of the clusters to coalesce and form the distinctive 'islands'. The capillary force induced by the solvent is thought to be as high as 80, 85 or 90 nN. that is clearly sufficient to horizontally reposition the bases of the nanoclusters and enlarge the gaps between the clusters. In this regard, the solvent such as ethanol or methanol clearly provides an environment in which zinc and oxygen atoms can detach from the crystallite surface and migrate on the surface of nanoparticles before settling on an atomic site that is energetically more favourable. This migration of atoms, and atomic re-arrangement, removes the smaller particles, enables the growth of larger particles and allows the particles to 'fuse' together or coalesce at points-of-contact, and especially where oriented attachments can develop. The same effect can also be seen with other solvents such as DMF and toluene.

In order to improve the properties of the thin film structure an additive can be added. The additive can improve one or more of the structural integrity, conductivity, photodetection performance, UV detecting repeatability and fast photo-response kinetics. In an embodiment, the additive is carbon nanotubes (CNT). In an embodiment, the additive is a polymer such as a conducting polymer.

In an embodiment, the polymer additive added to the solvent is a PEDOT (poly(3,4-ethylenedioxythiophene)). This is a conducting polymer made up of repeating units of 3,4-ethylenedioxythiophene. PEDOT is known for its electrical conductivity, making it useful in various applications such as organic electronics, sensors, and conductive coatings. The PEDOT can be used with PSS (poly(styrenesulfonate)). PSS is a polyelectrolyte consisting of repeating units of styrene sulfonate. It is often used as a dopant or stabilizing agent in combination with PEDOT to enhance the material's solubility, processability, and stability. PEDOT:PSS is commonly used as a transparent conductive layer in organic electronic devices, such as organic solar cells, organic light-emitting diodes (OLEDs), and organic field-effect transistors (OFETs). Its properties make it suitable for applications where flexible and transparent conductive coatings are needed. The combination of the conducting PEDOT and the stabilizing PSS results in a material that can be easily processed into thin films and coatings for various electronic devices. Its use in the present thin film can improve the performance characteristics of the resultant product.

The invention also includes devices or products manufactured with the thin film as herein described.

5 **Brief Description of the Figures**

Embodiments of the invention will now be described with reference to the accompanying drawings which are not drawn to scale and which are exemplary only and in which:

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Figure 1 Schematics of process diagram for preparing ZnO_UNN and ZnO_CFI thin films.

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Figure 2: Figure 2A is an SEM images of the top of ZnO_UNN. Figure 2B is an SEM image of the side of ZnO_UNN prior to wetting with ethanol. Figure 2C is an SEM images of the top of ZnO_CFI after wetting with ethanol. Figure 2D is an SEM image of the side of ZnO_CFI after wetting with ethanol. Figure 2E is a TEM image of ZnO_UNN and Figure 2F is a TEM image of ZnO_CFI. The insets are the corresponding particle size distribution plots.

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Figure 3: Screenshots showing the morphology transformation from ZnO UNN to ZnO CFI under the capillary force exerting on the flame-made ZnO thin films.

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Figure 4: The XRD patterns (A) and photoluminescence spectra (B) of ZnO_UNN and ZnO_CFI.

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Figure 5: The FTIR (A) and optical transmittance (B, C), reflectance (D) and absorption (E) spectra of ZnO_UNN and ZnO_CFI.

Figure 6: The top view of ZnO_CFI SEM images.

Figure 7: (A) The UV photo response dynamic curves of ZnO_UNN and ZnO_CFI under 375 nm illumination with the light density $1 \text{ mW}\cdot\text{cm}^{-2}$ at 1 V. (B) the

normalised photo response kinetics based on the second UV on and off cycle. (C) Time-dependent photodetection response of ZnO_UNN and ZnO_CFI UV photodetectors under 375 nm illumination with the light density of $1.0 \text{ mW}\cdot\text{cm}^{-2}$ at an applied bias of 1 V; and b) the normalized photocurrent dynamics for rise and decay times investigation.

Figure 8: The UV detection dynamic curves of ZnO_CFI at different voltage under 325 nm illumination with the light density of $1 \text{ mW}\cdot\text{cm}^{-2}$ (A), and averaged photocurrent density versus the applied bias (B). (C) The time-dependant photoresponse and (D) corresponding photocurrent density NMCAs UV photodetector at different applied bias from 0.1 to 2 V under the same light illumination conditions mentioned above. (E) The photocurrent and (F)) its density of NMCAs under a series of light density from 0.5 to $2.0 \text{ mW}\cdot\text{cm}^{-2}$ at the basis of 0.5 and 1 V accordingly. g) 45 cycles of photoresponse dynamic test for NMCAs devices at the applied bias of 0.5 and 1 V, respectively. (H) The photoresponse dynamic of NMCA devices under $1.0 \text{ mW}\cdot\text{cm}^{-2}$ of 375 nm illumination at a series of low bias (0.01 to 0.05 V).

Figure 9 is a table showing details of state-of-art visible blind UV photodetectors based on nanostructured ZnO.

Figure 10 is a schematic of the flame spray pyrolysis (FSP) process showing HAB.

Figure 11 shows SEM images of ultraporous films.

Figure 12 shows the schematic (Figure 12A to C) as well as scanning electron microscope (SEM) images of UNN (Figure 2D, G) and CFI (Figure 2E, F, H, I) devices before and after deformation induced by capillary force.

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Figure 13 shows X-ray diffraction (XRD) patterns of deposited films (UNN, CFI and CFI-CNT) on Si substrates

Figure 14 shows the photoluminescence spectra of the fabricated UNN and

CFI-0CNT and CFI-0.1CNT films at room temperature.

Figure 15 are graphs showing the data resulting for experiments performed on the photodetectors in accordance with an embodiment the present invention.

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Figure 16 is a schematic showing how the photodetector can work.

Figure 17 presents the time-dependent response of UNN and CFI photodetectors under the illumination of 365 nm, the light density of 1mW.cm^{-2} and 0.5V applied bias.

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Figure 18 presents the SEM images of ZnO films fabricated via FSP with non-12 cm HAB settings: (A,B) 8 cm; (C,D) 9 cm and (E,F) 14 cm, insets are their corresponding cross-sectional views. Images on the left- (A,C,E) and -right handed (B,D,F) refer to before and after the liquid capillary treatment, respectively. The scale bars are 10 μm , otherwise noted accordingly.

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Figure 19 presents the SEM images of ZnO films treated with (A-C) 2 μL and D) 10 μL of ethanol droplet.

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Figure 20 is a schematic showing the meniscus bridge and resulting capillary force between neighbouring spheric nanoparticles.

Figure 21 presents The SEM images of flame-made DNCs on different substrates: a) Si wafer, b) Glass substrate featuring Pt IDEs, and c) Cu foil. All scale bars are 10 μm .

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Figure 22 is a schematic of a) Flame Spray Pyrolysis (FSP), and b) the evolution of UNNs upon increasing deposition time. c) The cross-sectional SEM image of deposited UNNs film after 100 s spraying at the HAB of 12 cm. d-g) Illustrations of the key morphological transformation process from the UNNs to CFI with frozen frames of the actual morphology under the video metrological investigation. All scale bars are 10 μm .

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Figure 23 is an SEM image of ZnO thin film treated by a droplet of DMF.

Figure 24 is an SEM image of SnO₂ thin film treated by a droplet of ethanol.

5 Figure 25 is an SEM image of ZnO thin film treated by a droplet of methanol.

Figure 26 is an SEM image of ZnO thin film treated by a droplet of methanol and added polymer (PEDOT:PSS).

10 Figure 27 is an SEM image of SnO₂ thin film treated by a droplet of toluene.

Detailed Description of Embodiments of the Invention

Experimental Section

15 *Synthesis of UNN ZnO thin film featuring dendrite-like nanoclusters and stump-like (Capillary Force Induced) CFI ZnO thin films*

i. Nanoparticle aerosols self-assembly:

A flame spray pyrolysis (FSP) system was used for the synthesis and direct
20 deposition of ZnO nanoparticle aerosols onto silicon wafers and glasses featuring interdigitated platinum electrodes (IDE), the latter ones were used as the UV photodetectors.

The ZnO nanoparticles were prepared as follows: Zinc Naphthenate (10% Zn, Strem Chemicals) was diluted in Xylene (Sigma Aldrich) with a total metal atom
25 concentration of 0.3 mol·L⁻¹ for Zn. The prepared solution was supplied at a rate of 5 mL·min⁻¹ through a syringe pump and dispersed into a fine spray with 5 L·min⁻¹ oxygen at a constant pressure drop of 2 bars. The spray was ignited by supporting premixed methane/oxygen flames (CH₄ = 1.25 L·min⁻¹, O₂ = 1.3 L·min⁻¹). A water-
30 cooled substrate holder placed at 12 cm height above the burner (HAB) was utilized to keep the substrate temperature below 220 °C (**Figure 1A**). Figure 21 also shows the uniform coverage of dendrite-like nanoclusters (DNCs) of ZnO bring vertically grown by atomisation, nucleation, and thermophoretic-driven deposition of ZnO nanoparticles on a water-cooled glass substrate using flame spray pyrolysis

(FSP). **Figure 10** also shows a schematic of the ZnO thin film photodetector being synthesized by atomization, combustion, and nucleation of zinc naphthenate liquid precursor solution diluted in X-xylene using one-step flame spray pyrolysis (FSP) synthesis.

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Height above burner (HAB) is through to affect the thickness of the ZnO film, but also, affects the morphology of the ZnO film. For a short HAB of 8 cm (Figure 18A), the film exhibits an average thickness of 3.05 μm (Figure 18A, inset) after spraying for 60 s, featuring a very dense microstructure without apparent pores. The ZnO_UNN characteristics begin to appear when the HAB increased to 9 cm (100 s spraying, Figure 18C), and disappears as the HAB further increased toward to 14 cm (Figure 18E, 100 s spraying). For the HAB of 14 cm, it depicts the classic flame-made ultraporous morphological features as reported previously.

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ZnO films prepared at a lowered HAB (8-9 cm) show intact (Figure 18B) or negligible (Figure 18D) impacts after the ethanol capillary action. However, the ZnO film prepared with the HAB of 14 cm fails to resist the “hit” of ethanol “tsunami” and collapses arbitrarily on the substrate with intuitive cracks under SEM (as white arrows pointed, Figure 18F). It is evident that, HAB of 12 cm can both obtain the ZnO_UNN structures (Figure 2B) with the high porous characteristic (Figure 2A, inset) and maintain the appreciable agility and mechanical strength to form ZnO_CFI (Figure 2C-D) after the capillary treatment.

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Meanwhile, the HAB of 12 cm can also offer the fastest growth rate of 11.1 $\mu\text{m}\cdot\text{min}^{-1}$, suggesting a high product yield compared to the 3.05, 8.6 and 9.6 $\mu\text{m}\cdot\text{min}^{-1}$ growth rates for HAB of 8, 9 and 14 cm, respectively. Overall, the HAB = 12 cm was found to be the optimized parameter in this work to generate ZnO_UNN while keeping the rest conditions same herein.

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As expected, the reduced HAB of 12 cm has produced more robust layers that can withstand capillary forces. This quasi-columnar morphology of the ZnO_UNN layers are more similar to the self-assembled ‘tree-like’ structures reported for layers produced with a HAB of 10 cm, than the ultra-porous fractal-like nanostructures typically seen at a HAB of 20 cm.

After spraying 100 s, a UNN ZnO thin film was deposited on the substrates. All the as-prepared samples were annealed (Compact muffle/tube 2-in-1 furnace, Zhengzhou TCH) at 300 °C for 12 hours at ambient pressure to stabilize the nanoparticle size and avoid resistive-sintering during the photo-detection measurements (**Figure 1B**). This annealing step has no effects on the film morphology and crystallinity, and the prepared samples are named as ZnO UNN (**Figure 1C**).

10 *ii. Capillary force induced self-assembly:*

5 μ L ethanol (Pure, 200 proof, Sigma Aldrich) was dropped next to the edge of the thin film with an active surface area of 0.418 cm² (0.76 cm × 0.55 cm) on the substrate (**Figure 1D**) to prepare capillary forced induced stump-like nano/micro-clusters (**Figure 1E**). The samples were left to dry in ambient environment for 2
15 hours before UV photodetection and denoted as ZnO CFI.

The volumes of ethanol droplet of 2 and 10 μ L were investigated to emphasize the sensible droplet size of 5 μ L in this project. The SEM images show insufficient volume of ethanol droplet (2 μ L) could not guarantee the fully spreading of ethanol solvent to the whole film tested but terminated somewhere halfway due to its fast evaporation and thus left a distinguishable stopping line (Figure 19A). The intact section retains the ZnO_UNN cloudy and fluffy features (Figure 19C), while the adjacent section on the other side of the stopping line displays an immeasurably vast difference. Whereas the agglomerated bridges composing fluffy nanoparticle clusters are presented (Figure 19B), this is might be driven by the process of vapour sintering as ethanol evaporates. In the case of 10 μ L, the excessive mass of solvent crushes the ZnO_UNN film and causes it to collapse with visible cracks everywhere under SEM (Figure 19B).

30 *iii. Addition of Multi-walled Carbon nanotube*

Different concentrations (0.02, 0.05, 0.1, 0.2 and 0.4 mg.ml⁻¹) of Multi-walled Carbon nanotube (MWCNT, 10-40 nm × 0.5-1.5 mm, Sigma Aldrich) dispersed in ethanol (Pure, 200 proof, Sigma Aldrich) were prepared via ultrasonic bath at room

temperature. The CNTs were dispersed in the droplet of ethanol resulting in CNTs dispersion into metal oxide film through ethanol infiltration.

Characterization and UV photodetection

- 5 The morphology and patterning characteristics of the deposited particles and films were investigated by a field emission scanning electron microscope (FESEM, JEOL JSM7100F, 15 kV) and transmission electron microscope (TEM, Philips CM10, 100 kV).
- 10 The crystal phases, crystal size (d_{XRD}), and surface compositions were characterized by X-ray diffraction using Bruker system (XRD, D2 Phaser, USA) equipped with Cu K α radiation of average wavelength of 1.54059 Å. Photoluminescence (PL, Cary Eclipse, Agilent Technologies, excited at 325 nm), Fourier transform infrared spectroscopy (FTIR, iD5 ATR, Thermo Scientific) and
- 15 Raman scattering (LabRam HR Evolution, Horiba, 473 nm) spectra studies were performed to understand the band structure and non-resonant and resonant vibration properties of fabricated nanocomposites.

- Photodetection test:* Absorbance spectra of all films were measured using a
- 20 Perkin–Elmer (Lambda 265 UV/Vis) Spectrophotometer. DC photocurrents were measured using a picoammeter/voltage source (Model 6487, Keithley). Mounted LED (M375L4, ThorLabs) were used as the UV light source to provide 375 nm of UV illumination at the power density of 1 mW cm⁻². All optical and electric measurements were carried out at room temperature under atmospheric condition.
- 25

Results and Discussion

- The capability of FSP to fast prepare a homogeneous metal oxide thin layer featuring a smooth surface (**Figure 2A**) and nanoparticle networked 3D structures with consistent surface appearance and uniform micro- and nano-scale
- 30 morphological features (**Figure 2A and B, inset**) is shown in the images on the left of Figure 2. Images on right in Figure 2 are post contact with volatile solvent.

The porosity computed from the SEM cross-sectional thickness and deposited film mass density was found to be around 95% with HAB = 12 cm. The film thickness of

18.5 μm (**Figure 2B**) reveals that film growth rate ($11.1 \mu\text{m}\cdot\text{min}^{-1}$) is twice as fast as HAB = 20 cm (growth rate $\sim 5.5 \mu\text{m}\cdot\text{min}^{-1}$) most likely due to a shortened particle deposition path, therefore more particles are captured and deposited on the substrate. Interestingly, a side view of the film (**Figure 2B**) shows that a shortened
5 HAB can generate a thin film with dendrite-like patterns. This may be caused by partial sintering of the primary nanoparticles due to high temperature.

The transmission electron microscopy (TEM) analysis of the collected samples reveals a spherical shape and a visible primary particle diameter (d_{TEM}) of 15.54
10 nm in average (**Figure 2E, inset**), which is in good agreement with previous reports on the flame made ZnO nanoparticles.

By introducing at least one microlitre-sized droplet of ethanol to the flame made ZnO thin film, the morphology can be starkly transformed. The capacity of
15 nanoparticle agglomerates cohesion in enhancing charge carrier transduction and photoreaction performance of UNN devices was investigated. Firstly, the 3D nanoparticle networked thin film converts to a uniformly distributed stump-like micro-cluster arrays with average size of 16.0 μm in diameter on the surface (**Figure 2D**). Secondly, the film thickness was decreased from 18.5 μm of flame
20 made thin film to 16.0 μm (**Figure 2D**), resulting in a 1 % reduction in the average film porosity from 95 % to 94% consequently. No cracks were created during the morphology transformation, suggesting a crack-free top-down approach to manipulate the morphology. Thirdly, the primary particle size was increased 10% from 15.44 nm to 17.10 nm as demonstrated from TEM measurement (**Figure 2F,**
25 **inset**), the reduced quantity of small nanoparticles ($\leq 15 \text{ nm}$) from 49% to 38% but overall increased larger size counterpart demonstrating the Ostwald ripening process was accountable for the primary particle size increase may be driven by overwhelmingly prominent capillary force exerting on the small sized nanoparticles. Screen shots of the capillary force of ethanol exerting on a UNN ZnO thin film are
30 shown in **Figure 3**. Before the application of ethanol, the quasi-columnar dendrite-like nanoclusters are seen standing vertically on the substrate surface. Soon after releasing the microlitre-sized droplet of ethanol under the microscope, the ethanol solvent infiltrated through the 3D networked nanoparticle agglomerates by capillary force (**Figure 3A.i-ii**). At the same time, the force bridged the nearby quasi-

columnar dendrite-like nanoclusters to lean inward and shift, causing neighbouring nanoclusters to coalesce and consequently forming stump-like micro-clusters. leaving small gaps between the microclusters (**Figure 3B.i-ii**).

- 5 As the ethanol started to evaporate (shortly after spreading over the whole thin film), the bases of the nano-micro cluster arrays (NMCAs) are also seen to coalesce to form distinctive islanding in a shape that is reminiscent of 'tree stumps'. The nanoclusters leaned and shifted further inwards and consequently the gaps between the micro-clusters grew larger to reduce the surface tension and maintain
- 10 a minimum Gibbs free energy at the surface (**Figure 3C.i-ii**). Most of the ZnO nanoparticles/nanoclusters are seen to be contained within these structures, though a continuous thin film of ZnO may form directly above the substrate.

- Application of the ethanol droplet can change the characteristics of the thin film.
- 15 The thickness of layer is found to decrease from 18.5 μm to 16.5 μm , while the average film porosity is found to reduce from 95% to 94.4%. The average nanoparticle size increases from 15.4 nm in ZnO_UNN (Figure 2E inset) to 17.10 nm in the case of ZnO_CFI (Figure 2F inset), and the number of nanoparticles below 15 nm is found to decrease from 49% to 38% in the ZnO_UNN and
- 20 ZnO_CFI structures, respectively (insets in Figure 2E,F). These observations suggest that the application of ethanol is not only responsible for bringing the ZnO_UNN clusters together, but is also responsible for significant nanoparticle coalescence, and restructuring at the atomic level. Selected area electron diffraction (SAED) of the ZnO_UNN and the ZnO_CFI show characteristic 'ring'
- 25 patterns commensurate with polydisperse crystalline ZnO. Meanwhile, the ring-like diffraction patterns slightly changed from the more diffused style of the DNC layers to be the more scattered mode in NMCA layers, indicating some randomly orientated small crystals are becoming bigger and more oriented particles after the capillary action, providing further evidence of the microstructural transformation
- 30 induced by of the application of ethanol.

The video shows no more visible morphological changes could be observed under microscope after 1 min since the ethanol was dropped, indicating a high evaporation rate ($\sim 5 \mu\text{l}\cdot\text{min}^{-1}$) of ethanol within this thin film in open air at room

temperature. Giving enough time for ethanol to dry completely will result in uniformly distributed stump-like micro-clusters on substrate (**Figure 3D.i-ii**).

The capillary force of ethanol exerting on a neighbour dendrite-like nanoclusters/agglomerates was estimated via simplified model (**Figure 3A.iii**) here, where the quasi-columnar nanoclusters was symbolised as columns (filled with grey gradient slashes) with diameter of 20 μm (2R) and distance of 30 μm (X) by following equation:

$$F_{c-c} = \frac{\pi\gamma R^2 \cos^2 \alpha}{\sqrt{\left(\frac{X}{2}\right)^2 - R^2}}$$

Where γ is the surface tension of ethanol (γ , 21.4 $\text{mN}\cdot\text{m}^{-1}$ at 25 $^{\circ}\text{C}$) [28] and $\alpha = 72^{\circ}$ is the contact angle, herein the F_{clu} was calculated to be 57.4 nN, which can easily overcome the elastic restoring force. Therefore, it is postulated that the dendrite-like nanoclusters can be forced to shift and lean inwards and keep the stump-like structures.

At the nano scale, the van der Waals force between two adjacent identical spheric nanoparticles can be estimated via the equation given below:

$$F_{vdw} = \frac{A_H r}{12D^2}$$

Where A_H , r , and D are the Hamaker constant (9.2×10^{-20} J for ZnO), radius of the nanoparticle (7.5 nm, half of d_{TEM}) and the interparticle distance (which is generally assumed to be in the range of 0.3 nm), respectively. Therefore $F_{vdw} \approx 0.64$ nN. In the case of adjacent nanoparticles of different size (r_1, r_2), the F_{vdw} can be estimated by replacing r with $r = \frac{2r_1 r_2}{r_1 + r_2}$. For nanoparticles with the radius of 5 nm and 7.5 nm in radius for instance, the F_{vdw} is calculated to be ~ 0.51 nN.

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Meanwhile, at the nano scale, the capillary force between neighbouring spherical nanoparticles (Figure 20) in the nanoclusters (F_{p-p}) are significantly strengthened as estimated by equation (2) due to distance between them is getting closer and closer [30]:

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$$F_{p-p} = -\frac{2\pi r\gamma \cos \theta}{1+\left(\frac{D}{2d}\right)},$$

Where r is the radius of the sphere, θ is the contact angle, D is the separation distance between the two spheres, and d is the immersion length given by

$$d = \left(\frac{D}{2}\right) \times \left(\sqrt{1 + \frac{2V}{\pi r D^2}} - 1\right)$$

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where V is the liquid volume.

This capillary force is proportional to the interfacial tension of the liquid (γ) and the particle size, but inversely correlates to the spacing between the neighbouring agglomerates. As the two dendrites are driven closer to each other during the drying step, the capillary force becomes larger. For example, a 0.06 nN capillary force could be generated for a typical case that $V = 1 \times 10^3 \text{ nm}^3$, $\theta = 72^\circ$ [29] with $D = 10 \text{ nm}$ and $R = 6 \text{ nm}$, and the force can reach over ~0.2 nN when the spacing between neighbouring agglomerates reduces down to 2 nm during the dying process.

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Such remarkably high capillary force between two neighbouring nanoparticles can generate strong compress pressure (contact area is close to 0) which could lead them to weld together to either generate necking between nanoparticles or to form larger sized nanoparticles.

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Figure 4A shows X-ray diffraction (XRD) patterns of both ZnO UNN and ZnO CFI films on Si substrates. All the XRD spectra correspond to the hexagonal wurtzite ZnO (JCPDS No. 36-1451) structure with no secondary and amorphous components observed, which is in line with previous reports. Two outstanding extraneous peaks appearing at $\sim 33^\circ$ and $\sim 62^\circ$ for ZnO_CFI are originated from the

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Si wafer substrate (Blue diamond symbols). The average crystalline size of ZnO was estimated by means of the Scherrer equation:

$$d_{XRD} = \frac{0.9\lambda}{\beta \cdot \cos \theta}$$

where λ is the incidence X-ray wavelength, β is the full width at half maximum (FWHM) of the peaks, and θ is the diffraction angle of the corresponding peaks.

The nanoparticle size of ZnO_UNN is 14.6 nm, which is about 25% larger than the crystal size reported in previous works ($d_{xrd} = 11.7$ nm for the HAB of 20 cm) indicating significant interparticle sintering and grain boundary necking effect during the thin film deposition due to the higher deposition temperature of 500 °C with HAB = 12 cm which is about 100 °C higher than HAB = 20 cm. This outcome may be due to the increased energy present during deposition.

Furthermore, the average ZnO nanoparticle size further increased 11.5% to 16.5 nm after CFI process, showing a significant growth of ZnO crystal size due to the ethanol infiltration and evaporation effects. Using the (002) plane, a tensile stress of 6.3 GPa was calculated for the ZnO_UNN layers, a value nearly twice that of the ZnO_CFI layers where the residual stress is only 3.3 GPa. The diffraction angle (2θ) of ZnO-CFI samples exhibit a 0.24° downshift (**Figure 4, inset**) towards the bulk ZnO ($c_0 = 5.207$ Å), reflecting that the inner compressive stress is cured via CFI effect. This can be calculated by using the biaxial strain model analysis as follows:

$$\sigma = -4.53 \times 10^{11} \frac{c - c_0}{c_0}$$

where c can be calculated by means of the Bragg equation $c_0 = \frac{\lambda}{\sin \theta}$.

It is thought that the ethanol treatment has in some way enabled this relaxation in stress and the formation of an energetically favourable structure that is more stable.

It is worth mentioning that the appearance of Si peaks in ZnO_CFI is likely attributed to the impact of capillary force in forming the ZnO micro-clusters from nearby dendrite-like ZnO nanoparticle network, therefore leaving abundant gaps between stump-like ZnO micro-clusters. Others have reported the appearance of a rod-like structure detectable by an increase in the aspect ratio between the (100) and (002) peaks. Here, the (100)/(002) planes aspect ratio was found to be close to unity (1.06 ± 0.07) which is in line with the predominant spherical shape observed by TEM analysis (**Figure 2E, F**), indicating homogenous particle growth by condensation and Brownian coagulation.

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Photoluminescence (PL) and Fourier Transfer Infra-Red (FTIR) spectroscopy of both ZnO_UNN and ZnO_CFI layers identified features expected to be seen from pure ZnO nanoparticles. Despite the significant changes in morphology of the nanoclusters, there are not significant differences in the PL and FTIR investigations before (ZnO_UNN) and after (ZnO_CFI) the treatment with ethanol, indicating that the treatment has not chemically contaminated the layers.

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The state of defects in ZnO thin film was investigated by photoluminescence (PL) spectroscopy, and the spectra are displayed in **Figure 4B**. Two dominant peaks at 391 and 445 nm and a small peak at ~360 nm stand out in both samples. The end of the UV emission peak centered at 391 nm is a Near Band Emission (NBE), originating from the recombination of the free excitons through an exciton-exciton collision process, and is attributed to the presence of structural defects. The slightly weakened NBE intensity of ZnO_CFI indicates the CFI process are able to quench or remove the structural defects among the thin film, which may relate to the ZnO nanoparticle size increase.

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Around this dominating peak, from 365 nm to 435 nm, four discerned peaks located at ~383, ~393, ~404 and ~412 nm can be well deconvoluted via Gaussian function as depicted in **Figure 4B**. The ~383 and ~393 nm UV emission bands are the exaction recombination related near-band edge (NBE) emission or free exciton emission of nanostructured ZnO. Two violet emissions centered at ~404 and ~420 nm are ascribed to an electron transition from a shallow donor level of the Zn_i to the top level of the valence band. The blue emission band at 445 nm is a Deep

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Level Emission (DLE) assigned to band-to-band transitions and is originated from interstitial zinc ions of ZnO nanofilms. The small UV emission band at ~360 nm might originate from the ultra-small sized ZnO (<10 nm) Nanoparticles among the thin films (TEM images of **Figure 2E,F**), as this short wavelength NBE is often
5 found in the ZnO quantum dots (QDs) under 325 nm excitation.

The slightly decreased intensity of ZnO_CFI is in good agreement with the reduced ultra-small sized ZnO Nanoparticles in **Figure 2E,F**, indicating some of the ultra-small ZnO Nanoparticles redeposited and merged into nearby bigger ZnO
10 Nanoparticles via Ostwald ripening during the CFI process.

Similarly, the surface defect and impurity contents of the ZnO_UNN and ZnO_CFI were characterized by Fourier Transfer InfraRed (FTIR) spectroscopy (**Figure 5A**). The broad peak at 3420 cm^{-1} is ascribed to O–H stretching and bending vibrations
15 of water molecules respectively, which is attributed to adsorption of atmospheric moisture. The peaks which appeared at 2340 cm^{-1} correspond to the CO_2 adsorbed on the surface of the fabricated films. Two peaks appeared at 1080 and 1118 cm^{-1} which may originate from C–N–C stretching vibration. Another two peaks at 1600 and 1400 cm^{-1} are attributed to the asymmetrical and symmetrical stretching of
20 zinc carboxylate, respectively. The Zn–O stretching peaks can be also captured at $\sim 900\text{ cm}^{-1}$ and $\sim 600\text{ cm}^{-1}$, which is in line with previous studies and confirms the achievement of a highly pure ZnO nanofilms.

The optical transmittance spectra over a wavelength range of 200–800 nm for
25 ZnO_UNN and ZnO_CFI is displayed in **Figure 5B**. Both films exhibited less than 14% optical transmissivity due to the nature of relatively thick ZnO thin-films and compromised less porosity. The sharp cut-off wavelength approaching the end of the visible spectrum and well within the UV-A range of 400–320 nm at around 380 nm (**Figure 5B** and **inset**), indicates the characteristic intrinsic solar-blind property
30 of ZnO nanomaterials. In addition, the UV light transmittance, at a wavelength of 375 nm increases from 0.01% for UNN ZnO (**Figure 5B**, dark line) to 3.8% for CFI ZnO film (**Figure 5B**, red line) indicating a significant light transmittance improved via CFI process. Similar trend was observed within the visible range, with 40 times higher transparency for ZnO_CFI compared to the ZnO_UNN film. Optical images of

the films placed over a printed paper (**Figure 5B**, inset) illustrating this higher visible range transparency for ZnO_CFI in contrast to ZnO_UNN nanostructure.

The optical transmittance, reflectance and absorption spectra for DNC (also referred to as ZnO_UNN) and NMCA (ZnO_CFI) layers in the 200-800 nm wavelength range, are presented in **Figure 5C-F**. In the case of the ZnO_UNN layers, there is observed very high optical absorption between 200 and 370 nm, and a sharp reduction in absorption from 370 to 400 nm. From very low values below 370 nm, both transmission and reflection rapidly increase with increasing wavelength, with transmission reaching 44% at 450 nm, before more gradually reaching ~75% at 800 nm. This excellent transparency across the visible wavelength is in good agreement with flame-made ultraporous ZnO layers that had a slightly higher transmittance (~84%) in the visible wavelengths, corresponding to their higher porosity (>98%). This strong absorption in the UV-A range (320 - 400 nm) indicates the intrinsic value of ZnO films for use in solar-blind UV photodetectors. In the case of the ZnO_CFI layers, the transmittance, reflection and absorption spectra show broadly similar features, but with an increase in transmittance (of between 10% and 20%) across the 200 to 800 nm range. This increase in transmittance is readily explained by the microstructural features of the ZnO_CFI (Figure 2C, 2D and 2F), where the formation of the 'tree-stump' like micron-scale-clusters also produces optically significant gaps in the ZnO layers that reveal a significant percentage of the substrate. The increased transmission in the ZnO_CFI layers relative to the ZnO_UNN layers, obviously impacts the corresponding reflectance and absorbance data, specifically, in the UV region (<400 nm), where the absorbance is reduced by between 10 and 15%, while in the visible region (>400 nm) the reflectance is reduced by between 15 and 20%.

In the case of both the ZnO_UNN and ZNN_CFI layers, the measure of 'absorbance' in the visible region (450 to 650 nm) is not negligible, with typical values of 10% for the ZnO_UNN layers, and 5% for the ZNN_CFI layers. The calculation of absorbance ($A = 100 - R - T$) does not exclude other optical losses that might, for instance, include parasitic absorption or scattering losses, and values in this low absorption range should be treated with caution. The absorption coefficient in the near-bandgap region has been extracted to produce Tauc plots

(Figure 5E, inset). By extrapolating the linear part of the Tauc plots, a bandgap of 3.26 eV for the ZnO_UNN layers and 3.21 eV in the case of the ZnO_CFI layers is found. This change can be attributed to the enlarged particle size and tensile stress release.

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A typical ZnO_CFI on glass substrate featuring interdigitated platinum electrodes (Pt IDEs) is displayed in **Figure 6**, the stump-like ZnO micro-clusters were well duplicated on the substrate, each the clusters cover 2-5 Pt electrodes to ensure sufficient channels for UV excited carriers. Real time UV photo-detecting dynamic curves of ZnO_UNN (dark line) and ZnO_CFI (red line) under 375 nm light illumination with the power density of $1 \text{ mW} \cdot \text{cm}^{-2}$ at 1 V for six cycles are present in **Figure 7A**. When the UV light is on, the current of ZnO_UNN immediately increases from baseline (25 nA) to its maximum value 4.5 μA then decreases gradually, which cause the phenomenal photocurrent growth decay issue (**Figure 7B**).

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Others have fabricated a 3D ZnO UV photodetector based on PVA-capped ZnO nanowire (NW) arrays via aqueous chemically grown (ACG) process. Introducing PVA in earlier work was aimed at reducing the surface photocarrier relaxation thereby troubleshooting the photocurrent growth decay under steady UV illumination. It was found that with PVA-capping, the maximum photocurrent was greatly enhanced from 9.7 μA to 62.5 μA and most importantly only 12% photocurrent decreased within 15 min steady UV illumination which is four time less comparing to the as-grown ZnO NWs arrays.

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In stark contrast, without introducing excess materials, such as PVA or dopants, the photocurrent of ZnO_CFI in the present process increases from baseline ($\sim 1 \mu\text{A}$) to as high as 103.7 μA on average. This is 23 times higher than the photocurrent of ZnO_UNN. Moreover, the photocurrent continues to be stable before the UV light is off. The cyclic curve in **Figure 7A** (and further 20 times and 50 times repeating under the same light condition but at the bias of 1 V and 0.5 V respectively) (SI) shows ZnO_CFI is outstandingly stable with only negligible fluctuation.

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In another example, **Figure 7C** shows the current of ZnO_UNN increases upon illumination from an initial dark current of ~90 nA to a maximum photocurrent of 6.8 μ A. In comparison, the photocurrent of ZnO_CFI increasing from ~110 nA to a maximum of 115.4 μ A, representing an approximate 17-fold increase in photocurrent.

The UV sensing photocurrent of ZnO thin film is thought to work in the following way. Atmospheric oxygen molecules will be absorbed on the surface of ZnO nanoparticles extracting the free electrons from ZnO nanoparticles to form negatively charged oxygen species (O_2^- , O^- and/or O^{2-}). This also causing the ZnO nanoparticles to be fully electrically depleted in a dark condition due to the primary nanoparticle size of both ZnO_UNN and ZnO_CFI being smaller than twice the Debye Length ($d \leq 2\delta \approx 38 \text{ nm}$). This is thought to provide the thin film with an overall low dark current. Electron and hole pairs are generated upon UV light exposure. The holes migrate to the surface to neutralise the negatively charged oxygen species and desorb molecular oxygen back to the environment. The electrons reduce the depletion region and contribute to the rapid increased photocurrent.

Responsivity and response time (rise and decay time) are widely used to assess the performance of UV photodetection. The Responsivity (Res.) is the ratio of photocurrent obtained by a device per unit area to the incident light power at a given wavelength, which can be calculated as follows:

$$Res. = \frac{I_{UV} - I_{dark}}{LD \times S_A}$$

where I_{UV} and I_{dark} are the photocurrent and dark current respectively, LD is the corresponding UV light density and S_A is the effective sensing surface area (0.418 cm^2).

Here, the light density (LD) was kept constantly at 1 $\text{mW}\cdot\text{cm}^{-2}$. The calculated responsivity of ZnO_UNN and ZnO_CFI are 11.2 and 245.7 $\text{mW}\cdot\text{A}^{-1}$. The rise time

is defined as the time for the current increase from 10% to 90% of its saturation value, and the decay time is vice versa.

The normalised current of a second UV on/off dynamic curve in **Figure 7B** displays remarkable enhanced UV detecting kinetics. The rise and decay times of ZnO_UNN are 36.4 s and ~60 s respectively, which is tremendously faster than previously reported UNN ZnO with porosity as high as 98% due to the longer HAB setup in flame spraying (**Figure 10**), showing the fact that lowering the HAB to prepare less porous ZnO thin films can prompt the charge carriers flow therefore faster UV detecting kinetic will be featured.

Moreover, the CFI process further improves the response kinetics with rise and decay times being 13.4 s and 7.5 s, respectively, which are about threefold and eightfold faster than ZnO_UNN. The formation of stump-like ZnO nano-micro clusters accounts for this improvement. Firstly, the further reduced porosity has shortened conductive channels so the charge carriers can circulate more easily from one end to another; secondly, the stump-like micro clusters are thought to create stronger adhesion for ZnO nanoparticles to the substrate; thirdly, the further grown ZnO nanoparticle during the CFI process are thought to at least partially remove the structural defects in the film, therefore there may be less traps for photo carrier charges resulting in higher photocurrent and faster response times.

In another example, Figure 7D shows the photo-response for a single on/off illumination cycle, in which the responses of ZnO_UNN and ZnO_CFI devices are normalised to allow a comparison of the device response times. The rise time (T_r) and decay time (T_d) are determined by the time elapsed as the current changes from 10% to 90% of the maximum value, and vice versa. Even without significant high temperature annealing as a typical routine for flame-made ultraporous ZnO films, the UV photodetectors fabricated with a HAB of 12 cm show significantly improved response dynamics (~1.5 time faster). In the case of the ZnO_UNN devices, rise time and decay time are found to be 164.5 s and 159.2 s, while the ZnO_CFI devices show over twice as fast with rise time and decay time found to be 88.2 s and 68.9 s, respectively.

The photodetection of ZnO_CFI was performed under different voltages from 1 V to as low as 0.01 V (**Figure 8A**), the photocurrent reduced proportionally against the decreasing voltage with about 1.16 μA and 0.48 μA at 0.02 V and 0.01 V respectively. A near linear relationship between photocurrent density and applied bias in **Figure 8B** shows the ZnO_CFI is excellently stabile and repeatable.

In **Figure 8C-H**, in an example, the UV photoresponse of ZnO_CFI devices exhibit excellent stability, with little variation in the signal photocurrent over time applied voltages in the range 0.01 to 2 V (**Figure 8C and 8H**). The relationship of photocurrent density versus the applied voltage (0.01-2V) shows a slightly non-linear characteristic (**Figure 8D**) as would be expected for a symmetrical metal-semiconductor-metal (MSM) design, i.e., Pt (electrode)-ZnO-Pt (electrode) (**Figure 8D**, bottom right inset). Here, the near-linear relationship between the photocurrent density in a relatively low applied voltage range (0.01-0.05 V, **Figure 8D**, top left inset) indicates a promising energy-saving feature of these devices for UV photodetection. The well preserved stable photoresponse at nominal zero applied voltage (**Figure 8H**) suggests potential as a self-powered device. The UV photoresponse depicts photocurrent enhanced linearly with the light density gradually increased from 0.5 to 2 $\text{mW}\cdot\text{cm}^{-2}$ regardless of the applied bias (**Figure 8E-F**), showing a very reliable response towards the incident UV light. The stability of the NMCA devices was further investigated across 45 on/off cycles at 0.5 and 1 V applied voltages (**Figure 8G**). These results reveal excellent repeatability and remarkable stability.

25 **Introducing CNT**

Figure 11B,C shows the cross-section and top view SEM images of ultraporous films obtained by 100s exposure of the substrate to thermophoretic-driven deposition of ZnO aerosols. Here, to achieve sufficient mechanical stability, the deposition distance from the burner was decreased from 20 cm as employed in previous studies to 12 cm, resulting in 9% reduction in average film porosity from 98% of film deposited at HAB = 20 cm to 89% of HAB = 12 cm. The film porosity was computed from the SEM cross-sectional thickness and deposited film mass density. The fabricated films were then post-sintered at 300 °C for 12h to increase

the film mechanical stability and decrease grain boundary barriers to electron conduction within the film.

Figure 12 shows the schematic (**Figure 12A to C**) as well as scanning electron microscope (SEM) images of UNN (**Figure 2D, G**) and CFI (**Figure 2E, F, H, I**) devices before and after deformation induced by capillary force. As the ethanol evaporates from the UNN surface during drying, a meniscus forms between nanoparticles agglomerates, yielding a relatively strong capillary force to drive the nearby quasi-columnar deposited nanoparticle network into contact forming the morphology deformation from homogeneous UNN to be stump-like structure with 10-30 μm size stump in diameter (**Figure 2E,F**) and relatively similar sized gaps between nearby stumps (**Figure 2H,I**). The capillary force between to neighbouring agglomerates can be calculated. This capillary force is proportional to the interfacial tension of the liquid, (γ), the cross-section area of the agglomerates, and the spacing between the neighbouring agglomerates. As the two agglomerates are driven closer to each other during the drying step, the capillary force becomes larger. Such remarkably high capillary force between two neighbouring agglomerates on nanoscale can significantly enhance the electrical contact between randomly deposited nanoparticles on the substrate's surface, tackling the long-standing conductivity issue in these ultraporous nanostructured metal oxide devices.

To introduce carbon nanotubes (CNT) the CNT were added to the ethanol solution prior to application of the droplet. Experiments comprising CNT are referred to as CFI-CNT. The average film thickness was decreased from 18.5 μm of UNN (**Figure 12D**) to 11.6 μm of CFI (**Figure 12E**). A further reduction in the average film thickness (down to 11 μm) was observed for CFI-CNTs samples, (**Figure 2F**). The transmission electron microscopy (TEM) analysis of the collected samples from the surface reveals a spherical shape and a visible primary particle diameter (d_{TEM}) of 18 $\pm$ 1 nm. The primary particle size was increased from 18 nm of UNN to 22 nm CFI samples, demonstrating that the capillary force was overwhelmingly prominent among the CFI ZnO films to minimize the interfacial energy.

Figure 13A shows X-ray diffraction (XRD) patterns of deposited films (UNN, CFI and CFI-CNT) on Si substrates. All the XRD spectra correspond to the hexagonal wurtzite ZnO (JCPDS No. 36-1451) structure with no secondary and amorphous components observed. Two outstanding extraneous peaks appearing at $\sim 33^\circ$ and $\sim 62^\circ$ for both CFI samples originated from the Si wafer substrate (dark yellow spectrum). All the XRD patterns corresponded to the wurtzite ZnO phase (JCPDS No. 36–1451) composed of alternating planes of Zn and O atoms growing along the (100) axis with no secondary and amorphous components observed. The appearance of a rod-like structure has been detectable by an increase in the aspect ratio between the (100) and (002) peaks. Here, the (100)/(002) planes aspect ratio was found to be close to unity ($1.0x \pm 0.0x$) which is in line with the predominant spherical shape observed by TEM analysis (**Figure 12J to L**), indicating homogenous particle growth by condensation and Brownian coagulation.

An average crystal size of 12.9 ± 1 nm was calculated for flame-made ZnO nanoparticles deposited at the HAB of 12 cm (**Figure 13A**). This is 10% larger than the crystal size reported in previous works ($d_{\text{xrd}} = 11.7$ nm for the HAB of 20cm) indicating interparticle sintering and grain boundary necking, which is attributed to the higher deposition temperature for lower HAB. The average crystal size for ZnO nanoparticles increased from 12.9 nm of UNN to 15.5 nm of CFI samples, indicating a significant growth of 20% in ZnO crystal size after CFI process. Furthermore, the diffraction angle (2θ) of all the CFI samples shows a downshift trend (**Figure 13a**, inset), reflecting the inner compressive stress increases due to the morphology transformation from weak connection of UNN to stronger aggregation state via CFI treatment.

It is worth mentioning that the appearance of Si peaks in CFI samples (Figure 13a, CFI-ZnO and CFI-0.1CNT) are attributed to the impact of capillary force in washing off ZnO nanoparticles from the substrate and therefore thin coverage of ZnO nanoparticles at the stump-to-stump gaps.

Raman spectroscopy was performed to provide information on the vibration structure, crystallinity, and electronic properties of the fabricated films. As presented in **Figure 13b**, the two characteristic sharp peaks positioned at ~ 99 cm^{-1}

and $\sim 439\text{ cm}^{-1}$ are assigned to the $E_2^{(\text{low})}$ and $E_2^{(\text{high})}$ modes from the vibration of heavy zinc sublattice and oxygen atoms, respectively. These sharp peaks are attributed to the crystalline and defect-free state, indicating a perfect crystal quality of the fabricated films. Multi-phonon peak of $E_2^{(\text{low})}$ and $E_2^{(\text{high})}$ can be found at ~ 334
5 cm^{-1} . Acoustic transverse optical mode, $A_1(\text{TO})$, can also be observed at ~ 380 cm^{-1} . A weak shoulder peak in the low frequency direction of intense vibration at 439 cm^{-1} is correspond to the $E_1(\text{TO})$ mode. Both obvious asymmetric peaks at $\sim 580\text{ cm}^{-1}$ and $\sim 1150\text{ cm}^{-1}$ are attributed to the overlapping of the E_1 and A_1 longitudinal optical (LO) modes and the resonance behaviour of the main second-
10 order structure (2LO). Double humps located at $\sim 218\text{ cm}^{-1}$ and $\sim 278\text{ cm}^{-1}$ are associated with the second-order Raman spectrum arising from zone-boundary phonons (2TA) and disorder-activated silent B1 mode, respectively. A broad hump observed at around 650 cm^{-1} is assigned to other multi-phonon processes occurring for phonon wavevectors considerably removed from the centre of the
15 Brillion zone. The peak at around 987 cm^{-1} might be attributed to the A_1 and E_2 optical combination.

The characteristic D and G bands for CNTs can be observed in the nanocomposite at $\sim 1370\text{ cm}^{-1}$ and $\sim 1590\text{ cm}^{-1}$, respectively (the bottom red line), where D band is
20 activated by the presence of disorder in carbon systems, and G band is assigned to the in-plane vibration of the C–C bond, indicating the successful loading of CNTs into the UNN ZnO matrix.

The defect and impurity content of the deposited ZnO UNN were characterized by
25 Fourier Transfer InfraRed (FTIR) spectroscopy (**Figure 13C**). The broad peaks at 3420 cm^{-1} and 1600 cm^{-1} are ascribed to O–H stretching and bending vibrations of water molecules respectively, which is attributed to adsorption of atmospheric moisture. The peaks appeared at 2340 cm^{-1} correspond to the CO_2 adsorbed on the surface of the fabricated films. The two peaks at 1600 and 1400 cm^{-1} are
30 attributed to the asymmetrical and symmetrical stretching of zinc carboxylate, respectively. The two small peaks at 900 cm^{-1} and 600 cm^{-1} are ascribed to Zn–O stretching, which is line with previous studies and confirms the achievement of a highly pure ZnO nanofilms.

Figure 14A presents the photoluminescence spectra of the fabricated UNN and CFI-0CNT and CFI-0.1CNT films at room temperature. The synthesised UNN, CFI and CFI-CNT nanofilms demonstrate the same characteristics with two dominant peaks at 391 and 445 nm (Figure 4A). The UV emission peak centered at 391 nm is a Near Band Emission (NBE), originated from the recombination of the free excitons through an exciton-exciton collision process, and is attributed to the presence of structural defects. The weak and broad blue emission band at 445 nm is a Deep Level Emission (DLE) assigned to band-to-band transitions and originates from the oxygen vacancies or interstitial zinc ions of ZnO nanofilms. The presence of these emission peaks for the UNN, CFI and CFI-CNT samples demonstrates the successful attachment of the CNT into the ZnO nanoparticles by CFI self-assembly process. However, the emission intensity of the CFI and CFI-CNT is lower than that of UNN ZnO which is attributed to a better electron-transfer of the excited electrons in CFI samples, resulting in a reduction in the fluorescence emission. The I_{NBE}/I_{DLE} ratio decreased from 7.13 of UNN ZnO to 6.17 and 5.59 of CFI and CFI-CNT films, indicating the formation of some structural defects in the fabricated films by CFI self-assembly process.

Figure 14B shows the optical transmittance spectra of the UNN and CFI-0CNT and CFI-0.1CNT films deposited on blank glass substrates over a wavelength range of 250-800nm. Both UNN and CFI ZnO films were highly transparent to visible light with a relatively sharp cut-off below 375 nm. This is relatively close to the end of the visible spectrum 400 nm and well within the UV-A range of 400–320 nm. The film average optical transmittance for visible light was computed by subtraction of the fraction lost through the glass substrates indicating a transmission of visible light and absorption of incoming UV radiation.

Figure 15A shows the spectral responsivity of the photodetectors as a function of the illumination wavelength from 265 to 850 nm with light density of 1 mW.cm^{-2} at an applied bias of 0.5 V. By definition, responsivity is the ratio of photo-current obtained by a device per unit area to the incident light power at a given wavelength, which can be calculated as follows:

$$R = \frac{\Delta I}{P}$$

It was observed that decreasing the wavelength below 400 nm sharply increased the responsivity that reached its peak value at about 365 nm. The sharp cut-off at wavelength of 365 nm is in good agreement with the ZnO bandgap of 3.37 eV ($\lambda =$ 368 nm) confirming that these ZnO photodetectors are inherently visible-blind. All samples had negligible response to visible light ($\lambda > 400$ nm). The device responsivity increased drastically with the illumination wavelength decreasing from 400 to 365 nm and peaked at 18 A.W^{-1} for the CPI-0.1CNT device under a light illumination with the wavelength of 365 nm. This high responsivity corresponds to a responsivity nearly 6000 times as high as that of the pure UNN ZnO device ($\approx 3 \text{ mA/W}$).

Figure 15B presents the photocurrent density of UNN and CFI samples with different concentration of CNTs from 0 to 0.4%, as a function of applied bias from 0 to 2 V under a wavelength of 375 nm. All the samples had very low dark currents up to a bias of 2V. This is attributed to both the strong impact of surface states on the ZnO conductivity and to the very high film porosity (89%) that results in large electron depleted region.

A linear I - V response indicating an Ohmic behaviour was observed with sufficient availability of charge carriers. Similar to the responsivity, a significant enhancement in photocurrent density (165 folds) was observed already after applying CFI self-assembly resulting in a photocurrent density of 1.35 mA.cm^{-2} of CFI-0CNT compared to $8.25 \text{ }\mu\text{A.cm}^{-2}$ of pure UNN ZnO film. This is attributed to the major reduction in nanoparticles junction resistance due to the nanoparticles' cold-welding.

As the schematic in **Figure 16A-B** shows, the oxygen molecules adsorb on the nanoparticle surface of the UNN_ZnO in dark and capture free electrons from the semiconductor conduction. This results in the formation of poorly conductive depletion layer near the surface of the ZnO, which suppresses the dark-current of these nanostructures to sub nA. Upon UV illumination, the photogenerated holes can travel to the surface along potential gradient and desorb oxygen molecules from the surface, resulting in an increase in the free carrier concentration within this

depletion layer. [ref] However, the nanoparticles are held together by weak van der Waals force in the UNN_ZnO, hindering charge carriers transfer between the grains, resulting in high electrical resistance and poor photo-response of these ultraporous nanostructured films.

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For the CFI samples, on the other hand, the nanoparticles cold-welding results in a significant increase in charge transport. This nanoscale cold-welding is attributed to the formation of meniscus shaped capillary bridge between nanoparticles during the ethanol evaporation at the nanoparticle's junction, yielding an interparticle attractive force, and subsequently compressive pressure between nanoparticles pulling them into contact. This welding effect is extremely strong when two particles begin to form contact, and the effect is especially strong on nanoscales, leading to a gigantic enhancement in photocurrent density of the CFI samples compared to the UNN structure.

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A further increase in photocurrent density was observed by adding CNT into the CFI self-assembled films resulting in the photocurrent density of 4.68 mA.cm^{-2} of CFI-0.1CNT sample which is 720 times higher than of the pure UNN ZnO. This further improvement in photoreaction performance is ascribed to the superior electron transportation of CNTs in CFI-CNT sample, leading to a quick drift of unpaired electrons to the electrode by external bias voltage. However, further increasing the CNT concentration to 0.2 and 0.4 decreased the photocurrent density to 3.05 and 2.32 mA.cm^{-2} , respectively. This is tentatively attributed to the absorption and back-scattering of UV light from the CNTs. which is not efficiently contributing to the enhancement of the conductivity of the nanostructured photodetectors.

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In addition to increasing the photocurrent density, the dark-current density slightly increased from 0.38 nA of the UNN_ZnO to 0.6 nA of CFI_0.1ZnO sample (**Figure 15C**, inset). However, this higher dark-current density had negligible impact on signal-to-noise ratio ($I_{\text{photo}}/I_{\text{dark}}$) of the CFI_ZnO photodetectors. **Figure 15C** shows the $I_{\text{photo}}/I_{\text{dark}}$ ratio of the UNN_ZnO as well as CFI_0.1ZnO samples under UV light illumination of 375 nm as a function of applied bias. The $I_{\text{photo}}/I_{\text{dark}}$ ratios increase

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from 2.5×10^5 of UNN_ZnO to 4×10^6 of CFI_0.1CNT sample at the applied bias of 2V.

Figure 15D shows the photocurrent density of the fabricated samples under UV light illumination with light density of 1 to 20 mW.cm². A linear *I*-*V* response is observed for different light density, indicating an Ohmic behaviour with sufficient availability of charge carriers. This demonstrates a disproportional enhancement in charge carrier photogeneration efficiency towards applied photon flux [ref]. In fact, the photocurrent density reaches its saturation point when the light density passes 20 mW.cm².

Figure 17A-C presents the time-dependent response of UNN and CFI photodetectors under the illumination of 365 nm, the light density of 1mW.cm⁻² and 0.5V applied bias. For all devices, the photo-current initially increased rapidly and thereafter gradually saturated under illumination, and then descended as the illumination was switched off. Upon light illumination, electron-hole pairs are generated in the ZnO nanostructured film resulting in initial photocurrent overshoot during the light-on cycle. However, this photocurrent is not sustained in the UNN-ZnO sample leading to continuous photocurrent growth decay under steady light illumination (Figure 17a). This is attributed to the competition between charge carrier generation and recombination, when the recombination rate at the deep defect states overcome the electron-hole pairs generation rate at the surface states. As the charge carrier recombination have a longer lifetime, the recombined electrons cannot be generated as fast as recombination occurs, resulting in a decrement in the photocurrent (**Figure 17a**). This is undesirable for many applications. Here, nanostructure modification via CFI process results in a significant enhancement in particles-particles connection and subsequently a higher electrical percolation in CFI nanostructure.

The normalized photocurrent dynamics of UV photodetectors under the bias of 0.5V, and illumination density of 1 mW.cm⁻² is presented in Figure 16D. Rise and decay times were computed from the time taken for the current to increase from 10% to 90% of the peak value and vice versa, respectively. The rise time significantly increases from 30.3s of UNN-ZnO to 96.4 s of CFI-ZnO, while a

reduction in decay time was observed from 43.9s of UNN-ZnO to 11.1s of CFI-ZnO.

In summary, lower the HAB to be 12 cm and UNN thin film with a porosity of 95% can be produced with a unique dendrite-like microstructure on different substrates. UV photodetectors deposited with this UNN ZnO thin film exhibits high photocurrent responsivity of $11.2 \text{ mA} \cdot \text{W}^{-1}$ and fast response kinetics under 70s. Furthermore, simply introducing a drop of ethanol to the UNN ZnO thin film can convert a novel stump-like ZnO micro-cluster network driven by capillary force of ethanol with negligible porosity compromise. The unique patterns formed by the capillary force induced (CFI) self-assembly can create a UV detector having a high photocurrent. In embodiments, when irradiated at 375 nm UV light illumination with a light density of $1 \text{ mW} \cdot \text{cm}^{-2}$ at 1 V, the photocurrent can be about $100 \mu\text{A}$, which is 21-fold higher than flame made UNN ZnO formed under the same conditions without the present process. Meanwhile, the ZnO can have stable and fast UV photodetection kinetics with about 13.4s and about 7.5s for raise and decay times respectively, which is about three and seven times faster, respectively, than the flame made UNN ZnO formed without the present process. Further increase in photocurrent density was observed by adding CNT into the CFI self-assembled films resulting in the photocurrent density of $4.68 \text{ mA} \cdot \text{cm}^{-2}$ of CFI-0.1CNT sample which is 720 times higher than of the pure UNN ZnO. This further improvement in photoreaction performance is ascribed to the superior electron transportation of CNTs in CFI-CNT sample, leading to a quick drift of unpaired electrons to the electrode by external bias voltage. This new technique of employing capillary force to form thin films sheds new light on the avenue towards modifying and manipulating high performance optoelectronic devices and designs.

Other metal oxide thin films and solvents

It should be understood that while ZnO has been used as an exemplary thin metal oxide film, other metal oxides will behave in the same or substantially similar ways. Furthermore, other solvents can achieve the same or a similar effect. The images of **Figures 23** show the effect of DMF solvent on a ZnO film prepared according to the teachings herein. The stump like microstructure can be seen. These structures

are also seen when methanol is used as shown in **Figure 25**. In **Figure 26** conducting polymer is added to the methanol.

5 The ZnO film treated with DMF undergoes a more intense morphological transformation compared to methanol treatment, attributed to DMF's higher capillarity impacts and potentially more intensive chemical interaction with the nanoparticles due to its higher surface tension and polarizability. As a result, DMF-treated ZnO film exhibits higher nanocluster crosslinking, forming corroded tree stump or island microcluster arrays. Each microcluster has an average diameter of
10 10 μm with an estimated 5 μm gap between nearby arrays (**Figure 23**). Conversely, methanol-treated ZnO films display incomplete transformation, with numerous ZnO nanoparticles remaining among the gaps, resulting in a denser layer on the substrate with a mountainous topology and negligible cracks along the ridges. While these microclusters have a similar diameter of 10 μm , the gaps are
15 approximately 10 μm wide as well.

The formation of the micro-clusters on SnO₂ films is shown in **Figure 24** (ethanol) and **Figure 27** (toluene) exemplifying that the teaching herein is not limited only to ZnO films. When SnO₂ is treated with a toluene droplet, the microstructures which
20 form are continental plate-like microclusters joined by ravines. This process yields a flat plate surface with shallow gaps between neighboring coalescent microclusters. While the morphology differs slightly from that of ZnO films treated with a corresponding solvent, the microclusters formed on SnO₂ exhibit similar island-and-valley features, resembling large stumps joined by ravines.

25 It will of course be realized that while the foregoing has been given by way of illustrative example of this invention, all such and other modifications and variations thereto as would be apparent to persons skilled in the art are deemed to fall within the broad scope and ambit of this invention as is herein set forth.

30 It is to be understood that, if any prior art publication is referred to herein, such reference does not constitute an admission that the publication forms a part of the common general knowledge in the art, in Australia or any other country.

In the claims which follow and in the preceding description of the invention, except where the context requires otherwise due to express language or necessary implication, the word “comprise” or variations such as “comprises” or “comprising” is used in an inclusive sense, i.e. to specify the presence of the stated features but
5 not to preclude the presence or addition of further features in various embodiments of the invention.

Any promises made in the present description should be understood to relate to some embodiments of the invention and are not intended to be promises made
10 about the invention as a whole. Where there are promises that are deemed to apply to all embodiments of the invention, the applicant/patentee reserves the right to later delete them from the description and does not rely on these promises for the acceptance or subsequent grant of a patent in any country.

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CLAIMS

1. A process for forming a nanostructured metal oxide micro-cluster, the process comprising the steps of:
 - 5 obtaining a thin film of metal oxide attached to an underlying surface, the thin film having a peripheral edge;
 - adding a droplet of volatile solvent adjacent to the peripheral edge of the thin film;
 - allowing the droplet of volatile solvent to wet the thin film of metal oxide and subsequently evaporate, thereby allowing capillary force induced self-assembly to change the thin film structure.
- 10 2. The process according to claim 1, wherein the metal oxide is selected from one of zinc oxide, tin oxide, titanium oxide and copper oxide.
- 15 3. The process of claim 2, wherein the metal oxide is zinc oxide.
4. The process of any one of the preceding claims, wherein the step of obtaining the thin film of metal oxide comprises forming the thin film of metal oxide by flame spray pyrolysis (FSP).
- 20 5. The process of claim 4 when dependent on claim 3, wherein the height above burner in the FSP process is in the range of from about 9 to about 14 cm, preferably 12cm.
- 25 6. The process of any one of the preceding claims, wherein the volatile solvent used in the adding a droplet step is an alcohol, preferably ethanol.
7. The process of any one of the preceding claims, wherein carbon nanotubes are added to the volatile solvent prior to adding the droplet of volatile solvent.
- 30 8. The process of claim 7, wherein the carbon nanotubes are added in an amount in a range of from about 0.02 to about 0.4 mg.ml⁻¹.

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9. The process of any one of the preceding claims, wherein a conductive polymeric additive is added to the volatile solvent prior to adding the droplet of volatile solvent.
- 5 10. The process of any one of the preceding claims, wherein the step of adding a droplet of volatile solvent comprises adding about 1 μ L of volatile solvent per 0.1 cm² of thin film
- 10 11. The process of any one of the preceding claims, wherein the method further includes the step of annealing the thin film at a temperature of at least about 150, 200, 250 or 300 °C for a period of at least about 6, 10 or 12 hours at ambient pressure.
- 15 12. The process of any one of the preceding claims, wherein the step of obtaining a thin film of metal oxide comprises forming the thin film on an underlying surface comprise interdigitated platinum electrodes (IDE) thereon so that the resultant thin film can be useable as a photodetector
- 20 13. A thin film of metal oxide having stump like micro-clusters of metal oxide distributed over a surface.
14. The thin film of claim 12, wherein the metal oxide is zinc oxide.
- 25 15. The thin film of claim 13, wherein the stump-like clusters have one or more of:
- a. an average height of at least about 12, 16, or 20 μ m.
 - b. an average top diameter of at least about 16, 20 or 24 μ m.
 - c. an average bottom diameter of at least about 20, 25 or 30 μ m.
 - 30 d. an average distance between stumps of at least about 8, 10, 12 μ m.
16. The thin film of any one of claims 12 to 14, wherein each stump is surrounded by at least about 5, 7, 9, 11 other stumps or there are least about 1 million stumps on every mm² of area.
- 35 17. The thin film of any one of claims 12 to 16, wherein the thin film comprises

stump like micro-clusters of metal oxide and carbon nanotubes.

18. The thin film of any one of claims 12 to 17 when formed by the process of any one of claims 1 to 11.

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19. The thin film of any one of claims 12 to 18 wherein the average particle size of the metal oxide is about 16.5 nm.

20. A photodetector comprising the thin film of any one of claims 12 to 19.

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