

METHOD FOR TRANSFERRING GRAPHENE-BASED MATERIALS USING HYDROGEL

FIELD OF THE INVENTION

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Embodiments of the present invention relate to a method for transferring graphenous layer and more particularly to a method for transferring graphene-based materials using hydrogel on a target substrate. Further, it is a facile, efficient, repeatable and environmental friendly method. Also, it provides an advantage of low-production cost.

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BACKGROUND OF THE INVENTION

In recent years, research and development of carbon materials including fullerene, carbon nanotubes, graphite, graphene and graphene oxide (GO) have been actively conducted. Among these, graphene-based materials have been gaining scientific and technical attention because of their versatility in wide range of applications such as in the field of energy, telecommunication, and chemical/biological sensor.

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Numerous techniques for transferring graphene on to target substrate have been developed. Various techniques known in the art for transferring graphene include roll-to-roll method, thermal release tape, hot press, wet etching, wafer scale epitaxial graphene transfer, and micro-patterned elastomeric stamp. Evolvement of the roll-to-roll method has credited merit over the thermal release tape method in minimizing damage of graphene layer. In the roll-to-roll method the graphene layer is removed from polymer by applying heat and pressure. However, subjection of speedy rolling speed induces shear stress which could still cause damage to the graphene layer.

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Conventional method for transferring large area graphene layer includes a wafer on which a graphene layer is grown and is adhered to a polydimethylsiloxane (PDMS) substrate or polymer and while being immersed in an etching solution, the graphene layer is transferred to the PDMS substrate by means of catalytic etching. Through a process of transferring the graphene layer of the PDMS to substrates, such as polyethylene terephthalate, polyimide film,

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and glass, of various electronic devices, the large area transfer of the graphene layer can be made. In this method the catalytic etching is performed in FeCl_3 , $\text{Fe}(\text{NO}_3)_3$, or $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solutions and thus, a lot of time for etching is required.

5 US 20120258311 A1 describes a graphene roll-to-roll transfer method which is capable of transferring a large-area graphene layer to various kinds of flexible and/or extensible substrates, a graphene roll-to-roll transfer apparatus, a graphene roll manufactured by the graphene roll-to-roll transfer method, and uses thereof. The apparatus includes a first roller unit that forms a layered structure
10 including substrate-graphene layer-first flexible substrate and a second roller unit that removes the substrate from the layered structure by immersing the layered structure provided by the first roller unit into an etching solution and transfers the graphene layer onto the first flexible substrate.

15 US 20120244358 A1 describes a method for dry graphene transfer from metal foils. Graphene is grown on a growth substrate and a transfer substrate is chemically modified to enhance its adhesion to graphene. The graphene on the growth substrate is contacted with the transfer substrate and the transfer substrate with attached graphene from the growth substrate is separated. The
20 growth substrate may be copper foil. The transfer substrate may be a polymer, such as polystyrene or polyethylene, or an inorganic substrate.

US 20140174640 A1 describes a method of transferring graphene wherein a sacrificial layer and a graphene layer is formed sequentially on a first substrate.
25 The graphene layer is bonded to a target layer and the sacrificial layer is removed using a laser and then the first substrate is separated from the graphene layer.

In particular, at least one advantage of the conventional method for transferring the layer of graphene-based material is that they can remove the layer
30 of graphene-based material from polymer support and then transfers the layer of graphene-based material on the target substrate. Also, the conventional method uses the graphene which is electrically, mechanically and chemically stable and has excellent conductivity.

While conventional method for transferring the layer of graphene-based material can provide various advantages, such as those described above, conventional methods are limited in various other matters such as damage of the graphene layer resulted from the influences of heat and pressurization leads to deterioration of conductivity of the layer of graphene-based material . Further, these methods can cause cracks, tears, ripples, and folds during growth and cooling process of graphene. Furthermore, these methods require the target substrate to be flat to transfer the graphene from sacrificial substrate. Also, requirement of long-time etching process may result in time inefficiency and high cost in mass production of film and thus, it may be difficult to apply to actual production.

Accordingly, there remains a need in the prior art to have an improved method for transferring graphene-based material which overcomes the aforesaid problems and shortcomings.

However, there remains a need in the art for a method for transferring graphene-based materials such as graphene oxide (GO) using hydrogel on the target substrate of varying degree of contours and geometries. Further, the proposed method is free from etching, heating or use of any hazardous solvents in detaching the layer of graphene-based material from the hydrogel. Also, it is a facile, efficient and environmental friendly method.

DISCLOSURE OF THE INVENTION

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Embodiments of the present invention aim to provide a method for transferring graphene-based materials using hydrogel on the target substrate of varying degree of contours and geometries compared to the conventional method of transferring the layer of graphene-based material onto its target substrate by using heat and pressure. Further, the use of present invention eliminates the risk of any damage to the layer of graphene-based material during its detachment from the hydrogel without the necessity of heating and etching. The method for transferring graphene-based materials is performed by the steps as mentioned in claim 1. The invention may additionally be performed by performing the steps of claim 1 in any appropriate order.

In accordance with an embodiment of the present invention, the method for transferring graphene-based materials comprising the steps of providing a layer of graphene-based material being formed on a holding substrate, pouring a hydrogel solution on the layer of graphene-based material to form a layered structure of graphene-based material-hydrogel having the layer of graphene-based material and a hydrogel layer, peeling off the layered structure of graphene-based material-hydrogel from the holding substrate, immersing the layered structure of graphene-based material-hydrogel into water for initiating release of the layer of graphene-based material from the hydrogel layer and transferring the released layer of graphene-based material onto an active substrate.

In accordance with an embodiment of the present invention, the graphene-based materials are selected from a group consisting of graphene, graphene nanoribbons and graphene oxide (GO). Preferably, the graphene-based material is graphene oxide (GO).

In accordance with an embodiment of the present invention, the graphene oxide (GO) is reduced to form a reduced graphene oxide (rGO). Further, the reduced graphene oxide (rGO) is functionalized to form a functionalized reduced graphene oxide (rGO).

In accordance with an embodiment of the present invention, the functionalization is a covalent functionalization.

In accordance with an embodiment of the present invention, the functionalization is a non-covalent functionalization.

In accordance with an embodiment of the present invention, the functionalized reduced graphene oxide (rGO) has increased solubility in polar solvents.

In accordance with an embodiment of the present invention, the functionalized reduced graphene oxide (rGO) has increased solubility in non-polar solvents.

In accordance with an embodiment of the present invention, the hydrogel layer is having, but not limited to, polyvinyl alcohol (PVA) flakes.

5 In accordance with an embodiment of the present invention, the layered structure of graphene-based material -hydrogel is prepared by effect of Van der Waals forces between the layer of graphene-based material and the hydrogel layer.

10 In accordance with an embodiment of the present invention, the active substrate is selected from, but not limited to, a group consisting of *Indium tin oxide* (ITO) glass, copper foil and aluminum foil. The active substrate has different shapes with different angles ranging from 0-360°. Further, the shapes are, but not limited to, cylindrical, spherical etc.

15 In accordance with an embodiment of the present invention, the holding substrate is, but not limited to, a lidded dish. Preferably, the lidded dish is a petri dish.

20 While the present invention is described herein by way of example using embodiments and illustrative drawings, those skilled in the art will recognize that the invention is not limited to the embodiments of drawing or drawings described, and are not intended to represent the scale of the various components. Further, some components that may form a part of the invention may not be illustrated in
25 certain figures, for ease of illustration, and such omissions do not limit the embodiments outlined in any way. It should be understood that the drawings and detailed description thereto are not intended to limit the invention to the particular form disclosed, but on the contrary, the invention is to cover all modification/s, equivalent/s and alternative/s falling within the scope of the present invention as
30 defined by the appended claim. The headings used herein are for organizational purposes only and are not meant to be used to limit the scope of the description or the claim. As used throughout this description, the word "may" is used in a permissive sense (i.e. meaning having the potential to), rather than the mandatory sense (i.e. meaning must). Further, the words "a" or "an" mean "at least one"
35 unless otherwise mentioned. Furthermore, the terminology and phraseology used

herein is solely used for descriptive purposes and should not be construed as limiting in scope. Language such as "including," "comprising," "having," "containing," or "involving," and variations thereof, is intended to be broad and encompass the subject matter listed thereafter, equivalents, and additional subject matter not recited, and is not intended to exclude other additives, components, integers or steps. Likewise, the term "comprising" is considered synonymous with the terms "including" or "containing" for applicable legal purposes. Any discussion of documents, acts, materials, devices, articles and the like is included in the specification solely for the purpose of providing a context for the present invention.

It is not suggested or represented that any or all of these matters form part of the prior art base or were common general knowledge in the field relevant to the present invention.

In this disclosure, whenever a composition or an element or a group of elements is preceded with the transitional phrase "comprising", it is understood that we also contemplate the same composition, element or group of elements with transitional phrases "consisting of", "consisting", "selected from the group of consisting of", "including", or "is" preceding the recitation of the composition, element or group of elements and vice versa.

DESCRIPTION OF DRAWINGS AND BEST MODE FOR CARRYING OUT THE INVENTION

So that the manner in which the above recited features of the present invention can be understood in detail, a more particular description of the invention, briefly summarized above, may have been referred to embodiments, some of which are illustrated in the appended drawings. It is to be noted, however, that the appended drawing illustrate only typical embodiments of this invention and are therefore not to be considered limiting of its scope, for the invention may admit to other equally effective embodiments.

These and other features, benefits and advantages of the present invention will become apparent by reference to the following text figure, with like reference numbers referring to like structures across the views, wherein:

Fig. 1(a) to 1(d) are perspective views illustrating method of transferring graphene oxide (GO) via hydrogel formation in accordance with an embodiment of the present invention.

5 Fig. 2 is a graph showing CV profiles of (a) 0.5 M GO, 1.0 M GO, 1.5 M GO, and GO on bare ITO (b) 1.5 M GO drop casted and transferred on ITO glass (c) photographic images of transferred GO on ITO glass slides.

10 Fig. 3 is a graph showing CV profiles of (a) bare Cu, 1.5 M transferred GO, and 1.5 M drop casted GO (b) bare Al, 1.5 M transferred GO, and 1.5 M drop casted GO on Cu and Al substrates, respectively (c) Images of bare Cu foil and Al foil, transferred GO, and drop casted GO on different substrates.

15 The present invention is described hereinafter by various embodiments with reference to the accompanying drawing, wherein reference numerals used in the accompanying drawing correspond to the like elements throughout the description. This invention may, however, be embodied in many different forms and should not be construed as limited to the embodiment set forth herein. Rather, the embodiment is provided so that this disclosure will be thorough and
20 complete and will fully convey the scope of the invention to those skilled in the art. In the following detailed description, numeric values and ranges are provided for various aspects of the implementations described. These values and ranges are to be treated as examples only, and are not intended to limit the scope of the claims. In addition, a number of materials are identified as suitable for various
25 facets of the implementations. These materials are to be treated as exemplary, and are not intended to limit the scope of the invention.

Embodiments of the present invention aim to provide a method for transferring graphene-based materials using hydrogel on the target substrate of
30 varying degree of contours and geometries. The present invention is able to provide an alternative method for transferring graphene-based materials to replace the conventional method of transferring graphene by using heat and pressure. Further, the disclosed method eliminates the risk of any damage to the layer of graphene-based material during its detachment from the hydrogel. The
35 layer of graphene-based material is transferred to the target substrate such as

ITO glass, copper foil and aluminum foil without the necessity of heating and etching. Furthermore, it is a facile, efficient, repeatable and environmental friendly method. Also, it provides an advantage of low-production cost.

5 Referring to the drawings, the invention will now be described in more detail. In accordance with an embodiment of the present invention, the method (100) for transferring graphene-based materials, as shown in in figure 1, comprising forming a layer of graphene-based material (102) on a holding substrate (104) and
10 pouring a hydrogel solution on the layer of the graphene-based material (102) to form a layered structure of graphene-based material-hydrogel (106) having the layer of graphene-based material (102) and a hydrogel layer (108). Further, the layered structure of graphene-based material-hydrogel (106) is peeled off from the holding substrate (104) and immersed into water for initiating release of the layer of graphene-based material (102) from the hydrogel layer (108). Furthermore, the
15 released layer of graphene-based material (102) is transferred onto an active substrate (110).

As shown in figure 1(a) hydrogel is spread on a dried layer of graphene-based material and is left to dry. Subsequently, figure 1(b) shows immersion of
20 layered structure of graphene-based material-hydrogel (106) that is performed to initiate detachment of the layer of graphene-based material (102) from the hydrogel layer (108). The hydrogel gets swollen upon immersion in water to weaken the adhesiveness of graphene-based material-hydrogel interface, as shown in figure 1(c). Detached graphene-based material film is finally transferred
25 onto an ITO glass for cyclic voltammetry investigation, as shown in figure 1(d). Hydrogel has tense cross-linked networks, which arises as an excellent water swollen yet non-dissolvable gel. This is due to its hydrophilic functional groups that are aligning along the polymer backbone, which acted as water molecules absorbing enhancements, while the firm cross-linked between network chains
30 restrains the dissolution of hydrogel in water. Thus, swollen hydrogel weakens the adhesion force on graphene-based material surface and enabled the layer of graphene-based material (102) to be peeled off from the hydrogel layer (108) with ease.

In accordance with an embodiment of the present invention, the hydrogel layer (108) includes polyvinyl alcohol (PVA) flakes. The PVA flakes were stirred on hot plate stirrer with the supply of sufficient heat so that these flakes get dissolved.

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In accordance with an embodiment of the present invention, the layered structure of graphene-based material-hydrogel (106) is formed by the effect of Van der Waals forces between the layer of graphene-based material (102) and the hydrogel layer (108).

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In accordance with an embodiment of the present invention, the active substrate (110) is selected from, but not limited to, the group consisting of ITO glass, copper foil and aluminum foil. The active substrate has different shapes with different angles ranging from 0-360°. Further, the shapes are, but not limited to, cylindrical, spherical etc.

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In accordance with an embodiment of the present invention, the holding substrate (104) is, but not limited to, a petri dish. The graphene-based material is prepared in the petri dish by Hummer's method and left to dry. Graphene-based material possesses large surface area which enhances the charge transfer performance, owing to the ease and surmount of electrolyte ions facilitation. The hydrogel solution is poured on dried layer of graphene-based material and it is also left to dry to form a stacked structure of layer of graphene-based material-hydrogel layer.

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In accordance with an embodiment of the present invention, the graphene-based materials are selected from a group consisting of graphene, graphene nanoribbons and graphene oxide (GO). Preferably, the layer of graphene-based material (102) is graphene oxide (GO) layer.

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In accordance with an embodiment of the present invention, the graphene oxide is reduced to form reduced graphene oxide (rGO). Reduced graphene oxide (rGO) has properties similar to graphene such as conductivity.

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In accordance with an embodiment of the present invention, the reduced graphene oxide (rGO) is functionalized to form a functionalized reduced graphene oxide (rGO). The reduced graphene oxide (rGO) is covalently and non-covalently functionalized. The functionalized reduced graphene oxide (rGO) has increased solubility in polar and non-polar solvents that enables adhesion with the hydrogel layer (108). Further, it is able to restore the porosity of graphenous framework and thus prevents agglomeration of rGO sheets due to loss of oxygenous groups. In addition, it enhances hydrogen bond interlocking between the functionalized rGO and the hydrogel.

Hereinafter, an example of the present invention will be provided for more detailed explanation.

EXAMPLES

Example 1

1. Preparation of graphene oxide (GO)

The graphene oxide (GO) was prepared via Simplified Hummer's method, where oxidation reaction was carried out by mixing H_2SO_4 : H_3PO_4 (360 ml:40 ml), graphite flakes, and KMnO_4 at room temperature. This mixture was stirred for 3 days to allow complete oxidation of the graphite. H_2O_2 was added to the mixture to cease the oxidation process and the color of mixture turned bright yellow. Graphite oxide was then washed with 1 M HCl aqueous solution 3 times and with deionized water 10 times using centrifugation technique until a pH of 4-5 was achieved and GO was formed.

2. Preparation of hydrogel

0.1- 20% of polyvinyl alcohol (PVA) was prepared and stirred on hot plate stirrer at ambient temperature ranging from room temperature to 200°C to dissolve PVA flakes. 0.1-20 M potassium hydroxide solution was prepared. Preferably, 1 M of potassium hydroxide (KOH) solution and 1 ml of glycerin were then added and stirred for homogeneity.

3. Preparation of graphene oxide (GO) transfer

0.5 M, 1.0 M, and 1.5 M of GO was prepared in a petri dish and was left to dry. The prepared hydrogel solution as described in above protocol was poured on dried GO surface and left to dry. The GO-hydrogel could be easily peel off from the petri dish, thus transferring the layer of GO onto the hydrogel. A small piece of GO thin film was cut and was immersed in water to initiate release of the GO from hydrogel. Detached GO layer was then transferred to an ITO glass, copper foil and aluminum foil.

4. Electrochemical Measurements

Electrochemical performances of transferred graphene oxide films were investigated using cyclic voltammetry (CV) via VersaSTAT 3 electrochemical system (Princeton Applied Research). CV test was performed using a three-electrode system, in which the transferred substrate was used as a working electrode, an Ag/AgCl electrode worked as a reference electrode, and a platinum wire as a counter electrode in the range of -0.1 to -0.8 V (versus reference electrode) at scan rates of 50 mV/s.

Results

1. Cyclic voltammetry study

Cyclic voltammetry (CV) tests were performed to investigate capacitive behavior of the transferred substrates at the scan rate of 50mV/s in the range of -0.1 V to -0.8 V in Dulbecco's phosphate buffered saline, which acted as an electrolyte. Figure 2(a) reflects the influences of GO concentration against the electrocatalytic-activity of transferred GO. A nearly rectangular voltammograms of 0.5 M, 1.0 M, and 1.5 M GO on ITO glasses were displayed, as shown in figure 2(a), an indication of the contribution of the electrical double layer capacitance (EDLC) nature of graphenous layer, in which the EDLC attributes to the cyclic stability performances. In addition, it shows that the loop of 1.5 M GO voltammogram is the largest as opposed to 1.0 M GO and 0.5 M GO, respectively. This phenomenon could be due to the thickness of GO that enhances the facilitation of electrolyte ions. The formation of an almost rectangular voltammogram, regardless of its surface area, firmly displayed the enduring catalytic activity of transferred GO. In addition, a comparison

has been made between bare ITO, transferred GO (1.5 M) via hydrogel formation and direct drop casted GO (1.5 M) on the ITO glass to prove the workability of hydrogel transfer method, as depicted in figure 2(b). The manifestation of an almost ideal voltammogram of both methods hence proved the sustainability, sensitivity, and workability of electrocatalytic-activity performances of GO even after the transfer as the conductivity of both the loops (transferred GO via hydrogel formation and direct drop casted GO in figure 2(b)) portrayed an indistinguishable alteration. Photographic images of transferred GO at various concentrations are depicted in figure 2(c).

Figure 3(a) and (b) present CV profiles of directly transferred and drop casted techniques of GO (1.5 M) on copper and aluminum foils, respectively at scan rate of 50 mV/s to gauge the versatility of transfer technique on different substrate surfaces. Likewise, both the techniques depicted nearly identical voltammograms as shown in figure 3(a) and (b). Synchronicity of the voltammograms of directly transferred and drop casted GO proves the sustainability of the electroactivity of transferred GO, regardless of the substrates being used.

The CV analysis has proven the efficiencies, sustainability, workability, and versatility of GO transfer via hydrogel formation technique as the sensitivity and electroactivity of GO were able to be retained significantly. Figure 3(c) shows the images of bare substrates, transferred and drop casted GO on various substrates.

Conclusion

A method for transferring graphene-based materials using hydrogel has been successfully performed by transferring GO thin film from hydrogel to ITO glass, copper and aluminum foils. The CV voltammograms have provided firm evident to prove the workability of this method, as seen the conductivity of GO film is still preserving. This method is expected to be applicable to all graphenous materials such as rGO, graphene, functionalized graphene and graphene-based nanocomposites as the exertion of Van der Waals forces, electrostatic repulsion, and hydrogen bond formation between grapheneuos and hydrogel interfaces

render adhesion excellency. The thickness of grapheneous materials can be controlled. Further, the method is facile, environmental friendly and provides an advantage of low-cost. Also, the method, without the usage of toxic solvents and etchants, is envisioned to be able to produce large scale graphene-based films
5 that are able to fulfill industrial demands.

The exemplary implementation described above is illustrated with specific shapes, dimensions, and other characteristics, but the scope of the invention includes various other shapes, dimensions, and characteristics. Also, the method
10 for transferring graphene-based materials using hydrogel as described above could be fabricated in various other ways and could include various other materials, including various other substrates, electrodes, polymers etc.

Similarly, the exemplary implementations described above include specific
15 examples of substrates, electrodes, polymers etc., but a wide variety of other such steps of fabrication could be used within the scope of the invention, including additional steps, omission of some steps, or performing process in a different order.

Various modifications to these embodiments are apparent to those skilled in
20 the art from the description and the accompanying drawings. The principles associated with the various embodiments described herein may be applied to other embodiments. Therefore, the description is not intended to be limited to the embodiments shown along with the accompanying drawings but is to be providing
25 broadest scope of consistent with the principles and the novel and inventive features disclosed or suggested herein. Accordingly, the invention is anticipated to hold on to all other such alternatives, modifications, and variations that fall within the scope of the present invention and appended claim.

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CLAIMS

1. A method for transferring graphene-based materials, comprising the steps of:
 - 5 providing a layer of graphene-based material (102) being formed on a holding substrate (104);
pouring a hydrogel solution on said layer of graphene-based material (102) to form a layered structure of graphene-based material-hydrogel (106) having said layer of graphene-based material (102) and a hydrogel layer (108);
 - 10 peeling off said layered structure of graphene-based material-hydrogel (106) from said holding substrate (104);
immersing said layered structure of graphene-based material-hydrogel (106) into water for initiating release of said layer of graphene-based material (102) from said hydrogel layer (108); and
 - 15 transferring said released layer of graphene-based material (102) onto an active substrate (110).
2. The method as claimed in claim 1, wherein said graphene-based materials are selected from a group consisting of graphene, graphene nanoribbons and
20 graphene oxide (GO).
3. The method as claimed in claim 1, wherein said layer of graphene-based material is a graphene oxide (GO) layer.
- 25 4. The method as claimed in claim 2, wherein said graphene oxide (GO) is reduced to form a reduced graphene oxide (rGO).
5. The method as claimed in claim 4, wherein said reduced graphene oxide (rGO) is functionalized to form a functionalized reduced graphene oxide (rGO).
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6. The method as claimed in claim 5, wherein said functionalization is a covalent functionalization.
7. The method as claimed in claim 5, wherein said functionalization is a non-
35 covalent functionalization.

8. The method as claimed in claim 5, wherein said functionalized reduced graphene oxide (rGO) has increased solubility in polar solvents.

5 9. The method as claimed in claim 5, wherein said functionalized reduced graphene oxide (rGO) has increased solubility in non-polar solvents.

10. The method as claimed in claim 1, wherein said hydrogel layer (108) is having polyvinyl alcohol (PVA) flakes.

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11. The method as claimed in claim 1, wherein said layered structure of graphene-based material -hydrogel (106) is prepared by effect of Van der Waals forces between said layer of graphene-based material (102) and said hydrogel layer (108).

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12. The method as claimed in claim 1, wherein said active substrate (110) is selected from a group consisting of *Indium tin oxide* (ITO) glass, copper foil and aluminum foil.

20 13. The method as claimed in claim 12, wherein said active substrate has different shapes with different angles ranging from 0-360°.

14. The method as claimed in claim 12, wherein said active substrate is of cylindrical shape.

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15. The method as claimed in claim 12, wherein said active substrate is of spherical shape.

30 16. The method as claimed in claim 1, wherein said holding substrate (104) is a lidded dish.

17. The method as claimed in claim 16, wherein said lidded dish is a petri dish.

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