

MULTIFUNCTIONAL SUPERHYDROPHILIC AND UNDERWATER
SUPEROLEOPHOBIC ACTIVATED GLASS DERIVED FROM WASTE GLASS

Cross-Reference To Related Application

- 5 [0001] This application claims the benefit of priority of Singapore Patent Application No. 10201606456U, filed 4 August 2016, the content of it being hereby incorporated by reference in its entirety for all purposes.

Technical Field

- 10 [0002] The present disclosure relates to a glass material which is superhydrophilic at least in air and superoleophobic when submerged in water. The present disclosure also relates to one or more methods for making such a glass material.

Background

- 15 [0003] The fast growing global energy demand and industrial production have intensified the exploitation of crude oil. In the meantime, increased oil leakage and oil spill accidents have become one of the top environmental concerns. Marine resources are quite vulnerable to such anthropogenic disasters. For example, the Exxon Valdez massive oil spill accident brought fatal damage to nearly 300,000 living species in the habitat, and its long-term ecological impact still remains. Therefore, oil/water separation is an emerging and rapidly growing concern.

- 20 [0004] Conventional countermeasures to massive oil spill accidents include degradation with chemical dispersants, in-situ burning, vacuum suction, and polymer oil absorbents. However, these methods tend to be expensive, inefficient and may cause secondary pollution. More importantly, it is almost impossible to reclaim the precious oil resources with these conventional methods. The development of novel materials that can separate oil/water mixture in a selective, efficient and eco-friendly manner is thus a pressing topic.

- 25 [0005] In recent years, novel materials with special wettability (or special wettable materials) have been developed as promising materials for selective oil/water separation. Special wettable materials refer to materials that have opposite affinity towards water and oil. Specifically, two kinds of special wettable materials are
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suitable for oil/water separation, i.e. hydrophobic and oleophilic materials (i.e. “hate” water and “like” oil), and hydrophilic and oleophobic materials (i.e. “like” water and “hate” oil). In order to further promote separation efficiency and practical applicability of these two types of special wettable materials, significant amount of efforts have been devoted to enhance the wetting and anti-wetting properties to super-wetting and super-anti-wetting properties.

[0006] From a theoretical perspective of mathematical equations and model, wetting behavior is determined by surface chemistry of materials and further enhanced via suitable surface architectures. For example, if surface tension of a material is lower than that of water and higher than those of oil(s) [i.e. between surface tension of water and oil(s)], the material tends to show hydrophobicity and oleophilicity. With a suitable surface texture, wetting behavior of a material may be tuned to become superhydrophobic and superoleophilic.

[0007] Guided by the above principle, significant amount of research have been carried out to develop novel materials with super-wetting and super-anti-wetting properties, inter alia, superhydrophobic and superoleophilic materials being most commonly explored and reported. For the present disclosure, this type of material is referred herein as *type 1 materials*.

[0008] *Type 1 materials* tend to have high affinity towards oils and repel water at the same time. Therefore, in oil/water separation process (e.g. a filtration process), the oil phase may pass through a filter of *type 1 material* while water phase may be retained. However, there are several severe problems with *type 1 materials* in terms of their practical applications.

[0009] Firstly, due to their high affinity towards oils, filters are likely to foul more easily, especially so when processing real viscous spilled oil. This leads to costly maintenance and frequent replacement of filters. A second issue that may occur when superhydrophobic *type 1 materials* are fully adsorbed with oil on their surface is that they lose their superhydrophobicity, in turn compromising separation efficiency. Thirdly, reported methods for fabrication of superhydrophobic *type 1 materials* are extremely complicated (i.e. multiple reaction stages), expensive and environmentally toxic e.g. most of their methods and approaches require corrosive reagents (strong acid or base) and highly toxic elements (sulfur, fluorine etc.).

[0010] To solve the first two issues of *type 1 materials*, hydrophilic and oleophobic materials have been explored. This type of materials tend to have high affinity towards water and repel oil at the same time (referred herein as *type 2 materials*). The water phase thus passes through *type 2 materials* while oil phase is retained.

5 [0011] From a chemistry point of view, to fabricate *type 2 materials*, the material itself should have a surface energy higher than water and lower than oil at the same time. However, this requirement is theoretically impossible to satisfy, as water has a higher surface tension than most oils. For this reason, only a handful of work have been reported for *type 2 materials*, and unfortunately, these reported works are based
10 on complex multi-constituent polymers that are extremely complicated and expensive to make.

[0012] More recently, superhydrophilic and underwater superoleophobic materials (denoted herein as *type 3 materials*), which overcome problem of oil-fouling, have been proposed. By creating suitable surface architectures on the hydrophilic materials,
15 superhydrophilic materials may be achieved. A superhydrophilic material in air typically demonstrates superoleophobic property when submerged under the water. This is because the superhydrophilic surface tends to trap water molecules onto its hierarchical surface structure to reach a low-energy state. When in contact with oil, since it is energetically unfavorable for oil to replace water molecules, the *type 3*
20 *materials* tend to display superoleophobicity under water. These *type 3 materials* have thus attracted intensive research attention.

[0013] Conventionally, there are two approaches to fabricate *type 3 materials*. In the first approach, hydrophilic polymers are coated onto a rough substrate. In the second approach, high surface energy metal oxides are grown onto substrates. Unfortunately,
25 there are several major hurdles to these two approaches.

[0014] Regarding the first approach, preparation of special polymers is expensive and this approach's scalability is not reportedly known. The polymers are also destroyed under high temperature, which make them practically non-usable for processing most industrial oil/water mixtures that tend to be at elevated temperatures of about 80°C to
30 90°C. Regarding the second approach of using metal oxide, expensive metal precursors and complicated preparation process are required. In addition, effluent from such production process contains excess metal ions (e.g. Zn^{2+} , Cu^{2+} , etc.) which

damage the environment. Apart from these issues, preparation methods that require etchants to create surface architectures may be harmful to the environment as the etchants may be corrosive.

5 [0015] Having discussed the research status of various materials for oil/water separation, it is vital to note that water contamination by heavy metal ions and soluble organics is another critical problem which calls for innovative solutions. In many industries, their effluent may contain both insoluble oils and soluble ions. In this regard, conventional wastewater treatment processes require several stages to treat different contaminants separately. Such treatment processes are expensive and require
10 large footprint.

[0016] To overcome the issues as mentioned above, there is thus a need to provide for multifunctional material(s) that can separate oil/water mixture and remove soluble water contaminants at the same time. The multifunctional material needs to be superhydrophilic (at least in air) and superoleophobic (when submerged in water) to
15 resolve and/or ameliorate the issues mentioned above.

[0017] There is also a need to provide for one or more methods to synthesize such multifunctional superhydrophilic (at least in air) and superoleophobic (when submerged in water) materials which ameliorate one or more of the issues as mentioned above.

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Summary

[0018] In one aspect, there is provided for a glass material which is superhydrophilic at least in air and superoleophobic when submerged in water, wherein the glass material comprises a porous layer comprising interconnected silica fibers.

25 [0019] In another aspect, there is provided for a method for making a glass material which is superhydrophilic at least in air and superoleophobic when submerged in water, comprising: providing a dispersion comprising silica particles in a powder form dispersed in an organic solvent or aqueous solvent; coating the dispersion on a substrate; drying the coated substrate; and subjecting the dried substrate to a
30 hydrothermal treatment for less than 24 hours in the presence of an aqueous medium.

[0020] In another aspect, there is provided for a method for making a glass material which is superhydrophilic at least in air and superoleophobic when submerged in

water, comprising: providing silica particles in a powder form; and subjecting the silica particles in the powder form to a hydrothermal treatment for less than 24 hours in the presence of an aqueous medium.

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Brief Description of the Drawings

[0021] The drawings are not necessarily to scale, emphasis instead generally being placed upon illustrating the principles of the invention. In the following description, various embodiments of the present disclosure are described with reference to the following drawings, in which:

10 [0022] FIG. 1 is a schematic illustration of the preparation process for the activated glass (AG) coated stainless steel (SS) mesh filter, starting from raw glass slides. The AG coated SS mesh may be called a superhydrophilic and underwater superoleophobic (SHUWSO) SS mesh or an AG coated SHUWSO SS mesh as described herein.

15 [0023] FIG. 2a shows a scanning electron microscope (SEM) image of a pristine SS mesh (100 mesh). The scale bar represents 100 μm .

[0024] FIG. 2b shows a SEM image of AG coated SHUWSO SS mesh. The scale bar represents 100 μm and the magnification is 100x.

20 [0025] FIG. 2c shows a higher magnification SEM image of the AG coated SHUWSO SS mesh of FIG. 2b. The scale bar represents 10 μm and the magnification is 750x.

[0026] FIG. 2d shows an even higher magnification SEM image of the AG coated SHUWSO SS mesh of FIG. 2b. The scale bar represents 500 nm and the magnification is 35000x.

25 [0027] FIG. 2e shows the energy-dispersive X-ray spectroscopy elemental mapping result of Fe element for the AG coated SS mesh. The scale bar represents 200 μm .

[0028] FIG. 2f shows the energy-dispersive X-ray spectroscopy elemental mapping result of the uniformly coated glass (AG) (i.e. the SHUWSO glass) on SS mesh. The scale bar represents 200 μm .

30 [0029] FIG. 2g is a transmission electron microscopy (TEM) image showing the wire-shaped activated glass. The scale bar represents 200 nm and the magnification is

6000x. These wire-shaped activated glass may be called glass fibers or silica fibers in the present disclosure.

[0030] FIG. 2h is a higher magnification TEM image of FIG. 2g. The scale bar represents 50 nm and the magnification is at 50000x. The higher magnification TEM image of FIG. 2h revealed that the micro-wires are made of bundles of even smaller nanofibers. The inset of FIG. 2h shows the Selected Area Electron Diffraction (SAED) pattern of one of the smaller nanofibers. This SAED pattern is taken via a TEM equipment. The pattern shows the crystallinity of the nanofiber rather than its morphology, which indicates that the nanofibers (and hence the present AG material) are amorphous. The scale bar of the SAED inset represents 2 nm^{-1} .

[0031] FIG. 2i shows a plot of the X-ray diffraction (XRD) patterns indicating that the AG (i.e. SHUWSO) material of the present disclosure has a structure that is amorphous, which is same as raw glass powder.

[0032] FIG. 3a shows the water contact angle in air for the SHUWSO mesh.

[0033] FIG. 3b shows the underwater oil (chloroform) contact angle for the SHUWSO mesh.

[0034] FIG. 3c shows the water contact angle in air for pristine SS mesh.

[0035] FIG. 3d shows the underwater oil contact angle for pristine SS mesh.

[0036] FIG. 4a shows a SEM image of the AG coated SS mesh (i.e. SHUWSO SS mesh) before hydrothermal treatment (i.e. 0 hour). The magnification of FIG. 4a and its inset is 5000x and 10000x, respectively. The scale bars of FIG. 4a and its inset represent $1 \mu\text{m}$.

[0037] FIG. 4b shows a SEM image of the AG coated SS mesh after hydrothermal treatment of 2 hours. The magnification of FIG. 4b and its inset is 5000x and 10000x, respectively. The scale bars of FIG. 4b and its inset represent $1 \mu\text{m}$.

[0038] FIG. 4c shows a SEM image of the AG coated SS mesh after hydrothermal treatment of 6 hours. The scale bar represents $1 \mu\text{m}$.

[0039] FIG. 4d shows a SEM image of the AG coated SS mesh after hydrothermal treatment of 10 hours. The scale bar represents $1 \mu\text{m}$.

[0040] FIG. 4e shows a SEM image of the AG coated SS mesh after hydrothermal treatment of 24 hours. The magnification of FIG. 4e and its inset is 5000x and 10000x, respectively. The scale bars of FIG. 4e and its inset represent $1 \mu\text{m}$.

[0041] FIG. 4f shows a plot of the water capture percentage of the AG coated SS meshes with different hydrothermal treatment durations compared to original SS mesh.

5 [0042] FIG. 5a shows a SEM image of the porous structure of an original AG product (i.e. the SHUWSO material). The scale bar represents 1 μm .

[0043] FIG. 5b shows a SEM image of the porous structure of the AG product after being heated at 300°C for 2 hours. The scale bar represents 1 μm .

[0044] FIG. 5c shows a SEM image of the porous structure of the AG product after being submerged in acid solution (pH 1) for 10 days. The scale bar represents 1 μm .

10 [0045] FIG. 5d shows a SEM image of the porous structure of the AG product after being submerged in basic solution (pH 14) for 10 days. The scale bar represents 1 μm .

[0046] FIG. 5e shows the underwater oil contact angle measurements for the AG coated SS mesh with different oils and organic solvents.

15 [0047] FIG. 6a shows a SEM image of AG coated SHUWSO mesh prepared from a glass container (see inset of FIG. 6b). The scale bar represents 10 μm and the magnification is 2000x.

[0048] FIG. 6b shows a higher magnification SEM image of the AG coated SHUWSO mesh of FIG. 6a. The scale bar represents 1 μm and the magnification is 10000x. The inset shows a glass container.

20 [0049] FIG. 6c shows a SEM image of AG coated SHUWSO mesh prepared from laboratory petri dish (see inset of FIG. 6d). The scale bar represents 10 μm and the magnification is 2000x.

25 [0050] FIG. 6d shows a higher magnification SEM image of the AG coated SHUWSO mesh of FIG. 6c. The scale bar represents 1 μm and the magnification is 10000x. The inset shows a glass petri dish.

[0051] FIG. 7a shows a SEM image of superhydrophilic and underwater superoleophobic material with AG coated on cotton fabrics. The scale bar represents 100 μm and the magnification is 100x. The inset is a SEM image of FIG. 7a at higher magnification of 2300x and the inset scale bar represents 10 μm .

30 [0052] FIG. 7b shows a SEM image of superhydrophilic and underwater superoleophobic material with AG coated on filter papers. The scale bar represents

100 μm and the magnification is 200x. The inset is a SEM image of FIG. 7b at higher magnification of 2700x and the inset scale bar represents 10 μm .

[0053] FIG. 7c shows a SEM image of superhydrophilic and underwater superoleophobic materials with AG coated on polyvinylidene fluoride (PVDF) membranes. The scale bar represents 100 μm and the magnification is 200x. The inset is a SEM image of FIG. 7c at higher magnification of 5000x and the inset scale bar represents 5 μm .

[0054] FIG. 8 shows digital photographs depicting the process (from left to right) of oil/water separation using AG coated SS mesh. The layered oil/water mixture was prepared with hexane (dyed with Oil Red) and water (dyed with methylene blue) at a volume ratio 1:2. The filter was pre-wetted with water. The hexane is retained by the mesh, while water freely passes through the mesh. The entire separation process is completed within 15 seconds.

[0055] FIG. 9a is a photo of a lab-scale prototype designed device of a colander incorporated with the AG mesh.

[0056] FIG. 9b is a photo of the process of collecting oil from oil/water mixture using the device of FIG. 9a, specifically dipping the device into the oil/water mixture.

[0057] FIG. 9c is a photo of the process of collecting oil from oil/water mixture using the device of FIG. 9a, specifically lifting up the device and the water leaks from the mesh bottom.

[0058] FIG. 9d is a photo of the process of collecting oil from oil/water mixture using the device of FIG. 9a, specifically transporting the retained oil. The inset is a close up photo showing that only oil is retained by the device of FIG. 9a.

[0059] FIG. 10a is a SEM image of the 500 mesh AG filter for separation of oil-in-water emulsion. The scale bar represents 100 μm and the magnification is 100x.

[0060] FIG. 10b is a higher magnification SEM image of the filter of FIG. 10a where the mesh holes are completely sealed with only pores of several micrometers left, which are formed by the porous network of AG. The scale bar represents 10 μm and the magnification is 500x.

[0061] FIG. 10c is an even higher magnification SEM image of the filter of FIG. 10b where the mesh holes are completely sealed, with only pores of several micrometers

left, which are formed by the porous network of AG. The scale bar represents 1 μm and the magnification is 5000x.

[0062] FIG. 10d is an optical microscope image showing the oil droplet before filtration. The scale bar represents 10 μm .

5 [0063] FIG. 10e is a digital photograph showing the oil/water emulsion before (left) and after (right) filtration.

[0064] FIG. 10f is an optical microscope image showing the absence of oil droplets after filtration. The scale bar represents 10 μm .

10 [0065] FIG. 11a shows digital photographs of the oil/water separation and removal of methylene blue from water via one filtration process.

[0066] FIG. 11b shows the UV-vis absorbance spectra of the water before and after filtration. The insets show digital photographs of the oil/water mixture with methylene blue contaminated water (left), the filtered water processed through the mesh after filtration (middle), and the mesh after the filtration process.

15 [0067] FIG. 12a shows the Zeta potential characterization of the AG.

[0068] FIG. 12b shows the FTIR spectra of raw glass and AG.

[0069] FIG. 13a shows adsorption capacity of AG for various heavy metal ions.

20 [0070] FIG. 13b shows the UV-vis absorbance spectra of water before and after adsorption of methylene blue by the AG adsorbents. The inset photographs show the water before (left) and after (right) adsorption process.

[0071] FIG. 13c shows time profile of adsorption kinetics for Pb^{2+} with initial concentration of 500 mg L^{-1} . The inset shows a fitting of pseudo-second-order adsorption kinetics by plotting (t/Q_t) against time, wherein t stands for time and Q_t stands for the amount of adsorbate per adsorbent at time t .

25 [0072] FIG. 13d shows time profile of adsorption kinetics for methylene blue with initial concentration of 200 mg L^{-1} . The inset shows a fitting of pseudo-second-order adsorption kinetics by plotting (t/Q_t) against time, wherein t stands for time and Q_t stands for the amount of adsorbate per adsorbent at time t .

30 [0073] FIG. 13e shows digital photographs of the AG adsorbent fabricated into various shapes using suitable moulds.

[0074] FIG. 14a shows the underwater oil sliding angle measurement. Specifically, 3 μl chloroform droplet could easily move and roll off the AG coated surface within 2°

of stage tilting. The arrow in the middle picture indicates the direction of the oil droplet movement. The oil droplet rolls off the AG mesh at very small tilting angle.

[0075] FIG. 14b shows the underwater oil adhesion measurement. Specifically, 5 μ l chloroform suspended on the needle tip is contacted with the AG coated surface and then released. The arrows indicate the moving direction of the stage. The oil droplet shows almost no adhesion on AG mesh.

[0076] FIG. 14c shows pristine steel mesh as a comparison to FIG. 14a where the oil droplet does not roll off the pristine steel mesh easily even at 50°.

[0077] FIG. 14d shows pristine steel mesh as a comparison to FIG. 14b where the oil droplet adheres to the pristine steel mesh upon contact and breaks away from the needle tip.

[0078] FIG. 15a shows the underwater oil contact angle (UWOCA) measurements of AG coated SS mesh (and their respective insets) against various corrosive organic solvents.

[0079] FIG. 15b shows the UWOCA measurements of AG coated SS mesh against various annealing temperatures.

[0080] FIG. 15c shows the UWOCA measurements (left vertical axis) and residual oil content (in ppm) (right vertical axis) of the AG coated SS mesh against various pH.

[0081] FIG. 15d shows the residual oil content in water filtered through the AG coated SS mesh for 5 cycles usage after subjected to various conditions (organic solvent treatment with THF, high temperature treatment and strong acid treatment).

[0082] FIG. 16a is an image of AG showing stable underwater superoleophobicity when directly immersed in 1 M HCl.

[0083] FIG. 16b is an image of AG showing stable underwater superoleophobicity when directly immersed in 1 M NaCl.

[0084] FIG. 16c is an image of AG showing stable underwater superoleophobicity when directly immersed in 1 M NaOH.

[0085] FIG. 17a shows a plot of the oil content in filtrate obtained from various layered oil/water mixture and oil/water emulsion using AG on 100 SS mesh and AG on 500 SS mesh.

[0086] FIG. 17b shows a plot of the oil content in filtrate obtained from a layered oil/water mixture and an oil/water emulsion for 5 cycles using AG on 100 SS mesh and AG on 500 SS mesh.

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Detailed Description

[0087] The following detailed description refers to the accompanying drawings that show, by way of illustration, specific details and embodiments in which the invention may be practised. These embodiments are described in sufficient detail to enable those skilled in the art to practise the invention. Other embodiments may be utilized and changes may be made without departing from the scope of the invention. The various
10 embodiments are not necessarily mutually exclusive, as some embodiments can be combined with one or more other embodiments to form new embodiments.

[0088] Features that are described in the context of an embodiment may correspondingly be applicable to the same or similar features in the other
15 embodiments. Features that are described in the context of an embodiment may correspondingly be applicable to the other embodiments, even if not explicitly described in these other embodiments. Furthermore, additions and/or combinations and/or alternatives as described for a feature in the context of an embodiment may correspondingly be applicable to the same or similar feature in the other
20 embodiments.

[0089] The present disclosure provides for a glass material which is superhydrophilic at least in air and superoleophobic when submerged in water, wherein the glass material comprises a porous layer comprising interconnected silica fibers.

[0090] The present disclosure also provides for one or more methods for making such
25 a glass material. Embodiments described in the context of the glass material are analogously valid for the method(s) described herein, and vice versa. The presently described glass material may be called an activated glass (AG) because it is produced or treated, based on the method(s) described herein, to become superhydrophilic at least in air and superoleophobic when submerged in water.

30 [0091] The as-developed AG technology, i.e. the present glass material and method(s), is low-cost compared with existing methods. Waste glass as the raw material and pure water as the etchants are used. These are cheaper compared to

existing materials and methods utilizing either synthetic polymers or metal oxide as precursors, which are much more expensive.

[0092] The as-developed AG technology is environmental friendly compared to existing methods. Existing methods tend to require heavy metal ions as precursors that
5 lead to water contamination by their effluent. Some existing methods require corrosive chemicals and solvents during the etching process to create surface architectures. The present method(s) and the present glass material are environmentally friendly because they are derived from non-toxic solid waste i.e. waste glass, and only water is used as the etchant.

10 [0093] Advantageously, the as-developed AG technology, when being coated onto stainless steel (SS) meshes and used as filters, separates different oil/water mixtures, including both layered oil/water mixtures and oil/water emulsions. A layered oil/water mixture is one where the oil and water are formed as discrete layers whereas an oil/water emulsion is a mixture where the oil phase may be encapsulated in the water
15 phase or vice versa. For example, the oil may exist as a droplet in water. Such an oil droplet may or may not contain water internally. In another example, the water may exist as the droplet in oil. The water droplet may or may not contain oil internally. The separation of various types of oil/water mixtures is possible because the present method effectively controls the sealing and opening of the mesh holes, while
20 maintaining a porous AG networks. In contrast, conventional mesh-based filters are generally not applicable for separation of oil/water emulsions due to their larger filter holes' size when compared to the small oil droplet in the emulsion.

[0094] The as-developed AG technology is also multifunctional in that it separates oil/water mixtures and removes water soluble contaminants at the same time through
25 adsorption. In addition, a high performance AG adsorbent can be fabricated through the present method without coating onto a SS mesh, demonstrating the present method is also versatile.

[0095] The as-developed AG technology is further advantageously stable under harsh working conditions, including high temperatures, extreme acidic and alkaline
30 conditions. Conventional *type 3 materials* are not able to withstand high temperatures or corrosive environments. The exact temperature at which conventional *type 3* materials fail may vary according to the materials. For example, polymer hydrogel

based *type 3* materials tend to be specifically stable at room temperature while metal hydroxide based *type 3* materials tend to gradually decompose when temperature exceeds 200°C, or even 100°C.

5 [0096] The as-developed AG technology, when being used as AG filters, can be prepared on various different substrates, including but not limited to, SS meshes, filter papers, cotton fabrics, polymeric membranes etc.

[0097] The as-developed AG technology, when being used as AG adsorbent, demonstrated better adsorption performance compared to other conventional low-cost and natural adsorbents e.g. activated carbon.

10 [0098] Having outlined various advantages of the present glass material and method(s), definitions of certain terms are first discussed before going into details of the various embodiments.

[0099] In the context of the present disclosure, the term “superhydrophilic” refers to a material having a water contact angle less than 5°.

15 [00100] In the context of the present disclosure, the phrase “superoleophobic” refers to a material having an oil contact angle of more than 150°.

[00101] In the context of the present disclosure, the phrase “underwater oil contact angle” refers to the contact angle measured for a material with respect to an oil droplet when the material is immersed in an aqueous solution or a mixture comprising an aqueous medium.

20 [00102] The word “substantially” does not exclude “completely” e.g. a composition which is “substantially free” from Y may be completely free from Y. Where necessary, the word “substantially” may be omitted from the definition of the invention.

25 [00103] In the context of various embodiments, the articles “a”, “an” and “the” as used with regard to a feature or element include a reference to one or more of the features or elements.

[00104] In the context of various embodiments, the term “about” or “approximately” as applied to a numeric value encompasses the exact value and a reasonable variance.

30 [00105] As used herein, the term “and/or” includes any and all combinations of one or more of the associated listed items.

[00106] As used herein, the phrase of the form of “at least one of A and B” may include A or B or both A and B. Correspondingly, the phrase of the form of “at least one of A and B and C”, or including further listed items, may include any and all combinations of one or more of the associated listed items.

5 [00107] Unless specified otherwise, the terms "comprising" and "comprise", and grammatical variants thereof, are intended to represent "open" or "inclusive" language such that they include recited elements but also permit inclusion of additional, unrecited elements.

[00108] Having defined the various terms as mentioned above, details of the various
10 embodiments are now described below.

[00109] In the present disclosure, there is a glass material which is superhydrophilic at least in air and superoleophobic when submerged in water, wherein the glass material comprises a porous layer comprising interconnected silica fibers. The glass material described as superhydrophilic at least in air implies that the glass material is
15 also superhydrophilic when submerged in water or aqueous medium. This allows the present glass material to filter off oil and water soluble contaminants when water passes through the present glass material.

[00110] The presently described glass material may be known interchangeably as a superhydrophilic and underwater superoleophobic (SHUWSO) glass material in the
20 present disclosure. This abbreviated terminology has already been explained above. To reiterate, the present glass material may be referred to as SHUWSO because it is a superhydrophilic material in air that demonstrates superoleophobic property when submerged in water. The superhydrophilic surface tends to trap water molecules onto its hierarchical surface structure to reach a low-energy state. When in contact with oil,
25 since it may be energetically unfavorable for oil to replace water molecules, the present glass material then displays superoleophobicity under water.

[00111] According to various embodiments, the present glass material may comprise at least one type of glass. A non-limiting example is waste glass. The present glass material is thus environmentally sustainable because it can be constructed from waste
30 glass material.

[00112] Regardless of the type of glass material used, the present glass material may comprise or consist of a porous layer. This porous layer, in many embodiments, may

comprise or may be formed from a network of interconnected glass fibers. Interconnected glass fibers may refer to glass fibers that are linked to each other in no particular order or in a haphazard manner. In other words, the interconnected glass fibers do not exist in any arranged nor organized manner. The interconnected fibers may also include intertwined glass fibers. Intertwined glass fibers specifically refer to glass fibers that may be bundled and/or twisted together. In various embodiments, the porous layer may comprise or consist of interconnected fibers.

[00113] The interconnected and/or intertwined glass fibers may comprise or consist of silica. In various embodiments, the interconnected glass fibers may be interconnected silica fibers. These silica fibers form a three-dimensional (3D) network of silica fibers, thereby forming the porous layer. The porous layer may have a rough surface due to the network of silica fibers. The network of silica fibers may attract water more strongly compared to non-silica fibers and/or silica that is not of the fiber form, thereby making the water purification process more stable. These silica fibers may be known as micro-wires in the present disclosure. These micro-wires may have diameter larger than 100 nm.

[00114] The porous layer of interconnected silica fibers may be superhydrophilic at least in air and superoleophobic when submerged in water. In this regard, the porous layer may have a water contact angle less than 5° according to various embodiments. The porous layer may have an underwater oil contact angle more than 150° or at least 153° in the same embodiments. This range of oil contact angle may be present in other embodiments. With these water and oil contact angles, the porous layer is thus superhydrophilic at least in air and superoleophobic when submerged in water. This implies the porous layer is capable of repelling oil and adsorbing water-soluble contaminants while allowing water to pass through. In other words, apart from filtration, the present glass material is usable for adsorption.

[00115] Regarding the silica fibers, they may have a diameter of 100 nm to 200 nm, 100 nm to 150 nm or 150 to 200 nm. In the present disclosure, the term “diameter” when used to describe the glass and silica fibers, may be used interchangeably with the term “width”.

[00116] Regarding the silica fibers, they may comprise or consist of SiO_2 . In various embodiments, the silica fibers, however, may not be pure SiO_2 as they may be derived

from waste glass materials. Waste glass materials may contain metal ions, which may include those of, but not limited to, alkali metals or alkaline earth metals. Such metal ions may include Na^+ , K^+ , Ca^{2+} , Mg^{2+} and/or Al^{3+} etc. Accordingly, in certain embodiments, the silica fibers may comprise Na^+ , K^+ , Ca^{2+} , Mg^{2+} and/or Al^{3+} . These metal ions, advantageously, can be exchanged with heavy metal ions, thus reducing heavy metal ion pollutants in water or other process streams to be treated. In contrast, pure SiO_2 fibers absent of such metal ions may lack the ability to remove the heavy metal ions from wastewater through such ion exchange mechanism and rely on adsorption of heavy metal ion pollutants instead. Apart from containing such metal ions, as the present glass material is producible from waste glass, it is more economical compared to conventional materials that require costly precursors e.g. tetraethyl orthosilicate (TEOS).

[00117] When the present glass material is used in water separation processes, by virtue of its superhydrophilicity and superoleophobicity, it advantageously purifies water from a mixture comprising water, oil(s) and water soluble contaminants at the same time, i.e. without the need to separately filter the oil and water soluble contaminants.

[00118] The oil may be in the form of a layered oil/water mixture and/or oil/water emulsion. The oil may comprise petroleum, canola oil, pump oil, hexane, chloroform etc. Other organic substances not miscible with water may be present in the oil, and such organic substances may be separated by the present glass material.

[00119] The water soluble contaminants may comprise heavy metal ions and water soluble organic dyes. The heavy metal ions may be pollutants that exist in waste and wastewater. The heavy metal ions may be known to a person skilled in the art. Such heavy metal ions may include, but not limited to, arsenic, cadmium, chromium, copper, iron, lead, mercury, silver, or other metal ions that may be toxic when ingested by mammals. Meanwhile, water soluble organic dyes may comprise or may be selected from the group consisting of methylene blue, basic organic dyes and cationic dyes. Basic organic dyes may include organic dyes that are likely to be stable in alkaline solutions, e.g. up to pH 14. Cationic dyes may also be alkaline. Non-limiting examples of cationic dyes may include azo dyes, triarylmethane dyes,

anthraquinone dyes, and dyes composed of heterocyclic compounds. Such basic organic dyes and cationic dyes may be known to a person skilled in the art.

[00120] To filter water, the present glass material may be used as it is, i.e. standalone glass material. In other embodiments, the present glass material may further comprise
5 or consist of a substrate, wherein the porous layer of interconnected silica fibers may be deposited or coated on the substrate. The substrate, advantageously, provides better mechanical strength, flexibility and further serves as an additional filter layer where the pore sizes and shapes can be selected, thereby making it conveniently integrable into other devices.

10 [00121] The substrate may be selected from the group consisting of a metal mesh, a filter paper, a cotton fabric and a polymeric membrane. The metal mesh may be a stainless steel mesh.

[00122] In the present disclosure, there is also a method for making a glass material which is superhydrophilic at least in air and superoleophobic when submerged in
15 water, comprising: providing a dispersion comprising silica particles in a powder form dispersed in an organic solvent or aqueous solvent; coating the dispersion on a substrate; drying the coated substrate; and subjecting the dried substrate to a hydrothermal treatment for less than 24 hours in the presence of an aqueous medium.

[00123] The present method leads to production of intertwined/interconnected silica
20 fibers as described above. These silica fibers form a 3D porous network with a rough surface which holds water more strongly as compared to conventional materials. Meanwhile, conventional processes may require additional step(s) just to even achieve silica fibers that do not even have the SHUWSO property. Even with additional step(s), conventional processes may not achieve the interconnected silica fibers as
25 described herein due to rigidity of silica materials. Conventional processes may also lead to pure SiO₂ which lack the ability to remove heavy metal ions from water through the exchange mechanism as mentioned. The present method is, accordingly, advantageous over conventional processes.

[00124] In the step of providing the dispersion, this step may comprise cleaning a
30 glass precursor material with water and/or an alcohol, and/or subjecting the glass precursor material to ball milling to obtain the silica particles in the powder form. Advantageously, providing silica particles in the powder form speeds up subsequent

reaction(s) or processes as the powder form has higher surface area compared to glass or glass precursor materials in their bulk shape form (i.e. those that have not undergone any size reduction process or reduced to a powder form). The silica particles (e.g. in powder form) may then be dispersed in an organic solvent or aqueous solvent to form the dispersion.

[00125] The glass precursor material may comprise at least one type of glass material. That is to say, the present glass material may be made from any type of glass precursor material, i.e. a single glass precursor material or a mixture of glass precursor materials. A non-limiting example of such a glass precursor material may include waste glass. Another example of a glass precursor material may be objects made of glass, such as a laboratory microscope glass slide etc. The method is thus versatile and environmentally sustainable in that the present glass material can be constructed from any type of glass precursor materials (e.g. glass based materials), including utilizing only waste glass, thereby offering the opportunity for recycling waste glass materials. Waste glass materials may comprise metal ions as described above, which do not lose its ability for extracting heavy metal ion pollutants from water when such waste glass materials are processed via the present method.

[00126] As the glass precursor material may be of a size that is not immediately usable for the present method e.g. for coating onto a substrate, there is then the need to reduce the size of the glass precursor material. In this regard, apart from ball milling as mentioned above, other size reduction means known to a skilled person may be used. Any crushing and/or grinding machine capable of reducing size of the glass precursor material known to a person skilled in the art may be used. By reducing size of the glass precursor material, subsequent fabrication steps may be easier and/or faster because smaller sizes of glass precursor material have higher surface area for reaction e.g. with water during hydrothermal treatment.

[00127] The present method, which involves a size reduction step, may be called a top down approach. In such top down approach, the size reduction process is physically carried out without any chemical reaction, advantageously circumventing expensive precursors or harmful reagents commonly used in conventional bottom up approach. Whereas in bottom up approaches, silica particles may be synthesized from liquid polymer precursors (e.g. TEOS) in the presence of ammonia, which inevitably

renders waste glass unexploitable since such bottom up approaches do not include any means to reduce size of waste glass. The present method, on the other hand, is a top down approach that allows for recycling of waste glass into a highly porous network of silica fibers with SHUWSO property.

5 **[00128]** In various embodiments where ball milling is adopted, the ball milling may be carried out in two sequential stages. For example, the ball milling may be conducted at a low-speed milling of 150 rpm to 250 rpm for 30 minutes followed by high-speed milling of 550 rpm to 650 rpm for 30 minutes. This advantageously prevents densification and solid-state sintering of the silica particles. The silica
10 particles may also be called glass powders or silica powders in the present disclosure because they may exist in the powder form after a size reduction process, such as ball milling. The milling speed and duration may be selected by a person skilled in the art based on processing needs.

[00129] The silica particles in the powder form may comprise metal ions as described
15 above. According to certain embodiments, the silica particles (e.g. powder form) may not be pure SiO_2 but may comprise metal ions such as Na^+ , K^+ , Ca^{2+} , Mg^{2+} and/or Al^{3+} etc. These ions additionally allow extraction of heavy metal ions via the exchange mechanism as disclosed above.

[00130] After obtaining the silica particles, they may be dispersed in an organic
20 solvent or aqueous solvent to form the dispersion as mentioned above. The organic solvent may be an alcohol. The organic solvent may comprise acetone, ethanol and/or methanol. Meanwhile, the aqueous solvent may comprise water.

[00131] Thereafter, the dispersion may be coated onto a substrate. This coating step may be repeated for more than once, or for 2 to 5 times to control loading of the silica
25 particles (e.g. in powder form) on the substrate. The substrate has already been described above. The coating step may be carried out by dipping the tip of a brush in the dispersion and then painting the substrate with the dipped brush so as to deposit the silica particles onto the substrate. Other deposition or coating means known to a skilled person, capable of depositing the silica particles onto the substrate, may be
30 applied. For instance, spray coating, dip coating or drop casting may be employed. Although dip coating may be used, the quality (e.g. uniformity and loading amount) of such a coating method may be lower compared to the brush coating used herein.

This is because dip coating may produce unevenly spread portion(s) such that a portion of the dip coated dispersion exists as an undesirable chunk of particles. In another conventional method such as layer by layer (LBL) assembly, it may be similar to dip coating except for more repeated cycles carried out and involving use of electrostatically attractive co-coating species. This means two materials are needed to form coated silica particles instead of just using a glass precursor material to form silica particles (e.g. in the form of powder).

[00132] After coating the substrate, the coated substrate may be dried. The drying may be carried out above room temperatures to accelerate the production process. The temperatures may be between 80°C to 200°C (including 80°C and 200°C) or any other temperatures falling within this range. Advantageously, the drying does not need to take place in any special environment. For example, the drying does not require an inert environment. Higher drying temperatures above 200°C may require special oven or equipment while lower drying temperatures below 80°C may require longer duration.

[00133] Once the coated substrate is dried, the dried substrate may be subjected to hydrothermal treatment in the presence of an aqueous medium. The aqueous medium may comprise or consist of water. The water may be deionized water. The water may remain as liquid water throughout hydrothermal treatment and hence steam is not needed.

[00134] The hydrothermal treatment may be carried out in an autoclave. The hydrothermal treatment may be carried out between 150°C to 200°C (including 150°C and 200°C), and/or for less than 2 hours, less than 6 hours, less than 10 hours or even less than 24 hours. If the duration goes above 24 hours, the porous layer of interconnected silica fibers (i.e. the 3D network of silica fibers) may collapse. If temperature below 150°C is used, the hydrothermal reaction may not proceed or may require significantly longer duration, meaning that the interconnected silica fibers may not be formed. On the other hand, temperatures above 200°C may accelerate interconnected silica fibers formation but specialized autoclaves may be required.

[00135] During hydrothermal treatment, the silica particles may be etched by the aqueous medium while converting to silica fibers. This creates the interconnected porous network of silica fibers. Advantageously, only the aqueous medium, which

may consist only of water, is required to produce the present 3D porous network of interconnected silica fibers.

[00136] In the present disclosure, there is further, a method for making a glass material which is superhydrophilic at least in air and superoleophobic when submerged in water, comprising: providing silica particles in a powder form; and
5 subjecting the silica particles in the powder form to a hydrothermal treatment for less than 24 hours in the presence of an aqueous medium. Advantageously, providing silica particles in the powder form speeds up subsequent reaction(s) or processes as the powder form has higher surface area compared to glass or glass precursor
10 materials in their bulk shape form (i.e. those that have not undergone any size reduction process or reduced to a powder form).

[00137] In some embodiments, the glass material may be a glass adsorbent. The present method is advantageous for making a glass adsorbent of the present glass material because it can do so without the steps associated with coating i.e. preparation
15 of silica particles in dispersion, coating the dispersion onto a substrate and then drying the substrate. That is to say, the silica powders can be subjected to hydrothermal treatment directly. The resultant adsorbent is especially effective for removing heavy metal ions and dyes from water.

[00138] In various embodiments of the further method, the providing step may
20 comprise subjecting a glass precursor material to ball milling to obtain the silica particles in the powder form. The glass precursor material has been described above.

[00139] In various embodiments where ball milling is adopted, the ball milling may be carried out in two sequential stages. For example, the ball milling may be conducted at a low-speed milling of 150 rpm to 250 rpm for 30 minutes followed by
25 high-speed milling of 550 rpm to 650 rpm for 30 minutes. This advantageously prevents densification and solid-state sintering of the silica particles (e.g. in their powder form). Other milling speeds and duration may be used.

[00140] The silica particles in their powder form may contain pure SiO_2 in some embodiments. In other embodiments, the silica particles in their powder form may not
30 be pure SiO_2 and may comprise metal ions as described above. Such metal ions may include, but not limited to, Na^+ , K^+ , Ca^{2+} , Mg^{2+} and/or Al^{3+} . These metal ions allow for extracting heavy metal ions in waste and wastewater by way of ion exchange

mechanism. In this regard, the present method, which allows for recycling of waste glass containing such metal ions, advantageously produces silica fibers that can additionally extract heavy metal ions by ion exchange instead of solely through adsorption, when purifying water.

- 5 **[00141]** When making the adsorbent, the silica particles (e.g. powders) may be subjected to hydrothermal treatment carried out between 150°C to 200°C (including 150°C and 200°C), and/or for less than 2 hours, less than 6 hours, less than 10 hours or even less than 24 hours. If the duration goes above 24 hours, the porous layer of interconnected silica fibers (i.e. the 3D network of silica fibers) may collapse. If
10 temperatures below 150°C is used, the hydrothermal reaction may not proceed or may take a significantly longer time. On the other hand, temperatures above 200°C may accelerate interconnected silica fibers formation but specialized autoclaves may be required.

- [00142]** During hydrothermal treatment, the silica particles (e.g. in powder form) may
15 be etched by the aqueous medium while converting to silica fibers. This creates the interconnected porous network of silica fibers. Advantageously, only the aqueous medium, which may consist only of water, is needed to produce the present silica fibers. The aqueous medium may comprise or consist of water. The water may be deionized water. The water may remain as liquid water throughout hydrothermal
20 treatment and hence steam is not needed.

- [00143]** While the methods described above are illustrated and described as a series of steps or events, it will be appreciated that any ordering of such steps or events are not to be interpreted in a limiting sense. For example, some steps may occur in different orders and/or concurrently with other steps or events apart from those
25 illustrated and/or described herein. In addition, not all illustrated steps may be required to implement one or more aspects or embodiments described herein. Also, one or more of the steps depicted herein may be carried out in one or more separate acts and/or phases.

Examples

[00144] There are at least three major aspects of breakthroughs that the present superhydrophilic (at least in air) and superoleophobic (when submerged in water) glass material, and the present method(s), provide over conventional technologies.

5 [00145] First, the as-developed superhydrophilic and underwater superoleophobic (SHUWSO) AG as well as the method(s) are highly environmentally sustainable. This is because solid municipal waste can be utilized as the raw materials (i.e. waste glass) for making the present glass material. This not only converts waste into useful materials but also reduces the problem of land invasion by solid waste. So far,
10 preparation of super-wetting or super-anti-wetting materials using waste materials is not reportedly known. The present disclosure unconventionally utilizes common solid waste as raw materials to fabricate SHUWSO. More importantly, the entire preparation process uses only water as the etchant and does not involve corrosive and/or toxic solvents that are inevitable in reported methods and materials.

15 [00146] Second, the as-developed AG is multifunctional. As will be shown in the examples below, the AG not only separates various kinds of oil/water mixtures but also removes soluble water contaminants (soluble organic dyes, heavy metal ions etc.) from water. More excitingly, the simultaneous separation of oil from water and the purification of the permeated water can be achieved at one go. This is not reportedly
20 demonstrated.

[00147] Third, the as-developed AG is extremely stable under various harsh working conditions, such as high temperature and extreme pH conditions. As the practical application conditions are very likely to be at elevated temperatures, and in the presence of corrosive water, the present AG exhibits high potential for practical usage
25 in such harsh environment. This, again, is hardly achieved by conventional materials. As an example, polymer based *type 3 materials* are generally unstable at high temperature while metal oxide based *type 3 materials* are easily corroded under acidic conditions. The major component of our AG being silica, makes the present material very stable against high temperature and most strong acids. Although silica may be
30 etched by base, it is an extremely slow process which makes the etching almost non-existent, and therefore the present AG is regarded as stable in basic solution as well.

As shown in the examples below, the AG is not destroyed when immersed in NaOH solution (pH 14) for 10 days.

[00148] Apart from these three major breakthroughs, the as-developed AG shows many other advantages over existing technologies, such as being low-cost, and generally applicable on different types of substrates, which are elaborated in the examples below.

[00149] Example 1: An Exemplary Embodiment of the Present Method Using Glass Slide

[00150] In a non-limiting example of the present method, optical microscope glass slides were used as the starting materials for fabrication of multifunctional activated glass (AG). This type of glass was selected as its chemical constituents are known and is the most suitable representative of waste glass. The present method developed is also suitable and/or compatible using other glasses, which is shown in further examples below. Details of the present method are now described.

[00151] The glass slides were first sonicated in deionized water and ethanol to remove dirt on the slide surfaces. Then, the cleaned glass slides were ground into powders using a ball milling machine. The ball milling process was performed in two sub-steps: a low-speed milling at 200 rotation per minute (rpm) for 30 minutes, followed by high-speed milling at 600 rpm for another 30 minutes. Through this specific manner, the resultant glass powders then possess relatively smaller sizes with a narrower size distribution. These parameters are carefully adjusted to prevent densification and solid-state sintering of glass powders during milling process. After milling, the transparent glass slides turned into white glass powders.

[00152] To fabricate a superhydrophilic and underwater superoleophobic (SHUWSO) AG filter, the as-prepared glass powders were first weighed and then dispersed into ethanol to form a uniform dispersion with concentration of about 2 mg ml⁻¹ to 10 mg ml⁻¹. A brush was dipped into the glass powder dispersion whose tip is to be fully soaked with the glass powder. Then, the glass powder dispersion, which functioned as the “ink”, was “painted” onto various substrates using the brush, e.g. stainless steel (SS) meshes, paper filter, cotton fabrics, polymeric membranes etc. The “dipping and painting” process could be repeated for 1 to 5 times in order to control amount of glass powder loading required. Instead of this painting method, the coating process

can also be achieved by a spray coating method. Subsequently, the glass powder coated substrates were completely dried in an oven using temperatures around 80°C to 200°C, depending on the substrate used. The drying process simultaneously promotes stronger adhesion between glass powder coatings and substrate. After the glass powder coated filters were dried, they were hydrothermally treated with 10 ml deionized (DI) water in a 20 ml autoclave at about 180°C for 2 hours to 24 hours. After the hydrothermal process, the resultant SHUWSO AG filters were taken out from the autoclave and dried for subsequent characterizations and applications. The entire fabrication process is illustrated in FIG. 1.

10 **[00153] Example 2: Scanning Electron Microscope (SEM) and Water Contact Angle (WCA) Characterization**

[00154] A non-limiting example of the present SHUWSO AG filter based on stainless steel (SS) mesh as the substrate was characterized in detail and is used as a representative illustration herein.

15 **[00155]** FIG. 2a shows that the surface of the pristine SS mesh (100 mesh) is quite smooth. On the contrary, surface of the SHUWSO AG coated SS mesh is very rough (FIG. 2b). High magnification SEM image reveals that the SHUWSO mesh surface is fully covered with intertwined micro-wires, which are about 100 nm to 200 nm in width. The micro-wires interconnect with each other to form a 3D porous network, which creates a rough and porous architecture on the coated SS fibrous surface (FIG. 2c and FIG. 2d).

[00156] Due to the highly porous network, the mesh surface becomes very rough and the as-obtained mesh showed superhydrophilicity (at least in air) and underwater superoleophobicity. The water droplet can quickly spread over the mesh surface within 1 second, with a WCA of 0°, indicating superhydrophilicity (FIG. 3a). When the mesh is submerged in water, an oil droplet can form a spherical shape standing on the mesh surface, with an underwater oil contact angle (UWOCA) of around 153°, indicating its superoleophobicity under the water (FIG. 3b).

25 **[00157]** As a comparison, the pristine raw SS mesh shows hydrophobic property in air (WCA of about 120°) and underwater oleophilic property (UWOCA of about 20°) (FIG. 3c and FIG. 3d), which are completely different from the SHUWSO mesh made from AG.

[00158] The above characterizations confirm a successfully fabricated superhydrophilic (at least in air) and underwater superoleophobic mesh using waste glass.

[00159] Additionally, the EDX results of FIG. 2e and FIG. 2f demonstrate the AG is successfully and uniformly coated on the steel fibers of the SS mesh. The TEM images of FIG. 2g and FIG. 2h further illustrate the wire-shaped activated glass. The XRD results of FIG. 2i show the structure of AG is amorphous, which is the same as glass.

[00160] **Example 3: Characterization by Water Capture Ability and Hydrothermal Treatment Duration**

[00161] More detailed characterization of the filter described above is presented in this example.

[00162] The water capture ability is another key criteria to evaluate the affinity of the mesh towards water. The water capture percentage increased with duration of the hydrothermal process until around 10 hours. When the hydrothermal process was further continued to more than 24 hours, the water capture percentage drops. In order to understand this, SEM characterizations on the AG coated mesh samples for different hydrothermal durations were carried out.

[00163] From FIG. 4a to FIG. 4e, morphological change of AG coated meshes is clearly observable for different hydrothermal durations. Before hydrothermal treatment, the glass particles are coated on the surface of the SS fibers, with a relatively smooth surface observed (FIG. 4a). After 2 hours of hydrothermal treatment, surface of the glass particles becomes much rougher (FIG. 4b). With further hydrothermal processing, the micro-sized wires start to form on the top of the glass coatings (FIG. 4c). After 10 hours of hydrothermal treatment, all glass particles transformed into micro-sized wires which interconnect with each other to form a porous network (FIG. 4d).

[00164] However, if the hydrothermal process is carried out for 24 hours or more, the micro-sized wires start to fuse together and the porous network collapses (FIG. 4e). Based on the above characterizations, it is deduced that the highly porous network is responsible for the high water capture ability of the as-developed mesh. It is also important to note that for all AG coated SS meshes subjected to different

hydrothermal durations, their water capture abilities are higher than that of the pristine SS mesh (FIG. 4f).

[00165] Example 4a: Structural Characterization with Different pH

[00166] Currently, two approaches have been conventionally adopted to fabricate *type 3 materials*, which are coating of hydrophilic polymers onto rough substrates and growth of metal oxide or hydroxide onto substrates. The materials fabricated from either approach are, however, unstable against certain environment e.g. the polymers in the first approach tend to be deformed or even decomposed under high temperature while the metal oxide or hydroxide in the second approach is easily corroded under acidic condition. These are concerns in practical applications, especially wastewater treatment sectors, where oily water is usually present or processed at elevated temperatures to promote their thermal separation, and to decrease viscosity of the wastewater. Moreover, it is common that wastewater to be treated is not at neutral pH level. This highlights the importance of developing *type 3 materials* with excellent stability under harsh conditions.

[00167] On the other hand, the as-developed AG of the present disclosure is stable at high temperature and extreme pH conditions. As shown in FIG. 5b, the interconnected micro-wires maintained its porous structure after being heated at 300°C for 2 hours, thereby demonstrating excellent thermal stability. In addition, the unique micro-wired porous structure is retained after the AG was submerged into strong acidic (pH 1) and strong basic solutions (pH 14) for 10 days, thereby demonstrating excellent pH stability (FIG. 5c and FIG. 5d, respectively). Hence, the AG promotes continuous passage of water even at different conditions.

[00168] Example 4b: Characterization with Different Oils and Organic Solvents

[00169] More oils and organic solvents are tested using the AG coated SS mesh. The AG coated SS mesh shows superhydrophilic (at least in air) and underwater superoleophobic property for all the tested oils and solvents in FIG. 5e. The underwater superoleophobic property is observed when oil contact angle measured for a material submerged in water [i.e. underwater oil contact angle (UWOCA)] is more than 150°. The present glass materials with superhydrophilic (at least in air) and underwater superoleophobic property are advantageous in that they effectively separate any form of oil/water mixtures by specifically letting water permeate while

repelling oil and/or other contaminants, which in turn reduce fouling of filters composed of such glass materials at the same time, thereby reducing maintenance cost of such filters.

[00170] Example 5: Applicability with Different Waste Glass

5 **[00171]** In practical situations, instead of a glass slide as exemplified above, waste glass is likely to be a mixture of different types of waste glass that are being disposed from various sources. Notably, the as-developed method of the present disclosure for fabrication of AG also works for other types of waste glass. For example, as shown in FIG. 6b and FIG. 6d, two other types of waste glass, i.e. household glass cups and
10 laboratory petri dishes, can be recycled and processed into AG coated SHUWSO mesh. Similarly, the highly interconnected and porous network of micro-wires are clearly observed on the surface of SS fibres (FIG. 6a and FIG. 6c). This demonstrates that the present method(s) is advantageously versatile in that a wide range of waste glass for obtaining the practically usable AG coated SHUWSO mesh as disclosed
15 herein can be utilized instead of being limited to a specific type of glass.

[00172] Example 6: Applicability with Different Substrates

[00173] Although the above characterizations were performed based on SS mesh substrate, different kinds of substrates can also be coated with AG. Each type of substrate offers its unique advantages, and therefore, according to different
20 application requirements, different substrates can be chosen. For example, metal mesh offers high filtration flux and rigid mechanical property, filter papers and cotton fabrics offer flexibility while polymeric membranes allow the size control of micro-pores. Therefore, it is vital that the as-developed materials and method(s) of the present disclosure are compatibly functional with or applicable onto various substrates
25 to modify the substrates' wetting property into superhydrophilic and underwater superoleophobic. FIG. 7a to FIG. 7c show the SEM images of three different substrates after hydrothermal processing of the AG coating. Similarly, a rough surface with porous architectures is observed.

[00174] Example 7a: Commercial Application as Filter Material - Separation of
30 **Layered Oil/Water Mixture**

[00175] Layered oil/water mixture is frequently encountered in cases such as crude oil spill over the sea, oil drilling process, food processing industries etc. It is thus of significant importance to be able to separate floating oil from water.

[00176] Conventionally, superhydrophobic filters are fabricated to selectively
5 separate layered oil/water mixture by letting oil phase pass through the filters while blocking the water phase. This approach, however, suffers from two fatal problems. First, due to oleophilic property of the superhydrophobic filter, such filters tend to interact strongly with the oil, and the filters are thus easily fouled by the oil, which significantly reduces the filtration rate. Second, for many superhydrophobic materials,
10 once the surface is wetted by oil, they tend to lose their ability to repel water and become wettable by water. In this case, separation efficiency is significantly compromised. These problems are overcome by the superhydrophilic and underwater superoleophobic filters (SHUWSO) of the present disclosure.

[00177] Such SHUWSO filter can selectively let water pass through while blocking
15 the oil. When the filter is wetted by water, water can be trapped within the porous rough surface of the filters. Due to its strong affinity towards water, it is energetically unfavorable for the oil to replace the captured water film, which renders such type of filter superoleophobic in water. Therefore, the filter can hardly be fouled by oil during the filtration separation process. FIG. 8 shows the separation process of layered
20 oil/water mixture. Even though the oil was first poured into the funnel, it cannot pass through the mesh and is retained above. However, as soon as the water came into contact with the mesh, it immediately flows through. Due to the large grid holes (i.e. the gaps between the woven steel fibers) of 100 mesh stainless steel, water permeates the filter very rapidly. 14 ml of water passes through the filter in about 4 seconds,
25 corresponding to an extremely high water flux of about $62667 \text{ L h}^{-1} \text{ m}^{-2}$, which is larger than traditional membrane-based filtration process. It is also very important to note that the separation process is purely driven by gravity of the water itself, without any external pressure applied. Therefore, such separation process using the as-developed mesh is highly energy conservative.

30 [00178] **Example 7b: Commercial Application in a Filter Device - Separation of Layered Oil/Water Mixture**

[00179] Besides the usage of AG mesh in a filtration assembly, in order to widen the AG mesh's potential in more applications, a new device design utilizing the mesh is developed. As shown in FIG. 9a to FIG. 9d, a lab-scale prototype is demonstrated. The tub is constructed from solid wall, with its bottom sealed by the superhydrophilic and underwater superoleophobic AG mesh. The tub is connected to a mechanical arm or handler. The overall lab-scale prototype resembles the shape of a “colander”.

[00180] When the device is dipped into and subsequently lifted up from the oil/water mixture, the tub is filled with the oil/water mixture. Since the bottom of tub is a mesh that is superhydrophilic, the water quickly leaks out, specifically leaving behind the oil in the device. The captured oil can then be easily transferred to other containers by the arm. In such a way, the oil layer above the water is easily removed and collected for desired storage. Advantageously, this kind of device can provide more insight into alternatives and serves as a powerful alternative for cleaning up oil spill over the sea.

[00181] **Example 8: Commercial Application - Separation of Oil/Water Emulsion**

[00182] Besides the layered oil/water mixture, oil/water emulsion is another type of mixture that is more frequently encountered in oil refinery industry and in wastewater effluent. The efficient separation of oil/water emulsion is of significant importance in terms of environmental protection. Traditionally, oil/water emulsion is separated using polymeric membranes. However, as polymeric membranes are easily fouled by the oils, the separation efficiency is thus low. On the other hand, conventional mesh based filter fails to effectively separate oil/water emulsions due to their much larger holes than the oil droplets. Accordingly, the developed preparation method as disclosed herein offers the ability of controlling the amount of glass powder coated onto the mesh substrate, which allows a mesh to be conveniently prepared with all the mesh holes sealed by simply increasing amount of the coatings.

[00183] FIG. 10a to FIG. 10c show the SEM images of a 500 mesh completely coated with AG derived from waste glass. High magnification SEM images reveal that although the mesh holes were completely sealed, the porous network formed by the interconnected micro-sized wires still exists. Water could still pass through the porous filter. However, the oil droplets will be blocked.

[00184] FIG. 10e shows an oil-in-water emulsion purified after passing through the filter. Before filtration, the emulsion appears to be milky white and opaque, due to the light scattering effect by the large amount of small oil droplets within the emulsion. However, after filtration, the filtrate becomes colorless and transparent, indicating removal of oil droplets.

[00185] Furthermore, optical microscopic characterizations of the emulsion before and after filtration were performed (FIG. 10d and FIG. 10f). It is clearly observed that the oil droplets of diameter ranging from a few tens of micrometers to hundreds of micrometers can all be removed from the feed emulsion after filtration with the AG mesh filter of the present disclosure, which is one of the major advantages compared to known mesh-based filters that are not successfully applicable for separating oil/water emulsions (due to limitation of their fabrication method which can hardly seal the mesh hole completely while producing micro-sized pores at the same time).

[00186] Example 9: Commercial Application - Removal of Water Soluble Contaminants

[00187] In various modern production industries, it is not uncommon that their effluent discharge contains multiple pollutants, including both oils (either free floating oils, emulsified oils, or a mixture of both) and soluble pollutants, such as organic dyes (e.g. from textile industry, painting and coloring industry or food industry), and heavy metal ions (from mining industry, electroplating industry, electronics industry etc.).

[00188] To treat such complicated wastewater, a combination of different techniques and multi-stages treatment processes which are expensive, poorly efficient and requiring a large footprint are conventionally needed. Therefore, it is highly desirable to develop materials and techniques that treat different water contaminants at one pass. In this regard, the as-developed materials not only separate different types of oil/water mixtures with high efficiency but also remove the soluble contaminants from the filtrated water simultaneously via one filtration process. FIG. 11a and FIG. 11b show the layered oil/water mixture with water contaminated by organic dyes (methylene blue) can be purified with one single filtration process. The 500 mesh fully covered with AG micro-wires is used in this process. This is because the water flux is lower, which provides enough contact time between the pollutant and AG coating so that the pollutant can be fully adsorbed by the AG. It is clear that after the

filtration process (FIG. 11a), the oil is retained above the mesh, while the water passes through the mesh and becomes colorless, indicating the removal of organic dyes from the water.

[00189] From the UV-vis spectra (e.g. FIG. 11b), disappearance of the characteristic peak of methylene blue after the filtration process is clearly indicated, suggesting the dyes are removed from the permeated water. In addition, the photograph of the AG filter after the filtration process clearly shows that the area where water permeated turns blue, further indicating that the methylene blue is adsorbed by the AG. Similarly, water contaminated by heavy metal ions can also be purified in a similar process.

[00190] Example 10a: Characterization of AG Mesh Behaviour towards Organic Dyes and Heavy Metal Ions

[00191] In order to understand adsorption behavior of AG towards both organic dyes and heavy metal ions, more detailed characterizations are performed. FIG. 12b shows the Fourier transform infrared (FTIR) spectra of raw glass powders and AG. Peaks around 3500 cm^{-1} and 1600 cm^{-1} are observed to be stronger with hydrothermal treatment, indicating more Si-OH bond formation. The Si-OH bonds are electrostatically negatively charged, which is proven by the zeta potential characterization (FIG. 12a), and could strongly interact with positively charged water contaminants, such as methylene blue and heavy metal ions due to the electrostatic attraction force. Therefore, based on the above characterization, it is demonstrated that the superhydrophilic property as well as the strong negative charges of the AG contribute to the multifunctional water purification ability in addition to contribution from the ion exchange ability of the AG, especially when waste glass comprising the metal ions (e.g. Na^+ , K^+ , Ca^{2+} , Mg^{2+} and/or Al^{3+}) are used.

[00192] Example 10b: Quantitative Analysis of AG Adsorption Capacity towards Organic Dyes and Heavy Metal Ions

[00193] In order to quantitatively understand the adsorption capacity of AG towards organic dyes and heavy metal ions, pure AG without coating onto mesh substrate was synthesized. This is to exclude the effect of different substrates, if any. By doing so, other possible applications of AG could be demonstrated e.g. as a low cost adsorbent for removing water soluble pollutants, or as a potential replacement for commercial

activated carbons (AC). FIG. 13a shows the adsorption capacity of the AG (24 hours hydrothermal treatment) towards a wide range of heavy metal ions. FIG. 13b indicates the ability of AG adsorbent to remove organic dyes from water within 5 hours. The kinetic adsorption studies of Pb(II) and methylene blue show both adsorptions fit into the pseudo-second-order adsorption kinetics (FIG. 13c and FIG. 13d). The adsorption capacity of methylene blue under testing condition is about 46 mg g⁻¹.

[00194] Interestingly, it is worth mentioning that the AG adsorbent fabricated without the coating process could form a freestanding monolith rather than in the form of powder. This is advantageous over other powdery adsorbents, such as activated carbon or polymer dispersants, in terms of handling, collecting and recycling, as powdery materials easily fly around or flow around due to their fluffy nature. With proper mould, shape of the AG adsorbents can be changed as well (FIG. 13e).

[00195] **Example 11: Commercial Application - Anti-fouling and Anti-Adhesion**

[00196] Underwater superoleophobic materials have also shown great promise in the field of anti-fouling and anti-adhesion applications, such as oil-repellent coatings, anti-crawling materials, self-cleaning of marine equipment, anti-oil treatment of oil pipelines and anti-bioadhesion. Due to its strong repellence towards oil, the as-developed AG could also be used as coating materials for marine equipment in order to prevent oil-fouling, adhesion of bio-organisms, and thus facilitate underwater self-cleaning. The ultra-low underwater oil adhesion of AG coated mesh was investigated by both sliding angles and oil adhesion measurements. FIG. 14a shows that the oil droplet can roll off very easily even when the AG mesh is only tilted or shaken slightly (about 2°), indicating an ultralow adhesion between the surface and oil droplet under water. This was compared with pristine steel mesh in FIG. 14c.

[00197] The oil adhesion can also be assessed by the oil adhesion experiment, as shown in FIG. 14b. 5 µl chloroform droplet is first extruded from a needle and suspended on the needle tip. Then, the as-prepared AG coated surface is contacted with the oil droplet by slowly moving the substrate stage upwards. Then, the substrate stage is lowered again to release the oil contact with the surface. As can be seen, the suspending oil droplet cannot be detached from the needle tip onto the surface even when the droplet was severely deformed by the upward pushing force produced by the leveling of the stage. This indicates the excellent oil-repellence of the AG-coated

surface. In addition, as the stage moves downward, the oil droplet maintains its substantial spherical shape without deforming even in the presence of a drag force produced by the leaving stage. This again shows the ultra-low oil adhesion property of the AG-coated surface. This was compared with pristine steel mesh in FIG. 14d.

5 **[00198] Example 12: Stability Test**

[00199] Stability tests of the AG mesh under various harsh environments are also conducted. The results are depicted in FIG. 15a to FIG. 15d.

[00200] From the results of FIG. 15a, AG is stable against various corrosive organic solvents (THF: tetrahydrofuran, NMP: N-methyl-2-pyrrolidone, DMF: dimethylformamide, DMK: dimethyl ketone, and TCM: chloroform). From FIG. 15b, AG is stable up to temperatures of 400°C. From FIG. 15c, AG is stable against both acidic and alkaline solutions. From FIG. 15d, the oil content in the filtrated water from 5 cycles of filtration using the AG meshes, after the AG meshes are treated under different harsh conditions, demonstrates that the AG meshes are stable against various harsh conditions.

[00201] FIG. 16a to FIG. 16c demonstrate that AG shows stable underwater superoleophobicity even when directly immersed in strong acid, high salinity and strong alkali.

[00202] The above conditions as tested may be commonly encountered in practical daily situations. The test is carried out to demonstrate that the AG, when exposed to the tested conditions, maintains its superhydrophilicity (at least in air) and underwater superoleophobicity. Conventional materials, on the other hand, tend to fail in one or more of the tested conditions.

[00203] Example 13: Separation Efficiency of Different AG Mesh

25 **[00204]** Further quantitative study of the separation efficiency for different AG mesh is carried out (FIG. 17a and FIG. 17b). The separation efficiency for 100 and 500 AG mesh is tested with different oils and organic solvents (FIG. 17a). For the tested AG meshes, the separation efficiency is stable for at least 5 experiment cycles (FIG. 17b).

[00205] While the invention has been particularly shown and described with reference to specific embodiments, it should be understood by those skilled in the art that various changes in form and detail may be made therein without departing from the spirit and scope of the invention as defined by the appended claims. The scope of

the invention is thus indicated by the appended claims and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced.

CLAIMS

1. A method for making a glass material which is superhydrophilic at least in air and superoleophobic when submerged in water, comprising:
 - providing a dispersion comprising silica particles in a powder form dispersed in an organic solvent or aqueous solvent;
 - coating the dispersion on a substrate;
 - drying the coated substrate; and
 - subjecting the dried substrate to a hydrothermal treatment for less than 24 hours in the presence of an aqueous medium.
2. The method of claim 1, wherein the providing step comprises subjecting a glass precursor material to ball milling to obtain the silica particles in the powder form.
3. The method of claim 1 or 2, wherein the ball milling is carried out at low-speed milling of 150 rpm to 250 rpm for 30 minutes followed by high-speed milling of 550 rpm to 650 rpm for 30 minutes.
4. The method of any one of claims 1 to 3, wherein the silica particles in the powder form comprise Na^+ , K^+ , Ca^{2+} , Mg^{2+} and/or Al^{3+} .
5. The method of any one of claims 1 to 4, wherein the organic solvent comprises acetone, ethanol or methanol.
6. The method of any one of claims 1 to 4, wherein the aqueous solvent comprises water.
7. The method of any one of claims 1 to 6, wherein the coating step is repeated for more than once.

8. The method of any one of claims 1 to 7, wherein the drying step occurs between 80°C to 200°C.
9. The method of any one of claims 1 to 8, wherein the hydrothermal treatment is carried out between 150°C to 200°C.
10. The method of any one of claims 1 to 9, wherein the aqueous medium comprises liquid deionized water.