

ANTI-MICROBIAL COATINGS, COATING SOLUTIONS AND METHODS OF PRODUCING THE SAME

Technical Field

5 The present invention generally relates to anti-microbial coatings and coating solutions. The present invention also relates to methods for producing said anti-microbial coating solution.

Background

10 Anti-microbial coatings and solutions are fast receiving attention due to the growing demand for better quality of life and better living hygiene. Such coatings and solutions are especially purposeful in industries
15 such as those that deal with medical devices and water filtration devices.

 To address the demand for anti-microbial coatings and solutions, an increased number of research resources are placed in developing anti-microbial coatings and
20 solutions. To date several anti-microbial coatings and solutions as well as methods of producing the same have been developed. However, these coatings and solutions as well as methods of producing the same have not reached the levels which are required in the medical devices and
25 water filtration industries.

 Many of the known anti-microbial coatings and solutions contain metal oxide particles to take advantage of the known anti-microbial properties of these metal oxide particles. However, when applied to articles, these
30 coatings and solutions do not work as effectively as desired. More often than not, the anti-microbial effect

of these coatings and solutions appears considerably suppressed. While not being bound by theory, it is believed that the metal oxide particles which are present in the coatings or solutions, are being fully encapsulated by the other components of the coatings and solutions, thereby reducing the possibility of direct contact of the metal oxide particles with external microorganisms. As a result, most of the known anti-microbial coatings have to work in tandem with an external Ultra Violet light source to boost the anti-microbial properties of the coated article in question.

Other drawbacks of known anti-microbial coatings and solutions include formation of cracks on the coated surfaces of articles when these coatings and solutions are used to coat the surfaces of articles. The formation cracks on the coated surfaces eventually results in the flaking of the coating from the surfaces of the article, thereby causing the article to lose its anti-microbial property over time.

In addition, the metal oxide particles present within known anti-microbial coating solutions tend to agglomerate together, resulting in an uneven dispersion of metal oxide particles within the solution. This phenomenon can sometimes be detected by the naked eye as solutions that contain agglomerated metal oxide particles appear to be cloudy at times. Due to the uneven dispersion of metal oxide particles within the solution, application of such coating solutions to an article may result in parts of the article having little or no anti-microbial effect. Large masses of agglomerated metal oxide particles within the formed coating on the surface

of the article may also contribute to concentrated points of stress that would result in cracking and flaking of the coatings.

In view of the above, there is a need to provide anti-microbial coatings and coating solutions that overcome or at least ameliorate one or more of the disadvantages described above. There is also a need to provide a method to produce such anti-microbial coatings and coating solutions.

Summary

According to a first aspect, there is provided a coating solution comprising nano-sized or micro-sized metal or metalloid chalcogenide particles in a polymer matrix precursor solution, wherein the weight ratio of metal or metalloid chalcogenide particles to said polymer matrix precursor solution enables at least a portion of said metal or metalloid chalcogenide particles to project from the surface of a polymer matrix that has been formed during cross-linking of said polymer matrix precursor solution, to thereby inactivate micro-organisms in contact with said metal or metalloid chalcogenide particles. Advantageously, the coating solution when applied to an article, is capable of producing a coated article with enhanced anti-microbial effect. More advantageously, as at least a portion of said metal or metalloid chalcogenide particles projects from the surface of the polymer matrix that is formed, when coated onto the surface of an article, the projected parts of the metal or metalloid chalcogenide particles are able to

come into direct contact with external micro-organisms to thereby inactivate them.

5 In one embodiment, the metal or metalloid chalcogenide particles have an average diameter of from 50 nm to 150 nm. It has been surprisingly discovered by the inventors that this range of particle sizes is effective in producing a satisfactory anti-microbial effect when coated onto an article. The metal or metalloid chalcogenide particles may be selected from the group consisting of zinc oxide, titanium dioxide, silicon dioxide, magnesium oxide, copper oxide. It has also been discovered that this group of metal or metalloid chalcogenide particles are effective in deactivating micro-organisms.

15 The weight percentage of metal or metalloid chalcogenide particles to the polymer matrix precursor solution may be in the range of from about 0 to about 40%, from about 10% to about 30%, from about 10% to about 20% or from about 0 to about 15%. In one embodiment, the weight percentage of metal or metalloid chalcogenide particles to the polymer matrix precursor solution is no more than 15%. Advantageously, when the weight percentage of metal or metalloid chalcogenide particles to the polymer matrix precursor solution is no more than about 20 15%, the solution obtained will not be excessively viscous and can be easily applied to coat the surface of an article. The weight percentage of the metal or metalloid chalcogenide particles to the polymer matrix precursor solution may be from about 0.5 to about 10%. Advantageously, within this weight percentage range of the metal or metalloid chalcogenide particles to the

polymer matrix precursor solution, the coating solution will not be excessively viscous, but at same time is still able to achieve an effective anti-microbial effect. In one embodiment, the metal or metalloid chalcogenide particles and the polymer matrix precursor solution are in an amount such that the ratio of metal or metalloid chalcogenide particles to the polymer matrix ultimately formed is in the range of from about 0 to about 40%, from about 10% to about 30%, from about 10% to about 20% or from about 0 to about 15%.

In one embodiment, the polymer matrix precursor solution is capable of cross-linking to form a polymer matrix that is selected from the group consisting of epoxide containing polymer matrix, acrylate containing polymer matrix, ester containing polymer matrix, siloxane containing polymer matrix and combinations thereof. In one embodiment, the polymer matrix precursor solution comprise polydimethylsiloxane (PDMS). These polymer matrices are effective in forming a coating which is substantially crack free.

In one embodiment, the coating solution is substantially transparent. Advantageously, this provides a visual indication that the metal or metalloid oxide particles are substantially evenly distributed within the solution with little or no agglomeration.

According to a second aspect, there is provided a coating comprising nano-sized or micro-sized metal or metalloid chalcogenide particles bound to a polymer matrix, wherein at least a portion of the metal or metalloid chalcogenide particles project from the surface of said polymer matrix for inactivating micro-organisms

in contact with said metal or metalloid chalcogenide particles. Advantageously, the projected parts of the metal or metalloid chalcogenide particles are able to come into direct contact with external micro-organisms to thereby inactivate them. In one embodiment, the chalcogenide particles are bound to a polymer matrix via chemical bonds.

In one embodiment, at least about 5%, at least about 10%, at least about 15%, at least about 20% or at least about 30% of the surface area of the metal or metalloid chalcogenide particles are not encapsulated by said polymer matrix. In one embodiment, the surface area of the metal or metalloid chalcogenide particles which are not enclosed by said polymer matrix is from about 5% to about 20%. Advantageously, this increases the overall area of metal chalcogenide particles that are exposable to external micro-organism.

In another embodiment, the coating is substantially free from cracks. Advantageously, as the coating is substantially crack-free, there is a reduced likelihood of flaking of the coating. Hence, the coating may also be substantially resistant to peeling. Accordingly, the life of the coating is prolonged and the anti-microbial property of the article to which the coating is coated on, is also prolonged.

In one embodiment, the polymer matrix is substantially biodegradable. Advantageously, as the polymer matrix degrades over time, a larger surface area of the metal chalcogenide particles can be exposed to external micro-organisms, thereby increasing the anti-microbial effect of the coating. The polymer matrix may

also be porous. The porosity of the polymer matrix increases the surface area of contact of external micro-organisms with the metal chalcogenide particles.

According to a third aspect, there is provided a
5 method of producing an anti-microbial coating solution, said method comprises the steps of:

- a. providing a solution mixture comprising a organic precursor and a solvent;
- 10 b. precipitating nano-sized or micro-sized metal chalcogenide particles from the solution mixture of the providing step (a); and
- c. adding a polymer matrix precursor solution to said metal chalcogenide particles in the solution mixture to thereby bind said metal
15 chalcogenide particles to a polymer matrix during cross-linking of the polymer matrix precursor solution.

According to a fourth aspect, there is provided a
method of producing an anti-microbial coating solution,
20 said method comprises the steps of:

- f. pulverizing a composite material comprising nano-sized or micro-sized metal chalcogenide particles into a powdered form; and
- 25 g. adding a polymer matrix precursor solution to said powdered form of the composite material obtained in step (f) to thereby bind said metal chalcogenide particles present within said powders to a polymer matrix during cross-linking of the polymer matrix precursor
30 solution.

Advantageously, the methods of the third and fourth aspects are capable of producing the coating solution and coating of the first and second aspects. Advantageously, the addition of the pulverized composite powder from step
5 (f) to a polymer matrix in step (g) permits the powdered form of the composite material obtained in step (f), containing said metal or metalloid chalcogenide particles present within said powders, to bind to a polymer matrix during cross-linking of the polymer matrix precursor
10 solution in step (g) resulting in at least a portion of metal or metalloid chalcogenide particles projecting from the surface of the coating composition.

In one embodiment, the method of the fourth aspect further comprises prior to pulverizing step (f), the
15 steps of:

- a. providing a solution mixture comprising a organic precursor and a solvent;
- b. precipitating nano-sized or micro-sized metal chalcogenide particles from the solution
20 mixture of the providing step (a);
- c. gelating the solution mixture obtained in step (b) to obtain a gel comprising said nano-sized or micro-sized metal chalcogenide particles dispersed therewithin;
- d. aging of the gel obtained in step (c) to
25 increase the degree of polymerization within said gel; and
- e. drying the aged gel obtained from step (d) to form the composite material comprising nano-
30 sized or micro-sized metal chalcogenide particles of step (f).

Advantageously, these steps can be carried out easily on a laboratory scale without the need for sophisticated and costly equipment. Even more advantageously, this may reduce the overall production cost of the coating solution produced.

It is a further advantage that the methods of the third and fourth aspects are capable of producing a coating wherein at least a portion of the metal or metalloid chalcogenide particles is not encapsulated by said polymer matrix. It is a further advantage that the methods of the third, fourth and fifth aspects are capable of increasing the surface area of the metal or metalloid chalcogenide particles which are in contact with micro-organisms.

In one embodiment, the organic precursor is selected from the group consisting of propoxide containing precursor, acetate containing precursor, silane containing precursor and alkoxide containing precursor. In one embodiment, the organic precursor is a metallorganic precursor. The solvent may selected from the group consisting of organic solvents such as acetone and alcohols such as ethanol or isopropyl alcohol (IPA).

In another embodiment, the precipitation step (b) is carried out at a temperature of from about 20 degrees Celsius to about 200 degrees Celsius, about 25 degrees Celsius to about 150 degrees Celsius or about 30 degrees Celsius to about 100 degrees Celsius. In one embodiment, the precipitation step (b) is carried out at a temperature ranging from room temperature to about 150 degrees Celsius. The precipitation step (b) may be carried out at a a humidity of up to about 90%, up to

about 85%, up to about 80% or up to about 70%. The adding step (c) may be carried out at a temperature of from about 80 degrees Celsius to about 250 degrees Celsius, from about 100 degrees Celsius to about 200 degrees Celsius, from about 100 degrees Celsius to about 150 degrees Celsius, or from about 150 degrees Celsius to about 200 degrees Celsius.

According to a fifth aspect, there is provided a filter coated with a coating, said coating comprises nano-sized or micro-sized metal chalcogenide particles bound to a polymer matrix, wherein at least a portion of the metal chalcogenide particles project from the surface of the polymer matrix for inactivating micro-organisms can in contact with said metal chalcogenide particles.

According to a sixth aspect, there is provided use of a coating solution as defined herein for coating a water filtration device.

Definitions

The following words and terms used herein shall have the meaning indicated:

The terms "inactivate microorganisms" or "inactive microbes" and the like in the context of this specification is used herein to describe killing of micro-organisms or microbes, attenuating of micro-organisms or microbes, or reducing the activity of micro-organisms or microbes such that the micro-organisms or microbes are not capable of growing or at least have reduced growth or reduced proliferation or that have lost or have reduced activity that may aberrantly affect human or animal health. When describing a population of

microbes as being "inactivated" in the context of this specification, it does not mean that the whole population of microbes within the plant material are necessarily inactivated, although they may be, but means that at
5 least 90% of the total microbe population will be inactivated. More typically, at least 95% of the total microbe population will be inactivated and yet more typically, at least 98% of the total microbe population will be inactivated. The population of microbes can be
10 determined by measuring the colony forming unit (CFU) according to methods known to those in the art.

The term "chalcogen" is to be interpreted broadly to refer to atoms of Group VIA of the Periodic Table of Elements. More particularly, the term "chalcogen"
15 includes elements selected from the group consisting of oxygen (O), sulfur (S), selenium (Se), and tellurium (Te).

The term "chalcogenide" is to be interpreted broadly to refer to a binary or multinary compound containing at
20 least one chalcogen and at least one electropositive element or radical.

The term "metal or metalloid chalcogenide" is to be interpreted broadly to refer to a chalcogenide in which the at least one electropositive element is a metal or
25 metalloid cation.

The term "micro" as used herein is to be interpreted broadly to include dimensions between about 1 micron to about 1000 micron.

The term "nano" as used herein is to be interpreted
30 broadly to include dimensions less than about 1000 nm.

The term "metal", as used herein, is to be interpreted broadly to include all metals, including, for example, semimetals, alkali metals, alkaline earth metals, transition metals and metals selected from the main groups of the Periodic Table of the Elements.

The term "metalloid" as used herein is to be interpreted broadly to include elements that exhibit properties that are characteristic properties of metals and properties that are characteristic properties of non-metals.

The term "biodegradable" as used herein refers to the susceptibility of a substance to decomposition by living things (organisms/microorganisms) and/or natural environmental factors.

The term "transparent" refers to any substance that allows light easily pass through such that objects placed on the back can be fully seen through the substance.

The term "precursor", as used herein, is to be interpreted broadly to any substance which is used to derive the final desired product. For example, in the context of the present specification, the phrase "polymer matrix precursor solution" refers to a solution the polymer matrix is derived from. Likewise, the phrase "organic precursor" when referring to metal or metalloid chalcogenide particles in the present specification, refers to an organic substance that the metal or metalloid chalcogenide particles are derived from. The precursor may also have the same composition as the final desired product but only differs in the physical state from the final product.

The term "bind", "bound" or grammatical variants thereof as used herein, refers to the interaction between a corresponding pair of molecules which may be physical or chemical.

5 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.

10 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.

15 As used herein, the term "about", in the context of concentrations of components of the formulations, typically means +/- 5% of the stated value, more typically +/- 4% of the stated value, more typically +/- 3% of the stated value, more typically, +/- 2% of the
20 stated value, even more typically +/- 1% of the stated value, and even more typically +/- 0.5% of the stated value.

 Throughout this disclosure, certain embodiments may be disclosed in a range format. It should be understood
25 that the description in range format is merely for convenience and brevity and should not be construed as an inflexible limitation on the scope of the disclosed ranges. Accordingly, the description of a range should be considered to have specifically disclosed all the
30 possible sub-ranges as well as individual numerical values within that range. For example, description of a

range such as from 1 to 6 should be considered to have specifically disclosed sub-ranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6 etc., as well as individual numbers within that range, for example, 1, 2, 3, 4, 5, and 6. This applies regardless of the breadth of the range.

Detailed Disclosure of Embodiments

Exemplary, non-limiting embodiments of a coating solution, a coating, methods for producing anti-microbial coating solutions will now be disclosed.

The coating solution disclosed herein comprises coating solution comprising nano-sized or micro-sized metal or metalloid chalcogenide particles in a polymer matrix precursor solution, wherein the weight ratio of metal or metalloid chalcogenide particles to said polymer matrix precursor solution enables at least a portion of said metal or metalloid chalcogenide particles to project from the surface of a polymer matrix that has been formed during cross-linking of said polymer matrix precursor solution, to thereby inactivate micro-organisms in contact with said metal or metalloid chalcogenide particles.

The coating disclosed herein comprises nano-sized or micro-sized metal or metalloid chalcogenide particles bound to a polymer matrix, wherein at least a portion of the metal or metalloid chalcogenide particles project from the surface of said polymer matrix for inactivating micro-organisms in contact with said metal or metalloid chalcogenide particles. In one embodiment, the

chalcogenide particles are chemically bound to the polymer matrix.

The metal of the metal chalcogenide particles may be selected from the group consisting of alkali metals, alkaline earth metals, metals selected from the transition metals and metals selected from the main group of the Periodic Table of the Elements. Exemplary metals of the metal chalcogenide particles may include, but are not limited to, Mg, Ca, Sr, Ba, Ag, Zn, Fe, Cu, Co, Al, Ce, Sn, Zr, Nb, Ti and Cr.

The metal or metalloid chalcogenide may be selected from the group consisting of SiO_2 , Ag_2O , Mn_2O_3 , SrO , MgO , CaO , BaO , ZnS , ZnSe , ZnTe , PbS , PbSe , PbTe , CuS , CuSe , CuTe , CdS , CdSe , CdTe , MnS , MnSe , MnTe , Ag_2S , Ag_2Se , Ag_2Te , ZnO , ZrO_2 , TiO_2 , CeO_2 , SnO_2 , FeO , Fe_3O_4 , Fe_2O_3 , ZrO_2 , CuO , MnO , Cu_2O , Al_2O_3 , V_2O_3 , V_2O_5 , Nb_2O_5 , NiO , InO_3 , HfO_2 , Cr_2O_3 , Ta_2O_5 , Ga_2O_3 , Y_2O_3 , MoO_3 and Co_3O_4 . Preferably, the metal or metalloid chalcogenide particles disclosed herein are metal or metalloid oxide particles. In one embodiment, the metal or metalloid oxide particles are selected from the group consisting of MgO , CaO , BaO , TiO_2 , SrO , ZnO , Mn_2O_3 , Fe_2O_3 , FeO , ZrO_2 , V_2O_3 , V_2O_5 , CuO , NiO , Al_2O_3 , SiO_2 , ZnO , Ag_2O , mixed metal oxides such as $\text{MgO}/\text{Al}_2\text{O}_3$ and their mixtures thereof. More preferably, the metal or metalloid chalcogenide particles are selected from the group consisting of zinc oxide, titanium dioxide, silicon dioxide, magnesium oxide, copper oxide. The metal or metalloid oxide particles may be coated or uncoated.

The metal or metalloid chalcogenide particles may be substantially spherical in shape. The metal or metalloid

chalcogenide particles may have an average particle size of about 10 nm to about 200 nm; about 10 nm to about 150 nm; about 50 nm to about 140 nm; about 50 nm to about 130 nm and about 50 nm to about 120 nm, about 50 nm to about 110 nm, about 50 nm to about 100 nm, about 50 nm to about 90 nm, about 50 nm to about 80 nm, about 50 nm to about 70 nm, or about 50 nm to about 60 nm. In one embodiment, the metal or metalloid chalcogenide particles have an average particle size of from 50 nm to 150 nm. The metal or metalloid chalcogenide or metal or metalloid oxide particles may be completely solid, partially porous or completely porous. In one embodiment, the metal or metalloid chalcogenide or metal or metalloid oxide particles is mesoporous.

In one embodiment, the weight percentage of metal or metalloid chalcogenide particles to the polymer matrix precursor solution is no more than 15%. In another embodiment, the weight percentage of metal or metalloid chalcogenide particles to the polymer matrix precursor solution is from 0.5 to 10%. The weight percentage of metal or metalloid chalcogenide particles to the polymer matrix precursor solution may be from about 1% to about 10%, about 2% to about 9%, about 3% to about 8%, about 4% to about 7% or about 5% to about 6%.

In one embodiment, the weight percentage of metal or metalloid chalcogenide particles to the polymer matrix is no more than 15%. In another embodiment, the weight percentage of metal or metalloid chalcogenide particles to the polymer matrix is from 0.5 to 10%. The weight percentage of metal or metalloid chalcogenide particles to the polymer matrix may be from about 1% to about 10%,

about 2% to about 9%, about 3% to about 8%, about 4% to about 7% or about 5% to about 6%.

5 In one embodiment, at least about 5%, at least about 10%, at least about 15%, at least about 20% or at least about 30% of the surface area of the metal or metalloid chalcogenide particles are not encapsulated by said polymer matrix. In one embodiment, the surface area of the metal or metalloid chalcogenide particles which are not enclosed by said polymer matrix is from about 5% to
10 about 20%. In one embodiment, the metal or metalloid disclosed chalcogenide particles are obtained from a sol-gel method.

In one embodiment, the polymer matrix precursor solution is capable of cross-linking to form a polymer
15 matrix that is selected from the group consisting of epoxide containing polymer matrix, acrylate containing polymer matrix, ester containing polymers, siloxane containing polymer matrix and combinations thereof. The polymer matrix precursor solution may be selected from
20 the group consisting of epoxide containing precursor solution, acrylate containing precursor solution, ester precursor solution, siloxane containing precursor solution. In one embodiment, the polymer matrix precursor solution may also comprise a curing agent to aid in the
25 cross-linking.

In one embodiment, the coating solution is substantially transparent. The coating solution may have a light transmittance of from about 80 % to about 100%, from about 85 % to about 95% or from about 90 % to about
30 95%.

In one embodiment, the micro-organisms or microbes that may be inactivated are bacteria or fungi. The bacteria may further be selected from the group consisting of *Staphylococcus aureus* (*S. aureus*),
5 *Escherichia coli* (*E. coli*), Methicillin-resistant *Staphylococcus aureus* (MRSA) and *Propionibacterium acnes* (*P. acnes*), *Salmonella* sp., *Streptococcus* sp., *Shigella* sp., *Botulism* sp., *Actinomycetes*, *Nocardia*, *Staphylococcus*, *Enterobacter*, , *Bacillus* and Coliform
10 bacteria.

The fungi may be further selected from the group consisting of *Botrytis cinerea*, *Rhizomucor miehei*, *Pyricularia oryzae*, *Rhizopus oligosporus*, *Cercospora traversiana*, *Cercospora sorghii*, *Cercospora sesami*,
15 *Cercospora scirpicola*, *Cercospora kikuchii*, *Cercospora haji*, *Cercospora beticola*, *Sclerotinia fructicola*, *Aspergillus oryzae*, *Trichophyton*, *Microsporum*, *Epidermaphyton*, *Pichia* sp., *Torulopsis spherica*, *Rhodotorula aurantiaca*, *Rhodotorula glutinis*, *Rhodotorula minuta*, *Candida albicans*, *Trichoderma viride*, *Drechslera australiensis*, *Gibberella fugikuri*, *Phoma herbarum*, *Pycnoporus sangiuneus*, *Fusarium* such as *Fusarium culmorum*, *Fusarium decemcellulase*, *Fusarium acuminatum*, *Fusarium moniliforme*, *Fusarium sporotrichioides*, *Fusarium*
20 *poae*, *Fusarium fugikurai*, *Fusarium longipes*, *Penicillium* such as *Penicillium rotatum*, *Penicillium oxalicum*, *Penicillium crustosum*, *Penicillium implicatum*, *Penicillium lividum*, *Penicillium cyclopium*, *Penicillium digitatum*, *Penicillium toxicarium*, *Penicillium italicum*,
25 or *Aspergillus* such as *Aspergillus cervinus* and *Aspergillus cremens*.
30

In one embodiment, the disclosed coating is substantially free from cracks. The disclosed coating may also be biodegradable. The disclosed coating may also be substantially resistant to coating. In one embodiment the polymer matrix is porous. The pore size of the matrix may be less than 1 micron.

One method of producing an anti-microbial coating solution disclosed herein comprises the steps of:

- a. providing a solution mixture comprising a organic precursor and a solvent;
- b. precipitating nano-sized or micro-sized metal or metalloid chalcogenide particles from the solution mixture of the providing step (a); and
- c. adding a polymer matrix precursor solution to said metal or metalloid chalcogenide particles in the solution mixture to thereby bind said metal or metalloid chalcogenide particles to a polymer matrix during cross-linking of the polymer matrix precursor solution.

In another embodiment, the precipitation step (b) is carried out at a temperature of from about 20 degrees Celsius to about 200 degrees Celsius, about 25 degrees Celsius to about 150 degrees Celsius or about 30 degrees Celsius to about 100 degrees Celsius. In one embodiment, the precipitation step (b) is carried out at a temperature ranging from room temperature to about 150 degrees Celsius. The precipitation step (b) may be carried out at a humidity of up to about 90%, up to about 85%, up to about 80% or up to about 70%. The precipitation step may be carried out at room temperature and pressure.

In one embodiment, the adding step (c) is carried out at a temperature of from about 80 degrees Celsius to about 250 degrees Celsius, from about 100 degrees Celsius to about 200 degrees Celsius, from about 100 degrees Celsius to about 150 degrees Celsius, or from about 150 degrees Celsius to about 200 degrees Celsius. The adding step may be carried out at room temperature and pressure. In one embodiment, externally supplied metal or metalloid chalcogenide particles may be further added to the solution mixture of step (b) prior to the adding step (c).

Another method of producing an anti-microbial coating solution disclosed herein comprises the steps of:

- f. pulverizing a composite material comprising nano-sized or micro-sized metal or metalloid chalcogenide particles into a powdered form; and
- g. adding a polymer matrix precursor solution to said powdered form of the composite material obtained in step (f) to thereby bind said metal or metalloid chalcogenide particles present within said powders to a polymer matrix during cross-linking of the polymer matrix precursor solution.

In one embodiment, the pulverising step (f) is carried out at room temperature and pressure. In one embodiment, the composite material in step (f) is a material obtained by a sol gel method. The composite material may be a sol gel which has or has not been subjected to drying or densification.

The pulverizing step may be carried out by any physical means which result in high energy attrition. The pulverizing step may comprise at least one of ball milling, rod milling, vibratory grinding, jet milling, cone grinding, jaw crushing, and hammer milling or any other physical steps that are able to reduce the composite material into a powdered form.

Advantageously, the addition of the pulverized composite powder from step (f) to a polymer matrix in step (g) permits the powdered form of the composite material obtained in step (f), containing said metal or metalloid chalcogenide particles present within said powders, to bind to a polymer matrix during cross-linking of the polymer matrix precursor solution in step (g) resulting in at least a portion of metal or metalloid chalcogenide particles projecting from the surface of the coating composition.

Advantageously, in accordance with the method of the disclosure, at least a portion of the metal chalcogenide particles are not encapsulated by said polymer matrix. In one embodiment, the particles that are not encapsulated by the polymer matrix project from the surface of the polymer matrix for inactivating microorganisms in contact with said metal or metalloid chalcogenide particles. In one embodiment, at least about 5%, at least about 10%, at least about 15%, at least about 20% or at least about 30% of the surface area of the metal or metalloid chalcogenide particles are not encapsulated by said polymer matrix. In one embodiment, the surface area of the metal or metalloid chalcogenide particles which are not enclosed by said polymer matrix

is from about 5% to about 20%. Advantageously, this increases the overall surface area of metal chalcogenide particles that are exposed to external micro-organisms.

5 In one embodiment, prior to the pulverizing step (f), the method comprises the steps of:

- a. providing a solution mixture comprising a organic precursor and a solvent;
- b. precipitating nano-sized or micro-sized metal or metalloid chalcogenide particles from the
10 solution mixture of the providing step (a);
- c. gelating the solution mixture obtained in step (b) to obtain a gel comprising said nano-sized or micro-sized metal or metalloid chalcogenide particles dispersed therewithin;
- d. aging of the gel obtained in step (c) to
15 increase the degree of polymerization within said gel; and
- e. drying the aged gel obtained from step (d) to form the composite material comprising nano-sized or micro-sized metal or metalloid
20 chalcogenide particles of step (f).

The precipitation step (b) may be carried out at a temperature of from about 20 degrees Celsius to about 200 degrees Celsius, about 25 degrees Celsius to about 150
25 degrees Celsius or about 30 degrees Celsius to about 100 degrees Celsius. In one embodiment, the precipitation step (b) is carried out at a temperature ranging from room temperature to about 150 degrees Celsius. The precipitation step (b) may be carried out at a humidity
30 of up to about 90%, up to about 85%, up to about 80% or up to about 70%. The gelating step (c) may be carried

out at a temperature of from 20 degrees Celsius to from 60 degrees Celsius. In one embodiment, the gelation step (c) is carried out room temperature pressure. The aging step (d) may be carried out at a temperature of from 20 degrees Celsius to from 70 degrees Celsius. The drying step (e) may be carried out at a temperature of from 20 degrees Celsius to from 160 degrees Celsius.

In one embodiment, method of the disclosure provides a coating wherein at least a portion of the metal chalcogenide particles are not encapsulated by said polymer matrix. In one embodiment, the particles that are not encapsulated by the polymer matrix project from the surface of the polymer matrix for inactivating micro-organisms in contact with said metal chalcogenide particles. In one embodiment, at least about 5%, at least about 10%, at least about 15%, at least about 20% or at least about 30% of the surface area of the metal or metalloid chalcogenide particles are not encapsulated by said polymer matrix. In one embodiment, the surface area of the metal or metalloid chalcogenide particles which are not enclosed by said polymer matrix is from about 5% to about 20%. Advantageously, this increases the overall surface area of metal chalcogenide particles that are exposed to external micro-organisms.

The coating solution disclosed herein may be used to coat components of medical devices or water filtration devices such as a membrane filters. The coating solution may be coated on the article of interest by at least one of the following methods: spray coating, dip coating, whirl sintering, vapour deposition, sputtering and combinations thereof.

Brief Description Of Drawings

The accompanying drawings illustrate a disclosed embodiment and serves to explain the principles of the disclosed embodiment. It is to be understood, however, that the drawings are designed for purposes of illustration only, and not as a definition of the limits of the invention.

Fig. 1 is a Scanning Electron Microscope (SEM) image of the surface of one embodiment of the coating disclosed herein.

Fig. 2 is a schematic diagram outlining the steps of synthesis Of $\text{SiO}_2\text{-ZnO}$ glass in accordance to one embodiment disclosed herein.

Fig. 3a is a picture of a sol gel comprising 1% by weight of zinc acetate dehydrate, obtained after the wet drying step but before the dry drying step in accordance to Fig 2.

Fig. 3b is a picture of a sol gel comprising 5% by weight of zinc acetate dehydrate, obtained after the wet drying step but before the dry drying step in accordance to Fig 2.

Fig. 4 is a picture of the sol gels of Fig. 3a and 3b after the dry drying step.

Fig. 5a is a picture of a powders comprising 1% of $\text{SiO}_2\text{-ZnO}$ glass obtained after ball milling.

Fig. 5b is a picture of a powders comprising 5% of $\text{SiO}_2\text{-ZnO}$ glass obtained after ball milling.

Example

Synthesis Of SiO₂-ZnO glass

Referring to Fig 2. there is shown a schematic
5 diagram outlining the steps of synthesis Of SiO₂-ZnO
glass in accordance to one embodiment disclosed herein.
14.665 g of hydrochloric acid (HCl) was first mixed with
75.333 g of deionised water (100). This mixture was the
placed into a separatory funnel and allowed to drip into
10 a beaker for 10 minutes (101).

Tetraethyl Orthosilicate (TEOS) was then allowed to
drip into the beaker containing the HCl via the
separatory funnel for 30 minutes (102, 103). Thereafter,
0.742 g of Zinc Acetate Dihydrate (104) was added to the
15 beaker containing the mixture of TEOS and HCl and stirred
for a period of 120 minutes (105) until all of the
solutes in the beaker were dissolved to form a homogenous
sol solution. The homogenous sol solution was then poured
in to a beaker and covered with an aluminum foil (106).

20 The homogenous sol solution in the beaker was then
placed in a humidity chamber 1/4 filled with water for at
least 4 days to allow gelation to take place (108).

After gelation had completed, the humidity chamber
together with formed gel was placed into a Binder vacuum
25 oven for aging (110) where the temperature was increased
from 25°C to 60°C over 15 hours. The temperature was then
maintained at 60°C for 54 hours. Thereafter, the
temperature was then decreased from 60°C to 25°C over 15
hours. This marked the end of the aging process. During
30 the aging process, the pore liquor that was expelled was

subsequently removed but common laboratory techniques including pouring (112).

After the pore liquor had been removed, the aged gel then was then made to undergo wet drying (114). The temperature of the Binder vacuum oven was increased from 25°C to 60°C over 5 hours. The temperature was then maintained at 60°C for 10 hours. Thereafter, the temperature was then further increased from 60°C to 90°C over 10 hours before maintaining the temperature at 90°C for 12 hours. After which, the temperature was then further increased from 90°C to 140°C over 26 hours before maintaining the temperature at 140°C for 26 hours. Finally, the temperature was decreased from 140°C to 25°C over 16 hours. This resulted in the sol-gel shrinking in size. The shrunk sol-gel was also observed to have a glass like appearance (200 of Fig 3a).

To ensure that the sol-gel was completely dry, dry drying (116) was carried out by placing the sol gel in the Binder Vacuum Oven at 60°C for at least one day. This resulted in the sol-gel turning white in appearance (300 of Fig. 4). Optionally, further drying can be carried out by freeze drying (118).

Pulverizing dried sol gel

The dried sol-gel was then placed into a grinding jar that was 1/3 filled with Zirconium Oxide ball mills. The sol-gel was then ground at a speed of 300 rpm for 15 minutes intervals followed by a 10 minute break between each 15 mins interval until a total of 8 hours had lapsed. The final product obtained were fine powders having 1% by weight of SiO₂-ZnO glass particles (400 of

Fig 5a). The entire process described above can be repeated with 3.71g of Zinc Acetate Dihydrate, 7.42g of Zinc Acetate Dihydrate or 11.13g of Zinc Acetate Dihydrate to finally obtain fine powders having 5%, 15% and 10% by weight of SiO₂-ZnO glass particles respectively.

Preparing the coating solution.

The coating solution was then prepared using PDMS in its fluid state. The fluid PDMS was mixed with a curing agent in the ratio of 5:1. Thereafter, the fine powders comprising SiO₂-ZnO particles obtained from the steps outlined in the previous section was then added to the PDMS-curing agent mixture in the appropriate amount desired (dependent on the desired final SiO₂-ZnO particles concentration in the coating solution).

The coating solution mixture was then placed in a centrifugation mixer and stirred at a speed of 10000 rpm and at an angle of 45° to the horizontal until the fine powders comprising SiO₂-ZnO particles were substantially uniformly distributed throughout the solution mixture. The uniformly distributed solution mixture was then placed into a vacuum casting machine to remove the gas bubbles present in the solution. Once all of the gas bubbles had been removed, the coating solution mixture can be used for coating onto a substrate.

Coating of Substrate

For the purposes of this example, a glass slide was used as a substrate. The glass slide dipped into the coating solution mixture obtained from the previous section for a few seconds before removal from the solution. Thereafter, an air gun was used to dry the coated substrate at a temperature of 60°C.

After the coating on the glass slide had been dried up, a diamond cutting tool was used to remove the residual coatings present at the edges of the glass slide.

Detailed Description of Figures

Referring to Fig. 1, there is shown a Scanning Electron Microscope (SEM) image of the surface of one embodiment of the coating disclosed herein. As can be seen in the SEM, nanoparticles that are capable of inactivating microorganisms are present.

Referring to Fig. 3a and Fig. 3b, there are shown pictures of sol gels comprising 1% (200) and 5% (202) by weight of zinc acetate dehydrate respectively, obtained after the wet drying step but before the dry drying step in accordance to Fig 2. The sol gels (200 and 202) are substantially transparent.

Referring to Fig. 4, there is shown a picture of the sol gels (300) of Fig. 3a and 3b after the dry drying step. The sol gels (300) appear white in appearance.

Referring to Fig. 5a and Fig. 5b, there are provided pictures of a powders comprising 1% of SiO₂-ZnO glass (300) and 5% of SiO₂-ZnO glass (302) respectively

obtained after ball milling. The powders have a white and fine appearance.

Applications

5 It will be appreciated that the coating and coating solution disclosed herein are effective in inactivating micro-organisms and microbes. As the disclosed coatings comprise metal or metalloid chalcogenide particles which are not fully encapsulated by a matrix, a large surface
10 area of the metal or metalloid chalcogenide particles can be exposed to the external environment. Accordingly, these exposed surfaces of the metal or metalloid chalcogenide particles are capable of inactivating micro-organisms and microbes that come into direct contact with
15 them, thereby imparting an anti-microbial property to the articles being coated by such coatings.

 Advantageously, due to the effectiveness of the anti-microbial properties of these coatings, Ultra Violet light sources are not required to boost the anti-
20 microbial properties of the coated article in question. The articles coated with the disclosed coating or coating solution is still capable of inactivating micro-organisms or microbes even in the dark.

 Even more advantageously, there is little or no
25 formation of cracks on the coated surfaces of articles when these disclosed coatings and solutions are used to coat the surfaces of articles. Consequently, the likelihood of the flaking of the coating from the surfaces of the article is substantially reduced,
30 increasing the overall lifespan of the coatings.

The presently disclosed coating solution may also appear substantially transparent. This indicates substantially even dispersion of metal or metalloid chalcogenide particles within the solution. 5 Advantageously, there is also little or no agglomeration of metal or metalloid chalcogenide particles occurring within the solution, reducing stress concentration points that contribute to the flaking of the coatings.

10 The coating and coating solution may also be used to coat components of medical devices and water filtration devices where a high level of sterility is required.

15 The disclosed methods to produce the anti-microbial coatings and coating solutions can also be carried out on a laboratory scale under room temperature and without the need for sophisticated equipment. Accordingly, the disclosed methods are effective yet economical in producing the disclosed anti-microbial coatings and coating solutions.

20 While reasonable efforts have been employed to describe equivalent embodiments of the present invention, it will be apparent to the person skilled in the art after reading the foregoing disclosure, that various other modifications and adaptations of the invention may be made therein without departing from the spirit and 25 scope of the invention and it is intended that all such modifications and adaptations come within the scope of the appended claims.

30

Claims

1. A coating solution comprising nano-sized or micro-sized metal or metalloid chalcogenide particles in a polymer matrix precursor solution,
wherein said nano-sized or micro-sized metal or metalloid chalcogenide particles are pulverized sol-gel particles,
wherein the weight ratio of metal or metalloid chalcogenide particles to said polymer matrix precursor solution enables at least a portion of said metal or metalloid chalcogenide particles to project from the surface of a polymer matrix that has been formed during cross-linking of said polymer matrix precursor solution, to thereby inactivate micro-organisms in contact with said metal or metalloid chalcogenide particles.
2. The coating solution as claimed in claim 1, wherein said metal or metalloid chalcogenide particles have an average diameter of from 50 nm to 150 nm.
3. The coating solution as claimed in claims 1 or 2, wherein said metal or metalloid chalcogenide particles are selected from the group consisting of zinc oxide, titanium dioxide, silicon dioxide, magnesium oxide, copper oxide.
4. The coating solution as claimed in any one of the preceding claims, wherein the weight percentage of

metal or metalloid chalcogenide particles to the polymer matrix precursor solution is up to 40%.

- 5 5. The coating solution as claimed in claim 4, wherein the weight percentage of metal or metalloid chalcogenide particles to the polymer matrix precursor solution is no more than 15%.
- 10 6. The coating solution as claimed in any one of the preceding claims, wherein said polymer matrix precursor solution is capable of cross-linking to form a polymer matrix that is selected from the group consisting of epoxide containing polymer matrix, acrylate containing polymer matrix, ester containing
15 polymer matrix, siloxane containing matrix and combinations thereof.
- 20 7. The coating solution as claimed in any one of the preceding claims, wherein the coating solution is substantially transparent.
- 25 8. A coating comprising nano-sized or micro-sized metal or metalloid chalcogenide particles bound to a polymer matrix, wherein said nano-sized or micro-sized metal or metalloid chalcogenide particles are
30 pulverized sol-gel particles, wherein at least a portion of the metal or metalloid chalcogenide particles project from the surface of said polymer matrix for inactivating micro-organisms in contact with said metal or metalloid chalcogenide particles.

9. The coating as claimed in claim 8, wherein said metal or metalloid chalcogenide particles are chemically bonded to the polymer matrix.

5 10. The coating as claimed in any one of claims 8 to 9, wherein said metal or metalloid chalcogenide particles have an average diameter of from 50 to 150 nm.

10 11. The coating as claimed in any one of claims 8 to 10, wherein said metal or metalloid chalcogenide particles are selected from the group consisting of zinc oxide, titanium dioxide, silicon dioxide, magnesium oxide, copper oxide.

15 12. The coating as claimed in any one of claims 8 to 11, wherein the weight percentage of metal or metalloid chalcogenide particles to the polymer matrix is up to 40%.

20 13. The coating as claimed in claim 12, wherein the weight percentage of metal or metalloid chalcogenide particles to the polymer matrix is no more than 15%.

25 14. The coating as claimed in any one of claims 8 to 13, wherein said polymer matrix is selected from the group consisting of epoxide containing polymer matrix, acrylate containing polymer matrix, ester containing polymer matrix, siloxane containing matrix
30 and combinations thereof.

15. The coating as claimed in any one of claims 8 to 14,
wherein at least 5 % of the surface area of the metal
or metalloid chalcogenide particles are not
encapsulated by said polymer matrix.
- 5
16. The coating as claimed in any one of claims 8 to 15,
wherein said coating is substantially free from
cracks.
- 10
17. The coating as claimed in any one of claims 8 to 16,
wherein said polymer matrix is substantially
biodegradable.
18. The coating as claimed in any one of claims 8 to 17,
wherein said polymer matrix is porous.
- 15
19. The coating as claimed in any one of claims 8 to 18,
wherein said coating is substantially resistant to
peeling.
- 20
20. A method of producing an anti-microbial coating
solution according to any one of claims 1 to 19, said
method comprises the steps of:
- 25
- a. providing a solution mixture comprising a
organic precursor and a solvent;
 - b. precipitating nano-sized or micro-sized metal
or metalloid chalcogenide particles from the
solution mixture of the providing step (a);
 - c. gelating the solution mixture obtained in step
- 30
- (b) to obtain a gel comprising said nano-sized

or micro-sized metal or metalloid chalcogenide particles dispersed therewithin;

d. aging of the gel obtained in step (c) to increase the degree of polymerization within said gel;

e. drying the aged gel obtained from step (d) to form a dried sol-gel composite material comprising nano-sized or micro-sized metal or metalloid chalcogenide particles;

f. pulverizing the dried sol-gel composite material comprising nano-sized or micro-sized metal or metalloid chalcogenide particles into a powdered form; and

g. adding a polymer matrix precursor solution to said powdered form of the dried sol-gel composite material comprising metal or metalloid chalcogenide particles obtained in step (f) to thereby bind said metal or metalloid chalcogenide particles to a polymer matrix during cross-linking of the polymer matrix precursor solution, wherein at least a portion of the metal or metalloid chalcogenide particles project from the surface of the polymer matrix.

21. The method as claimed in claim 20, wherein the precipitation step (b) is carried out at a temperature of from 20 degrees Celsius to 200 degrees Celsius.

22. The method as claimed in any one of claims 20 to 21, wherein the precipitation step (b) is carried out at a humidity of up to 90%.
- 5 23. The method as claimed in any one of claims 20 to 22, wherein the adding step (c) is carried out at a temperature of from 80 degrees Celsius to 250 degrees Celsius.
- 10 24. The method as claimed in any one of claims 20 to 23, wherein said organic precursor is selected from the group consisting of propoxide containing precursor, acetate containing precursor, alkoxide containing precursor and silane containing precursor.
- 15 25. The method as claimed in any one of claims 20 to 23, or 24 wherein said solvent is selected from the group consisting of acetone and alcohols.
- 20 26. The method as claimed in any one of claims 20 to 25, wherein said metal or metalloid chalcogenide particles have an average diameter of from 50 to 150 nm.
- 25 27. The method as claimed in any one of claims 20 to 26, wherein said metal or metalloid chalcogenide particles are selected from the group consisting of zinc oxide, titanium dioxide, silicon dioxide, magnesium oxide, copper oxide.

30

28. The method as claimed in any one of claims 20 to 27, wherein the weight percentage of metal or metalloid chalcogenide particles to the polymer matrix is up to 40%.

5

29. The method as claimed in claim 28, wherein the weight percentage of metal or metalloid chalcogenide particles to the polymer matrix is no more than 15%.

10 30. The method as claimed in any one of claims 20 to 29, wherein said polymer matrix is selected from the group consisting of epoxide containing polymer matrix, acrylate containing polymer matrix, ester containing polymer matrix, siloxane containing
15 polymer matrix and combinations thereof.

31. A filter coated with a coating, said coating comprises nano-sized or micro-sized metal or metalloid chalcogenide particles bound to a polymer matrix,
20 wherein said nano-sized or micro-sized metal or metalloid chalcogenide particles are pulverized sol-gel particles,

wherein at least a portion of the metal or metalloid chalcogenide particles project from the
25 surface of the polymer matrix for inactivating micro-organisms in contact with said metal or metalloid chalcogenide particles.

32. Use of a coating solution as claimed in any one of
30 claims 1 to 7 for coating a water filtration device.