

Fabrication Of A Densely Packed Nano-Structured Photocatalyst For Environmental Applications

Technical Field

This invention relates to the purification of a fluid medium, and more particularly to the absorption, reduction or removal from water of organic pollutants.

Background Art

Titanium dioxide can be used in photocatalytic degradation of organic compounds, as described by J. H. Carey *et al* in "Photocatalytic degradation and subsequent adsorption characteristics of humic acids", *Water Science and Technology*, Vol. 34, No. 9, pp. 65-72, 1996. Carey *et al* described how humic acids, which are aromatic compounds, are degraded into less aromatic and simpler compounds through photocatalytic oxidation.

Most of the laboratory reactions involve forming a suspension of particulate titanium dioxide, or other photocatalytic semiconductor, in water containing organic pollutants that are to be converted into harmless by-products. A disadvantage of this procedure for commercial purification of water is that the particulate titanium dioxide would have to be subsequently removed before the water could be used, and this would be either impossible or prohibitively expensive, since titanium dioxide particles are extremely small in size and do not settle readily.

There is therefore a need for a photocatalyst which is highly effective in photochemical degradation of organic materials and which may be easily removed from the matrix in which those organic materials are located.

Objects of the Invention

It is an object of the present invention to ameliorate the disadvantage of the prior art. It is another object to satisfy the aforementioned need. A further object is to provide a practical fluid purification system for either commercial or domestic use.

Summary of Invention

In a first aspect, there is provided a photocatalytic assembly comprising:

- a first photocatalytic semiconductor layer; and
- a material selected from the group consisting of a metal, a metal alloy, a metal oxide and mixtures thereof, said material being disposed on and/or in said first layer.

The photocatalytic assembly may further comprise a second photocatalytic semiconductor layer disposed on and/or in said material.

- 10 The first and/or the second photocatalytic semiconductors may be nano-structured. The second photocatalytic semiconductor may be the same as the first photocatalytic semiconductor or it may be different, and the structure of the second photocatalytic semiconductor layer may be the same as the structure of the first photocatalytic semiconductor layer or it may be different. The first and/or the second photocatalytic semiconductor layers may comprise titanium dioxide or it may comprise zinc sulfide or it may comprise another suitable photocatalytic semiconductor. The first and/or second photocatalytic semiconductor layers may comprise nano-structured titanium dioxide. The titanium dioxide may have an anatase crystal structure. The first semiconductor layer may be doped with the material, or the material may form a layer on the first semiconductor layer or the first semiconductor layer may both be doped with the material and have a layer of the material thereon. The material may be a metal or a metal oxide or metal alloy, and may be selected from the group consisting of transition metals, Sn, Pt-Sn, Pt-Mo, Pt-Ru, Ni-Zr, Pt-Rh, Pt-Ir, Pt-Ru-W, Pt-Ru-Os, Pt-Ru-Sn, Pt-Ni-Ti, Pt-Ni-Zr, Pt-Ni-Nb, platinum group metal oxides, gold group metal oxides, tin oxides, tungsten oxides, iridium oxides, rhodium oxides, ruthenium oxides and mixtures thereof. The transition metals may include silver, platinum group metals, gold group metals, Ir, Ru, Os, Mo, Zr, Cu, Nb, and Rh.

- 30 In an embodiment, one or more additional photocatalytic semiconductor layers, and material disposed on and/or in said layers, may be present. The material in the additional layers may be the same as or different to the material in the layer on and/or in the first layer.

In one embodiment, there is provided a photocatalytic entity, which comprises:

- a substrate; and
- a photocatalytic assembly according to the first aspect, said assembly being
5 disposed on, in, or both in and on the substrate.

In a second aspect, there is provided a photocatalytic entity, which comprises

a substrate;

a photocatalytic assembly comprising a first photocatalytic semiconductor layer, and a
10 material selected from the group consisting of a metal, a metal alloy, a metal oxide and
mixtures thereof, said material being disposed on and/or in said first layer, said assembly
being disposed on, in, or both in and on the substrate; and
a second photocatalytic semiconductor layer disposed on, in, or both in and on said material;
wherein said second photocatalytic semiconductor layer has a finer microstructure than the
15 first photocatalytic semiconductor layer.

The photocatalytic assembly may further comprise a second photocatalytic layer disposed
on, in, or both in and on said material.

20 The photocatalytic assembly may be on the surface of the substrate or it may be within
pores in the substrate or it may be partly on the surface of the substrate and partly within
pores in the substrate or it may be attached to some other part of the substrate. The
photocatalytic assembly may partly coat the substrate or it may completely coat the
substrate.

25 In one embodiment, there is provided a process for making photocatalytic entity, said process
comprising the steps of:

- depositing a first photocatalytic semiconductor layer on a substrate; and
- depositing a material on, in, or both in and on said first layer, said material being
30 selected from the group consisting of a metal, a metal alloy, a metal oxide and
mixtures thereof.

In a third aspect, there is provided a process for making photocatalytic entity, said process comprising the steps of:

- depositing a first photocatalytic semiconductor layer on a substrate;
- depositing a material on, in, or both in and on said first layer, said material being selected from the group consisting of a metal, a metal alloy, a metal oxide and mixtures thereof; and
- depositing a second photocatalytic semiconductor layer on, in, or both in and on said material; wherein said second photocatalytic semiconductor layer has a finer microstructure than the first photocatalytic semiconductor layer.

In one embodiment, there is provided a process for making photocatalytic entity, said process comprising the steps of:

- depositing a first photocatalytic semiconductor layer on a substrate, said layer comprising a material on, in or both in and on said first layer, said material being selected from the group consisting of a metal, a metal alloy, a metal oxide and mixtures thereof.

In a fourth aspect, there is provided a process for making photocatalytic entity, said process comprising the step of:

- depositing a first photocatalytic semiconductor layer on a substrate, said layer comprising a material selected from the group consisting of a metal, a metal alloy, a metal oxide and mixtures thereof; and
- depositing a second photocatalytic semiconductor layer on, in, or both in and on said material; wherein said second photocatalytic semiconductor layer has a finer microstructure than the first photocatalytic semiconductor layer.

The processes above may further comprise the step of depositing a second photocatalytic semiconductor layer on, in or both in and on said material.

The process of depositing the first photocatalytic semiconductor layer may comprise one or more of the following steps:

- immersing the substrate in a solution of a hydrolysable titanium species in an organic solvent;
- 5 – removing the substrate from the solution;
- exposing the substrate to air or some other gas containing water vapour; and
- heating the substrate with a first layer.

10 The hydrolysable titanium species may be an a C₁ to C₆ straight chain or branched alkoxide, and may be a primary, secondary or tertiary alkoxide, or it may be some other hydrolysable titanium species.

15 The material may be a metal or a metal oxide or metal alloy, and may be selected from the group consisting of transition metals, Sn, Pt-Sn, Pt-Mo, Pt-Ru, Ni-Zr, Pt-Rh, Pt-Ir, Pt-Ru-W, Pt-Ru-Os, Pt-Ru-Sn, Pt-Ni-Ti, Pt-Ni-Zr, Pt-Ni-Nb, platinum group metal oxides, gold group metal oxides, tin oxides, tungsten oxides, iridium oxides, rhodium oxides, ruthenium oxides and mixtures thereof. The transition metals may include silver, platinum group metals, gold group metals, Ir, Ru, Os, Mo, Zr, Cu, Nb, and Rh.

20 The step of depositing a layer of material may be achieved by precipitation, impregnation, photodecomposition or sputter coating, or by some other convenient method.

25 The step of depositing a second photocatalytic semiconductor layer may comprise similar steps to the process of depositing the first layer, and the hydrolysable titanium species to be used in making the second photocatalytic semiconductor layer may be the same as or different to the hydrolysable titanium species to be used in making the first photocatalytic semiconductor layer.

30 In an embodiment, one or more additional layers of the material and of the first and/or the second semiconductor may be added to the substrate.

In a fifth aspect, there is provided a photocatalytic entity, when made by the process of the third aspect.

In a sixth aspect, there is provided a photocatalyst entity, comprising a plurality of photocatalytic entities according to the second or the fourth aspect. Some of the entities may be according to the second aspect and some may be according to the fourth aspect, or they may be all according to the second aspect or they may be all according to the fourth aspect, or they may be according to both the second and fourth aspects.

In a seventh, there is provided a method for degrading organic materials, halogens or ozone in a fluid comprising:

- contacting a photocatalyst according to the fifth aspect, and/or a photocatalytic entity according to the second or fourth aspects, with the fluid; and
- illuminating said photocatalyst and/or photocatalytic entity in contact with the fluid.

The halogens may comprise fluorine, chlorine, bromine or iodine.

The fluid may be water or it may be aqueous based or it may be some other liquid, or it may be steam or some other vapour, or it may be air or it may be some other gas. The illuminating may use a wavelength of light, or mixture of wavelengths, effective to degrade organic materials, halogens or ozone when in contact with the photocatalyst or photocatalytic entity. The illumination may be for a time suitable for the desired degree of degradation of organic matter, halogens or ozone in the fluid. The time may depend on the concentration and nature of organic matter in the fluid, the concentration of photocatalysts in the suspension, the size of the photocatalysts, the intensity and wavelength of the light, the geometry of the vessel in which the fluid is contained, temperature and other factors.

The contacting may be by means of suspending the photocatalyst in the fluid or it may be by passing the fluid through the photocatalyst or past the catalyst or it may be by some other means. The method may also include the step of separating the photocatalyst from the fluid. The separating may be by means of settling, filtration or centrifugation or some other suitable method.

In an embodiment, the photocatalytic entity is a surface at least partially coated with the photocatalytic assembly of the first aspect. The contacting may be by means of passing the fluid past, through or over the photocatalytic entity. A photocatalytic entity in the form of a surface may also be used in combination with a photocatalyst according to the sixth aspect.

The method may also include the step of at least partially removing products of degradation of organic materials from the fluid.

The photocatalytic assembly according to the first aspect or a photocatalytic entity according to the second or fifth aspects or a photocatalyst according to the sixth aspect can be used to degrade and/or adsorb one or more organic materials, halogens or ozone in a fluid.

In an eighth aspect, there is provided an apparatus comprising:

- a photocatalytic entity according to the second or fourth aspects and/or a photocatalyst according to the sixth aspect;
- a reactor in which a fluid may be contacted with the photocatalytic entity and/or photocatalyst; and
- a source of illumination disposed to illuminate the photocatalytic entity and/or photocatalyst in contact with the fluid with a wavelength of light, or mixture of wavelengths, effective to degrade organic materials, halogens or ozone when in contact with the first or the second photocatalytic semiconductor layer of the photocatalytic entity and/or photocatalyst.

The apparatus may be suitable for degrading organic materials, halogens or ozone in a fluid in accordance with the method of the seventh aspect. The apparatus may additionally comprise means to constrain the photocatalytic entity and/or photocatalyst within the apparatus, and may also comprise means for the fluid to enter and exit the apparatus.

The means to constrain the photocatalytic entity and/or photocatalyst may be for example a filter which is capable of preventing passage of the photocatalytic entity.

In an embodiment, there is a region in which the photocatalyst is suspended in the fluid, and the suspension illuminated by the source.

In another embodiment, the apparatus comprises a photocatalytic entity which is in the form of a surface at least partially coated with a photocatalytic assembly according to the first aspect. The means to constrain the photocatalytic entity may be an attachment between the photocatalytic entity and another portion of the apparatus. For example the photocatalytic entity may be attached to the walls of a reactor through which the fluid flows.

In a further embodiment, packed bed technology is used whereby the photocatalyst is constrained in a reactor column.

The apparatus according to the eighth aspect can be used to degrade organic materials in a fluid.

In a ninth aspect, there is provided a system for purification of a fluid comprising:

- an apparatus according to the eighth aspect of the invention, and
- a treatment module coupled to the reactor of the apparatus.

The treatment module comprises a separation membrane, and the separation membrane may be a filtration membrane, or a microfiltration membrane, or an ultrafiltration membrane, or a reverse osmosis membrane, or it may comprise a combination of membranes. The separation membrane may be capable of separating a fluid into a permeate and a concentrate. Alternatively the treatment module may comprise a deioniser or an ion exchanger or a distillation unit or some other purification unit. The fluid may be water or it may be aqueous based or it may be some other liquid, or it may be steam or some other vapour, or it may be air or it may be some other gas.

In an embodiment, the system is configured such that, in operation, effluent from the reactor passes from the reactor to the treatment module to enable the treatment module to purify the effluent from the reactor.

The system has means to recycle a portion of the fluid exiting from the treatment module to the reactor. For example, if the treatment module comprises a membrane, the concentrate may be recycled to the reactor and the permeate may be outputted from the system. The means to recycle may be, for example, a pipe leading from the treatment module to the reactor.

In another embodiment, the system is configured such that, in operation, fluid passes from the treatment module to the reactor. In this embodiment, the treatment module may act as a pre-treatment for the apparatus.

In yet another embodiment, there is more than one treatment module. The system may be for example configured such that, in operation, fluid passes through a first treatment module to the reactor, and from the reactor to a second treatment module. There may be means to recycle a portion of the fluid exiting from the second treatment module to the reactor.

In a tenth aspect, there is provided the use of the system according to the ninth aspect for the purification of a fluid.

In an eleventh aspect, there is provided a method for purifying a fluid comprising passing the fluid through a system according to the ninth aspect of the invention.

Disclosure of Invention

This invention relates to the purification of a fluid medium, for example air or water. More particularly, the invention relates to the adsorption and/or degradation of organic pollutants such as natural organic matter, volatile organic contents (VOCs), aromatic emissions, polychlorobiphenyls (PCB's), trihalomethanes, benzene, benzene derivatives, acetone, carbon monoxide, methyl ethyl ketone, styrene, toluene, acetaldehyde and formaldehyde, micro-organisms such as bacteria, viruses, fungi, mites and allergens, and

smells and odours such as tobacco smoke, pet smells, mouldy smell, stagnant air, ozone and halogens, and other organic compounds/organisms in air or water.

In another aspect relating to the purification of a fluid medium, the technology can also be applied to accelerate total organic carbon (TOC) reduction, chlorine destruction and also ozone destruction.

The invention describes a novel photocatalyst which comprises a layered nano-structured semiconductor (for example titanium dioxide), wherein at least the first semiconductor layer has disposed thereon and/or therein a material selected from the group consisting of a metal, a metal alloy, a metal oxide and mixtures thereof, and the nano-structured semiconductor is attached to a substrate. The novel photocatalyst may be used together with a light source with a wavelength that will activate the photocatalytic assembly for purification of fluids by adsorption and/or degradation of pollutants.

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An object of the present invention is to apply this invention to a practical fluid purification system for either commercial or domestic use, for example for the purification of potable water or for treating water from natural sources such as reservoirs, streams, groundwater or even wastewater for reuse.

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In its preferred form, the present invention addresses this problem by attaching a layered nano-structured titanium dioxide including a layer of infused metal on and/or in the surfaces of a porous substrate such as iron oxide, silica, alumina, activated carbon, general zeolite, zinc oxide or some other suitable material.

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The substrate

The substrate may be porous or it may be non-porous or it may be partially porous. A porous substrate may be suitable to act as an adsorbent for pollutants, inorganic or organic as well as acting as a substrate for a photocatalyst. The substrate may comprise silica or it may comprise iron oxide or it may comprise zinc oxide, alumina, activated carbon, general zeolite, or it may comprise some other suitable material or it may comprise a suitable mixture of materials. The substrate may be in the form of a microparticle, a hollow microparticle, a fibre, a bead, a plate or some other suitable form, and may be

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spherical, irregular or some other shape or it may be a surface. The substrate may be sufficiently large to enable it to separate from a fluid by either settling or flotation.

Alternatively the substrate may be sufficiently large to allow it to be removed from a fluid by filtration or centrifugation or by some other suitable method. The hydrodynamic

5 diameter of the substrate may be greater than 10 micron or greater than 20, 50, 100, 200 or 500 microns or greater than, 1, 2, 5 or 10 mm, and may be between 10 microns and 10 mm or between 100 microns and 5 mm or between 500 microns and 5 mm or between 1 and 5 mm, and may be about 10, 20, 50, 100, 200 or 500 microns for a substrate to be used in a slurry or in suspension, or about 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10 mm for a substrate
10 to be used as a packed bed. Alternatively, the substrate may be a surface. The substrate may conveniently have a large specific surface area for coating with the photocatalytic assembly. This may be achieved with a porous structure, wherein the fluid to be treated may thoroughly contact the photocatalytic assembly on and/or in the substrate. Also, the substrate may have sufficient transparency to light of a wavelength which activates the
15 photocatalytic assembly to ensure that a sufficient proportion of the coated surfaces receives said light at an adequate energy level for activation.

Examples of substrates that may conveniently be used in the present invention are:

20 1) iron oxide: iron oxide may conveniently be used as it is inexpensive and may be manufactured easily in a suitable form. Porous iron oxide in its preferred form (hematite) may be manufactured by reaction of iron chloride with sodium hydroxide in water or by other suitable methods. The desired porous hematite structure may be obtained for example by repeated accelerated drying using ethanol and methanol followed by calcining
25 at a temperature above 350°C or the temperature may be above 400, 450, 500 or 550°C, and may be between 350 and 650°C or between 400 and 600°C or between 450 and 550°C and may be about 350, 400, 450, 500, 550, 600 or 650°C. The iron oxide obtained using this method is porous and has a large specific surface area. The porous nature of the iron oxide facilitates adsorption of pollutants and also facilitates mass transfer of fluid
30 to photoreactive sites.

2) Silica or glass beads: silica or glass beads may also be used as substrates as silica has a high refractive index and is also inert and may be obtained in a porous form. The

hydrodynamic diameter of the beads may be greater than 10 micron or greater than 20, 50, 100, 200 or 500 microns or greater than, 1, 2, 5 or 10 mm, and may be between 10 microns and 10 mm or between 100 microns and 5 mm or between 500 microns and 5 mm or between 1 and 5 mm, and may be about 10, 20, 50, 100, 200 or 500 microns or
5 about 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10 mm and is preferably between 1 and 10 mm. For better adhesion between the substrate and the photocatalyst and also to increase the surface area of the substrate, the substrate can be conditioned as follows: Silica or glass beads in the preferred size range may be prepared for coating with the photocatalytic entity by etching the silica surface with hydrofluoric acid. In an example of this process, the beads are
10 immersed into a solution of between 1 and 10M HF, rinsed with ultrapure water and dried prior to the coating process. The immersion may be for a time between 0.5 and 5 hours or between 1 and 4 hours or between 2 and 3 hours, and may be about 0.5, 0.75, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5 or 5 hours, or it may be less than 0.5 hours or it may be greater than 5 hours. The temperature for drying may be greater than 100°C, or between 100 and 150°C or
15 between 110 and 150°C or between 120 and 140°C, and may be about 100, 110, 120, 130, 140 or 150°C. The time for drying may be between 1 and 6 hours and may be between 2 and 5 hours or between 3 and 4 hours and may be about 1, 2, 3, 4, 5 or 6 hours.

3) Commercially available particles or powders may also be used as a substrate. For
20 example alumina (Al_2O_3), zeolite, activated carbon, ceramic particles can be used as a substrate.

4) The substrate could also be surfaces in the form of glass fibers, the walls of the reactor in contact with the fluid medium which may be of glass or stainless steel construction, or
25 on the surface of the light source itself.

The photocatalytic assembly

The photocatalytic assembly of this invention comprises a layered photocatalytic semiconductor, doped with a layer of a material selected from the group consisting of a
30 metal, a metal alloy, a metal oxide and mixtures thereof, and which is disposed on and/or in at least one of the layers of semiconductor. The photocatalytic assembly may be bonded to the surface of a substrate.

The photocatalytic semiconductor may be titanium dioxide, although other photocatalytic semiconductors may be used, and it is preferably nano-structured. The second photocatalytic semiconductor may be the same as the first photocatalytic semiconductor or it may be different, and the structure of the second photocatalytic semiconductor layer may be the same as the structure of the first photocatalytic semiconductor layer or it may be different. A photocatalytic semiconductor which may be used in the present invention is titanium dioxide in the anatase form. If anatase is used as the photocatalytic semiconductor, a process which may be used for bonding it to the substrate is by an adaptation of the known sol-gel technique.

The material may be a metal or a metal oxide or metal alloy, and may be selected from the group consisting of Sn, Pt-Sn, Pt-Mo, Pt-Ru, Ni-Zr, Pt-Rh, Pt-Ir, Pt-Ru-W, Pt-Ru-Os, Pt-Ru-Sn, Pt-Ni-Ti, Pt-Ni-Zr, Pt-Ni-Nb, platinum group metal oxides, gold group metal oxides, tin oxides, tungsten oxides, iridium oxides, rhodium oxides, ruthenium oxides and mixtures thereof. The transition metals may be platinum group metals (Pd, Pt, Ni), gold group metals (Au, Ag, Cu), Ir, Ru, Os, Mo, Zr, Cu, Nb, Rh. Commonly the material may be silver or platinum. The material selected from the group consisting of a metal, a metal alloy, a metal oxide and mixtures thereof may be capable of inhibiting the recombination of photogenerated electron-hole pairs produced in one or more of the semiconductor layers. Said material may behave as an accelerator for transferring the photogenerated electrons to oxygen adsorbed on the surface of the photocatalytic entity, thereby reducing the recombination rate (Wang, C. M., Heller, A. and Gerischer, H (1992), *J. Am. Chem. Soc.*, Vol. 114, p 5230). There is an optimum loading rate of the material on a photocatalytic entity, and too much deposition may be detrimental for the reaction. The optimum loading rate will depend upon the nature of the material, and may be between 0.1 and 5% by weight, or between 0.5 and 4% or between 1 and 3% by weight, and may be about 0.1, 0.2, 0.5, 1, 2, 3, 4 or 5% by weight. When the material is silver, the optimum loading rate may be about 1% by weight.

In early work, it was unclear whether the metal was coated on the substrate particles, or whether it was present as separate particles. Furthermore, loss of the metal was detected after prolonged illumination of the photocatalyst. Relative to freshly prepared photocatalyst, the activity of reused photocatalyst was decreased. Nevertheless,

photocatalysts which contain a material layer similar to that of the present invention, have been observed to exhibit higher efficiency, even after repeated use, than photocatalysts which comprise a substrate and a photoreactive semiconductor but no such layer.

5 **Process for making a photocatalytic entity**

After application of a first semiconductor layer to a substrate, a layer of material selected from the group consisting of a metal, a metal alloy, a metal oxide and mixtures thereof is deposited on the first semiconductor layer, and subsequently a second semiconductor layer is deposited on the material. This process enables the material to perform its role in
10 the photocatalyst as an accelerator for transferring the photogenerated electrons away from the top layer of semiconductor, thereby reducing the recombination rate and improving efficiency. The material may be trapped between layers of semiconductor and may not be disassociated in the photocatalytic reaction.

15 Alternatively, the first semiconductor layer is first admixed with the material prior to deposition on the substrate as a first layer.

A photocatalytic semiconductor which may be used in the present invention is titanium dioxide in the anatase form. If anatase is used as the photocatalytic semiconductor, a
20 process which may be used for bonding it to the substrate is by an adaptation of the known sol-gel technique, described below. In this invention, the sol-gel bonding technique may be employed with different precursors for the first and second photocatalytic semiconductor layers in order to achieve different morphologies in the different layers.

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In an example, a titanium alkoxide, for example titanium ethoxide, is dissolved in an organic solvent and is then reacted with a controlled amount of an acid, such as aqueous nitric acid, to form a coating solution. This process may be used to achieve controlled or accelerated hydrolysis in order to obtain the required hydrolysis pathway such that
30 subsequent calcination produces the desired surface structure. Other methods may be used for forming a coating solution, however a common feature of the coating solution is that it contain a titanium alkoxide. In one method, the process for forming the first photocatalytic layer the titanium alkoxide is titanium isopropoxide (TIP). The organic

solvent may be an alcohol or a mixture of alcohols. It may be a mixture of ethanol and methanol and the proportion of methanol in the mixture may be between 0 and 50% by weight or by volume, or between 15 and 45% or between 20 and 40% or between 25 and 35% by weight or by volume, and it may be about 0, 10, 15, 20, 25, 30, 35, 40, 45 or 50% by weight or by volume. The ratio of the titanium alkoxide and organic solvent is also varied to achieve different end results, ie. Different surface morphology and different crystal growth. To achieve the desired result in this technology, the molar ratio of the titanium alkoxide to the solvent can vary from 1:4 to 1:100 but preferably in the range of 1:30 to 1:70.

The substrate may be dipped into the first coating solution. Alternatively the first coating solution may be passed through or over the substrate or some other method may be used to expose the substrate to the first coating solution. Subsequent exposure of the substrate to air or another gas results in a controlled or accelerated hydrolysis process to yield an amorphous titanium dioxide layer on the substrate surfaces. The air or other gas may contain sufficient water vapour to hydrolyse the hydrolysable titanium species remaining on the substrate after removing said substrate from the solution. The relative humidity of the air or other gas may conveniently be greater than 10% or it may be greater than 20, 30, 40, 50, 60, 70, 80 or 90%, and may be between 10 and 100% or between 20 and 100% or between 50 and 100%, and may be about 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 95 or 100%. The air or other gas may be for example air, nitrogen, carbon dioxide, argon or other suitable gas. The substrate may be left in the air or other gas for a time sufficient to effect at least partial hydrolysis of the hydrolysable titanium species. The length of time will depend on the relative humidity and the temperature, and may be between 1 hour and 10 hours or may be between 2 and 9 hours or between 3 and 8 hours or between 4 and 7 hours or between 5 and 6 hours, and may be about 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10 hours or it may be greater than 10 hours. The substrate may be exposed to air by resting in air, or by passing air through, past or over it or by some other convenient method.

After a period sufficient to effect at least partial hydrolysis of the hydrolysable titanium species, the coated substrate may be heated in order to convert the amorphous layer to the anatase crystal structure with the desired structure. The result is a very tight bonding of the anatase layer with, to or into the substrate, hence avoiding any significant amount of

anatase entering the fluid to which the photocatalytic entity may be subsequently be exposed. This bonding may involve a covalent bonding between the substrate and the anatase. Heating the substrate with the first layer may be effected at a temperature above 350°C or the temperature may be above 400, 450, 500, 550 or 600°C, and may be
5 between 350 and 650°C or between 400 and 600°C or between 450 and 550°C and may be about 350, 400, 450, 500, 550, 600 or 650°C. Heating may be for a time sufficient to convert the first layer to the anatase crystal structure, and may be for greater than 3 hours or greater than 4, 5 or 6 hours, or may be between 3 and 7 hours or between 3.5 and 6.5 hours or between 4 and 6 hours or between 4.5 and 5.5 hours, and may be about 3, 3.5, 4,
10 4.5, 5, 5.5, 6, 6.5 or 7 hours.

The process of depositing a first photocatalytic semiconductor layer using TIP results in a surface structure of interconnected crystals comprising irregular crystalline peaks, i.e. high peaks and valleys which may be detected using atomic force microscopy (AFM). An
15 example of an AFM image of a semiconductor layer according to the invention is shown in Fig. 5.

Following the depositing of a first photocatalytic semiconductor layer on the substrate, the material is deposited on and/or in the first layer. Commonly used methods for
20 depositing a material into and/or onto the first semiconductor layer include precipitation and impregnation. In addition, photodecomposition and sputter coating may also be used. These methods are documented in the open literature (for example Herrmann, J. M., and Mansot, J. L. "Analytical TEM study of the selective photocatalytic deposition of platinum on titania-silica mixtures and silica-supported titania." *J. Catal*, 121, no. 2
25 (1990): pp 340-8). Alternatively, an effective way of depositing the material on the first layer is to form a metal alkoxide (or any organo-metallic precursor) with the intended metal and subsequently introducing the metal via sol-gel coating method to the first layer. The coat is then allowed to dry and heated using the same procedure and profiles as described for the first coating layer.

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Yet in another procedure, the titania alkoxide and chosen metal alkoxide can be mixed in a certain ratio, together with the organic solvent ethanol or methanol to form the augmented first coating layer. The augmented coat is then allowed to dry and heated

using the same procedure and profiles as described for the first coating layer.
Subsequently the second coat is applied as described below.

A second photocatalytic semiconductor layer is then deposited on and/or in the material.

5 The process of depositing said second photocatalytic semiconductor layer is similar to the process described above for depositing a first photocatalytic semiconductor layer, however a common titanium alkoxide used in the sol-gel technique is titanium butoxide (TBT). TBT may be selected for making the second photocatalytic semiconductor layer because the resulting microstructure is finer with smaller and more uniform nanosized
10 crystal grains compared to the structure obtained from TIP. A finer microstructure with more crystal grains coated onto the first photocatalytic semiconductor layer with high peaks and valleys may produce a densely packed nano-structure which is well suited for photoreaction. With the embedded material performing the role as accelerator and reducing recombination of electron-hole pairs, the resulting densely packed nano-structured
15 photocatalytic assembly on a porous substrate is highly efficient.

The result of the process described above is a very tight bonding of a second anatase layer on the material hence avoiding any significant amount of anatase entering the fluid to which the matrix may subsequently be exposed.

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Ideally the first photocatalytic semiconductor layer has a surface structure of interconnected crystals with high peaks and valleys. This will be doped with a metal, metal alloy, metal oxide or mixture thereof and then coated with another layer of anatase crystal structure with a finer microstructure with smaller and more uniform nanosize
25 crystal grains to produce a densely packed novel nano-structured photocatalytic entity. Under ideal conditions, one coating of each layer is required, however it may be necessary to repeat the coating process of one or more layers in order to achieve adequate coverage.

30 **Method of degrading organic materials, ozone or halogens such as chlorine**

The method for degrading organic materials, chlorine or ozone in a fluid may comprising contacting a photocatalyst or a photocatalytic entity, with the fluid and illuminating the photocatalyst or photocatalytic entity in contact with the fluid.

The fluid may be water or it may be aqueous based or it may be some other liquid, or it may be steam or some other vapour, or it may be air or it may be some other gas. The fluid should contain sufficient oxygen to enable photooxidation of the organic materials, chlorine or ozone therein. The illuminating may use a wavelength of light, or mixture of wavelengths, effective to degrade organic materials, chlorine or ozone when in contact with the photocatalytic entity and/or photocatalyst. The wavelength of light may be associated with an energy greater than the band gap of the photocatalytic semiconductor of the photocatalyst or photocatalytic entity. For example, if the photocatalytic semiconductor is titanium dioxide, the light may be in the UV range, and its wavelength may be less than 400 nm or less than 380, 360, 340, 320, 300, 280, 260, 240, 220 or 160 nm, and it may be between 200 and 410 nm or between 225 and 400 nm or between 250 and 375 nm or between 275 and 350 nm or between 300 and 325 nm, and may be about 390, 380, 370, 360, 350, 340, 330, 320, 310, 300, 290, 280, 270, 260, 250, 240, 230, 220, 210 or 160nm, and is commonly 254 nm or 185nm which is provided in most commercial UV light sources, or it may comprise a mixture of wavelengths, at least one of which is in the UV range. For other photocatalytic semiconductors, the wavelength of the light used may be different to that used for titanium dioxide. The illumination may be for a time suitable for the desired degree of degradation of organic matter, chlorine or ozone in the fluid. The time may depend on the concentration and nature of organic matter or concentration of chlorine or ozone in the fluid, the concentration of photocatalytic entities in the suspension, the size of the photocatalytic entities, the intensity and wavelength of the illumination, the geometry of the vessel in which the fluid is contained, temperature and other factors.

25

In addition, the photocatalyst can also be applied to accelerate total organic carbon (TOC) reduction, chlorine destruction and also ozone destruction.

The time may be between 1 second and 1 hour, and may be between 10 seconds and 1 hour or between 30 seconds and 1 hour or between 1 minute and 1 hour or between 5 and 45 minutes or between 5 and 30 minutes or between 5 and 20 minutes and may be about 1, 5, 10, 20, 30 or 45 seconds or about 1, 2, 5, 10, 20, 30, 40, 50 or 60 minutes or it may be greater than 1 hour.

The contacting may be by means of suspending the photocatalyst or photocatalytic entity in the fluid or it may be by passing the fluid through or past the photocatalyst or photocatalytic entity or it may be by some other means. The method may also include the
5 step of separating the photocatalyst from the fluid. The separating may be by means of settling, filtration or centrifugation or some other suitable method.

Silica/glass beads commonly absorb only a small percentage of the light and are substantially transparent. One method for using a photocatalyst made from silica or glass
10 beads is to use a packed bed method whereby the photocatalyst is packed into a reactor column. Due to the high refractive index of silica/glass beads, the light from the source is able to penetrate the photocatalyst with relatively little attenuation and illuminate regions of the photocatalytic assembly that do not directly face the light source. This creates an efficient photocatalytic system.

15 Another method for practicing the invention is to suspend a photocatalyst in the fluid by agitation or some other convenient method. Due to the mixing of the suspension, illumination of a majority of the photocatalytic entities is achieved for a significant time. Optionally, the fluid may exit the reactor through a barrier that is capable of constraining
20 the photocatalyst within the region of illumination but may permit passage of the fluid. The barrier may be a filter or it may be a membrane or it may be a frit or it may be some other form of selective barrier.

In yet another method, the photocatalytic entity may be a surface at least partially coated
25 with the photoreactive material of the first aspect. The contacting may be by means of passing the fluid past, through or past the photocatalytic entity. A photocatalytic entity in the form of a surface may also be used in combination with a photocatalyst.

The method may also include the step of removing the products of degradation of organic
30 materials produced from the fluid.

Purification systems

An apparatus according to the invention, comprising a photocatalytic entity and/or a photocatalyst, a reactor and a source of illumination, may be used by itself to purify a fluid, or it may be used in combination with at least one other treatment module. Said treatment module(s) may comprise a filtration membrane, or a microfiltration membrane, or an ultrafiltration membrane, or a reverse osmosis membrane, or it may comprise a combination of membranes. The membranes may be hollow fibre membranes or they may be spiral wound or flat sheet. Alternatively a treatment module may comprise a deioniser or an ion exchanger or a distillation unit or some other purification unit.

Treatment modules may be used either for pre-treatment of the fluid before the fluid enters the reactor, or as treatment of the effluent from the reactor. In this specification, "effluent from the reactor" refers to fluid that exits the reactor. Pre-treatment may serve to remove some impurities in order to reduce the load of impurities entering the reactor, and treatment of the effluent from the reactor may remove some impurities that were not degraded or removed by the apparatus, or may remove some products of degradation of impurities, said products being formed in the reactor. If the treatment module is used for treatment of the effluent from the reactor, the use of the apparatus to at least partially degrade impurities in the fluid before they enter the treatment module may increase the life of the treatment module, or may reduce the required frequency of cleaning of the treatment module, relative to use of the treatment module alone. There may be more than one treatment module, and there may be separate modules to function as a pre-treatment module and as a treatment module for treatment of the effluent from the reactor.

Commonly a treatment module comprises a membrane. A membrane separates a fluid into a permeate and a concentrate. Conveniently, the concentrate may be recycled to the reactor in order to further degrade impurities in the fluid. Alternatively the concentrate may be passed through one or more further treatment modules before being either recycled to the reactor or being discharged. The permeate may be purified further using one or more treatment modules.

Brief Description of Drawings

The invention will now be described, by way of example, with reference to the accompanying drawings wherein:

Figure 1 is a diagrammatic representation of the process for making a photocatalyst according to the present invention;

Figure 2 is a diagrammatic representation of an apparatus for degrading organic materials in a fluid wherein a photocatalyst is suspended in the fluid;

Figure 3 is diagrammatic representation of an apparatus for degrading organic materials in a fluid wherein a photocatalytic entity in the form of a surface is attached to the apparatus;

Figure 3a is a diagrammatic representation of another apparatus for degrading organic materials in a fluid wherein a photocatalytic entity in the form of a surface is attached to the apparatus

Figure 4 is a diagrammatic representation of an apparatus for degrading organic materials in a fluid wherein a photocatalyst is constrained in a reactor column;

Figure 4a is a diagrammatic representation of another apparatus for degrading organic materials in a fluid wherein a photocatalyst is constrained in a reactor column;

Figure 5 is an AFM image of a semiconductor layer according to the invention;

Figure 6 is a diagrammatic representation of a system for purifying a fluid, wherein a treatment module comprising a membrane is used;

Figure 7 is a diagrammatic representation of another system for purifying a fluid, wherein a treatment module is used as pre-treatment; and

Figure 8 is a diagrammatic representation of yet another system for purifying a fluid, wherein two treatment modules are used.

Figure 9 is a graph of removal efficiency vs hydraulic retention time .

Figure 10 is a diagrammatic representation of a system for purifying air.

Best Mode And Other Modes For Carrying Out The Invention

Making the photocatalyst or photocatalytic entity

In this invention, the sol-gel bonding technique may be employed with different precursors for the first and second photocatalytic semiconductor layers in order to achieve different morphologies in the different layers.

With reference to Figure 1, a first coating solution 102 is made in a first coating vessel 104 as follows. A titanium alkoxide, is dissolved in an organic solvent to form a solution in the range of 1:30 to 1:70 by molar ratio, and is then reacted with a controlled amount of concentrated HCL or some other aqueous acid, to form coating solution 102. This process may be used to achieve controlled or accelerated hydrolysis in order to obtain the required hydrolysis pathway such that subsequent calcination produces the desired surface structure. Other methods may be used for forming coating solution 102, however a preferred feature of the coating solution is that it contain a titanium alkoxide. Preferably the titanium alkoxide is titanium isopropoxide (TIP). The organic solvent may be an alcohol or a mixture of alcohols. It may be a mixture of ethanol and methanol and the proportion of methanol in the mixture may be between 10 and 50% by weight or by volume.

Substrate 106 may be dipped into first coating solution 102. Alternatively first coating solution 102 may be passed through or over substrate 106 or some other method may be used to expose substrate 106 to coating solution 102. Substrate 106 may be in the form of a particulate material (as illustrated in Figure 1) or it may be in some other form.

Substrate 106 may for example comprise porous silica beads. Preferably the beads are sufficiently large to enable them to separate from a fluid by either settling or flotation.

Alternatively they may be sufficiently large to allow them to be removed from a fluid by filtration or centrifugation or by some other suitable method. The hydrodynamic diameter of substrate 106 may be between 10 microns and 10 mm. Alternatively, substrate 106

may be a surface. Substrate 106 is left in contact with first coating solution 102 for between 10 sec and 1 hour, and preferably for about 1 minutes.

After removal of substrate 106 from coating solution 102, exposure of substrate 106 to air
5 results in a controlled or accelerated hydrolysis process to yield an amorphous titanium dioxide layer on the substrate surfaces. The air may contain sufficient water vapour to hydrolyse the hydrolysable titanium species remaining on the substrate after removing said substrate from the solution. The relative humidity of the air may conveniently be greater than 10%. Substrate 106 may be left in air for a time sufficient to effect at least
10 partial hydrolysis of the hydrolysable titanium species. The length of time will depend on the relative humidity and the temperature, and may be between 1 minute and 1 hour. Substrate 106 may be exposed to air by resting substrate 106 in air, or by passing air through, past or over substrate 106 or by some other convenient method.

15 After at least partial hydrolysis of the hydrolysable titanium species, coated substrate 110 may be transferred to container 111 and heated in order to convert the amorphous layer to the anatase crystal structure with the desired structure. Heating may be conducted in furnace 112, or by some other means of heating. Heating may be effected at a temperature above 350°C. Heating may be for a time sufficient to convert the first layer to the anatase
20 crystal structure, and may be for between 3 and 7 hours.

Following the depositing of a first photocatalytic semiconductor layer on substrate 106 to form coated substrate 110, a material selected from the group consisting of a metal, a metal alloy, a metal oxide and mixtures thereof is deposited on and/or in the first
25 photocatalytic semiconductor layer. Commonly the material is silver or platinum. In an example, solution 114, containing silver nitrate, is added to coated substrate 110 in container 111 and an aqueous solution of sodium carbonate 115 is added. Solution 114 may be agitated during and/or after addition of solution 115. The liquid phase is then removed and metal coated substrate 126 in container 111 is placed in a furnace 116, and
30 heated. Heating may be effected at a temperature above 350°. Furnace 116 may be the same as or different to furnace 112.

A second photocatalytic semiconductor layer is then deposited on and/or in the layer of material. A second coating solution 122 is made in a second coating vessel 124 as follows. A titanium alkoxide, is dissolved in an organic solvent and is then reacted with a controlled amount of aqueous nitric acid or some other aqueous acid, to form second
5 coating solution 122. The conditions for forming the second semiconductor layer are similar to those used for forming the first semiconductor layer. This process may be used to achieve controlled or accelerated hydrolysis in order to obtain the required hydrolysis pathway such that subsequent calcination produces the desired surface structure. Other methods may be used for forming second coating solution 122, however a preferred
10 feature of second coating solution 122 is that it contain a titanium alkoxide. Preferably the titanium alkoxide is titanium butoxide (TBT). The organic solvent may be an alcohol or a mixture of alcohols. It may be a mixture of ethanol and methanol and the proportion of methanol in the mixture may be between 0% and 50% by weight or by volume. The process of depositing the second photocatalytic semiconductor layer is similar to the
15 process described above for depositing the first photocatalytic semiconductor layer. Metal coated substrate 126 may be dipped into second coating solution 122. Alternatively second coating solution 122 may be passed through or over metal coated substrate 126 or some other method may be used to expose it to second coating solution 122.

20 After removal of intermediate species 127 from coating solution 122, exposure of intermediate species 127 to air results in a controlled or accelerated hydrolysis process to yield an amorphous titanium dioxide layer on the substrate surfaces. The air may contain sufficient water vapour to hydrolyse the hydrolysable titanium species remaining on the substrate after removing said substrate from the solution. The relative humidity of the air
25 may conveniently be greater than 10%. Intermediate species 127 may be left in air for a time sufficient to effect at least partial hydrolysis of the hydrolysable titanium species. The length of time will depend on the relative humidity and the temperature, and may be between 1 minute and 1 hour. Intermediate species 127 may be exposed to air by resting it in air, or by passing air through, past or over it or by some other convenient method.

30 After at least partial hydrolysis of the hydrolysable titanium species, intermediate species 127 may be heated in order to convert the amorphous layer to the anatase crystal structure with the desired structure. Heating may be conducted in furnace 132, or by some other

means of heating. Heating may be effected at a temperature above 350°C. Heating may be for a time sufficient to convert the second photocatalytic semiconductor layer to the anatase crystal structure, and may be for between 3 and 7 hours in order to produce photocatalyst 130. Furnace 132 may be the same as or different to furnaces 112 and 116.

5

Method of degrading organic materials

Figure 2 is a diagrammatic representation of an apparatus for degrading organic materials in a fluid according to the present invention. In Figure 2 a reactor 212 is fitted with an inlet 205, an outlet 230. Inside reactor 212 is located a photocatalyst comprising small photocatalytic entities 215 capable of being suspended in fluid 210. A source of illumination 225 is disposed within reactor 212. Filters 207 and 235 are provided in outlet 230 to constrain the photocatalyst within reactor 212.

In use, fluid 210 to be treated enters reactor 212 through inlet 205. The photocatalyst may be maintained in suspension by means of the normal turbulence of fluid 210, or alternatively some other means may be used. Source 225 illuminates the photocatalyst in contact with the fluid 210, causing degradation of organic materials in fluid 210. The light may be in the near UV range, and its wavelength may be less than 400 nm. Treated fluid may exit reactor 212 through outlet 230. Filter 235 prevents the photocatalyst from leaving reactor 212.

Figure 3 is diagrammatic representation of an alternative apparatus for degrading organic materials in a fluid. In Figure 3, a reactor 312 is fitted with an inlet 305 and an outlet 330. Photocatalytic entity 315, in the form of a surface, comprises a portion of the inner surface of reactor 312, such that the photocatalytic assembly that is part of photocatalytic entity 315 is on the inside of reactor 312 so that it may contact fluid 310. A source of illumination 325 is disposed so that it is capable of illuminating at least a portion of the photocatalytic assembly in contact with fluid 310 within reactor 312.

In use, fluid 310 enters reactor 312 through inlet 305 and past photocatalytic entity 315. Source 325 illuminates at least a portion of the photocatalytic assembly in contact with fluid 310, causing degradation of organic materials in fluid 310. The light may be in the

near UV range, and its wavelength may be less than 400 nm. Treated fluid may exit reactor 312 through outlet 330.

Figure 3a is diagrammatic representation of another apparatus for degrading organic materials in a fluid. In Figure 3a, a cylindrical reactor 3112 is fitted with an inlet 3105 and an outlet 3130. Photocatalytic entity 3115, in the form of a surface, comprises a portion of the inner surface of reactor 3112, such that the photocatalytic assembly that is part of photocatalytic entity 3115 is on the inside of reactor 3112 so that it may contact fluid 3110. A cylindrical UV light source of illumination 3125 is disposed to illuminate at least a portion of the photocatalytic assembly in contact with fluid 3110 within reactor 3112.

In use, fluid 3110 enters reactor 3112 through inlet 3105 and flows past photocatalytic entity 3115. Source 3125 illuminates at least a portion of the photocatalytic assembly in contact with fluid 3110, causing degradation of organic materials in fluid 3110. The light may be in the near UV range, and its wavelength may be less than 400nm. Treated fluid may exit reactor 3112 through outlet 3130.

Figure 4 is a diagrammatic representation of yet another apparatus for degrading organic materials in a fluid. In Figure 4, a reactor column 412 is fitted with an inlet 405 and an outlet 430. The photocatalyst is in the form of a packed bed which comprises plurality of photocatalytic entities 415 and is located within reactor column 412. The photocatalyst is preferably made from porous silica or glass beads, or from some other material that may permit UV light to penetrate the plurality of photocatalytic entities 415. Porous barrier 435 is provided near the lower end of reactor column 412 to constrain the photocatalyst within reactor column 412. A source of illumination 425 is disposed within reactor column 412.

In use, fluid 410 enters reactor column 412 through inlet 405 and flows through the packed bed which comprises plurality of photocatalytic entities 415. Source 425 illuminates photocatalyst in contact with fluid 410, causing degradation of organic materials in fluid 410. The light may be in the near UV range, and its wavelength may be less than 400 nm. Treated fluid may exit reactor column 412 through outlet 430. Porous barrier 435 prevents the photocatalyst from leaving reactor column 412. Alternatively

fluid 410 may enter from the lower end of reactor column 412, through port 430, and exit reactor column 412 through port 405.

Figure 4a is a diagrammatic representation of another apparatus for degrading organic materials in a fluid. In Figure 4a, a reactor column 4112 is fitted with an inlet 4105 and an outlet 4130. The photocatalyst is in the form of a packed bed which comprises plurality of photocatalytic entities 4115 and is located within reactor column 4112. The photocatalyst is preferably made from porous silica or glass beads, or from some other material that may permit UV light to penetrate the plurality of photocatalytic entities 4115. Porous barrier 4135 is provided in inlet 4105 to constrain the photocatalyst within reactor column 4112. A source of illumination 4125 is disposed within reactor column 4112.

In use, fluid 4110 enters reactor column 4112 through inlet 4105 and flows through the packed bed which comprises plurality of photocatalytic entities 4115. Source 4125 illuminates photocatalyst in contact with fluid 4110, causing degradation of organic materials in fluid 4110. The light may be in the near UV range, and its wavelength may be less than 400 nm. Treated fluid may exit reactor column 4112 through outlet 4130.

Figure 5 is an Atomic Force Microscope image of a first semiconductor layer according to the invention. The surface is highly irregular and is characterised by high peaks and valleys. Typically the material deposited in and/or on the first semiconductor layer will predominantly deposit in the depressions or valleys of the structure shown.

Purification Systems

Figure 6 is a diagrammatic representation of a system 600 for purification of a fluid. System 600 comprises apparatus 610 and treatment module 630. Apparatus 610 comprises a light source 615, which is located within a reactor 620. Apparatus 610 also comprises a photocatalyst according to the invention (not shown), said photocatalyst being located within reactor 620. Treatment module 630 comprises a separation membrane 635, whereby fluid is purified by passing through the membrane, and impurities are rejected by the membrane. Reactor 620 is equipped with inlet pipe 650, connecting pipe 655, and recycle pipe 660. Pipes 655 and 660 are also connected to treatment module 630. Output pipe 665 is fitted to treatment module 630.

In operation, fluid containing impurities enters reactor 620 through inlet pipe 650. At least a portion of the impurities in the fluid is degraded by apparatus 610 under the influence of light from source 615 in combination with the photocatalyst. The fluid, which may
5 contain some undegraded impurities as well as some degradation products from the impurities, then passes out of reactor 610 through connecting pipe 655, and into treatment module 630. In treatment module 630, the fluid is divided by separation membrane 635 into a concentrate, which is recycled via recycle pipe 660 to reactor 620 for further photoreaction, and a permeate which exits system 600 through output pipe 665.

10

In Figure 7, system 700 comprises treatment module 710 and apparatus 720. Apparatus 720 comprises a light source 725, which is located within a reactor 730. Apparatus 720 also comprises a photocatalyst according to the invention (not shown), said photocatalyst being located within reactor 730. Treatment module 710 may be for example a deionising
15 unit or a distillation unit. Treatment module 710 is fitted with an inlet pipe 740, and a connecting pipe 745 which also connects to reactor 730. Reactor 730 is also fitted with output pipe 750.

In operation, fluid containing impurities enters treatment module 710 through inlet pipe
20 740, and is partly purified by treatment module 710. Fluid then passes from treatment module 710 through connecting pipe 745 to reactor 730. At least a portion of the impurities in the fluid are degraded by apparatus 720 under the influence of light from source 725. Purified fluid then exits system 700 through output pipe 750.

25 In Figure 8, system 800 comprises pre-treatment module 810, apparatus 830 and post-treatment module 850. Pre-treatment module 810 may be for example a deionising unit or a distillation unit. Apparatus 830 comprises a light source 835, which is located within a reactor 840. Apparatus 830 also comprises a photocatalyst according to the invention (not shown), said photocatalyst being located within reactor 840. Post-treatment module 850
30 comprises a separation membrane 855, whereby fluid is purified by passing through the membrane, and impurities are rejected by the membrane. Pre-treatment module 810 is fitted with inlet pipe 870, and is connected to reactor 840 by connecting pipe 875. Reactor

840 is fitted with transfer pipe 880 and recycle pipe 885, both of which connect to post-treatment module 850. Post-treatment module 850 is fitted with output pipe 890.

In operation, fluid containing impurities enters pre-treatment module 810 through inlet pipe 870, and is partly purified by pre-treatment module 810. Fluid then passes from pre-treatment module 810 through connecting pipe 875 to reactor 840. At least a portion of the impurities in the fluid are degraded by apparatus 830 under the influence of light from source 835. At least partially purified fluid then passes out of reactor 840 through transfer pipe 880. The fluid, which may contain some undegraded impurities as well as some degradation products from the impurities, then passes out of reactor 840 through transfer pipe 880, and into post-treatment module 850. In post-treatment module 850, the fluid is divided by separation membrane 855 into a concentrate, which is recycled via recycle pipe 885 to reactor 830 for further photoreaction, and a permeate which exits system 800 through output pipe 890.

Example

Packed bed Design

Fabrication of photocatalyst:

Glass beads 3mm in diameter were etched in 2M HF for 1 hour and dried at 105°C for 12 hours. First layer coating was achieved by immersing the etched beads in a coating solution consisting of TIP (68grams to 460 grams of organic solvent) in a mixture of ethanol and methanol.

The coated beads were dried in air at room temperature for 6 hours and then loaded into a furnace at room temperature and the furnace was then ramped at 3 °C/min to 450°C where it was kept for 4 hours.

In this example, silver was chosen as the metal to be doped on the first layer of anatase TiO₂. Silver was deposited onto the beads by immersing the beads in a solution of 0.1M AgNO₃. The beads were dried and heated at 450°C for 2 hours. Subsequently, the beads were cooled to room temperature and then immersed in a solution consisting of TBT in

ethanol (88grams to 460 grams organic solvent). The same heating profile and temperature as the first layer was used.

Use of the catalyst:

5 The coated beads were packed into the reactor as shown in Fig. 4a. The length of the column was 350mm and the internal diameter of the column was 55mm. A cylindrical UV lamp with main emission of 254nm was used. Humic acid was chosen as the model contaminant. A solution of 25mg/l of humic acid was prepared and fed into the reactor. A graph of removal efficiency vs hydraulic retention time is shown in Figure 9.

10

Advantageously, the photocatalyst can be used to enhance the treatment efficiency of existing UV systems for air or water, and more particularly to the adsorption and/or degradation of organic pollutants, such as natural organic matter, bacterial, viruses, polychlorobiphenyls (PCB's), trihalomethanes, benzene derivatives, and other organic
15 compounds/organisms in water. The photocatalyst can also be used to accelerate total organic carbon (TOC) reduction, chlorine destruction and ozone destruction.

A further advantage is that the photocatalyst can be applied on the reactor walls and UV lamp walls to remove fouling matter accumulating on the walls of the system, thereby
20 making it more efficient.

Indoor Air Treatment

Figure 10 is a diagrammatic representation of a system 900 for purification of air in a room. System 900 comprises a chamber 910 having an inlet 920, a suction device 930, a
25 pre-filter 940, a UV light source 950, a photocatalyst 960 according to the invention and outlet 970.

In operation, air containing impurities enters the chamber 910 through inlet 920. At least a portion of the impurities in the air is removed by the pre-filter 940. The remaining
30 impurities in the filtered air is degraded under the influence of UV light from light source 950 in combination with the photocatalyst 960.

The UV light source can be in the form of conventional UV lamps or UV LEDs (light emitting diodes). The use of UV LEDs can enable a small and portable air purification device to be created.

- 5 Such an air purification device can be used in the following applications:
- Removal of VOCs, tobacco smoke and odours (e.g., body odour) in cabins of vehicles such as cars, trucks, coaches, airplanes and trains.
 - Removal of VOCs, , tobacco smoke and odours (e.g., odour in the sewage area, odour in the cooking area and body odour) in homes.
 - 10 – Removal of VOCs, , tobacco smoke, ozone from photocopier machines and odours (e.g., odour in the sewage area, body odour, mouldy odour, and odour in stagnant air) in the office.

Claims

1. A photocatalytic assembly comprising:
a first photocatalytic semiconductor layer;
a material selected from the group consisting of a metal, a metal alloy, a metal oxide and mixtures thereof, said material being disposed on and/or in said first layer; and
a second photocatalytic semiconductor layer disposed on, in, or both in and on said material; wherein said second photocatalytic semiconductor layer has a finer microstructure than the first photocatalytic semiconductor layer.
2. A photocatalytic assembly according to claim 1 wherein one or more additional photocatalytic semiconductor layers, and material disposed on and/or in said layers, are present.
3. A photocatalytic assembly according to claim 1 wherein the first photocatalytic semiconductor layer is nano-structured.
4. A photocatalytic assembly according to claim 1 wherein the second photocatalytic semiconductor layer is nano-structured.
5. A photocatalytic assembly according to claim 1 wherein the first photocatalytic semiconductor layer comprises titanium dioxide.
6. A photocatalytic assembly according to claim 1 wherein the second photocatalytic semiconductor layer comprises titanium dioxide.
7. A photocatalytic assembly according to claim 1 wherein the first photocatalytic semiconductor layer comprises nano-structured titanium dioxide.
8. A photocatalytic assembly according to claim 1 wherein the second photocatalytic semiconductor layer comprises nano-structured titanium dioxide.

9. A photocatalytic assembly according to claim 1 wherein the material is selected from the group consisting of transition metals, Nb, Rh, Pt-Sn, Pt-Mo, Pt-Ru, Ni-Zr, Pt-Rh, Pt-Ir, Pt-Ru-W, Pt-Ru-Os, Pt-Ru-Sn, Pt-Ni-Ti, Pt-Ni-Zr, Pt-Ni-Nb, platinum group metal oxides, gold group metal oxides, tin oxides, tungsten oxides, indium oxides, rhodium oxides, ruthenium oxides and mixtures thereof.
10. A photocatalytic assembly according to claim 9 wherein the transitional metals are selected from the group consisting of silver, platinum group metals, gold group metals, Ir, Ru, Os, Mo, Zr and Cu.
11. A photocatalytic entity, which comprises:
 - a substrate;
 - a photocatalytic assembly comprising a first photocatalytic semiconductor layer, and a material selected from the group consisting of a metal, a metal alloy, a metal oxide and mixtures thereof, said material being disposed on and/or in said first layer, said assembly being disposed on, in, or both in and on the substrate; and
 - a second photocatalytic semiconductor layer disposed on, in, or both in and on said material; wherein said second photocatalytic semiconductor layer has a finer microstructure than the first photocatalytic semiconductor layer.
12. A photocatalytic entity according to claim 11 wherein one or more additional photocatalytic semiconductor layers, and material disposed on and/or in said layers, are present.
13. A photocatalytic entity according to claim 11 wherein the first photocatalytic semiconductor layer is nano-structured.
14. A photocatalytic entity according to claim 11 wherein the second photocatalytic semiconductor layer is nano-structured.
15. A photocatalytic entity according to claim 11 wherein the first photocatalytic semiconductor layer comprises titanium dioxide.

16. A photocatalytic entity according to claim 11 wherein the second photocatalytic semiconductor layer comprises titanium dioxide.
17. A photocatalytic entity according to claim 11 wherein the first photocatalytic semiconductor layer comprises nano-structured titanium dioxide.
18. A photocatalytic entity according to claim 11 wherein the second photocatalytic semiconductor layer comprises nano-structured titanium dioxide.
19. A photocatalytic entity according to claim 11 wherein the material is selected from the group consisting of transition metals, Sn, Pt-Sn, Pt-Mo, Pt-Ru, Ni-Zr, Pt-Rh, Pt-Ir, Pt-Ru-W, Pt-Ru-Os, Pt-Ru-Sn, Pt-Ni-Ti, Pt-Ni-Zr, Pt-Ni-Nb, platinum group metal oxides, gold group metal oxides, tin oxides, tungsten oxides, indium oxides, rhodium oxides, ruthenium oxides and mixtures thereof.
20. A photocatalytic entity according to claim 19 wherein the transition metals are selected from the group consisting of silver, platinum group metals, gold group metals, Ir, Ru, Os, Mo, Zr and Cu.
21. A process for making a photocatalytic entity, said process comprising the steps of:
 - depositing a first photocatalytic semiconductor layer on a substrate;
 - depositing a material on, in, or both in and on said first layer, said material being selected from the group consisting of a metal, a metal alloy, a metal oxide and mixtures thereof; and
 - depositing a second photocatalytic semiconductor layer on, in, or both in and on said material; wherein said second photocatalytic semiconductor layer has a finer microstructure than the first photocatalytic semiconductor layer.
22. A process according to Claim 21 further comprising the step of depositing one or more additional layers to the substrate, said layers being selected from the group consisting of the material, the first second semiconductor layer and the second semiconductor layer.

23. A process according to Claim 21 wherein the step of depositing a material on, in, or both in and on said first layer comprises selecting the material from the group consisting of transition metals, Sn, Pt-Sn, Pt-Mo, Pt-Ru, Ni-Zr, Pt-Rh, Pt-Ir, Pt-Ru-W, Pt-Ru-Os, Pt-Ru-Sn, Pt-Ni-Ti, Pt-Ni-Zr, Pt-Ni-Nb, platinum group metal oxides, gold group metal oxides, tin oxides, tungsten oxides, iridium oxides, rhodium oxides, ruthenium oxides and mixtures thereof.

24. A process according to claim 23 wherein the step of depositing a material on, in, or both in and on said first layer comprises selecting the material from transition metals comprising silver, platinum group metals, gold group metals, Ir, Ru, Os, Mo, Zr and Cu.

25. A process according to claim 21 wherein the first photocatalytic semiconductor layer comprises titanium dioxide.

26. A process according to claim 21 wherein the second photocatalytic semiconductor layer comprises titanium dioxide.

27. A process for making a photocatalytic entity, said process comprising the step of:

depositing a first photocatalytic semiconductor layer on a substrate, said layer comprising a material selected from the group consisting of a metal, a metal alloy, a metal oxide and mixtures thereof; and

depositing a second photocatalytic semiconductor layer on, in, or both in and on said material; wherein said second photocatalytic semiconductor layer has a finer microstructure than the first photocatalytic semiconductor layer.

28. A process according to Claim 27 further comprising the step of depositing one or more additional layers to the substrate, said layers being selected from the group consisting of the material, the first second semiconductor layer and the second semiconductor layer.

29. A process according to Claim 28 wherein the step of depositing a material on, in, or both in and on said first layer comprises selecting the material from the group consisting of transition metals, Sn, Pt-Sn, Pt-Mo, Pt-Ru, Ni-Zr, Pt-Rh, Pt-Ir, Pt-Ru-W, Pt-Ru-Os, Pt-Ru-Sn, Pt-Ni-Ti, Pt-Ni-Zr, Pt-Ni-Nb, platinum group metal oxides, gold group metal oxides,

tin oxides, tungsten oxides, iridium oxides, rhodium oxides, ruthenium oxides and mixtures thereof.

30. A process according to claim 29 wherein the step of depositing a material on, in, or both in and on said first layer comprises selecting the material from transition metals comprising silver, platinum group metals, gold group metals, Ir, Ru, Os, Mo, Zr and Cu.

31. A process according to claim 27 wherein the first photocatalytic semiconductor layer comprises titanium dioxide.

32. A process according to claim 27 wherein the second photocatalytic semiconductor layer comprises titanium dioxide.

33. A photocatalytic entity when made by the process of Claim 21 and 27.

34. A photocatalyst comprising a plurality of photocatalytic entities, each of said entities being according to claim 11.

35. A method for degrading organic materials, halogens or ozone in a fluid comprising:
contacting a photocatalytic entity according to Claim 11 with the fluid; and
illuminating said photocatalytic entity in contact with the fluid.

36. A method for degrading organic materials, halogens or ozone in a fluid comprising:
contacting a photocatalyst according to claim 34 with the fluid; and
illuminating said photocatalyst in contact with the fluid.

37. A method for degrading organic materials, halogens or ozone in a fluid comprising:
contacting a photocatalytic entity according to Claim 11 and a photocatalyst comprising a plurality of photocatalytic entities, each of said entities being according to claim 11, with the fluid; and
illuminating said photocatalytic entity and said photocatalyst in contact with the fluid.

38. A method according to any one of claims 35 to 37 additionally comprising at least

partially removing products of degradation of organic materials, halogens or ozone from the fluid.

39. An apparatus comprising:

- a photocatalytic entity according to Claim 11;
- a reactor in which a fluid may be contacted with the photocatalytic entity; and
- a source of illumination disposed to illuminate the photocatalytic entity in contact with the fluid with a wavelength of light, or mixture of wavelengths, effective to degrade organic materials, halogens or ozone when in contact with the first or the second photocatalytic semiconductor layer of the photocatalytic entity.

40. An apparatus comprising:

- a photocatalyst according to claim 34;
- a reactor in which a fluid may be contacted with the photocatalyst; and
- a source of illumination disposed to illuminate the photocatalyst in contact with the fluid with a wavelength of light, or mixture of wavelengths, effective to degrade organic materials, chlorine or ozone when in contact with the first or the second photocatalytic semiconductor layer of the photocatalyst.

41. An apparatus comprising:

- a photocatalytic entity according to Claim 11 and a photocatalyst comprising a plurality of photocatalytic entities, each of said entities being according to claim 11;
- a reactor in which a fluid may be contacted with the photocatalytic entity and the photocatalyst; and
- a source of illumination disposed to illuminate the photocatalytic entity and the photocatalyst in contact with the fluid with a wavelength of light, or mixture of wavelengths, effective to degrade organic materials, halogens or ozone when in contact with the first or the second photocatalytic semiconductor layer of the photocatalytic entity and of the photocatalyst.

42. An apparatus according to claim 40 or 41 whereby the photocatalyst is constrained in a reactor column.

43. A system for purification of a fluid comprising:
an apparatus according to any one of claims 39 to 41; and
a treatment module coupled to the reactor.
44. A system for purification of a fluid comprising:
an apparatus according to any one of claims 39 to 41; and
a treatment module coupled to the reactor, wherein the treatment module comprises a separation membrane.
45. A system for purification of a fluid comprising:
an apparatus according to any one of claims 39 to 41; and
a treatment module coupled to the reactor, having means to recycle a portion of the fluid exiting from the treatment module to the reactor.
46. Use of a system for purification of a fluid comprising:
an apparatus according to any one of claims 39 to 41; and
a treatment module coupled to the reactor, for the purification of a fluid.
47. A method for purifying a fluid comprising passing the fluid through a system for purification of a fluid, said system comprising:
an apparatus according to any one of claims 39 to 41; and
a treatment module coupled to the reactor.