(54) Title: METAL OXIDE NANOFIBRE FILTER

(57) Abstract: A substantially ceramic nanofilter in the form of a hierarchical structure of layers of metal oxide nanofibre non-
woven meshes with increasing filtration ability on top of a mechanically strong but relatively porous substrate allows for high flux
with nanometre separation capability. The nanofilter has application in the water purification, dairy, pharmaceutical, petrochemical
and radioactive material processing industries. Particularly important, is the application of the nanofilter to filtering out viral and
bacterial pathogens from water and air.

1

TITLE

METAL OXIDE NANOFIBRE FILTER

FIELD OF THE INVENTION

The present invention relates to substantially ceramic filters, and more

5   particularly to metal oxide nanofibre filters.

BACKGROUND OF THE INVENTION

Ceramics have found a wide range of uses in today's society. They

have applications in the aerospace, medical, military and communications

industries. This versatility is due to their unique properties. Ceramic materials

10   are very stable chemically, thermally and mechanically, and in addition are

frequently bio-inert. Ceramic materials are generally porous and this means

they can be very useful as filters.

Simply, the medium to be filtered flows through the channels of the

filter carrier and particles are retained if their size exceeds the diameter of

15   the filter pores. The filtrate permeates through the pores and can then be

subjected to subsequent process stages. Ceramic materials are used as

filters in the water and air purification, pharmaceutical, dairy, radioactive

materials processing and chemical industries. Particularly important

applications of this technology are in wastewater processing, as air filters in

20   breathing equipment and in filtration of drinking water.

Every day, an estimated 3,000 to 6,000 people worldwide die from

diseases caused by contaminated water. Ceramic filters with nano-sized

pores which are capable of removing species larger than 60 nm have great

importance as a potential solution to this tragedy. Filters of this selectivity

2

allow the removal of bacteria and many pathogenic viruses from our water supply, air supply and even from our blood. The recent Severe Acute Respiratory Syndrome (SARS) and 'bird flu' epidemics resulted in many deaths and in affected areas people sought protection by the use of

5   respiratory masks which were capable of filtering out the virus. These viruses fall into the 80-200 nm range.

Already, ceramic microfilters and nanofilters are routinely used in most developed countries to clean wastewater before discharge. The biggest advantages of ceramic filters over others, such as polymer filters, are better

10   corrosion resistance, ability to withstand leaching and higher mechanical stability, all of which result in long operation lifetimes. Normal filtration at low temperature using organic filters causes fouling that has to be removed periodically. Steam cleaning is one way to remove it but is not possible without damaging the polymer filters. The ability of ceramic filters to

15   withstand temperatures as high as 500°C means they are much easier to clean and thereby regenerate. The use of chemicals to remove fouling is also problematic for organic polymer filters because, unlike ceramic filters, they are not chemically inert.

Ceramic filters are typically produced through the sol-gel method

20   which is well known in the art. In this method, the inorganic precursors go through the formation of a colloidal suspension (sol) and gelation of the sol to form a network in a continuous liquid phase (gel). At the functional group level, three reactions are generally used to describe the sol-gel process: hydrolysis, alcohol condensation, and water condensation. The support layer

3

is generally thin and has a pore size of 1 μm while the uppermost layer has a pore size in the nanometre range. Typical materials used to create porous filters employing the sol gel process are alkoxysilanes, alumina (Al_2O_3), titania (TiO_2), silica (SiO_2), zirconia (ZrO_2) and mixed oxides.

5   One of the drawbacks of the sol gel method is that the control of pore size is often difficult due to formation of irregular shaped particles. Pinholes and cracks can also appear in the top layer during the drying phase. This means that many sol particle layers may have to be put down to achieve effective filtration. This increases the mean pore length through which the

10   filtrate must pass and so, as mentioned above, results in a greatly decreased flux. Low porosity and the presence of dead end pores which cannot contribute to filtration are also common problems. It is currently extremely difficult to obtain porous ceramic filters with both good selectivity and a sufficiently large filtration flux.

15   Tepper et al, US patent 6,838,005, teaches the use of aluminium hydroxide fibres to form a composite filter to remove nano size viruses and other particulates from drinking water and other fluids. The filter is formed from an alumina sol mulched with glass microfibers. The resulting filter can suffer from the weaknesses described above for sol gel produced filters. The

20   use of the glass is an attempt to compensate for the mechanical weakness of the filter. They found that attempts to double the thickness of the alumina filter resulted in a halving of the flow rate which means that a trade off must be made between the mechanical strength of the filter and the flow rates which can be achieved.

4

WO 1998/21164 employs a functionally gradient ceramic structure as a substrate in a ceramic filter and teaches a method of producing said filter. Two surfaces are provided with a decreasing pore size between the two. Again this filter is synthesised starting from a colloidal suspension of ceramic

5   particles. The control over the pore size in the resulting filter provided by this method is poor and the layers produced are relatively thick. This results in a decreased rate of flux and poor separation.

WO 2007/054040 teaches the use of a number of polymeric nanofibres to produce a filter for removing biological and physical impurities.

10   The disadvantages of polymeric nanofilters compared to ceramic nanofilters are well known and include shorter operational lifetimes, lower stability to varying temperatures, problems with swelling in various solvents and greater difficulty in introducing surface modifications.

OBJECT OF THE INVENTION

15   The object of the invention is to overcome or at least alleviate one or more of the above problems and to provide for substantially ceramic nanofilters which possess high selectivity and are also capable of good filtration rates.

SUMMARY OF THE INVENTION

20   In a first aspect, although it need not be the only or indeed the broadest form, the invention resides in a substantially ceramic nanofilter comprising:

(a)   a porous substrate;

(b)   one or more intermediate layers of nanofibre non-woven

5

meshes coated onto the substrate; and

(c)   a top layer of nanofibre non-woven mesh coated onto the upper surface of the one or more intermediate layers,

wherein the pore sizes of the nanofibre non-woven meshes decrease

5   in each consecutive layer to a desired minimum size in the top layer.

In a second aspect the invention resides in a process for generating a metal oxide nanofibre non-woven mesh including the steps of:

(a)   suspending nanofibres of metal oxides in an aqueous, alcohol or acetone solution to form a suspension;

10   (b)   treating the suspension to make it homogeneous;

(c)   coating the suspension onto a substrate;

(d)   drying the coating in air; and

(e)   calcining the coating to produce the non-woven mesh.

Advantageously, the metal oxides of the second aspect may be

15   selected from a wide range of suitable metal oxides such as aluminium oxides, titanium oxides, zinc oxides, rare earth oxides, copper oxides and the like.

In a third aspect, the invention resides in a process for producing a substantially ceramic nanofilter including the steps of:

20   (a)   coating a porous substrate with a first layer of nanofibres wherein the length of the nanofibres is greater than the pore size of the substrate;

(b)   coating the first layer of nanofibres with a second layer of nanofibres wherein the length of the nanofibres in the second

6

layer is greater than the pore size of the first layer; and

(c)   repeating the process of coating a new layer of nanofibres on top of the uppermost layer until the desired number of layers is achieved, wherein the length of the nanofibres in the new layer is greater than the pore size of the uppermost layer, to thereby produce a substantially ceramic nanofilter.

Further features of the present invention will become apparent from the following detailed description. The term nanofibres will be used in this specification when discussing the suspensions of metal oxides being used to generate the non-woven meshes of the nanofilter. It should be understood that this also includes nanorods, nanotubes, nanobelts and the like which are formed by certain of the metal oxides discussed herein.

Throughout this specification, unless the context requires otherwise, the words "comprise", "comprises" and "comprising" will be understood to imply the inclusion of a stated integer or group of integers but not the exclusion of any other integer or group of integers.

BRIEF DESCRIPTION OF THE FIGURES

In order that the invention may be readily understood and put into practical effect, preferred embodiments will now be described by way of example with reference to the accompanying figures wherein:

FIG 1 shows a Scanning Electron Micrograph (SEM) of (a) a cross-sectional view of a nanofilter according to one embodiment of the present invention, including SEM's of the intermediate, (b) and (c), and top layers (d);

FIG 2 shows (a) a schematic representation of the nanofilter of FIG 1

showing the substrate, intermediate and top layers and relating each of these layers to electron micrograph images (b)-(d);

FIG 3 shows a titanate fibre with anatase nanocrystals coated on its surface;

5   FIG 4 shows (a) a graphical representation of the changing flux (black squares) and selectivity (clear circles) of a nanofilter according to one embodiment of the present invention to a solution of 60 nm latex spheres, as it is built up from its various layers and (b) a latex sphere of 60 nm diameter filtered out by the top layer of the nanofilter;

10   FIG 5 (a) is an SEM of a solution of latex spheres of 60 nm diameter before and after (insert) filtration through a nanofilter of pore size less than 60 nm;

FIG 5 (b) is an SEM of a solution of latex spheres of 108 nm diameter before and after (insert) filtration through a nanofilter of pore size less than 15   60 nm;

FIG 5 (c) is an SEM of a solution of latex spheres of 200 nm diameter before and after (insert) filtration through a nanofilter of pore size less than 60 nm;

FIG 6 shows a graphical representation of the changing flux (black 20   squares) and selectivity (clear circles) of a nanofilter constructed on a porous glass substrate, according to one embodiment of the present invention, to a solution of 60 nm latex spheres, as it is built up from its various layers;

FIG 7 shows an SEM of praseodymium oxide nanorods;

FIG 8 shows an SEM of cerium oxide nanofibres;

8

FIG 9 shows an SEM of CuO nanorods;

FIG 10 shows an SEM of ZnO nanorods;

FIG 11 shows an SEM of microporous niobate $(Na_2Nb_2O_6 \cdot \frac{2}{3}H_2O)$ nanofibres; and

5 FIG 12 shows an SEM of anatase (TiO_2) nanofibres.

DETAILED DESCRIPTION OF THE INVENTION

The present inventors have developed a method of creating substantially ceramic nanofilters by generating metal oxide nanofibre non-woven meshes. These non-woven meshes can be created to give pore sizes

10 of diminishing diameters simply by the choice of the ceramic nanofibres used. The mesh layers are continuously constructed one on top of the other, layer upon layer, starting on a porous substrate base, to give nanofilters which have a filtration ability based on the pore size of the top layer.

It should be appreciated that while the pore size generally diminishes

15 in going from the porous substrate, through the one or more intermediate layers to the top layer, each nanofibre non-woven mesh which is put down does not necessarily have a smaller pore size than the one directly below it. This is because each of the one or more intermediate layers may be made up of a number of sub-layers e.g. three sub-layers of titanate nanofibres laid

20 down one on top of the other. Likewise the top layer may consist of a number of sub-layers e.g. three sub-layers of γ-alumina nanofibres.

The one or more sub-layers within the one or more intermediate layers and top layer, will often be produced using the same suspension of nanofibres and so the pore sizes of each individual sub-layer being coated

9

down are the same and all contribute to the filtration ability of the intermediate and/or top layers. Each intermediate layer and the top layer will, therefore, often contain more than one sub-layer of nanofibre non-woven mesh. As stated previously however, the pore size will decrease in going

5   from the substrate through to each of the one or more intermediate layers and, finally, to the top layer.

The term "layer" will, therefore, be used herein to describe a distinct section of the nanofilter i.e. individually, the one or more intermediate layers and the top layer. The term "sub-layer" will be used to describe each of the

10   individual nanofibre non-woven meshes which are laid down to collectively form each layer.

In the embodiments described herein the nanofilter is constructed from a porous substrate onto which is coated one or more sub-layers of the same metal oxide nanofibre non-woven mesh, to form the intermediate layer.

15   One or more sub-layers of a different metal oxide nanofibre non-woven mesh are then coated on top of this to form the top layer. However, it will be appreciated that it is possible, using the same process, to lay down a number of intermediate layers which may each comprise one or more sub-layers of the same or differing metal oxide nanofibre non-woven meshes. The use of a

20   number of intermediate layers of different metal oxide nanofibres may be structurally or functionally useful to support the application of a top layer of metal oxide nanofibres of desired dimensions.

It should be appreciated that the term "intermediate layer(s)" as used herein refers to the one or more layers the first of which is laid down upon

10

the porous substrate i.e. they are located between the porous substrate and the top layer. Each of these one or more intermediate layers may be made up of one or more sub-layers of nanofibre non-woven mesh.

The term "top layer" as used herein refers to the layer which is laid down on top of the uppermost intermediate layer. As referred to earlier the top layer may be made up of one or more sub-layers of nanofibre non-woven mesh.

The term "titanate nanofibres" as used herein refers to hydrogen titanate nanofibres ($H_2Ti_3O_7$). It would be understood by a person of skill in the art that these nanofibres can be converted to TiO_2(B) and anatase TiO_2 nanofibres upon heating above approximately 300 °C. These fibres are useful for catalytic degradation of organic compounds using UV light. Other titanates such as sodium titanate ($Na_2Ti_3O_7$), which can be converted to $Na_2Ti_6O_{13}$ upon heating above approximately 300 °C, are also considered suitable to form metal oxide nano-fibre non-woven meshes but were not used in the particular examples herein which recite the use of "titanate nanofibres".

FIG 1 is a composite Scanning Electron Micrograph (SEM) of a cross-sectional view of a ceramic nanofilter according to one embodiment of the present invention. Image (a) is a cross section through the nanofilter, exposing the layers used in its construction. The porous α-alumina substrate can be seen at the left of the image and coated onto its surface, forming the intermediate layer is the non-woven mesh of titanate nanofibres. The top layer, at the right hand side of the image is a non-woven mesh of γ-alumina

nanofibres. Image (b) is an SEM of the filter surface after the substrate has had one coating of a 0.05-1.0 wt% titanate nanofibre suspension applied to it. Hydrogen titanate is particularly useful in the embodiments described as it bonds well to both the substrate and other metal oxide nanofibres. This

5   image clearly shows the structure of the non-woven meshes of the present invention. Image (c) is an SEM of the filter surface after the substrate has had three coatings of a 0.05-1.0 wt% titanate nanofibre suspension applied to it, thereby demonstrating how the non-woven mesh intermediate layer has been built up from individual sub-layers in comparison to the single sub-layer

10   in image (b). Image (d) is an SEM of the filter surface after the titanate intermediate layer has been coated with a 0.05-1.0 wt% suspension of AlO(OH) nanofibres. The decrease in pore size compared to the images of the titanate layer is clearly visible.

        FIG 2 shows a schematic representation, in part (a), of the substrate,

15   intermediate and top layers of a ceramic nanofilter according to one embodiment of the present invention and relates each of these layers to actual electron micrograph images. Image (b) is an SEM of the surface of the substrate, in this case α-alumina, demonstrating a relatively loose organization of particles and indicating pore sizes in the micrometer range.

20   Image (c) is a Transmission Electron Micrograph (TEM) of the titanate nanofibres. The non-woven mesh structure can be seen and the relative position of this layer in the construction of the nanofilter is indicated in the schematic (a). Finally, image (d) is a TEM of the AlO(OH) nanofibres which are converted into γ-alumina nanofibres during subsequent calcinations,

12

forming the top layer of the nanofilter. This image indicates how the non-woven mesh has formed pore sizes capable of nano-filtration.

A suitable porous substrate should provide mechanical strength to the nanofilter and should have pore sizes sufficiently large to allow high flux but not so large as to prohibit the forming of a layer of nanofibres on its surface. Examples are porous glass, ZnO, α-alumina, ZrO_2, TiO_2, aluminosilicate and other ceramics. Suitably, the substrate is α-alumina or porous glass. The substrate will have pore diameters of 1-20 μm depending on the flux desired and the dimensions of the nanofibres chosen to be coated onto the surface of the substrate. In one form the substrate will have pore diameters of 5-18 μm. Preferably, the substrate will have pore diameters of 10-16 μm.

In an alternative embodiment the porous substrate is titanium micromesh. The pore size of the titanium micromesh will be between 75 to 150 μm. Typically, the titanium micromesh pore size is between 80 to 125 μm. In a preferred embodiment the titanium micromesh pore size is about 100 μm. The thickness of the mesh will be in the order of 1 mm.

The use of a titanium micromesh as the porous substrate provides a number of advantages to the final nanofilter. It provides a framework which allows for a very high flow rate, has great mechanical strength and allows for excellent binding with nanofibres and nanotubes. The one or more intermediate layers and top layer of non-woven mesh metal oxide nanofibres can be laid down upon the micromesh substrate to generate a substantially ceramic nanofilter.

The ceramic porous substrates e.g. alumina may be chemically

13

treated to enhance adhesion with the intermediate layer of non-woven mesh nanofibres. Non-limiting examples are the treatment of the substrate surface with acid or caustic soda to bring about activation. This involves the generation of hydroxyl groups on the surface which aid in bonding with the

5   intermediate layer in contact with the substrate during calcination. Advantageously, the surface of the substrate does not have to be made smooth as is required in some processes. This allows the use of a wider range of materials to act as the substrate and also reduces cost and time spent on preparation.

10   Advantageously, the metal oxides of the present invention may be selected from a wide range of suitable metal oxides such as aluminium oxides, titanium oxides (FIG 12), cerium oxides (FIG 8), zinc oxides (FIG 10), rare earth oxides, copper oxides (FIG 9), boehmite, alumina, cerium oxide, titanate, zirconium dioxide, niobate, rare earth oxides and the like to produce

15   non-woven meshes with differing pore sizes, thereby providing filtration selectivity. Figures 7-12 are a series of SEM's of different metal oxides in the form of nanofibres or nanorods which can be used to generate the non-woven meshes in the construction of a nanofilter. These images demonstrate some of the diversity available when selecting the metal oxide based on

20   dimensions and inherent properties.

The intermediate layer can be formed from a range of suitable metal oxide nanofibres. The material chosen will depend on the pore size of the substrate. Suitable nanofibres will have a length greater than the diameter of the substrates pores. The nanofibres selected for the intermediate layer will

14

have good compatibility with biological systems i.e. non-toxic, photostable and no dissolution in water. In one embodiment of the present invention, the intermediate layer is constructed from titanate nanofibres. ZnO nanorods (FIG 10), niobate nanofibres (FIG 11) and rare earth nanorods (FIG 7, 5 praseodymium oxide) with a length in the range 1-10 μm are further examples of materials suitable for use in the construction of this intermediate layer.

In another embodiment, the intermediate layer nanofibres are coated with a substance which enables the ceramic filters to photocatalytically 10 decompose organic or biological species such as viruses and bacteria. This may aid in clearing the pores and maintaining filtration functionality of the nanofilter. One non-limiting example of such a substance is the use of anatase (TiO_2) nanocrystals. FIG 3 shows how these nanocrystals can be coated onto the surface of a titanate nanofibre. As was mentioned 15 previously, the hydrogen titanate nanofibres themselves may also be converted by heating into TiO_2(B) or anatase nanofibres which are both effective in photocatalytic decomposition or organic matter and biological species. Other suitable examples are the painting of a layer of In_2O_3/Ta_2O_5, anatase, rutile or TiO_2(B) onto the chosen nanofibres to allow the 20 decomposition of organic pollutants in water using visible light.

The selected nanofibres are dispersed in a solution which is aqueous, acetone or an alcohol to form a suspension greater than 0.001 wt%. Preferably, the suspension is 0.05-1.0 wt%. In a preferred embodiment, the suspension is 0.2 wt%. Suitably, the solution is ethanol, an ethanol/water

15

mixture or acetone. The solution may already contain various additives such as are discussed below.

Substances such as polyelectrolytes and the like may be present in the suspension to assist electrostatic self-assembly of the nanofibres.

5   Surfactants may also be present to provide control over the viscosity of the coating suspension.

The suspension may be treated to form a homogeneous suspension by a number of chemical and physical means. One such example is sonication.

10   The suspension is then applied to the substrate. The suspension can be applied by a number of appropriate means such as are known in the art, for example, dip-coating and spin-coating. The coating process may be repeated a number of times resulting in a number of sub-layers of the same nanofibre being laid down and which together form the intermediate layer.

15   This allows the desired filtration capacity to be achieved. The layer is then dried in air at 323-523 K followed by calcination at 523-973 K. A non-woven mesh of nanofibres is formed with pore sizes substantially smaller than those of the substrate.

The top layer of the filter can be formed from a number of suitable

20   metal oxide nanofibres. The nanofibres are chosen so that their length is greater than the diameter of the pores of the intermediate layer. In one preferred embodiment, the nanofibres are boehmite (AlO(OH)) nanofibres. Small nanofibres of rare earth oxides, ZrO_2 and alumina nanofibres coated with other oxides are also suitable for forming the top layer.

16

The metal oxide nanofibres used to generate the top layer will also be chosen based on the functionality required from the nanofilter, which is related to the pore sizes achieved. For example, if the purpose of the nanofilter is to filter out bacteria and viruses then metal oxides which achieve pore sizes in the range of about 30 nm to about 60 nm in the top layer would be suitable. If the application of the nanofilter is to separate biological substances such as DNA or chlorophyll then metal oxide nanofibres which result in pore sizes of approximately 10 nm would be chosen.

In one embodiment the nanofibres of the top layer will result in a non-woven mesh with pore sizes of 1-100 nm. Suitably, the top layer will have pore sizes of 5-80 nm. Normally the pore sizes of the top layer will be between 10-60nm.

A number of metal oxide nanofibres are considered suitable for use in the nanofilter of the present invention. Some are particularly suitable for use in either the intermediate layer(s) or the top layer. It should be appreciated, however, that any metal oxide nanofibre may be useful in forming these layers and the particular one chosen will depend, in part, on the pore size of either the substrate (if laying down the nanofibre non-woven mesh directly upon this) or the last layer generated. The pore size the particular nanofibres form, their mechanical strength and desired functionality e.g. photocatalytic decomposers will all be taken into consideration when choosing the metal oxide nanofibres to form any one layer.

The top layer is formed in a similar manner to the intermediate layer. The selected nanofibres are dispersed in acetone, an alcohol or an aqueous

17

solution to form a suspension greater than 0.001 wt%. Preferably, the suspension formed is between 0.01-5.0 wt%. In a preferred embodiment, the suspension is 0.2 wt%. The suspension may be treated to form a homogeneous suspension by a number of chemical and physical means.

5   One such example is sonication. In addition, substances such as polyelectrolytes and the like may be present in the suspension to assist electrostatic self-assembly of the nanofibres. Further, the suspension may contain non-ionic polymers such as poly(ethylene)oxide, poly(ethylene)glycol and other water soluble polymers, to aid in controlling the thickness of the

10   top layer.

The suspension is then applied on top of the intermediate layer and the solvent evaporated to leave a non-woven mesh of nanofibres. The suspension can be applied to the upmost intermediate layer by a number of appropriate means such as are known in the art, for example, dip-coating

15   and spin-coating. The coating may be repeated a number of times resulting in a number of sub-layers. The resulting layer is then dried in air at between 323-523 K followed by calcination at between 523-923 K. In one embodiment, when using boehmite nanofibres, a temperature of 393 K is used for drying in air and the calcination is carried out at 723 K for 2h. During

20   calcination the boehmite nanofibres are converted to γ-alumina (Al_2O_3) nanofibres. The γ-alumina nanofibres retain a similar morphology to the parent boehmite nanofibres. This results in a non-woven mesh of nanofibres with smaller pore sizes than the intermediate layer on which it is generated.

Thus, a hierarchical structure of non-woven meshes with increasing

18

filtration ability on top of a mechanically strong but relatively porous substrate is achieved.

Further, post-construction, modification of the surface of the nanofilter can confer additional, desirable properties on the nanofilter. For example,

5   grafting various silanes onto the filter surface by impregnation or gaseous reaction alters surface properties of the filter such as the relative hydrophobicity. Other chemical reactions on the filter surface can achieve fine-tuning of the porous structure and alter the affinity of the nanofibres for various elements.

10   These nanofibre non-woven meshes do not suffer from cracks or pinholes to the same degree as, for example, layers created by the sol gel process and, as a direct result of the mesh-like structure, have flow rates at 60 nm separation that are 10-100 times greater than those of conventional filters with similar separation ability. This is due to a number of factors

15   inherent in the non-woven meshes, for example the absence of dead-end pores and the fact that all the pores are interconnected. This can result in high porosity levels of 70% or greater. This is demonstrated graphically in FIG 4 (a) which shows the changing flux and selectivity of the filter as it is built up from its various sub-layers and layers. The filter selectivity was

20   determined based on the filtering of a solution containing latex spheres of 60 nm diameter. The different points represent the flux (black squares) and filtration (clear circles) of the layers as they are built, one upon the other. Therefore, S = substrate alone, T1 = one titanate coating (on the substrate), T2 = two titanate coatings, T3 = three titanate coatings and Al = 3 boehmite

coatings on top. The relatively high flux rates demonstrated can be achieved at lower pressures and so, with less energy consumption.

FIG 4 (b) shows how a latex sphere of 60 nm diameter from the above filtration solution has been filtered out by the non-woven mesh of γ-alumina

5   nanofibres forming the upper layer of the nanofilter.

FIG 5 (a)-(c) is a series of SEM's from three different solutions of latex spheres before and after (insert) filtration through the nanofilter. In the image shown in (a) the spheres were of 60 nm diameter, in (b) 108 nm and in (c) 200 nm. A portion of the solutions before filtration were analysed by SEM

10   and these form the main part of each image. After filtration through a nanofilter with a γ-alumina top layer, and so, pore sizes of 60 nm or less, a portion of the filtrate was sampled and analysed by SEM. These images form the insert in the top right hand corner of the corresponding pre-filtration image (a)-(c). These images show that all species of diameter 200 nm or

15   greater are filtered off. Spheres of 108 nm are almost completely removed and even 60 nm diameter spheres are filtered off to a very large degree.

So that the invention may be more readily understood and put into practical effect, the skilled person is referred to the following non-limiting examples.

20   <u>EXAMPLES</u>

Example 1

Preparation of a ceramic nanofilter was performed using a porous α-alumina disk with a diameter of 30 mm and thickness of 2-3 mm as the substrate. The pore sizes of the α-alumina substrate are approximately 10

µm. Titanate fibres (20-30 µm long and 40-100 nm thick) were dispersed in ethanol to give a 0.2 wt% suspension and sonicated for 10 min using an ultrasonic finger to achieve a homogenous suspension. This suspension was used to coat the substrate using a spin-coat processor. The coating was

5   applied at a spinning velocity of 1000 r/min for 2 min and used approximately 0.5 mL of the fibre suspension for the coating.

The spin-coating process was repeated twice followed by drying in air at 393 K and then calcination at 773 K for 4 h. The heating rate employed is 1 K/min starting from 393 K. These three sub-layers collectively form the

10   intermediate layer.

A 0.2 wt% suspension of boehmite (AlO(OH)) nanofibres (60-100 nm long and 2-5 nm thick) in ethanol was then made up and applied on top of the calcined titanate nanofibre non-woven mesh in the same manner. After coating and drying in air at 393 K, calcining at 723 K for 2h then results in the

15   boehmite fibres being converted to γ -alumina nanofibres (Al_2O_3). The γ-alumina nanofibres form the top layer of the nanofilter and retain a similar morphology to the parent boehmite nanofibres. This process results in a non-woven mesh of γ-alumina nanofibres (top layer) with smaller pore sizes than the underlying titanate nanofibre non-woven mesh (intermediate layer) all

20   formed upon the α-alumina substrate. The result is shown in cross section in FIG 1 (a).

Example 2

The filtration properties of the titanate non-woven mesh (intermediate layer) formed from three coating cycles (three sub-layers) on the substrate

were tested before the boehmite top layer was applied by filtering an aqueous suspension of latex spheres. Suspensions of spheres of a variety of sizes were made up to be 0.1 wt% and were used in the following experiment. 30 mL of these suspensions were put through the titanate

5   nanofilter layer using a vacuum system which maintains a pressure difference between the feeding fluid and permeated fluid of 20 KPa.

The concentrations of the latex spheres in the original suspension and the filtrate were determined using both scanning electron microscopy (SEM) and UV-Visible spectroscopy. The titanate layer was able to filter out 100%

10   of latex spheres with a diameter of 200 nm or greater. It also retained a flux of about 800 L/m^2/h. The alumina substrate alone has a flux of about 1200 L/m^2/h. FIG 4 exemplifies these results for the 60 nm diameter latex sphere solution. For comparisons sake the filtration and flux were tested at each stage of filter construction i.e. on the substrate alone (S), one titanate coating

15   on the substrate (T1), two titanate coatings (T2), three titanate coatings (T3) (these three titanate coatings or sub-layers together make up the intermediate layer) and with the final γ-alumina layer on top (AI).

Example 3

The filtration capability of the completed filter (3 coatings of titanate

20   nanofibres on the α-alumina substrate followed by 3 coatings of the γ-alumina nanofibres on top) was tested.

A 10 wt% aqueous suspension of 60 nm latex spheres was diluted to 0.01 wt% with water. 30 mL of the dilution was used to test permeation of the filter. A pressure difference of 20 KPa between the feeding fluid and

22

permeated fluid was stably maintained by a vacuum system. The time taken for every 5 mL of fluid to filter through the filter under test was recorded.

The fluids before and after filtration were sampled for analysis. SEM images were collected on an FEI Quanta 200 Environmental SEM. A JEOL

5   JSM 6400F Field Emission SEM was also used to obtain images of high resolution. The samples are coated with gold using a BioRad SC500 sputter coater.

The specimens from the liquid samples were prepared by dropping 5 μl of solution on a glass slide and drying under vacuum. The efficiency of

10   filter separation could be estimated directly by comparing the numbers of latex spheres in images of the specimens taken before and after filtration. These images are shown in FIG 5 which demonstrates that at pore sizes less than 60 nm all spheres of diameter greater than 200nm are filtered off. Those of diameter 108nm are almost completely filtered off and spheres of

15   60 nm diameter are removed to a very large extent.

The morphology of the nanofibres was recorded on a Philips CM200 Transmission Electron Microscope. UV-visible spectroscopy on a Cary100 (Varian Inc.) spectrophotometer was also utilized to analyze the concentration change of the fluids before and after filtration. The intensity of

20   the absorption band at 200 nm was adopted to determine the concentration using a standard plotting curve.

In this case 96.8% of spheres with a diameter of 60 nm or greater were filtered out. The flux passing through the nanofilter was still found to be relatively high at 600 $L/m^2/h$. This is 70-80% that of the titanate non-woven

mesh filter alone and half that of the alumina substrate alone. It also represents a flux of 10-100 times greater than that of ceramic filters prepared in a more conventional manner exhibiting similar separation ability.

Example 4

5   A glass filter substrate was placed into 50 ml of a HNO_3 solution containing 0.5 g of HNO_3 and 49.5 g H_2O. It was sonicated for about 10 min in an ultrasonic bath and then washed with deionised water. The substrate was then dried in air at 393 K for 4 h.

A suspension of titanate nanofibres was prepared by dispersing 0.08

10   g of nanofibres into 50 ml ethanol with vigorous stirring to give a white suspension with a fibre content of 0.2 wt%. Stirring was continued for a further 30 min.

The pre-cleaned substrate was loaded on the chuck of a spin coat processor and the above suspension was dropped at a spin velocity of 1000

15   r/min. The coating process took 1 min. The coating process is repeated 2-4 times. The total consumption of one solution was about 0.4 g (using 0.5 ml of the suspension). The substrate surface was thereby covered with titanate nanofibres.

After spin-coating, the coated substrate is dried firstly at room

20   temperature for 12h and then at 393 K for 4 h. The substrate is then calcined at 773 K for 4 h to attach the non-woven mesh layer. The heating rate is 1 K/min, starting from 393 K.

Similarly, a 0.2 wt% suspension of boehmite nanofibres was applied on top of the calcined non-woven mesh of titanate nanofibres. The coating

24

process is repeated 2-4 times.

The nanofilter product was mounted on a filtration set-up to assess its separation efficiency. A 10 wt% aqueous dispersion of latex spheres of 60 nm diameter was diluted to 0.01 wt% with water. 30 mL of the dilution was

5   used to test permeation passing through a prepared filter. A pressure difference of 20 kPa was maintained between the feeding fluid and the filtrate, by a vacuum system, to drive the filtration. The time taken for each 5 mL of fluid to pass through the filter was recorded. The fluids before and after filtration were sampled for analysis.

10   UV-visible spectroscopy (UV-vis) on a Cary100 (Varian Inc.) spectrophotometer was utilized to analyse the concentration change of the latex spheres in the fluids before and after filtration. The intensity of the absorption band at 205 nm was adopted to determine the concentration using a standard plotting curve.

15   FIG 6 demonstrates the filtration flux and selectivity of this nanofilter as it is built up from its various layers by filtering a 0.01 wt% solution of 60 nm latex spheres (S is for the glass substrate alone; T1 represents the filter after the first coating with titanate nanofibres; T2 after the second coating with titanate nanofibres; T3 after the third coating with titanate nanofibres

20   and Al represents the filter after three coatings of γ-alumina nanofibres on top of the coatings of titanate nanofibres).

The completed filter comprising a non-woven mesh of titanate nanofibres (three coatings) and a non-woven mesh of alumina nanofibres (three coatings) is able to filter out 93 % of latex spheres with a diameter of

25

60 nm, with a maximum flux of 994 $L/m^2/h$. Such a flux is significantly greater than the flux of filters prepared under conventional approaches which exhibited similar separation. The glass substrate (pore size 10-16 μm) alone has a flux of more than 4000 $L/m^2/h$.

5   The nanofilter provided by the present invention will be useful for a range of applications in the water purification, dairy, pharmaceutical, petrochemical and radioactive material processing industries. Particularly important, is the application of the nanofilter to filtering out viral and bacterial pathogens from water and air. The hierarchical structure of non-woven mesh

10   layers with increasing filtration ability on top of a mechanically strong but relatively porous substrate allows for high flux with nanometre separation capability.

The surface of the substrate used does not have to be made smooth as is required in some processes thereby making the filter cheaper and

15   faster to produce.

Throughout the specification the aim has been to describe the preferred embodiments of the invention without limiting the invention to any one embodiment or specific collection of features. It will therefore be appreciated by those of skill in the art that, in light of the instant disclosure,

20   various modifications and changes can be made in the particular embodiments exemplified without departing from the scope of the present invention.

26

CLAIMS

1.   A substantially ceramic nanofilter comprising:

    (a)   a porous substrate;

    (b)   one or more intermediate layers of nanofibre non-woven meshes coated onto the substrate; and

    (c)   a top layer of nanofibre non-woven mesh coated onto the upper surface of the one or more intermediate layers,

    wherein the pore sizes of the nanofibre non-woven meshes decrease in each consecutive layer to a desired minimum size in the top layer.

2.   The nanofilter of claim 1 wherein the one or more intermediate layers and/or the top layer may each comprise more than one sub-layer in which the pore size does not decrease from that of the underlying sub-layer.

3.   The nanofilter of claim 1 wherein the porous substrate is selected from the group consisting of titanium micromesh, porous glass, ZnO, α-alumina, ZrO_2, TiO_2, and aluminosilicate porous substrates.

4.   The nanofilter of claim 1 wherein the porous substrate has been chemically treated to enhance adhesion.

5.   The nanofilter of claim 4 wherein the chemical treatment is an acid or base treatment.

6.   The nanofilter of claim 1 wherein the nanofibre non-woven meshes are formed from metal oxide nanofibres.

7.   The nanofilter of claim 6 wherein the metal oxide nanofibres are

27

selected from the group consisting of aluminium oxide nanofibres, boehmite nanofibres, alumina nanofibres, titanium oxide nanofibres, cerium oxide nanofibres, zinc oxide nanofibres, titanate nanofibres, zirconium dioxide nanofibres, niobate nanofibres, rare earth oxide nanofibres and copper oxide nanofibres.

8.   The nanofilter of claim 7 wherein the boehmite nanofibres are converted to a layer of substantially γ-alumina nanofibres by calcination.

9.   The nanofilter of claim 1 wherein the top layer of nanofibre non-woven mesh has pore sizes of between 1-100 nm.

10.   The nanofilter of claim 1 wherein the top layer of nanofibre non-woven mesh has pore sizes of between 5-80 nm.

11.   The nanofilter of claim 1 wherein the top layer of nanofibre non-woven mesh has pore sizes of between 10-60 nm.

12.   The nanofilter of claim 1 wherein the properties of the top layer of nanofibre non-woven mesh are modified by the addition of one or more silanes.

13.   The nanofilter of claim 1 wherein one or more of the layers of nanofibre non-woven mesh are coated with a substance which brings about the photocatalytic decomposition of organic compounds and/or biological species.

14.   The nanofilter of claim 13 wherein the substance is anatase, In_2O_3/Ta_2O_5, rutile or $TiO_2(B)$.

15.   The nanofilter of claim 1 for use in filtering substances from a fluid.

28

16.   The nanofilter of claim 15 wherein the fluid is water, blood, serum, milk, aqueous solutions, organic solvents or a gas.

17.   The nanofilter of claim 16 wherein the gas is air.

18.   A process for generating a metal oxide nanofibre non-woven mesh including the steps of:

   (a)   suspending nanofibres of metal oxides in an aqueous, alcohol or acetone solution to form a suspension;

   (b)   treating the suspension to make it homogeneous;

   (c)   coating the suspension onto a substrate;

   (d)   drying the coating in air; and

   (e)   calcining the coating to produce the non-woven mesh.

19.   The process of claim 18 wherein the nanofibres of metal oxides are dispersed in the solution to form a suspension which is greater than 0.001 wt%.

20.   The process of claim 18 wherein the nanofibres of metal oxides are dispersed in the solution to form a suspension which is between 0.01 to 5.0 wt%.

21.   The process of claim 18 wherein the nanofibres of metal oxides are dispersed in the solution to form a suspension which is between 0.05 to 1.0 wt%.

22.   The process of claim 18 wherein the nanofibres of metal oxides are dispersed in the solution to form a suspension which is about 0.2 wt%.

23.   The process of claim 18 wherein the aqueous solution is an ethanol/water solution and the alcohol solution is an ethanol solution.

29

24.   The process of claim 18 wherein the suspension further comprises
        additives selected from the group consisting of polyelectrolytes, non-
        ionic polymers, water-soluble polymers and surfactants.

25.   The process of claim 24 wherein the non-ionic polymers are
        poly(ethylene)oxide and/or poly(ethylene)glycol

26.   The process of claim 18 wherein the suspension is coated onto the
        substrate by dip-coating or spin-coating.

27.   The process of claim 18 wherein the drying in air is carried out at a
        temperature of between 323-523 K.

28.   The process of claim 18 wherein the calcining is carried out at a
        temperature of between 523-923 K.

29.   A process for producing a substantially ceramic nanofilter including
        the steps of:

        (a)   coating a porous substrate with a first layer of nanofibres
                wherein the length of the nanofibres is greater than the
                pore size of the substrate;

        (b)   coating the first layer of nanofibres with a second layer of
                nanofibres wherein the length of the nanofibres in the
                second layer is greater than the pore size of the first layer;
                and

        (c)   repeating the process of coating a new layer of nanofibres
                on top of the uppermost layer until the desired number of
                layers is achieved, wherein the length of the nanofibres in
                the new layer is greater than the pore size of the

uppermost layer, to thereby produce a substantially ceramic nanofilter.

30. The process of claim 29 wherein the porous substrate is selected from the group consisting of titanium micromesh, porous glass, ZnO, α-alumina, and aluminosilicate porous substrates.

31. The process of claim 29 wherein the nanofibres are metal oxide nanofibres selected from the group consisting of aluminium oxide nanofibres, boehmite nanofibres, titanium oxide nanofibres, cerium oxide nanofibres, zinc oxide nanofibres, titanate nanofibres, zirconium dioxide nanofibres, niobate nanofibres, rare earth oxide nanofibres and copper oxide nanofibres.
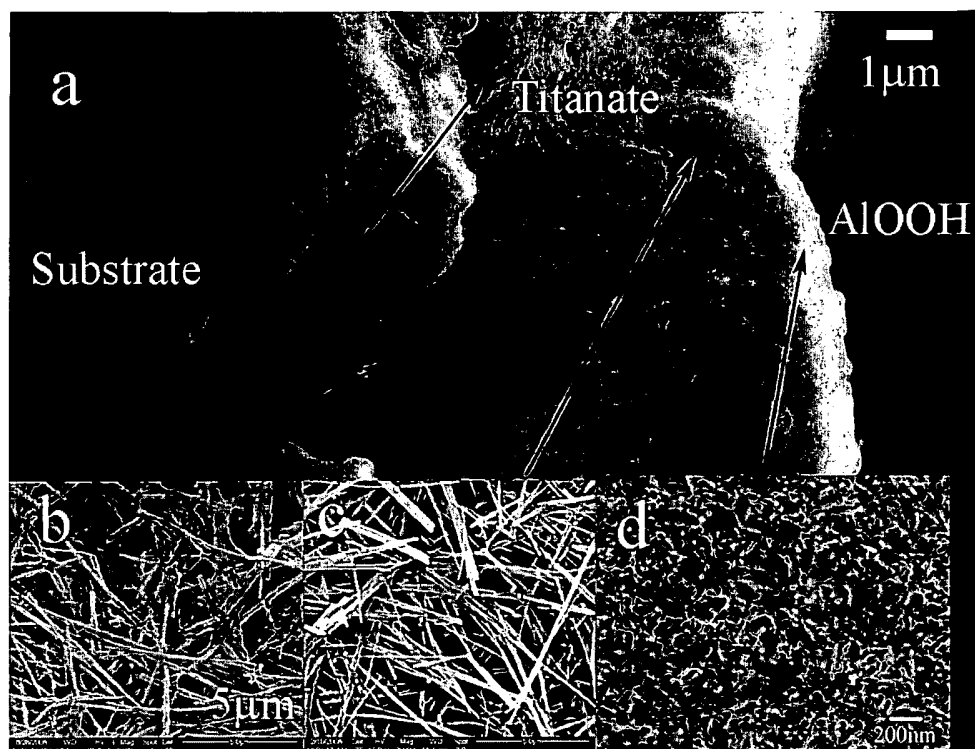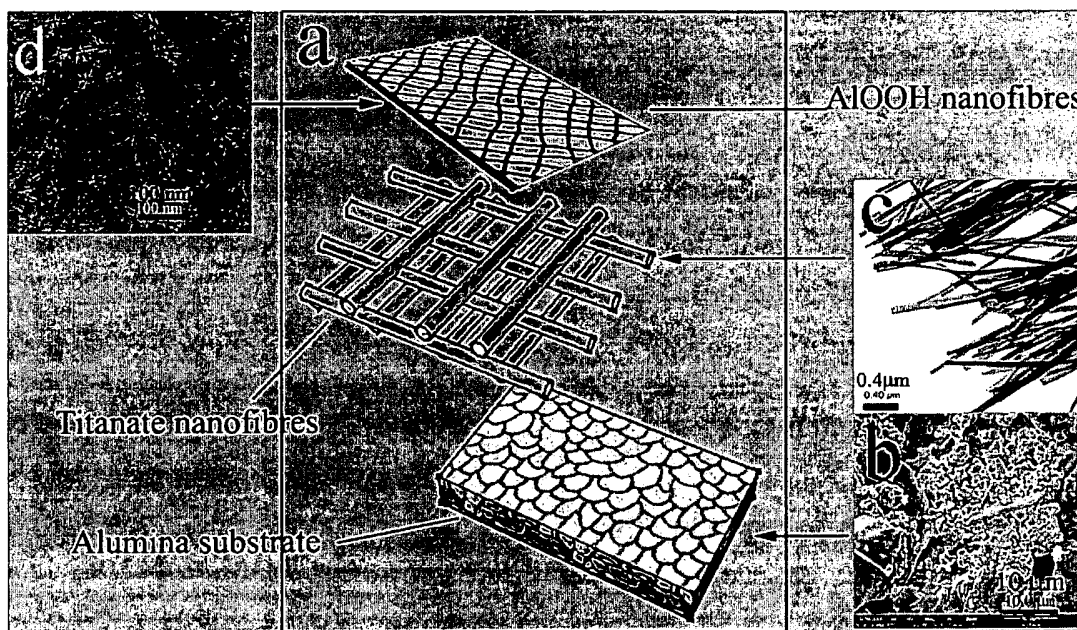
FIG 1

FIG 2
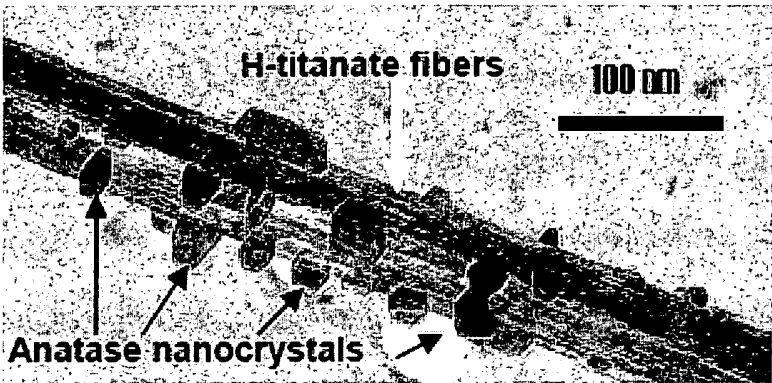
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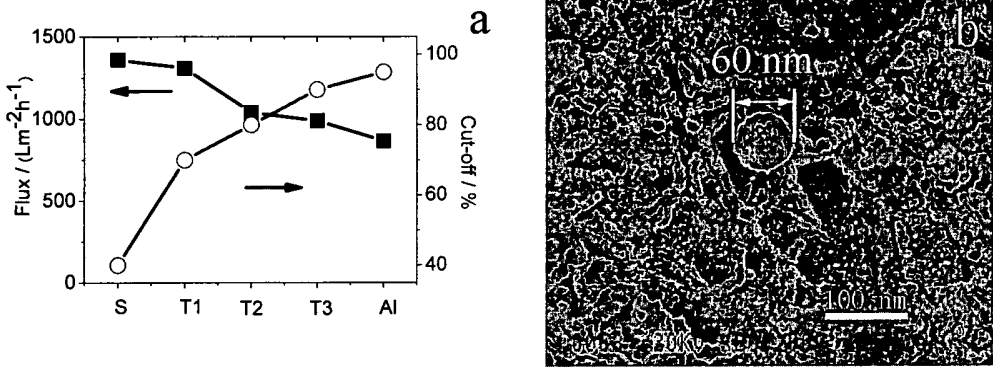
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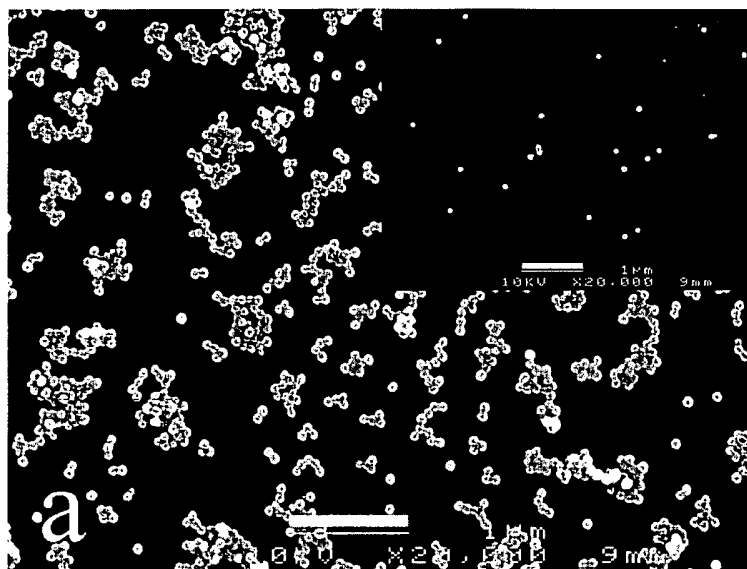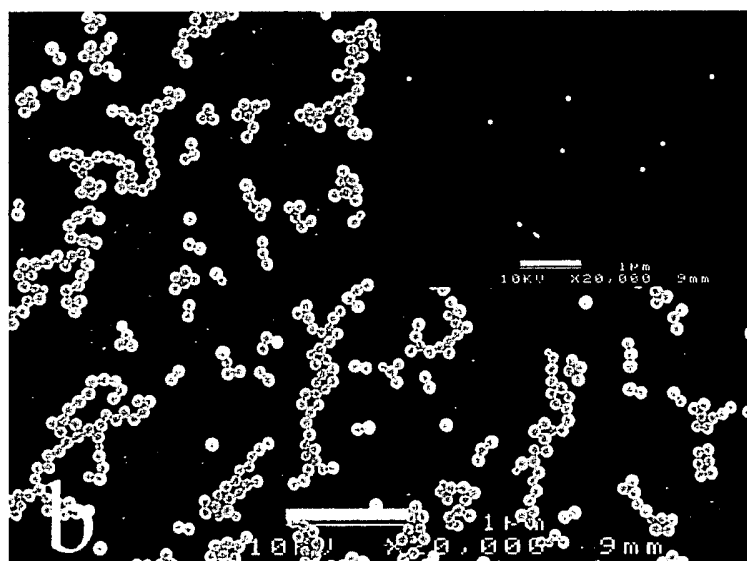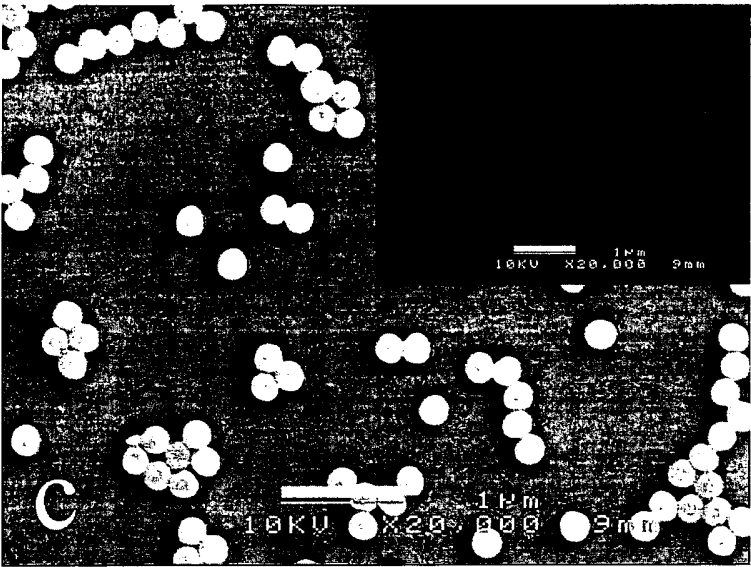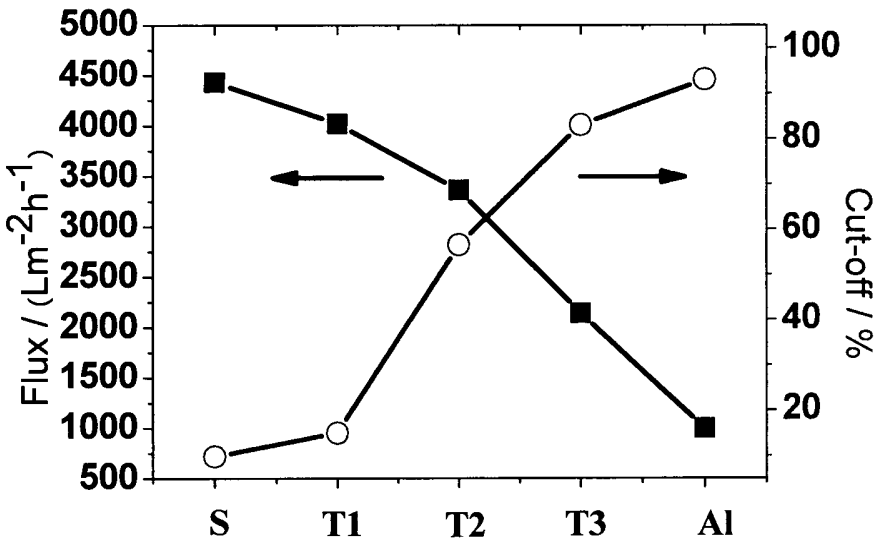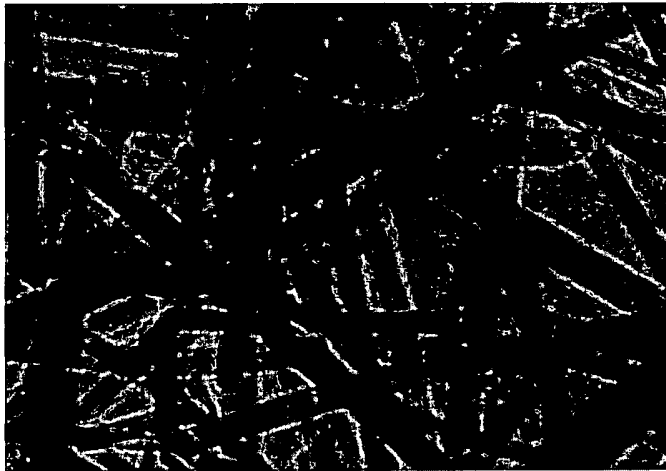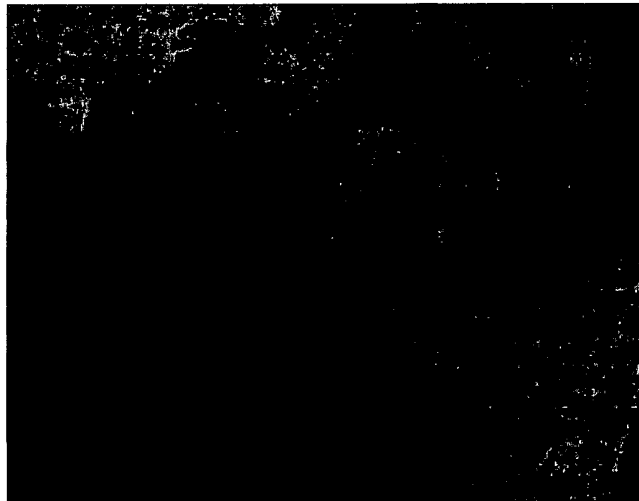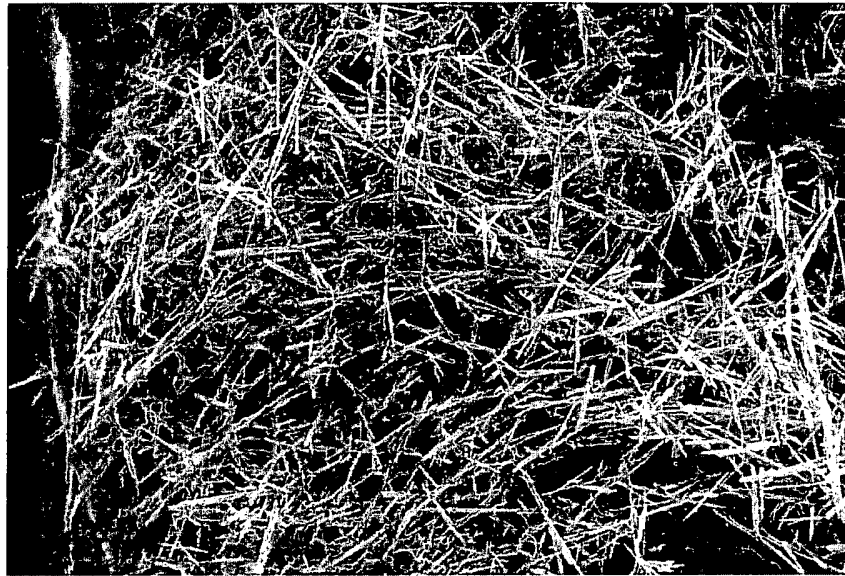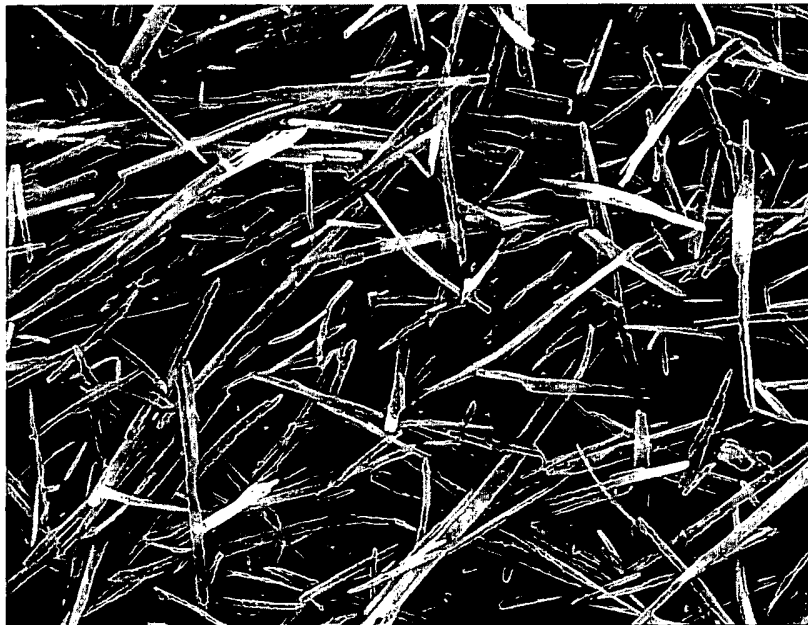
FIG 5 (a)

FIG 5 (b)

FIG 5 (c)

FIG 6
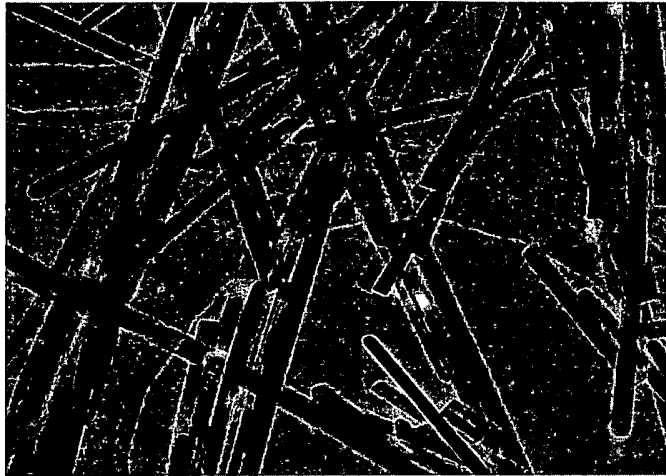
FIG 7

FIG 8

FIG 9

FIG 10

FIG 11

FIG 12

A.   CLASSIFICATION OF SUBJECT MATTER

Int. Cl.

B01D 39/00 (2006.01)   *B01D 61/14* (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B.   FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
REFER ELECTRONIC DATA BASE CONSULTED

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
DWPI IPC B01D 39/IC, 61/14 & Key words (nano+, ceramic, fibre or fibre)

C.   DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 1998/21164 A1 (NATIONAL RESEARCH COUNCIL OF CANADA) 22 May 1998 whole document	1-31
A,P	WO 2007/054040 A2 (ELMARCO) 18 May 2007 whole document	1-31
A	US 2005/0026526 A1 (VERDEGAN et al) 3 February 2005 whole document	1-31

☐ Further documents are listed in the continuation of Box C	☒ See patent family annex

*	Special categories of cited documents:		
"A"	document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E"	earlier application or patent but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search	Date of mailing of the international search report
04 December 2007	12 DEC 2007

Name and mailing address of the ISA/AU	Authorized officer
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This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member			
WO	199821164	CA	2272852		
WO	2007054040	CZ	297697		
US	20050026526	GB	2404347	DE	102004036440

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

END OF ANNEX