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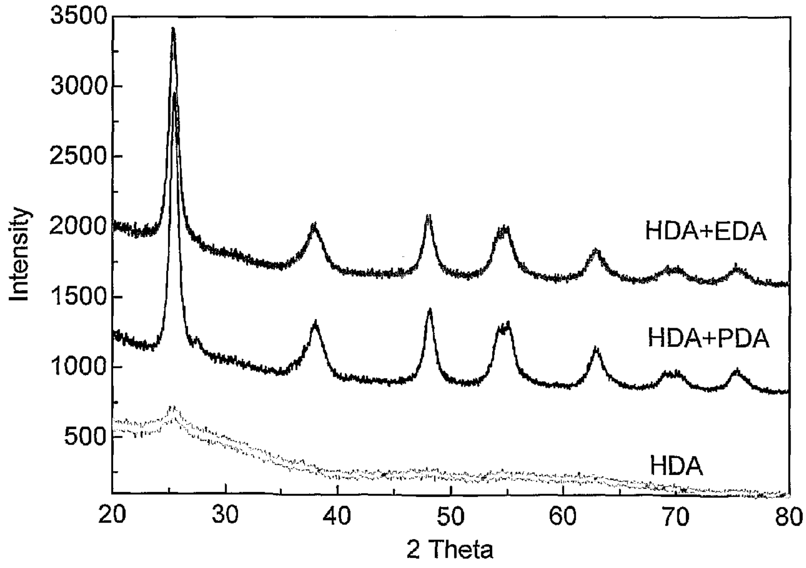
(54) Title: METAL OXYNITRIDE



(57) Abstract: A process for preparing a metal oxynitride, said process comprising: a) forming a solution of a metal compound and a compound having a nitrogen-containing functional group in a polar organic solvent, and b) converting said solution into a solid residue.

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Metal Oxynitride

The present invention relates to a process for preparing a metal oxynitride. The present invention also relates to a metal oxynitride obtainable by such a process, a photocatalyst comprising the metal oxynitride and a method of purifying a medium, such as water or air, which involves contacting the medium with the photocatalyst.

When photocatalytic materials are exposed to light, electron-hole pairs develop. These generate highly reactive free radicals on the surface of the material. Titanium dioxide is an example of a photocatalytic material.

Titanium dioxide is routinely used as a photocatalyst in the purification of water and/or air. In a typical purification process, water or air is contacted with titanium dioxide. When the titanium dioxide is activated with UV light, organic contaminants or bacteria in the water or air are oxidised and converted into harmless end-products.

Although titanium dioxide is an effective photocatalyst, it is only activated by UV light. As a result, it can only be activated using a relatively small proportion of the radiation from sunlight; for example, titanium dioxide shows little catalytic activity under visible light.

Various attempts have been made to shift the optical response of titanium dioxide to improve its photocatalytic efficiency. In particular, a number of techniques have been developed to shift the optical response of titanium dioxide to the visible spectral range, so that a greater proportion of solar radiation may be used for catalyst activation. In one such technique, titanium dioxide is doped with metals, such as V, Pt, Cr and Fe. The doped material, however, tends to be thermally unstable. Moreover, the doped metal centres tend to act as electron traps, reducing the material's photocatalytic activity.

Titanium dioxide may also be reacted with nitrogen to enhance its photocatalytic activity in the visible range. For example, titanium dioxide may be calcined in a flow of ammonia at a temperature of over 600°C to produce titanium oxynitride. Alternatively, titanium nitride may be oxidised at elevated temperatures in a flow of an oxygen-containing gas to produce titanium oxynitride. These methods, however, tend to produce heterogeneous products, with nitrogen intercalation confined predominantly to the surface of the material. Moreover, the resultant oxy-nitride has a tendency to have a relatively low surface area.

A new process for preparing a metal oxynitride has now been developed. In particular, the process of the present invention enables the metal oxynitride to be produced under relatively mild reaction conditions, such as mild temperatures and pressures. Moreover, the process can be used to produce a substantially homogeneous product, with nitrogen intercalation occurring throughout the bulk phase of the material. The resultant product typically has a high surface area.

According to the present invention, there is provided a process for preparing a metal oxynitride, said process comprising:

a. forming a solution of a metal compound and a compound having a nitrogen-containing functional group (nitrogen-containing compound) in a polar organic solvent, and

b. converting said solution into a solid residue.

The present invention also provides a metal oxynitride obtainable by the above process. The metal oxynitride of the present invention generally has the formula $MO_{n-x}N_x$. In one embodiment, the metal oxynitride is titanium oxynitride of the formula $TiO_{2-x}N_x$. In another embodiment, the metal oxynitride is tin oxynitride of the formula $SnO_{2-x}N_x$. The metal oxynitride may also be a mixed metal oxynitrides.

In part a) of the process of the present invention, a metal compound and a nitrogen-containing compound are dissolved in a polar organic solvent. Preferably, a homogenous solution of the metal compound and nitrogen-containing compound is formed. The nitrogen-containing compound reacts with the metal compound in the solution phase to form a metal oxynitride/metal oxynitride precursor. As the reaction takes place in solution, the reaction between the nitrogen-containing compound and the metal compound is not confined to the surface of the metal compound. As a result, a substantially homogeneous metal oxynitride product may be produced.

In one embodiment, the metal compound and the compound having a nitrogen-containing functional group may be dissolved in the polar organic solvent in a single step. Preferably, however, the metal compound may first be dissolved in the polar organic solvent, and the nitrogen-containing compound, subsequently added. Preferably, the nitrogen-containing compound is added gradually with stirring. More preferably, the nitrogen-containing compound is added in a drop-wise manner, whilst the mixture is stirred vigorously. Additionally or alternatively, the mixture may be irradiated with ultrasonic radiation. As well as acting as a stirring aid, the ultrasound treatment may also improve the crystallization of the product and limit the aggregation of the product particles. This is believed to be due to the sudden formation and collapse of low pressure bubbles in the mixture by ultrasound (i.e. cavitation effect of ultrasound).

In yet another alternative, the nitrogen-containing compound may first be dissolved in the polar organic solvent. The metal compound may then be added to the resultant solution. Preferably, the metal compound is added slowly with stirring. More preferably, the metal compound is added in a drop-wise manner, whilst the mixture is stirred vigorously. Additionally or alternatively, the mixture may be irradiated with ultrasonic radiation. As well as acting as a stirring aid, the ultrasound treatment may also improve the crystallization of the product and limit the aggregation of the product particles. This is believed to be due to the cavitation effect of ultrasound.

Any suitable nitrogen-containing compound may be employed. Preferably, the nitrogen-containing functional group is selected from at least one of an $-NH_x$ containing functional group, wherein x is 0, 1, 2, 3 or 4, and an -N=N- functional group. Specific examples of $-NH_x$ groups include $-NH_2$ and -NH-. Preferably, the nitrogen-containing compound is selected from at least one of urea, ammonia, ammonium salts, an organic amine, amide, imine, imide and hydrazine. Examples of suitable amines include monoamines and diamines, such as ethylene diamine and propylene diamine. Suitable ammonium salts include ammonium acetate; ammonium halides, such as ammonium chloride, ammonium fluoride and ammonium bromide; ammonium carbonate, ammonium sulfate and ammonium phosphate. EDTA may also be used. Most preferably, urea is employed. Amino acids, such as L-Alanine, L-Arginine, L-Asparagine, L-Aspartic acid, L-Cysteine, L-Glutamic acid, L-Glutamine, Glycine, L-Histadine, L-Isoleucine, L-Leucine, L-Lysine, L-Methionine, L-Phenylalanine, L-Proline, L-Serine, L-Threonine, L-Tryptophan, L-Tyrosine and L-Valine may be employed. Of the amino acids, Glycine is preferred.

The nitrogen-containing compound may be used in the form of a solution. For example, an aqueous solution of the nitrogen-containing compound may be used. Alternatively or additionally, the nitrogen-containing compound may be dissolved in a polar organic solvent. The polar organic solvent used to form this solution may be the same polar organic solvent used to dissolve both metal compound and nitrogen-containing compound in step a) of the present invention. Preferably, the polar organic solvent is an alcohol, such as ethanol. Examples of other suitable polar organic solvents are described below.

Any suitable metal compound may be employed. A mixture of two or more metal compounds may be used. The metal compound may be a compound of at least one metal selected from Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Re, Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt, Ag, Cu, Au, Zn, Ga, In, Bi, Sn, Sb, Ta and Nb. Preferably, the metal compound is a compound of W, Zn, Zr, Sn, Mo and/or Ti. More preferably, a Ti or Sn compound is used. The Ti compound may used in combination with another metal compound, such as a W, Zn, Zr, Sn, La, Ce, Ni and/or Mo compound. The Sn compound may used in combination with another metal compound, such as a W, Zn, Zr, Ti, La, Ce, Ni and/or Mo compound. In one embodiment, a titanium compound is used in combination with another metal compound, such as a transition metal or lanthanide metal compound. The resulting metal oxynitride is a mixed metal oxynitrides, such as a transition metal-titanium oxynitride or a lanthanide metal-titanium oxynitride. Specific examples include W/Ti, Zn/Ti, Zr/Ti, Sn/Ti, La/Ti, Ce/Ti, Ni/Ti and/or Mo/Ti oxynitrides.

The metal compound may be any metal compound that may dissolve in a solvent consisting essentially or containing a polar organic solvent (e.g. a mixture of a polar organic solvent and water). For example, a metal chelate, an inorganic salt or an organometallic compound may be employed.

Suitable metal chelates include chelation compounds formed using at least one of the following ligands: isopropoxybis(acetylacetonate), isopropoxybis(triethanolaminato), n-butoxybis (triethanolaminato), (2-ethylhexyloxy)bis(2-ethyl-1,3-hexanediolate), isopropoxy (2-ethyl-1,3-hexanediolate), tetraacetylacetonate and hydroxybis(lactato). Specific examples include titanium diisopropoxybis(acetylacetonate), titanium diisopropoxybis(triethanolaminato), titanium di-n-butoxybis(triethanolaminato), titanium di(2-ethylhexyloxy)bis(2-ethyl-1,3-hexanediolate), titanium isopropoxy (2-ethyl-1,3-hexanediolate), titanium tetraacetylacetonate and titanium hydroxybis(lactato).

Suitable inorganic salts include oxysulfates, sulfates, chlorides, nitrates, hydrogensulfates, phosphates, orthophosphates, dihydrogenphosphates and/or acetates. Mixtures of two or more of such salts may be employed. Examples of suitable metal salts include $TiCl_4$, $TiCl_3$, $Ti(NO_3)3$, $TiO(NO_3)2$,$Ti(NO3)4$, $Ti(CH_3COO)_4$, $Ti_3(PO_4)_4$, $TiHPO_4$, $Ti(H_2PO_4)_2$ and $TiO(SO_4)_2$. Other examples include $SnCl_4$ and $SnCl_2$. Further examples include $MoCl_5$, $Zn(NO_3)_2 \cdot xH_2O$ and $ZnCl_2$.

Suitable organometallic compounds include metal alkoxides. Suitable metal alkoxides include compounds of the formula $M(C_nH_{2n+1}O)_x$, wherein x is 1 to 10, preferably 2 to 6, and n is 1 to 20, preferably 2 to 18. Metal methoxides, ethoxides, propoxides and/or butoxides are preferred. For example, titanium tetramethoxide, titanium tetraethoxide, titanium tetra-n-propoxide, titanium tetra-isopropoxide, titanium tetra-n-butoxide, titanium tetra-isobutoxide, titanium tetra-sec-butoxide, and/or titanium tetra-t-butoxide may be employed. Metal ethylhexyloxide and stearyloxides may also be used. Examples include titanium tetra-2-ethylhexyloxide and a titanium tetra-stearyloxide.

Examples of suitable organotin compounds include $C_6H_{12}O_2Sn$ (cyclohexanestannoic acid); $C_4H_{10}O_2Sn$(e.g. 1-butanestannoic acid; butyltin hydroxide oxide; butylstannoic acid), $Sn(CnH_{2n+1}O)_4$, $C_{20}H_{40}O_4Sn$ (e.g. diethyldiiodostannane, diethyltin dicaprylate); $C_8H_{18}OSn$, $C_{12}H_{24}OSn$, $C_{32}H_{64}O_4Sn$, $C_{12}H_{20}O_4Sn$, $C_{12}H_{20}O_4Sn$, $C_{24}H_{48}O_4Sn$, $C_{24}H_{48}O_4Sn$, $C_{24}H_{40}O_8Sn$, $C_{34}H_{60}O_8Sn$, $C_{16}H_{24}O_8Sn$, $C_{32}H_{64}O_4Sn$, $C_{16}H_{34}O\ Sn$, $C_{20}H_{40}O_4Sn$, $C_{40}H_{30}O_4Sn$, $C_{20}H_{36}O_4Sn$, $C_{32}H_{36}O_8Sn$, $C_{40}H_{72}O_8Sn$, $C_{27}H_{44}O_8Sn$,$C_{32}H_{56}O_8Sn$, $C_{12}H_{22}OSn$, $C_8H_{18}O_2Sn$, $C_6H_{16}OSn$, $C_{11}H_{22}O_2Sn$, $C_{12}H_{21}C_{13}O_2Sn$, $C_{24}H_{54}O_2\ Sn_2$, $C_{30}H_{58}O_2Sn$, $C_{19}H_{32}O_2Sn$, $C_{19}H_{32}O_3Sn$, $C_{16}H_{32}O_2Sn$, $C_{24}H_{50}O_2Sn$, $C_{30}H_{60}O_2Sn$, $C_{20}H_{42}O_2Sn$, $C_{18}H_{34}OSn$, $C_{18}H_{16}OSn$ and $C_{20}H_{18}O_2Sn$.

Suitable organozinc compounds include $Zn(OAc)_2$ and $Zn(OC_nH_{2n+1})_2$.

As mentioned above, mixtures of two or more metal compounds may be employed. Examples of such mixtures include mixtures of $Ti(OC_4H_9)_4$ and $SnCl_4$ and mixtures of $Ti(OC_4H_9)_4$ and $MoCl_5$. The mole ratio of $Ti(OC_4H_9)_4$ to $SnCl_4$ in the mixture may range from 1 to 200. Accordingly, compounds ranging from $Ti_{0.5}Sn_{0.5}O_{2-x}N_x$ to $Ti_{0.995}Sn_{0.005}O_{2-x}N_x$ may be formed. The mole ratio of $Ti(OC_4H_9)_4$ to $MoCl_5$ may range from 1 to 200. Accordingly, compounds ranging from $Ti_{0.5}Mo_{0.5}O_{2-x}N_x$ to $Ti_{0.995}Mo_{0.005}O_{2-x}N_x$ may be formed.

The metal compound(s) may be provided in the form of a solution. In certain embodiments, for example, the metal compound may be dissolved in water. Alternatively or additionally, the metal compound may be dissolved in a polar organic solvent. The polar organic solvent used to form this solution may be the same polar organic solvent used to dissolve both metal compound and nitrogen-containing compound in step a) of the present invention. Preferably, the solvent is an alcohol, such as ethanol. Examples of other suitable polar organic solvents are described below.

Any suitable polar organic solvent may be used in part a) of the process of the present invention. Preferably, the solvent is one that is capable of dissolving both the nitrogen-containing compound and the metal compound as a homogeneous solution. By selecting an appropriate solvent, the reaction between the nitrogen-containing compound and the metal compound may be controlled. Examples of suitable solvents include alcohols, ketones, carboxylic acids, dimethyl sulfoxide (DMSO) and chloroform. Preferably, an alcohol, such as ethanol, is employed. In certain embodiments of the present invention, the polar organic solvent is used in combination with water.

Optionally, a surfactant may be used to aid the formation of the solution of the metal compound and compound having a nitrogen-containing functional group in step a). Any suitable surfactant may be employed. Examples include linear organic amines, such as hexadecylamine (HAD). Other examples include polyethylene glycol, polyethylene oxide and polymeric non-ionic surfactants having primary hydroxyl groups, such as Plutonic P123. The surfactant may form 0.01 to 30 weight % of the solution of step a), preferably 0.1 to 15 weight % of the solution of step a).

Prior to reaction, the initial concentration of the metal compound in the solution formed in part a) may be 0.1-40 weight %, preferably 0.5-20 weight %, more preferably 10-15 weight%.

Prior to reaction, the initial concentration of nitrogen-containing compound in the solution formed in part a) may vary depending, for example, on the nature of the metal compound and the desired nitrogen content of the target material. Typically, the initial concentration of nitrogen-containing compound in the solution may be 0.1-40 weight % preferably 0.5-20 weight %, 0.5-20 weight %, more preferably 10-15 weight %.

In step a) of the process of the present invention, the mole ratio of metal compound to nitrogen-containing compound in the polar organic solvent may be 100:1 to 1:10. Preferably, the mole ratio of metal compound to nitrogen-containing compound is 50:4 to 1:8, more preferably, 25:4 to 1:4.

Step a) of the process of the present invention may be carried out at any suitable temperature. Suitable temperatures range from -10 to 100°C, preferably 0 to 80°C, more preferably 20 to 60°C. In a preferred embodiment, temperatures of 20 to 40°C are employed. It is an advantage of at least some embodiments of the present invention that the metal oxynitride may be formed under relatively mild temperature conditions.

Step a) of the process of the present invention may be carried out at any suitable pressure. Suitable pressures range from ambient to 100 bar. It is an advantage of at least some embodiments of the present invention that the metal oxynitride may be formed under relatively mild pressure conditions.

As mentioned above, the nitrogen-containing compound reacts with the metal compound in step a) of the present invention to form a metal oxynitride or metal oxynitride precursor depending on nitrogen-containing compounds used. The metal oxynitride typically remains in solution as a sol or gel. Step b) of the present invention, therefore, involves converting the product (e.g. sol or gel) formed in part a) into a solid residue.

Any suitable method may be used to convert the solution formed in step a) into a solid residue. For example, the solution may be heated at an elevated temperature, optionally, under pressure. The pressure may be generated purely as a result of the heating step (self-generated pressure). Suitable temperatures range from 30 to 350°C, preferably 50 to 280°C, more preferably 80 to 250°C. The heating step may be carried out in an autoclave. The heating step may be carried out for 1 to 1000 hours, preferably 1 to 10 hours.

Additionally or alternatively, step b) may be carried out by subjecting the solution to ultrasonic radiation. For example, the solution from step a) may be subjected to at least 10W, preferably at least 40W, for example 40 to 1000W of ultrasonic radiation. This ultrasonic treatment step may last from 5 minutes to 10 hours, preferably 10 minutes to 2 hours. As mentioned above, the ultrasound treatment may improve the crystallization of the product and limit the aggregation of the product particles. This is believed to be due to the cavitation effect of ultrasound.

Additionally or alternatively, step b) may be carried out by subjecting the solution to microwave radiation. For example, the solution from step a) may be subjected to at least 10mW to 100 kW, preferably at least 50W to 100 kW, for example 50W to 2 kW of microwave radiation. This microwave treatment step may last from 5 minutes to 10 hours, preferably 10 minutes to 3 hours.

Additionally or alternatively, step b) may also be carried out by combusting the solution from step a). The combustion step may be carried out by burning the solution in an oxygen-containing gas, such as air. The combustion step may be carried out at a temperature of at least 200°C, preferably at least 250°C, for example 300 to 600°C.

Once a solid residue is obtained from step b), the solid residue may be washed with a suitable solvent. An example of a suitable solvent is water. Other examples include alcohols, such as ethanol. The solid residue may be alternately washed with ethanol and then water. This washing step may be carried out using a hot solvent, for example, a solvent at 10 to 80 °C, preferably 20 to 50 °C.

The solid residue from step b) may also be calcined. The calcinations may be carried out at a temperature in excess of 150°C, preferably from 200 to 600°C, for example, 400°C. The calcination step may be carried out in an inert atmosphere or in the presence of air. The calcination step may take 0.5 to 1000 hours, for example, 1 to 10 hours. Where the solid residue from step b) is washed, calcination may be carried out after the washing step.

In a preferred embodiment of the invention, a metal compound solution is formed by dissolving at least one metal compound (e.g. two) in ethanol. A solution of the nitrogen-containing compound is also formed by dissolving the nitrogen-containing compound in ethanol. For example, a saturated aqueous solution of urea may be dissolved in ethanol. The solution of the nitrogen-containing compound may then be added to the metal compound solution in a drop-wise manner with stirring. The resulting gel may then be transferred to an autoclave and heated at an elevated temperature of, for example, 30 to 300°C, preferably 80 to 120°C. The heating step may be carried out for 0.5 to 200 hours. The solid residue produced may then be retrieved (e.g. by filtration) and washed, for example, alternately with ethanol and distilled water. The washed product may then be dried and/or calcined at elevated temperatures of, for example, 200 to 600°C.

The metal oxynitride produced by the process of the present invention is characterised by a strong absorbance band in the visible region. The absorbance edge typically expands from 380nm to at least 400nm according the calcination temperature and composition of samples. Accordingly, the metal oxynitrides of the present invention have a strong optical response in the visible region. They can therefore be activated by exposure to visible light and are particularly useful as photocatalysts. Accordingly, a further aspect of the present invention provides a photocatalyst comprising the metal oxynitride of the present invention. Preferably, the photocatalyst is supported on a support material.

Suitable catalyst supports include inert supports or active supports.

Examples of suitable supports include solid oxides, carbides, zeolites, carbon and boronitride, especially alumina, modified alumina, spinel oxides, silica, modified silica, magnesia, titania, zirconia, a molecular sieve, a zeolite, β-aluminate and forms of carbon. The support may also be formed of and/or coated with glass, tiles, stones, concrete, plastic, ceramic, polymer, resin and/or fabric. Where alumina or modified alumina supports are used, the alumina or modified alumina may be, for example, α-alumina, β-alumina or γ-alumina. β-alumina and spinel oxides such as barium hexaaluminate have been found to be particularly useful in view of their stability. The carbon may be in the form, for example, of active carbon or carbon nanotubes. A zeolite may be chosen depending on the desired final product. Thus, for example, it may comprise pores or channels. Suitable zeolites are zeolites A, X, Y, ZSMs, MCMs or $AlPO_4$.

Suitable catalyst support precursors may be derived from $Al(NO_3)_3.9H_2O$ or $Mg(NO_3)_2$. Suitable catalyst precursors are described in further detail in Gonzales et al, Catalysis Today, 35 (1997), 293 - 317 and J. Livage, Catalysis Today, 41 (1998), 3 - 19.

The catalyst support employed is preferably porous. The particle size is desirably 0.1μm to 20mm, preferably, 0.2 μm to 5 mm, depending on the application. The surface area is desirably greater than 5 m^2/g, preferably greater than 10 m^2/g, more preferably greater than 50 m^2/g, for example, greater than 200 m^2/g. One or a mixture of two or more catalyst supports may be used.

The metal oxynitride may be loaded onto the support at a loading of 0.01 to 50 weight %, preferably 1 to 20 weight %. Conventional loading methods may be employed.

The metal oxynitride may take any crystal form. For example, in the case of titanium oxynitride ($TiO_{2-x}N_x$), the titanium oxynitride may be in anatase form. The particle size of the metaloxynitride crystals may be in the nanoparticles size range. For example, the metal oxynitride may take the form of nanocrystals. The nanocrystals may have a mean particle size of less than 1000 nm, preferably less than 500 nm, more preferably less than 200 nm, for example, less than 100 nm. In one embodiment, the nanocrystals have a mean particle size of at least 1 nm, preferably, at least 10 nm, more preferably at least 20 nm, yet more preferably at least 30 or 40 nm.

The metal oxynitride may be mesoporous. For example, the metal oxynitride may have a pore size of 1 to 100 nm, for example, 2 to 50 nm.

The present invention further provides a method of purifying a medium, such as air, hydrocarbon or water, which method comprises contacting the medium with the photocatalyst, and activating the photocatalyst by exposing the photocatalyst to visible light. In one embodiment, the photocatalyst is used to purify a hydrocarbon fuel, such as diesel or petrol. The photocatalyst may also be used in a method of deodorising or purifying air or other fluid (i.e. gaseous or liquid) medium, for example, by removing NO_x or SO_x from the air or other fluid medium. The photocatalyst may be contacted with a medium to provide anti-fouling, self-cleaning, anti-mould and/or anti-bacterial treatment.

The metal oxynitride obtainable by the process of the present invention may also be used as part of a solar cell cathode.

Examples

Example 1:

In this Example, a metal compound solution was formed by dissolving 3.4g $Ti(OBu)_4$ in 25ml ethanol. A solution of a nitrogen-containing compound was formed by dissolving 1ml of a saturated urea aqueous solution in 10ml ethanol. The ethanolic urea solution was then added drop-wise with stirring to the solution of $Ti(OBu)_4$. The resulting gel was then transferred to a 40ml autoclave and heated at 80°C for 12 hours. The solid residue produced was washed several times, alternately with distilled water and ethanol. The washed product was then calcined at 450 °C for 3 hours.

The final product ($TiO_{2-x}N_x$) was light grey. 0.1g of the product discoloured 15ml of a 30ppm methyl blue solution under visible light in 12 hours.

Example 2:

The procedure of Example 1 was repeated. However, the solution of the nitrogen-containing compound was formed by dissolving 2ml of a saturated urea aqueous solution in ethanol. 10 ml of this ethanolic solution was produced.

The final product ($TiO_{2-x}N_x$) was light yellow. 0.1g of the final product discoloured 15ml of a 30ppm methyl blue solution under visible light in 10 hours.

Example 3:

The procedure of Example 1 was repeated. However, the solution of the nitrogen-containing compound was formed by dissolving 3ml of a saturated urea aqueous solution in ethanol. 10 ml of this ethanolic solution was produced.

The product ($TiO_{2-x}N_x$) was light yellow. 0.1g of the final product discoloured 15ml of a 30ppm methyl blue solution under visible light in 6 hours.

Example 4:

The procedure of Example 1 was repeated. However, the solution of the nitrogen-containing compound was formed by dissolving 4ml of a saturated urea aqueous solution in ethanol. 10 ml of this ethanolic solution was produced.

The product ($TiO_{2-x}N_x$) was light yellow. 0.1g of the final product discoloured 15ml of a 30ppm methyl blue solution under visible light in 15 hours.

Example 5:

The procedure of Example 1 was repeated. However, the solution of the nitrogen-containing compound was formed by dissolving 5ml of a saturated urea aqueous solution in ethanol. 10 ml of this ethanolic solution was produced.

The product ($TiO_{2-x}N_x$) was light yellow. 0.1g of the final product discoloured 15ml of a 30ppm methyl blue solution under visible light in 10 hours.

Example 6:

The procedure of Example 1 was repeated. However, the solution of the nitrogen-containing compound was formed by dissolving 6ml of a saturated urea aqueous solution in ethanol. 10 ml of this ethanolic solution was produced.

The product ($TiO_{2-x}N_x$) was light yellow. 0.1g of the final product discoloured 15ml of a 30ppm methyl blue solution under visible light in 15 hours.

Example 7:

The procedure of Example 1 was repeated. However, the solution of the nitrogen-containing compound was formed by dissolving 7ml of a saturated urea aqueous solution in ethanol. 10 ml of this ethanolic solution was produced.

The product ($TiO_{2-x}N_x$) was bright yellow. 0.1g of the final product discoloured 15ml of a 30ppm methyl blue solution under visible light in 24 hours.

Example 8:

Example 3 was repeated. However, the gel produced upon reacting the metal compound solution and the solution of the nitrogen-containing compound was transferred to a 40ml autoclave and heated at 100°C for 12 hours.

Example 9:

Example 8 was repeated. However, the gel was transferred to a 40ml autoclave and heated at 120°C for 12 hours.

Example 10:

Example 9 was repeated. However, the gel was transferred to a 40ml autoclave and heated at 140°C for 12 hours.

Example 11:

Example 3 was repeated. However, the metal compound solution of Example 3 was replaced with a solution formed by dissolving 2.8g $Ti(OBu)_4$ and 0.52g $SnCl_4$ in 25mL ethanol.

The final product has the nominal formula $Ti_{0.8}Sn_{0.2}O_{2-y}N_y$.

Example 12:

Example 11 was repeated. However, the metal compound solution was formed by dissolving 2.04g $Ti(OBu)_4$ and 1.04g $SnCl_4$ in 25mL ethanol.

The final product has the nominal formula $Ti_{0.6}Sn_{0.4}O_{2-y}N_y$.

Example 13:

Example 11 was repeated. However, the metal compound solution was formed by dissolving 1.36g $Ti(OBu)_4$ and 1.56g $SnCl_4$ in 25mL ethanol.

The final product has the nominal formula $Ti_{0.4}Sn_{0.6}O_{2-y}N_y$.

Example 14:

Example 11 was repeated. However, the metal compound solution was formed by dissolving 0.68g $Ti(OBu)_4$ and 2.08g $SnCl_4$ in 25mL ethanol.

The final product has the nominal formula $Ti_{0.2}Sn_{0.8}O_{2-y}N_y$.

Example 15:

Example 11 was repeated. However, the metal compound solution was formed by dissolving 2.6g $SnCl_4$ in 25mL ethanol.

The final product has the nominal formula $SnO_{2-y}N_y$-15.

Example 16:

Example 11 was repeated. However, the metal compound solution was formed by dissolving 2.8g $Ti(OBu)_4$ and 0.8g $MoCl_5$ in 25mL ethanol.

The final product has the nominal composition, $Ti_{0.85}Mo_{0.15}O_{2-y}N_y$.

0.1g of the product was mixed with 10 ml of diesel oil containing 500 ppm sulfur and 60 ppm nitrogen and 1 ml of water in the presence of air. The mixture was stirred under 5W visible light irradiation for 2 hours. The sulfur and nitrogen content of the treated diesel was decreased to 210 ppm and 10 ppm, respectively.

Example 17:

In this Example, Hexadecylamine (HDA, 1.7g) was dissolved in 15ml ethanol. $Ti(OBu)_4$ (10mmol, 3.4g) was then added and the mixture was stirred rigorously for 30minutes. 4mmol ethylene diamine (EDA, 0.24g) or propylene diamine (PDA, 0.29g) were then added and the mixture was stirred rigorously to form a clear solution.

The solution was left for 2 to 500 hours until a yellowish gel was obtained. The resultant gel was heat treated at 300 to 100 degrees C to produce a mesoporous titanium oxynitride with a targeted N-content. Figure 1 shows an X-ray Diffraction (XRD) pattern of $TiO_{2-x}N_x$ precursors prepared in this Example. Figure 2 shows an XRD of the $TiO_{2-x}N_x$ prepared in this Example after calcinations at 450 degrees C. Figure 3 shows N_2 adsorption-desorption isotherms at specific surface areas for the $TiO_{2-x}N_x$ produced in this Example after calcinations at 450 degrees C.

Example 18:

Hexadecylamine(HAD, 1.7g) was dissolved in 15ml ethanol. $Ti(OBu)_4$ (10mmol, 3.4g) was then added and the mixture was stirred rigorously for 30minutes. 4mmol ethylene diamine (EDA, 0.24g) or 4mmol propylene diamine (PDA, 0.29g) were then added and the mixture was stirred rigorously to form a clear solution. The solution was coated as a film or membrane on a glass substrate. Optionally, this coating step may be repeated using ceramic or fabric as a substrate.

Figure 4 shows an x-ray diffraction pattern of the $TiO_{2-x}N_x$ film on the glass substrate after calcination at 450 degrees C for 1 hour. The sharp peaks show that the thin film is in anatase form. The yellowish colour of the film provides evidence that the film is a titanium oxynitride film.

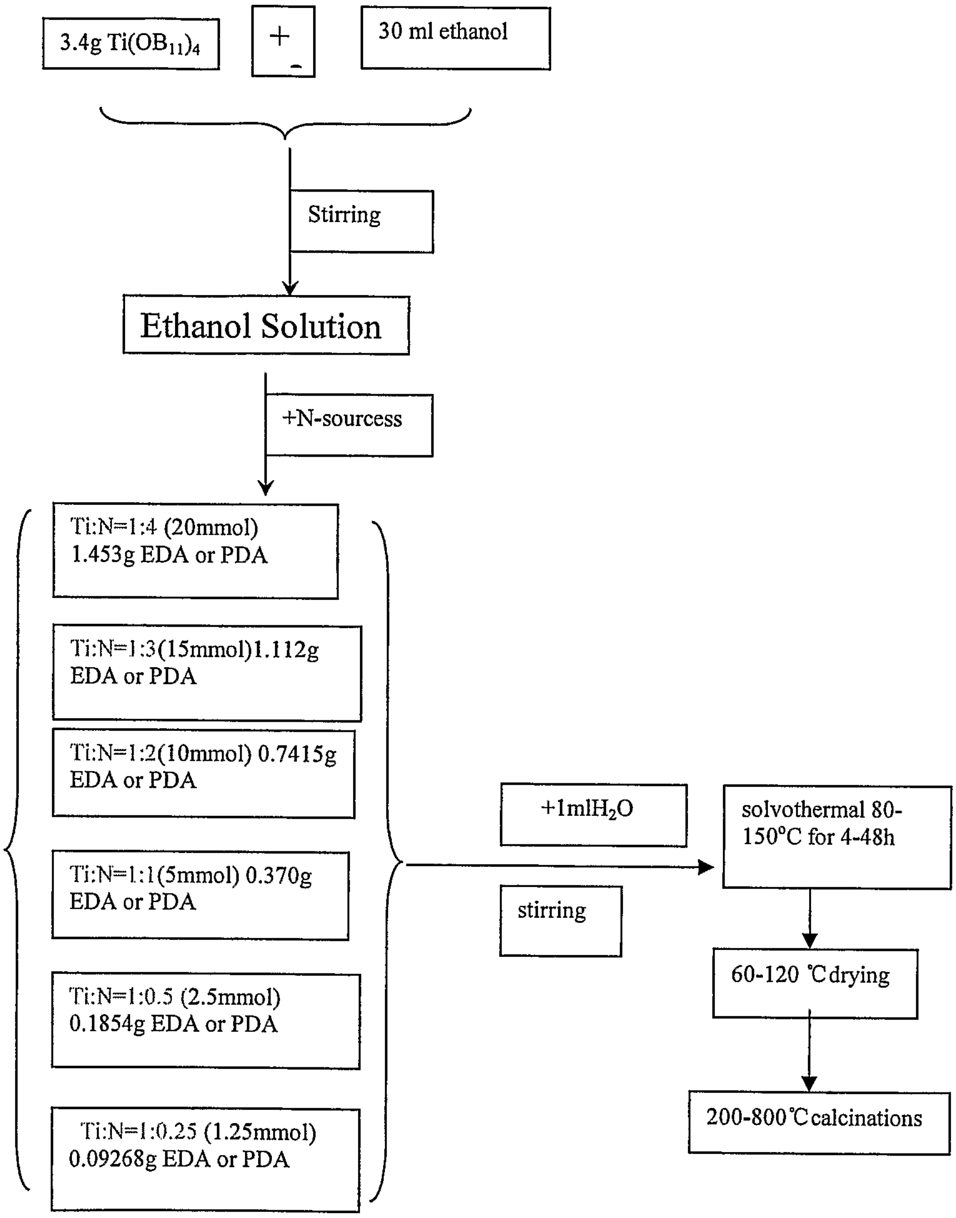
Example 19:

In this Example, $TiO_{2-x}N_x$ nano-crystals were synthesized at low temperature using an amino acid as a nitrogen-containing compound.

0.2 g glycine were dissolved in 5ml distilled water and the resulting glycine solution was added dropwise to a 30 mL ethanol solution to dissolve 3.4g $Ti(OBu)_4$. A white sol formed during the addition step. After stirring for 30min, the sol was transferred to an autoclave lined with PTFH (Polytetrafluorothylene) and heated at 120°C for 12 hours. The resultant precipitates were washed several times and dried at 120 °C. XRD characterization shows that a crystal anatase phase of $TiO_{2-x}N_x$ (Fig.5). Continuing calcinations at 450 °C for 4h did not induce strong sintering. When the amount of glycine was increased, a slight change in the $TiO_{2-x}N_x$ diffraction pattern was observed (Fig.6).

Example 20:

In this Example, clear yellow solutions containing specific amounts of EDA or PDA (adjusted according to the Ti/N ratio), 3.4g $Ti(OBu)_4$ and 30 mL ethanol were formed. After stirring for 30min, 1g distilled water was added dropwise. After further stirring for 30min, the sol was transfer to an autoclave lined with PTFH (Polytetrafluorothylene) and heated at 80-150°C for 4-48h, typically, 24h. The resultant gels were washed with water and ethanol and dried at 120 °C. The procedure used is shown in the flow chart below.



Notes: sample IDs: 1：Ti: N=1:4; 2：Ti:N=1:3 ; 3：Ti:N=1:2; 4：Ti:N=1:1; 5：Ti:N=1:0.5; 6: Ti:N=1:0.25

Figure 7 shows the XRD patterns of the $TiO_{2-x}N_x$ aged at 60 degrees for 24hours. The XRD pattern showed that the $TiO_{2-x}N_x$ was in anatase form. Figure 8 shows the XRD patterns of the $TiO_{2-x}N_x$ aged at 120 degrees C for 24hours. Figure 9 shows the XRD patterns of the $TiO_{2-x}N_x$ aged at 150 degrees C for 24hours. Calcinations at 200-800 °C (typically 450 °C) for 4h did not induce strong sintering.

Example 21:

In this Example, transition metal-Ti oxynitride composites were prepared using urea combustion methods.

A specific amount of zinc nitrate was added to a urea-water saturated solution (typically 2ml). The solution was then mixed with 20 mL ethanol solution containing 3.4g $Ti(OBu)_4$ to form a clear yellow solution. After stirring for 30min, the solution was left to stand at room temperature for 5-48h, typically 24h, to form a gel. The obtained gels were calcined at 300-800°C temperatures for 3-10h to form metal doped titanium oxynitride. The XRD results indicate that the nature of the metal affected the XRD phase structures of the metal oxynitride significantly (see Figures 10 and 11). The procedure may be repeated using, for example, cerium, lanthanum or nickel nitrate in place of the zinc nitrate.

Example 22:

In this Example, a solvotherm method was used to synthesise mesoporous $TiO_{2-x}N_x$

A specific amount of HAD and EDA or PDA (adjusted according to the Ti/N ratio) was dissolved in 30 mL ethanol solution. 3.4g $Ti(OBu)_4$ were added to form a clear yellow solution. After stirring for 30min, 1g distilled water was added dropwise. After further stirring for 30min, the sol was transferred to autoclave lined with PTFH (Polytetrafluorothylene) and heated at 80-150°C for 4-48h, typically, 24h. The resultant gels were washed with water and ethanol and dried at 120 °C. Further continuous calcination at 450 °C for 4h was carried out to form anatase phase.

CLAIMS

1. A process for preparing a metal oxynitride, said process comprising:

   a. forming a solution of a metal compound and a compound having a nitrogen-containing functional group in a polar organic solvent, and

   b. converting said solution into a solid residue.

2. A process as claimed in claim 1, wherein the nitrogen-containing functional group is selected from at least one of an $-NH_x$ containing functional group, wherein x is 0, 1, 2, 3 or 4, and an -N=N- functional group.

3. A process as claimed in claim 2, wherein the compound having a nitrogen-containing functional group is selected from at least one of urea, ammonia, an organic amine, amide, imide, imine and hydrazine.

4. A process as claimed in any one of the preceding claims, wherein the solution formed in part a. of the claim is a homogeneous solution.

5. A process as claimed in any one of the preceding claims, wherein the solution of the metal compound and the compound having a nitrogen-containing functional group is formed by dissolving the metal compound in the polar organic solvent, and dissolving the compound having nitrogen-containing functional group in the resultant solution.

6. A process as claimed in any one of the preceding claims, wherein step b) is carried out by heating the

solution at an elevated temperature, optionally, in an autoclave.

7. A process as claimed in any one of claims 1 to 5, wherein step b) is carried out by subjecting the solution to ultrasonic or microwave radiation.

8. A process as claimed in any one of claims 1 to 5, wherein step b) is carried out by combusting the solution.

9. A process as claimed in any one of the preceding claims, which further comprises calcining the solid residue at a temperature in excess of 150°C.

10. A process as claimed in any one of the preceding claims, wherein the metal compound is a compound of at least one metal selected from Ti, Sn, Sb, Ta, Nb, Zr, Mn, Co, Fe, Re, Ga, Ni, Mo, W, Bi, Pt, Rh, Pd, Ag, Ir, Au, Cu and Zn.

11. A process as claimed in claim 10, wherein the metal compound is a compound of Sn and/or Ti.

12. A process as claimed in any one of the preceding claims, wherein the metal compound is an organometallic compound, sulfate, chloride, nitrate, hydrogensulfate, phosphate, orthophosphate, dihydrogenphosphate and/or acetate.

13. A process as claimed in claim 1, wherein the metal compound is selected from at least one of $Ti(C_4H_9O)_4$, $Ti(C_2H_5O)_4$, $Ti(C_3H_7O)_4$, $TiCl_4$, $TiCl_3$, $Ti(NO_3)_3$, $Ti(NO_3)_3$, $Ti(CH_3COO)_4$, $Ti_3(PO_4)_4$, $TiHPO_4$, $Ti(H_2PO_4)_2$ and $TiO(SO_4)_2$.

14. A process as claimed in any one of the preceding claims, wherein two or more metal compounds are employed.

15. A process as claimed in any one of the preceding claims, wherein the organic polar solvent is selected from at least one of an alcohol, ketone, carboxylic acid, dimethyl sulfoxide (DMSO) and chloroform.

16. A process as claimed in claim 15, wherein the organic polar solvent is ethanol.

17. A process as claimed in any one of the preceding claims, wherein the organic polar solvent is used in combination with water.

18. A process as claimed in any one of the preceding claims, wherein step a. is carried out at a temperature of 10 to 100°C.

19. A process as claimed in any one of the preceding claims, wherein step a. is carried out at a pressure of up to 100 bar.

20. A metal oxynitride obtainable by a process as claimed in any one of the preceding claims.

21. A photocatalyst comprising a metal oxynitride as claimed in claim 20.

22. A photocatalyst as claimed in claim 21, wherein the metal oxynitride is deposited on a catalyst support.

23. A method of purifying a medium, said method comprising contacting said medium with a photocatalyst as claimed in claim 21 or 22, and activating the photocatalyst by exposing the photocatalyst to visible light.

24. A method as claimed in claim 23, wherein the medium is water, hydrocarbon or air.

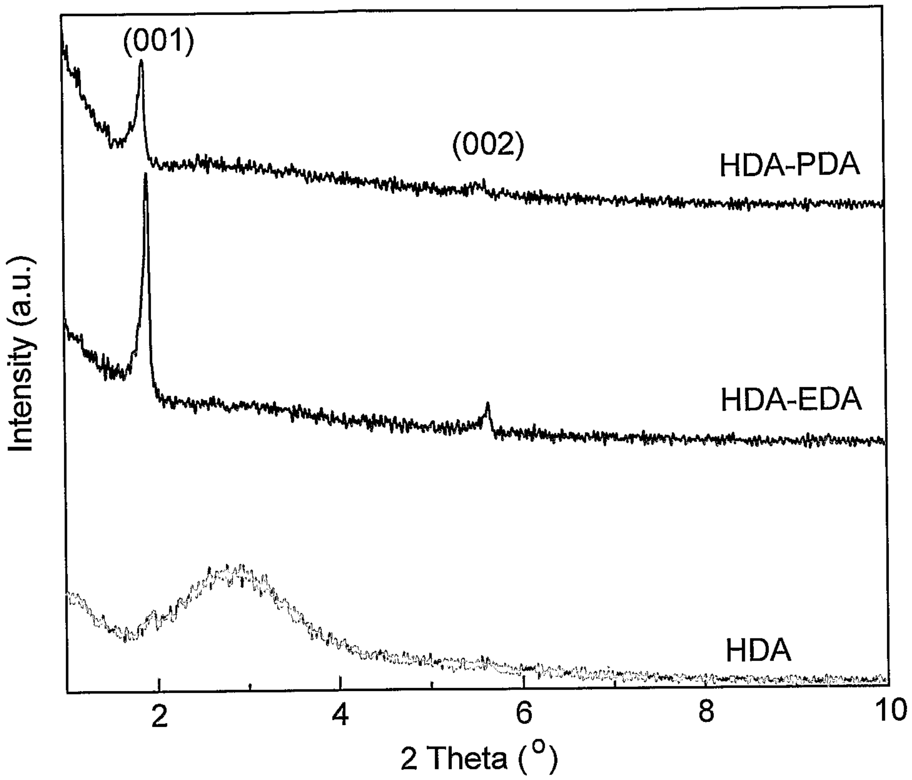

(001)
(002)
HDA-PDA
HDA-EDA
HDA
Intensity (a.u.)
2
4
6
8
10
2 Theta (°)

FIG. 1

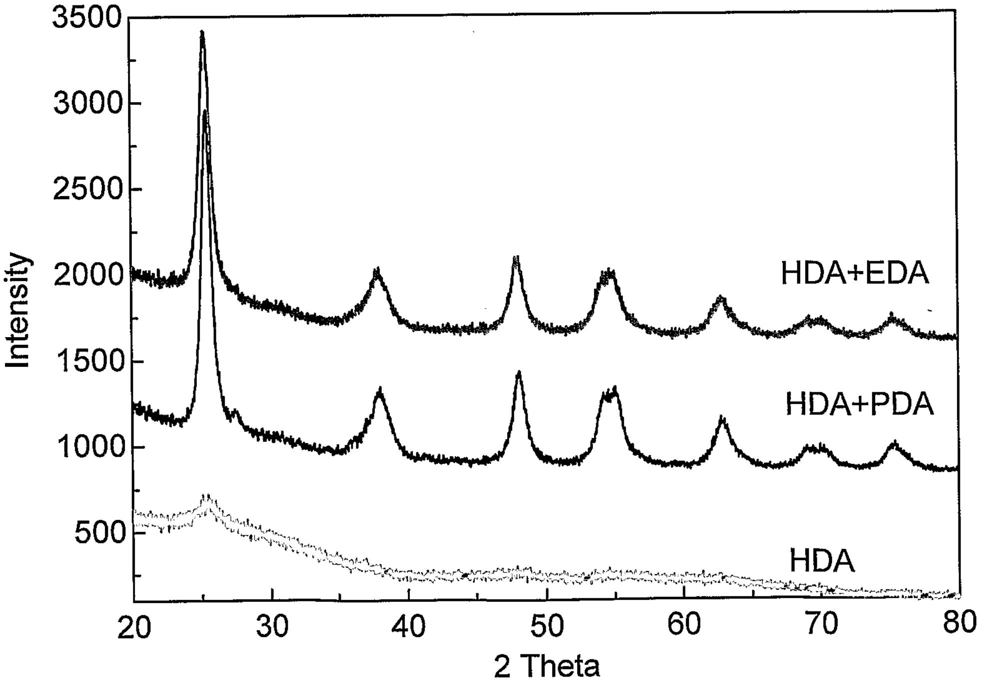
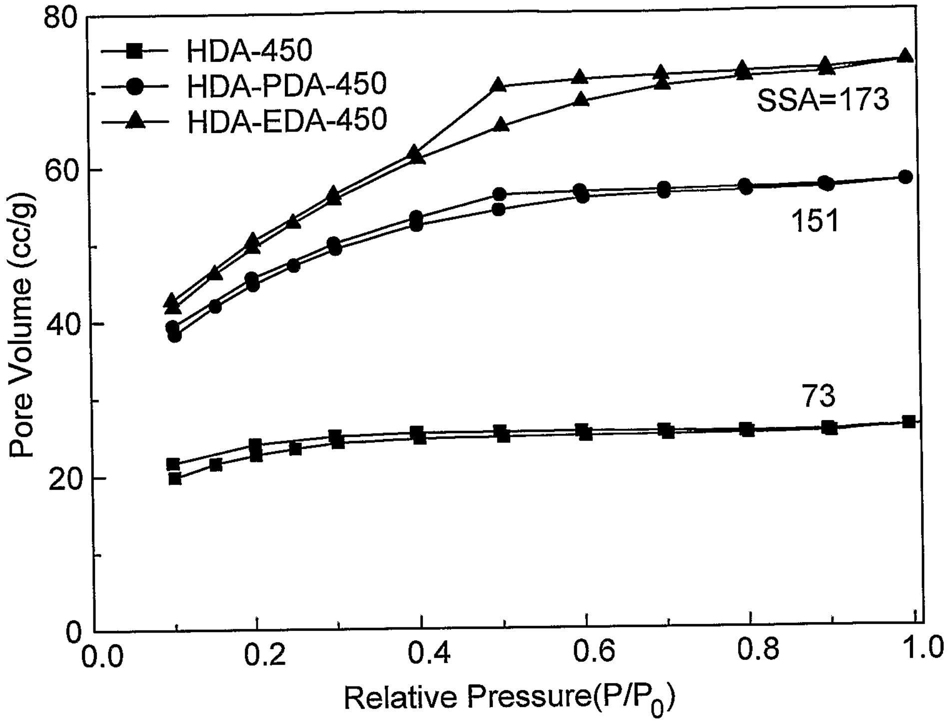
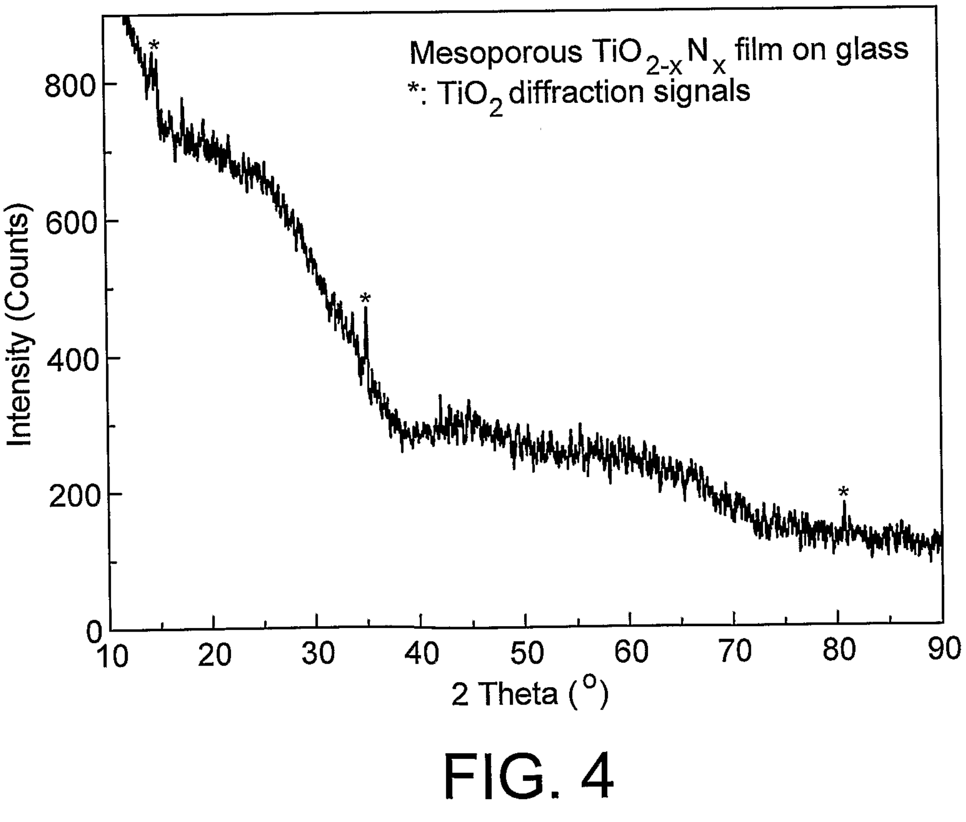

3500
3000
2500
2000
1500
1000
500
Intensity
HDA+EDA
HDA+PDA
HDA
20
30
40
50
60
70
80
2 Theta

FIG. 2



80
60
40
20
0
Pore Volume (cc/g)
0.0
0.2
0.4
0.6
0.8
1.0
Relative Pressure(P/P0)
HDA-450
HDA-PDA-450
HDA-EDA-450
SSA=173
151
73

FIG. 3



Mesoporous TiO2-xNx film on glass
*: TiO2 diffraction signals
*
*
*
800
600
400
200
0
Intensity (Counts)
10
20
30
40
50
60
70
80
90
2 Theta (°)

FIG. 4

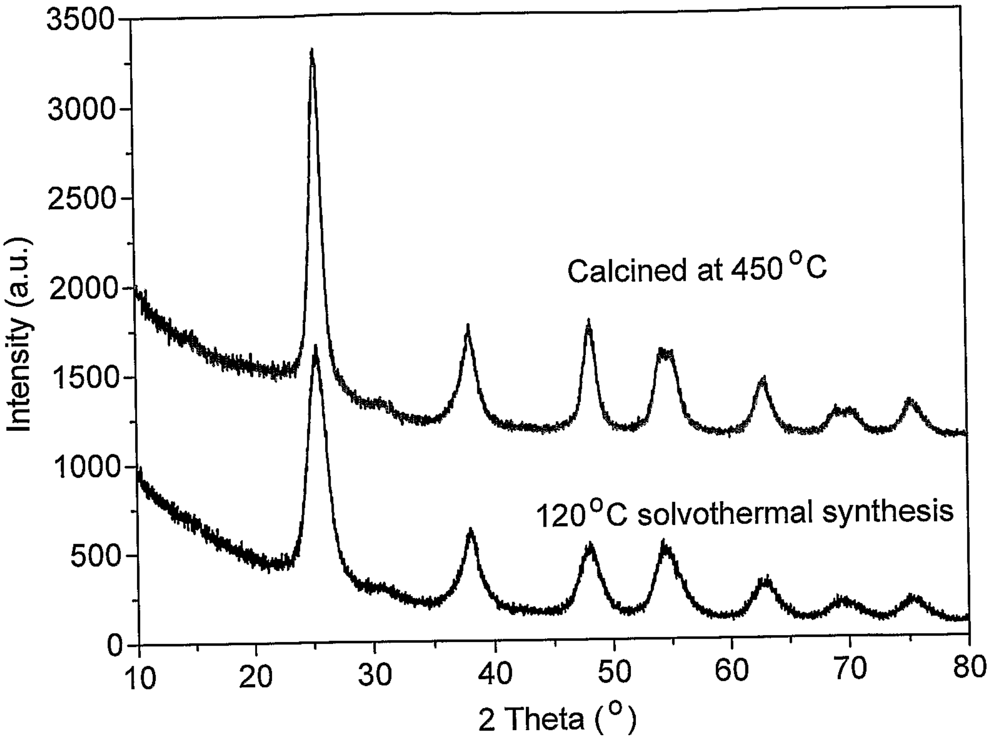
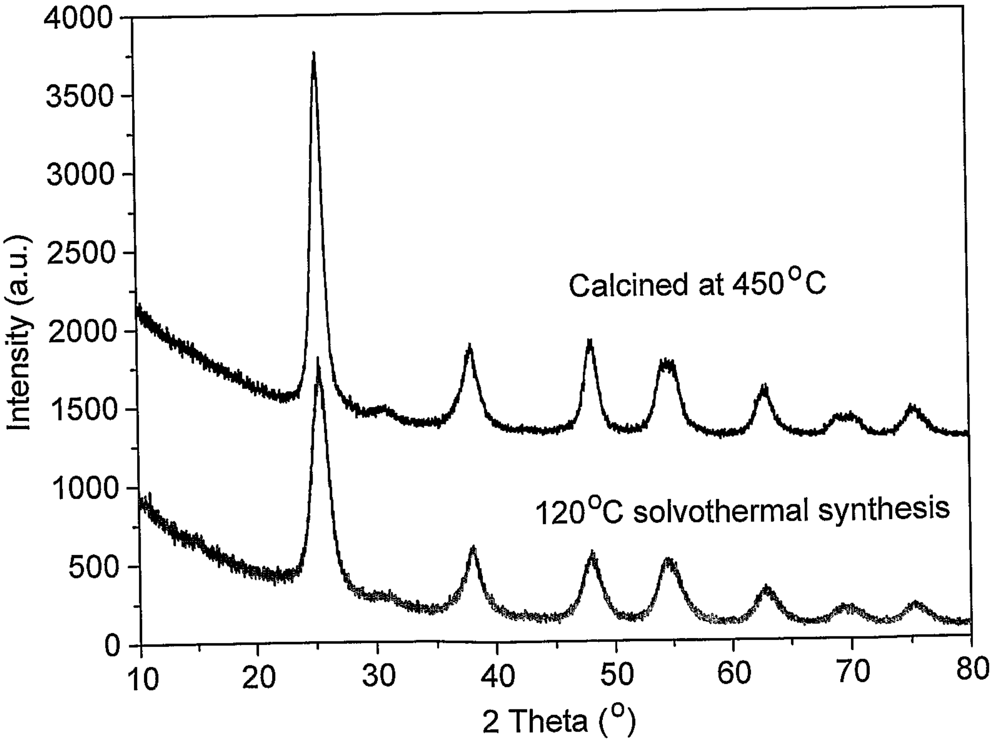

3500
3000
2500
2000
1500
1000
500
0
Intensity (a.u.)
Calcined at 450 °C
120°C solvothermal synthesis
10
20
30
40
50
60
70
80
2 Theta (°)

FIG. 5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3500
3000
2500
2000
1500
1000
500
0
Intensity (a.u.)
Calcined at 450°C
120°C solvothermal synthesis
10
20
30
40
50
60
70
80
2 Theta (°)

FIG. 6

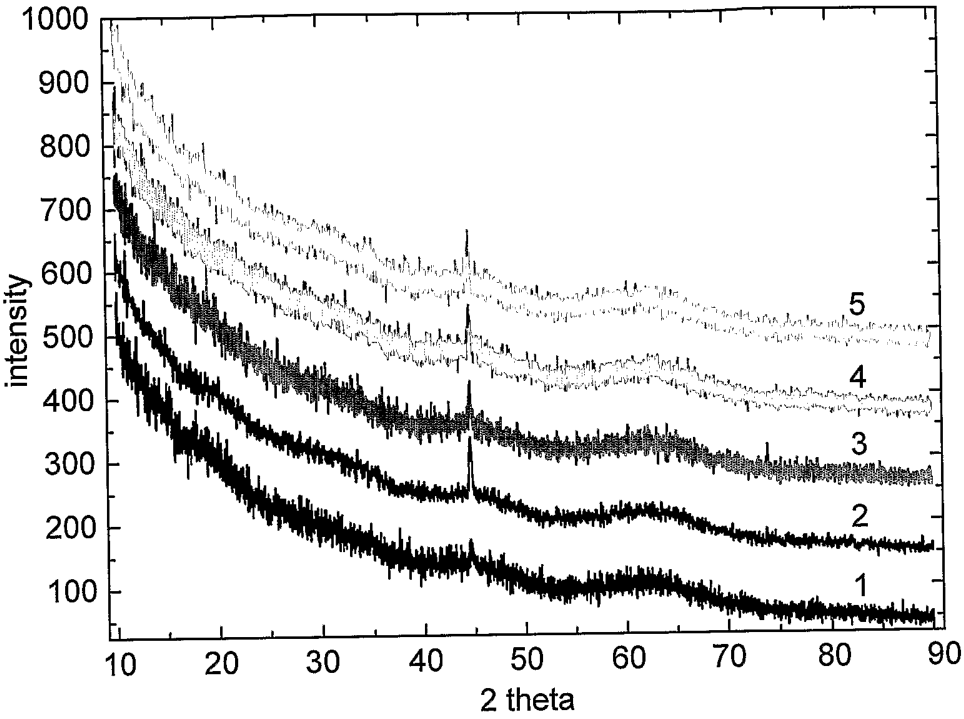
1000
900
800
700
600
500
400
300
200
100
intensity
10
20
30
40
50
60
70
80
90
2 theta
5
4
3
2
1

FIG. 7

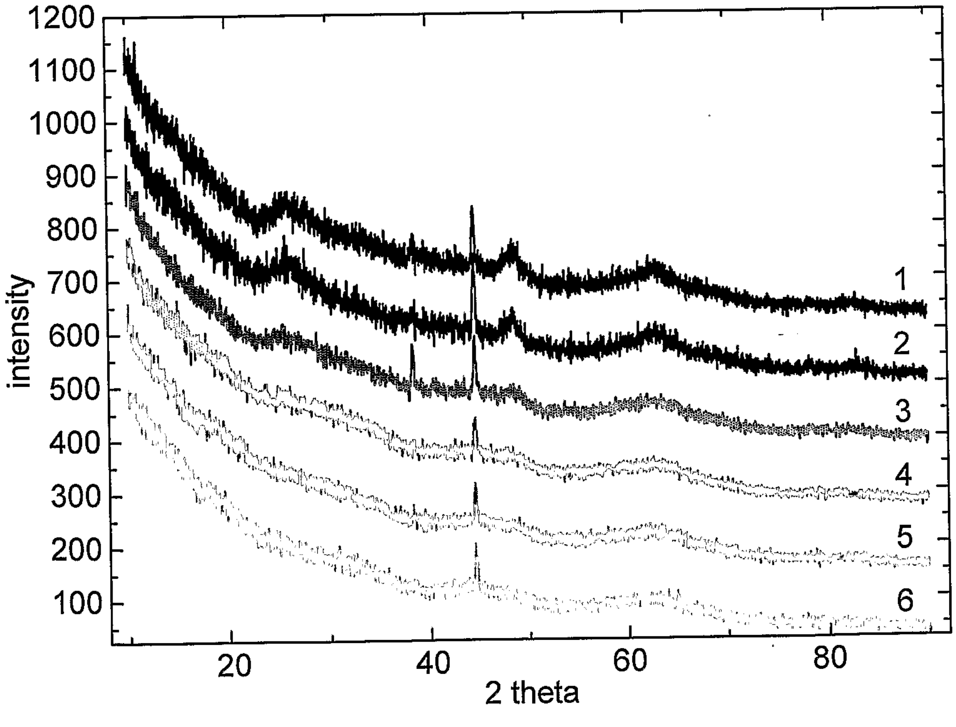
1200
1100
1000
900
800
700
600
500
400
300
200
100
intensity
20
40
60
80
2 theta
1
2
3
4
5
6

FIG. 8

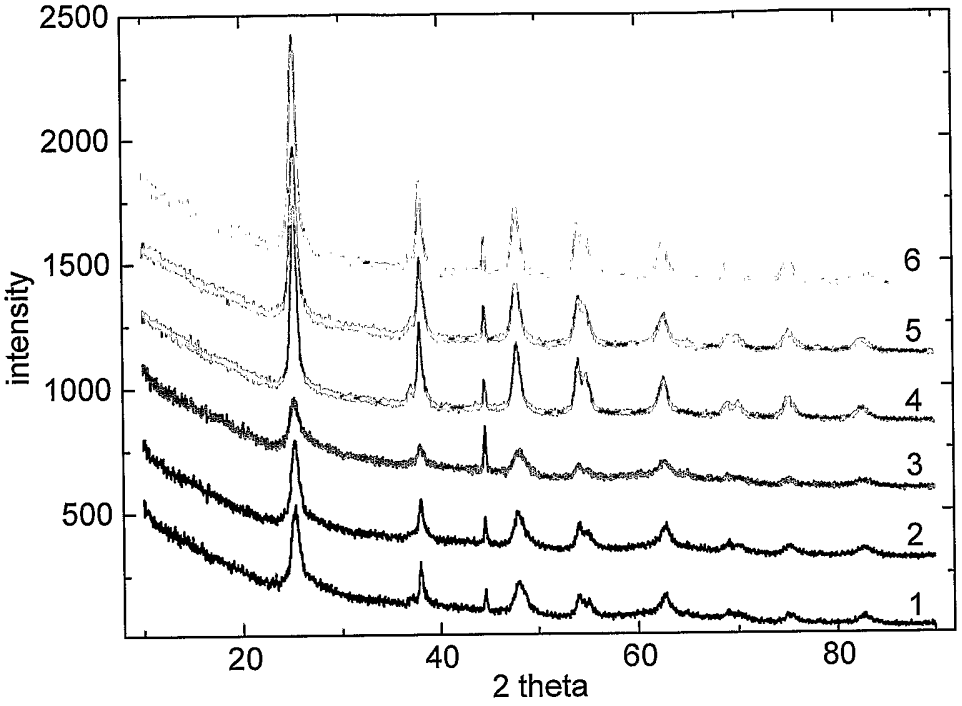
2500
2000
1500
1000
500
intensity
20
40
60
80
2 theta
6
5
4
3
2
1

FIG. 9

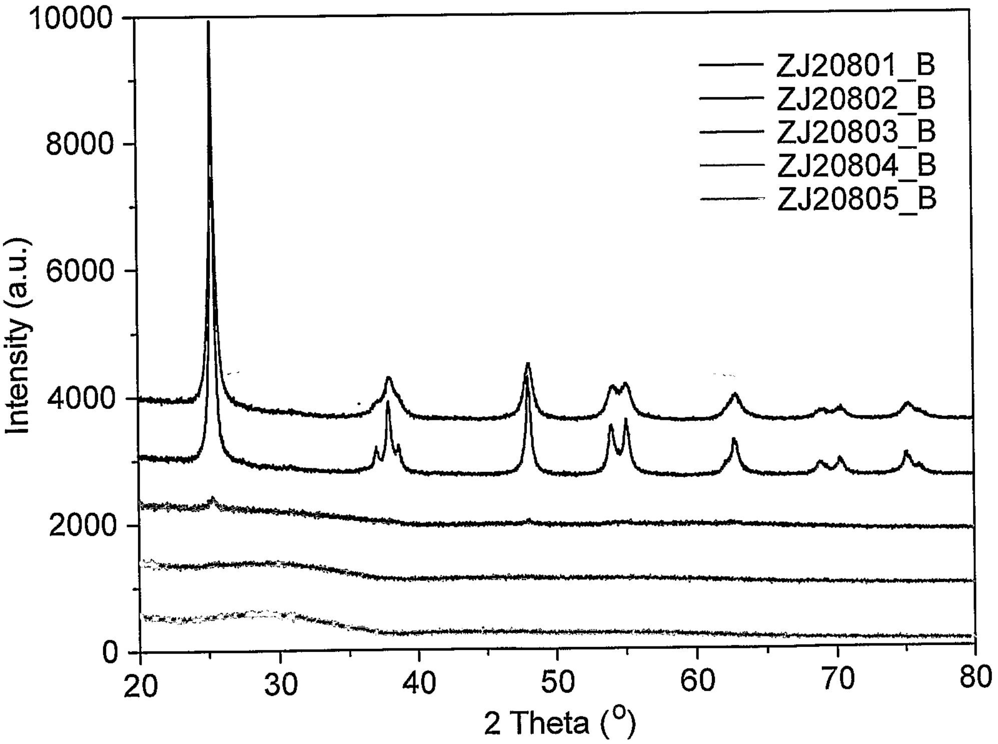
10000
8000
6000
4000
2000
0
Intensity (a.u.)
20
30
40
50
60
70
80
2 Theta (°)
ZJ20801_B
ZJ20802_B
ZJ20803_B
ZJ20804_B
ZJ20805_B

FIG. 10

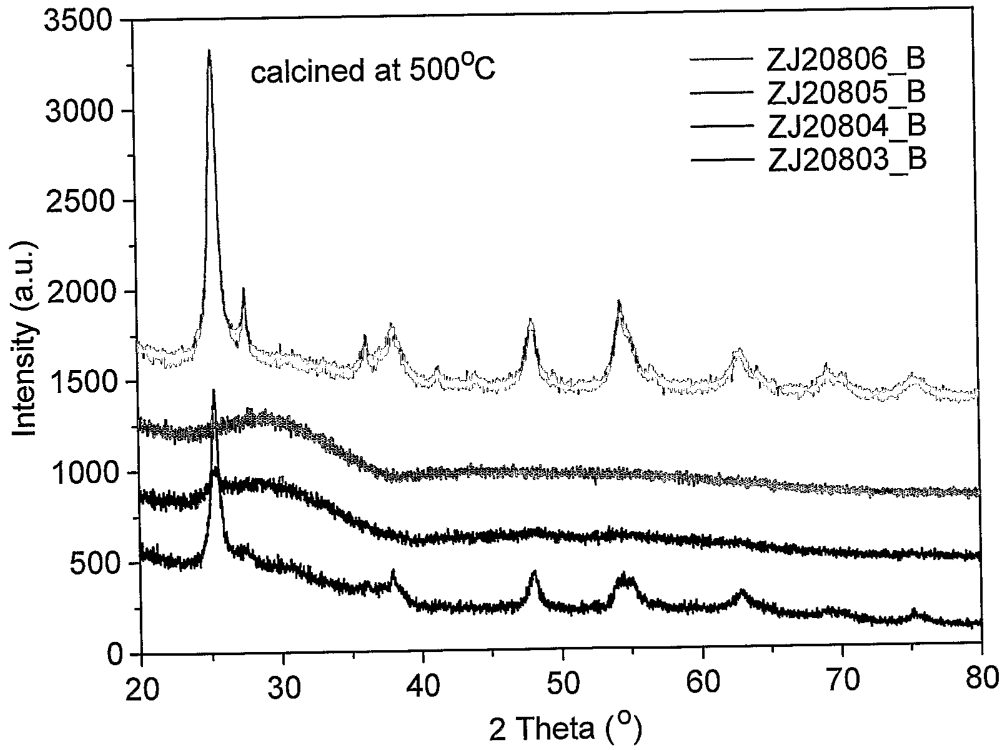
calcined at 500°C
ZJ20806_B
ZJ20805_B
ZJ20804_B
ZJ20803_B
Intensity (a.u.)
0
500
1000
1500
2000
2500
3000
3500
20
30
40
50
60
70
80
2 Theta (°)

FIG. 11

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2007/002695

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01B21/082 C01G19/00 C01G23/00 C01G39/00 B01J27/24
B01J35/00

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)
C01B C01G B01J

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 practical, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2003/216252 A1 (GOLE JAMES L [US]) 20 November 2003 (2003-11-20) page 1, paragraphs 3,4,6,7 page 3, paragraphs 34,36-46 example 1	1-24
X	US 2002/151434 A1 (DOMEN KAZUNARI [JP] ET AL) 17 October 2002 (2002-10-17)	20-23
A	examples	1
X	US 5 444 173 A (OYAMA SHIGEO T [US] ET AL) 22 August 1995 (1995-08-22)	20
A	examples	1

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

* Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"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

"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

"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.

"&" document member of the same patent family

Date of the actual completion of the international search 28 November 2007	Date of mailing of the international search report 05/12/2007
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Besana, Sonia

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/GB2007/002695

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2003216252 A1	20-11-2003	US 2006159609 A1	20-07-2006
US 2002151434 A1	17-10-2002	EP 1314477 A1	28-05-2003
		WO 0218048 A1	07-03-2002
		JP 2002066333 A	05-03-2002
US 5444173 A	22-08-1995	WO 9513870 A1	26-05-1995