Anatase TiO_2 semiconductor has a band gap of more than 3 eV and has been widely used as a catalytic material, for example, as a catalyst or a support material for active metal and metal oxide catalysts. TiO_2 has been successfully applied as a heterogeneous UV-sensitive photocatalyst, which has attracted the attention of people interested in developing new photocatalytic materials at the nano-scale. TiO_2 for water treatment also attracts much research attention due to its low cost, that no additional chemicals are needed, the process is environmental friendly, and the potential ability to conduct the process using direct sunlight. However, currently available photocatalysts, such as the widely referred to Degussa P-25 titanium dioxide, are not entirely satisfactory in the above applications due to low efficiency.

Summary of Invention

This invention discloses highly efficient titanium dioxide TiO_2 photocatalysts able to degrade organic substances in reverse osmosis concentrate (ROC) under UV-visible light or sunlight to improve the ratio of purified water to reverse osmosis membrane product from 70% to greater than or equal to 95%, and at the same time reducing the brackish waste from 30% to less than or equal to 5%.

This invention enables the possibility of producing an additional 200,000 cubic meters (m^3) clean water every day at a minimal cost for a city with a population of 5-million people, having wastewater reclamation facilities ordinarily capable of producing 550,000 cubic meters (m^3) reclaimed water every day, which is 30% of such a city's daily water usage, while also reducing the amount of brackish waste by 200,000 cubic meters (m^3). Since an additional 200,000 cubic meters (m^3) clean water accounts for 11% of such a city's daily water usage, this invention may have significant economic and social advantages for major cities around the world.

In a first aspect of the invention, there is provided a composition comprising TiO_2 nanocrystals in the form of agglomerates and/or aggregates; and an anionic species associated with the TiO_2 agglomerates/aggregates, wherein the diameter of the TiO_2 agglomerates/aggregates is from 0.02 μm to 5.0 μm; the diameter of the TiO_2 nanocrystals is from 4 to 70 nm; and the BET surface area of the composition is from 6 to 250 m^2/g~~/m^2~~ (e.g. the diameter of the TiO_2 agglomerates/aggregates is from 0.02 μm to 3.0 μm; the diameter of the TiO_2 nanocrystals is from 4 to 70 nm; and the BET surface area of the composition is from 6 to 170 m^2/g~~/m^2~~).

In still further embodiments, the diameter of the agglomerates/aggregates may be from 0.05 μm to 3.0 μm (e.g. from 0.1 μm to 1.0 μm); and/or the diameter of the TiO_2 nanocrystals may be from 5 to 50 nm (e.g. from 5 to 30 nm, such as from 9 to 26 nm or from 5.7 to 6.4 nm).

In yet further embodiments, the BET surface area of the composition may be from 6.0 to 9.0 m^2/g~~/m^2~~; or the BET surface area of the composition may be from 20.0 to 90.0 m^2/g~~/m^2~~; or the BET surface area of the composition may be from 115 to 250 m^2/g~~/m^2~~ (e.g. from 6.5 to 7.0 m^2/g~~/m^2~~; or the BET surface area of the composition may be from 30.0 to 70.0 m^2/g~~/m^2~~; or the BET surface area of the composition may be from 145 to 170 m^2/g~~/m^2~~).

In still further embodiments of the invention, the majority of the anionic species may be associated with the surface of the TiO_2 agglomerates/aggregates. For example, the ratio of the anionic species on the surface of the TiO_2 agglomerates/aggregates compared to the anionic species within the interior volume of the TiO_2 agglomerates/aggregates is from 1.5:1 to 30:1, optionally from 2:1 to 10:1, such as from 3:1 to 8:1 (e.g. from 5:1 to 8:1).

In still further embodiments of the invention, 0.1 wt% of the composition reduces the dissolved organic carbon in 99.9 wt% of reverse osmosis concentrate by from 70% to 80% after 6 hours of photocatalytic reaction.

In a second aspect of the invention, there is provided a method of preparing TiO_2 nanocrystals, the method comprising the steps of:

(a) hydrolysing a titanium source in a water/solvent mixture to form a hydrous TiO_2 material;

(b) filtering the hydrous TiO_2 material and washing the filtered hydrous TiO_2 material with a washing solution;

(c) drying and grinding the filtered and washed hydrous TiO_2 material into a powder;

(d) calcinating the powder to form anhydrous TiO_2 nanocrystals; and

(e) optionally further grinding the anhydrous TiO_2 nanocrystals.

In embodiments of the invention, the titanium source may be one or more of the group selected from titanyl sulfate, $TiCl_3$, $TiCl_4$, oxalotitanic acid, titanium ethoxide, titanium n-propoxide, titanium isopropoxide, and titanium n-butoxide. For example, the titanium source is titanyl sulfate.

the diameter of the TiO_2 agglomerates/aggregates is from 0.02 μm to 5.0 μm (e.g. from 0.02 μm to 3.0 μm);

the diameter of the TiO_2 nanocrystals is from 4 to 70 nm; and

the BET surface area of the composition is from 6 to 250 m^2/g~~/m²~~ (e.g. from 6 to 170 m^2/g~~/m²~~).

2. The composition according to Clause 1, wherein the direct band gap of the TiO_2 nanocrystals is from 3.00 to 3.70 eV and/or the indirect band gap of the TiO_2 nanocrystals may be from 2.90 to 3.50 eV (e.g. 3.34 to 3.50 eV and/or the indirect band gap of the TiO_2 nanocrystals is from 3.17 to 3.30 eV, such as the direct band gap of the TiO_2 nanocrystals is from 3.35 to 3.45 eV and/or the indirect band gap of the TiO_2 nanocrystals is from 3.20 to 3.26 eV).

3. The composition according to Clause 1 or Clause 2, wherein the TiO_2 nanocrystals are substantially in the anatase form (e.g. the TiO_2 nanocrystals may be in the anatase form, though they may contain surface defects and secondary structures).

4. The composition according to any one of the preceding clauses, wherein the anionic species is selected from one or more of the group consisting of SO_4^{2-}, Cl^-, F^-, Br^-, I^-, PO_4^{3-}, NO_3^-, BO_3^{3-}, and SiO_3^{2-} (e.g. SO_4^{2-}).

5. The composition of Clause 4, wherein:

Ti is present in an amount of from 50.9 wt% to 63.9 wt% (e.g. Ti is present in an amount of from 55.9 wt% to 59.49 wt%); and/or

O is present in an amount of from 36.09 wt% to 44.5 wt% (e.g. O is present in an amount of from 40.5 wt% to 41.5 wt%); and/or

S is present in an amount of from 0.01 wt% to 4.6 wt% (e.g. S is present in an amount of from 0.01 wt% to 2.6 wt%).

6. The composition of Clause 5, wherein:

Ti is present in an amount of from 55.9 wt% to 59.0 wt%; and/or

O is present in an amount of from 40.5 wt% to 41.5 wt%; and/or

S is present in an amount of from 0.5 wt% to 2.6 wt%.

7. The composition of Clause 6, wherein:

Ti is present in an amount of from 57.3 wt% to 58.5 wt%; and/or

O is present in an amount of from 40.5 wt% to 40.9 wt%; and/or

S is present in an amount of from 1.0 wt% to 1.8 wt%.

8. The composition of any one of Clauses 4 to 7, wherein the composition has FTIR peaks at approximately 3620-3850 cm^{-1}, 3159 cm^{-1}, 1400 cm^{-1}, 1215 cm^{-1}, 1148 cm^{-1}, 1051 cm^{-1} and 980 cm^{-1}.

9. The composition of any one of Clauses 4 to 9, wherein:

the proportion of Ti-OH species compared to Ti-OSO_3 species of the surface of the aggregates/agglomerates, as measured using the Ti $2p_{3/2}$ peaks using X-ray photoelectron spectroscopy, is from 1.5:1 to 2:1; and/or

the proportion of Ti-OH species compared to Ti-OSO_3 species of the surface of the aggregates/agglomerates, as measured using the O 1s peaks using X-ray photoelectron spectroscopy, is from 1.5:1 to 2:1; and/or

the proportion of Ti-O(O=S=O)O-Ti species compared to Ti-OO(O=S=O) species of the surface of the aggregates/agglomerates, as measured using the S $2p_{3/2}$ peaks using X-ray photoelectron spectroscopy, is from 4:1 to 5:1.

10. The composition according to any one of the preceding clauses, wherein:

the diameter of the agglomerates/aggregates is from 0.05 μm to 3.0 μm (e.g. from 0.1 μm to 1.0 μm); and/or

the diameter of the TiO_2 nanocrystals is from 5 to 50 nm (e.g. from 5 to 30 nm, such as from 9 to 26 nm or 5.7 to 6.4 nm).

11. The composition according to any one of the preceding clauses, wherein the BET surface area of the composition is from 6.0 to 9.0 m^2/g~~$/m^2$~~; or the BET surface area of the composition is from 20.0 to 90.0 m^2/g~~$/m^2$~~; or the BET surface area of the composition is from 115 to 250 m^2/g~~$/m^2$~~ (e.g. from 6.5 to 7.0 m^2/g~~$/m^2$~~; or the BET surface area of the composition may be from 30.0 to 70.0 m^2/g~~$/m^2$~~; or the BET surface area of the composition may be from 145 to 170 m^2/g~~$/m^2$~~).

12. The composition according to any one of the preceding clauses, wherein the majority of the anionic species is associated with the surface of the TiO_2 agglomerates/aggregates.

13. The composition according to Clause 12, wherein the ratio of the anionic species on the surface of the TiO_2 agglomerates/aggregates compared to the anionic species within the

B. The composition of Clause A, wherein the anionic species is selected from one or more of the group consisting of SO_4^{2-}, Cl^-, F^-, Br^-, I^-, PO_4^{3-}, NO_3^-, BO_3^{3-}, and SiO_3^{2-} (e.g. SO_4^{2-}).

C. The composition of any one of the preceding clauses, wherein:

(a) the amount of the anionic species on the surface of the TiO_2 agglomerates/aggregates compared to the anionic species within the interior volume of the TiO_2 agglomerates/aggregates is from 1.5:1 to 30:1, optionally from 2:1 to 10:1, such as from 3:1 to 8:1; and/or

(b) the diameter of the agglomerates/aggregates is from 0.02 μm to 5.0 μm (e.g. 0.02 μm (or 0.05 μm) to 3.0 μm, such as from 0.1 μm to 1.0 μm); and/or

(c) the diameter of the TiO_2 nanocrystals is from 5 to 50 nm (e.g. from 5 to 30 nm, such as from 9 to 26 nm); and/or

(d) the BET surface area of the composition is from 6 to 250 m^2/g~~/m²~~ (e.g. from 6.0 to 9.0 m^2/g~~/m²~~; or from 20.0 to 90.0 m^2/g~~/m²~~; or from 115 to 250 m^2/g~~/m²~~ (such as from 6.5 to 7.0 m^2/g~~/m²~~; or from 30.0 to 70.0 m^2/g~~/m²~~; or from 145 to 170 m^2/g~~/m²~~); and/or

(e) the direct band gap of the TiO_2 nanocrystals is from 3.00 to 3.70 eV (e.g. 3.34 to 3.50 eV) and/or the indirect band gap of the TiO_2 nanocrystals may be from 2.90 to 3.50 eV (3.17 to 3.30 eV), optionally wherein the direct band gap of the TiO_2 nanocrystals is from 3.35 to 3.45 eV and the indirect band gap of the TiO_2 nanocrystals is from 3.20 to 3.26 eV; and/or

(f) the TiO_2 nanocrystals are substantially in the anatase form.

Description of Figures

The invention will now be described in further detail below, with the aid of the following figures.

Fig. 1: Photocatalytic reaction set-up for the treatment of reverse osmosis concentrate (ROC).

Fig. 2: Total Organic Concentration (TOC) in ROC following reaction with various photocatalysts for 6 hours.

Fig. 3: TOC in ROC following reaction with E20W80 for 24 hours.

Fig. 4: (a) DOC conversion (C/C_0) of ROC after 6 hours photocatalytic reaction over Degussa P25 pure TiO_2 and SO_4^{2-}/TiO_2 catalyst prepared from different

associated with the TiO_2 agglomerates/aggregates, wherein the diameter of the TiO_2 agglomerates/aggregates is from 0.02 μm to 5.0 μm; the diameter of the TiO_2 nanocrystals is from 4 to 70 nm; and the BET surface area of the composition is from 6 to 250 m^2/g~~/m²~~, results in photocatalysts with particularly good properties. Preferably, the introduction of the anionic species is born as a by-product of the method of manufacture of the nanocrystals.

When used herein, the term "primary particles", refers to individual crystals that may or may not associate together form secondary particles. "Secondary particles", when referred to herein are either agglomerates (particles that are physically-bound together; rigidly) or aggregates (particles that are chemically or sinter-bound together; loosely). When used herein, the term "associated" may refer to any type of bonding, such as covalent bonding, Van der Waals attraction or, more particularly, ionic bonding.

When used herein "substantially" refers to the situation where all or almost all of a composition (or component thereof) is in a single form, though minor impurities and/or minor amounts (e.g. less than 1 wt%) of another form (or forms) may exist.

When used herein, the term "comprising" (an open-ended term) is intended to cover the terms "consists of" or "consists essentially of" or equivalents of such phrases (closed terms). This specification explicitly contemplates the situation where the term "comprising" can be replaced by the terms "consists of" or "consists essentially of" or equivalents of such phrases or *vice-versa*. That is, any open-ended term may be replaced by a closed term or *vice-versa*.

When used herein, the term "optionally" refers to a feature that may be present, but can be removed.

In the disclosed compositions the direct band gap of the TiO_2 nanocrystals can be from 3.00 to 3.70 eV (e.g. 3.34 to 3.50 eV) and/or the indirect band gap of the TiO_2 nanocrystals may be from 2.90 to 3.50 eV (3.17 to 3.30 eV). For example, the direct band gap of the TiO_2 nanocrystals may be from 3.35 to 3.45 eV and/or the indirect band gap of the TiO_2 nanocrystals is from 3.20 to 3.26 eV.

While the TiO_2 nanocrystalline compositions may contain different crystalline forms, it is preferred that the TiO_2 nanocrystalline compositions are substantially in the anatase form. For example, the TiO_2 nanocrystalline compositions are entirely in the anatase form, though

diameter of the TiO_2 nanocrystals (i.e. the primary particles) may be from 5 to 50 nm (e.g. from 5 to 30 nm, from 9 to 26 nm or from 5.7 to 6.4 nm).

In certain embodiments, the BET surface area of the composition may be from 6 to 170 m^2/g~~/m²~~, such as from 6.0 to 9.0 m^2/g~~/m²~~, or from 20.0 to 90.0 m^2/g~~/m²~~ or from 115 to 250 m^2/g~~/m²~~ (e.g. from 6.5 to 7.0 m^2/g~~/m²~~, or may be from 30.0 to 70.0 m^2/g~~/m²~~ or from 145 to 170 m^2/g~~/m²~~). While it would be generally expected that a composition with a high surface area may result in better catalytic activity, it has surprisingly been found that the compositions of the current invention may have a relatively low surface area as compared to Degussa P-25 and yet retain a catalytic activity that is many times higher than said catalyst.

While not wishing to be bound by theory, it is suspected that the unexpectedly good catalytic activity of the current compounds may be associated with the presence of a relatively high proportion of Ti-OH and anionic species on the surface of the secondary particles (e.g. as measured by FTIR and/or XPS). In certain embodiments, (e.g. in embodiments where the composition has a BET surface area of from 6.5 to 7.0 m^2/g~~/m²~~), the ratio of the anionic species on the surface of the TiO_2 agglomerates/aggregates compared to the anionic species within the interior volume of the TiO_2 agglomerates/aggregates is from 1.5:1 to 30:1, optionally from 2:1 to 10:1, such as from 3:1 to 8:1 (e.g. from 5:1 to 8:1).

In certain embodiments, 0.1 wt% of the composition can reduce the dissolved organic carbon in 99.9 wt% of reverse osmosis concentrate by from 70% to 80% after 6 hours of photocatalytic reaction.

The compositions described herein before may be prepared using a method comprising the steps of:

(a) hydrolysing a titanium source in a water/solvent mixture to form a hydrous TiO_2 material;

(b) filtering the hydrous TiO_2 material and washing the filtered hydrous TiO_2 material with a washing solution;

(c) drying and grinding the filtered and washed hydrous TiO_2 material into a powder; and

(d) calcinating the powder to form anhydrous TiO_2 nanocrystals.

It is intended that steps (a) to (d) be run consecutively. In addition, the anhydrous TiO_2 nanocrystals obtained in step (d) may be optionally subjected to further grinding.

Claims

1. A composition comprising:

TiO_2 nanocrystals in the form of agglomerates and/or aggregates; and

an SO_4^{2-} as an anionic species associated with the TiO_2 agglomerates/aggregates, wherein:

the diameter of the TiO_2 agglomerates/aggregates is from 0.02 μm to 5.0 μm;

the diameter of the TiO_2 nanocrystals is from 4 to 70 nm; ~~and~~

the BET surface area of the composition is from 6 to 250 ~~g/~~m^2/g;

the TiO_2 nanocrystals are substantially in the anatase form;

Ti is present in an amount of from 55.9 wt% to 59.0 wt%;

O is present in an amount of from 40.5 wt% to 41.5 wt%;

S is present in an amount of from 0.1 wt% to 2.6 wt%;

the ratio of the SO_4^{2-} on the surface of the TiO_2 agglomerates/aggregates compared to the SO_4^{2-} within the interior volume of the TiO_2 agglomerates/aggregates is from 2:1 to 10:1.

~~2. The composition according to Claim 1, wherein the TiO_2 nanocrystals are substantially in the anatase form.~~

~~3. The composition according to Claim 1, wherein the anionic species is selected from one or more of the group consisting of SO_4^{2-}, Cl^-, F^-, Br^-, I^-, PO_4^{3-}, NO_3^-, BO_3^{3-}, and SiO_3^{2-}.~~

~~4. The composition of Claim 3, wherein, when the anionic species is SO_4^{2-}:~~

~~Ti is present in an amount of from 50.9 wt% to 63.9 wt%; and/or~~

~~O is present in an amount of from 36.09 wt% to 44.5 wt%; and/or~~

~~S is present in an amount of from 0.01 wt% to 4.6 wt%.~~

2. The composition according to Claim 1, wherein the direct band gap of the TiO_2 nanocrystals is from 3.00 to 3.70 eV and/or the indirect band gap of the TiO_2 nanocrystals may be from 2.90 to 3.50 eV.

~~5~~3. The composition of ~~Claim 3~~Claim 1 or Claim 2, wherein~~, when the anionic species is SO_4^{2-},~~ the composition has FTIR peaks at approximately 3620-3850 cm^{-1}, 3159 cm^{-1}, 1400 cm^{-1}, 1215 cm^{-1}, 1148 cm^{-1}, 1051 cm^{-1} and 980 cm^{-1}.

~~6~~4. The composition according to any one of the preceding claims~~Claim 1~~, wherein:

the diameter of the agglomerates/aggregates is from 0.05 μm to 3.0 μm; and/or
the diameter of the TiO_2 nanocrystals is from 5 to 50 nm.

~~7~~5. The composition according to any one of the preceding claims~~Claim 1~~, wherein the BET surface area of the composition is from 6.0 to 9.0 ~~g/~~m^2/g, or from 20.0 to 90.0 ~~g/~~m^2/g or from 115 to 250 ~~g/~~m^2/g.

~~8. The composition according to Claim 1, wherein the majority of the anionic species is associated with the surface of the TiO_2 agglomerates/aggregates.~~

~~9~~6. The composition according to any one of the preceding claims~~Claim 8~~, wherein the ratio of the anionic species on the surface of the TiO_2 agglomerates/aggregates compared to the anionic species within the interior volume of the TiO_2 agglomerates/aggregates is from 3:1 to 8:1~~1.5:1 to 30:1~~.

7. The composition according to Claim 6, wherein the ratio of the anionic species on the surface of the TiO_2 agglomerates/aggregates compared to the anionic species within the interior volume of the TiO_2 agglomerates/aggregates is from 5:1 to 8:1.

~~10~~8. The composition according to any one of the preceding claims~~Claim 1~~, wherein 0.1 wt% of the composition reduces the dissolved organic carbon in 99.9 wt% of reverse osmosis concentrate by from 70% to 80% after 6 hours of photocatalytic reaction.

~~11~~9. A method of preparing TiO_2 nanocrystals according to any one of Claims 1 to 8, the method comprising the steps of:

(a) hydrolysing a titanium source in a water/solvent mixture to form a hydrous TiO_2 material;
(b) filtering the hydrous TiO_2 material and washing the filtered hydrous TiO_2 material with a washing solution;
(b) drying and grinding the filtered and washed hydrous TiO_2 material into a powder;
(c) calcinating the powder to form anhydrous TiO_2 nanocrystals; and
(d) optionally further grinding the anhydrous TiO_2 nanocrystals, wherein

the titanium source is titanyl sulfate;
the solvent used in the hydrolysis reaction is ethanol; and
the water/solvent ratio is from 2:1 to 4:1, or only water is used.

~~12. The method of Claim 11, wherein the titanium source is one or more of the group selected from titanyl sulfate, $TiCl_3$, $TiCl_4$, oxalotitanic acid, titanium ethoxide, titanium n-propoxide, titanium isopropoxide, and titanium n-butoxide.~~

~~13~~10. The method of Claim ~~11~~9, wherein the hydrolysis is conducted at from 25 to 190°C and/or the calcination step is conducted at a temperature of from 100°C to 1000°C using a temperature ramp of from 0.1°C to 100°C per minute for from 0.1 to 48 hours..

~~14. The method of any one of Claim 11, wherein the solvent used in the hydrolysis reaction is one or more selected from methanol, ethanol, n-propanol, isopropanol, acetone, acetylacetone, methyl ethyl ketone, methyl propyl ketone, methyl isobutyl ketone, methyl pentyl ketone, butyrolactone, methyl formate, ethyl formate, propyl formate, butyl formate, methyl acetate, oxaloacetate, ethyl acetate, propyl acetate, butyl acetate, and dibasic ester.~~

~~15~~11. The method of Claim ~~11~~9 or Claim 10, wherein ~~the water/solvent ratio is from 1:10 to 20:1 or only water is used and/or~~ the weight ratio of the titanium source to the solvent/water in the hydrolysis step is from 1:1000 to 10:1.

~~16~~12. The method of any one of Claims 9 to 11, wherein the washing solution is selected from one or more of 0.01 to 5 M ammonia (aq), methanol, ethanol, isopropanol, acetone, methyl ethyl ketone, methyl isobutyl ketone, methyl formate, ethyl formate, methyl acetate, and ethyl acetate.

~~17~~13. The method of any one of Claims 9 to 12~~1~~, wherein step (a) further comprises adding a anionic source to the titanium source and water/solvent mixture, optionally wherein the anionic source contains one or more (or is capable of producing one or more) anions selected from the group consisting of F^-, Br^-, I^-, PO_4^{3-}, NO_3^-, BO_3^{3-}, and SiO_3^{2-}.

~~18~~14. A composition made by the process of any one of Claims 9 to 13~~11~~.

~~19~~15. Use of the composition or any one of Claims 1 to 8 or Claim 1~~4~~8 as a photocatalyst.

~~20~~16. The use of Claim ~~19~~15, wherein the photocatalyst is used for:

the treatment of any one of wastewater, drinking water and ROC;

air purification; or

surface self-cleaning.