[0005] The need exists for improved methods for producing novel types of rutile titanium dioxide (TiO_2) nanoparticles which have high surface areas, e.g., in the range of from 120 m^2/g to 160 m^2/g, and high refractive indices for improved UV blocking capability and which demonstrate high performance levels in catalysis, e.g., biomass conversion, and in electronic applications, such as lithium ion batteries and fuel cells.

SUMMARY OF THE INVENTION

[0006] The described and claimed inventive concepts(s) comprise in one embodiment a method for preparing a novel form of rutile TiO_2 nanoparticles which are ordered acicular aggregates of elongated TiO_2 crystallites. The elongated TiO_2 crystallites are rod-like, e.g., slender and/or needle-like, having a thickness of from 3 nm to 5 nm and a length which can vary from 20 nm up to 50 nm, although longer and shorter lengths may also be present. However, the elongated TiO_2 crystallites assemble together during the process in a manner which results in ordered acicular aggregates that resemble nano-sized flower bouquets or triangular funnels. The largest dimension of the funnel-shaped nano-particles is about 100 nm.

[0007] The method comprises:

(a) forming an aqueous solution of a soluble titanium compound at a titanium concentration of from 0.1 to 1.5 moles per liter, although a concentration range of from 0.5 to 1.0 moles per liter is preferred, optionally in the presence of a mineral acid;

(~~c~~b) introducing a morphology controlling agent, or a mixture thereof, selected from an α-hydroxy carboxylic acid of the formula R-CH(OH)COOH, an α-hydroxy carboxamide of the formula R-CH(OH)$CONH_2$, or an α-amino acid of the formula R-CH(NH_2)COOH, wherein R is an alkane, alkene, alkyne, arene, or cycloalkane group having 6 or more carbon atoms, into the solution at an acid- or carboxamide-to-titanium molar ratio of from 0.02 to 0.2 while simultaneously heating the solution to a temperature in the range of from 60°C to 80°C with constant stirring;

(d) introducing TiO_2 seeds into the stirred solution at a seed-to-TiO_2 molar ratio of from 0.0005 to 0.0015 and maintaining the stirred solution at a temperature in the range of from 60°C to 80°C for a period of from one to 3 hours;

(de) elevating the temperature of the stirred solution to a value of from 100°C to the refluxing temperature of the stirred solution and maintaining said temperature for a period of from 2 hours to 4 hours to form a reaction product;

(ef) cooling the reaction mixture from step (e) to room or ambient temperature;

(fg) optionally neutralizing the reaction mixture; and

(gh) separating and drying the reaction product.

[0008] The reaction product can then be calcined. Calcining, which can be adjusted over a wide range for time and temperature, operates to enhance the properties of the resulting nanoparticles by expanding or opening the pore structure and/or increasing the refractive index.

[0009] Soluble titanium compounds useful according to the described method include, but are not limited to, titanium oxychloride ($TiOCl_2$), titanium oxybromide ($TiOBr_2$), titanium oxyiodide ($TiOI_2$), titanium oxynitrate ($TiO(NO_3)_2$), titanium trichloride ($TiCl_3$), titanium tribromide($TiBr_3$), titanium oxalate ($Ti_2(C_2O_4)_3$), potassium hexafluorotitanate(K_2TiF_6), ammonium hexafluorotitanate ($(NH_4)_2TiF_6$), potassium titanyloxolate ($K_2TiO(C_2O_4)_2$), ammonium titanyloxolate ($(NH_4)_2TiO(C_2O_4)_2$), titanium bis(ammonium lactate) dihydroxide ($[CH_3CH(O)COONH_4]_2Ti(OH)_2$), and mixtures thereof.

[0010] Morphology controlling agents as described above with R groups having 6 or more carbon atoms include, but are not limited to, mandelic acid ($C_6H_5CH(OH)COOH$), 4-hydroxymandelic acid ($C_6H_4(OH)CH(OH)COOH$), benzilic acid ($(C_6H_5)_2C(OH)COOH$), 2-hydroxy-4-phenylbutyric acid ($C_6H_5CH_2CH_2CH(OH)COOH$), 2-hydroxy-2-phenylpropionic acid ($(C_6H_5)(CH_3)C(OH)COOH$), 2-hydroxyoctanoic acid ($CH_3CH_2CH_2CH_2CH_2CH_2CH(OH)COOH$), mandelamide ($C_6H_5CH(OH)CONH_2$), phenylalanine ($C_6H_5CH_2CH(NH_2)COOH$), tyrosine ($C_6H_4(OH)CH_2CH(NH_2)COOH$), and combinations and mixtures thereof. In addition, ammonium (NH_4+), sodium (Na+) and potassium (K+) salts of the above-listed α-hydroxy carboxylic acids (R-CH(OH)COOH) may also be used with satisfactory results.

[0011] The described and claimed inventive concepts(s) embrace, in a second embodiment, novel rutile TiO_2 nanoparticles which are produced by the described method. The rutile TiO_2 nanoparticles, i.e., the reaction product, are ordered acicular aggregates of elongated, i.e., rod-like, TiO_2 crystallites. The individual crystallites have a thickness in the range of from 3 nm to 5 nm, and one end of each of the rod-

What is claimed is:

1. A method for preparing rutile TiO_2 nanoparticles which are aggregates of elongated TiO_2 crystallites comprising:

(a) forming an aqueous solution of a soluble titanium compound at a titanium concentration of from 0.5 to 1.0 moles per liter, optionally in the presence of a mineral acid;

(b) introducing a morphology controlling agent or a mixture thereof selected from (i) an α-hydroxy carboxylic acid of the formula R-CH(OH)COOH, (ii) an α-hydroxy carboxamide of the formula R-CH(OH)$CONH_2$ or (iii) an α-amino acid of the formula R-CH(NH_2)COOH, wherein R is an alkane, alkene, alkyne, arene, or cycloalkane group having 6 or more carbon atoms, into the solution at an acid- or carboxamide-to-titanium molar ratio of from 0.02 to 0.2 while simultaneously heating the solution to a temperature in the range of from 60°C to 80°C with constant stirring;

(cd) introducing TiO_2 seeds into the stirred solution at a seed-to-TiO_2 molar ratio of from 0.0005 to 0.0015 and maintaining the stirred solution at a temperature in the range of from 60°C to 80°C for a period of from one to 3 hours;

(de) elevating the temperature of the stirred solution to a value of from 100°C to the refluxing temperature of the stirred solution and maintaining said temperature for a period of from 2 hours to 4 hours to form a reaction product;

(ef) cooling the reaction mixture which results from step (e) to room or ambient temperature;

(fg) optionally neutralizing the reaction mixture; and

(gh) separating and drying the reaction product.

2. The method of claim 1 wherein said elongated TiO_2 crystallites have a thickness of from 3 nm to 5 nm and a length of from 20 nm to 50 nm.

3. The method of claim 2 wherein said rutile TiO_2 nanoparticles are aggregates wherein one set of ends of said elongated TiO_2 crystallites of each aggregate are joined in a cluster and the opposite ends of said crystallites fan outwardly in the general shape of a funnel having a diameter in the range of 50 nm and a height in the range of from 50 nm to 100 nm.

4. The method of claim 1 wherein said morphology controlling agent is selected from mandelic acid ($C_6H_5CH(OH)COOH$); 4-hydroxymandelic acid ($C_6H_4(OH)CH(OH)COOH$); benzilic acid ($(C_6H_5)_2C(OH)COOH$); 2-hydroxy-4-phenylbutyric acid ($C_6H_5CH_2CH_2CH(OH)COOH$); 2-hydroxy-2-phenylpropionic acid ($(C_6H_5)(CH_3)C(OH)COOH$); 2-hydroxyoctanoic acid ($CH_3CH_2CH_2CH_2CH_2CH_2CH(OH)COOH$); mandelamide ($C_6H_5CH(OH)CONH_2$); phenylalanine ($C_6H_5CH_2CH(NH_2)COOH$); tyrosine ($C_6H_4(OH)CH_2CH(NH_2)COOH$); and ammonium ($NH_4+$), sodium (Na+) and potassium (K+) salts thereof and mixtures thereof.

5. The method of claim 1 wherein said soluble titanium compound is selected from titanium oxychloride ($TiOCl_2$), titanium oxybromide ($TiOBr_2$), titanium oxyiodide ($TiOI_2$), titanium oxynitrate ($TiO(NO_3)_2$), titanium trichloride ($TiCl_3$), titanium tribromide($TiBr_3$), titanium oxalate ($Ti_2(C_2O_4)_3$), potassium hexafluorotitanate(K_2TiF_6), ammonium hexafluorotitanate ($(NH_4)_2TiF_6$), potassium titanyloxolate ($K_2TiO(C_2O_4)_2$), ammonium titanyloxolate ($(NH_4)_2TiO(C_2O_4)_2$), titanium bis(ammonium lactate) dihydroxide ($[CH_3CH(O)COONH_4]_2Ti(OH)_2$) and mixtures thereof.

6. The method of claim 4 wherein said soluble titanium compound is selected from titanium oxychloride ($TiOCl_2$), titanium oxybromide ($TiOBr_2$), titanium oxyiodide ($TiOI_2$), titanium oxynitrate ($TiO(NO_3)_2$), titanium trichloride ($TiCl_3$), titanium tribromide($TiBr_3$), titanium oxalate ($Ti_2(C_2O_4)_3$), potassium hexafluorotitanate(K_2TiF_6), ammonium hexafluorotitanate ($(NH_4)_2TiF_6$), potassium titanyloxolate ($K_2TiO(C_2O_4)_2$), ammonium titanyloxolate ($(NH_4)_2TiO(C_2O_4)_2$), titanium bis(ammonium lactate) dihydroxide ($[CH_3CH(O)COONH_4]_2Ti(OH)_2$) and mixtures thereof.

7. The method of claim 6 wherein said morphology controlling agent is mandelic acid ($C_6H_5CH(OH)COOH$), said soluble titanium compound is titanium oxychloride ($TiOCl_2$), and said TiO_2 seeds comprise a slurry containing 0.2g TiO_2 in anatase phase.

8. The method of claim ~~6~~7 wherein said morphology controlling agent is phenylalanine ($C_6H_5CH_2CH(NH_2)COOH$).

9. Rutile TiO_2 nanoparticles which are ordered acicular aggregates of elongated TiO_2 crystallites having a thickness in the range of from 3 nm to 5 nm in which one end of each of said elongated TiO_2 crystallites are joined into a cluster such that the opposite ends of each of said elongated TiO_2 crystallites extend outwardly in the shape of a nano-sized funnel structure having a diameter in the range of 50 nm and a height in the range of from 50 nm to 100 nm.

10. The rutile TiO_2 nanoparticles of claim 9 which are produced by the process of:

(a) forming an aqueous solution of a soluble titanium compound at a titanium concentration of from 0.5 to 1.0 moles per liter;

(b) introducing a morphology controlling agent or a mixture thereof selected from (i) an α-hydroxy carboxylic acid of the formula R-CH(OH)COOH, (ii) an α-hydroxy carboxamide of the formula R-CH(OH)$CONH_2$ or (iii) an α-amino acid of the formula R-CH(NH_2)COOH, wherein R is an alkane, alkene, alkyne, arene, or cycloalkane group having 6 or more carbon atoms, into the solution at an acid- or carboxamide-to-titanium molar ratio of from 0.02 to 0.2 while simultaneously heating the solution to a temperature in the range of from 60°C to 80°C with constant stirring;

(cd) introducing TiO_2 seeds into the stirred solution at a seed to TiO_2 molar ratio of from 0.0005 to 0.0015 while maintaining the solution at a temperature in the range of from 60°C to 80°C for a period of from one to 3 hours;

(de) elevating the temperature of the stirred solution to a value of from 100°C to the refluxing temperature of the stirred solution and maintaining said temperature for a period of from 2 hours to 4 hours to form a reaction product;

(ef) cooling the reaction mixture which results from step (e) to room or ambient temperature;

(fg) optionally neutralizing the reaction mixture; and

(gh) separating and drying the reaction product.

11. The rutile TiO_2 nanoparticles of claim 10 wherein:

(a) said morphology controlling agent is selected from mandelic acid ($C_6H_5CH(OH)COOH$); 4-hydroxymandelic acid ($C_6H_4(OH)CH(OH)COOH$); benzilic acid ($(C_6H_5)_2C(OH)COOH$); 2-hydroxy-4-phenylbutyric acid ($C_6H_5CH_2CH_2CH(OH)COOH$); 2-hydroxy-2-phenylpropionic acid

($(C_6H_5)(CH_3)C(OH)COOH$); 2-hydroxyoctanoic acid ($CH_3CH_2CH_2CH_2CH_2CH_2CH(OH)COOH$); mandelamide ($C_6H_5CH(OH)CONH_2$); phenylalanine ($C_6H_5CH_2CH(NH_2)COOH$); tyrosine ($C_6H_4(OH)CH_2CH(NH_2)COOH$); and ammonium ($NH_4+$), sodium (Na+) and potassium (K+) salts thereof and mixtures thereof, and

(b) said soluble titanium compound is selected from titanium oxychloride ($TiOCl_2$), titanium oxybromide ($TiOBr_2$), titanium oxyiodide ($TiOI_2$), titanium oxynitrate ($TiO(NO_3)_2$), titanium trichloride ($TiCl_3$), titanium tribromide($TiBr_3$), titanium oxalate ($Ti_2(C_2O_4)_3$), potassium hexafluorotitanate(K_2TiF_6), ammonium hexafluorotitanate ($(NH_4)_2TiF_6$), potassium titanyloxolate ($K_2TiO(C_2O_4)_2$), ammonium titanyloxolate ($(NH_4)_2TiO(C_2O_4)_2$), titanium bis(ammonium lactate) dihydroxide ($[CH_3CH(O)COONH_4]_2Ti(OH)_2$) and mixtures thereof.

12. The rutile TiO_2 nanoparticles of claim 10 wherein:

(a) said morphology controlling agent is selected from phenylalanine ($C_6H_5CH_2CH(NH_2)COOH$) and mandelic acid ($C_6H_5CH(OH)COOH$) or a mixture thereof; and

(b) said soluble titanium compound is titanium oxychloride ($TiOCl_2$).