

COATED GLASS MICROSPHERE AND METHOD OF FORMING THE SAME**CROSS-REFERENCE TO RELATED APPLICATION**

[0001] This application claims the benefit of priority of Singapore application No. 10202301522P filed May 30, 2023, the contents of it being hereby incorporated by reference in its entirety for all purposes.

TECHNICAL FIELD

[0002] Various embodiments of this disclosure may relate to a coated glass microsphere. Various embodiments of this disclosure may relate to a method of forming a coated glass microsphere.

BACKGROUND

[0003] Reflective insulation coatings, capable of reflecting more sunlight (i.e. solar reflectance) and absorbing or transferring less heat (i.e. thermal insulation), provide one of the most feasible, affordable and sustainable ways for the coated buildings to reduce the cooling burden during hot seasons, which in turn decreases the energy consumption by air conditioning systems and improves environmental sustainability. FIG. 1 is a schematic illustrating the principle of using reflective insulation coatings to cool buildings. As shown in FIG. 1, the reflective insulation coatings serve to provide (A) solar reflectance and (B) thermal insulation. The key pigments in reflective insulation coatings can be divided into two main categories: thermal insulation pigments and reflective pigments.

[0004] Hollow glass microspheres are a type of thermal insulation pigments widely used in paints and coatings. The air trapped inside the hollow cavity reduces thermal conductivity. However, hollow glass microspheres tend to absorb infrared and visible radiation, which undermines their thermal insulation properties. Titanium dioxide (TiO₂) or titania is a type of

reflective pigment and exhibits high visible and infrared reflectance. TiO_2 is then combined with hollow glass microspheres to improve the radiation properties of the latter.

[0005] Physical mixing of hollow glass microspheres and TiO_2 particles often suffers from inhomogeneity due to the large density difference between these two types of pigments. Agglomeration and sedimentation of TiO_2 particles also occur quite often during storage in many paints.

[0006] To solve the inhomogeneity problem, conventional processes involve chemical binding of TiO_2 particles to the surface of hollow glass microspheres through binders or coupling agents.

[0007] A more effective strategy is to precipitate TiO_2 onto the surface of hollow glass microspheres to fabricate core-shell structured pigments. Numerous studies show that surface modification/activation of hollow glass microspheres is essential for TiO_2 deposition. The hollow glass microspheres are etched with alkali or hydrogen fluoride (HF) for increasing the surface roughness and making the surface more hydrophilic, modified by surfactants or silane coupling agents for improving the affinity between hollow glass microspheres and TiO_2 , or treated by both methods before TiO_2 deposition. In chemical precipitation methods without surface modification/activation of hollow glass microspheres, the precipitation of TiO_2 occurs at room temperature and neutral pH conditions; catalyst of water is added at proper intervals of time for uniform TiO_2 shell deposition surrounding hollow glass microspheres rather than homogeneous precipitation in the solution.

[0008] Up to now, the combination of TiO_2 and hollow glass microspheres are limited to physical mixtures and core-shell structures. In fact, TiO_2 has a rich variety of zero, one, two, and three-dimensional architectures and exceptional electrical, optical, and chemical properties, and has been used in energy and environmental applications, for example, in photovoltaics, water splitting, photo-/electrochromics, hydrogen storage, photocatalysis and sensors.

Developing facile and easily controllable routes for the growth of other architectures of TiO_2 on the hollow glass microspheres remains challenging.

SUMMARY

[0009] Various embodiments may relate to a method of forming a coated glass microspheres. The method may include providing a titanium precursor to a glass microsphere in presence of water to form the coated glass microsphere via partial hydrolysis of the titanium precursor. The coated microsphere may include a plurality of titania rods, the plurality of titania rods being amorphous, on a surface of the glass microsphere.

[0010] Various embodiments may relate to a coated glass microsphere. The coated glass microsphere may include a glass microsphere, and a plurality of titania rods, the plurality of titania rods being amorphous, on a surface of the glass microsphere.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] In the drawings, like reference characters generally refer to the same parts throughout the different views. The drawings are not necessarily drawn to scale, emphasis instead generally being placed upon illustrating the principles of various embodiments. In the following description, various embodiments of the invention are described with reference to the following drawings.

FIG. 1 is a schematic illustrating the principle of using reflective insulation coatings to cool buildings.

FIG. 2 shows a general illustration of a method of forming a coated glass microsphere according to various embodiments.

FIG. 3 shows a general illustration of a coated glass microsphere according to various embodiments.

FIG. 4A shows the scanning electron microscopy (SEM) images of a hollow glass microsphere (HGM) (i.e., HGM_#1) at (top) a first magnification (middle) a second magnification and (bottom) at a cut interface of the hollow glass microsphere.

FIG. 4B shows the scanning electron microscopy (SEM) images of a titania rods-coated hollow glass microsphere prepared with 7.1 mmol of titanium butoxide per square meter (m^2) of a hollow glass microsphere (HGM) (HGM_#1@TiO₂_7.1) at (top) a first magnification (middle) a second magnification and (bottom) at a cut interface of the coated hollow glass microsphere according to various embodiments.

FIG. 4C shows the scanning electron microscopy (SEM) images of a titania rods-coated hollow glass microsphere prepared with 10.6 mmol of titanium butoxide per square meter (m^2) of a hollow glass microsphere (HGM) (HGM_#1@TiO₂_10.6) at (top) a first magnification (middle) a second magnification and (bottom) at a cut interface of the coated hollow glass microsphere according to various embodiments.

FIG. 4D shows the scanning electron microscopy (SEM) images of a titania rods-coated hollow glass microsphere prepared with 14.1 mmol of titanium butoxide per square meter (m^2) of a hollow glass microsphere (HGM) (HGM_#1@TiO₂_14.1) at (top) a first magnification (middle) a second magnification and (bottom) at a cut interface of the coated hollow glass microsphere according to various embodiments.

FIG. 4E shows the scanning electron microscopy (SEM) images of a core-shell titania-coated hollow glass microsphere prepared with 16.3 mmol of titanium butoxide per square meter (m^2) of a hollow glass microsphere (HGM) (HGM_#1@TiO₂_16.3) at (top) a first magnification (middle) a second magnification and (bottom) at a cut interface of the coated hollow glass microsphere.

FIG. 4F shows the scanning electron microscopy (SEM) images of a core-shell titania-coated hollow glass microsphere prepared with 17.7 mmol of titanium butoxide per square meter (m^2)

of a hollow glass microsphere (HGM) (HGM_#1@TiO₂_17.7) at (top) a first magnification (middle) a second magnification and (bottom) at a cut interface of the coated hollow glass microsphere.

FIG. 5 shows a plot of amount of titania TiO₂ (in percent or %) as a function of ratio of titanium precursors (Ti(OBu)₄) and the surface area of hollow glass microspheres (HGM) (in milli-moles per square meter or mmol/m²) illustrating the relationship between the surface accessibility of the hollow glass microspheres to titanium precursors (Ti(OBu)₄/HGM), the loading of titania TiO₂, and the morphology of titania TiO₂ in the composite structure or pigment according to various embodiments.

FIG. 6 shows (a) low magnification and (b) high magnification of scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) mapping images for silicon (Si) and titanium (Ti) elements in the rod-like titania TiO₂ -coated hollow glass microspheres (HGM_#1@TiO₂_14.1) according to various embodiments.

FIG. 7A shows a plot of reflectance (in percent or %) as a function of wavelength (in nanometer or nm) illustrating the ultraviolet (UV)-visible (VIS)-near infrared (NIR) diffuse reflectance spectra of bare hollow glass microspheres and titania TiO₂ -coated hollow glass microspheres according to various embodiments.

FIG. 7B shows a table comparing the parameters (diffuse reflectance spectra, bandgap and morphology) of bare hollow glass microspheres and titania TiO₂ -coated hollow glass microspheres according to various embodiments.

FIG. 8A shows a plot of reflectance (in percent or %) as a function of wavelength (in nanometers or nm) illustrating the diffuse reflectance spectra of bare hollow glass microspheres and titania TiO₂ -coated hollow glass microspheres according to various embodiments in the ultraviolet A/B wavelengths (280 nm – 400 nm).

FIG. 8B shows a plot of Kubelka-Munk remission function $F(R^\infty)h\nu)^{1/2}$ as a function of bandgap $h\nu$ (in electron-volts or eV) illustrating the bandgap of bare hollow glass microspheres and titania TiO_2 -coated hollow glass microspheres according to various embodiments as determined by the $F(R^\infty)h\nu)^{1/2}$ plots.

FIG. 9A shows a table illustrating the formulation and morphology of titania TiO_2 -coated hollow glass microspheres according to various embodiments fabricated from the first batch of hollow glass microspheres (HGM_#1).

FIG. 9B shows a table illustrating the formulation and morphology of titania TiO_2 -coated hollow glass microspheres according to various embodiments fabricated from the second batch of hollow glass microspheres (HGM_#2).

FIG. 9C shows a table illustrating the formulation and morphology of titania TiO_2 -coated hollow glass microspheres according to various embodiments fabricated from the third batch of hollow glass microspheres (HGM_#3).

DESCRIPTION

[0012] The following detailed description refers to the accompanying drawings that show, by way of illustration, specific details and embodiments in which the invention may be practiced. These embodiments are described in sufficient detail to enable those skilled in the art to practice the invention. Other embodiments may be utilized and structural, logical, and electrical changes may be made without departing from the scope of the invention. The various embodiments are not necessarily mutually exclusive, as some embodiments can be combined with one or more other embodiments to form new embodiments.

[0013] Features that are described in the context of an embodiment may correspondingly be applicable to the same or similar features in the other embodiments. Features that are described in the context of an embodiment may correspondingly be applicable to the other embodiments,

even if not explicitly described in these other embodiments. Furthermore, additions and/or combinations and/or alternatives as described for a feature in the context of an embodiment may correspondingly be applicable to the same or similar feature in the other embodiments.

[0014] In the context of various embodiments, the articles “a”, “an” and “the” as used with regard to a feature or element include a reference to one or more of the features or elements.

[0015] In the context of various embodiments, the term “about” or “approximately” as applied to a numeric value encompasses the exact value and a reasonable variance, e.g. within 10% of the specified value.

[0016] As used herein, the term “and/or” includes any and all combinations of one or more of the associated listed items.

[0017] By “comprising” it is meant including, but not limited to, whatever follows the word “comprising”. Thus, use of the term “comprising” indicates that the listed elements are required or mandatory, but that other elements are optional and may or may not be present.

[0018] By “consisting of” is meant including, and limited to, whatever follows the phrase “consisting of”. Thus, the phrase “consisting of” indicates that the listed elements are required or mandatory, and that no other elements may be present.

[0019] Embodiments described in the context of one of the coated glass microspheres are analogously valid for the other coated glass microspheres, embodiments described in the context of a method are analogously valid for a coated glass microsphere, and vice versa.

[0020] FIG. 2 shows a general illustration of a method of forming a coated glass microsphere according to various embodiments. The method may provide, in 202, providing a titanium precursor to a glass microsphere in presence of water to form the coated glass microsphere via partial hydrolysis of the titanium precursor. The coated glass microsphere may include a plurality of titania rods, the plurality of titania rods being amorphous, on a surface of the glass microsphere.

[0021] In other words, various embodiments may relate to forming a glass microsphere coated with a plurality of amorphous titania (i.e. titanium dioxide) rods via a partial hydrolysis process.

[0022] For avoidance of doubt, a “glass microsphere” may refer to a glass structure having a spherical or substantially spherical shape. In various embodiments, a diameter of the glass microsphere may be of a value selected from a range from 500 nm to 100 μm , e.g. from 1 μm to 40 μm . The glass microsphere may include silica or silicon dioxide (SiO_2).

[0023] In various embodiments, the glass microsphere may have a hollow core. The hollow core may include a suitable fluid such as air. In various other embodiments, the glass microsphere may have a solid core. Coated solid core glass microspheres may also be used in similar applications, such as reflective insulation pigments. However, as coated hollow core glass microspheres include air trapped in the core, coated hollow core glass microspheres may have better insulation property compared to coated solid core glass microspheres.

[0024] In various embodiments, providing the titanium precursor to the glass microsphere in presence of water may include adding the glass microsphere to ethanol to form a microsphere-ethanol suspension before the microsphere-ethanol suspension is shaken. In various embodiments, the titanium precursor may be added dropwise to the microsphere-ethanol suspension under shaking.

[0025] In various embodiments, providing the titanium precursor to the glass microsphere in presence of water may further include adding the titanium precursor to the microsphere-ethanol suspension to form a precursor-microsphere-ethanol suspension.

[0026] In various embodiments, providing the titanium precursor to the glass microsphere in presence of water may additionally include adding the water to the precursor-microsphere-ethanol suspension, after a first predetermined period of time of shaking, to form a water-precursor-microsphere-ethanol suspension. The water-precursor-microsphere-ethanol

suspension may be shaken for a second predetermined period of time. The water may be added directly to the precursor-microsphere-ethanol suspension.

[0027] In various embodiments, the first predetermined period of time may be any value selected from a range from 1.5 to 2.5 hours. In various embodiments, the second predetermined period of time may be any value selected from a range from 23 hours to 25 hours.

[0028] In various embodiments, the shaking may be carried out at a value selected from a range from 150 rpm (revolutions per minute) to 250 rpm. In other words, the shaking during the first determined period of time of shaking and the second determined period of time of shaking may be any value selected from a range from 150 rpm to 250 rpm.

[0029] In various embodiments, the titanium precursor may be or include a titanium alkoxide. In various embodiments, the titanium precursor may be any one precursor selected from a group consisting of methoxides, ethoxides, n-propoxides, iso-propoxides, n-butoxides, sec-butoxides and ter-butoxides of titanium. For instance, the titanium precursor may be titanium (IV) butoxide $\text{Ti}(\text{OBu})_4$.

[0030] In various embodiments, the method may further include filtering the water-precursor-microsphere-ethanol suspension after the water-precursor-microsphere-ethanol suspension is shaken for the second predetermined period of time. A wet powder may be collected after filtering. The method may also include drying the wet powder at a suitable temperature, such as a temperature selected from a range from 20 °C to 80 °C, e.g. room temperature.

[0031] For avoidance of doubt, a “rod” as described herein may refer to any structure in which one dimension (i.e. length) is longer than each of the remaining dimensions. The plurality of titania rods may be long-grain rice-like. In various embodiments, the plurality of rods may each have a circular or substantially circular cross-section perpendicular to the length of the rod. In various embodiments, the length of the titania rod may be any value selected from a

range from 3 times to 5 times relative to a diameter of the titania rod. As mentioned above, the plurality of titania rods may be amorphous. In other words, the titanium oxide materials included in the titania rods may lack long-range order in their atomic arrangement. Titania may be referred to by the formula TiO_2 .

[0032] In various embodiments, the plurality of titania rods may be arranged parallel to the surface of the glass microsphere. In various embodiments, the plurality of titania rods may be arranged substantially parallel to the surface of the glass microsphere, e.g., a value selected from a range from 80° to 110° from the normal of the surface of the glass microsphere. The plurality of titania rods may be arranged in tangent to the surface of the glass microsphere, or near tangent to the surface of the glass microsphere, e.g., 80° to 110° from the normal of the surface. For avoidance of doubt, in various other embodiments, the plurality of titania rods may be arranged outside the range from 80° to 110° from the normal of the surface of the glass microsphere, including but not limited to situations where the surface of the glass microsphere is not perfectly spherical. In various embodiments, the plurality of titania rods may grow in a random pattern.

[0033] The long-grain rice-like morphology may generate i) a rough and irregular surface with a large interface area between the silicate glass microsphere and titania that increases the solar reflectance at the interface; and ii) a large amount of Si-O-Ti bonds at the interface (between the hollow glass microsphere and titania) associated with an increased ultraviolet (UV) light reflectance. Various embodiments may have an ultraviolet (UV) light reflectance of more than 85%, e.g., more than 88%, e.g. close to 90%. The UV light reflectance may pertain to UV light having wavelengths from 280 nm to 400 nm. This level of UV light reflectance may not be present in crystalline titania.

[0034] As mentioned above, there may be chemical bonds between the titania rods and the hollow glass microsphere. The chemical bonds may attach the titania rods to the hollow glass microsphere.

[0035] In various embodiments, an amount of the titanium precursor relative to a surface area of the glass microsphere may be of any suitable value such that the plurality of titania rods is able to form on the surface of the glass microsphere. In various embodiments, an amount of the titanium precursor relative to a surface area of the glass microsphere may be selected from a range from 3 mmol/m² (milli-moles per square meter) to 14.5 mmol/m², e.g., from 7 mmol/m² to 14.5 mmol/m².

[0036] In various embodiments, a mole ratio of water to the titanium precursor may be such that partial hydrolysis occurs. The mole ratio of water to the titanium precursor may be less than the stoichiometric ratio (i.e., 4 : 1) required for complete hydrolysis. In various embodiments, a mole ratio of water to the titanium precursor may be selected from a range from 0.05 : 1 to 2 : 1, e.g. from 1 : 1 to 2 : 1.

[0037] According to various embodiments, the growth of the plurality of titania rods may start from the formation of Si-O-Ti bonds. In various embodiments, a seeding layer may not be required. In other words, the coated microsphere may be free of a seeding layer that is required to form crystalline TiO₂ in conventional methods. In such conventional methods, the substrate may be pre-deposited with a seeding layer, which provides an epitaxial effect on initiating the formation of crystalline titania. The anisotropic growth which is driven by crystalline titania may tend to expose its lowest-energy facets for minimizing total potential energy.

[0038] In contrast, the anisotropic growth of the titania rods according to various embodiments may be driven by the partial hydrolysis of titania with the formation of one dimensional (1D) anisotropic amorphous titania parallel or substantially parallel to the substrate surface. As mentioned above, no seeding layer may be required. Due to the Si-O-Ti bonds, there

may be a significant blueshift in the ultraviolet (UV) absorption edge generated associated with an increase in UV light reflectance of around 85% - 90% as mentioned above. Due to the parallel or substantially parallel orientation of the titania rods, a rough and irregular surface with a large interface area may be generated between the silicate glass microsphere and titania that increases the solar reflectance at the interface.

[0039] In various embodiments, the plurality of titania rods may have an average diameter selected from a range from 40 nm to 140 nm. In various embodiments, the plurality of titania rods may have an average length selected from a range from 150 nm to 650 nm.

[0040] In various embodiments, the water may be tap water, distilled water, or deionized water. In various embodiments, the partial hydrolysis may be conducted at a pH value selected from a range from 6.5 to 7.5.

[0041] In various embodiments, the partial hydrolysis may be conducted at a temperature selected from a range from 10 °C to 30 °C.

[0042] FIG. 3 shows a general illustration of a coated glass microsphere according to various embodiments. The coated glass microsphere may include a glass microsphere 302. The coated glass microsphere may include a plurality of titania rods 304, the plurality of titania rods 304 being amorphous on a surface of the glass microsphere 302.

[0043] In other words, various embodiments may relate to a glass microsphere 302 coated with amorphous titania rods 304.

[0044] For avoidance of doubt, FIG. 3 is intended to illustrate some features in accordance to various embodiments, and is not intended to limit the shape of the various features. For instance, while FIG. 3 shows a spherical glass structure 302, various embodiments may include a near spherical structure instead of a perfect spherical structure. The plurality of titania rods 304 are also illustrated in FIG. 3 as a general layer, and in various embodiments, a "rod" as described herein may refer to any elongated structure, i.e., any structure in which one dimension

(i.e. length) is longer than each of the remaining dimensions as mentioned above. FIG. 3 is also not intended to limit, for instance, the size, dimensions (e.g. thicknesses), proportions (e.g. relative thicknesses) etc. of the various features.

[0045] In various embodiments, the plurality of titania rods 304 may be arranged parallel or substantially parallel to the surface of the glass microsphere 302.

[0046] In various embodiments, a diameter of the glass microsphere 302 may be of a value selected from a range from 500 nm to 100 μm , e.g., from a range from 1 μm to 40 μm .

[0047] In various embodiments, the glass microsphere 302 may have a hollow core.

[0048] In various embodiments, the plurality of titania rods 304 may have an average diameter selected from a range from 40 nm to 140 nm. In various embodiments, the plurality of titania rods 304 may have an average length selected from a range from 150 nm to 650 nm.

[0049] Various embodiments may relate to a method of forming rod-like titania-coated hollow glass microspheres. The growth of rod-like titania structures or particles on the surface of hollow glass microsphere substrate may follow a heterogeneous nucleation process. The heterogeneous growth process may require the diffusion and attachment of hydrated titanium species in solution to the substrate surface. Therefore, the surface accessibility of hollow glass microspheres to titanium precursors and the content of water for hydrolysis may be critical parameters for controlling the deposition and morphology of TiO_2 .

[0050] FIG. 4A shows the scanning electron microscopy (SEM) images of a hollow glass microsphere (HGM) (i.e., HGM_#1) at (top) a first magnification (middle) a second magnification and (bottom) at a cut interface of the hollow glass microsphere.

[0051] FIG. 4B shows the scanning electron microscopy (SEM) images of a titania rods-coated hollow glass microsphere prepared with 7.1 mmol of titanium butoxide per square meter (m^2) of a hollow glass microsphere (HGM) (HGM_#1@ TiO_2 _7.1) at (top) a first magnification

(middle) a second magnification and (bottom) at a cut interface of the coated hollow glass microsphere according to various embodiments.

[0052] FIG. 4C shows the scanning electron microscopy (SEM) images of a titania rods-coated hollow glass microsphere prepared with 10.6 mmol of titanium butoxide per square meter (m^2) of a hollow glass microsphere (HGM) (HGM_#1@TiO₂_10.6) at (top) a first magnification (middle) a second magnification and (bottom) at a cut interface of the coated hollow glass microsphere according to various embodiments.

[0053] FIG. 4D shows the scanning electron microscopy (SEM) images of a titania rods-coated hollow glass microsphere prepared with 14.1 mmol of titanium butoxide per square meter (m^2) of a hollow glass microsphere (HGM) (HGM_#1@TiO₂_14.1) at (top) a first magnification (middle) a second magnification and (bottom) at a cut interface of the coated hollow glass microsphere according to various embodiments.

[0054] FIG. 4E shows the scanning electron microscopy (SEM) images of a core-shell titania-coated hollow glass microsphere prepared with 16.3 mmol of titanium butoxide per square meter (m^2) of a hollow glass microsphere (HGM) (HGM_#1@TiO₂_16.3) at (top) a first magnification (middle) a second magnification and (bottom) at a cut interface of the coated hollow glass microsphere.

[0055] FIG. 4F shows the scanning electron microscopy (SEM) images of a core-shell titania-coated hollow glass microsphere prepared with 17.7 mmol of titanium butoxide per square meter (m^2) of a hollow glass microsphere (HGM) (HGM_#1@TiO₂_17.7) at (top) a first magnification (middle) a second magnification and (bottom) at a cut interface of the coated hollow glass microsphere.

[0056] Hollow glass microspheres used may preferably have diameters from 500 nm to 100 μm , e.g., from 1 μm to 40 μm . In a first batch, the hollow glass microspheres may have an average size of $14 \pm 6 \mu\text{m}$, with specific surface area of $0.69 \text{ m}^2/\text{g}$ (HGM_#1), which are shown

in FIGS. 4A-F. In a second batch, the hollow glass microspheres may have an average size of $13 \pm 4 \mu\text{m}$, with specific surface area of $0.63 \text{ m}^2/\text{g}$ (HGM_#2). In a third batch, the hollow glass microspheres may have an average size of $29 \pm 17 \mu\text{m}$, with specific surface area of $0.49 \text{ m}^2/\text{g}$ (HGM_#3). No surface treatment of these hollow glass microspheres by alkali or hydrofluoric (HF) acid may be required.

[0057] In various embodiments, the titanium precursor may be or include a titanium alkoxide. In various embodiments, the titanium precursor may be selected from a group consisting of methoxides, ethoxides, n-propoxides, iso-propoxides, n-butoxides, sec-butoxides and ter-butoxides of titanium.

[0058] The ratio between the amount of titanium precursors and the surface area of hollow glass microspheres, in the unit of mmol/m^2 , may be used to reflect the surface accessibility of hollow glass microspheres to titanium precursors. Too low ratios may result in no or poor deposition of TiO_2 due to the condition of supersaturation not being met. Too high ratios may result in excessive hydrated titanium species in the local solution near the silicate surfaces, leading to a quick nucleation and nucleus coalescence at small thickness with the formation of a continuous TiO_2 shell on the silicate surface. Only at a suitable range of ratios, rod-like TiO_2 structures or particles may be formed on hollow glass microspheres. In various embodiments, the ratio of titanium n-butoxide ($\text{Ti}(\text{OBu})_4$) to HGM_#1 may be in the range of $3 \text{ mmol}/\text{m}^2$ to $14.5 \text{ mmol}/\text{m}^2$ for the rod-like TiO_2 deposition. FIG. 5 shows a plot of amount of titania TiO_2 (in percent or %) as a function of ratio of titanium precursors ($\text{Ti}(\text{OBu})_4$) and the surface area of hollow glass microspheres (HGM) (in milli-moles per square meter or mmol/m^2) illustrating the relationship between the surface accessibility of the hollow glass microspheres to titanium precursors ($\text{Ti}(\text{OBu})_4/\text{HGM}$), the loading of titania TiO_2 , and the morphology of titania TiO_2 in the composite structure or pigment according to various embodiments. $\text{TiO}_2(\text{r})$ refers to rod-like TiO_2 , while $\text{TiO}_2(\text{s})$ refers to TiO_2 shell.

[0059] As mentioned above, the ratio of titanium n-butoxide ($\text{Ti}(\text{OBu})_4$) to HGM_#1 may be in the range of 3 mmol/m² to 14.5 mmol/m² for the rod-like TiO_2 deposition. The ratio of titanium n-butoxide ($\text{Ti}(\text{OBu})_4$) to HGM_#2 may be in the range of 7 mmol/m² to 14.5 mmol/m² for the rod-like TiO_2 deposition, while the ratio of titanium n-butoxide ($\text{Ti}(\text{OBu})_4$) to HGM_#3 may be in the range of 7 mmol/m² to 14.5 mmol/m² for the rod-like TiO_2 deposition.

[0060] Both diameters and lengths of the rod-like TiO_2 structures or particles may increase with increase in the ratio of titanium precursors to hollow glass microspheres. In various embodiments, when the ratio of $\text{Ti}(\text{OBu})_4/\text{HGM}$ is 7.1 mmol/m², rod-like TiO_2 structures or particles of 40 - 50 nm in diameters and 150 - 250 nm in lengths may be deposited on the hollow glass microspheres (FIG. 4B). In various other embodiments, rod-like TiO_2 structures or particles of 50 - 80 nm in diameters and 250 - 300 nm in lengths may be deposited at the $\text{Ti}(\text{OBu})_4/\text{HGM}$ ratio of 10.6 mmol/m² (FIG. 4C). In yet various other embodiments, rod-like TiO_2 structures or particles of 130 - 140 nm in diameters and 450 - 650 nm in lengths may be deposited at the $\text{Ti}(\text{OBu})_4/\text{HGM}$ ratio of 14.1 mmol/m² (FIG. 4D). Meanwhile, the rod-like TiO_2 structures or particles may have typical aspect ratios of around 3 - 5 : 1.

[0061] When the ratio of $\text{Ti}(\text{OBu})_4/\text{HGM}$ is beyond the proper range, the formation of a continuous and uniform shell with high TiO_2 loading in the final structure may be favored. Core-shell structured TiO_2 -coated hollow glass microspheres may be formed when the ratio of $\text{Ti}(\text{OBu})_4/\text{HGM}$ is 16.3 mmol/m² and above (FIGS. 4E-F). A cut or broken sphere may provide further insight into the core-shell structure. Microcrack structures may appear with the thickening of TiO_2 shells, induced by the increased mismatch strain of thermal expansion between the TiO_2 coating and the underlying hollow glass microsphere.

[0062] In various embodiments, TiO_2 may be exclusively and uniformly deposited onto the surface of the hollow glass microspheres prior to the formation of freestanding TiO_2 structures. FIG. 6 shows (a) low magnification and (b) high magnification of scanning electron microscopy

with energy dispersive X-ray spectroscopy (SEM-EDX) mapping images for silicon (Si) and titanium (Ti) elements in the rod-like titania TiO_2 -coated hollow glass microspheres (HGM_#1@ TiO_2 _14.1) according to various embodiments.

[0063] Another important controlling factor to consider may be the molar ratio of water to titanium precursors. The catalyst of water may be selected from tap water, distilled water and deionized water. The molar ratio of water to titanium precursors may be in the range from 0.05 to 2, e.g. in the range from 1 to 2. It may be less than the required stoichiometric ratio for hydrolysis (i.e., 4), leading to incomplete hydrolysis between water and titanium precursors. The condensation reaction may occur between these partially hydrolyzed precursors favoring the formation of chain-like structures. The interchain bonding between unreacted OR^- groups may direct the anisotropic growth of structures or particles with rod-like shape. Further in-depth understanding of the nucleation and oriented growth of TiO_2 on hollow glass microspheres may greatly be desired for fully revealing the rod-like formation process.

[0064] The ultraviolet (UV)-visible (VIS)-near infrared (NIR) diffuse reflectance spectra of titania TiO_2 -coated hollow glass microspheres is illustrated by FIGS. 7A - B. FIG. 7A shows a plot of reflectance (in percent or %) as a function of wavelength (in nanometer or nm) illustrating the ultraviolet (UV)-visible (VIS)-near infrared (NIR) diffuse reflectance spectra of bare hollow glass microspheres and titania TiO_2 -coated hollow glass microspheres according to various embodiments. FIG. 7B shows a table comparing the parameters (diffuse reflectance spectra, bandgap and morphology) of bare hollow glass microspheres and titania TiO_2 -coated hollow glass microspheres according to various embodiments. A diffuse solar reflectance > 100% may mean higher reflectance than the barium sulphate (BaSO_4) reference used.

[0065] Due to a strong absorbance of TiO_2 in the UV region, the UV reflectance of hollow glass microspheres often experiences a decrease with TiO_2 coating, as what has been observed for the core-shell TiO_2 - coated hollow glass microspheres (FIG. 7B, HGM_#1@ TiO_2 _16.3 and

HGM_#1@TiO₂_17.7). The rod-like TiO₂ structures or particles surprisingly exhibit negligible alteration of reflectance in the UVA/B region of 280 – 400 (FIG. 7B, HGM_#1@TiO₂_7.1, HGM_#1@TiO₂_10.6 and HGM_#1@TiO₂_14.1). This may be ascribed to an obvious blueshift in the UV absorption edge and an increase in the optical band gap of the rod-like TiO₂ structures or particles as compared with its shell counterparts.

[0066] FIG. 8A shows a plot of reflectance (in percent or %) as a function of wavelength (in nanometers or nm) illustrating the diffuse reflectance spectra of bare hollow glass microspheres and titania TiO₂ -coated hollow glass microspheres according to various embodiments in the ultraviolet A/B wavelengths (280 nm – 400 nm). FIG. 8B shows a plot of Kubelka-Munk remission function $F(R^\infty)h\nu)^{1/2}$ as a function of bandgap $h\nu$ (in electron-volts or eV) illustrating the bandgap of bare hollow glass microspheres and titania TiO₂ -coated hollow glass microspheres according to various embodiments as determined by the $F(R^\infty)h\nu)^{1/2}$ plots.

[0067] The significant blueshift in the UV absorption edge and optical band gap may be attributed to a combination of the quantum-size effect and the interface interaction between the rod-like TiO₂ structures or particles and the silicate substrate, with the latter probably being more important. The surface hydroxyls (-OH) of hollow glass microspheres may generally act as the adsorptive/reactive sites for titanium precursors because of their hydrophilic character. Thus, the titanium atoms may bind to the silicate surface via oxygen as a bridge with the formation of Ti-O-Si bonds. The distribution capacity of these Ti-O-Si bonds may increase when the concentration of -OH on the silicate surface is high and the concentration of titanium precursors is low, which is consistent with the formation conditions for rod-like TiO₂ structures or particles. A higher distribution of Ti-O-Si bonds at the interface may strongly modify the electronic structure of the Ti atoms and increase the effective positive charge on the Ti atoms, giving rise to a significant blueshift in the UV absorption edge and increase in the optical band gap.

[0068] Moreover, due to the relatively large diameters and lengths, the rod-like TiO_2 particles would act as scattering material and reflect solar light. As shown in FIG. 7B, the reflectance in both NIR and visible regions may be increased with increasing diameters and lengths of the rod dimension, which may then decline when the morphology of TiO_2 changes from rod-like to shell structures, even though the TiO_2 content in the core-shell structured composite pigments is higher. In various embodiments, the dimensions of the rod-like TiO_2 structures or particles as a light scattering material may be of a diameter selected from a range from 130 nm to 140 nm, and of a length selected from a range from 450 nm to 650 nm (HGM_#1@ TiO_2 _14.1).

[0069] The process may take place at neutral pH and ambient temperature, therefore reducing energy costs.

[0070] The above results demonstrate that the described rod-like TiO_2 -coated hollow glass microspheres may be promising for multilevel solar reflectance and scattering with a synergy of excellent light scattering effect and suitable band gap structure of TiO_2 , and may represent a clear advancement towards efficient solar reflective materials for reflective insulation coatings with low cost.

[0071] Example

[0072] Preparation of TiO_2 -Coated Hollow Glass Microspheres

[0073] 0.6 g of hollow glass microspheres are added to 72 mL of ethanol and shaken at 200 rpm. Varying amounts of $\text{Ti}(\text{O}i\text{Bu})_4$ is added dropwise into the hollow glass microsphere suspension under shaking. After 2 hours of shaking, Varying amount of water is added to the suspension. It is shaken for another 24 hours. The suspension is filtered and the obtained wet powder is dried at room temperature. The powder is labelled as HGM_a@ TiO_2 _b, where a is #1 - #3 corresponding to different types of hollow glass microspheres, and b is the $\text{Ti}(\text{O}i\text{Bu})_4$ /HGM ratio. FIG. 9A shows a table illustrating the formulation and morphology of

titania TiO_2 -coated hollow glass microspheres according to various embodiments fabricated from the first batch of hollow glass microspheres (HGM_#1). FIG. 9B shows a table illustrating the formulation and morphology of titania TiO_2 -coated hollow glass microspheres according to various embodiments fabricated from the second batch of hollow glass microspheres (HGM_#2). FIG. 9C shows a table illustrating the formulation and morphology of titania TiO_2 -coated hollow glass microspheres according to various embodiments fabricated from the third batch of hollow glass microspheres (HGM_#3).

[0074] Test Methods

[0075] Morphology and composition of the TiO_2 -coated hollow glass microspheres are studied by a Field Emission Scanning Electron Microscopes (FE-SEM, JEOL JSM-7600) equipped with an Energy Dispersive X-Ray spectroscopy (EDX, Oxford Aztec Synergy). The TiO_2 content in the TiO_2 -coated hollow glass microspheres is studied by an Inductively Coupled Plasma Optical Emission spectroscopy (ICP-OES, PerkinElmer Avio 500). The diffuse solar reflectance is measured by a UV-VIS-NIR spectrophotometer (Shimadzu UV-3600) equipped with an integrating sphere (ISR 3100).

[0076] Various embodiments may relate to rod-like titania-coated hollow glass microspheres. Various embodiments may relate to rod-like titania-coated hollow glass microspheres having multilevel solar reflectance and scattering. Various embodiments may relate to a method of forming rod-like titania-coated hollow glass microspheres.

[0077] Various embodiments may relate to a method of uniform growth of rod-like titania particles on the surface of hollow glass microspheres through controllable surface accessibility of hollow glass microspheres to titanium precursors and controlled partial hydrolysis for oriented growth of titania structures or particles. The hollow glass microspheres may have diameters from 500 nm to 100 μm , e.g., from 1 μm to 40 μm . The ratio between the amount of titanium precursors and the surface area of hollow glass microspheres may be from 3 mmol/ m^2

to 14.5 mmol/m², e.g., from 7 mmol/m² to 14.5 mmol/m². The mole ratio of water to titanium precursors may be from 0.05 to 2, e.g., from 1 to 2. The titania structures or particles may have a rod-like morphology. The rod-like titania structures or particles may be homogeneously distributed on the surface of the hollow glass microspheres. Various embodiments may relate to a method of forming one-dimensional (1D) anisotropic amorphous titania parallel or substantially parallel to the surface of the hollow glass microsphere. The formation may neither start from an epitaxial growth of a seeding layer nor involve crystalline anisotropic growth. Instead, various embodiments may involve growth of 1D anisotropic titania starting from formation of Si-O-Ti bonds. The anisotropic growth may be driven by partial hydrolysis of precursors with the formation of 1D anisotropic amorphous titania parallel or substantially parallel to the surface of the hollow glass microspheres.

[0078] The heterostructures of rod-like titania structures/particles and hollow glass microspheres may increase the probability of multilevel reflection and scattering of light. The heterostructures may have high UV reflectance of ~ 90%. Various embodiments may have an increased bandgap of TiO₂ (> 3.70 eV). Various embodiments may offer opportunities for developing solar reflective and thermal insulation pigments that can be applied for reflective insulation coatings.

[0079] The method of forming the coated hollow glass microspheres as described herein may have the advantages of (i) conducting at neutral pH and ambient temperature (no surfactants required and no surface modification of the hollow glass microspheres needed); (ii) dimensions of the rod-like titania structures or particles being easily adjustable; (iii) uniform growth of rod-like titania structures or particles on the surface of microspheres; and/or multilevel solar reflectance and scattering arising from the rod-like titania structures.

CLAIMS

1. A method of forming a coated glass microsphere, the method comprising:
providing a titanium precursor to a glass microsphere in presence of water to form the coated glass microsphere via partial hydrolysis of the titanium precursor;
wherein the coated glass microsphere includes a plurality of titania rods, the plurality of titania rods being amorphous, on a surface of the glass microsphere.
2. The method according to claim 1,
wherein providing the titanium precursor to the glass microsphere in presence of water comprises adding the glass microsphere to ethanol to form a microsphere-ethanol suspension before the microsphere-ethanol suspension is shaken;
wherein providing the titanium precursor to the glass microsphere in presence of water further comprises adding the titanium precursor to the microsphere-ethanol suspension to form a precursor-microsphere-ethanol suspension; and
wherein providing the titanium precursor to the glass microsphere in presence of water further comprises adding the water to the precursor-microsphere-ethanol suspension, after a first predetermined period of time of shaking, to form a water-precursor-microsphere-ethanol suspension;
wherein the water- precursor-microsphere-ethanol suspension is shaken for a second predetermined period of time.
3. The method according to claim 2,
wherein the titanium precursor is added dropwise to the microsphere-ethanol suspension under shaking.
4. The method according to claim 2 or claim 3,
wherein the first predetermined period of time is any value selected from a range from 1.5 to 2.5 hours; and
wherein the second predetermined period of time is any value selected from a range from 23 hours to 25 hours.
5. The method according to any one of claims 2 to 4,
wherein the shaking is carried out at a value selected from a range from 150 rpm to 250 rpm.
6. The method according to any one of claims 2 to 5, further comprising:

filtering the water- precursor-microsphere-ethanol suspension after the water- precursor-microsphere-ethanol suspension is shaken for the second predetermined period of time.

7. The method according to any one of claims 1 to 6,
wherein the plurality of titania rods is arranged parallel to the surface of the glass microsphere.
8. The method according to any one of claims 1 to 7,
wherein the plurality of titania rods has an ultraviolet light reflectance of more than 85%.
9. The method according to any one of claims 1 to 8,
wherein a diameter of the glass microsphere is of a value selected from a range from 500 nm to 100 μm .
10. The method according to claim 9,
wherein the diameter of the glass microsphere is of a value selected from a range from 1 μm to 40 μm .
11. The method according to any one of claims 1 to 10,
wherein an amount of the titanium precursor relative to a surface area of the glass microsphere is selected from a range from 3 mmol/m² to 14.5 mmol/m².
12. The method according to claim 11,
wherein the amount of the titanium precursor relative to the surface area of the glass microsphere is selected from a range from 7 mmol/m² to 14.5 mmol/m².
13. The method according to any one of claims 1 to 12,
wherein a mole ratio of water to the titanium precursor is selected from a range from 0.05 : 1 to 2 : 1.
14. The method according to claim 13,
wherein the mole ratio of water to the titanium precursor is selected from a range from 1 : 1 to 2 : 1.
15. The method according to any one of claims 1 to 14,
wherein the glass microsphere has a hollow core.

16. The method according to any one of claims 1 to 15,
wherein the plurality of titania rods has an average diameter selected from a range
from 40 nm to 140 nm; and
wherein the plurality of titania rods has an average length selected from a range from
150 nm to 650 nm.
17. The method according to any one of claims to 16,
wherein the water is tap water, distilled water, or deionized water.
18. The method according to any one of claims 1 to 17,
wherein the partial hydrolysis is conducted at a pH value selected from a range from
6.5 to 7.5.
19. The method according to any one of claims 1 to 18,
wherein the partial hydrolysis is conducted at a temperature selected from a range
from 10 °C to 30 °C.
20. The method according to any one of claims 1 to 19,
wherein the coated glass microsphere is free of a seeding layer.
21. A coated glass microsphere comprising:
a glass microsphere; and
a plurality of titania rods, the plurality of titania rods being amorphous, on a surface of
the glass microsphere.
22. The coated glass microsphere according to claim 21,
wherein the plurality of titania rods is arranged parallel to the surface of the glass
microsphere.
23. The coated glass microsphere according to claim 21 or claim 22,
wherein a diameter of the glass microsphere is of a value selected from a range from
500 nm to 100 µm.
24. The coated glass microsphere according to claim 23,
wherein the diameter of the glass microsphere is of a value selected from a range
from 1 µm to 40 µm.

25. The coated glass microsphere according to any one of claims 21 to 24,
wherein the glass microsphere has a hollow core.
26. The coated glass microsphere according to any one of claims 21 to 25,
wherein the plurality of titania rods has an average diameter selected from a range
from 40 nm to 140 nm; and
wherein the plurality of titania rods has an average length selected from a range from
150 nm to 650 nm.