performance. Metal oxide-coatings are widely used for protective, decorative and functional purposes. Titania ($TiO_2$) is an inorganic additive that features high reflectance throughout the entire solar spectrum. Its high refractive index improves the scattering of solar radiation. Thus, the addition of $TiO_2$ to hollow glass beads enhances the reflective performance of reflective coatings.

Some methods for addition of $TiO_2$ to hollow glass beads involve physical mixing of hollow glass beads and $TiO_2$. However, such physical methods generally suffer from inhomogeneity in mixing due to the large differences in density, agglomeration of $TiO_2$ particles, and low refractive index difference at the interface between hollow glass beads and binder. Other methods involve coating of $TiO_2$ onto hollow glass beads. The direct deposition of $TiO_2$ onto the surface of hollow glass beads is difficult due to the lack of affinity between hollow glass beads and $TiO_2$. As a result, surface modification of hollow glass beads is very common for improving the dispersion of hollow glass beads in the suspension and the uniformity of $TiO_2$ deposition onto the surface of hollow glass beads. Conventional surface modification methods include modifying the surface of hollow glass beads with hydroxides (for example, sodium hydroxide, potassium hydroxide and ammonium hydroxide) for surface activation. Other surface modification methods involve using urea for the growth of quasi-spherical $TiO_2$ on the surface of hollow glass beads, or using calcium hydroxide for treating the surface of hollow glass beads to increase roughness and subsequently introducing $TiCl_4$ under acidic conditions. Still other surface modification methods involve etching hollow glass beads with alkali followed by modification of the surface with a silane coupling agent. However, these methods not only involve surface modification of hollow glass beads, but also involve heating and calcination, harsh pH conditions and the use of surfactants (e.g., sodium dodecylbenzenesulfonate) for dispersion of hollow glass beads. However, the resultant $TiO_2$ coatings suffer from low uniformity and low yield which leads to high production costs.

There is therefore a need to provide a method for forming titania-coated substrates that overcomes, or at least ameliorates, one or more of the disadvantages described above.

## Summary

In one aspect, the present disclosure refers to a method of forming a titania-coated inorganic particle comprising the steps of:

(a) agitating a mixture of inorganic particle and organic solvent;
(b) adding titania precursor dropwise into the mixture of step (a) under agitation; and
(c) adding catalyst to the mixture of step (b) two or more times at predetermined time intervals, wherein each time interval is at least 0.5 hours apart, thereby converting said titania precursor to titania which then forms a coating on said inorganic particle;
wherein steps (a) to (c) are performed at neutral pH range of about 6.0 to about 8.0 without adding any acid/base and ambient temperature.

Advantageously, the disclosed methods may provide a uniform titania-coating on the surface of an inorganic particle or substrate material.

Further advantageously, the loading of titania precursors may be easily adjusted, thereby maximizing utilization of the titania precursors.

Also advantageously, the disclosed methods may produce substrates which are uniformly coated with titania. Having a highly uniform titania-coating is beneficial as it leads to an increase in the interfacial area with refractive index difference, which increases solar light reflectance. Another advantage of having a more uniform titania coating is that the interface between the titania coating and the substrate is better utilized for increasing solar light reflectance performance, photolytic antimicrobial activity or ultraviolet(UV)-shielding ability.

Further advantageously, the disclosed methods result in high yield of titania such as above 90 %, which provides cost savings advantage.

Also advantageously, the thickness of the titania coating on the substrate may be easily tuned by adjusting the ratio of substrate material to metal oxide precursor in the surface reactions.

Further advantageously, the disclosed method may be undertaken at ambient conditions, such as at neutral pH and ambient temperature. This is a departure from some attempted methods which rely heavily on pH adjustment (either highly acidic or highly basic), or temperature adjustment (heating or cooling), surfactant utilization, precipitator utilization, preheating or post annealing treatment of the substrate materials to form $TiO_2$ from precursor. These controls and treatments usually result in more operation procedures and equipment usage. The disclosed methods advantageously do not require the use of any surfactant.

Also advantageously, the disclosed method is cost effective while allowing the ability to tune the uniformity and thickness of the titania-coating without any obvious freestanding $TiO_2$ agglomerates which advantageously increases the solar light reflectance property of the titania-coated substrates.

# Definitions

The following words and terms used herein shall have the meaning indicated:

As used herein, the term ‘titania’ is to be used interchangeably with titanium dioxide, or titanium (IV) oxide, and has the chemical formula $TiO_2$. Titania can exist in the amorphous form, or may be in crystalline form such as rutile, anatase, brookite, or mixtures thereof. Titania can exist as a mixture of amorphous or crystal forms, or a mixture of different amorphous forms, or a mixture of different crystal forms.

As used herein, the term “dropwise” refers to any method of incrementally adding one solution to another solution discontinuously and intermittently via discrete and/or separate aliquots.

The word “substantially” does not exclude “completely” e.g. a composition which is “substantially free” from Y may be completely free from Y. Where necessary, the word “substantially” may be omitted from the definition of the invention.

Unless specified otherwise, the terms "comprising" and "comprise", and grammatical variants thereof, are intended to represent "open" or "inclusive" language such that they include recited elements but also permit inclusion of additional, unrecited elements.

As used herein, the term "about", in the context of concentrations of components of the formulations, typically means +/- 5% of the stated value, more typically +/- 4% of the stated value, more typically +/- 3% of the stated value, more typically, +/- 2% of the stated value, even more typically +/- 1% of the stated value, and even more typically +/- 0.5% of the stated value.

Throughout this disclosure, certain embodiments may be disclosed in a range format. It should be understood that the description in range format is merely for convenience and brevity and should not be construed as an inflexible limitation on the scope of the disclosed ranges. Accordingly, the description of a range should be considered to have specifically disclosed all the possible sub-ranges as well as individual numerical values within that range. For example, description of a range such as from 1 to 6 should be considered to have

# Claims

1. A method of forming a titania-coated inorganic particle comprising the steps of:
(a) agitating a mixture of inorganic particle and organic solvent;
(b) adding titania precursor dropwise into the mixture of step (a) under agitation; and
(c) adding catalyst to the mixture of step (b) two or more times at predetermined time intervals, wherein each time interval is at least 0.5 hours apart,
thereby converting said titania precursor to titania which then forms a coating on said inorganic particle;
wherein steps (a) to (c) are performed at neutral pH range of about 6.0 to about 8.0 without adding any acid/base and ambient temperature.

2. The method according to claim 1, wherein in step (a), the mass ratio of inorganic particle to organic solvent is in the range of 0.02:1 to 0.1:1.

3. The method according to any one of the preceding claims, wherein in step (b), the mass ratio of titania precursor to organic solvent is in the range of 0.01:1 to 0.12:1.

4. The method according to any one of the preceding claims, wherein in step (b), said titania precursor is added dropwise to the mixture of step (a) at a rate in the range from 0.1 g/min to 5 g/min.

5. The method according to any one of the preceding claims, wherein in step (c), the mass ratio of total amount of catalyst added over predetermined time intervals to organic solvent is in the range of 0.006:1 to 0.1:1.

6. The method according to any one of the preceding claims, wherein the ratio of titania precursor to inorganic particle is in the range of about 1:1 to 7:1 (mmol/g).

7. The method according to any one of the preceding claims, wherein the molar ratio of catalyst to titania precursor is in the range of about 9:1 to about 16:1.

8. The method according to any one of the preceding claims, wherein said titania precursor is a titanium alkoxide.

9. The method according to any one of the preceding claims, wherein said inorganic particle is selected from the group consisting of hollow glass beads, silicate platelets, silica glass particles, borosilicate glass particles, aluminosilicate glass particles, and mixtures thereof.

10. The method according to any one of the preceding claims, wherein said organic solvent is selected from the group consisting of alcohols, ketones, ethers, and mixtures thereof.

11. The method according to any one of the preceding claims, wherein said catalyst is selected from the group comprising of tap water, distilled water and deionized water.

12. The method according to claim 11, further comprising the step of:
(d) annealing the particles at a temperature of 200 °C to 1000 °C for 2 hours at a heating rate of 1 °C $min^{-1}$m, thereby obtaining titania-coated particles that are coated with crystalline titania.

13. The method according to any one of the preceding claims, wherein the yield of titania is above 90%.

14. The method of any one of the preceding claims, wherein the titania-coated particle is coated with a uniform titania coating.

15. The method of any one of the preceding claims, wherein said titania-coated particle is coated with titania with a thickness in the range of 20 nm to 500 nm.