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(54) Title: MICROENCAPSULATED THERMOCHROMIC MATERIALS AND USES THEREOF

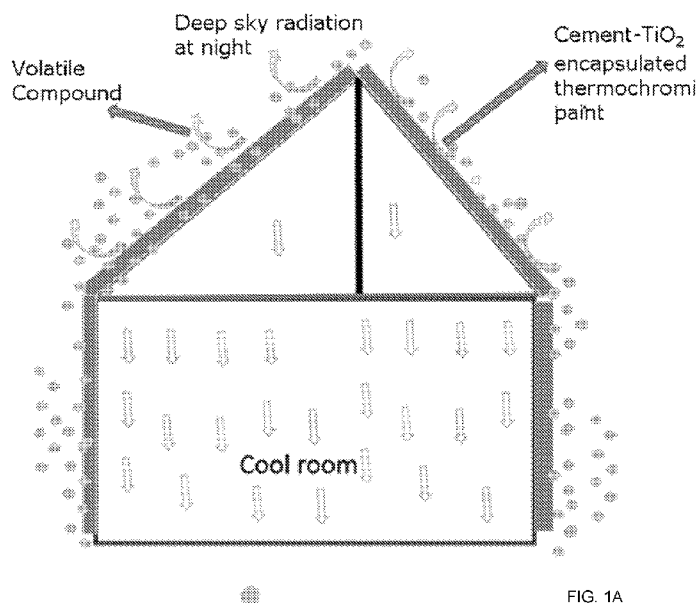
The cement-TiO₂ paint coated building in night

FIG. 1A

(57) **Abstract:** A variety of particles forming microencapsulated thermochromic materials are provided. The particles can include a thermochromic core and a metal oxide shell encapsulating the thermochromic core. The thermochromic core can include one or both of an organic thermochromic material and an inorganic salt thermochromic material. In some aspects, the particles include a dye selected from a crystal violet lactone dye, a fluoran dye, and a combination thereof. In still further aspects, the particles include a color developer selected from a hydroxybenzoate, a 4, 4'-dihydroxydiphenyl propane, a hydroxycoumarin derivative, a lauryl gallate, and a combination thereof. In some aspects, the metal oxide shell is a TiO₂ shell. The particles can be used in cements and paints and for a variety of building materials. Methods of making the particles and building materials and methods of use, for example, for removing a volatile organic carbon from a building material, are also provided.



OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

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Declarations under Rule 4.17:

- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
- *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

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MICROENCAPSULATED THERMOCHROMIC MATERIALS AND USES THEREOF

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to, and the benefit of, co-pending U.S. provisional application entitled “MICROENCAPSULATED THERMOCHROMIC MATERIALS AND USES THEREOF” having serial no. 62/500,669, filed May 3, 2017, the contents of which are incorporated by reference in their entirety.

TECHNICAL FIELD

[0002] The present disclosure generally relates to thermochromic materials and uses thereof.

BACKGROUND

[0003] Buildings use almost 40% of the world's energy and are responsible for about 70% of emitted sulphur oxides and 50% of CO₂ [1]. In the US alone, air-conditioning use has increased substantially with 87% of homes already being air-conditioned with 185 billion kilowatt hours of energy expended annually for residential cooling [2]. Many cities around the world suffer from the urban heat island (cluster of buildings) effect with an average daylight temperature greater than 3°C compared to rural areas [3-6]. There is great need to develop a technology that can be used to regulate the surface optical properties of coatings (paint) or building materials with temperature and solar radiation [7, 8]. The optical properties of a thermochromic material reversibly change as the temperature changes. The change in the color of a thermochromic material occurs due to change in doping or change in the proton-donor or electron acceptor concentrations in the thermochromic composition. The thermochromic material also changes its atomic arrangement as the temperature changes, due to the neutral or acidic conditions in the molecular environment. Thermochromic materials find applications in temperature sensors, thermometers and in improving the energy efficiency of buildings [9, 10]. Studies of microencapsulated thermochromic materials for cooling of buildings and urban structures have been previously reported in the literature [6, 7, 11-15].

SUMMARY

[0004] In various aspects, particles are provided including a thermochromic core and a metal oxide shell encapsulating the thermochromic core. The thermochromic core can include, for

example, an organic thermochromic material or an inorganic salt thermochromic material. The metal oxide shell can protect the thermochromic core and, in some aspects, can provide useful catalytic properties. As one example, a titanium oxide shell can provide for the photocatalytic decomposition of organic materials.

[0005] In some aspects, a particle is provided having a thermochromic core containing an organic thermochromic material; and a shell containing TiO_2 . The organic thermochromic material can include (i) a dye such as crystal violet lactone, a fluoran dye, or a combination thereof; (ii) a color developer such as a hydroxybenzoate, a 4, 4'-dihydroxydiphenyl propane, a hydroxycoumarin derivative, a lauryl gallate, or a combination thereof; and (iii) a solvent such as alcohol, phenol, ester, or a mixture thereof.

[0006] In some aspects, a particle is provided including a thermochromic core containing an inorganic salt thermochromic material; and a shell containing TiO_2 . The inorganic salt thermochromic material can include silver mercury iodide, cuprous mercury iodide, bis(diethylammonium) tetrachloronickelate, benzimidazolium tetrachlorocuprate, or a combination thereof.

[0007] In some aspects, the core includes an organic thermochromic material. Organic thermochromic materials can include a dye, a color developer, and a solvent. Suitable dyes can include, but are not limited to, a crystal violet lactone dye, a fluoran dye, or a combination thereof. Suitable color developers can include, but are not limited to, a hydroxybenzoate, a 4, 4'-dihydroxydiphenyl propane, a hydroxycoumarin derivative, a lauryl gallate, or a combination thereof. Suitable solvents can include, but are not limited to, alcohol, phenol, ester, or a mixture thereof.

[0008] The particles can include a variety of metal oxide shell materials. For example, suitable metal oxides can be titanium dioxide (TiO_2), zinc oxide (ZnO), silicon oxide (SiO_2), tungsten oxide (WO_3), manganese oxide (MnO_2), indium oxide (In_2O_3), aluminum oxide (Al_2O_3), iron oxide (Fe_2O_3), molybdenum oxide (MoO_2), or a combination thereof.

[0009] The particles can be made having a variety of sizes. The particles can be nanoparticles or microparticles. In some aspects, the particles are microparticles having a diameter of about 2 μm to 10 μm .

[0010] Methods of making the particles are also provided. The methods can include dispersing a thermochromic material using a surfactant to form an aqueous dispersion, and adding a metal

isopropoxide and a base to the dispersion to convert the metal isopropoxide into a corresponding metal oxide, thereby forming the particle having the thermochromic material in a core of the particle and the metal oxide in a shell encapsulating the core. Suitable surfactants can include quaternary ammonium surfactant such as cetyltrimethylammonium bromide. The dispersion can be created by forming a first solution containing the thermochromic material, surfactant, and an organic solvent such as 2-propanol; and combining the first solution with water to form the aqueous dispersion comprising the thermochromic material, surfactant, and organic solvent dispersed within the water. Converting the metal isopropoxide into the corresponding metal oxide can include reacting the metal isopropoxide and the base for a period of time from about 6 hours to 36 hours. Suitable bases can include, but are not limited to, ammonia and sodium hydroxide.

[0011] Compositions containing the particles are also provided. The compositions can include a plurality of the particles dispersed in a suitable binder. A variety of binders might be used depending upon the application. In some aspects, the binder includes a hydraulic or cementitious binder. For example, the binder can include Portland cement, high alumina cement, calcium aluminate cement, calcium sulfoaluminate cement, magnesium phosphate cement, magnesium potassium phosphate cement, activated fly ash, activated clay, or slag cement. In some aspects, the binder can include a polymeric resin. Suitable polymeric resins can include an acrylic polymer resin, an alkyd polymer resin, an epoxy polymer resin, or a combination thereof. The compositions can include one or more additives as for example, a filler, a pigment, an extender, a solvent, a dispersant, a silicone, a drying agent, a bactericide, a fungicide, an algicide, an anti-foaming agent, or a combination thereof. The particles and compositions thereof can be used to make a variety of building materials such as cement based paints, roof tiles, or cement based concrete.

[0012] Methods of using the particles and compositions are also provided. For example, a method of cleaning a building or other surface are provided. The methods can include removing volatile organic carbons from the material. By radiating a composition or particle provided herein with a light source, the metal oxide can be excited to produce a radical. The radical can react with the volatile organic carbon to oxidize the volatile organic carbon, for example, to produce H_2O , CO_2 , a combination thereof, or a combination thereof with one or more additional decomposition products. The excitation can be promoted by ultraviolet radiation, for example UV light contained in solar radiation. The ultraviolet radiation can excite the metal oxide, such as TiO_2 , to produce radical species such as $\bullet\text{OH}$, $\bullet\text{O}_2^-$, or a combination thereof.

[0013] Other systems, methods, features, and advantages of particles and methods of making and using thereof will be or become apparent to one with skills in the art upon examination of the following drawings and detailed description. It is intended that all such additional systems, methods, features, and advantages be included within this description, be within the scope of the present disclosure, and be protected by the accompanying claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] Further aspects of the present disclosure will be readily appreciated upon review of the detailed description of its various embodiments, described below, when taken in conjunction with the accompanying drawings.

[0015] FIGS. 1A-1B show a building's roof and walls coated with cement-TiO₂ paint: (FIG. 1A) night time (FIG. 1B) daytime.

[0016] FIG. 2 shows the titanium oxide encapsulant with the thermochromic material.

[0017] FIG. 3 shows cement that contains TiO₂ encapsulated thermochromic material: (left) shows the distribution of TiO₂ encapsulated thermochromic material in cement particles, and (right) shows the change of the TiO₂ encapsulated thermochromic material in cement as the temperature increases during day time.

[0018] FIG. 4 shows a schematic of the apparatus that can be used to test gas remediation by the TiO₂ encapsulated thermochromic paint coating the interior surface of a hollow cylinder.

[0019] FIG. 5 shows the FTIR spectra of: curve 1 (thermochromic material) and curve 2 (TiO₂ coated (encapsulated) thermochromic material).

[0020] FIG. 6 shows a TiO₂ encapsulated thermochromic film on glass as a function of temperature, at 550 nm wavelength of light, showing the change in the absorption magnitude.

[0021] FIG. 7 shows a TiO₂ coated thermochromic film on glass cooled at a 550 nm light wavelength showing the change (increase) in the absorption magnitude with decrease in temperature.

DETAILED DESCRIPTION

[0022] In various aspects, particles are provided including a thermochromic material in the core and a metal oxide shell encapsulating the core. Methods of making and methods of using the particles and compositions thereof are also provided.

[0023] Before the present disclosure is described in greater detail, it is to be understood that this disclosure is not limited to the particular embodiments described, and as such may, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only, and is not intended to be limiting. The skilled artisan will recognize many variants and adaptations of the embodiments described herein. These variants and adaptations are intended to be included in the teachings of this disclosure and be encompassed by the claims herein.

[0024] All publications and patents cited in this specification are cited to disclose and describe the methods and/or materials in connection with which the publications are cited. All such publications and patents are herein incorporated in the references, as if each individual publication or patent were specifically and individually indicated to be incorporated by reference. Such incorporation by reference is expressly limited to the methods and/or materials described in the cited publications and patents and does not extend to any lexicographical definitions from the cited publications and patents. Any lexicographical definition in the publications and patents cited that is not also expressly repeated in the instant specification should not be treated as such and should not be read as defining any terms appearing in the accompanying claims. The citation of any publication is for its disclosure prior to the filing date and should not be construed as an admission that the present disclosure is not entitled to antedate such publication by virtue of prior disclosure. Further, the dates of publication provided could be different from the actual publication dates that may need to be independently confirmed.

[0025] Although any methods and materials similar or equivalent to those described herein can also be used in the practice or testing of the present disclosure, the preferred methods and materials are now described. Functions or constructions well-known in the art may not be described in detail for brevity and/or clarity. Embodiments of the present disclosure will employ, unless otherwise indicated, techniques of nanotechnology, organic chemistry, material science and engineering and the like, which are within the skill of the art. Such techniques are explained fully in the literature.

[0026] It should be noted that ratios, concentrations, amounts, and other numerical data can be expressed herein in a range format. It is to be understood that such a range format is used for convenience and brevity, and thus, should be interpreted in a flexible manner to include not only the numerical values explicitly recited as the limits of the range, but also to include all the individual numerical values or sub-ranges encompassed within that range as if each numerical

value and sub-range is explicitly recited. To illustrate, a numerical range of “about 0.1% to about 5%” should be interpreted to include not only the explicitly recited values of about 0.1% to about 5%, but also include individual values (e.g., 1%, 2%, 3%, and 4%) and the sub-ranges (e.g., 0.5%, 1.1%, 2.2%, 3.3%, and 4.4%) within the indicated range. Where the stated range includes one or both of the limits, ranges excluding either or both of those included limits are also included in the disclosure, e.g. the phrase “x to y” includes the range from ‘x’ to ‘y’ as well as the range greater than ‘x’ and less than ‘y’. The range can also be expressed as an upper limit, e.g. ‘about x, y, z, or less’ and should be interpreted to include the specific ranges of ‘about x’, ‘about y’, and ‘about z’ as well as the ranges of ‘less than x’, less than y’, and ‘less than z’. Likewise, the phrase ‘about x, y, z, or greater’ should be interpreted to include the specific ranges of ‘about x’, ‘about y’, and ‘about z’ as well as the ranges of ‘greater than x’, greater than y’, and ‘greater than z’. In some embodiments, the term “about” can include traditional rounding according to significant figures of the numerical value. In addition, the phrase “about ‘x’ to ‘y’”, where ‘x’ and ‘y’ are numerical values, includes “about ‘x’ to about ‘y’”.

Definitions

[0027] Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this disclosure belongs. It will be further understood that terms, such as those defined in commonly used dictionaries, should be interpreted as having a meaning that is consistent with their meaning in the context of the specification and relevant art and should not be interpreted in an idealized or overly formal sense unless expressly defined herein.

[0028] The articles “a” and “an,” as used herein, mean one or more when applied to any feature in embodiments of the present invention described in the specification and claims. The use of “a” and “an” does not limit the meaning to a single feature unless such a limit is specifically stated. The article “the” preceding singular or plural nouns or noun phrases denotes a particular specified feature or particular specified features and may have a singular or plural connotation depending upon the context in which it is used.

Particles and Compositions Thereof

[0029] In various aspects, particles are provided including a thermochromic core and a metal oxide shell encapsulating the thermochromic core. The thermochromic core can include, for example, an organic thermochromic material or an inorganic salt thermochromic material. The metal oxide shell can protect the thermochromic core and, in some aspects, can provide useful

catalytic properties. As one example, a titanium oxide shell can provide for the photocatalytic decomposition of organic materials.

[0030] In some aspects, a particle is provided having a thermochromic core containing an organic thermochromic material; and a shell containing TiO₂. The organic thermochromic material can include (i) a dye selected such as a crystal violet lactone dye, a fluoran dye, or a combination thereof; (ii) a color developer such as a hydroxybenzoate, a 4, 4'-dihydroxydiphenyl propane, a hydroxycoumarin derivative, a lauryl gallate, or a combination thereof; and (iii) a solvent such as an alcohol, a phenol, an ester, or a mixture thereof.

[0031] In some aspects, a particle is provided including a thermochromic core containing an inorganic salt thermochromic material; and a shell containing TiO₂. The inorganic salt thermochromic material can include a silver mercury iodide, cuprous mercury iodide, bis(diethylammonium) tetrachloronickelate, benzimidazolium tetrachlorocuprate, or a combination thereof.

[0032] In some aspects, the core includes an organic thermochromic material. Organic thermochromic materials can include a dye, a color developer, and a solvent. Suitable dyes can include, but are not limited to, a crystal violet lactone dye, a fluoran dye, or a combination thereof. Suitable color developers can include, but are not limited to, a hydroxybenzoate, a 4, 4'-dihydroxydiphenyl propane, a hydroxycoumarin derivative, a lauryl gallate, or a combination thereof. Suitable solvents can include, but are not limited to, an alcohol, a phenol, an ester, or a mixture thereof.

[0033] The particles can include a variety of metal oxide shell materials. Suitable metal oxides can include, for example, TiO₂, ZnO, SiO₂, WO₃, MnO₂, In₂O₃, Al₂O₃, and a combination thereof.

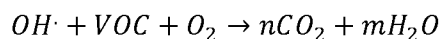
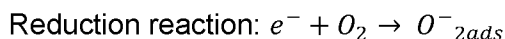
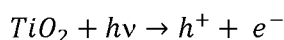
[0034] The particles can be made having a variety of sizes. The particles can be nanoparticles or microparticles. In some aspects, the particles are microparticles having a diameter of about 2 μm to 10 μm.

[0035] Compositions containing the particles are also provided. The compositions can include a plurality of the particles dispersed in a suitable binder. A variety of binders might be used depending upon the application. In some aspects, the binder includes a hydraulic or cementitious binder. For example, the binder can include Portland cement, high alumina cement, calcium aluminate cement, calcium sulfoaluminate cement, magnesium phosphate cement, magnesium potassium phosphate cement, activated fly ash, activated clay, and slag

cement. In some aspects, the binder can include a polymeric resin. Suitable polymeric resins can include acrylic polymer resin, alkyd polymer resin, epoxy polymer resin, or a combination thereof. The compositions can include one or more additives, for example a filler, a pigment, an extender, a solvent, a dispersant, a silicone, a drying agent, a bactericide, a fungicide, an algicide, an anti-foaming agent, or a combination thereof. The particles and compositions thereof can be used to make a variety of building materials such as cement based paints, roof tiles, or cement based concrete.

Encapsulation of a thermochromic material with TiO₂

[0036] In one example of particles that can obtain the desired reflective and self-cleaning properties during the daytime and night time periods, TiO₂ is used to encapsulate a thermochromic material. The thermochromic material can be used to produce surface color change and improve the surface reflective, emissive and radiative properties. Photocatalytic TiO₂ can be used to encapsulate the thermochromic material and thus: (a) protect the thermochromic materials from reacting with the environment (cement); and (b) enable the surface to destroy any organic pollutants that come in contact with the surface through the following reactions [16]:



[0037] TiO₂ does not react with cement.

Thermochromic material

[0038] There are four types of thermochromic materials such as dye based, conjugated polymer, inorganic salt and metal oxides. The thermochromic organic material incorporates electron-donating for color former, electron acceptor as color developer and a solvent. Generally, the color former is called leuco dye (example: spiroilacones, fluorans, crystal violet, thymolphthalein, spiropyran). The color developer is generally hydroxybenzoates, 4, 4'-dihydroxydiphenyl propane, and hydroxycoumarin derivatives and lauryl gallate. The solvents are generally alcohol, phenol and ester derivatives [17]. Table 1 shows various materials used to develop leuco dye based thermochromic materials. The thermochromic materials can be

synthesized using Crystal Violet Lactone, Lauryl Gallate and different solvents such as ,N - Dimethylformamide (DMF), Arachidic Acid, Propylene Carbonate , Ethylene Carbonate, Dimethyl Sulphoxide , Tetrahydrofuran, N-Methylpyrrolidine, Triton, hexadecanol, and their combination.

[0039] The inorganic salt (e.g. silver mercury iodide, cuprous mercury iodide, bis(diethylammonium) tetrachloronickelate, benzimidazolium tetrachlorocuprate) changes color, different temperatures depending upon the composition of the material. The conjugated polymers (polyacetylenes polythiophenes, (poly 2-methoxy-5-(2- ethylhexyloxy-1,4-phenylenevinylene) are common thermochromic materials but are unsuitable for building applications because of UV degradation and environment instability. The metal oxides (aluminum oxide, zinc oxide, indium oxide, chromium (III) oxide, vanadium oxides (VO_2 , V_2O_3 , V_2O_5 , V_6O_{11})) are common transition metal oxides thermochromic material due to their thermal behavior and semiconductor to metal phase transitions at different temperatures[18, 19]. With the exception of VO_2 , most of the metal oxides have been used for high temperature applications.

[0040] From the available organic thermochromic materials, examples include the crystal violet lactone and the fluoran dyes. An inorganic metal salt thermochromic material can also be used, such as benimidazolelium tertrachlorocuprate, due to its stability. In addition, VO_2 can be used as a standard to compare the thermochromic properties of organic and inorganic salt based materials.

[0041] The thermochromic properties of dye based materials is lost if it is simply mixed with cement. Therefore, microencapsulation can be important to protect the thermochromic properties of the material when mixed with cement in paint or concrete applications. The microencapsulation also helps the durability of the material. Organic based thermochromic dyes are also unstable under UV-vis radiation. The microencapsulation of leuco dyes in a polymeric matrix has been attempted in the textile industry [20, 21].

Methods of making particles and composition thereof

[0042] Methods of making the particles are also provided. The methods can include dispersing a thermochromic material using a surfactant to form an aqueous dispersion; and adding a metal isopropoxide and a base to the dispersion to convert the metal isopropoxide into a corresponding metal oxide, thereby forming the particle having the thermochromic material in a

core of the particle and the metal oxide in a shell encapsulating the core. Suitable surfactants can include quaternary ammonium surfactant such as cetyltrimethylammonium bromide. The dispersion can be created by forming a first solution containing the thermochromic material, surfactant, and an organic solvent such as 2-propanol; and combining the first solution with water to form the aqueous dispersion comprising the thermochromic material, surfactant, and organic solvent dispersed within the water. Converting the metal isopropoxide into the corresponding metal oxide can include reacting the metal isopropoxide and the base for a period of time from about 6 hours to 36 hours. Suitable bases can include, but are not limited to, ammonia and sodium hydroxide.

[0043] We have already developed a method to encapsulate phase change materials with SiO_2 . This method can be used with some variations to encapsulate thermochromic materials [22, 23]. Leuco dyes and inorganic salt based thermochromic materials can be used and encapsulated with metal oxide shells such as TiO_2 . The thermal and optical properties of thermochromic materials mixed with cement can provide thermochromic responses in the 20-50°C temperature range. **FIG. 2** shows the titanium oxide (TiO_2) encapsulant with thermochromic materials containing electron donors and electron acceptors.

Table 1: Examples of important organic thermochromic materials

Pigments	Color-developing agent	Solvent	Percentage	Ref
Crystal violet lactone	4,4'-dihydroxydiphenyl propane	Phenol Alcohol	1:5:30,	[24]
Crystal violet lactone	lauryl gallate,	Acetonitrile with acetic acid	75–95 mol% solvent,	[25]
Crystal violet lactone	Lauryl gallate	1-octadecanol	1: 6: 40.	[26]
Crystal violet lactone	Propyl gallate, octyl gallate or lauryl gallate	1-tetradecanol, 1-hexadecanol or 1-octadecanol		[27]
Crystal violet lactone, 3,3-bis-(1-n-butyl-2-methyl-3-indolyl)-phthalide	Bisphenol A, Lauryl gallate, Ethylgallate and p-Hydroxybenzoic acid	1-octanoic acid Methyl ester	Various ratios	[28]
Fluoran, Vinylphthalide, Luorene Crystal Violet lactone	Bisphenol A	Stearic acid,	1:2:50	[29]
Crystal Violet Lactone	Lauryl Gallate	Acetonitrile + Acetic acid	1:3:40	Our method
Crystal Violet Lactone	Lauryl Gallate	,N - Dimethylformamide (DMF)	1:3:40	Our method
Crystal Violet Lactone	Lauryl Gallate	Arachidic Acid	1:3:40	Our method
Crystal Violet Lactone	Lauryl Gallate	Propylene Carbonate	1:3:40	Our method

Table 1 (Continued): Examples of important organic thermochromic materials

Pigments	Color-developing agent	Solvent	Percentage	Ref
Crystal Violet Lactone	Lauryl Gallate	Ethylene Carbonate	1:3:40	Our method
Crystal Violet Lactone	Lauryl Gallate	Dimethyl Sulphoxide (commercial)	1:3:40	Our method
Crystal Violet Lactone	Lauryl Gallate	Tetrahydrofuran	1:3:40	Our method
Crystal Violet Lactone	Lauryl Gallate	N-Methylpyrrolidine	1:3:40	Our method
Crystal Violet Lactone	Lauryl Gallate	Triton	1:3:40	Our method

Synthesis and characterization of thermochromic materials

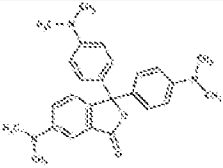
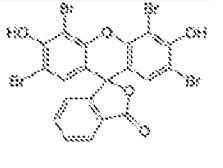
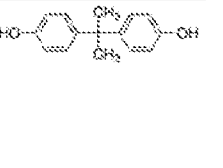
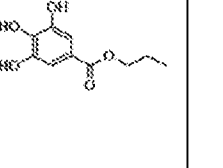
[0044] Two leuco dyes (crystal violet lactone and Fluoran) and one inorganic salt as benimidazolelium tetrachlorocuprate thermochromic materials can be synthesized as described below. The standard tungsten doped VO₂ is selected for comparison of the organic and inorganic salt based thermochromic material. Organic based thermochromic primers can be crystal violet lactone and Fluoran.

- a. **Synthesis of the dye based material.** Commercial leuco dyes (-5 °C to 60 °C with a change of temperature) are procured. The stoichiometry of a leuco dye is dependent on the acidity of developer (lauryl gallate), co-solvent acidity and compositions. The electron-donating phthalide in leuco dyes has reversible thermochromic properties and is dependent on the amount of lauryl gallate added to the dyes. So, various combinations of dye with developer and solvent

are used. The solvent as fatty acid as well as alkyl alcohol are selected for developing the organic thermochromic properties materials. Table 2 shows the chemicals and their structures used to synthesize thermochromic materials.

- b. **Synthesis of inorganic salt based thermochromic material:** Various concentrations of hydrated copper chloride mixed with benzimidazole in hydrochloric acid solution can be prepared. The reactant is concentrated and later kept to crystallize benzimidazolium tetrachlorocuprate. The yellow to orange colors can be developed by changing the concentrations of the precursor 'hydrated copper chloride', and the developer 'benzimidazole' in hydrochloric acid [30].
- c. **Synthesis of tungsten doped VO₂:** The tungsten doped VO₂ can be synthesized using the sol-gel technique. Tungsten doped VO₂ works well within a building's temperature range.

Table 2: Chemicals and their structures used to synthesize thermochromic materials

				$(C_7H_7N_2)_2CuCl_4$
Crystal violet lactone	Fluoran	Bisphenol A	Lauryl gallate	benzimidazolium tetrachlorocuprate

Encapsulation of thermochromic materials and characterization

[0045] The microencapsulation techniques used are emulsion, vacuum metallization, liquid-wall microencapsulation, hydrothermal, spray drying, interfacial coacervation [20-23].

[0046] The TiO₂ encapsulation over the dye can be synthesized through a hydrothermal process and subsequent heat treatment in air using our earlier methods with modification [22, 23]. The leuco dyes are insoluble in water so they are well dispersed with the use of the surfactant cetyltrimethylammonium bromide (CTAB). The thermochromic material can be developed by dispersing in water with the addition of CTAB, using a 2-propanol solution in a round bottom flask. The solution is stirred and then heated for one hour. Next, titanium

isopropoxide can be added dropwise to the solution, and the reaction continued for 30 minutes. The aqueous ammonia of sodium hydroxide at a concentration of 25 wt % is then added to the resulting solution and stirred for an additional 4 hours. The solution can be allowed to cool and mechanically stirred for 12 to 24 hrs. Subsequently, the precipitate is filtered, washed with alcohol, and dried at 100°C to remove any moisture; later (depending on the melting temperature of the pigment), the precipitate is dried to remove any residual 2-propanol. This process produces a TiO₂ layer over the thermochromic material. The TiO₂ coated thermochromic material can be characterized using FTIR, thermal diffusivity, SEM and X-ray diffraction measurements.

[0047] However, the experiment such as encapsulation process with titanium oxide was made on thermochromic material which contained the solvent hexadecanol. The encapsulation of TiO₂ was performed over thermochromic material.

[0048] In one aspect, a TiO₂ encapsulation is accomplished via heating with magnetic stirring, followed by the addition of 50ml of HCl 0.1M and 25ml methanol. About 100 mg of CTAB surfactant is added, followed by the thermochromic material (TC) (1 : 3 : 40). The solution is stirred and then heated. Next, TiCl₄ 1ml is added and the reaction continued. 2M NaOH 1 ml is then added to the resulting solution with stirring.

[0049] In a second aspect, a TiO₂ encapsulation is accomplished via heating at 60°C with magnetic stirring followed by the addition of 50ml of HCl 0.1M and 25ml methanol. About 50 mg of CTAB surfactant is added and stirred for 30 minutes. Next 2M NaOH 1ml is added as well as TiCl₄ 1ml, and the reaction continued for 30 minutes. After 30 min Ti isopropoxide was added as well. After another 30 minutes, the thermochromic material (TC) (1 : 3 : 40) was added.

[0050] In a third aspect, a TiO₂ encapsulation is accomplished via heating at 60-70°C with magnetic stirring followed by the addition of 50ml of HCl 0.1M and 25ml methanol. About 50 mg of CTAB surfactant is added along with 0.5M NaOH 1ml and TiCl₄ 1ml. After 30 min Ti isopropoxide was added as well. After another 30 minutes, the thermochromic material (TC) (1 : 3 : 40) was added. TC was mixed with polyethylene oxide to see if it would be protected from the encapsulation reaction

[0051] In a fourth aspect, a TiO₂ encapsulation is accomplished via heating at 60-70°C with magnetic stirring followed by the addition of 50ml of HCl 0.1M and 25ml methanol. About 50 mg of CTAB surfactant is added, followed by the thermochromic material (TC) (1 : 6 : 40). The TC was mixed with polyethylene oxide to see if it would be protected from the encapsulation

reaction. TiCl_4 1ml was then added, followed by 0.5M NaOH 1ml and the reaction was allowed to continue. After 30 min Ti isopropoxide was added as well.

[0052] In a fifth aspect, a TiO_2 encapsulation is accomplished via a method similar to the first aspects but halving the volume of solution, including heating at 45-55°C with magnetic stirring. followed by the addition of 25ml of HCl 0.1M and 12.5ml methanol. About 50 mg of CTAB surfactant is added, followed by the thermochromic material (TC) (1 : 3 : 40) about 10 g. The solution is stirred and then heated. Next, TiCl_4 0.5ml is added and the reaction continued. 2M NaOH 2.5 ml is then added to the resulting solution with stirring.

[0053] In a sixth aspect, a TiO_2 encapsulation is accomplished via heating 25 ml of HCl 0.1M + 12.5ml methanol to 50°C. The liquid thermochromic material (TC) (1 : 3 : 40) is then added; around 8ml with stirring. The surfactant 115 mg poly(styrene sulfonate) (PSS) is then added, followed by TiCl_4 0.5ml and 2M NaOH 2ml. The beaker was then left and the reaction allowed to continue without heating for 3 hours and then put into condenser at 60°C for 30 min.

[0054] In a seventh aspect, TiO_2 encapsulation is accomplished by combining 25ml of HCl 0.1M + 12.5ml methanol, and then adding the thermochromic material (TC) (1 : 3 : 40); around 5ml. The surfactant 50mg poly(styrene sulfonate) (PSS) is then added, followed by TiCl_4 0.5ml and 2M NaOH 2ml. The reaction is allowed to continue in a condenser for 20 min at 70°C.

[0055] In an eighth aspect, TiO_2 encapsulation is accomplished by combining 5 ml of HCl 0.1M + 12.5ml methanol with heating at 30°C. The liquid thermochromic material (TC) (1 : 3 : 40) is then added. The surfactant 115 mg poly(styrene sulfonate) (PSS) is then added, followed by TiCl_4 0.5ml and 2M NaOH 2ml. The reaction was allowed to continue in a condenser at 60°C for 70 min and the dried and filtered.

[0056] In a ninth aspect, TiO_2 encapsulation is accomplished by combining 5 ml of HCl 0.1M + 12.5ml methanol with heating at 30°C. The material produces from the eighth aspects is then added along with an additional 115 mg PSS surfactant followed by TiCl_4 0.5ml and 2M NaOH 2ml. This reaction was put into a condenser at 80°C for 30 min. The product as put into a beaker to cool and then filtered.

[0057] In a tenth aspect, TiO_2 encapsulation is accomplished by combining 5 ml of HCl 0.1M + 12.5ml methanol followed by 115 mg PSS surfactant. TiCl_4 1ml and 2M NaOH 3ml are added along with the liquid thermochromic material (TC) (1 : 3 : 40); around 10ml. The reaction was

allowed to continue in a condenser at 80 - 90°C for 70 min, poured into a beaker, and then filtered.

[0058] In an eleventh aspect, TiO₂ encapsulation is accomplished by combining 5 ml of HCl 0.1M + 12.5ml methanol followed by 115 mg PSS surfactant. The TiCl₄ 0.25ml and 2M NaOH 1ml is then added along with the product from the sixth aspect above. The reaction was then allowed to continue in a condenser at 80 - 90°C for 70 min, poured into a beaker, and then filtered.

Optimization of composition of cement and thermochromic material, coating and characterization

[0059] The thermochromic cement can be prepared by dispersing the encapsulated thermochromic material in cement. The cement containing thermochromic material can be coated over glass, slate and pebble. The amount of the material can be varied from 1% to 20% of the total weight of the cement. The compositions can include the surfactant and plasticizer flattening agents. The nickel and zinc based stabilizers, such as [3-(2-benzotriazolyl)-2-hydroxy-1-naphthoate], (2,4-dihydroxybenzophenone-3-carboxylates), [5-(2-benzotriazolyl)-2,4-dihydroxybenzoates], can be used as a stabilizer against the UV-light for the leuco dye based thermochromic material [31, 32]. The coating can be made by a number of techniques, such as roller, brush coating, etc. Color change temperatures from 20°C to 50°C can be prepared using suitable leuco dye based thermochromic pigments.

Methods of using particles and compositions thereof

[0060] Methods of using the particles and compositions are also provided. For example, a method of cleaning a building or other surface are provided. The methods can include removing volatile organic carbons from the material. By radiating a composition or particle provided herein with a light source, the metal oxide can be excited to produce a radical. The radical can react with the volatile organic carbon to oxidize the volatile organic carbon, for example to produce H₂O, CO₂, a combination thereof, or a combination thereof with one or more additional decomposition products. The excitation can be achieved by ultraviolet radiation, as for example UV light contained in solar radiation. The ultraviolet radiation excites electrons in a metal oxide, such as TiO₂, and react with water molecules in the air to produce radical species such as •OH, •O₂⁻, or a combination thereof.

Thermal and reflective properties of a thermochromic coatings

[0061] Reflection measurements can follow the Byk model Dospermat N1 disperser with cowls disk test with a paint coating of $\sim 75 \mu\text{m}$ on various surfaces [33]. The UV-vis spectrophotometer can be used to measure the reflectance of various samples. The experimental setup for temperature measurements used IR lamps irradiating the coated plates. The temperature measured using a temperature sensor can indicate the thermal and reflective properties of the coated surface. The temperature of the surface exposed to a thermal environment (a thermal lamp) can be measured by a temperature sensor as a function of time. The increase in the coated surface temperature can affect the reflectivity and thermal insulation of the coated surface. In addition, IR imaging can be performed to determine the temperature profile at various temperatures. Spectral reflectance measurement at different sample temperatures are made to understand any changes in coatings of the same color [7].

Self-cleaning tests of cement – thermochromic coating

[0062] The test chamber can be designed using a set up similar to that proposed by Mo et al [16]. The inner surface of the cylinder can be coated with the cement – thermochromic coating material. The airflow with known toluene or other gases can be used as inlet gas, and remediated air is tested as a function of time using gas chromatography. **FIG. 4** shows a schematic of the setup that can be used for gas remediation by the cylinder interiorsurface coating.

EXAMPLES

[0063] Now having described the embodiments of the present disclosure, in general, the following examples describe some additional embodiments. While embodiments of the present disclosure are described in the following examples and corresponding text and figures, there is no intent to limit the embodiments of the present disclosure to this descriptions. On the contrary, the intent is to cover all alternatives, modifications, and equivalents included within the spirit and scope of embodiments of the present disclosure.

Example 1: Thermochromic experimental results

Experimental Results

[0064] The microencapsulated (e.g. TiO_2 coated) thermochromic material has been characterized using FTIR, UV-vis and thermal heating tests.

[0065] The thermochromic and TiO₂ coated (encapsulated) thermochromic materials are used to measure the Fourier transform infrared spectrometer (FTIR) spectra. **FIG. 5** (curve 1) shows the FTIR characteristics peaks of the thermochromic material at 3893, 3322, 3228, 2921, 2850, 2640, 2484, 2421, 2327, 2031, 1894, 1445, 1689, 1689, 1641, 1465, 1310, 1244, 1105, 1055, 874, 813, 614, 544 and 477 cm⁻¹. **FIG. 5** (curve 2) shows the FTIR spectra of TiO₂ coated thermochromic material. Figure 1 (curve 1) shows infrared bands at 3893, 3322, 3228, 2921, 2850, 2640, 2484, 2421, 2327, 2031, 1894, 1745, 1689, 1689, 1641, 1465, 1404, 1310, 1244, 1105, 1055, 874, 803, 685, 544 and 477 cm⁻¹. The band at 3476 cm⁻¹ is due to hydroxyl group which is linked to Ti⁴⁺-OH vacancies. The bands at 803 and 685 are due to Ti-O and Ti-O-Ti indicating the presence of the TiO₂ encapsulating the thermochromic material.

[0066] **FIG. 6** shows the change in the absorption curve at 550 nm of the TiO₂ microencapsulated thermochromic film on glass as a function of temperature. The absorption magnitude changes from ~0.6 to ~0.3 at a temperature of ~50°C. However, we have observed that the change in absorption at 550 nm can vary from 30 - 50°C in various other encapsulated thermochromic materials.

[0067] **FIG. 7** shows the change in the absorption magnitude at 550 nm as the temperature of the encapsulated thermochromic film is cooled to room temperature. There is an increase in the absorption magnitude as the temperature decreases from ~50°C to room temperature.

[0068] The TiO₂ encapsulated thermochromic material was applied to a filter paper and heated from room temperature to 50°C. The color of the TiO₂ coated thermochromic material on filter paper changed from dark blue green to light yellow when heated from room temperature to 50°C. The color change was observed to be completely reversible.

TiO₂ encapsulated thermochromic material

[0069] The thermochromic behavior and the stability of the TiO₂ coated thermochromic material is dependent on the thickness of the encapsulating layer. The thickness of the encapsulating material can be increased by applying 2 or 3 layers (multiple TiO₂ encapsulating layers).

Metal oxide encapsulants of thermochromic materials

[0070] In addition to TiO₂, a number of metal oxides such as zinc oxide (ZnO), silicon oxide (SiO₂), tungsten oxide (WO₃), manganese oxide (MnO₂), indium oxide (In₂O₃), aluminum oxide (Al₂O₃), or combinations of metal oxides can be used for encapsulating thermochromic materials using our method.

[0071] It should be emphasized that the above-described embodiments of the present disclosure are merely possible examples of implementations, and are set forth only for a clear understanding of the principles of the disclosure. Many variations and modifications may be made to the above-described embodiments of the disclosure without departing substantially from the spirit and principles of the disclosure. All such modifications and variations are intended to be included herein within the scope of this disclosure.

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We claim:

1. A particle comprising:

a thermochromic core comprising one or both of an organic thermochromic material and an inorganic salt thermochromic material; and

a metal oxide shell encapsulating the thermochromic core.

2. The particle according to claim 1, wherein the thermochromic core comprises an organic thermochromic material;

wherein the organic thermochromic material comprises

(i) a dye selected from the group consisting of a crystal violet lactone dye, a fluoran dye, and a combination thereof;

(ii) a color developer selected from the group consisting of a hydroxybenzoate, a 4, 4'-dihydroxydiphenyl propane, a hydroxycoumarin derivative, a lauryl gallate, and a combination thereof; and

(iii) a solvent selected from the group consisting of an alcohol, a phenol, an ester, and a mixture thereof; and

wherein the metal oxide shell comprises TiO_2 .

3. The particle according to claim 1, wherein the thermochromic core comprises an organic thermochromic material.

4. The particle according to claim 3, wherein the organic thermochromic material comprises a dye, a color developer, and a solvent.

5. The particle according to claim 4, wherein the dye is selected from the group consisting of a crystal violet lactone dye, a fluoran dye, and a combination thereof.

6. The particle according to claim 4, wherein the color developer is selected from the group consisting of a hydroxybenzoate, a 4, 4'-dihydroxydiphenyl propane, a hydroxycoumarin derivative, a lauryl gallate, and a combination thereof.

7. The particle according to claim 4, wherein the solvent is selected from the group consisting of an alcohol, a phenol, an ester, and a mixture thereof.

8. The particle according to claim 1, wherein the thermochromic core comprises an inorganic salt thermochromic material;

wherein the inorganic salt thermochromic material is selected from the group consisting of silver mercury iodide, cuprous mercury iodide, bis(diethylammonium) tetrachloronickelate, benzimidazolium tetrachlorocuprate, and a combination thereof; and

wherein the metal oxide shell comprises TiO_2 .

9. The particle according to claim 1, wherein the thermochromic core comprises an inorganic salt thermochromic material.

10. The particle according to claim 9, wherein the inorganic salt thermochromic material is selected from the group consisting of silver mercury iodide, cuprous mercury iodide, bis(diethylammonium) tetrachloronickelate, benzimidazolium tetrachlorocuprate, and a combination thereof.

11. The particle according to any one of claims 1, 3-7, and 9-10, wherein the metal oxide shell comprises a metal oxide selected from the group consisting of titanium dioxide (TiO_2), zinc oxide (ZnO), silicon oxide (SiO_2), tungsten oxide (WO_3), manganese oxide (MnO_2), indium oxide (In_2O_3), aluminum oxide (Al_2O_3), iron oxide (Fe_2O_3), molybdenum oxide (MoO_2), and a combination thereof.

12. The particle according to any one of claims 1, 3-7, and 9-10, wherein the metal oxide shell comprises TiO_2 .
13. The particle according to claim 1, wherein the particle has a radius of about 2 μm to 10 μm .
14. A composition comprising a plurality of particles according to any one of claims 1-13 dispersed in a suitable binder.
15. The composition according to claim 14, wherein the composition is a cement paint, and wherein the binder is a Portland cement.
16. The composition according to claim 14, wherein the binder is a hydraulic or cementitious binder.
17. The composition according to claim 16, wherein the binder is selected from the group consisting of a Portland cement, a high alumina cement, a calcium aluminate cement, a calciumsulfoaluminate cement, a magnesium phosphate cement, a magnesium potassium phosphate cement, an activated fly ash, an activated clay, and a slag cement.
18. The composition according to claim 14, wherein the binder is a polymeric resin.
19. The composition according to claim 18, wherein the binder is selected from the group consisting of an acrylic polymer resin, an alkyd polymer resin, an epoxy polymer resin, and a combination thereof.
20. The composition according to any one of claims 14-19, further comprising one or more additives selected from the group consisting of a filler, a pigment, an extender, a solvent, a

dispersant, a silicone, a drying agent, a bactericide, a fungicide, a algacide, an anti-foaming agent, and a combination thereof.

21. The composition according to any one of claims 14-19, wherein the binder is present at a concentration of about 25 wt% to 75 wt % based upon a total weight of the composition.

22. The composition according to any one of claims 14-19, wherein the plurality of particles are present at a concentration of about 15 wt % to about 30 wt % based upon a total weight of the composition.

23. A method of making a particle according to any one of claims 1-13, wherein the method comprises

dispersing a thermochromic material using a surfactant to form an aqueous dispersion;

adding a metal isopropoxide and a base to the dispersion to convert the metal isopropoxide into a corresponding metal oxide, thereby forming the particle having the thermochromic material in a core of the particle and the metal oxide in a shell encapsulating the core.

24. The method according to claim 23, wherein the surfactant comprises a quaternary ammonium surfactant.

25. The method according to claim 23, wherein the surfactant comprises cetyltrimethylammonium bromide.

26. The method according to any one of claims 23-25, wherein the dispersing step comprises forming a first solution containing the thermochromic material, surfactant, and an organic solvent such as 2-propanol; and

combining the first solution with water to form the aqueous dispersion comprising the thermochromic material, surfactant, and organic solvent dispersed within the water.

27. The method according to any one of claims 23-25, wherein the converting the metal isopropoxide into the corresponding metal oxide comprises reacting the metal isopropoxide and the base for a period of time from about 6 hours to 36 hours.

28. The method according to claim 27, wherein the base is selected from ammonia, sodium hydroxide, or a combination thereof.

29. The method according to any one of claims 23-25, wherein the metal isopropoxide is selected from the group consisting of titanium isopropoxide, a zinc isopropoxide, a silicon isopropoxide, a tungsten isopropoxide, a manganese isopropoxide, an indium isopropoxide, an aluminum isopropoxide, and a combination thereof.

30. The method according to any one of claims 23-25, wherein the corresponding metal oxide is selected from the group consisting of TiO_2 , ZnO , SiO_2 , WO_3 , MnO_2 , In_2O_3 , Al_2O_3 , and a combination thereof.

31. A building material comprising a plurality of particles according to any one of claims 1-13 or a composition according to any one of claims 14-22.

32. The building material according to claim 31, wherein the building material is a cement based paint, a roof tile, or a cement based concrete.

33. A method of removing a volatile organic carbon from a building material according to claim 31 or claim 32, the method comprising:

radiating the composition with a light source to excite the metal oxide to produce a radical, and

reaction of the radical with the volatile organic carbon to oxidize the volatile organic carbon.

34. The method according to claim 33, wherein the light source comprises ultraviolet radiation.
35. The method according to claim 33, wherein the light source comprises solar radiation.
36. The method according to claim 33, wherein the radical comprises $\bullet\text{OH}$, $\bullet\text{O}_2^-$, or a combination thereof.
37. The method according to any one of claims 33-36, wherein the volatile organic carbon is oxidized to produce H_2O , CO_2 , a combination thereof, or a combination thereof with one or more additional decomposition products.

The cement-TiO₂ paint coated building in night

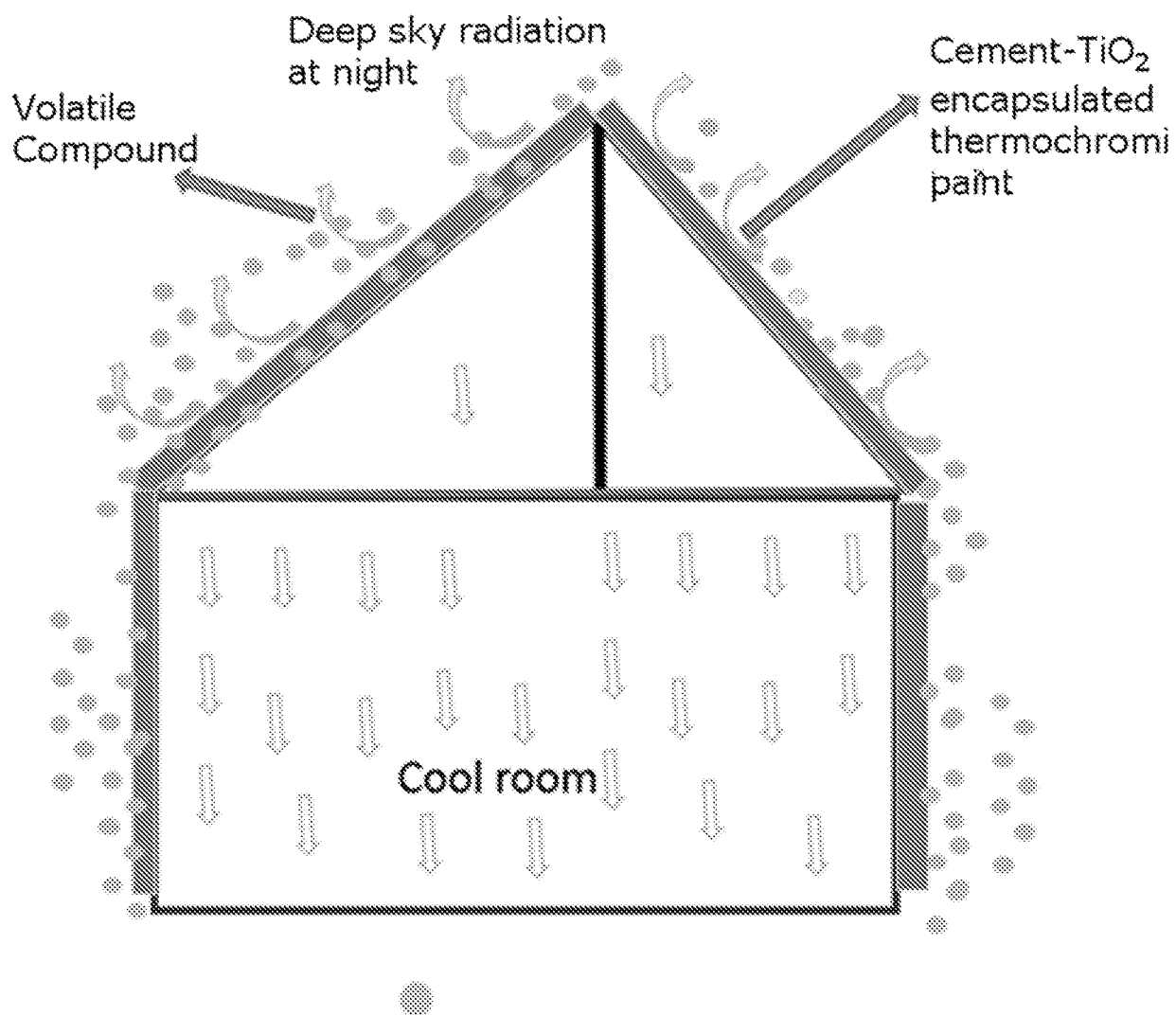


FIG. 1A

The cement-TiO₂ paint coated building in day

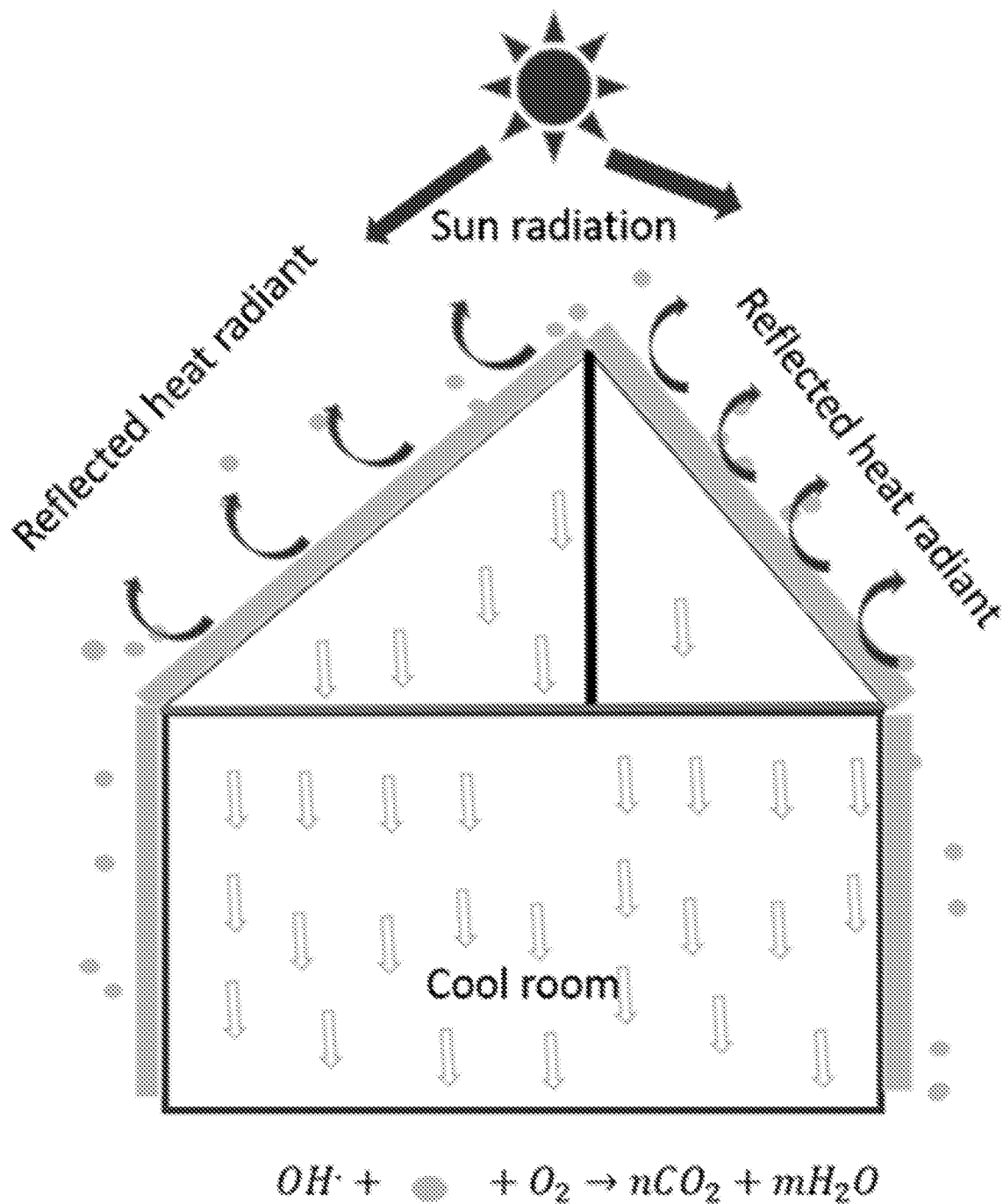


FIG. 1B

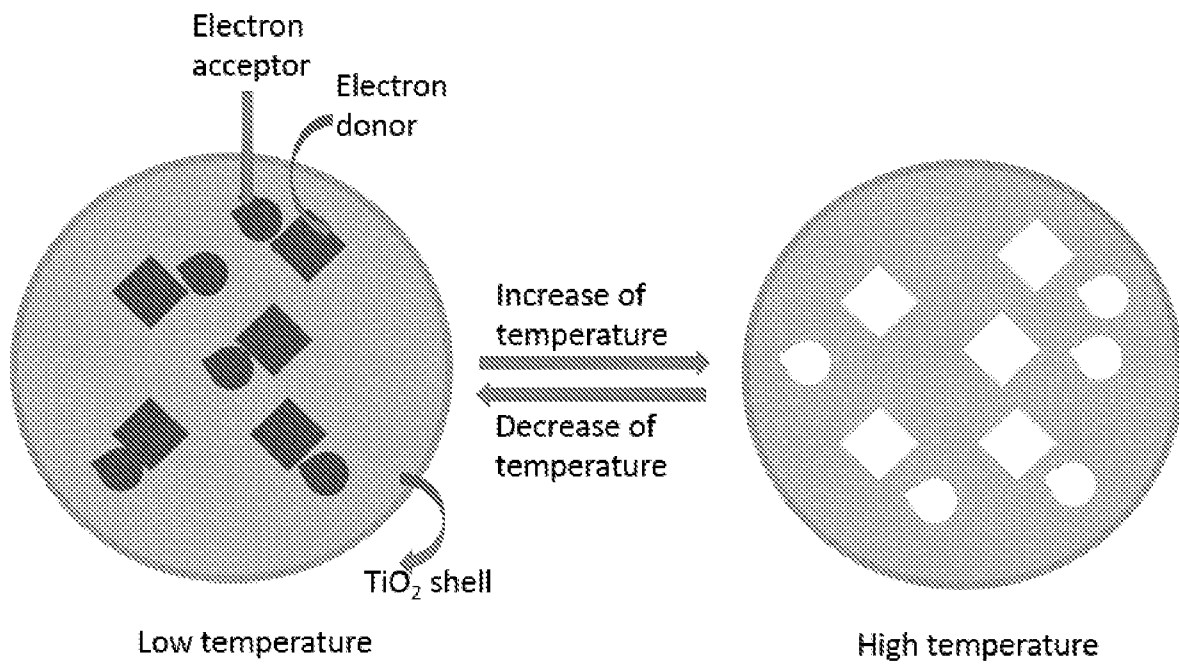


FIG. 2

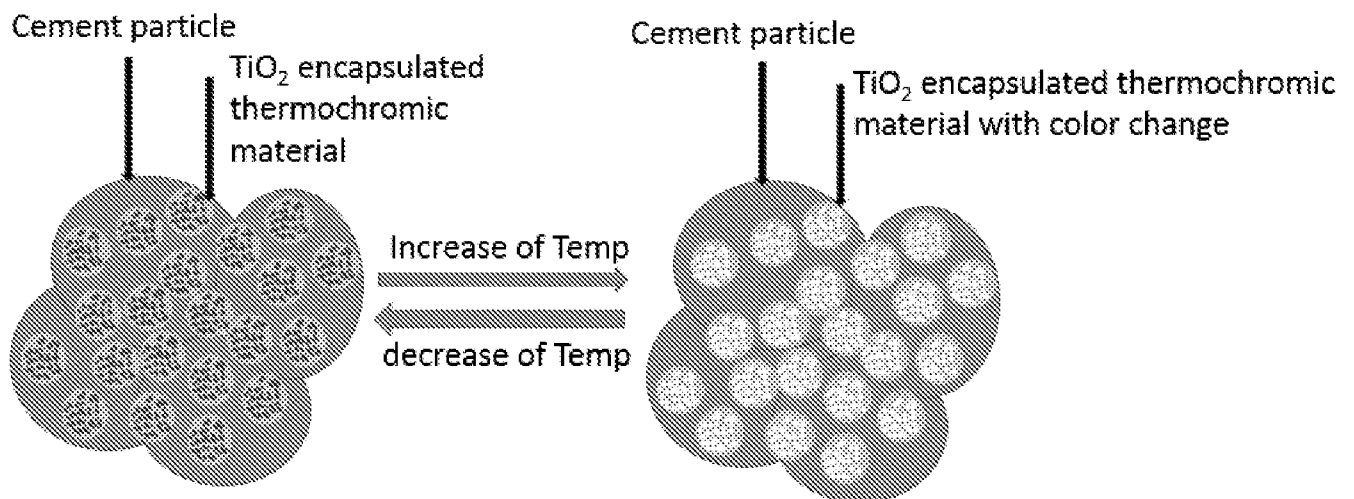


FIG. 3

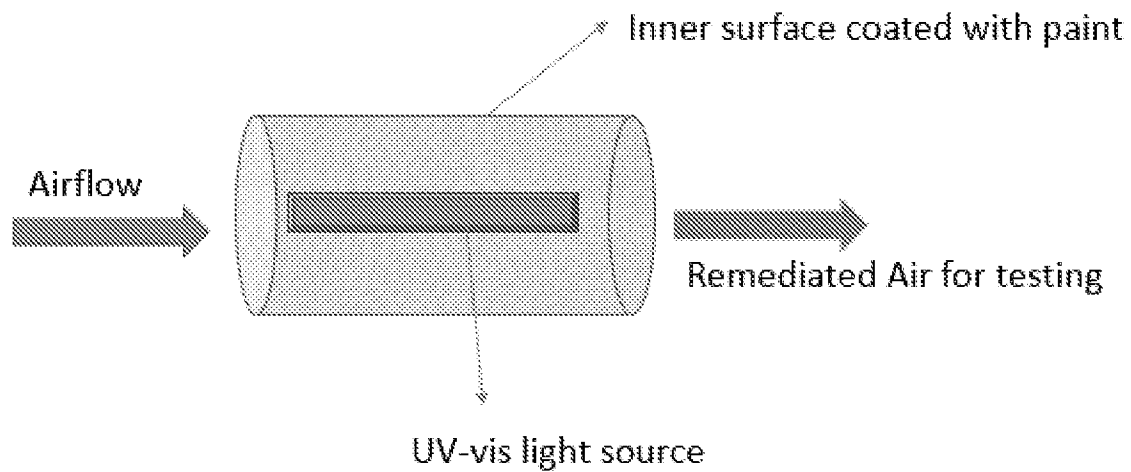


FIG. 4

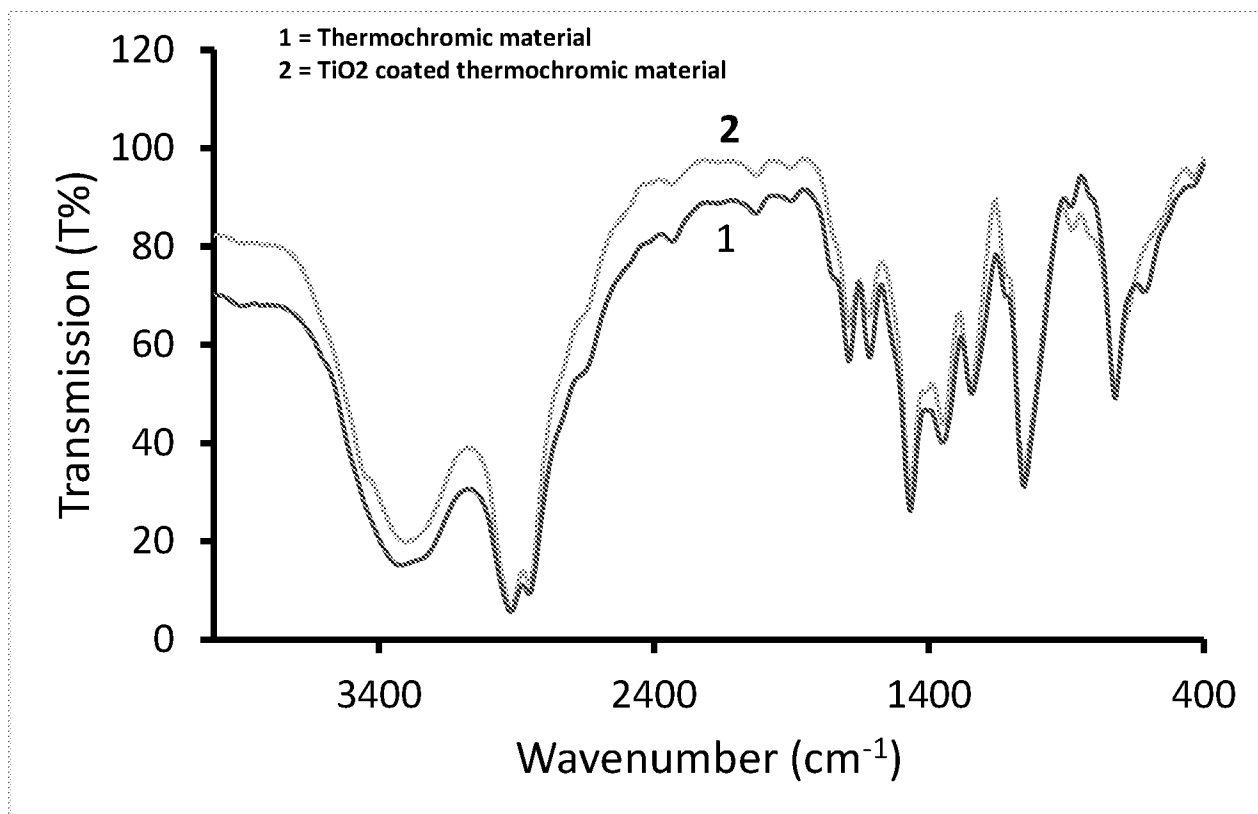


FIG. 5

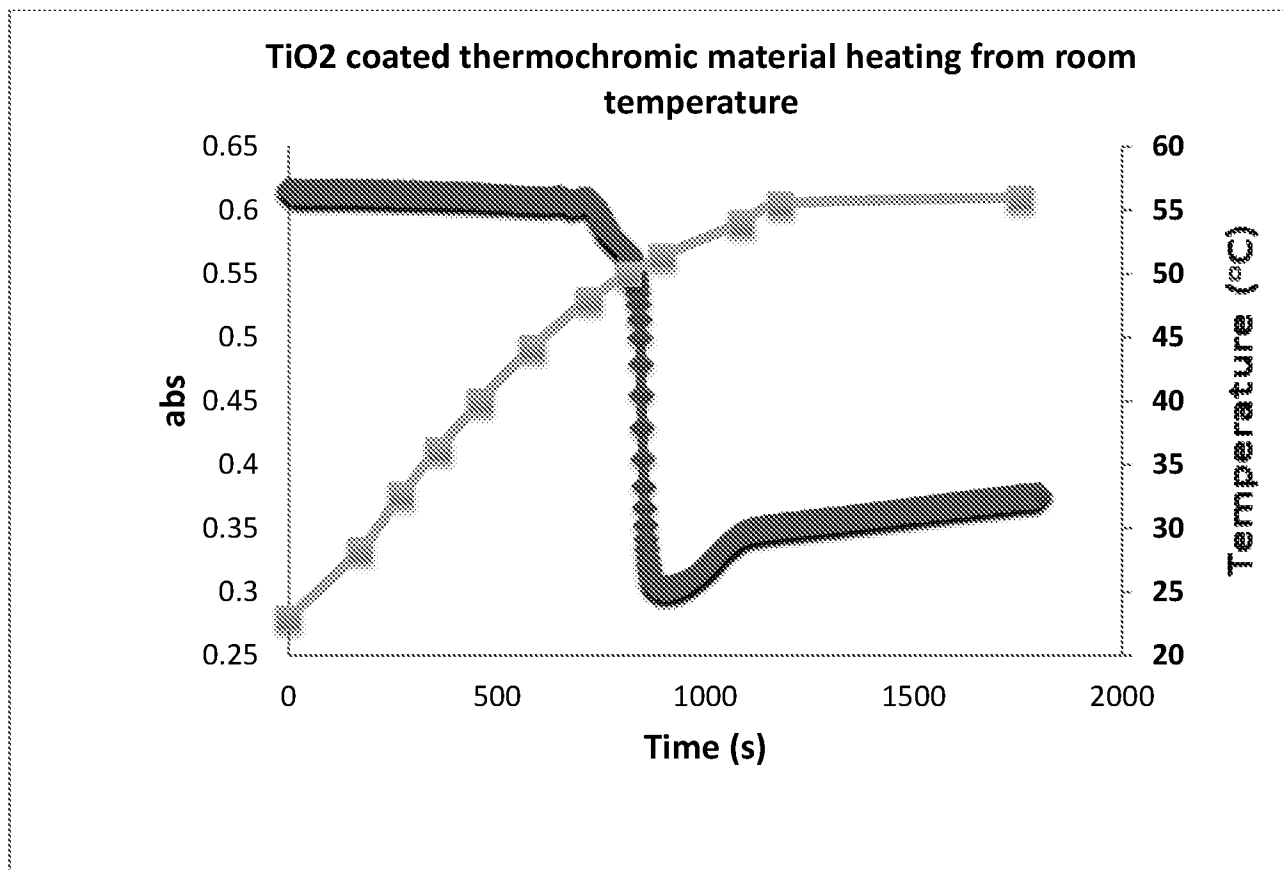


FIG. 6

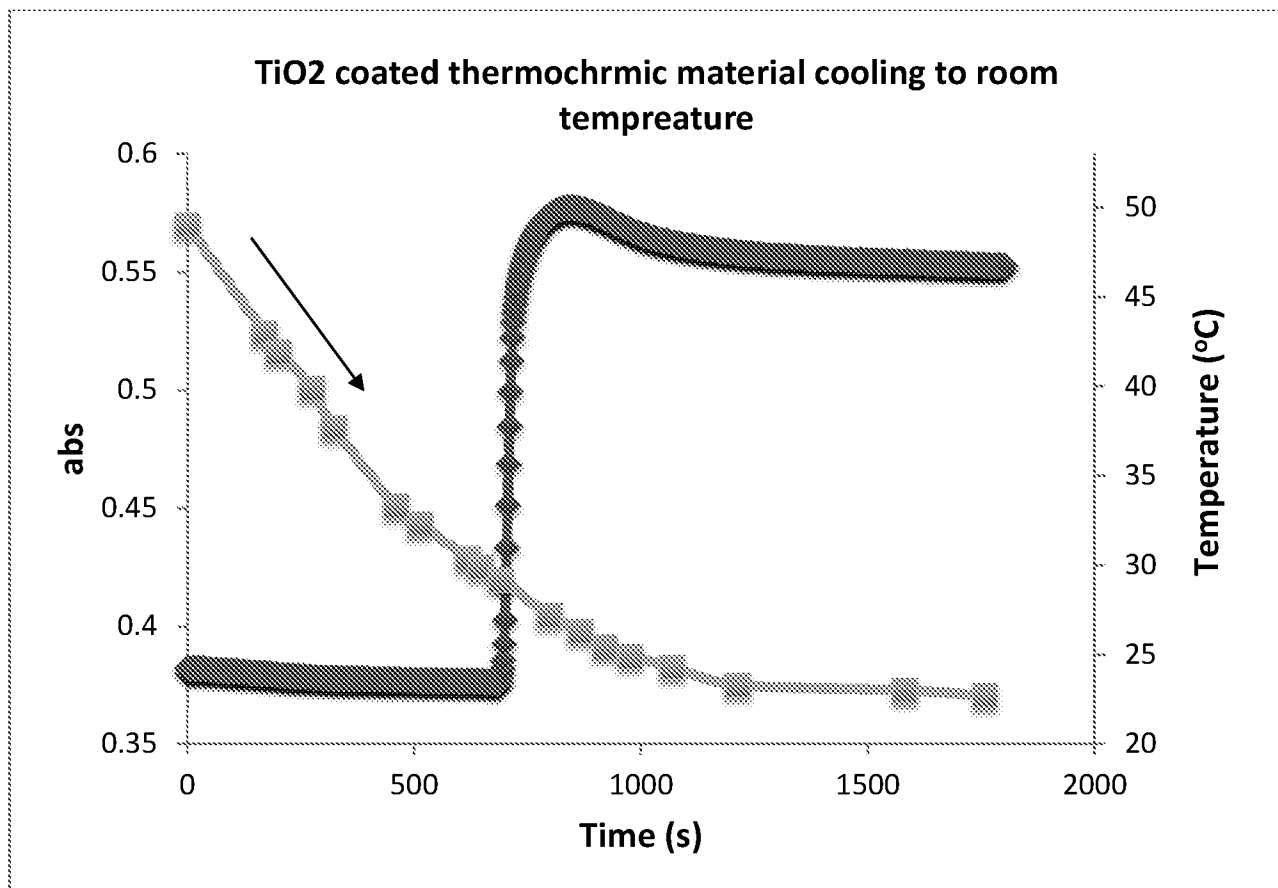


FIG. 7

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US18/30886

A. CLASSIFICATION OF SUBJECT MATTER

IPC - B41M 5/28; C09D 11/17, 11/50, 5/26; C09K 9/02; G01K 11/12 (2018.01)

CPC - B41M 5/284, 5/282, 5/283, 5/305, 5/287; C09D 11/17, 5/26, 11/50; C09K 9/02; G01K 11/16, 11/165, 11/18, 11/14, 11/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

See Search History document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

See Search History document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	WO 2016/046216 A1 (PHILIPS LIGHTING HOLDING B.V.) March 31, 2016; figure 1A; pages 8, 30, 43, 45-46, 48	1, 3, 8-10, 11/1, 11/3, 11/9, 11/10, 12/1, 12/3, 12/9, 12/10, 13 2, 4-7, 11/4-11/7, 12/4-12/7
Y	US 2009/0301382 A1 (PATEL, G) December 10, 2009; paragraphs [0782], [0976], [0985]-[0988]	2, 4-7, 11/4-11/7, 12/4-12/7
A	US 2016/0297975 A1 (CASE WESTERN RESERVE UNIVERSITY) October 13, 2016; entire document	1-13

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

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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

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

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

03 July 2018 (03.07.2018)

Date of mailing of the international search report

20 JUL 2018

Name and mailing address of the ISA/

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-8300

Authorized officer

Shane Thomas

PCT Helpdesk: 571-272-4300
PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US18/30886

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 14-37
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.