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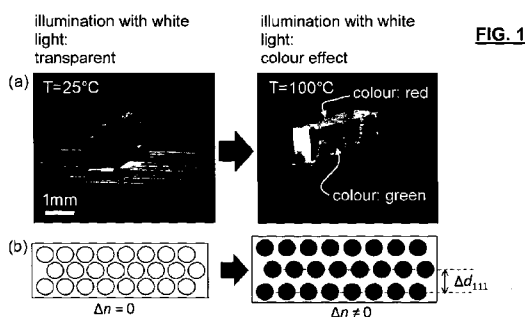
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(54) **Title:** COMPOSITE OPTICAL MATERIALS. USES OF COMPOSITE OPTICAL MATERIALS AND METHODS FOR THE MANUFACTURE OF COMPOSITE OPTICAL MATERIALS



(57) **Abstract:** A thermochromic composite optical body formed of a composite optical material. The material has a three dimensionally periodic arrangement of particles of a first material having refractive index n_1 disposed in a matrix of a second material, different to the first material, having refractive index n_2 . The material is capable of being modified by an external stimulus to provide an optical effect based on the three dimensionally periodic arrangement of particles. At a first condition of the external stimulus, the body is substantially transparent and satisfies at least one of: formula (1) and $\Delta n < 0.001$ (2). Δn is the modulus of the difference between n_1 and n_2 at the first condition of the external stimulus. n_a is the volume average refractive index of the body at the first condition of the external stimulus, λ is a wavelength of light corresponding to the three dimensionally periodic arrangement of particles. L is the thickness of the body at the first condition of the external stimulus. At a second condition of the external stimulus, different from the first condition, the body provides a colour effect due to a corresponding change in n_1 and/or n_2 .

**COMPOSITE OPTICAL MATERIALS, USES OF COMPOSITE OPTICAL MATERIALS
AND METHODS FOR THE MANUFACTURE OF COMPOSITE OPTICAL MATERIALS**

BACKGROUND TO THE INVENTION

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Field of the invention

The present invention relates to composite optical materials, uses of composite optical materials and methods for the manufacture of composite optical materials. The invention
10 has particular, but not exclusive, applicability to materials which change colour in response to a stimulus, for use for example in sensor applications.

Related art

15 Natural opal is built up from domains consisting of monodisperse silica spheres of diameter 150-400 nm. These spheres are close-packed and therefore form a regular three dimensional lattice structure within each domain. The colour play of such opals is created by Bragg-like scattering of the incident light at the lattice planes of the domains.

20 It is known to produce synthetic opal-like materials. For example, US-A-4,703,020 discloses the formation of such materials by allowing silica spheres to sediment from an aqueous dispersion. This sediment is then dried and calcined at 800 degrees C. Subsequently, a solution of zirconium alkoxide is allowed to penetrate into the interstices in the sediment and zirconium oxide is precipitated in the interstices by hydrolysis. The
25 material is then calcined again to leave a structure in which silica spheres are arranged in a three dimensional lattice with zirconium oxide in the interstices. Forming opal-like materials in this way is exceptionally time-consuming and expensive. It is not an industrially-applicable route for the manufacture of significant quantities of materials.

US 2004/0253443 (equivalent to WO03025035) discloses moulded bodies formed from core-shell particles. Each particle is formed of a solid core, and the solid cores have a monodisperse particle size distribution. Each particle has a shell formed surrounding the core. The core and shell have different refractive indices. In one embodiment in this document, the core is formed of crosslinked polystyrene and the shell is formed of a polyacrylate such as polymethyl methacrylate (PMMA). In this case, the core has a relatively high refractive index and the shell has a relatively low refractive index. A polymer interlayer may be provided between the core and shell, in order to adhere the shell to the core. Granules of the core-shell particles are heated and pressed to give a film. In this heating and pressing step shell material is flowable but the core material remains solid. The cores form a three dimensional periodic lattice arrangement, and the shell material becomes a matrix material. The resultant material demonstrates an optical opalescent effect. Inorganic nanoparticles (e.g. metal nanoparticles or semiconductor nanoparticles) can be incorporated in the interstices between cores to provide enhanced functionality to the material. US 2004/0253443 suggests mechanisms to explain the ordering of the core particles in the matrix, but these are not fully explained.

US 2005/0142343 (equivalent to WO03064062) provides similar disclosure to US 2004/0253443. However, additionally, a contrast material such as a pigment is stored in the matrix, in order to enhance the optical effect.

US 2005/0228072 (equivalent to WO03106557) provides similar disclosure to US 2004/0253443. However, additionally, a further material is added in order to control the mechanical properties of the composite material. The further material is, for example a thermoplastic rubber polymer.

WO2004096894 provides similar disclosure to US 2004/0253443, and additionally proposes extruding the composite material as a sheet and subsequently rolling the

material. The result is reported to be a uniform colour effect depending on the viewing angle.

US2006/0292344 (equivalent to WO2005028396) discloses the formation of moulded
5 bodies using core-shell particles as disclosed above. The moulded bodies incorporate homogeneous, regularly arranged cavities. The cavities are formed by removal of the core particles from the composite material.

US2007/0160521 (equivalent to WO2005056622) provides similar disclosure to
10 US2006/0292344 above except that the core particles are formed of a degradable polymer and the shell material is pyrolysed to give a carbon matrix.

WO2005056621 provides similar disclosure to US 2004/0253443. However, in this case, the matrix material is brittle.

15 US2007/0178307 (equivalent to WO2005080475) provides similar disclosure to US 2004/0253443. However, the core particles are formed of inorganic material, and the shell material is removed to leave the core particles arranged in corresponding cavities bounded by walls. Depending on the nature of the core particles, they may be aligned
20 using electric or magnetic fields.

WO2006097173 provides similar disclosure to US 2004/0253443. In addition, composite bodies formed from the core-shell particles are used as optical elongation and compression sensors.

25 Pursiainen et al [O. Pursiainen, J. Baumberg, H. Winkler, B. Viel, P. Spahn and T. Ruhl "Nanoparticle-tuned structural color from polymer opals" Optics Express, 23 July 2007, Vol. 15, No. 15, 9553] discuss the effect of the incorporation of nanoparticles on the optical properties of flexible polymer opals formed using core-shell polymeric particles.

They conclude that incorporating sub-50nm nanoparticles into the interstices of the face centered cubic (fcc) lattice dramatically changes the colour perceived from the composite material without affecting the lattice quality. Contrary to iridescence based on Bragg diffraction, colour generation arises through spectrally-resonant scattering inside the composite material. Viewing angles are shown to widen beyond 40°, removing the strong dependence of the perceived colour on the position of light sources or the viewer, thereby greatly enhancing the colour appearance.

SUMMARY OF THE INVENTION

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The present inventors have realised that it may be possible to provide a visible change in a composite optical material. This change may be produced, for example, in response to a stimulus.

15

It is known to produce materials which have optical properties which can vary in response to a stimulus. For example, WO0244728 discloses crystalline colloidal arrays encapsulated in polymer matrix. The material provides shifts in its photonic band gap in response to a change in temperature or in response to an applied mechanical force, for example.

20

US2003122112 provides similar disclosure to WO0244728, but concentrates on the effect of the application of stress to the composite material of crystalline colloidal particles embedded in a polymer matrix.

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WO2009050448 discloses the use of photonic materials as security devices, in particular as security labels having two photonic crystal structures with differing optical properties. WO2008017869 provides a similar disclosure to WO2009050448 except that the photonic crystal security device gives a different response to light incident from different

directions. WO08017864 provides a similar disclosure to WO2009050448 except that the security device generates two optically different effects depending on external stimuli.

WO2009042207 discloses the use of photonic crystals as temperature sensors. The photonic crystals are formed from lamellae of diblock copolymers. The photonic crystals are therefore periodic in only one dimension. The spacing between lamellae can be affected by external stimuli, such as by the preferential absorption of water in one part of the diblock copolymer.

US6950584 discloses the formation of material with one dimensional periodicity, such as layers of SiO₂ and TiO₂ of appropriate wavelength so that the material is non-transparent at a particular wavelength of light.

US2008095664 discloses the use of a colloidal crystal as a vapour-sensing device.

US6847477 discloses the use of sequential colloidal crystals to alter the wavelength of an incident beam, and give temperature or strain measurement by comparing input and output beam.

WO0073795 discloses a sensor for detecting changes in conditions such as temperature, chemical conditions (including pH and ion levels), biological antigens, radiation levels, electrical field and pressure applied to the sensor. The sensor body is formed from a material which incorporates an evenly dispersed matrix of light-scattering elements. However, the light-scattering elements are not periodically arranged.

WO0126611 discloses a dental composite including a dispersed phase and reinforcing, translucent filler. About 25-80 % by volume of the filler particles have a particle size in the range from about 0.2 µm to about 0.6 µm. The composite has a self-opalescing

quality. The refractive indices of the resin and the translucent filler are the same or substantially similar, e.g. being within the range of 1.45-1.60.

5 WO0244301 discloses solid colloidal crystals of monodispersed spheres, the materials exhibiting opalescence.

WO0021905 discloses materials formed by the self-assembly of three dimensionally periodic structures of spherical particles. Colour changes are induced by changes of refractive index of the components of the materials, and/or by changes in the lattice
10 parameters of the periodic structures.

The present inventors have realised that it would be advantageous to provide a material that responds to an external stimulus by providing a visible change from substantially transparent to coloured, when viewed in ambient light conditions.

15

Accordingly, in a general aspect of the invention, particles of a first material are arranged in a three dimensionally periodic arrangement in a matrix of a second material, the refractive index of the first and second materials being substantially matched at a first condition of an external stimulus, and at a second condition of the external stimulus,
20 there being provided a colour effect due to a corresponding change in the relative refractive indices of the first and second materials.

In a first preferred aspect of the invention, there is provided a composite optical body formed of a composite optical material having a three dimensionally periodic
25 arrangement of particles of a first material having refractive index n_1 disposed in a matrix of a second material, different to the first material, having refractive index n_2 , wherein the material is capable of being modified by an external stimulus to provide an optical effect based on the three dimensionally periodic arrangement of particles, wherein, at a first

condition of the external stimulus, the body is substantially transparent and satisfies at least one of inequality (1) and inequality (2):

$$\Delta n < \frac{n_{va} \lambda}{L} \quad (1)$$

5

$$\Delta n < 0.001 \quad (2)$$

where: Δn is the modulus of the difference between n_1 and n_2 at the first condition of the external stimulus; n_{va} is the volume average refractive index of the body at the first

10 condition of the external stimulus; λ is a wavelength of light corresponding to the three dimensionally periodic arrangement of particles; and L is the thickness of the body at the first condition of the external stimulus,

and wherein, at a second condition of the external stimulus, different from the first condition, the body provides a colour effect due to a corresponding change in n_1 and/or

15 n_2 .

In a second preferred aspect of the invention, there is provided a use of a composite optical body formed of a composite optical material having a three dimensionally periodic arrangement of particles of a first material having refractive index n_1 disposed in a matrix

20 of a second material, different to the first material, having refractive index n_2 , the use including the step of modifying the material using an external stimulus to provide an optical effect based on the three dimensionally periodic arrangement of particles, wherein, at a first condition of the external stimulus, the body is substantially transparent and satisfies at least one of inequality (1) and inequality (2):

25

$$\Delta n < \frac{n_{va} \lambda}{L} \quad (1)$$

$$\Delta n < 0.001 \quad (2)$$

where: Δn is the modulus of the difference between n_1 and n_2 at the first condition of the external stimulus; n_{va} is the volume average refractive index of the body at the first condition of the external stimulus; λ is a wavelength of light corresponding to the three dimensionally periodic arrangement of particles; and L is the thickness of the body at the first condition of the external stimulus,
and wherein, at a second condition of the external stimulus, different from the first condition, the body provides a colour effect due to a corresponding change in n_1 and/or n_2 .

In a third preferred aspect of the invention, there is provided a method of forming a composite optical body, including providing a population of core-shell particles, each particle including a core and a shell material surrounding the core, heating the population to a temperature at which the shell material is flowable and subjecting the population to the action of a mechanical force to provide a three dimensionally periodic arrangement of core particles in a matrix of the shell material, wherein the core particles have refractive index n_1 and the shell material has refractive index n_2 , different from n_1 ,
and either:

(i) the population of core-shell particles satisfies inequality (2):

$$\Delta n < 0.001 \quad (2)$$

or

(ii) the body satisfies at least one of inequality (1) and inequality (2):

$$\Delta n < \frac{n_{va}\lambda}{L} \quad (1)$$

$$\Delta n < 0.001 \quad (2)$$

where: Δn is the modulus of the difference between n_1 and n_2 at a first condition of an external stimulus; n_{va} is the volume average refractive index of the body at the first condition of the external stimulus; λ is a wavelength of light corresponding to the three dimensionally periodic arrangement of particles; and L is the thickness of the body at the first condition of the external stimulus.

In a fourth preferred aspect of the invention, there is provided a sensor device including at least one composite optical body according to the first aspect, the sensor device being operable to detect a change in an external stimulus by providing a change of the composite optical body from transparent to coloured between first and second conditions of the external stimulus.

Preferred and/or optional features of the invention will now be set out. These are applicable singly or in any combination with any aspect of the invention.

λ is typically a wavelength of light corresponding to a colour of light. In order to provide the colour effect, Bragg reflection occurs. This can be thought of as being based on reflections from corresponding notional planes of the three dimensionally periodic lattice. The colour effect seen depends on the spacing of these planes. Thus, λ corresponds to the colour effect seen based on the three dimensionally periodic lattice. As is explained in more detail below, this is not necessarily strongly dependent on the viewing angle.

Inequality (1) expresses the preferred requirement that when the composite optical body satisfies this inequality, the lattice scattering colour will not be visible (or will substantially not be visible) to the observer. Thus, the body may not appear completely transparent (there may be some attenuation of light intensity during transmission of light through the body, for example) but preferably it will not appear to be coloured. The basis for inequality (1) is that the effective penetration of light at the strongest colour available

from the body (corresponding to λ) is $\frac{n_{va}\lambda}{\Delta n}$ and this should be smaller than the sample thickness L to allow suitable colour scattering to build up.

Preferably, the core particles (also referred to herein as the particles of the first material) have a substantially monodisperse size distribution. Preferably, the core material (or the first material) is either not flowable or becomes flowable at a temperature above the melting point of the shell material. This can be achieved through the use of polymeric materials having a correspondingly high glass transition temperature (T_g). For example, crosslinked polymers may be used. Alternatively, although this is not preferred, inorganic core materials may be used. This is typically not preferred due to the difficulty in tuning the matching of the refractive indices of the core material and the shell material.

Preferably, the shell of the core-shell particles is bonded to the core via an interlayer.

Preferably, at least at the second condition of the external stimulus, the body exhibits opalescence.

Preferably, the temperature at which the method is carried out is at least 40°C, more preferably at least 60°C, above the glass transition temperature of the shell material of the core-shell particles.

Preferably, the flowable core-shell particles are cooled under the action of the mechanical force to a temperature at which the shell is no longer flowable.

The action of mechanical force can be the action of a force which is used in known processing steps of polymers. For example, the action of mechanical force may take place via one or more of: uniaxial pressing (e.g. forming a film or plate); injection-

moulding; transfer moulding; extrusion; co-extrusion; calendering; lamination; blowing; fibre-drawing; embossing; and nano-imprinting.

When the action of force takes place through uniaxial pressing, the body is preferably a film. Suitable films can preferably also be produced by calendering, film blowing or flat-film extrusion.

When the body is produced by injection moulding, it is particularly preferred for the demoulding not to take place until after the mould with moulding inside has cooled.

When carried out in industry, it is advantageous to employ moulds having a large cooling-channel cross section since the cooling can then take place in a relatively short time. The mould may advantageously be heated before the injection operation.

The body may comprise auxiliaries and/or additives. These can serve in order to provide desired properties of the body. Examples of auxiliaries and/or additives of this type are antioxidants, UV stabilisers, biocides, plasticisers, film-formation auxiliaries, flow-control agents, fillers, melting assistants, adhesives, release agents, application auxiliaries, demoulding auxiliaries and viscosity modifiers, for example thickeners.

In order to achieve the preferred optical effect, it is desirable for the core particles to have a mean particle diameter in the range from about 5 nm to about 2000 nm. More preferably, the core particles have a mean particle diameter in the region of about 50-500 nm, more preferably 100-500 nm. Still more preferably, the core particles have a mean particle diameter of at least 150 nm. The core particles may have a mean particle diameter of at most 400 nm, or at most 300 nm, or at most 250 nm.

Preferably, one or more species of nanoparticles is included in the matrix material, in addition to the cores of the core-shell particles. These particles are selected with respect to their particle size in such a way that they fit into the cavities of the packing (e.g. sphere

packing) of the core particles and thus cause only little change in the arrangement of the core particles. Through specific selection of corresponding materials and/or the particle size, it is firstly possible to modify the optical effects of the mouldings, for example to increase their intensity. Secondly, it is possible through incorporation of suitable

- 5 "quantum dots", to functionalise the matrix. Preferred materials are inorganic nanoparticles, in particular carbon nanoparticles, nanoparticles of metals or of II-VI or III-V semiconductors or of materials which influence the magnetic/electrical (electronic) properties of the materials. Examples of further preferred nanoparticles are noble metals, such as silver, gold and platinum, semiconductors or insulators, such as zinc
- 10 chalcogenides and cadmium chalcogenides, oxides, such as haematite, magnetite or perovskite, or metal pnictides, for example gallium nitride, or mixed phases of these materials.

- Preferably, the nanoparticles have an average particle size of 50 nm or less. The
- 15 nanoparticles may have an average particle size of at least 5 nm. An average particle size in the range 10-50 nm (e.g. about 20 nm) has been found to guide suitable results. Preferably, the proportion by weight of the nanoparticles in the composite is less than 1%, more preferably less than 0.5%, less than 0.1% and still more preferably less than 0.01%. The nanoparticles preferably are distributed uniformly in the matrix material.

20

- Preferably, the interlayer is a layer of crosslinked or at least partially crosslinked polymers. The crosslinking of the interlayer here can take place via free radicals, for example induced by UV irradiation, or preferably via di- or oligofunctional monomers. Preferred interlayers in this embodiment comprise from 0.01 to 100% by weight,
- 25 particularly preferably from 0.25 to 10% by weight, of di- or oligofunctional monomers. Preferred di- or oligofunctional monomers are, in particular, isoprene and allyl methacrylate (ALMA). Such an interlayer of crosslinked or at least partially crosslinked polymers preferably has a thickness in the range from 10 to 20 nm. Thicker interlayer materials may be possible, provided that the refractive index of the interlayer closely

matches the refractive index of the core material and/or the shell material. It is preferred that the refractive index of the interlayer, if present, is taken into account in inequality (1) and/or inequality (2).

- 5 Preferably the shell is formed of a thermoplastic or elastomeric polymer. Since the shell essentially determines the material properties and processing conditions of the core-shell particles, the person skilled in the art will select the shell material in accordance with the usual considerations in polymer technology, but with particular attention to the requirement to closely match the refractive index with that of the core material.

10

The core particles are preferably spherical, or substantially spherical, in shape. Preferably, the distribution of the diameter of the core particles is substantially monodisperse, e.g. with a standard deviation of 20% or less, more preferably 10% or less, still more preferably 5% or less.

15

Preferably the core particles are disposed in the composite material in a close packed three dimensional lattice. Specifically, preferably the core particles are disposed in the composite material in a face centred cubic lattice. Preferably, the (111) plane of the lattice is aligned substantially perpendicular to a direction of force used to form the body.

- 20 Typically, the (111) plane of the lattice is aligned substantially parallel with a surface of the body.

It can be advantageous for the core : shell weight ratio to be in the range from 2:1 to 1:5, preferably in the range from 3:2 to 1:3 and particularly preferably in the region below

- 25 1.2:1. In specific embodiments of the present invention, it is even preferred for the core:shell weight ratio to be less than 1:1, a typical upper limit for the shell content being at a core:shell weight ratio of 2:3.

The core may be formed, for example, from polymethylmethacrylate (PMMA). The shell may be formed from polyethylacrylate (PEA) and/or polybenzylmethacrylate (PBzMA).

More preferably, the shell may itself be a composite material, formed from PEA and PBzMA. For example, the shell may be formed from about 70% PEA and about 30%

5 PBzMA. In order to promote refractive index matching of the shell, core and/or interlayer (if present), it is possible to select suitable starting materials for these components and add refractive index modifiers to one or more of the components. For example, inorganic particles (e.g. particles of TiO_2 and/or SiO_2) may be added for this purpose. Such particles may have a small particle size, e.g. an average particle size of 10 nm or less,
10 e.g. 5 nm or less, typically about 3 nm.

Preferably the body satisfies both inequality (1) and inequality (2).

Preferably the thickness L of the body is at least 10 μm . Thinner bodies may not have
15 sufficient mechanical integrity for practical uses. Furthermore, thinner bodies typically will not provide sufficiently strong reflections in order to give a significant colour effect. L is more preferably at least 20 μm . L may be significantly greater than this, e.g. up to 1 mm or more. Preferably, for a body in the form of a film, L is at most 0.5 mm, or at most 0.3 mm.

20

Films are typically formed by uniaxial pressing, and/or or by rolling. Alternatively, fibres may be formed. Fibres may be formed by drawing, but are more preferably formed by extrusion. Fibre dimensions corresponding to L above may be used. Fibres are of interest because they can be further processed to form woven or non-woven articles, e.g.
25 labels, clothing, etc. Furthermore, such articles may provide a significantly greater surface area of composite material available for interaction with the environment, and therefore greater sensitivity for changes in the external stimulus.

Preferably, at the second condition of the external stimulus, inequality (1) and/or inequality (2) is no longer satisfied.

Preferably, at the second condition of the external stimulus, inequality (3) is satisfied:

5

$$\Delta n \geq \frac{n_{va} \lambda}{l_{scatt}} \quad (3)$$

where: l_{scatt} is the average scattering length of light of wavelength λ in the composite material. In this case, n_{va} and l_{scatt} are measured at the second condition of the external stimulus.

10

The average scattering length of typical materials for use with the present invention is in the range of about 1 μm to about 1 mm. Light is typically transmitted through a material, in the thickness direction, proportionally to $e^{-z/l_{scatt}}$, where z is the depth. Inequality (3) therefore defines a regime in which significant colour effects occur for the composite material

15

Typically, when the external stimulus changes from the first condition to the second condition, there is a change in the relative refractive index of the core particles and the matrix material. This allows Fresnel reflection from the interfaces in the composite material. Furthermore, the spacing between lattice planes in the composite material may change with the change in external stimulus. Since the spacing of the planes affects the peak wavelength of light affected by Bragg reflection in the material, the colour seen may also be affected with the change in external stimulus. In this manner, the body can provide not only a binary response, but can provide a continuum of responses for different conditions of the external stimulus, based on the observed colour.

20

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Preferably the external stimulus is one or more of: temperature, pH, a fluid, pressure (or stress), strain (e.g. shear, or uniaxial strain), electromagnetic radiation, electric field, magnetic field, a chemical agent, a biochemical agent, a biological agent.

- 5 The body may include a material which is swellable in the presence of a fluid. Such a material may be the matrix material, for example. The material may be swellable in the presence of water. In a first condition (in which water is absent) the body may be transparent. In a second condition (in which water is present), the water may swell the matrix material, affecting the relative refractive index of the matrix compared with the
- 10 core material, and also affecting the spacing of the lattice planes. The result is that the composite optical body provides a colour effect in the second condition, indicating the presence of water.

- Other fluids, chemical agents (e.g. HO^- ions, H^+ ions in the case of pH sensing),
- 15 biochemical agents, biological agents, etc., may provide a similar effect. In order for the body to provide a selective response to specific external stimuli such as these, it is preferred that the matrix (or, in some circumstances, the core) includes specific sites for selectively bonding with the external stimuli.

- 20 In a preferred embodiment, the external stimulus is temperature. The body may be transparent at room temperature and may exhibit a colour effect on heat and/or cooling from ambient temperature. Alternatively, the body may be transparent at a temperature different to room temperature (higher or lower), and may exhibit the colour effect when cooled or warmed to room temperature.

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In another embodiment, the external stimulus is electromagnetic radiation, e.g. microwave radiation. The composite material may include electromagnetic radiation-absorption elements. These preferably absorb electromagnetic radiation only within one or more specific frequency ranges. Typically, the energy absorbed is emitted as heat

energy, thereby raising the temperature of the material around the electromagnetic radiation-absorption elements. For example, in the case of microwave radiation, the electromagnetic radiation-absorption elements may be split ring resonators. These may be located in the core particles. Preferably, one such resonator may be included per
5 core particle. The temperature rise provided by the electromagnetic radiation-absorption elements can provide the necessary change in refractive index (and optionally an associated change in lattice plane spacing) in order to provide the colour effect.

Preferably, the colour effect viewable in the second condition of the external stimulus is
10 different depending on whether the body is viewed in reflection or transmission.

The device may be used at operating temperatures up to 150°C. It is preferred that at temperatures up to this limit, any colour effects observed are substantially reversible.

15 Additionally or alternatively, the body may be encapsulated prior to use, and operable to be exposed only at the point of use. In this way, the body can be kept from becoming contaminated up to the point of use, and then exposed to a fluid (or other external stimulus) of interest to determine whether a specific analyte is present.

20 The body may include an image. The image may be a pictorial representation, for example, a logo or other shape. More preferably, the image is an arrangement of one or more alphanumeric characters. The image may be formed by allowing the body to be formed using different constituents at the image part of the body compared with non-image parts of the body. These different constituents may provide the image part of the
25 body with a different refractive index or lattice spacing response in response to the external stimulus. Additionally or alternatively, the image may be formed by allowing a different amount of cross linking to occur in the image part of the body compared with non-image parts of the body. Suitable different amounts of cross linking affects the hardness, and thus can locally affect the expansion of the material. In turn, this can

affect the refractive index variation and/or the lattice spacing variation at the image part of the body compared with the non-image part of the body.

Further optional features of the invention are set out below.

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BRIEF DESCRIPTION OF THE DRAWINGS

Preferred embodiments of the invention will be set out by way of example with reference to the drawings, in which:

- 10 Fig. 1(a) shows images of a thermochromic composite body according to an embodiment of the invention. The left hand image is taken at 25°C and the right hand image at 100°C. The left hand image shows a transparent composite body. The right hand image shows a colour effect: the top face shows a red colour and the large side face shows a green colour. The small side face shows a combination of green and yellow colours. Fig. 1(b)
- 15 shows corresponding schematic views of a cross section through the composite body, indicating the isotropic expansion with refractive index changes on heating.
- Fig. 2 shows scattering spectra of (a) a balanced composite optical material ($\Delta n=0$) at $T=20^\circ\text{C}$ and (b) non-balanced composite optical material ($\Delta n=0.1$ at $T=20^\circ\text{C}$). The materials are 0.05wt% carbon-doped polymer opals from $T = 45^\circ\text{C}$ to 150°C in 5°C steps.
- 20 The spectra are normalised to white diffuser plates.
- Fig. 3 shows (a) normalised scattering spectra of balanced thermochromic polymer opals at 150°C and (b) peak scattering strength against temperature, for samples with increasing carbon nanoparticle doping up to 0.2% by weight. Dashed line shows non-balanced opal (right axis); dotted line shows quadratic fit to scattering against
- 25 temperature. (c) Peak scattered wavelength against temperature for balanced (solid) and non-balanced samples (dashed), both with (labelled w) and without (labelled w/o) carbon nanoparticle doping.

**DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS, FURTHER
OPTIONAL FEATURES OF THE INVENTION**

The present inventors have devised a new class of thermochromic materials, in one
5 embodiment of the invention. These materials are fabricated using large-scale shear-
ordering of polymer photonic crystals. By balancing the refractive index of the core
(PMMA) and composite shell components at room temperature, transparent films are
created which become coloured on heating, for example to 150°C. Since this scattering-
based structural colour depends only on resonant Bragg scattering of the un-pigmented
10 components, it can be tuned to any desired optical wavelength. The present inventors
have found that the observed colour shifts with temperature are not simply accounted for
by theory and are sensitive to the constituents.

Man-made thermochromic materials can be considered to fall into two categories. Phase
15 transition thermochromics [References 1-4] realign their atomic crystal structure on
reaching a critical temperature thus changing their colour, and are found in products such
as disposable battery indicators [Reference 5]. Other types (particularly thermochromic
liquid crystals) change colour continuously, but only within a small ΔT range [References
6-9] and have been widely used to map surface temperature distributions [Reference 10].
20 Similar results have been reported for meta-stable gels of block-copolymers that form a
lamellar phase whose Bragg reflection can be temperature tuned [Reference 11].
Neither category describes the preferred new materials disclosed here, which preferably
show little colour shift but display a thermally-induced continuous change from
transparency to spectrally-resonant scattering. Such materials are examples of a new
25 class of structural colour nano-composites with tunable properties.

The preferred thermochromic polymer opals disclosed here are based on flexible
monolithic photonic crystals formed from hard polymer spheres dispersed in a softer
sticky elastomer matrix [see References 12 and 13]. As typical for opaline photonic

crystals [References 14-16], when the spheres self-assemble into an fcc lattice they can be colour-tuned by changing the size of the constituent spheres. Using spheres of diameter about 20 nm produces Bragg peaks in the visible spectral range, whilst the elastomeric composition gives flexible films with enhanced structural control of colour. A
5 major strength of this work is the ability to form these opals by shear-assembly in extrusion or compression which allows efficient production on industrial scales.

Here, polymer opals with striking thermochromic properties may be produced by designing sphere and matrix to have equal refractive indices at room temperature, hence
10 suppressing Fresnel reflections at the sphere surfaces and leading to transparent films, plates, fibres or bodies. As the temperature is increased these refractive indices change at different rates. Hence a strong structural colour progressively appears (Fig.1), arising from the resonant Bragg scattering, which is reversed on cooling. This thermochromic mechanism can be harnessed in a wide variety of ways by tuning core and shell sizes
15 and compositions.

Thermochromic polymer opals with $\Delta n=0$ at room temperature ('balanced opals') are produced from monodisperse precursor core/shell spheres comprised of a polymethylmethacrylate (PMMA) core and a composite shell of 70% polyethylacrylate
20 (PEA) and 30% polybenzylmethacrylate (PBzMA), grown using similar methods to previous core-shell precursors [see References 17 and 18]. This material is then sheared by being extruded and then pressed (at 150°C and 1.9 MPa) for five minutes). When the polymer opal material is pressed against a flat plate, the shell material fuses into a matrix and the spheres shear-assemble into a lattice with the (111) plane parallel to the surface.
25 In previous work [References 12 and 13], it has been shown that doping polymer opals with < 0.1% by weight of sub-50nm carbon nanoparticles (which uniformly incorporate in the outer matrix) dramatically enhances the resonant Bragg scattering so that specific colours emerge in a broad scattering cone. The balanced thermochromic samples are compared with our previous versions which have $\Delta n=0.1$ at room temperature ('non-

balanced opals') and consist of a polystyrene (PS) inner core and a PEA shell, providing strong structural colour at room temperature. In this work, therefore, four types of samples are contrasted: with and without refractive index contrast at room temperature, and with and without carbon doping that can enhance structural colour.

5

Optical scattering spectra of different samples were quantified by mounting them on a heated stage and recording confocally-collected dark-field spectra on a modified microscope. Data was normalised to the scattering spectra taken under identical conditions on white diffuser plates which have a broadband Lambertian spectrum. The collected spot diameter at the sample is 10 μm using x20 objectives (numerical aperture of 0.45), with light in a dark field configuration incident at 27° and collected at normal incidence ($\theta < 20^\circ$).

Balanced thermochromic samples (Fig.2a) have a weak featureless scattering spectrum at room temperature, but a significant scattering peak emerges around $\lambda_{pk} = 580\text{nm}$ on heating, as refractive index contrast develops between the shell-derived matrix and 220 nm diameter spheres. This reflects the transition from transparent to green colour observed for the sample in Fig. 1. Similarly, heating a non-balanced polymer opal to 150°C raises the pre-existing scattering peak by 9% (Fig. 2b). The difference in the resonant linewidth between these two samples originates in the thickness and degree of order of the opal and reflects the non-optimised shear-ordering for the balanced shell composition. However it is clear that in both materials, increasing reflection at each sphere interface creates a new type of thermochromic effect which is limited in temperature range only by the decomposition temperatures of the constituent polymers.

25

In all cases, the scattering increases quadratically with temperature (Fig. 3a), both for the balanced ($\Delta n = 0$) and non-balanced ($\Delta n = 0.1$) opals. This accords with a simple theory presented below, although the inventors do not wish to be bound by this theory. Carbon doping affects both scattered intensity and λ_{pk} , with the addition of carbon nanoparticles

in all cases leading to extra absorption reducing the scattered light emerging. Examining the spectra at $T = 150^\circ\text{C}$ (Fig. 3b) shows a surprising increase in Bragg wavelength, λ_{pk} , on adding carbon nanoparticles implying that despite the low levels of loading and undisrupted lattice, the average lattice spacing increases. This effect is also seen in the original non-balanced opals, and may arise because the nanoparticles modify the rheology during the shear-ordering process [Reference 19].

Extracting the peak scattering λ_{pk} as temperature increases reveals a wide range of behaviours (Fig. 3c). Resonant Bragg scattering is controlled by the condition

$\lambda_{pk} = 2n_{va}d_{111} \sin \theta$ where n_{va} is the volume-weighted average refractive index. Whilst thermal expansion increases the lattice spacing, it reduces the refractive index, leading to competing control over λ_{pk} . The glass transition temperature of PEA is 0°C and of PMMA is 110°C , hence the heavily cross-linked PMMA has an expansivity (κ_s) less than a third that of PEA (κ_m) in this temperature range [Reference 20]. For small temperature changes ΔT :

$$\Delta f = f(1-f)(\kappa_s - \kappa_m)\Delta T \quad (\text{A})$$

$$\Delta d_{111} = \left(\frac{2g+1}{3} \right) \bar{\kappa} \Delta T d_{111} \quad (\text{B})$$

where the sphere fill fraction $f = 0.55$ and the volume-averaged expansivity

$\bar{\kappa} = f\kappa_c + (1-f)\kappa_s$. The extent to which the film is allowed to expand laterally as

compared to vertically is parameterised by g , which is 0 for isotropic expansion and 1 for vertical expansion only (film pinned laterally to the substrate).

As the material expands, its optical density falls according to the Clausius-Mossotti equation [see Reference 21] which with equation (A) above yields for the dielectric

constant in each medium:

$$\varepsilon(T + \Delta T) = \varepsilon(T) - \kappa \Delta T [\varepsilon(T) - 1] [\varepsilon(T) + 2] / 3 \quad (\text{C})$$

$$\Delta n \cong - \bar{\kappa} \Delta T (n_{va}^2 - 1)(n_{va}^2 + 2) / 6n_{va} \quad (\text{D})$$

where Δn is the thermally induced change in refractive index contrast. For small refractive index contrasts between matrix and spheres in a typical balanced opal material:

$$\frac{\Delta \lambda_{pk}}{\lambda_{pk}} = \frac{\Delta n}{n_{va}} + \frac{\Delta d_{111}}{d_{111}} \cong \bar{\kappa} \Delta T \left(\frac{2g}{3} - 0.055 \right) \quad (E)$$

- 5 As $\bar{\kappa} = 4.01 \times 10^{-4} \text{ cm}^3/\text{gK}$ [Reference 20] the wavelength shift should lie between 2.45% and -0.219% for $\Delta T = 100\text{K}$. Fig. 3(c) shows red shifts up to 5% and blue shifts up to 0.08% which is thus accounted for by different sample constraints on the expansion. But it does not explain the significant dependence on carbon nanoparticle loading, nor the nonlinear behaviour of the wavelength shift. One likely origin of this failure is the way the
- 10 current model assumes that strain is uniformly spatially distributed within this heterogeneous nano-composite, when local compression and relaxation are possible.

Despite these anomalies, this simple model successfully predicts a quadratic temperature-dependent increase in optical scattering strength (c.f. Fig. 3a). While the

15 reflected intensity at each sphere-matrix interface increases as Δn^2 , optical scattering is proportional to $[\Delta \epsilon / (\epsilon_s + 2\epsilon_m)]^2$ [Reference 22]. The present inventors thus predict that the maximum scattering $S_{\max} \propto \Delta \kappa \Delta T^2$ independent of the original refractive index contrast, in good agreement with the present data at small temperature rises.

- 20 The spectral linewidth of the Bragg peaks is unaffected by temperature, remaining 50 nm in these thermochromic opals independent of the carbon loading. Since the Bragg linewidth is mainly a function of the disorder and not the index contrast, this confirms structural electron microscopy that carbon nanoparticles do not affect the basic internal opal structure [Reference 13] even if they slightly affect the spacing between spheres.
- 25 This is also confirmed in the 1D DBR model, in which the linewidth increases little with refractive index contrast despite increased optical penetration through the structure.

In summary, the present inventors have demonstrated a novel thermochromic material with scattering strength increasing continuously with increasing temperature, but without strong colour shifts. Balanced thermochromic opals are transparent at room temperature and their colours appear not because of a change in material phase, but because of a temperature-dependent change in refraction. Emerging refractive index contrast produces structural colour, with wavelength shifts that can be tuned by modifying the composition and cross-linking of the sphere and matrix polymers. Incorporation of other (e.g. emissive) nanoparticles thus provides a range of applications in sensing, displays, and structural colour materials.

The embodiments set out above have been described by way of example. On reading this disclosure, modifications of these embodiments, further embodiments and modifications thereof will be apparent to the skilled person and as such are within the scope of the present invention.

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- 25

CLAIMS

1. A composite optical body formed of a composite optical material having a three dimensionally periodic arrangement of particles of a first material having refractive index n_1 disposed in a matrix of a second material, different to the first material, having refractive index n_2 , wherein the material is capable of being modified by an external stimulus to provide an optical effect based on the three dimensionally periodic arrangement of particles, wherein, at a first condition of the external stimulus, the body is substantially transparent and satisfies at least one of inequality (1) and inequality (2):

$$\Delta n < \frac{n_{va}\lambda}{L} \quad (1)$$

$$\Delta n < 0.001 \quad (2)$$

where: Δn is the modulus of the difference between n_1 and n_2 at the first condition of the external stimulus; n_{va} is the volume average refractive index of the body at the first condition of the external stimulus; λ is a wavelength of light corresponding to the three dimensionally periodic arrangement of particles; and L is the thickness of the body at the first condition of the external stimulus,

and wherein, at a second condition of the external stimulus, different from the first condition, the body provides a colour effect due to a corresponding change in n_1 and/or n_2 .

2. A composite optical body according to claim 1 wherein, at the second condition of the external stimulus, inequality (3) is satisfied:

$$\Delta n \geq \frac{n_{va}\lambda}{l_{scatt}} \quad (3)$$

where: l_{scatt} is the average scattering length of light of wavelength λ in the composite material.

3. A composite optical body according to claim 1 or claim 2 wherein the particles of the first material have a substantially monodisperse size distribution.

4. A composite optical body according to any one of claims 1 to 3 wherein the particles of the first material are substantially equi-axed in shape, e.g. spherical.

5. A composite optical body according to any one of claims 1 to 4 wherein the particles of the first material are disposed in a face centred cubic lattice.

6. A composite optical body according to claim 5 wherein the (111) plane of the lattice is aligned substantially perpendicular to a direction of force used to form the body.

7. A composite optical body according to claim 5 or claim 6 wherein the (111) plane of the lattice is aligned substantially parallel with a surface of the body.

8. A composite optical body according to any one of claims 1 to 7 wherein the particles of the first material have a mean particle diameter in the range 50-500 nm.

9. A composite optical body according to any one of claims 1 to 8 wherein one or more species of nanoparticles is included in the matrix material, in addition to the particles of the first material.

10. A composite optical body according to claim 9 wherein the nanoparticles are carbon nanoparticles.

11. A composite optical body according to claim 9 or claim 10 wherein the nanoparticles have an average particle size in the range 10-50 nm.

12. A composite optical body according to any one of claims 9 to 11 herein the proportion by weight of the nanoparticles in the composite is less than 1%.

13. A composite optical body according to any one of claims 1 to 12 wherein the particles of the first material are surrounded by an interlayer material, adhering the particles of the first material to the matrix material.

10

14. A composite optical body according to any one of claims 1 to 13 wherein the matrix is formed of a thermoplastic or elastomeric polymer.

15. A composite optical body according to any one of claims 1 to 14 wherein the first material is polymethylmethacrylate (PMMA) and the matrix material is polyethylacrylate (PEA) and/or polybenzylmethacrylate (PBzMA)

16. A composite optical body according to any one of claims 1 to 15 wherein the body satisfies both inequality (1) and inequality (2).

20

17. A composite optical body according to any one of claims 1 to 16 wherein the thickness L of the body is at least 10 μm .

18. A composite optical body according to any one of claims 1 to 17, in the form of a film or plate.

25

19. A composite optical body according to any one of claims 1 to 17 in the form of a fibre or fibres.

20. A composite optical body according to any one of claims 1 to 19 wherein the body is substantially shielded from external stimuli other than the stimulus intended to produce the colour effect.

5 21. A composite optical body according to any one of claims 1 to 19 wherein the body is encapsulated prior to use, and operable to be exposed only at the point of use.

22. A composite optical body according to any one of claims 1 to 21 further including an image.

10

23. A composite optical body according to claim 22 wherein the image is formed by allowing the body to be formed using different constituents at the image part of the body compared with non-image parts of the body.

15 24. A composite optical body according to claim 22 wherein the image is formed by allowing a different amount of cross linking to occur in the image part of the body compared with non-image parts of the body.

20 25. A sensor device including at least one composite optical body according to any one of claims 1 to 24, the sensor device being operable to detect a change in an external stimulus by providing a change of the composite optical body from transparent to coloured between first and second conditions of the external stimulus.

25 26. Use of a composite optical body formed of a composite optical material having a three dimensionally periodic arrangement of particles of a first material having refractive index n_1 disposed in a matrix of a second material, different to the first material, having refractive index n_2 , the use including the step of modifying the material using an external stimulus to provide an optical effect based on the three dimensionally periodic

arrangement of particles, wherein, at a first condition of the external stimulus, the body is substantially transparent and satisfies at least one of inequality (1) and inequality (2):

$$\Delta n < \frac{n_{va}\lambda}{L} \quad (1)$$

5

$$\Delta n < 0.001 \quad (2)$$

where: Δn is the modulus of the difference between n_1 and n_2 at the first condition of the external stimulus; n_{va} is the volume average refractive index of the body at the first

10 condition of the external stimulus; λ is a wavelength of light corresponding to the three dimensionally periodic arrangement of particles; and L is the thickness of the body at the first condition of the external stimulus,

and wherein, at a second condition of the external stimulus, different from the first condition, the body provides a colour effect due to a corresponding change in n_1 and/or

15 n_2 .

27. Use according to claim 26 wherein the external stimulus is one or more of: temperature, pH, a fluid, pressure, electromagnetic radiation, electric field, magnetic field, a chemical agent, a biochemical agent, a biological agent.

20

28. Use according to claim 26 wherein the external stimulus is temperature.

29. Use according to any one of claims 26 to 28 wherein the colour effect viewable in the second condition of the external stimulus is different depending on whether the body

25 is viewed in reflection or transmission.

30. Use according to any one of claims 26 to 29 wherein the composite optical body is used at operating temperatures up to 150°C.

31. A method of forming a composite optical body, including providing a population of core-shell particles, each particle including a core and a shell material surrounding the core, heating the population to a temperature at which the shell material is flowable and
 5 subjecting the population to the action of a mechanical force to provide a three dimensionally periodic arrangement of core particles in a matrix of the shell material, wherein the core particles have refractive index n_1 and the shell material has refractive index n_2 , different from n_1 ,
 and either:

10 (i) the population of core-shell particles satisfies inequality (2):

$$\Delta n < 0.001 \quad (2)$$

or

15 (ii) the body satisfies at least one of inequality (1) and inequality (2):

$$\Delta n < \frac{n_{va}\lambda}{L} \quad (1)$$

$$\Delta n < 0.001 \quad (2)$$

20

where: Δn is the modulus of the difference between n_1 and n_2 at a first condition of an external stimulus; n_{va} is the volume average refractive index of the body at the first condition of the external stimulus; λ is a wavelength of light corresponding to the three dimensionally periodic arrangement of particles; and L is the thickness of the body at the
 25 first condition of the external stimulus.

32. A method according to claim 31 wherein the core material is either not flowable or only becomes flowable at a temperature above the melting point of the shell material.

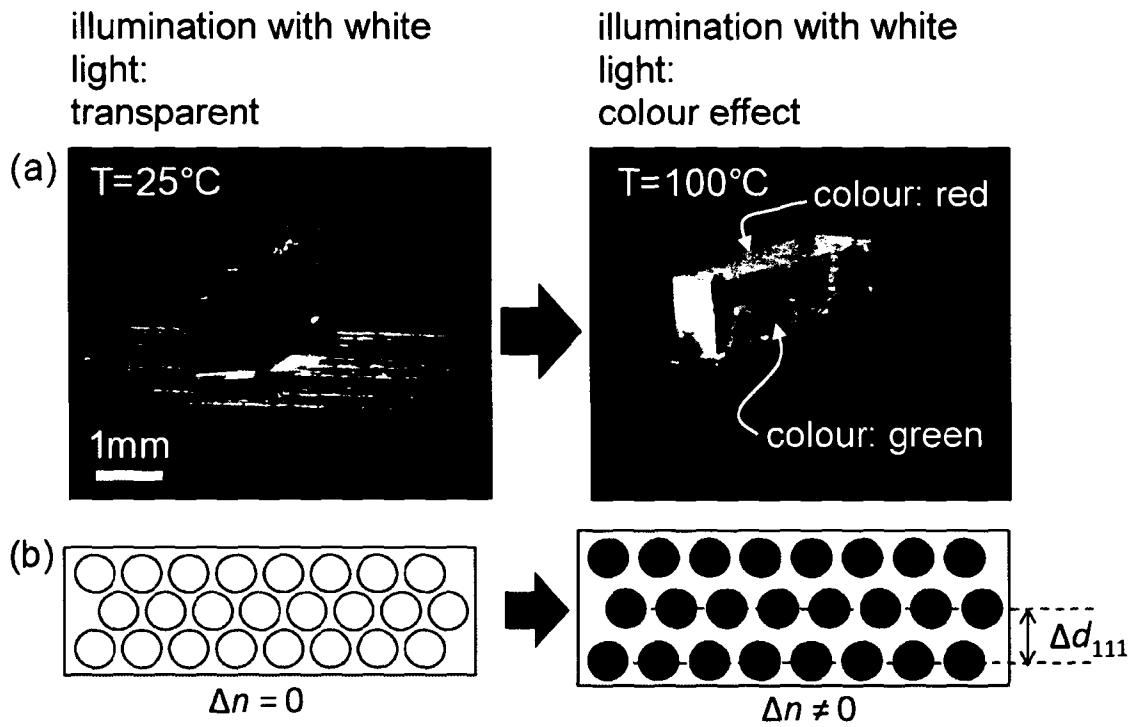
33. A method according to claim 31 or claim 32 wherein the method is carried out at least 40°C above the glass transition temperature of the shell material of the core-shell particles.

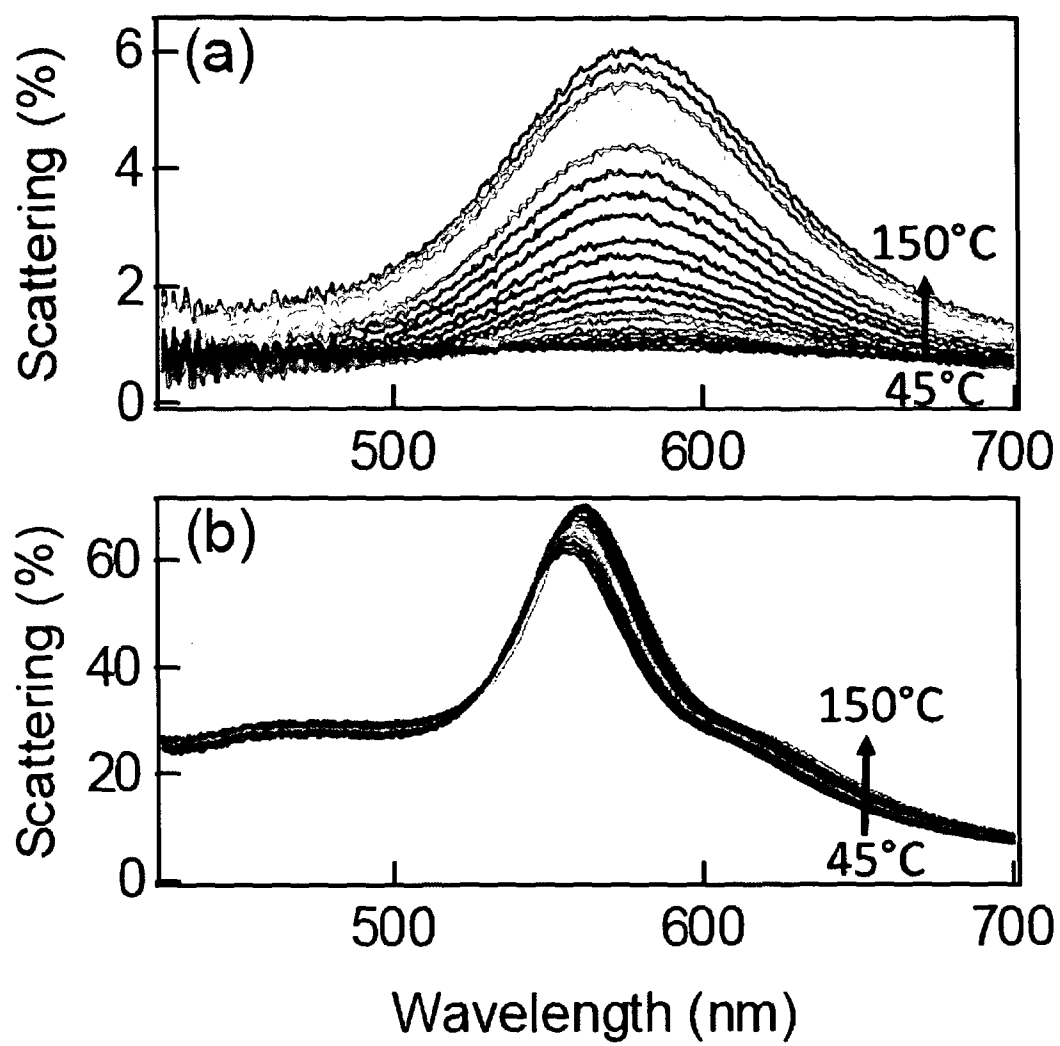
5

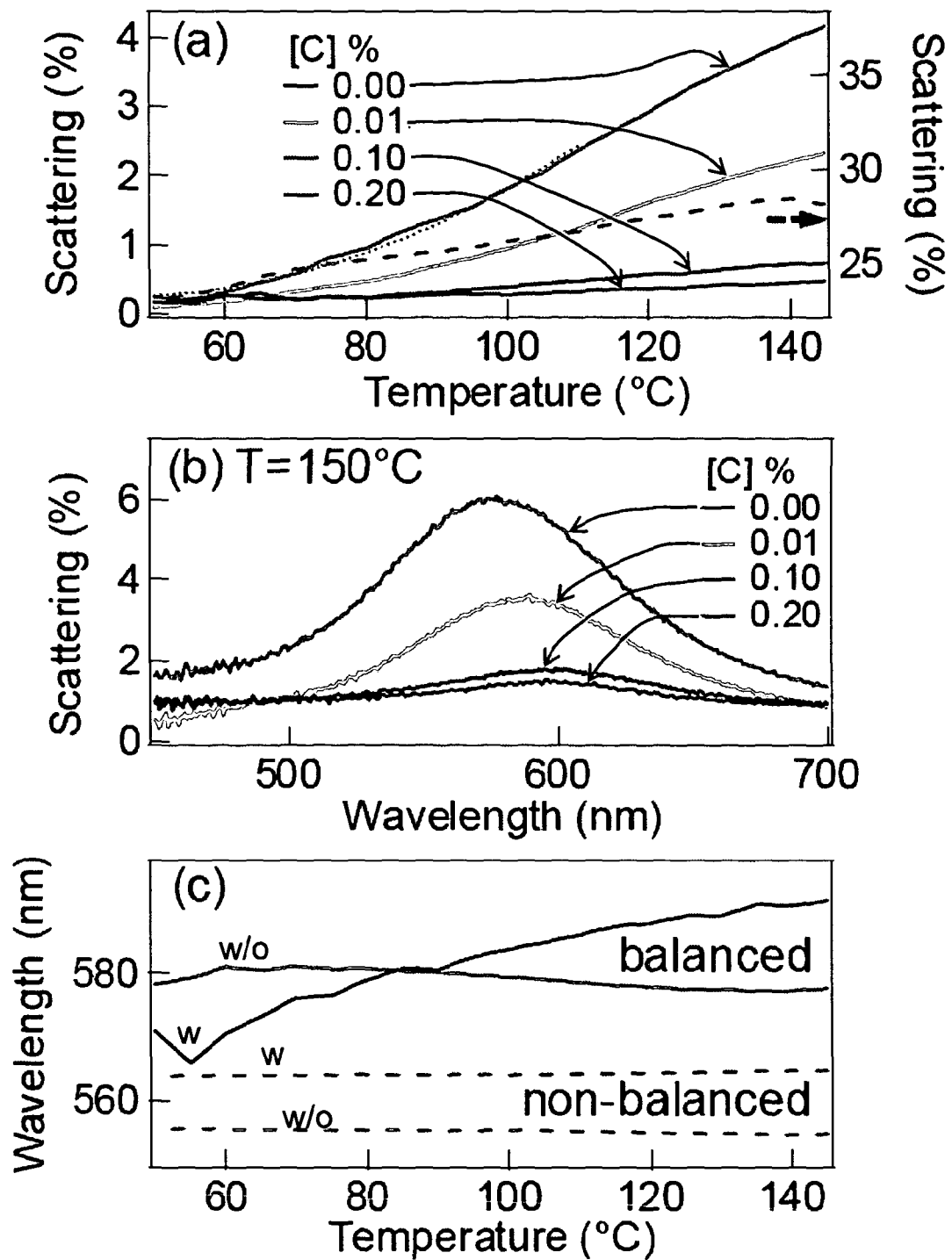
34. A method according to any one of claims 31 to 33 wherein the flowable core-shell particles are cooled under the action of the mechanical force to a temperature at which the shell is no longer flowable.

10 35. A method according to any one of claims 31 to 34 wherein the action of mechanical force takes place via one or more of: uniaxial pressing (e.g. forming a film or plate); injection-moulding; blowing; transfer moulding; extrusion; co-extrusion; calendering; lamination; blowing; fibre-drawing; embossing; and nano-imprinting.

15

**FIG. 1**

**FIG. 2**

**FIG. 3**

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2010/001596

A. CLASSIFICATION OF SUBJECT MATTER

INV. G02F1/01 G02B5/18 G02B5/22

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)

G02B G02F B01D

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

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

EPO-Internal, INSPEC, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 165 389 A (ASHER SANFORD A [US] ET AL) 26 December 2000 (2000-12-26) the whole document	1-35
A	US 2009/034051 A1 (ARSENAULT ANDRE [CA] ET AL ARSENAULT ANDRE [CA] ET AL) 5 February 2009 (2009-02-05) abstract	1,26,31
A	US 2008/030837 A1 (ASHRIT PANDURANG [CA] ET AL) 7 February 2008 (2008-02-07) abstract	1,26,31
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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
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- *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
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- *&* document member of the same patent family

Date of the actual completion of the international search

30 November 2010

Date of mailing of the international search report

29/12/2010

Name and mailing address of the ISA/

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Lehtiniemi, Henry

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2010/001596

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	RAHMAN F ET AL: "Thermochromic effect in synthetic opal/polyaniline composite structures" APPLIED PHYSICS A: MATERIALS SCIENCE & PROCESSING, vol. 94, no. 2, 2 August 2008 (2008-08-02), pages 405-410, XP002612060 SPRINGER BERLIN GERMANY ISSN: 0947-8396 DOI: 10.1007/S00339-008-4822-6 the whole document -----	1,26,31

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/GB2010/001596

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