MATERIAL FUNCTIONALISED WITH A POLYMER

Abstract: The present invention relates to an ink composition comprising a functionalised material, a pH regulating agent, and an aqueous solvent, wherein the functionalised material comprises a carbon material or layered oxide, nitride or transition metal dichalcogenide functionalised with a pH responsive polymer.
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MATERIAL FUNCTIONALISED WITH A POLYMER

TECHNICAL FIELD

The present invention relates to an ink composition comprising a functionalised carbon material, or layered oxide, nitride or transition metal dichalcogenide, a method of preparing it, methods of printing an article with the ink composition and a functionalised material comprising carbon material, or layered oxide, nitride or transition metal dichalcogenide.

BACKGROUND

The field of 3D printing and additive manufacturing for the printing of carbon material-based products is underdeveloped when compared to the printing of polymer or metal products. Printing inks for 3D objects often require complicated formulations with multiple additives, for example dispersants, binders, that are specifically formulated for each material to be printed. The inks also require the fine control of pH, and/or mixtures of volatile solvents. There is therefore a need for simplified inks which have the required resolution and structural stability for printing 3D articles from carbon materials or layered oxides, nitrides or transition metal dichalcogenides.

SUMMARY OF THE INVENTION

It has been determined that an ink composition comprising a carbon material or layered oxide, nitride or transition metal dichalcogenide functionalised with a pH responsive polymer, provides an ink which has the required resolution and structural stability for the printing of 3D articles.

Accordingly, in a first aspect, the present invention provides an ink composition comprising a functionalised material, a pH regulating agent, and an aqueous solvent, wherein the functionalised material comprises a carbon material, layered oxide, nitride or transition metal dichalcogenide functionalised with a pH responsive polymer.

In a second aspect, the present invention provides a method of preparing an ink composition comprising the steps of

(a) preparing a functionalised material according to the first aspect by mixing an aqueous suspension of carbon material, layered oxide, nitride or transition metal dichalcogenide with an aqueous solution of a pH responsive polymer;
(b) adding a pH regulating agent.

In a third aspect, the present invention relates to the use of a composition according to the first aspect as an ink for 3D printing.

In a fourth aspect, the present invention relates to a method of printing a carbon material, layered oxide, nitride or transition metal dichalcogenide article comprising the steps of

(a) preparing an ink composition according to the first aspect;

(b) printing the ink into an article;

(c) drying the printed article; and optionally

(d) curing the printed article.

In a fifth aspect, the present invention relates to an article obtainable by printing a composition according to the first aspect.

In a sixth aspect, the present invention relates to a functionalised material comprising a carbon material, a layered oxide, nitride or transition metal dichalcogenide functionalised with a pH responsive branched polymer.

In a seventh aspect, the present invention relates to a method of preparing the functionalised material according to the sixth aspect, comprising the steps of mixing an aqueous suspension of carbon material, layered oxide, nitride or transition metal dichalcogenide with an aqueous suspension of a pH responsive branched polymer, at a pH of at least 7.

In an eighth aspect, the present invention relates to an aqueous suspension comprising the functionalised material according to the sixth aspect.

**BRIEF DESCRIPTION OF THE FIGURES**

In the context of the following figures, detailed discussion and examples, an exemplary pH-responsive polymer may be referred to as a pH-responsive branched copolymer surfactant (BCS).

Figure 1 is a schematic illustration of the BCS and graphene oxide structures at basic pH.

Figure 2 is a schematic illustration of the structure of BCS-functionalised graphene oxide at basic and acidic pH.

Figure 3(a) shows the adsorption behaviour of BCS on GO sheets at pH 9.
Figure 3(b) shows the Temkin model of the adsorption behaviour of BCS on GO sheets at pH 9.

Figure 4 shows the kinetics of assembly of the BCS-functionalised graphene oxide.

Figure 5 shows the viscoelastic properties of the BCS-GO suspension before assembly.

Figure 6 shows the printing of a filament pile through a 200μm tip, SEM image of the structure of the print and details of the filaments in the structure after thermal reduction after 950 °C in Ar/H₂ (10%) atmosphere.

Figure 7 shows 3D-printed graphene structures using a robotic assisted deposition machine.

Figure 8 shows printed freestanding graphene oxide articles and their microstructure.

Figure 9 shows SEM, Raman spectroscopy and EDS analysis of the graphene oxide printed objects after thermal reduction.

**DETAILED DESCRIPTION**

The following definitions pertain to chemical structures, molecular segments and substituents:

The term "alkyl" as used herein refers to a branched or unbranched saturated hydrocarbon group which may contain from 1 to 20 or 1 to 12 carbon atoms. Preferably, a lower alkyl group contains from 1 to 6, preferably 1 to 4 carbon atoms. Methyl, ethyl and propyl groups are especially preferred. "Substituted alkyl" refers to alkyl substituted with one or more substituent groups. Typical substituent groups include, for example, halogen atoms, nitro, cyano, hydroxyl, cycloalkyl, alkyl, alkenyl, haloalkyl, alkoxy, haloalkoxy, amino, alkylamino, dialkylamino, formyl, alkoxy carbonyl, carboxyl, alkanoyl, alkyldioxy, alkylsulfinyl, alkylsulfonyl, alkylsulfonato, aroylsulfonil, aroylsulfonyl, aroylsulfonato, phosphinyl, phosphinyl, carbamoyl, amido, alkylamido, aryl, aralkyl and quaternary ammonium groups, such as betaine groups. Of these substituent groups, halogen atoms, cyano, hydroxyl, alkyl, haloalkyl, alkoxy, haloalkoxy, amino, carboxyl, amido and quaternary ammonium groups, such as betaine groups, are particularly preferred. When any of the foregoing substituents represents or contains an alkyl or alkenyl substituent group, this may be linear or branched and may contain up to 12, preferably up to 6, and especially up to 4, carbon atoms. A cycloalkyl group may contain from 3 to 8, preferably from 3 to 6, carbon atoms. An aryl group or moiety may contain from 6 to 10 carbon atoms, phenyl groups being especially preferred. A halogen atom may be a fluorine, chlorine, bromine or iodine atom and any group which contains a
halo moiety, such as a haloalkyl group, may thus contain any one or more of these halogen atoms.

Terms such as "(meth) acrylic acid" embrace both methacrylic acid and acrylic acid. Analogous terms should be construed similarly.

Terms such as "alk/aryl" embrace alkyl, alkaryl, aralkyl (e.g. benzyl) and aryl groups and moieties.

Molar percentages are based on the total monofunctional monomer content.

Molecular weights of monomers and polymers are expressed as weight average molecular weights, except where otherwise specified.

An ink composition according to the present invention comprises a functionalised material, a pH regulating agent and an aqueous solvent, wherein the functionalised material comprises a carbon material or a layered oxide, nitride or transition metal dichalcogenide functionalised with a pH responsive polymer.

The functionalised material comprises carbon material or layered oxide, nitride or transition metal dichalcogenide with pH responsive polymer bound thereto. Binding may be covalent, by adsorption of hydrophobic groups to the carbon or layered material, or a combination thereof. Accordingly, the functionalised material may comprise covalent bonding between the carbon material, layered oxide, nitride or transition metal dichalcogenide and the pH responsive polymer.

Carbon materials according to the present invention include, but are not limited to, graphite, graphene, graphene oxide, carbon nanotubes or carbon fullerenes. The carbon material may also include multi-layered material comprising two or more layers of graphene, including graphite nanoplatelets (GNP), chemically modified graphene materials and materials made using graphene or another graphene material as a precursor. Carbon materials may be nanomaterials. Nanomaterials are materials with at least one external dimension in the size range from about 1 to 100 nm. Carbon nanomaterials are carbon materials with at least one external dimension in the size range from about 1 to 100 nm.

Graphene is a single-atom thick sheet of hexagonally arranged, sp²-bonded carbon atoms. Graphene may have a specific surface area of up to 2600 m²/g. Graphite nanoplatelets (GNP) are stacks of graphene sheets. They may have a thickness and/or lateral dimension less than 100 nm. They may be stacks with a total thickness of each graphite platelet of around about 2 nm and an average diameter of 1 to 2 µm. GNP s have a high aspect ratio.
Graphene nanoribbons may be single-atom-thick strips of hexagonally arranged, sp2-bonded carbon atoms and which have a longer lateral dimension which exceeds the shorter lateral dimension by at least an order of magnitude.

Graphene oxide (GO) is an oxidized form of graphene. Graphene oxide may be prepared by oxidation and exfoliation of graphite. Graphene oxide may comprise, for example, at least 20 atomic % oxygen. Graphene oxide may be provided as a multi-layered material comprising two or more layers of oxidized graphene. The graphene oxide may also be exfoliated into individual layers. Graphene oxide may be provided as flakes. Flakes of graphene oxide may comprise single monolayers of graphene oxide or several layers. The flakes may have an average thickness of several nanometres (for example up to 10 nm). The flakes may have an average lateral dimension (maximum diameter) of up to 30 μm, preferably up to 25 μm, for example about 20 μm.

Preferably, the ink composition comprises 0.5 to 5 wt/wt% graphene oxide. More preferably, the composition comprises 2-3 wt/wt% graphene oxide.

Carbon nanotubes, according to the present invention, include, but are not limited to single-wall carbon nanotubes (SWNTs or SWCNTs), double-wall carbon nanotubes (DWNTs or DWCNTs), multi-wall carbon nanotubes (MWNTs or MWCNTs), small diameter carbon nanotubes, large wall carbon nanotubes, and combinations thereof. Carbon nanotubes may be any type of nanotube, that is, it may be any hollow tubular structure having at least one dimension measuring on the nanometer scale. For example, the nanotube may have a smallest inner diameter measuring between about 0.5 nm to about 50 nm, such as about 0.5 nm to about 20 nm, for example between about 0.7 nm to about 10 nm, e.g. between about 0.8 nm to about 2 nm. Small diameter multi-wall carbon nanotubes may be medium-sized carbon nanotubes with diameters of around 5 to 10 nm and lengths of several micrometers.

Large diameter multi-wall carbon nanotubes may be large nanotubes with diameters of around about 100 nm and lengths of several tens of micrometers. The nanotube may be of any length. For example, the nanotube may have a length between about 5 nm to about 2 mm, for example, about 5 to about 500 μm. The nanotube may have a length of 2 mm. The specific surface area of these small diameter multi-wall carbon nanotubes may be around 250 m²/g for 10 nm tubes, and 500 m²/g for 5 nm tubes.

The functionalised material may alternatively comprise a layered material selected from layered oxides, layered nitrides and layered transition metal dichalcogenides. A layered oxide as described herein is a metal (generally a transition metal, such as one or more of Ti, Nb, Mn, Ta, W) oxide material comprising a layered structure. Layered oxides include multi-
layered material comprising two or more layers of oxide or individual oxide layers. The oxide layers may comprise a geometrical, such as octahedral, arrangement of atoms and may comprise alkali metal cations (K⁺, Rb⁺, Cs⁺) occupying the interlayer space. The layered oxides according to the present invention include, but are not limited to, calcium niobium oxide, manganese oxide, niobium oxide, caesium tungsten oxide or molybdenum trioxide. The precursors of the layered oxides may be described as M₀₆ octahedral units where M may be Ti, Nb, Mn, Ta, V, W) and alkali metal cations (K⁺, Rb⁺, Cs⁺) occupying the interlayer space. The layered oxides may be exfoliated into individual layers and thus may be provided as a multi-layered material or as an individual layer.

A layered nitride as described herein is a metal (generally a transition metal such as Ti, Zr, Sr, or metalloid, such as boron) nitride material comprising a layered structure. Layered nitrides include multi-layered material comprising two or more layers of nitrides or individual nitride layers. Layered nitrides may be functionalise with oxygen prior to functionalisation with the pH responsive polymer. An example of a layered nitride is boron nitride.

A layered transition metal dichalcogenide (i.e. comprising ME₂, wherein M is a transition metal e.g. Ti, Nb, Mn, Ta, V, W, Zr, Sr) and E is a chalcogenide, (e.g. S, Se, Te)) may be provided as a multi-layered material or as an individual layer.

A pH responsive polymer is characterised by a reversible response to an external stimuli, i.e. pH. A pH responsive polymer is a polymer whose solubility in a solvent (usually an aqueous solvent) changes dependent upon solution pH. Accordingly, a solution or suspension of a pH responsive polymer will have different rheological properties at different pH values.

The following definitions of the pH responsive polymer apply to all aspects and embodiments of the invention described herein.

The pH responsive polymer may be a copolymer.

The pH responsive polymer may be a branched copolymer.

The pH responsive polymer may comprise at least one residue of a chain transfer agent.

Preferably, the polymer further comprises poly(ethylene glycol) and methacrylic acid residues.

Preferably, the polymer further comprises ethylene glycol dimethacrylate residues.

A chain transfer agent (CTA) is a molecule which may reduce the molecular weight of the polymer during a free-radical polymerisation via a chain transfer mechanism and prevents
polymer gelation. The CTA may be a molecule comprising a thiol group and can be either monofunctional or multifunctional. The CTA may be a hydrophobic monomer. Examples of hydrophobic CTAs include, but are not limited to linear and branched alkyl (e.g. C_{2-18} alkyl) and aryl thiols (e.g. mono- or di-thiols) such as dodecanethiol (DDT), octadecyl mercaptan, 2-methyl-1-butanethiol and 1,9-nonanedithiol. The residue of the chain transfer agent may comprise 0.05 to 30 mole % of the copolymer (based on the number of moles of monofunctional monomer).

The polymer may be, for example, as described in US 2012/0059069, US 2011/0313054, EP 2102256, US 2011/0172314, which are hereby incorporated by reference.

The pH responsive copolymer may comprise

(a) at least one ethylenically monounsaturated monomer;

(b) at least one ethylenically polyunsaturated monomer;

(c) at least one residue of a chain transfer agent;

(d) at least two chains formed from (a) being covalently linked, other than at its ends, by a bridge at residue (b); and wherein

(i) at least one of (a) to (c) comprises a hydrophilic residue;

(ii) at least one of (a) to (c) comprises a hydrophobic residue;

(iii) at least one of (a) to (c) comprises a moiety capable of forming a non-covalent bond with at least one of (a) to (c).

In the present invention, ethylenically monounsaturated monomer may be referred to as "monofunctional monomer". The ethylenically polyunsaturated monomer may be referred to as "multifunctional monomer".

The pH responsive branched copolymer may comprise the general formula (I)
in which

E and E' each independently represent a residue of a chain transfer agent or an initiator;

G and J each independently represent a residue of a monofunctional monomer having one polymerisable double bond per molecule;

L is a residue of a multifunctional monomer having at least two polymerisable double bonds per molecule;

each R, independently, represents a hydrogen atom or an optionally substituted alkyl group;

X and X' each independently represent a terminal group derived from a termination reaction;

g, j and I represent the molar ratio of each residue normalised so that g + j = 100, wherein g and j each independently represent 0 to 100, and I is \( \geq 0.05 \); and m and n are each independently \( \geq 1 \);

at least one of E, E', G, J and L is a hydrophilic residue; and at least one of E, E', G, J and L is a hydrophobic residue.

G may be 0-10, preferably 1 to 10, more preferably 4-6. J may be 90-100, preferably 94-96. L may be 10. Preferably, G may be a poly(ethyleneglycol) residue. J may be a methacrylic acid residue. E and E' may be a residue of dodecanethiol.

Preferably, the polymer may have a composition according to formula (II)
wherein $G'$ is poly(ethylene glycol), $J'$ is carboxyl, $E$ and $E'$ each independently represent a residue of a chain transfer agent or an initiator, $X$ and $X'$ each independently represent a terminal group derived from a termination reaction, $L$ is ethyleneglycoldiester, and $g$, $j$, $i$, $m$ and $n$ are as defined for formula (I).

g may be 0-10, preferably 4-6. $J$ may be 90-100, preferably 94-96. $L$ may be 10. Preferably, $G$ may be a poly(ethyleneglycol) residue. $J$ may be a methacrylic acid residue. $E$ and $E'$ may be a residue of dodecanethiol.

The monofunctional monomer may comprise any carbon-carbon unsaturated compound which can be polymerised by an addition polymerisation mechanism, for example vinyl and allyl compounds. The monofunctional monomer may be hydrophilic, hydrophobic, amphiphilic, anionic, cationic, neutral or zwitterionic in nature. The monofunctional monomer may be selected from but not limited to monomers such as vinyl acids, vinyl acid esters, vinyl aryl compounds, vinyl acid anhydrides, vinyl amides, vinyl ethers, vinyl amines, vinyl aryl amines, vinyl nitriles, vinyl ketones, and derivatives of the aforementioned compounds as well as corresponding allyl variants thereof. Other suitable monofunctional monomers include hydroxyl-containing monomers and monomers which can be post-reacted to form hydroxyl groups, acid-containing or acid-functional monomers, zwitterionic monomers and quaternised amino monomers. Oligomeric, polymeric and di- or multi-functionalised monomers may also be used, especially oligomeric or polymeric (meth)acrylic acid esters such as mono(alk/aryl) (meth)acrylic acid esters of polyalkyleneglycol or polydimethylsiloxane or any other mono-vinyl or allyl adduct of a low molecular weight oligomer. Mixtures of more than one monomer may also be used to give statistical, graft,
gradient or alternating copolymers. Thus, G and J each independently represent a residue of a monofunctional monomer as described above.

Vinyl acids and derivatives thereof include (meth)acrylic acid, fumaric acid, maleic acid, itaconic acid and acid halides thereof such as (meth)acryloyl chloride. Vinyl acid esters and derivatives thereof include C₅₋₇alkyl(meth)acrylates (linear and branched) such as methyl(meth)acrylate, stearyl(meth)acrylate and 2-ethyl hexyl(meth) acrylate aryl(meth)acrylates such as benzyl(meth)acrylate, tri(alkoxy)silylalkyl(meth)acrylates such as trimethoxysilylpropyl(meth)acrylate and activated esters of (meth)acrylic acid such as N-hydroxysuccinamido(meth)acrylate. Vinyl aryl compounds and derivatives thereof include: styrene, acetoxy styrene, styrene sulfonic acid, vinyl pyridine, vinlybenzyl chloride and vinyl benzoic acid. Vinyl acid anhydrides and derivatives thereof include maleic anhydride. Vinyl amides and derivatives thereof include (meth)acrylamide, N-(2-hydroxypropyl)methacrylamide, N-vinyl pyrrolidone, N-vinyl formamide, (meth)acrylamidopropyl trimethyl ammonium chloride, [3-((meth) unctional)propyl]dimethyl ammonium chloride, 3-[N-(3-(meth)acrylamidopropyl)-N,N-dimethyl]aminopropane sulfonate, methyl (meth)acrylamido glycolate methyl ether and N-isopropyl(meth)acrylamide. Vinyl ethers and derivatives thereof include methyl vinyl ether. Vinyl amines and derivatives thereof include: dimethylaminoethyl(meth)acrylate, diethylaminoethyl(meth)acrylate, diisopropylaminoethyl(meth)acrylate, mono-t-butylaminoethyl(meth)acrylate, morpholinoethyl(meth)acrylate and monomers which can be post-reacted to form amine groups, such as vinyl formamide. Vinyl aryl amines and derivatives thereof include: vinyl aniline, vinyl pyridine, N-vinyl carbazole and vinyl imidazole. Vinyl nitriles and derivatives thereof include (meth)acrylonitrile. Vinyl ketones and derivatives thereof include acrolein.

Hydroxyl-containing monomers include: vinyl hydroxyl monomers such as hydroxyethyl (meth)acrylate, unctional propyl (meth)acrylate, glycerol mono(meth)acrylate and sugar mono(meth)acrylates such as glucose mono(meth)acrylate. Monomers which can be post-reacted to form hydroxyl groups include vinyl acetate, acetoxy styrene and glycidyl (meth)acrylate. Acid-containing or acid functional monomers include: (meth)acrylic acid, styrene sulfonic acid, vinyl phosphonic acid, vinyl benzoic acid, maleic acid, fumaric acid, itaconic acid, 2-(meth) unctional 2-ethyl propanesulfonic acid, mono-2-((meth)acryloyloxy)ethyl succinate and ammonium sulfatoethyl (meth)acrylate. Zwitterionic monomers include (meth)acryloyl oxyethylphosphoryl choline and betaines, such as [2-((meth)acryloyloxy)ethyl]dimethyl-(3-sulfo propyl)ammonium hydroxide. Quaternised amino monomers include (meth)acryloyloxyethyltri-(alkylaryl) ammonium halides such as
(meth)acryloyloxyethyltrimethyl ammonium chloride.

Oligomeric and polymeric monomers include oligomeric and polymeric (meth)acyric acid esters such as mono(alk/aryl)oxypolyalkyleneglycol(meth)acrylates and mono(alklaryl)oxypolydimethyl-siloxane(meth)acrylates. These esters include: monomethoxy oligo(ethylene glycol) mono(meth)acrylate, monomethoxyoligo(propyleneglycol) mono(meth)acrylate, monohydroxy oligo(ethylene glycol) mono(meth)acrylate, monomethoxy poly(ethylene glycol) mono(meth)acrylate, monomethoxy poly(propyleneglycol) mono(meth)acrylate, monohydroxy poly(ethylene glycol) mono(meth)acrylate and monohydroxy poly(propyleneglycol) mono(meth)acrylate. Further examples include: vinyl or allyl esters, amides or ethers of pre-formed oligomers or polymers formed via ring-opening polymerisation such as oligo(caprolactam), oligo(caprolactone), poly(caprolactam) or poly(caprolactone), or oligomers or polymers formed via a living polymerisation technique such as poly(1,4-butadiene).

The corresponding allyl monomers to those listed above can also be used where appropriate.

Examples of monofunctional monomers are: amide-containing monomers such as (meth)acrylamide, N-(2-hydroxypropyl)methacrylamide, N,N’-dimethyl(meth)acrylamide, N and/or N’-di(alkyl or aryl) (meth)acrylamide, N-vinyl pyrrolidone, [3-((meth)unctional) propyl] trimethyl ammonium chloride, 3-(dimethylamino)propyl(meth)acrylamide, 3[N-(3-(meth)acrylamidopropyl)-N,N-diethyl]aminopropane sulfonate, methyl(meth)acrylamidoglycololate methyl ether and N-isopropyl(meth)acrylamide; (Meth)acrylic acid and derivatives thereof such as (meth)acrylic acid, (meth)acryloyl chloride (or any halide), (alkyl/aryl)(meth)acrylate, functionalised oligomeric or polymeric monomers such as monomethoxy oligo(ethylene glycol) mono(meth)acrylate, monomethoxy oligo(propyleneglycol) mono(meth)acrylate, monohydroxy oligo(ethylene glycol) mono(meth)acrylate, monohydroxy oligo(propyleneglycol) mono(meth)acrylate. Monomethoxy poly(ethylene glycol) mono(meth)acrylate, monomethoxy poly(propyleneglycol) mono(meth)acrylate, monohydroxy poly(ethylene glycol) mono(meth)acrylate, monohydroxy poly(propyleneglycol) mono(meth)acrylate. Glycerol mono(meth)acrylate and sugar mono(meth)acrylates such as glucose mono(meth)acrylate; vinyl amines such as aminoethyl (meth)acrylate, dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, diisopropylaminoethyl (meth)acrylate, mono-tbutylamino
(meth)acrylate, morpholinoethyl(meth)acrylate, vinyl aryl amines such as vinyl aniline, vinyl pyridine, N-vinyl carbazole, vinyl imidazole, and monomers which can be post-reacted to form amine groups, such as vinyl formamide; vinyl aryl monomers such as styrene, vinyl benzyl chloride, vinyl toluene, cx-methyl styrene, styrene sulfonic acid and vinyl benzoic acid; vinyl hydroxyl monomers such as hydroxyethyl (meth)acrylate, function propyl (meth)acrylate, glycerol mono(meth)acrylate or monomers which can be post-functionalised into hydroxyl groups such as vinyl acetate, acetoxy styrene and glycidyl(meth)acrylate; acid-containing monomers such as (meth)acrylic acid, styrene sulfonic acid, vinyl phosphonic acid, vinyl benzoic acid, maleic acid, fumaric acid, itaconic acid, 2-

(meth)functional 2-ethylpropanesulfonic acid and mono-2-((meth)acyloyloxy)ethyl succinate or acid anhydrides such as maleic anhydride; zwitterionic monomers such as (meth)acyloyl oxyethylphosphoryl choline and betainecontaining monomers, such as [2-((meth)acyloyloxy)ethyl]dimethyl-(3-sulfopropyl)ammonium hydroxide; quaternised amino monomers such as (meth)acyloyloxyethyltrimethyl ammonium chloride.

The corresponding allyl monomer, where applicable, can also be used in each case.

Functional monomers, that is monomers with reactive pendant groups which can be post or pre-modified with another moiety following polymerisation can also be used such as glycidyl (meth)acrylate, tri(alkoxy)silylalkyl (meth)acrylates such as trimethoxysilylpropyl(meth)acrylate, (meth)acyloyl chloride, maleic anhydride, hydroxyalkyl (meth)acrylates, (meth)acrylic acid, vinylbenzyl chloride, activated esters of (meth)acrylic acid such as N-hydroxysuccinamido m(meth)acrylate and acetoxy-styrene.

Functional monomers, that is monomers with reactive pendant groups which can be post or pre-modified with another moiety following polymerisation can also be used such as glycidyl (meth)acrylate, tri(alkoxy)silylalkyl (meth)acrylates such as trimethoxysilylpropyl(meth)acrylate, (meth)acyloyl chloride, maleic anhydride, hydroxyalkyl (meth)acrylates, (meth)acrylic acid, vinylbenzyl chloride, activated esters of (meth)acrylic acid such as N-hydroxysuccinamido m(meth)acrylate and acetoxy-styrene.

When the monofunctional monomer is providing the necessary hydrophilicity in the copolymer, it is preferred that the monofunctional monomer is a residue of a hydrophilic monofunctional monomer, preferably having a molecular weight of at least 1000 Daltons.

Macromonomers (monomers having a molecular weight of at least 1000 Daltons) are generally formed by linking a polymerisable moiety, such as a vinyl or allyl group, to a pre-
formed monofunctional polymer via a suitable linking unit such as an ester, an amide or an ether. Examples of suitable polymers include mono functional poly (alkylene oxides) such as monomethoxy [poly (ethylene glycol) ] or monomethoxy [poly (propylene glycol) ] , silicones such as poly (dimethylsiloxane) s, polymers formed by ring-opening polymerisation such as poly (caprolactone) or poly (caprolactam) or mono-functional polymers formed via living polymerisation such as poly (1, 4-butadiene).

Preferred macromonomers include monomethoxy [poly (ethylene glycol) ] mono (methacrylate) , monomethoxy [poly (propylene glycol) ] mono (methacrylate) and mono (meth) acryloxypropyl-terminated poly (dimethylsiloxane).

When the monofunctional monomer is providing the necessary hydrophilicity in the copolymer, it is preferred that G and/or J is a residue of a hydrophilic monofunctional monomer, preferably having a molecular weight of at least 1000 Daltons.

Hydrophilic monofunctional monomers contain hydrogen bonding and/or permanent or transient charges. Hydrophilic monofunctional monomers include (meth) acryloyl chloride, N-hydroxysuccinamido (meth) acrylate, styrene sulfonic acid, maleic anhydride, (meth) acrylamide, N- (2- hydroxypropyl) methacrylamide, N-vinyl pyrroldinone, N- vinyl formamide, quaternised amino monomers such as (meth) acrylamidopropyl trimethyl ammonium chloride, [3- (meth) unfunctional propyl] trimethyl ammonium chloride and (meth) acryloyloxyethyltrimethyl ammonium chloride, 3- [N- (3- (meth) acrylamidopropyl) -N, N-dimethyl] aminopropane sulfonate, methyl (meth) acrylamidoglycolate methyl ether, glycerol mono (meth) acrylate, monomethoxy and monohydroxy oligo (ethylene oxide) (meth) acrylate, sugar mono (meth) acrylates such as glucose mono (meth) acrylate, (meth) acrylic acid, styrene sulfonic acid, vinyl phosphonic acid, fumaric acid, itaconic acid, 2- (meth) unfunctional 2- ethyl propanesulfonic acid, mono-2- ( (meth) acryloyloxy) ethyl succinate, ammonium sulfatoethyl (meth) acrylate, (meth) acryloyl oxyethylphosphoryl choline and betaine- containing monomers such as [2- ( (meth) acryloyloxy) ethyl] dimethyl- (3-sulfo propyl) ammonium hydroxide. Hydrophilic macromonomers may also be used and include monomethoxy and monohydroxy poly (ethylene oxide) (meth) acrylate and other hydrophilic polymers with terminal functional groups which can be post-functionalised with a polymerisable moiety such as (meth) acrylate, (meth) acrylamide or styrenic groups. Hydrophobic monofunctional monomers include C₆₋₂₀ alkyl (meth) acrylates (linear and branched and (meth) acrylamides, such as methyl (meth) acrylate and stearyl (meth) acrylate, aryl (meth) acrylates such as benzyl (meth) acrylate, tri (alkyloxy) silylalkyl (meth)
acrylates such as trimethoxysilylpropyl (meth) acrylate, styrene, acetoxy styrene, vinyl benzyl chloride, methyl vinyl ether, vinyl formamide, (meth) acrylonitrile, acrewlin, 1- and 2-hydroxy propyl (meth) acrylate, vinyl acetate, glycidyl (meth) acrylate and maleic acid. Hydrophobic macromonomers may also be used and include monomethoxy and monohydroxy poly (butylene oxide) (meth) acrylate and other hydrophobic polymers with terminal functional groups which can be post-functionalised with a polymerisable moiety such as (meth) acrylate, (meth) acrylamide or styrenic groups.

Hydrophilic monofunctional monomers include: (meth) acryloyl chloride, N-hydroxysuccinamido (meth) acrylate, styrene sulfonic acid, maleic anhydride, (meth) acrylamide, N-(2-hydroxypropyl)methacrylamide, N-vinyl pyrrolidinone, N-vinyl formamide, quaternised amino monomers such as (meth)acrylamidopropyl trimethyl ammonium chloride, [3-((meth)acrylamido)propyl]trimethyl ammonium chloride and (meth)acryloyloxyethyltrimethyl ammonium chloride, 3-[N-(3-(meth)acrylamidopropyl)-N,N-dimethyljaminopropane sulfonate, methyl (meth) acrylamidoglycolate methyl ether, glycerol mono(meth)acrylate, monomethoxy and monohydroxy oligo(ethylene oxide) (meth) acrylate, sugar mono(meth)acrylates such as glucose mono(meth)acrylate, (meth) acrylic acid, vinyl phosphoric acid, fumaric acid, itaconic acid, 2-(meth)acrylamido 2-ethyl propanesulfonic acid, mono-2-((meth)acryloyloxy)ethyl succinate, ammonium sulfatoethyl (meth)acrylate, (meth)acryloyl oxyethylphosphoryl choline and betaine-containing monomers such as [2-((meth)acryloyloxy)ethylj dimethyl-(3-sulfopropyl)ammonium hydroxide. Hydrophilic macromonomers may also be used and include monomethoxy and monohydroxy poly(ethylene oxide) (meth) acrylate and other hydrophilic polymers with terminal functional groups which can be post-functionalised with a polymerisable moiety such as (meth) acrylate, (meth) acrylamide or styrenic groups.

Hydrophobic monofunctional monomers include C_1-C_25 alkyl(meth)acrylates (linear and branched and (meth)acrylamides, such as methyl(meth)acrylate and stearyl(meth)acrylate, aryl(meth)acrylates such as benzyl(meth)acrylate, trimethoxy(silylalkyl(meth)acrylates such as tri-methoxy(silylpropyl)(meth)acrylate, styrene, acetoxy styrene, vinyl benzyl chloride, methyl vinyl ether, vinyl formamide, (meth) acrylonitrile, acrewlin, 1- and 2-hydroxy propyl(meth)acrylate, vinyl acetate, and glycidyl(meth)acrylate. Hydrophobic macromonomers may also be used and include monomethoxy and monohydroxy poly(butylene oxide) (meth)acrylate and other hydrophobic polymers with terminal functional groups which can be post-functionalised with a polymerisable moiety such as (meth) acrylate, (meth) acrylamide or styrenic groups.
Responsive monofunctional monomers include (meth)acrylic acid, 2- and 4-vinyl pyridine, vinyl benzoic acid, N-isopropyl(meth)acrylamide, tertiary amine (meth)acrylates and (meth)acrylamides such as 2-(dimethyl)aminoethyl (meth)acrylate, 2-(diethylamino)ethyl (meth)acrylate, diisopropylaminoethyl (meth)acrylate, mono-t-butyraminoethyl (meth)acrylate and N-morpholinoethyl (meth)acrylate, vinyl aniline, vinyl pyridine, N-vinyl carbazole, vinyl imidazole, hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, maleic acid, fumaric acid, itaconic acid and vinyl benzoic acid. Responsive macromonomers may also be used and include monomethoxy and monohydroxy poly(propylene oxide) (meth)acrylate and other responsive polymers with terminal functional groups which can be post-functionalised with a polymerisable moiety such as (meth)acrylate, (meth)acrylamide or styrenic groups.

The multifunctional monomer or brancher may comprise a molecule containing at least two vinyl groups which may be polymerised via addition polymerisation. The molecule may be hydrophilic, hydrophobic, amphiphilic, neutral, cationic, zwitterionic, oligomeric or polymeric. Such molecules are often known as cross-linking agents in the art and may be prepared by reacting any di- or multifunctional molecule with a suitably reactive monomer. Examples include di- or multivinyl esters, di- or multivinyl amides, di- or multivinyl aryl compounds, di- or multivinyl alkaryl ethers. Typically, in the case of oligomeric or polymeric di- or multifunctional branching agents, a linking reaction is used to attach a polymerisable moiety to a di- or multifunctional oligomer or polymer. The brancher may itself have more than one branching point, such as T-shaped divinyl oligomers or polymers. In some cases, more than one multifunctional monomer may be used. When the multifunctional monomer is providing the necessary hydrophilicity in the copolymer, it is preferred that the multifunctional monomer has a molecular weight of at least 1000 Daltons.

The corresponding allyl monomers to those listed above can also be used where appropriate.

Preferred multifunctional monomers include but are not limited to divinyl aryl monomers such as divinyl benzene; (meth)acrylate diesters such as ethylene glycol di(meth)acrylate, propyleneglycol di(meth)acrylate and 1,3-butylenedi(meth)acrylate; polyalkylene oxide di(meth)acrylates such as tetraethyleneglycol di(meth)acrylate, poly(ethyleneglycol) di(meth)acrylate and poly(propyleneglycol) di(meth)acrylate; divinyl (meth)acrylamides such as methylene bisacrylamide; silicone-containing divinyl esters or amides such as (meth)acryloxypropyl-terminated poly(dimethylsiloxane); divinyl ethers such as
poly(ethyleneglycol)divinyl ether; and tetra- or tri-(meth)acrylate esters such as
pentaerythritol tetra(meth)acrylate, trimethylolpropane tri(meth) acrylate or glucose di-
to penta(meth)acrylate. Further examples include vinyl or ally esters, amides or ethers of pre-
formed oligomers or polymers formed via ring-opening polymerisation such as
oligo(caprolactam), oligo(caprolactone), poly(caprolactam) or poly(caprolactone), or
oligomers or polymers formed via a living polymerisation technique such as oligo- or
poly(1,4-butadiene). Macrocrosslinkers or macrobranchers (multifunctional monomers
having a molecular weight of at least 1000 Daltons) are generally formed by linking a
polymerisable moiety, such as a vinyl or aryl group, to a pre-formed multifunctional polymer
via a suitable linking unit such as an ester, an amide or an ether. Examples of suitable
polymers include di-functional poly(alkylene oxides) such as poly(ethyleneglycol) or
poly(propyleneglycol), silicones such as poly(dimethysiloxane)s, polymers formed by ring-
opening polymerisation such as poly(caprolactone) or poly(caprolactam) or polyfunctional
polymers formed via living polymerisation such as poly(1,4-butadiene).

Macrocrosslinkers or macrobranchers (multifunctional monomers having a molecular weight
of at least 1000 Daltons) are generally formed by linking a polymerisable moiety, such as a
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(alkylene oxides) such as poly (ethyleneglycol) or poly (propyleneglycol) , silicones such as
poly (dimethysiloxane) s, polymers formed by ring- opening polymerisation such as poly
(caprolactone) or poly (caprolactam) or poly-functional polymers formed via living
polymerisation such as poly (1, 4-butadiene).

Preferred macrobranchers include poly (ethyleneglycol) di (meth) acrylate, poly
(propyleneglycol) di (meth) acrylate, methacryloxypropyl-terminated poly (dimethysiloxane),
poly (caprolactone) di (meth) acrylate and poly (caprolactam) di (meth) acrylamide.

Preferred macrobranchers include poly(ethyleneglycol) di(meth)acrylate,
poly(propyleneglycol) di(meth)acrylate, methacryloxypropyl-terminated
poly(dimethysiloxane), poly(caprolactone) di(meth)acrylate and poly(caprolactam)
di(meth)acrylamide.

Hydrophilic branchers contain hydrogen bonding and/or permanent or transient charges.
Hydrophilic branchers include methylene bisacrylamide, glycerol di (meth) acrylate, glucose
di- and tri (meth) acrylate, oligo (caprolactam) and oligo (caprolactone). Multi end-
functionalised hydrophilic polymers may also be functionalised using a suitable
polymerisable moiety such as a (meth) acrylate, (meth) acrylamide or styrenic group.

Hydrophobic branchers include divinyl benzene, (meth) acrylate esters such as ethyleneglycol di (meth) acrylate, propyleneglycol di (meth) acrylate and 1,3- butylene di (meth) acrylate, oligo (ethylene glycol) di (meth) acrylates such as tetraethylene glycol di (meth) acrylate, tetra- or tri- (meth) acrylate esters such as pentaerythritol tetra (meth) acrylate, trimethylolpropane tri (meth) acrylate and glucose penta (meth) acrylate. Multi end-functionalised hydrophobic polymers may also be functionalised using a suitable polymerisable moiety such as a (meth) acrylate, (meth) acrylamide or styrenic group.

Branchers include: methylene bisacrylamide, glycerol di(meth)acrylate, glucose di- and tri(meth)acrylate, oligo(caprolactam) and oligo(caprolactone). Multi end-functionalised hydrophilic polymers may also be functionalised using a suitable polymerisable moiety such as a (meth)acrylate, (meth)acrylamide or styrenic group.

Further branchers include: divinyl benzene, (meth)acrylate esters such as ethyleneglycol di(meth)acrylate, propyleneglycol di(meth)acrylate and 1,3-butylene di(meth)acrylate, oligo(ethylene glycol) di(meth)acrylates such as tetraethylene glycol di(meth)acrylate, tetra- or tri-(meth)acrylate esters such as pentaerythritol tetra(meth)acrylate, trimethylolpropane tri(meth)acrylate and glucose penta(meth)acrylate. Multi end-functionalised hydrophobic polymers may also be functionalised using a suitable polymerisable moiety such as a (meth)acrylate, (meth)acrylamide or styrenic group.

Branched polymers are polymers comprising at least two non-linearly linked polymer chains, i.e. with a structure comprising a polymer chain and at least one further polymeric chain branching off the main chain.

Branched polymers of the invention are polymer molecules which are engineered to have a finite size. Branched polymers are soluble addition polymers and include statistical, graft, gradient and alternating branched polymers. Cross-linked polymers, unlike branched polymers of the invention, generally grow while monomers are available and can be arbitrarily large. Cross-linked polymers generally form gels.

Branched polymers according to the present invention are obtainable by an addition polymerization process. An addition polymerisation process may be a conventional free-radical polymerisation method. A branched copolymer may be prepared using a free-radical polymerisation method by polymerising a monofunctional monomer with a multifunctional monomer in the presence of a chain transfer agent and a free radical initiator. Preferably,
the molar ratio of the multifunctional monomer to the monofunctional monomer is between 0.0005 and 1.

Multifunctional responsive polymers may also be functionalised using a suitable polymerisable moiety such as a (meth)acrylate, (meth)acrylamide or styrenic group such as polypropylene oxide di(meth)acrylate.

Thus, L is a residue of a multifunctional monomer as described above. The copolymer must contain a multifunctional monomer. In other words, \( l \) is \( \geq 0.05 \) in formula (I). It is preferably 0.05 to 50, more preferably 0.05 to 40, particularly 0.05 to 30 and especially 0.05 to 15.

It is preferred that \( R \) and \( R' \) in formula (I) each independently represent a hydrogen atom or an optionally substituted lower alkyl group (preferably an unsubstituted \( \text{C}_{1-4} \) alkyl group).

X and \( X' \) each independently represent a terminal group derived from a termination reaction. During conventional radical polymerisation, some inherent and unavoidable termination reactions occur. Common termination reactions between free-radicals are typically bimolecular combination and disproportionation reactions which vary depending on the monomer structure and result in the annihilation of two radicals. Disproportionation reactions are thought to be the most common, especially for the polymerisation of (meth) acrylates, and involve two dead primary chains, one with a hydrogen terminus (\( X \) or \( X = \text{H} \)) and the other with a carbon-carbon double bond (\( X \) or \( X = -\text{C} = \text{CH}_2 \)). When the termination reaction is a chain transfer reaction, \( X \) or \( X' \) is typically an easily abstractable atom, commonly hydrogen. Thus, for instance, when the chain transfer agent is a thiol, \( X \) and/or \( X' \) can be a hydrogen atom.

As will be apparent from formula (I), \( m + l \) equals the number of polymerisable groups in \( L \) and \( n \) is the total number of repeat units in the copolymer. Preferably, \( m \) is 1 to 6, more preferably 1 to 4.

A preferred branched pH responsive copolymer may comprise at least two ethylenically monounsaturated monomers, wherein one of the ethylenically monounsaturated monomers is (meth)acrylic acid or a (meth)acrylic acid derivative, and wherein one of the ethylenically monounsaturated monomers is a poly(ethyleneglycol)(meth)acrylate or a poly(ethyleneglycol) derivative.

A preferred branched pH responsive copolymer according to the invention may be a branched copolymer comprising residues of the ethylenically monounsaturated monomer
methacrylic acid (MAA) and polyethylene glycol methacrylate (PEGMA), the ethyleneically polyunsaturated monomer ethyleneglycol dimethacrylate (EGDMA), and the chain transfer agent dodecanethiol (DDT).

pH responsive copolymers may be described using the following nomenclature:

\[(\text{monofunctional monomer } G)_g (\text{monofunctional monomer } J)_j (\text{multifunctional monomer } L)_i (\text{chain transfer agent})_d\]

wherein the values in subscript are the molar ratios of each constituent normalised to give the monofunctional monomer value as 100, that is, \(g + j = 100\). The degree of branching is denoted by \(i\). The subscript \(d\) refers to the molar ratio of the chain transfer agent.

In one embodiment, the monofunctional monomer \(G\) may be PEGMA, the monofunctional monomer \(J\) may be MAA, the multifunctional monomer \(L\) may be EGDMA, and the chain transfer agent may be DDT.

In a preferred embodiment, the polymer may be

\[\text{PEGMA}_g\text{MAA}_j\text{EGDMA}_i\text{DDT}_d\]

wherein \(g\) may be 4-6, \(j\) may be 94-96, \(i\) may be 10 and \(d\) may be 10. In a more preferred embodiment, the polymer may be \(\text{PEGMA}_g\text{MAA}_{85}\text{EGDMA}_{10}\text{DDT}_{10}\).

Preferably, the polymer has the formula \(\text{MFM}_{10}\text{EDGMA}_{10}\text{DDT}_{10}\), wherein \(\text{MFM}\) is a monofunctional monomer and is nominally set to a molar value of 100, and EGDMA is present in molar equivalent of 10 relative to the total \(\text{MFM}\). More preferably, the \(\text{MFM}\) may be methacrylic acid, poly(ethylene glycol) methacrylate, or mixtures thereof.

The initiator is a free-radical initiator and can be any molecule known to initiate free-radical polymerisation such as azo-containing molecules, persulfates, redox initiators, peroxides, benzyl ketones. These may be activated via thermal, photolytic or chemical means. Examples of these include but are not limited to 2, 2'-azobisisobutyronitrile (AIBN), azobisisobutyronitrile (4-cyanovaleric acid), benzoyl peroxide, cumylperoxide, 1-hydroxycyclohexyl phenyl ketone, hydrogenperoxide/ascorbic acid. Initiators such as benzyl- \(\text{N}\), N-diethylthiocarbamate can also be used. In some cases, more than one initiator may be used. The initiator may be a macroinitiator having a molecular weight of at least 1000 Daltons. In this case, the macroinitiator may be hydrophilic or hydrophobic. Preferably, the residue of the initiator in a free-radical polymerisation comprises 0 to 5% w/w, preferably 0.01 to 5% w/w and especially 0.01 to 3% w/w, of the copolymer based on the total weight of the monomers.
The use of a chain transfer agent and an initiator is preferred. However, some molecules can perform both functions.

The non-covalent bond in the branched polymer may be a hydrogen bond. The non-covalent bond may be formed by Van der Waal forces, by ionic interactions, or by pi-pi interactions.

In a preferred embodiment, the copolymers comprise a functionality that can hydrogen-bond with each other in response to external stimulus. This hydrogen-bonding requires the presence of hydrogen-bonding donor and acceptor groups of the branched copolymer. An example of a branched copolymer capable of hydrogen bonding comprises ethyleneglycol and meth(acrylic) acid residues.

The copolymer may be responsive to a change in external stimulus. Preferably, the stimulus is a change in pH. The change in pH allows a change in the properties, for example the rheological properties, of the polymer in an aqueous solution. For example, in their neutral form, the polymers are dehydrated, compact and non-hydrophobic. In their ionic form, they are hydrated, swollen and hydrophilic. The change in pH allows the ionisation or deionisation of the moieties on the polymer by protonating or deprotonating them. For example, carboxylic moieties may be deprotonated at high pH, leading to an increased electrostatic interaction between the branches. When the polymer is covalently bound to a particle, this allows an electrostatic interaction at high pH to occur between the positively charged particle surface.

The aqueous solvent may be water or a mixed solvent system comprising water and one or more other solvents (which are preferably miscible with water). Preferably, the solvent is water. An aqueous solvent enables the full formation of hydrogen bonds to obtain a change in the rheological properties of the functionalised material. Small amounts of organic solvent, for example methanol or ethanol, may be used.

The pH regulating agent is any substance which when dissolved in aqueous solution alters the pH of the solution. It may be an acid or a base or a compound which dissolves in aqueous solution to form an acid or base (i.e. by hydrolysis). Preferably, the pH regulating agent is an acid or a compound which dissolves to form an acid. In a preferred embodiment, the pH regulating agent may be a sugar acid or a compound which dissolves in aqueous solution form a sugar acid. The ink composition may comprise a graphene oxide to glucono-
δ-lactone ratio of 0.1 to 5, preferably, the graphene oxide to glucono-5-lactone ratio is 1:6 (by weight).

A more preferred embodiment comprises glucono-0-lactone as a pH regulating agent. The glucono-5-lactone dissolves to gluconic acid and then the gluconic acid drops the pH. This leads to a homogenous drop of pH. Preferably, the ink composition comprises 0.1 to 10 wt/wt% glucono-5-lactone/GO. More preferably, the composition comprises 0.2 to 5 wt/wt% glucono-5-lactone. Preferably, the composition comprises 1 to 4 wt/v% glucono-5-lactone. More preferably, the composition comprises a graphene oxide to glucono-5-lactone ratio of 1:6.

The ink compositions may be prepared by mixing an aqueous suspension of carbon material, layered oxide, nitride or transition metal dichalcogenide with an aqueous solution of BCS. The pH of the resulting mixture may be adjusted to at least 7 and the mixture may be stirred for at least 10 minutes. In one embodiment, the pH is adjusted to at least 9. In one embodiment, the mixture may be stirred for at least 30 minutes. The mixture may be stirred for up to 4 hours, preferably up to 60 minutes.

To further eliminate bubbles, the BCS/functionaldised carbon material, layered oxide, nitride or transition metal dichalcogenide/pH regulating agent suspension may be conditioned using a planetary mixer.

In order to print self-supporting 3D structures, an ink must have well controlled viscoelastic properties that enable a stable flow through the deposition nozzle and then "set" immediately retaining the shape. The inks must have a shear thinning behaviour (viscosity decreases with shear stress) so they can be easily injected through a small nozzle. At the same time, they should exhibit a solid-like (G'>G") behaviour, and high values of viscoelastic properties (storage modulus, G').

As the pH of the composition decreases, the functionalised material forms a weak gel-like network. Network formation is established where the storage (G') and loss (G") moduli are equal. As the pH is further decreased, more links are established until the hydrogen bonds create a strong network.

The storage modulus is measured by oscillation measurement, using a parallel plate with 40 mm diameter. The oscillation measurement is performed with a solvent trap cover to prevent solvent evaporation. The oscillation settings are: amplitude sweep at 0.1 Hz, under strains from 0.0001 up to 1000.
Preferably, the storage moduli $G'$ of the ink composition may be at least 1 kPa at a strain below 1%. The storage moduli $G'$ may be at least 5 kPa, 10 kPa, 20 kPa, 30 kPa at a strain below 1%.

At a pH value below 7, preferably below 6, the hydrophobic groups in the BCS branch and the carbon material edges protonate and enable the formation of multiple hydrogen bonds between the hydrophobic groups and the hydrophilic groups in the BCS molecules. Moreover, there is an adsorptive interaction between the hydrophobic groups and the hydrophobic carbon material surface. This allows the formation of a carbon material/BCS 3D network linked by non-covalent interactions and an increase in the loss and storage modulus. The non-covalent nature of the interactions allows the network links to break down under shear enabling the flow of the resulting ink composition, for example, through nozzles. The links heal once the stress is released and the carbon material/BCS networks recover their gel-like structure and set after printing. If the ink is passed through a nozzle, the ink sets immediately after passing through the nozzle and retains the shape of the filament, holding the printed structure.

When the polymer has structure PEGMA$_{60}$/MAA$_{95}$-EGDMA$_{18}$-DDT$_{10}$, at pH 9.68, the degree of protonation ($\alpha$) is 0. No MAA residues in the BCS are protonated at pH 9.68 or above. There is no aggregation of the BCS. At pH 6.46, the degree of protonation ($\alpha$) is 0.5, indicating that 50% of the MAA residues in the BCS are protonated at pH 6.46. At pH 3.88, the degree of protonation ($\alpha$) is 1, indicating that 100% of the MAA residues in the BCS are protonated at pH 3.88 or below, which means full aggregation of the BCS.

Preferably, the pH of the composition is less than the pKa of the ionisable groups in the polymer.

Preferably, the pH of the composition is less than 6.

In another embodiment, the invention provides an ink composition precursor which may comprise the formulation of the ink composition as defined in any embodiment of the first aspect of the invention absent the pH-regulating agent.

The invention provides a method for printing an article comprising the steps printing the ink to form an article; drying the printed article; and optionally curing the printed article.

The method may further comprise the step of preparing an ink composition according to the first aspect.
Rheological properties of an ink composition according to the invention enable its use for production of three dimensional articles. The ink composition is preferably for use in 3D printing and is of particular use in extrusion filament printing. The ink composition may also be used for coating, injection moulding and tape casting.

Preferably, the printing may be extrusion filament printing. In extrusion filament printing, an ink composition is printed by extrusion of a filament of the ink composition through a printing nozzle. Printing of thin filaments is possible and the printing nozzle may have a diameter of, for example, 100-1000 µm, preferably 100-500 µm (giving a corresponding printed filament diameter).

Filaments can be built up in layers to provide a 3D printed article. The ink may be used for continuous extrusion.

The drying may be according to methods known in the art. Drying may be in a convective oven with or without humidity control. Drying may also take place in a microwave oven. The drying step may comprise lyophilising the printed article. Freeze-drying, or lyophilising helps avoid shrinkage and allows the formation of 3D objects with smooth surfaces while preserving fine printing features down to the low micrometre range.

The curing may comprise the step of heating the graphene article. The heating temperature may be between 200-2400 °C. Preferably, the heating may be at a temperature of between 900-1000°C. The heating may be under a reducing environment. These reduction conditions allow BSC to be removed and the reduction of GO to restore the properties of graphene.

Preferably, the curing comprises the step of heating the graphene article at a temperature of between 200-2400 °C under a reducing atmosphere.

Preferably, when the article is a graphene oxide article, the article is chemically reduced to a graphene article. Preferably, the reduction of the graphene oxide article may take place under a reducing atmosphere with an argon/H₂ atmosphere comprising 10% H₂.

The article may be chemically reduced to a graphene article. Chemical reduction may involve reduction in the presence of hydrazine or ascorbic acid. The reducing atmosphere may comprise argon/H₂ atmosphere comprising 10% H₂.

In a sixth aspect, the present invention relates to a functionalised material comprising a carbon material, layered oxide, nitride or transition metal dichalcogenide functionalised with a pH responsive branched polymer.
Preferably, the functionalised material comprises covalent binding between the carbon material, layered oxide, nitride or transition metal dichalcogenide and the pH responsive branched polymer.

Preferably, the functionalised material is a carbon material. More preferably, the carbon material is graphene oxide.

Preferably, the polymer is as defined in the first aspect of the invention.

The present invention relates to a method of preparing the functionalised material according to the sixth aspect, comprising the steps of mixing an aqueous suspension of carbon material, layered oxide, nitride or transition metal dichalcogenide with an aqueous suspension of a branched polymer, at a pH of at least 7, preferably at least 8 or at least 9.

Preferably, the carbon material comprises graphene oxide. Preferably, the graphene oxide suspension comprises 0.5-5 wt/wt% graphene oxide in an aqueous solution. More preferably the graphene oxide suspension comprises 2-3 wt/wt% graphene oxide in an aqueous solution. Preferably, the graphene oxide to polymer ratio is 0.5:1 to 20:1 graphene oxide:BCS. Preferably, the graphene oxide to polymer ratio is 6:1 (by weight).

The present invention relates to an aqueous suspension comprising the functionalised material according to the sixth aspect.

The present invention will now be explained in more detail by reference to the following non-limiting examples:

Examples

The pH responsive polymer, with a ratio of ethylene glycol(EG) to methacrylic acid residues (MAA) is 1:1:1, was synthesised as follows:

A mixture of PEGMA (6.732 g, 6 mM, 5 molar equivalents), MA (10.000 g, 116 mM, 95 molar equivalents), ethylene glycol dimethacrylate (EGDMA, 2.42 g, 12 mM, 10 molar equivalents), and 1-dodecanethiol (DDT, 2.472 g, 12 mM, 10 molar equivalents) was degassed. Ethanol (200 ml) was degassed separately and added to the monomer mixture. After heating to 70 °C, the polymerization was initiated by addition of AIBN (200 mg) and was left stirring for 48 h. Ethanol was then removed by distillation and the polymer was washed with cold diethyl ether and dried.

A pH responsive polymer (BCS) stock solution with a concentration of 8 wt/v% was prepared in distilled water at pH 12.
GO solutions were prepared using the modified Hummers method. GO/BCS solutions were prepared by mixing different amounts of BCS stock solution and GO suspension, keeping the GO/BCS ratio 6 to 1. Printable GO networks were prepared by lowering the pH of GO/BCS suspensions, with glucono-δ-lactone (G6L). The total content of organics was fixed at 1.3 (GO/organic content).

For example, BCS-GO ink compositions are prepared by mixing 10 g of GO suspension (containing 2 or 3 wt% GO in water) with 412 or 625 μl BCS stock solution (containing 8 wt% BCS in water). The pH value of the GO/BCS solution is subsequently adjusted to 9-10 by adding 300-450 μl NaOH (1 mol/l). The suspensions are stirred for 30-60 minutes. GO-BCS networks with viscoelastic properties suitable for printing are obtained by adding 120 or 180 mg glucono-δ-lactone (G6L).

Figure 1 shows a schematic illustration of BCS functionalised graphene oxide in solution at basic pH. At the top, the BCS scheme shows the different functional groups, PMA, and PEG in the branches cross-linked by PEGMA. The branches are ended with hydrophobic anchoring group DDT. At the bottom, the graphene oxide structure shows the functional group distribution on the basal plane (hydroxyl, epoxy and un-oxidized graphitic islands).

Figure 2 shows a schematic illustration of the directed assembly mechanism. BCS molecules attach to the basal plane of GO sheets at basic pH by esterification of OH groups and hydrophobic interactions between DDT anchoring groups and graphitic islands. When lowering the pH below 5, the protonation of COO⁻ groups in BCS branches and GO sheets leads to the establishment of multiple hydrogen-bonds and directs the assembly of GO sheets into a 3D network.

The degree of interaction between the hydroxyl groups on the graphene oxide plane and the PMA functional groups in BC can be quantified by measuring the attachment of BCSr molecules (BCS with a fluorescent dye in the branched architecture, rhodamine).

Rhodamine was incorporated into the branched architecture in order to quantify pH responsive polymer (BCS) concentrations with UV-visible spectroscopy. Standard solutions of BCS (BCS-rhodamine) with concentrations ranging from 0.001 to 5wt/v% were prepared in distilled water at pH 8 and measured in UV-visible spectrometer to obtain the calibration curve by plotting the absorbance vs. concentration at 566 nm. Afterwards, the supernatants of GO/BCSr suspensions containing 0.2 wt% GO sheets and increasing amounts of BCSr (ranging from 0.001 to 5 wt/v%) were analysed by UV-visible spectroscopy after
centrifugation. The BCS adsorption isotherm onto GO sheets was determined by comparing the UV-visible absorbance at the excitation wavelength for rhodamine (566 nm).

At low initial BCS concentrations (between 0.5 and 2mg/ml at pH 8, and GO/BCS ratios between 4 and 1 respectively), all of the BCS molecules are adsorbed onto GO sheets (Figure 3a). Figure 3(a) shows the adsorption behaviour of BCS on GO sheets at pH 9. The graph shows the adsorption data against the initial equilibrium amphiphile concentration (Co). The dotted line indicates the limit at which all BCS molecules are absorbed on GO. At low concentrations there is complete adsorption of BCS onto GO surfaces, not being possible to detect free BCS molecules. In this concentration range, used to formulate GO/BCS inks, it is not possible to detect free BCS in the supernatants. As the BCS concentration increases (between 4 and 20mg/ml), the adsorption behaviour does not follow the ideal Langmuir model. Instead, they show a good linear correlation with the Temkin model (Figure 3b). Figure 3(b) shows the Temkin model showing the equilibrium adsorption capacity (qe, mg.g⁻¹) of GO (variation between initial (Co, mg/mL) and equilibrium concentration (Ce, mg/mL) per unit weight of the adsorbent, calculated by (Co-Ce)/Co) vs. the logarithm of the equilibrium concentration (Ce, equilibrium concentrations in aqueous phase after the adsorption of BCSr on GO)). Data were obtained for 0.2 wt/v% GO suspensions. According to this model adsorption is strongly affected by electrostatic interactions between the adsorbed BCS molecules.

At basic pH (>8) the PMA functional groups in BCS, are deprotonated providing electrostatic repulsion with the PEG branches and GO edges. The BCS-functionalized GO sheets are well dispersed by the repulsions between the BCS molecules functionalizing the basal plane of the sheets and the GO ionized edges. As a result it is possible to prepare stable suspensions with relatively high GO contents (up to 3 wt/v%).

Figure 4 shows the viscoelastic properties (amplitude sweep) of GO-BCS suspension before and after assembly (green and blue symbols respectively). At low pH, the formation of a network between GO sheets increases the magnitude of the storage and loss modulus (G’ and G”). The linear viscosity region (LVR) also changes with pH, GO suspensions break down at strains above 10%, while the GO/BCS networks exhibit solid-like behaviour and LVR below 1% strain. Higher amplitudes break down the network structure.

The GO/BCS suspensions at basic pH show a shear thinning behaviour as well as predominantly elastic response at strains below 10% (G’>G”, Figure 5). Despite this viscoelastic behaviour, the magnitude of the elastic component is not high enough to enable printing of 3D objects by continuous extrusion. The filaments do not retain their shape after
flowing through the nozzle and are too weak to hold a printed structure. However, when the pH is decreased (to a value below the pKₐ of BCS) the PMA groups in BCS branches and also GO edges protonate and enable the formation of multiple hydrogen bonds between the carboxylic functional groups in both (GO and BCS) and the PEG groups in the BCS molecules. The pH drop (below ~6.5 - pKₐ of the BCS molecules) can be triggered by the addition of glucono-5-lactone (G5L). G5L dissolves and then hydrolyses in water to gluconic acid, thus providing a gradual and homogeneous pH decrease. The consequence is the formation of a GO/BCS 3D network linked by noncovalent interactions and an increase in the loss and storage modulus of more than 5 orders of magnitude (above 100kPa, Figure 4).

This network forms a water-based 'pseudo-gel' with shear thinning behaviour and a predominantly solid-like behaviour at strains up to 1% (Figure 5). The non-covalent nature of the interactions within the GO/BCS network allows the network-links to break down under shear (Figure 5) enabling the easy flow of the gel through nozzles down to 100 µm in diameter. The links heal once the stress is released, the GO/BCS networks recover their 'pseudo-gel' structure and set immediately after passing through the nozzle retaining the shape of the filament and holding the printed structure. In this way it is possible to build 3D objects layer-by-layer using continuous extrusion.

The flow behaviour and viscoelastic properties of GO suspensions (pH>8) and inks (pH<5) were measured in a Discovery Hybrid Rheometer HR1 (TA Instruments). The flow experiments were carried out with a parallel plate (θ=40 mm) and a solvent trap cover under steady sensing. Viscoelastic behaviour and linear viscosity region (LVR) were evaluated with stress controlled amplitude sweeps at frequencies of 0.1 Hz under strains from 0.0001 up to 1000. The self-assembly process was monitored by measuring the viscoelastic properties (G', G'') over time, immediately after lowering the pH of GO-BCS suspensions. The oscillation measurements (time sweep with fixed frequency (0.1 Hz) and strain (γ=1%)) were applied immediately after adding the pH trigger. The solvent trap cover prevented evaporation of the solvent, while the axial force control allowed identifying changes in volume as well as automatically adjusting the gap.

GO/BCS inks were used to print 3D objects using a robotic deposition device (Robocad 3.0, 3-D Inks, Stillwater, OK). The diameter of the printing nozzles ranged from 100 to 500 pm (EFD precision tips, EFD, East Providence, RI).

Inks containing 2 or 3 wt/wt% GO and small amounts of additives (GO/BCS ratio of 6/1, G5L/BCS ratio around 3.8, and GO/organics ratio of 1.3) were printed through nozzles with internal diameters ranging from 100 to 500 pm. Filament piles, rings and woodpile
structures with different shapes were printed in air at speeds ranging between 4 and 10
mms\(^{-1}\) under controlled pressure in the range of 1-3 bar, depending on the ink formulation
and viscoelastic properties.

Figure 7 shows 3D printed graphene structures using a robotic assisted deposition machine.
Images showing parallel piles and crossed woodpile structures: Figure 7 (a) and (c) shows
structures printed with a 250 pm nozzle. Figure (b) shows a macroscopic image of the very
fine details of piled up lines printed by continuous extrusion through a nozzle with a diameter
of 100 \(\mu\)m.

2 to 3 wt/wt% of GO was dispensed in water using BCS functionalization. In order to
provide accurate dimensional control of printed articles, it is necessary to manage shrinkage
during drying. The large aspect ratio of GO limits its concentration in solution. Freeze drying
after printing helps to avoid shrinkage and form 3D objects with smooth surfaces while
preserving fine printing features down to the low micrometre range (Figure 8, 9). This
approach also allows the formation of highly porous printed lines, providing an additional
level of architectural control (Figure 8c and (d)).

3D printed GO structures were frozen in liquid nitrogen and subsequently dried (Freezone
4.5, Labconco Corporation). Once dried, samples were reduced in a tubular furnace
(Carbolite Furnaces) at 950°C in a 10%H\(_2\)/90%Ar atmosphere. Reduction is accompanied by
a 75% mass loss and -20% shrinkage while maintaining the printed lines. The resulted rGO
objects (Figure 9) are ultralight and retain their shape and structural integrity. Their Raman
spectra confirm the formation of predominantly crystalline rGO upon thermal reduction
(Figure 9) with conductivity restored to values between 10 and 20 S m\(^{-1}\) for printed lines with
densities varying between 25 and 65 mg/cm\(^3\).

The microstructure and chemical composition were studied by field emission scanning
electron microscopy on a LEO Gemini 1525 FEGSEM equipped with an energy dispersive
spectroscopy (EDS) microprobe (INCA Sight Oxford Instruments, UK). Raman spectroscopy
was performed using a Renishaw RM2000 equipped with a 514nm laser.

Figure 8 shows freestanding graphene oxide 3D articles and their microstructure. Figure 8a)
shows freeze-dried samples before reduction. Figure 8b) shows the detail of the junction
between lines in a woodpile structure fabricated with a 500 pm nozzle showing good
bonding. Figures 8c-(d) show microstructure of the printed lines from a transversal section in
a woodpile structure. The lines have densities ranging from 25 to 65 mg cm\(^{-3}\) depending on
ink formulation. The ice crystals formed during freeze-drying template the inner architecture (c-d), creating highly porous structures (d) with smooth surfaces (b).

Figure 9 shows the SEM, Raman spectroscopy and EDS analysis of the graphene oxide printed objects after thermal reduction. Figure 9(a) shows images of rGO filament pile (top) and ring (bottom) structures. The fine detail of the printed lines can be macroscopically identified in the ring structure. Figures 9(b), (c) show SEM images of the microstructural detail of the junctions between printed lines. There is good bonding and an interfacial region exhibiting surface porosity. Figure 9(d) shows the Raman spectrum, which confirms the recrystallization of graphene upon thermal reduction. The letters D, G and 2D represent characteristic Raman active modes for graphene. Figure 9(e) shows EDS analysis of the presence of C but is unable to detect any impurities. The densities of the rGO (reduced graphene oxide) objects range between 10 and 30 mg cm\(^{-3}\).

The above demonstrates that a pH trigger activates the controlled aggregation of the GO. The addition of glucono-5-lactone homogeneously drops the pH in the slurries. The hydrolysis of this sugar to gluconic acid homogeneously drops the pH throughout the suspension. At this point the protonated surfactant molecules "turn on" the hydrogen bonds, establishing multiple links between the branches from one GO flake to those in the neighbourhood. The suspension gradually aggregates forming a stronger solid as the pH drops and more bonds between the surfactant molecules occur. The coagulation kinetics can be manipulated through the concentration of polymer, temperature, sugar and solid loading. The rheological properties of this hybrid graphene/polymer network can be tuned for ink-filament 3D printing. The links within the networks are non-covalent and therefore they can self-heal. For instance, the hydrogen bonds can be broken during extrusion and re-bond afterwards.

While preferred embodiments of the present invention have been shown and described herein, it will be apparent to those skilled in the art that such embodiments are provided by way of example only. Numerous variations, changes, and substitutions will now occur to those skilled in the art without departing from the invention. It should be understood that various alternatives to the embodiments of the invention described herein may be employed in practicing the invention and that methods and structures within the scope of these claims and their equivalents be covered thereby.

The work leading to this invention has received funding from the People Programme (Marie Curie Actions) of the European Union's Seventh Framework Programme (FP7/2007-2013) under REA grant agreement n° 301909.
CLAIMS

1. An ink composition comprising a functionalised material, a pH regulating agent, and an aqueous solvent, wherein the functionalised material comprises a carbon material or layered oxide, nitride or transition metal dichalcogenide functionalised with a pH responsive polymer.

2. The ink composition according to claim 1, wherein the functionalised material comprises covalent binding between the carbon material or layered oxide, nitride or transition metal dichalcogenide and the pH responsive polymer.

3. The ink composition according to claim 2, wherein the carbon material is graphene oxide.

4. The ink composition according to claim 1 or 2, wherein the layered oxide is selected from the group of calcium niobium oxide, manganese oxide, niobium oxide, caesium tungsten oxide or molybdenum trioxide.

5. The ink composition according to claim 3, wherein the composition comprises 0.5 to 5 wt/wt% graphene oxide.

6. The ink composition according to claim 4, wherein the composition comprises 2-3 wt/wt% graphene oxide.

7. The ink composition according to any one of claims 1-6, wherein the polymer is a copolymer.

8. The ink composition according to any preceding claim, wherein the pH responsive copolymer comprises

   (a) at least one ethylenically monounsaturated monomer;

   (b) at least one ethylenically polyunsaturated monomer;

   (c) at least one residue of a chain transfer agent;

   (d) at least two chains formed from (a) being covalently linked, other than at its ends, by a bridge at residue (b); and wherein

   (i) at least one of (a) to (c) comprises a hydrophilic residue;
(i) at least one of (a) to (c) comprises a hydrophobic residue;

(iii) at least one of (a) to (c) comprises a moiety capable of forming a non-
covalent bond with at least one of (a) to (c).

9. The ink composition according to any one of claims 1-7, wherein the pH responsive
branched copolymer may comprise the general formula (I)

```
E' \[\begin{array}{c}
  (G)_g \\
  \hline
  (J)_j \\
  \hline
  -CH_2 - \\
  \hline
  R \\
  \hline
  L \\
  \hline
  R \\
  \hline
  \end{array}\] X
```

in which

E and E' each independently represent a residue of a chain transfer agent or an
initiator;

G and J each independently represent a residue of a monofunctional monomer
having one polymerisable double bond per molecule;

L is a residue of a multifunctional monomer having at least two polymerisable double
bonds per molecule;

each R, independently, represents a hydrogen atom or an optionally substituted alkyl
group;

X and X' each independently represent a terminal group derived from a termination
reaction;

\(g, j \text{ and } l \text{ represent the molar ratio of each residue normalised so that } g + j = 100,\)
\[\text{wherein } g \text{ and } j \text{ each independently represent } 0 \text{ to } 100, \text{ and } l \geq 0.05; \text{ and } m \text{ and } n \]
\[\text{are each independently } \geq 1;\]
at least one of $E$, $E'$, $G$, $J$ and $L$ is a hydrophilic residue; and at least one of $E$, $E'$, $G$, $J$ and $L$ is a hydrophobic residue.

10. The ink composition according to any preceding claim, wherein the pH responsive polymer is a branched pH responsive polymer comprising at least one residue of a chain transfer agent, optionally wherein the polymer further comprises poly(ethylene glycol) and methacrylic acid residues, optionally wherein the polymer further comprises ethylene glycol dimethacrylate residues.

11. The ink composition according to claim 10, wherein the polymer has the formula 
\[ \text{PEG-MAg/MAA}_{100} \text{-EGDMA}_{100} \text{-DDT}_{d}, \]
wherein $g$ and $j$ = 100 nominally set to a molar value of 100, and $l$ is 10 molar equivalent relative to $\text{PEGMA/MAA}$.

12. The ink composition according to claim 11, wherein $g$ is 4-6, $j$ is 94-96, $l$ is 10 and $d$ is 10.

13. The ink composition according to claim 7, wherein the polymer has a composition according to formula (I)

\[ \text{PEG-MAg/MAA}_{100} \text{-EGDMA}_{100} \text{-DDT}_{d}, \]
wherein $G'$ is poly(ethylene glycol), $J'$ is carboxyl, $E$ and $E'$ each independently represent a residue of a chain transfer agent or an initiator, $X$ and $X'$ each independently represent a terminal group derived from a termination reaction, $g$, $j$ and $l$ represent the molar ratio of each residue normalised so that $g + j = 100$, wherein $g$ and $j$ each independently represent 0 to 100, and $l$ is $\geq 0.05$; and $m$ and $n$ are each independently $\geq 1$.
14. The ink composition according to any one of claims 1-3, or 5-13, wherein the graphene oxide to polymer ratio is 0.5:1 to 20:1 graphene oxide:polymer, optionally 6:1 graphene oxide:polymer.

15. The ink composition according to any preceding claim, wherein the storage moduli $G'$ of the ink composition is at least 1kPa at a strain below 1%.

16. A method of preparing an ink composition comprising the steps of:

(a) preparing a functionalised material according to any one of claims 1-15 by mixing an aqueous suspension of carbon material, layered oxide, nitride or transition metal dichalcogenide with an aqueous solution of a pH responsive polymer;

(b) adding a pH regulating agent.

17. The ink composition according to any one of claims 1-15 or the method according to claim 16, wherein the pH regulating agent is an acid, base or substance which dissolves in an aqueous solution to form an acid or base.

18. The ink composition or the method according to claim 17, wherein the pH regulating agent is glucono-6-lactone.

19. The ink composition or the method according to claim 18, wherein the graphene oxide to glucono-6-lactone ratio is 0.1 to 5.

20. The ink composition or the method according to claim 19, wherein the graphene oxide to glucono-6-lactone ratio is 1:6.

21. The ink composition according to any one of claims 1-15 or 17-20 or the method according to claim 16-20, wherein the pH of the composition is less than the pKa of the ionisable groups in the polymer.

22. The ink composition according to any one of claims 1-15 or 17-20 or the method according to claim 16-20, wherein the pH of the composition is less than 6.

23. Use of a composition according to any one of claims 1-15 or 17-22 as an ink for 3D printing.

24. A method of producing a printed article comprising the steps of:
(a) printing an ink composition according to any one of claims 1-15 or 17-22
to form an article;
(b) drying the printed article; and optionally
(c) curing the printed article.

25. The method according to claim 24, wherein the method further comprises the step of
preparing an ink composition according to any one of claims 1-15, or 17-22, prior to step (a).

26. The method according to any one of claims 24-25, wherein the drying comprises
lyophilising the printed article.

27. The method according to any one of claims 24-26, wherein the curing comprises the
step of heating the article at a temperature of between 200-2400 °C under a reducing
atmosphere.

28. The method according to any one of claims 24-27, wherein curing comprises
chemical reduction of the printed article.

29. The method according to claim 28, wherein the reducing atmosphere comprises
under an argon/H₂ atmosphere comprising 10% H₂.

30. The method according to any one of claims 28-30 wherein the ink composition
comprises functionalised graphene oxide and wherein curing step (c) reduces the printed
graphene oxide article produced in step (a) to form a graphene article.

31. The method according to any one of claims 24-30, wherein the printing is extrusion
filament printing.

32. The method according to any one of claims 24-31, wherein printing is a three-
dimensional printing method, to produce a three-dimensional printed article.

33. An article obtainable by printing a composition according to claim 1-15 or 17-22 or as
produced by a method of any one of claims 24-32.

34. A functionalised material comprising a carbon material, layered oxide, nitride or
transition metal dichalcogenide functionalised with a pH responsive branched polymer.

35. The functionalised material according to claim 34, wherein the functionalised material
comprises covalent binding between the carbon material, or layered oxide, nitride or
transition metal dichalcogenide and the pH responsive branched polymer.
36. The functionalised material according to any one of claims 34-35, wherein the carbon material is graphene oxide.

37. The functionalised material according to claims 34-36, wherein the polymer is as defined in any one of claims 7-13.

38. A method of preparing the functionalised material of any one of claims 34-37, comprising the steps of mixing an aqueous suspension of carbon material, layered oxide, nitride or transition metal dichalcogenide with an aqueous suspension of a pH responsive branched polymer, at a pH of at least 7.

39. The method according to claim 38, wherein the carbon material comprises graphene oxide.

40. The method according to any one of claims 38-39, wherein the graphene oxide suspension comprises 0.5-5 wt/wt% graphene oxide in an aqueous solution.

41. The method according to claim 40, wherein the graphene oxide suspension comprises 2-3 wt/wt% graphene oxide in an aqueous solution.

42. The method according to any one of claims 38-41, wherein the graphene oxide to polymer ratio is 0.5:1 to 20:1 graphene oxide:pH-responsive polymer.

43. The method according to claim 42, wherein the graphene oxide to polymer ratio is 6:1.

44. An aqueous suspension comprising the functionalised material according to any one of claims 34-37.

45. A composition, method, use or material as substantially described herein with reference to or as illustrated in one or more of the examples or accompanying figures.
Figure 1

[Diagram showing molecular structures labeled BCS, PMA, DDT, PEG, PEGMA, GO, COO-, with dimensions 50 nm and 10 μm.]
Figure 2

GO/BCS network
Figure 3

(a)

(b)
Figure 4

Graph showing the change of $G'$ and $G''$ with time ($t$/min) on a logarithmic scale. The graph includes a inset showing the range of values for $G'$ and $G''$. The axes are labeled as $G', G''/Pa$ and $t$/min respectively.
Figure 5

Graph of $G', G''$ vs. strain $\gamma$, with regions marked for pH<5 and pH>8.
Figure 6
Figure 7
Figure 9
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

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<th>Inv.</th>
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<th>C09D11/037</th>
<th>C09D11/10</th>
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ADD.

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)

C09D

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 practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<td>A</td>
<td>paragraphs [0018], [0110], [0159], [0190], [0266]; claims 1-7,15-17,40, ; figure 27; examples 12-16</td>
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<td>X</td>
<td>GB 1 466 702 A (SANDOZ LTD) 9 March 1977 (1977-03-09)</td>
<td>34,35, 37</td>
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<td>claims 1-7; example 1</td>
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<td>CN 103 623 709 A (UNIV SOUTH CHINA TECH) 12 March 2014 (2014-03-12)</td>
<td>34-37, 44</td>
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Further documents are listed in the continuation of Box C.

X 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

*S* document member of the same patent family

Date of the actual completion of the international search: 16 November 2015

Date of mailing of the international search report: 25/11/2015

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL-2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fac. (+31-70) 340-3016

Authorized officer

Fel'dmann, Gabri el e
**INTERNATIONAL SEARCH REPORT**

**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.:
   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:

see additional sheet

1. ☐ 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 an 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.:

   l-45(partial)

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.
This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-45 (partly)

An ink composition as claimed in Cls. 1-15 and Cl. 17 comprising a carbon material functionalised with a pH responsive polymer. Furthermore, a method for preparing the said ink (Cls. 16-22), the use of the said ink for 3D printing (Cl. 23), a method for providing a printed article by printing the said ink (Cls. 24-32), an article obtained by printing the said ink (Cl. 33), a carbon material functionalised with a pH responsive branched polymer (Cl. 34), a method for providing the said functionalised material (Cls. 38-43) and an aqueous suspension of the functionalised material (Cl. 44) are claimed.

2. Claims: 1-45 (partly)

An ink composition as claimed in Cls. 1-15 and Cl. 17 comprising a layered oxide functionalised with a pH responsive polymer. Furthermore, a method for preparing the said ink (Cls. 16-22), the use of the said ink for 3D printing (Cl. 23), a method for providing a printed article by printing the said ink (Cls. 24-32), an article obtained by printing the said ink (Cl. 33), a layered oxide functionalised with a pH responsive branched polymer (Cl. 34), a method for providing the said functionalised material (Cls. 38-43) and an aqueous suspension of the functionalised material (Cl. 44) are claimed.

3. Claims: 1-45 (partly)

An ink composition as claimed in Cls. 1-15 and Cl. 17 comprising a nitride functionalised with a pH responsive polymer. Furthermore, a method for preparing the said ink (Cls. 16-22), the use of the said ink for 3D printing (Cl. 23), a method for providing a printed article by printing the said ink (Cls. 24-32), an article obtained by printing the said ink (Cl. 33), a nitride functionalised with a pH responsive branched polymer (Cl. 34), a method for providing the said functionalised material (Cls. 38-43) and an aqueous suspension of the functionalised material (Cl. 44) are claimed.

4. Claims: 1-45 (partly)

An ink composition as claimed in Cls. 1-15 and Cl. 17 comprising a transition metal dichalcogenide functionalised with a pH responsive polymer. Furthermore, a method for preparing the said ink (Cls. 16-22), the use of the said ink for 3D printing (Cl. 23), a method for providing a printed article by printing the said ink (Cls. 24-32), an article obtained by printing the said ink (Cl. 33), a transition metal dichalcogenide functionalised with a pH responsive branched polymer (Cl. 34), a method for providing the said functionalised material (Cls. 38-43) and an aqueous suspension of the functionalised material (Cl. 44) are claimed.
article by printing the said ink (Cl. 24-32), an article obtained by printing the said ink (Cl. 33), a transition metal dichalcogenide functionalised with a pH responsive branched polymer (Cl. 34), a method for providing the said functionalised material (Cl. S. 38-43) and an aqueous suspension of the functionalised material (Cl. 44) are claimed.
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<td>WO 2007/112503 A1 (UNIV SYDNEY [AU]; HAWKETT BRIAN STANLEY [AU]; SUCH CHRISTOPHER HENRY [AU]) 11 October 2007 (2007-10-11) page 34, lines 14-26; claims 1,6,13,19; examples 1-6</td>
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<td>EP 1 939 689 A1 (DSM IP ASSETS BV [NL]) 2 July 2008 (2008-07-02) paragraphs [0011], [0019] - [0023], [0028]; claims 1,3</td>
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