

CEMENT COMPOSITIONS WITH 3D GRAPHENE CARBONS

RELATED APPLICATIONS

[0001] This Patent Application claims priority to U.S. Provisional Patent Application No. 63/316,597 entitled “USING 3D GRAPHENES TO REGULATE NUCLEATION AND TIME-LAPSED GROWTH DURING GELATION/FORMATION OF POLYMERIZED CHAINS IN CEMENTS” and filed on March 4, 2022, and to U.S. Provisional Application No. 63/447,984 entitled “CEMENT COMPOSITIONS WITH 3D GRAPHENE CARBONS” and filed on February 24, 2023, all of which are assigned to the assignee hereof. The disclosures of all prior Applications are considered part of and are incorporated by reference in this Patent Application in their respective entireties.

TECHNICAL FIELD

[0002] This disclosure relates generally to cement compositions, and, more particularly, to cement compositions that include aggregates of functionalized 3-dimensional graphene carbons (3DG carbons).

DESCRIPTION OF RELATED ART

[0003] Recent developments in cement compositions are focused on decreasing CO₂ emissions of processes used for making and using cement. However, further improvements in cement compositions are desired.

SUMMARY

[0004] This Summary is provided to introduce in a simplified form a selection of concepts that are further described below in the Detailed Description. This Summary is not intended to identify key features or essential features of the claimed subject matter, nor is it intended to limit the scope of the claimed subject matter.

[0005] In some implementations, an example cement composition may include ordinary Portland cement, a secondary cementitious material (“SCM”) including pozzolan, in an amount corresponding to up to approximately 70% replacement level of ordinary Portland cement, and aggregates of carbon nanoparticles having graphene nanoplatelets such as 3-dimensional graphene (“3DG carbons”). The graphene nanoplatelets may include graphene

nanoplatelets which may be orthogonally joined to each other to form a 3D porous graphene scaffold structure. The amount of 3DG carbons may be between about 0.05% bwoc and 2% bwoc. The graphene nanoplatelets may include one or more of single layer graphene (SLG), few layer graphene (FLG), or many layer graphene (MLG). The aggregates may be further defined by an interconnected porous network disposed within and between the aggregates. The pozzolan may include between approximately 50 wt% and approximately 70 wt% SiO_2 , between approximately 10 wt% and 20 wt% Al_2O_3 , and less than approximately 10 wt% each of Fe_2O_3 and MgO . The loss on ignition (LOI) of the pozzolan may be less than approximately 10 wt%. The 3DG carbons may be characterized by a Raman spectroscopy signature having an I_D/I_G ratio between approximately 0.95 and approximately 1.05.

[0006] In some implementation, an example cement composition may include ordinary Portland cement, a SCM including one or more of metakaolin, slag, fly ash, pyroclastic ash, or limestone, in an amount corresponding to up to approximately 70% replacement level of ordinary Portland cement, and 3DG carbons. The graphene nanoplatelets may include graphene nanoplatelets which may be orthogonally joined to each other to form a 3D porous graphene scaffold structure. The amount of 3DG carbons may be between approximately 0.05% bwoc and approximately 2% bwoc. The amount of 3DG carbons may be between approximately 0.05% bwoc and approximately 1 % bwoc. The graphene nanoplatelets may include one or more of single layer graphene (SLG), few layer graphene (FLG), or many layer graphene (MLG). The aggregates may be further defined by an interconnected porous network disposed within and between the aggregates. The 3DG carbons may be surface functionalized with one or more of silicate compounds or nano-silica. The SCM may include between approximately 50 wt% and approximately 70 wt% SiO_2 , between approximately 10 wt% and approximately 20 wt% Al_2O_3 , and less than approximately 10 wt% each of Fe_2O_3 and MgO . The loss on ignition (LOI) of the SCM may be less than approximately 10 wt%. The 3DG carbons may be characterized by a Raman spectroscopy signature having an I_D/I_G ratio between approximately 0.95 and approximately 1.05. The silicate compounds or nano-silica may be anchored to the surface of the 3DG carbons, micro-confined within the interconnected porous open scaffold structure of the aggregates in 3DG carbons, or nano-confined in the scaffold structure formed by orthogonally joined graphene nanoplatelets in 3DG carbons. The 3DG carbons may be surface functionalized with one or more of silicon, sulfur, oxygen, nitrogen, silicon, lithium, sodium or potassium. The 3DG carbons surface functionalized with nano-silica may include between approximately 20 at. wt% and

approximately 65 at. wt% Si, and between approximately 15 at. wt% and approximately 40 at. wt% O. The O/Si ratio of the 3DG carbons surface functionalized with nano-silica may be between approximately 1.5 and approximately 3.

[0007] In some implementations, an example cement composition may include ordinary Portland cement, a SCM including one or more of metakaolin, limestone, or gypsum, in an amount corresponding to up to approximately 70% replacement level of ordinary Portland cement, a superplasticizer in a concentration range of between approximately 0.05% by weight of cement (“bwoc”) and approximately 2% bwoc, and 3DG carbons. The graphene nanoplatelets may include graphene nanoplatelets, which may be orthogonally joined to each other to form a 3D porous graphene scaffold structure. The amount of 3DG carbons may be between about 0.05% bwoc and 2% bwoc. The amount of 3DG carbons may be between about 0.05% bwoc and 1 % bwoc. The graphene nanoplatelets may include one or more of single layer graphene (SLG), few layer graphene (FLG), or many layer graphene (MLG). The amount of gypsum may be between about 0.5 wt% and approximately 3.5 wt%. The superplasticizer may include a polycarboxylate ether, for example, Arkema’s Ethacryl product or BASF’s Liquiment product. The superplasticizer may be added to the cement paste during hydration as a dispersant. The example cement composition may further include rheology modifiers, that include, but are not limited to, hydroxyethylcellulose in a concentration range of between approximately 0.05% bwoc and approximately 1.0% bwoc. The 3DG carbons may be surface functionalized with one or more of silicate compounds or nano-silica. The SCM may include approximately 65 wt% metakaolin (or generally pozzolan), approximately 32 wt% limestone, and approximately 3 wt% gypsum. The SCM may include approximately 97 wt% of one or more of metakaolin or limestone, and approximately 3 wt% gypsum.

[0008] In some implementations, an example cement composition may include ordinary Portland cement, a secondary cementitious material (SCM) including one or more of pyroclastic ash, slag, fly ash, metakaolin, or limestone in an amount corresponding to at least approximately 70% replacement level of ordinary Portland cement, and 3DG carbons. The amount of 3DG carbons may be between approximately 0.05% bwoc and approximately 2% bwoc. The amount of 3DG carbons may be between approximately 0.05% bwoc and approximately 1% bwoc. The 3DG carbons may include aggregates of carbon nanoparticles including graphene nanoplatelets. The carbon nanoparticles may be characterized by a plurality of porous concentric shells including graphene, where each shell may enclose a

porous carbon region. An interconnected porous network may be disposed in each carbon region and in fluid communication with contiguous carbon regions. The SCM may include between approximately 50 wt% and approximately 70 wt% SiO_2 , between approximately 10 wt% and 20 wt% Al_2O_3 , and less than approximately 10 wt% each of Fe_2O_3 and MgO . The loss on ignition (LOI) of the pozzolan may be less than approximately 10 wt%. The 3DG carbons may be characterized by a Raman spectroscopy signature having an I_D/I_G ratio between about 0.95 and about 1.05. The size of the carbon nanoparticles may be between about 20 nm and about 750 nm. The size of the aggregates of carbon nanoparticles may be between about 50 nm and about 1500 nm. The size of the aggregates of carbon nanoparticles may be greater than about 2 μm . The 3DG carbons may surface etched using CO_2 etching. The 3DG carbons may be surface oxidized or functionalized with ozone. The 3DG carbons may be surface functionalized with one or more of silicate compounds or nano-silica. The 3DG carbons surface functionalized with one or more of silicate compounds or nano-silica may include between approximately 20 at. wt% and approximately 65 at. wt% Si, and between approximately 15 at. wt% and approximately 40 at. wt% O. The O/Si ratio in the surface functionalized 3DG carbons may be between approximately 1.5 and approximately 3. The 3DG carbons may be surface functionalized with one or more of oxygen, nitrogen, silicon, sodium or potassium.

[0009] In some implementations, an example method for regulating calcium-silicate-hydrate (“CSH”) nucleation and time-lapsed growth during the initial hydration of cement comprising may include providing one or more of the cement compositions as described above in this disclosure that include 3DG carbons and mixing with water, where the water to cement ratio by weight may be approximately between about 0.3 and approximately 0.5.

[0010] Details of one or more implementations of the subject matter described in this disclosure are set forth in the accompanying drawings and the description below. Other features, aspects, and advantages will become apparent from the description, the drawings, and the claims. Note that the relative dimensions of the following figures may not be drawn to scale.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] Figure 1A shows a diagram of 3-dimensional graphene carbons (3DG carbons) having an interconnected porous network and graphene platelets orthogonally joined to form a 3D porous graphene scaffold structure, according to some implementations.

[0012] Figure 1B shows a diagram of nano-confinement of a dopant in the space between orthogonally joined graphene platelets of Figure 1A, according to some implementations.

[0013] Figure 2A shows another diagram of example 3DG carbons, according to some implementations.

[0014] Figure 2B shows a TEM micrograph of 3DG carbons, according to some implementations.

[0015] Figure 2C shows a SEM micrograph of 3DG carbons, according to some implementations.

[0016] Figure 3 shows a diagram of calcium-aluminosilicate hydrates including polymerized fibrous materials supported by 3DG carbons, according to some implementations.

[0017] Figure 4 shows a box plot representation of compositions of pyroclastic ash SCM with known pozzolanic activity.

[0018] Figure 5 shows micrographs of 3DG carbons functionalized with nano-silica particles and clusters, according to some implementations.

[0019] Figure 6A shows a SEM/EDS micrograph of 3DG carbons prior to functionalization, according to some implementations.

[0020] Figures 6B-6D show elemental composition maps measured during SEM/EDS analysis of 3DG carbons after nano-silica functionalization, according to some implementations.

[0021] Figure 7A shows elemental composition intensity (counts) measured during SEM/EDS analysis of 3DG carbons functionalized with nano-silica, according to some implementations.

[0022] Figure 7B shows a box plot of elemental composition distribution measured by SEM/EDS analysis of various 3DG carbons functionalized with nano-silica, according to some implementations.

[0023] Figure 8 shows a thermogram of example cement compositions functionalized with nano-silica, according to some implementations.

[0024] Figure 9A shows a diagram of an example primary carbon particle in 3DG carbons, according to some implementations.

[0025] Figure 9B shows a TEM image of primary particles and aggregates in 3DG carbons, according to some implementations.

[0026] Figure 9C shows a TEM image of 3DG carbon agglomerates, according to some implementations.

[0027] Figure 10 shows a diagram of another example primary carbon particle in 3DG carbons, according to some implementations.

[0028] Like reference numbers and designations in the various drawings indicate like elements.

DETAILED DESCRIPTION

[0029] The following description is directed to some example implementations for the purpose of describing the innovative aspects of this disclosure. However, a person having ordinary skill in the art will readily recognize that the teachings herein can be applied in a multitude of different ways. The described implementations can be implemented in cement compositions for a variety of applications and may be tailored to compensate for various performance related deficiencies. As such, the disclosed implementations are not to be limited by the examples provided herein, but rather encompass all implementations contemplated by the attached claims. Additionally, well-known elements of the disclosure will not be described in detail or will be omitted so as not to obscure the relevant details of the disclosure.

[0030] Various aspects of the novel compositions and methods are described more fully herein with reference to the accompanying drawings. These aspects are provided so that this disclosure will be thorough and complete, and will fully convey the scope of the disclosure to those skilled in the art. Although some examples and aspects are described herein, many variations and permutations of these examples fall within the scope of the disclosure. Although some benefits and advantages of the various aspects are mentioned, the scope of the disclosure is not intended to be limited to benefits, uses, or objectives. The detailed description and drawings are merely illustrative of the disclosure rather than limiting, the scope of the disclosure being defined by the appended claims and equivalents thereof.

[0031] Ordinary Portland cement (“OPC”) is produced by calcining limestone (CaCO_3) with clay (aluminosilicates) in a kiln at about 1500 °C to form a sintered product commonly known as clinker. Portland cement is used as a cementitious material (binder) in cement products such as concrete. ASTM standard specification (ASTM C150) requires that Portland cement “must have the following chemical compositions: aluminum oxide, ferric oxide, magnesium oxide, sulfur trioxide, tricalcium silicate (“C3S”), dicalcium silicate (“C2S”), tricalcium aluminate (“C3A”), and tetracalcium aluminoferrite.” When mixed with water, the calcium silicates and aluminates are hydrated via several hydration and gelation reactions to primarily form calcium-silicate-hydrate (“CSH”) paste, which gradually bonds sand and gravel particles in concrete together and hardens to form a solid water-resistant product via a process known as setting. After initial setting, concrete continues to harden and develop its mechanical strength over a period of about 30 days. About less than 5 wt% gypsum (hydrated calcium sulfate) may be added to clinker and ground to fine powder in a ball mill. Gypsum is added primarily to retard the setting time of cement by slowing down the hydration rates of the C2S, C3S and C3A, and more importantly, the exothermic hydration of C3A by preventing “flash setting.”

[0032] In addition to forming CSH, hydration typically forms a byproduct known as Portlandite, which is composed of calcium hydroxide (“CH”). Portlandite does not have cementitious properties and may cause an undesirable increase in the permeability of concrete to water, which reduces the mechanical strength of concrete. To mitigate this effect, supplementary cementitious materials (“SCM”) commonly known as pozzolans may be added to Portland cement or concrete prior to hydration, to react with CH and water during hydration via the pozzolanic reaction, which also has the beneficial effect of forming additional CSH cementitious compounds.

[0033] An SCM may be defined as “an inorganic material that contributes to the properties of a cementitious mixture through hydraulic or pozzolanic activity, or both.” See, for example, ASTM 2015, Paper FHWA-HIF-16-001, U.S. Department of Transportation. The type and amount of SCMs may be varied to reduce the amount of Portland cement in concrete (or increase the replacement levels of cement), without sacrificing mechanical strength. SCMs may contribute to the formation of cementitious materials by both hydraulic activity and pozzolanic activity. SCMs (and cements) that have hydraulic properties, harden during hydration, and that hardening process does not require drying. SCMs with pozzolanic activity require both water and CH as reactants to form CSH.

[0034] As previously described, undesirable CH produced by hydraulic activity (for example, hydration of Portland cement), may be consumed during pozzolanic activity provided by SCMs to produce additional amounts of cementitious compounds like CSH. Examples of SCMs may include fly ash (byproduct of coal fired furnaces), blast furnace slag, silica fume, and natural pozzolans like metakaolin. Other SCMs such as slag may exhibit hydraulic activity and produce cementitious compounds during hydration. Slag cement does not exhibit pozzolanic activity but consumes CH by binding alkalis in its hydration products. Therefore, although it is a hydraulic cement, slag cement provides the benefits of a pozzolan. SCMs are also used to improve concrete performance in its fresh and hardened state and also to improve the workability, durability and strength of concrete.

[0035] The amount of fly ash in concrete may vary from 5% to 65% by mass of the cementitious materials. The amount of slag may vary from 20% to 70% by mass of the cementitious materials. The amount of silica fume may vary from 5% to 12% by mass of cementitious materials. Natural pozzolans that exhibit pozzolanic activity may include metakaolin, calcined shale, or clay. The amount of metakaolin may vary from 5% to 70% by mass of cementitious materials. Higher amounts (percentage by mass) of calcined shale or clay may be used. See, for example, paper CIP30–SCMs, National Ready Mixed Concrete Association, 2000. While fly ash and slag increase initial set time and setting time of concrete, silica fume accelerates the hydration of Portland cement by providing nucleation sites for the formation of hydration products like CSH.

[0036] The cement industry contributes to about 8% of global greenhouse gas (CO₂) emissions. About 90% of these emissions are produced during the high temperature calcination process of limestone and clay materials at amounts of about 0.8 tons CO₂ per ton of OPC, which includes the amount of CO₂ produced by combustion of fuels used to heat the kilns. Accounting for CO₂ emissions from quarry-to-point-of-use, approximately 1 ton of CO₂ is produced per ton of OPC. Therefore, considerable research and development has been directed to reduce the amount of Portland cement in concrete and increase the replacement levels of cement. As described above, using SCM additives is one approach to increase the replacement levels of cement and realize reductions in CO₂ emissions.

[0037] Researchers at Exeter University (United Kingdom) have reported that graphene additives to cement may increase the replacement level of cement in concrete by as much as 50% and lead to significant reduction in CO₂ emissions. Small amounts of graphene additives also increase the mechanical strength, durability, and the water resistance of

concrete. Graphene is a single layer of carbon atoms arranged in a hexagonal structure. Atomically thin shards of graphene may be suspended in water during mixing concrete. Additionally, researchers at the University of Manchester (United Kingdom) have reported that graphene not only provides mechanical strength, but also acts as a catalyst surface for initiating hydration reactions, which provides a finished cement product with improved strength, durability, and corrosion resistance.

[0038] PureGraph® (First Graphene, United Kingdom) is a graphene nanoplatelet powder additives with particle size (D_{v50}) from 5 μm to 50 μm . The graphene nanoplatelets are produced by electrochemical exfoliation of graphite. The powders are not aggregated and may be dispersed in water and added to cement. Reports suggest that 0.01% to 0.05% of graphene nanoplatelet powders in cement compositions provide the same or better mechanical strength as Portland cement in cementitious products while reducing the amount of clinker, required by about 20% to 30%. That is, the replacement level of OPC is about 20% to 30%. As such, CO₂ emission reduction of about 20% is possible even with small amounts of graphene additives.

[0039] Reports suggest that graphene physically and chemically interacts with cementitious binders and improves adhesion between the graphene basal planes and cement gel by Van der Waals forces, which reinforces the hydrated structure by preventing cracks from developing at a nanoscale. Changes in porosity and hydration at the graphene-cement interface have also been observed. When used as a water-based admixture in typical cement-based mortar at dosing levels of less than 0.1%, graphene was found to increase compression strength by 34% increase in and tensile strength by 7%. However, graphene produced by exfoliation of graphite is an expensive boutique additive. Reports suggest that in volumes approaching about 5 tons, the price range of the graphene nanoplatelet powders may be about \$250/kg–\$300/kg, which is about 2000x the U.S. price of Portland cement (of about \$125/ton). Less expensive additives and cement compositions which offer higher replacement levels of Portland cement, and which lead to reduced setting time without reduction in mechanical strength are required.

[0040] In some implementations, an example cement composition may include ordinary Portland cement (“OPC”), one or more SCM additives, and 3DG carbons as additives or fillers. Any one of the SCMs or combination of SCMs previously described in this disclosure may be used to form cement compositions in accordance with aspects of the present disclosure. The amount of 3DG carbons may be between approximately 0.05% bwoc and 2%

bwoc. The 3DG carbons may include aggregates of carbon nanoparticles having graphene nanoplatelets with an interconnected porous network. The 3DG carbons may include graphene nanoplatelets orthogonally joined to each other to form a 3D porous graphene scaffold structure. The graphene nanoplatelets may include one or more of single layer graphene (SLG), few layer graphene (FLG), or many layer graphene (MLG).

[0041] Figure 1A shows a diagram of 3-dimensional graphene (3DG) carbons 100A having an interconnected porous network and graphene platelets orthogonally joined to form a 3D porous graphene scaffold structure, according to some implementations. The 3DG carbons 100A shown in Figure 1A may be produced by high throughput, low-cost, cracking of a hydrocarbon gas such as natural gas, in an atmospheric microwave plasma reactor. An example microwave plasma reactor that can be used to produce the 3DG carbons 110 is disclosed in commonly-owned U.S. Pat. No. 9,767,992, which is incorporated by reference herein in its entirety. For example, particles 100A may be formed in-flight and grown by adding additional carbon-based materials derived from incoming carbon-containing gas within a microwave-plasma reaction chamber.

[0042] A plurality of primary particles produced by one or more methods including thermal cracking of a hydrocarbon gas or source material may be coalesced or joined to form aggregates of primary particles. An aggregate may be considered to be a discrete, colloidal entity that is the smallest dispersible unit, composed of coalesced primary nanoparticles. A primary particle may be considered to be a spheroidal shaped, non-discreet component of an aggregate, separable from aggregate only by fracturing. The primary particles may be connected together by one or more of Van der Waals forces, covalent bonds, ionic bonds, metallic bonds, or by other physical or chemical interactions. Additionally, a plurality of aggregates may be considered to be agglomerates. Since aggregates of at least 1 μm in size may be considered to be agglomerates, the term “aggregates” also includes “agglomerates” in this disclosure. A carbon aggregate may be characterized by a principal dimension (diameter, length, width) of greater than about 1 μm .

[0043] The 3DG carbons 100A may include electrically conductive three-dimensional (3D) aggregates or agglomerations of graphene platelets or sheets 130. In some aspects, the 3DG carbons 100A may include pores having a multi modal pore size distribution or space 110 between contiguous carbon particles or microstructures to define an open porous scaffold 120. The 3D aggregates may include a hierarchical structure 132 formed by successive graphene layer structures 140 disposed substantially orthogonal to each other. The graphene

platelet structure 132 may include multiple layers of graphene platelets or sheets 140 and may be orthogonally fused together for use as a self-supporting hierarchical structure 132 to improve the mechanical strength of a cementitious product. Carbon particles may be tuned in-flight by tuning reactor operating conditions to form various structures, including 2D graphene sheets or platelets, 3D graphene aggregates having interconnected porous networks, including interconnected 3D graphene aggregates 130 of multiple layers of graphene sheets or platelets 140.

[0044] In some implementations, the 3DG carbons 100A may include open porous scaffolds 120 that facilitate electrical conduction along and across contact points of the graphene sheets 140. Dopants such as sulfates, silicates and alkalis that beneficially impact cement hydration processes may be disposed on the surface of 3DG carbons 100A or micro-confined in the pores of scaffold structure 120 or nano-confined in the scaffold structure.

[0045] Figure 1B shows a diagram 100B of nano-confinement of a dopant in the spaces 110 between the orthogonally joined graphene platelets 101C of Figure 1A, according to some implementations. In some instances, the dopants may be nano-confined in the scaffold structure formed by orthogonally joined graphene nanoplatelets in 3DG carbons and released out as a function of time. Timed-release of nucleating agents may be tuned to impact the acceleration of the pozzolan reaction after the formation of Portlandite from the reaction of anhydrous calcium silicate with water. 3DG carbons 100A may also provide a flexible scaffold-type structure to manage material expansion and mitigate crack formation during hydration and curing of cement. The graphene platelet structure 130 may include 5 to 15 layers of graphene that are oriented in a stacked configuration to have a vertical height referred to as a stack height. In some configurations, the graphene nanoplatelets may include one or more of single layer graphene (“SLG”), few layer graphene (“FLG”) defined as ranging from 5 to 15 layers of graphene, or many layer graphene (“MLG”).

[0046] In some implementations, the 3DG carbons 100A may include a plurality of interconnected crinkled 3D graphene sheets, a plurality of non-hollow carbonaceous spherical particles (“NHCS”), flat graphene, wrinkled graphene, a plurality of carbon nanotubes (“CNTs”), or a plurality of carbon nano-onions (“CNOs”). In some implementations, 3DG carbons 100A may include wavy or flexible graphene platelets that resemble crinkled paper and may be produced using microwave processes. The graphene platelets may be flexible as they may be fused with each other at sp^3 type defects in the sp^2 graphene lattice structure.

[0047] Figure 2A shows a diagram of 3DG carbons 201 having porous interconnected graphene nanoplatelets (“GNP”) and a scaffolded structure, according to some implementations. Figure 2B shows a TEM micrograph 202 of the 3DG carbons 201, according to some implementations. As shown, the 3D few-layer graphene (“FLG”) structure is aggregate at a 50 nm scale. FLG may refer to about 10 layers of graphene generally configured in a stacked orientation. Those skilled in the art will appreciate that the micrographs are shown by way of example only, and that other scales may exist without departing from the scope and spirit of the present implementations.

[0048] Figure 2C shows a SEM micrograph of 3DG carbons 203, according to other implementations. In some instances, plasma-based processing conditions applied or performed in a reactor such as a microwave reactor may be adjusted with a high degree of tunability to achieve 3DG carbons and graphene-on-graphene densification to yield the complex 3D carbons 203. The 3DG carbons 203 may be surface etched using methods such as CO₂ etching to create pores on the external surface of the aggregates and to increase the surface area of the aggregates.

[0049] The 3DG carbons described herein and characterized using Raman spectroscopy show a high degree of order and uniformity of structure. In this disclosure, “graphene” refers to an allotrope of carbon in the form of a two-dimensional, atomic-scale, hexagonal lattice in which one atom forms each vertex. The carbon atoms in graphene may be sp² hybridized carbon atoms. Additionally, graphene has a Raman spectrum with two main peaks: a G-mode at approximately 1580 cm⁻¹ and a D mode at approximately 1350 cm⁻¹ (when using a 532 nm excitation laser). The 3DG carbons may be characterized by a Raman spectroscopy signature having an I_D/I_G ratio between approximately 0.95 and approximately 1.05.

[0050] Figure 3 shows a diagram of calcium-aluminosilicate hydrates 300 including polymerized fibrous materials 301 supported by 3DG carbons 304, according to some implementations. Without being bound by any particular theory, hydration of OPC including gypsum (calcium sulfate) may form random needle-like ettringite (calcium sulfo-aluminate), tobermorite (calcium silicate hydrate) and calcium-aluminosilicate hydrates (“CASH”) in the form of entangled and branched polymerized fibrous material 301 of silicates and aluminates. Polymerized fibrous material 301 may include polymerized amorphous alumino-silicates 302 and crystalline alumino-silicates 303. 3DG carbons 304 may be used as fillers or seeding agents to anchor or serve as a “bridging agent” between polymerized CASH fibers, thereby leading to in higher compressive and tensile strength and greater resistance to fracture during

the setting of the hydrated cementitious product. The high surface area of 3DG carbons 304 may provide a high density of nucleating sites for CSH or CASH, which may then grow and polymerize to form fibrous material 301. 3DG carbons 304 may have a surface area between approximately 50 m²/g and 2,675 m²/g when measured in a dry state.

[0051] By kinetically controlling the hydration and authigenic formation of entangled, needle-like crystalline phases in the cementitious matrix, elasticity and toughness may be improved over conventional concrete. 3DG carbons 304 used in example cement compositions may further reduce the permeability of the hydrated cementitious product over and above the reduction in permeability possible with the use of only a pozzolan as SCM. 3DG carbons 304 when used as additives or fillers may also reduce shrinkage on cooling the cementitious product because 3DG carbons exhibit negative thermal expansion. That is, the 3DG carbons 304 increase in size when cooling and decrease in size when heating. In contrast, cementitious products without any 3DG carbons 304 are characterized by positive thermal expansion. Therefore, by varying the amount of 3DG carbons 304 used as fillers or additives, crack formation in the cementitious product due to repetitive ambient temperature thermal cycling may be reduced.

[0052] In some implementations, an example cement composition may include ordinary Portland cement (“OPC”), volcanic or pyroclastic (pozzolana) ash or metakaolin as a SCM at about 70% replacement level of OPC, and 3DG carbons. That is, about 70% of OPC by mass may be replaced by pyroclastic (pozzolana) ash. The replacement level of OPC with metakaolin may be greater than 70%. In this example cement composition, metakaolin having varying amounts of aluminosilicates may be considered to be an SCM with pozzolanic activity. OPC exhibits high autogenous temperature rise and corresponding high tensile shrinkage strains during the exothermic hydration process. In contrast, metakaolin including aluminosilicates, hydrate or gelate at lower temperatures and lower rates thereby reducing mechanical strains and micro-cracking and producing a more elastic and toughened cementitious product with higher chemical resistance, lower permeability to water and other chemicals. Without being bound by any particular theory, the 3DG carbons and functionalized 3DG carbons serve as nucleating agents for CSH and CASH formation, which helps to realize the 70% replacement of OPC in the example Portland cement / SCM blends as disclosed herein. Table 1 summarizes the anticipated benefits of cement compositions with 3DG carbons as fillers or additives.

Table 1. Summary of benefits of cement composition including 3DG carbons.

Material Property enhancement	Example mechanism
Improved tensile strength	3DG carbons may form nucleation sites for forming cement calcium silicate hydrate (CSH) gels during hydration which subsequently controls grain size and degree of crystallinity of the cementitious product such as concrete. The beneficial effect of 3DG carbons may be modulated by morphology, surface area and surface chemistry (e.g., functionalization) of 3DG carbons. 3DG carbon morphology, surface area and surface chemistry may be tuned.
3DG carbons may augment rebar or act as a substitute for rebar for mechanical reinforcement	Utilize the high tensile strength of 3DG carbons to improve the mechanical strength of the cementitious product. An electric field may be applied to the concrete mixture to align graphene particles in 3DG carbons to mimic rebar. Unlike rebar, the 3DG carbons may be more uniformly distributed throughout the thickness of the cementitious product. Reduced amounts of rebar may be required with cements including 3DG carbons.
Crack mitigation	3DG carbons may act as “roadblocks” to the propagation of micro-cracks, thus reducing or mitigating crack growth, and in particular, during ambient temperature thermal cycling.
Permeability reduction to O ₂ , H ₂ O, Cl ₂ , acids, which may enhance durability of concrete	3DG carbons interact with OPC, reducing grain size during hydration/curing, which may result in a dense matrix of cement grains. Porosity of the cementitious may be reduced. The conversion of Portlandite into hydrate cementitious material serves to reduce porosity in 3DG cements. The cementitious product may be more impervious to ambient air, water, chlorine, acids and sulfates commonly found in construction sites. The tortuous porous network in 3DG carbons may localize possible penetration of chemicals.
Crack healing (autogenous self-healing)	Crack healing may be realized via self-assembly of graphene at a crack location. Graphene may be chemically modified to have two separate surfaces: a hydrophobic and a hydrophilic surface.

[0053] Figure 4 shows a box plot representation 400 of compositions of pyroclastic ash SCM with known pozzolanic activity. Pyroclastic ashes or pumices materials result from explosive eruptions and show higher pozzolanic activity. The eruption type largely depends on the magma viscosity which is related to the “acidity” (i.e., SiO_2 content) of the magma. In general, more siliceous magma produces more explosive volcanism and products with better pozzolanic properties. Coarser highly vesicular pyroclastic material forms pumice-type deposits. Finely divided materials are transported further away from the volcanic source and are deposited as ash layers. Silica (SiO_2) content in most natural pumices and ashes fall in the intermediate range (approximately 50–70 wt% SiO_2) to acidic range (greater than approximately 70 wt% SiO_2). The pyroclastic ash may include between approximately 50 wt% and approximately 70 wt% SiO_2 , between approximately 10 wt% and 20 wt% Al_2O_3 , and less than approximately 10 wt% each of Fe_2O_3 and MgO . The loss on ignition (“LOI”) of the pyroclastic ash may be less than approximately 10 wt%.

[0054] The total alkali content may vary depending upon the regional type of volcanic activity and may reach at least approximately 11 wt% on an anhydrous basis in Neapolitan pozzolans. Pyroclastic ashes may contain Fe_2O_3 , CaO , and MgO in minor proportions. Loss on ignition (“LOI”) may exceed approximately 10 wt% in some ashes. See, for example, Snellings et al., “Supplementary Cementitious Materials,” Reviews in Mineralogy and Geochemistry, May 2012, which is incorporated herein in its entirety.

[0055] As previously described, the addition of gypsum to OPC prevents flash setting during hydration; however, gypsum retards the setting of the cementitious product. 3DG carbons may be functionalized using various methods to include specific dopants. 3DG carbons may include sulfur or sulfates anchored on the surface as shown in the example of Figure 3 or may be micro-confined within the interconnected porous open scaffold structure of the aggregates (as shown in Figure 1A) or nano-confined in the scaffold structure formed by orthogonally joined graphene nanoplatelets in 3DG carbons (as shown in Figure 1B). Sulfur compounds may be released in a controlled manner, that is, time released, into the CSH or CASH matrix during hydration facilitated by the tortuous interconnected porous network of the 3DG carbons. Sulfur-doped 3DG carbons enable regulated, local and distributed introduction of sulfate during the hydration process, which in turn enables control of the hydration rate and mitigates fast hydration, or flash set which adds stiffness. Controlling the hydration rate of cement can enhance elasticity and toughness without compromising the strength of the cementitious product.

[0056] Similarly, release of alkalis such as sodium or potassium from alkali-doped 3DG carbons may facilitate the formation of sodium aluminosilicate hydrate (“NASH”) chains, which in turn, may cross-link or entangle with CASH chains to enable strain hardening and strengthening of the cement matrix. Sodium hydroxide may behave as an alkali activator to reduce cement setting time and improve initial mechanical strength of the cement. Accordingly, in addition to sulfur, 3DG carbons may be doped with sodium, to offer synergistic benefits during initial hydration and setting processes.

[0057] In some implementations, an example cement composition may include ordinary Portland cement (“OPC”), volcanic or pyroclastic (pozzolana) ash with about 70% replacement level of OPC, and chemically functionalized 3DG carbons. An example cement composition may include 3DG carbons surface functionalized with an alkali such as sodium. Another example cement composition may include 3DG carbons functionalized with sulfur oxide (S–O) species. 3DG carbons may be functionalized with elements including oxygen, nitrogen, silicon, or hardening agents. 3DG carbons may be functionalized *in situ* – that is, within the reactor during the production of 3DG carbons. Alternately, 3DG carbons may be functionalized using separate post-production processing steps. For example, 3DG carbons may be treated with ozone to surface oxidize the carbon. Subsequently, the treated material may be further postprocessed to functionalize the oxidized surface of the carbon with silane through a modification of the Stobbe colloidal silica synthesis. Furthermore, the surfaces of 3DG carbons may be functionalized with silica, oxygen or nitrogen containing species which form bonds with polymers of the cementitious matrix, thus improving adhesion and providing strong binding to enhance the strength of cementitious product.

[0058] In some implementation, the 3DG carbons may be used without any post-production processing steps. In other implementations, the 3DG carbons may be subject to post-product processing steps. Example post-production processing steps may include one or more of mechanical processing steps such as ball milling, grinding, attrition milling, micro fluidizing, or other processes to reduce particle size. Post-production processing steps may also include one or more exfoliation processes such as sheer mixing, chemical etching, oxidizing (e.g., Hummer method), thermal annealing, doping by adding elements during annealing (e.g., sulfur, nitrogen), steaming, filtering, or lyophilizing, or other processes. Some other examples of post-production processing may include sintering processes such as one or more of spark plasma sintering (“SPS”), direct current sintering, microwave sintering, or ultraviolet (“UV”) sintering, which may be conducted at high pressure and temperature in

an inert gas. In some other implementations, multiple post-production processing methods may be used in any combination to achieve desired physical and chemical properties of the 3DG carbons. For example, post-production processing may yield functionalized 3DG carbons as disclosed herein.

[0059] In some implementations, the 3DG carbons may be subjected to post-production thermal annealing or sintering in an inert environment such as nitrogen or argon and at elevated temperatures, and at atmospheric pressure, or under vacuum. Post-production processing temperatures may range from approximately 500°C to 2500°C, or from approximately 500°C to 1500°C, or from approximately 800°C to 1500°C, or from approximately 800°C to 1200°C, or from approximately 800°C to 1000°C, or from approximately 2000°C to 2400°C, or approximately at 800°C, or approximately at 1000°C, or approximately at 1500°C, or approximately at 2000°C, or approximately at 2400°C.

[0060] In some implementations, an example cement composition may include ordinary Portland cement (“OPC”), one or more of pyroclastic ash or metakaolin (calcined clay) or limestone as SCMs, and 3DG carbons surface functionalized with nano-silica particles or clusters. The amount of 3DG carbons functionalized with nano-silica may be less than approximately 1 wt% of the cement composition. The replacement level of OPC by the SCMs may be at least approximately 70%. The replacement level of OPC by the SCMs may be approximately 80%. An example cement composition may include approximately 20% OPC, approximately 80% SCM (metakaolin and limestone) and less than approximately 1 wt% of 3DG carbons functionalized with nano-silica. OPC may conform to European standards EN 197-1 as CEM I 42.5R or the ASTM Type I standard. Metakaolin may be supplied by Burgess Pigment Company (Sandersville, GA) as Optipozz™ metakaolin. Limestone may be supplied by Omya, Inc. (Cincinnati, OH) as Durcal 15 powders.

[0061] Without being bound by any particular theory, nano-silica particles anchored in 3DG carbons surfaces or micro-confined in the 3DG carbons, or nano-confined in the scaffold structure formed by orthogonally joined graphene nanoplatelets in 3DG carbons act as a nucleating agent for CSH formed during the hydration process. Figure 5 shows micrographs 500 and 510 of 3DG carbons functionalized with respective nano-silica particles and clusters, according to some implementations. That is, nano-silica particles or nano-silica particle clusters 501 and 511 in 3DG carbons in the example cement compositions may function as distributed catalytic sites, and as such, as seeding agents for CSH during hydration and subsequent growth of CSH polymeric chains in the cement matrix. The

hydration process may be accelerated due to improved dissolution of C3S in water and acceleration of the pozzolanic activity of the SCMs to convert CH to CSH. Further 3DG carbons functionalized with nano-silica may anchor CSH polymeric chains and may provide structural reinforcement during hydration and setting.

[0062] In some implementations, an example cement composition may include ordinary Portland cement (“OPC”), one or more of pyroclastic ash or metakaolin or limestone as SCMs, and 3DG carbons surface functionalized with one or more of nano-silica and oxygen. The amount of 3DG carbons functionalized with one or more of nano-silica or oxygen may be less than approximately 1 wt% of the cement composition. The replacement level of OPC may be approximately 70%. 3DG carbons doped with oxygen may also nucleate CSH seeds via covalent bonding. The replacement level of OPC by the SCMs and functionalized 3DG carbons may be approximately 80%. An example cement composite may include approximately 20% OPC, approximately 80% SCM (metakaolin and limestone) and less than approximately 1 wt% of functionalized 3DG carbons functionalized with nano-silica and/or oxygen. OPC may conform to European standards EN 197-1 as CEM I 42.5R or ASTM Type I Portland cement. Metakaolin may be supplied by Burgess Pigment Company (Sandersville, GA) as Optipozz™ metakaolin. Limestone may be supplied by Omya, Inc. (Cincinnati, OH) as Durcal 15 powders.

[0063] In some implementations, an example cement composition may include ordinary Portland cement (“OPC”), one or more of pyroclastic ash, gypsum, limestone or metakaolin as SCMs, and 3DG carbons surface functionalized with one or more of nano-silica and oxygen. The replacement level of OPC may be at least approximately 70%. The amount of 3DG carbons functionalized with one or more of nano-silica or oxygen may be less than approximately 1 wt% of the cement composition. The amount of gypsum may range from approximately 0.5 wt% to 3.5 wt% of the cement composition. A superplasticizer may be used to improve workability. Superplasticizers may be added to the cement paste in concentrations ranging from 0.05% bwoc to 2% bwoc. The superplasticizer may include a polycarboxylate ether, for example, Arkema’s Ethacryl product or BASF’s Liquiment product. The superplasticizer may be added to the cement paste during hydration as a dispersant.

[0064] The example cement composition may further include rheology modifiers, that include, but are not limited to, hydroxyethylcellulose in a concentration range of between approximately 0.05% bwoc and approximately 1.0% bwoc. The replacement level of OPC

by the SCMs and functionalized 3DG carbons may be approximately 80%. An example cement composition may include approximately 20% OPC, approximately 80% SCM (metakaolin and limestone) and less than approximately 1 wt% of 3DG carbons functionalized with nano-silica and/or oxygen. OPC may conform to European standards EN 197-1 as CEM I 42.5R or ASTM Type I Portland cement.

[0065] In some implementations, an example cement composition may include ordinary Portland cement (“OPC”), one or more of pyroclastic ash, gypsum, or metakaolin as SCMs and 3DG carbons functionalized with one or more of nano-silica and oxygen. The replacement level of OPC may be at least approximately 70 wt%. The replacement level of OPC may be between approximately 70 wt% and approximately 80 wt%. An example SCM may include approximately 65 wt% metakaolin, approximately 32 wt% limestone, and approximately 3 wt% gypsum. A superplasticizer may be used to improve workability. The amount of 3DG carbons functionalized with one or more of nano-silica or oxygen may be less than approximately 1 wt% of the cement composition. OPC may conform to European standards EN 197-1 as CEM I 42.5R or ASTM Type I Portland cement. During initial hydration (cement slurry formation with water), the water to cement ratio may vary between approximately 0.3 and approximately 0.5.

[0066] 3DG carbons functionalized with nano-silica were analyzed using SEM/EDS for elemental analysis. Figure 6A shows a micrograph 600A of untreated 3DG carbons, and Figures 6B, 6C, and 6D show micrographs 600B, 600C and 600D that confirm the presence of O and Si elements on 3DG carbons that were functionalized by silica.

[0067] Figure 7A shows elemental composition intensity (counts) 700A measured during SEM/EDS analysis of 3DG carbons functionalized with nano-silica, according to some implementations, and Figure 7B shows a box plot 700B of elemental composition distribution measured by SEM/EDS analysis of various 3DG carbons functionalized with nano-silica, according to some implementations. Quantitative analysis of the elemental composition intensity may suggest an interquartile range for Si concentration of between approximately 22 at. wt% and approximately 64 at. wt%, with an average of approximately 44 at. wt%, and that for oxygen concentration of approximately between 18 at. wt% and approximately 38 at. wt%, with an average of approximately 29 at. wt%. The 3DG carbons surface functionalized with nano-silica may include between approximately 20 at. wt% and approximately 65 at. wt% Si, and between approximately 15 at. wt% and approximately 40 at. wt% O.

[0068] The presence of carbon during SEM/EDS analysis suggests that some areas of the 3DG carbons remain in an unfunctionalized state. The O/Si atomic ratio (not shown) had an interquartile range for Si concentration of between approximately 1.6 and approximately 2.8, with an average of approximately 2.5, which suggests that some elemental oxygen does not derive from silica (O/Si ratio of 2), but corresponds to oxygenated 3DG carbons (for example, graphene oxides). The O/Si ratio of 3DG carbons surface functionalized with nano-silica may be between approximately 1.5 and approximately 3.

[0069] Figure 8 shows a thermogram 800 of example cement compositions functionalized with nano-silica, according to some implementations. Samples of example cement compositions with 3DG carbons were subjected to thermogravimetry analysis (TGA). The example thermogram 800 of Figure 8 suggests that between approximately 250 °C and 450 °C, degradation of the chemical moiety that connects silica to the 3DG carbon surfaces occurs. Silanol groups present on the surface of nano-silica particles and clusters may degrade between approximately 450 °C and approximately 700 °C and carbon may degrade at between approximately 700 °C and approximately 1000 °C leaving behind inorganic silica residue.

[0070] In some implementations, an example method for regulating CSH nucleation and time-lapsed growth during the initial hydration of cement may include providing one or more of the example compositions previously described and mixing and mixing with water, where the water to cement ratio by weight may be vary between approximately about 0.3 and about 0.5. For example, a cement composition may include ordinary Portland cement, a secondary cementitious material (SCM) including one or more of metakaolin or limestone or gypsum in an amount corresponding to at least approximately 70% replacement level of ordinary Portland cement, and less than approximately 1 wt% of 3DG carbons. The 3DG carbons may include few layer graphene ("FLG") nanoplatelets orthogonally joined to each other to form a 3D porous graphene scaffold structure, where the 3DG carbons are surface functionalized with one or more of nano-silica or oxygen. An SCM may include approximately 65 wt% metakaolin, approximately 32 wt% limestone, and approximately 3 wt% gypsum.

[0071] In some implementations, 3DG carbons may include aggregates of primary carbon particles that include carbon nano-onions (CNOs) and other allotropes. The primary carbon nanoparticles may include two or more connected multi-walled spherical fullerenes (MWSF). CNOs or multi-walled fullerenes are carbon nanoparticles, generally spherical in shape, and may include multiple concentric shells including graphene that defining a plurality of porous

regions or zones nested within each other. The primary carbon nanoparticles may be characterized by a high degree of order (e.g., a Raman signature with an I_D/I_G ratio from 0.95 to 1.05), and a high purity (e.g., the ratio of carbon to other elements, other than H, is greater than 99.9%). Layers of graphene may coat the connected CNOs in each primary carbon nanoparticle. The one or more shells and carbonaceous regions may include sp^2 -hybridized carbon (indicative of graphene) and may have minor islands of amorphous sp^3 -hybridized carbon.

[0072] Synthesis and/or growth of 3DG carbons including CNOs may be produced by thermal cracking of hydrocarbon feedstock as disclosed by Riso et al., “Cracking of a Process Gas,” U.S. Pat. No. 9,862,602, filed on March 27, 2017, Cook, et al., “Carbon Allotropes,” U.S. Pat. No. 10,112,837, filed on October 26, 2017, Cook et al. “Method and Apparatus for Cracking of a Process Gas,” U.S. Pat. No. 11,053,121, filed October 18, 2018, and Cook, et al. “Carbon Allotropes,” U.S. Pat. Pub. No. 2021/0292170, filed June 3, 2021, which are incorporated by reference herein in each of their entireties.

[0073] Figure 9A shows a diagram of an example primary carbon particle 900A in 3DG carbons, according to some implementations. The primary carbon particle 900A includes an inner region 911 surrounded by an outer region 912. The outer region 912 includes an outer boundary 910 of the primary carbon particle 900A. The inner region 911 may include a plurality of first pores 901 dispersed therein, and the outer region 912 may include a plurality of second pores 902 dispersed therein. The inner region 911 and outer region 912 may be interconnected by at least some of the first pores 901. The inner region 911 may be associated with a first pore density, and the outer region 912 may be associated with a second pore density that is different than the first pore density. The first pores 901 may be configured to confine dopants 916 to be released as a function of time (time release) during hydration of cement, and the second pores 902 may provide pathways or channels for transport of dopants 916 into and from the primary particle 900A (and for pre-loading dopants into the primary carbon particle 900A. Example primary carbon nanoparticles may be characterized by a size or principal dimension (diameter, length, width) of less than approximately 200 nm. In some instances, polysulfides 920 may be present within the primary carbon particle 900A.

[0074] Figure 9B shows a TEM image 900B of a carbon aggregate 930, according to some implementations. As shown, the carbon aggregate 930 may include a plurality of primary carbon nanoparticles 932 that resemble a “string-of-pearls.” In some

implementations, the size or principal dimension of carbon aggregate 930 may be between about 50 nm and 500 nm. Example primary carbon nanoparticles 932 may be characterized by a surface area of less than about 3000 m²/g. Primary carbon nanoparticles 932 may be of any shape, including one or more of spherical, spheroidal, dumbbell, cylindrical, elongated cylindrical type, rectangular prism, disk, wire, or irregular. In some implementations, the primary nanoparticles 932 may be formed of concentric, well-ordered spheres of sp²-hybridized carbon atoms as contrasted with spheres of poorly-ordered, non-uniform, amorphous carbon particles. In the primary nanoparticles 932, pore sizes may gradually decrease along a radial direction from the center of the particle to the outer boundary of the particle. In some example implementations, a multi-shell CNO primary particle may be characterized by a range of pore sizes and pore distributions in each region. The primary nanoparticles 932 and/or carbonaceous layers may also include one or more of few layer graphene (FLG) interconnected platelets, multi-layer graphene (MLG) interconnected platelets, graphite, carbon nano-tubes (CNTs), flat graphene, or wrinkled graphene. The example primary carbon nanoparticles 932 may be characterized as non-hollow carbon spherical particles. In some other implementations, the primary carbon nanoparticles 910 may also include tri-zone particles.

[0075] Figures 9C shows a TEM image of 3-dimensional carbon agglomerates 900C, according to some implementations. The agglomerates 900C may be dispersed in any one of the example cement compositions previously described. In some instances, 3DG carbons that form the agglomerates 900C may be functionalized, as previously described.

[0076] Figure 10 shows a diagram of another example primary carbon particle 1000 in 3DG carbons, according to some implementations. The example primary carbon particle 1000 may include a first zone 1051 nested within a second zone 1052, which in turn is nested within a third zone 1053. The first zone 1051 may include pores having a size or principal dimension (diameter, length width) of less than approximately 40 nm, the second zone 1052 may include pores having a principal dimension of less than approximately 35 nm, and the third zone 1053 may include pores having a principal dimension of less than approximately 30 nm. In some instances, the pores 1061 within the first zone 1051 may be characterized as macropores, the pores 1062 within the second zone may be characterized as mesopores, and the pores 1063 within the third zone 1053 may be characterized as micropores.

[0077] In some aspects, the principal dimension D1 of first zone 1051 may be less than approximately 100 nm, the principal dimension D2 of second zone 1052 may be less than

approximately 150 nm, and the principal dimension D3 of third zone 1053 may be approximately 200 nm. The relative dimensions, porosities, and electrical conductivities of the first zone 1051, the second zone 1052, and the third zone 1053 may be tuned by tuning reactor operating conditions to obtain desired particle or aggregate structure, porosity and particle density. The first zone 1051 may have a density of carbonaceous material of less than approximately 1 g/cc. The third zone 1053 is bounded by an outer shell 1055 and may have a density of carbonaceous material between approximately less than 1 g/cc and 3.5 g/cc. The second zone 1052 may have a density of carbonaceous material between approximately 0.5 g/cc and 3 g/cc. The one or more shells and carbonaceous regions may include sp²-hybridized carbon (indicative of graphene) and may have minor islands of amorphous sp³-hybridized carbon.

[0078] As used herein, a phrase referring to “at least one of” or “one or more of” a list of items refers to any combination of those items, including single members. For example, “at least one of: a, b, or c” is intended to cover the possibilities of: a only, b only, c only, a combination of a and b, a combination of a and c, a combination of b and c, and a combination of a and b and c. Unless otherwise specified in this disclosure, for construing the scope of the term “about” or “approximately,” the error bounds associated with the values (dimensions, operating conditions etc.) disclosed is $\pm 10\%$ of the values indicated in this disclosure. The error bounds associated with the values disclosed as percentages is $\pm 1\%$ of the percentages indicated. The word “substantially” used before a specific word includes the meanings “considerable in extent to that which is specified,” and “largely but not wholly that which is specified.”

[0079] Various modifications to the implementations described in this disclosure may be readily apparent to persons having ordinary skill in the art, and the generic principles defined herein may be applied to other implementations without departing from the spirit or scope of this disclosure. Thus, the claims are not intended to be limited to the implementations shown herein but are to be accorded the widest scope consistent with this disclosure, the principles and the novel features disclosed herein.

[0080] Additionally, various features that are described in this specification in the context of separate implementations also can be implemented in combination in a single implementation. Conversely, various features that are described in the context of a single implementation also can be implemented in multiple implementations separately or in any suitable subcombination. As such, although features may be described above in combination

with one another, and even initially claimed as such, one or more features from a claimed combination can in some cases be excised from the combination, and the claimed combination may be directed to a subcombination or variation of a subcombination.

[0081] Similarly, while operations are depicted in the drawings in a particular order, this should not be understood as requiring that such operations be performed in the particular order shown or in sequential order, or that all illustrated operations be performed, to achieve desirable results. Further, the drawings may schematically depict one more example processes in the form of a flowchart or flow diagram. However, other operations that are not depicted can be incorporated in the example processes that are schematically illustrated. For example, one or more additional operations can be performed before, after, simultaneously, or between any of the illustrated operations. In some circumstances, multitasking and parallel processing may be advantageous. Moreover, the separation of various system components in the implementations described above should not be understood as requiring such separation in all implementations, and it should be understood that the described program components and systems can generally be integrated together in a single product or packaged into multiple products.

CLAIMS

What is claimed is:

1. A cement composition including:
ordinary Portland cement;
a secondary cementitious material (SCM) including pozzolan in an amount corresponding to up to approximately 70% replacement level of ordinary Portland cement;
and
aggregates of carbon nanoparticles including 3-dimensional graphene (3DG carbons) in an amount between approximately 0.05% bwoc and approximately 2% bwoc, wherein the 3DG carbons include graphene nanoplatelets orthogonally joined to each other to form a 3D porous graphene scaffold structure.
2. The cement composition of claim 1, wherein the graphene nanoplatelets include one or more of single layer graphene (SLG), few layer graphene (FLG), or many layer graphene (MLG).
3. The cement composition of claim 1, wherein the pozzolan includes between approximately 50 wt% and approximately 70 wt% SiO₂, between approximately 10 wt% and approximately 20 wt% Al₂O₃, and less than approximately 10 wt% each of Fe₂O₃ and MgO.
4. The cement composition of claim 1, wherein the loss on ignition (LOI) of the pozzolan is less than approximately 10 wt%.
5. The cement composition of claim 1, wherein the 3DG carbons are characterized by a Raman spectroscopy signature having an I_D/I_G ratio between approximately 0.95 and approximately 1.05.
6. A cement composition including:
ordinary Portland cement;
a secondary cementitious material (SCM) including one or more of metakaolin, slag, fly ash, pyroclastic ash, or limestone, in an amount corresponding to up to approximately 70% replacement level of ordinary Portland cement; and

aggregates of carbon nanoparticles (3DG carbons) in an amount between approximately 0.05% bwoc and approximately 2% bwoc, wherein the 3DG carbons include graphene nanoplatelets orthogonally joined to each other to form a 3D porous graphene scaffold structure, and wherein the 3DG carbons are functionalized with one or more of silicate compounds or nano-silica.

7. The cement composition of claim 6, wherein the graphene nanoplatelets include one or more of single layer graphene (SLG), few layer graphene (FLG), or many layer graphene (MLG).

8. The cement composition of claim 6, wherein the SCM includes between approximately 50 wt% and approximately 70 wt% SiO_2 , between approximately 10 wt% and approximately 20 wt% Al_2O_3 , and less than approximately 10 wt% each of Fe_2O_3 and MgO .

9. The cement composition of claim 6, wherein the loss on ignition (LOI) of the SCM is less than approximately 10 wt%.

10. The cement composition of claim 6, wherein the 3DG carbons are characterized by a Raman spectroscopy signature having an I_D/I_G ratio between approximately 0.95 and approximately 1.05.

11. The cement composition of claim 6, wherein the one or more of silicate compounds or nano-silica are anchored to the surface of the 3DG carbons, nano-confined in the scaffold structure formed by the orthogonally joined graphene nanoplatelets, or micro-confined within an interconnected porous network disposed within and between the aggregates.

12. The cement composition of claim 6, wherein the 3DG carbons functionalized with one or more of silicate compounds or nano-silica includes between approximately 20 at. wt% and approximately 65 at. wt% Si, and between approximately 15 at. wt% and approximately 40 at. wt% O.

13. The cement composition of claim 6, wherein the O/Si ratio of the 3DG carbons functionalized with one or more of silicate compounds or nano-silica is between approximately 1.5 and approximately 3.
14. The cement composition of claim 6, wherein the 3DG carbons are surface functionalized with one or more of oxygen, nitrogen, silicon, sodium, or potassium.
15. A cement composition including:
ordinary Portland cement;
a secondary cementitious material (SCM) including one or more of metakaolin, limestone, or gypsum in an amount corresponding to up to approximately 70% replacement level of ordinary Portland cement;
a superplasticizer in a concentration range of between approximately 0.05% bwoc and approximately 2% bwoc; and
aggregates of carbon nanoparticles (3DG carbons) in amounts of between approximately 0.05% bwoc and approximately 2% bwoc, wherein the 3DG carbons include graphene nanoplatelets orthogonally joined to each other to form a 3D porous graphene scaffold structure.
16. The cement composition of claim 15, wherein the graphene nanoplatelets include one or more of single layer graphene (SLG), few layer graphene (FLG), or many layer graphene (MLG).
17. The cement composition of claim 15, wherein the amount of gypsum is between approximately 0.5 wt% and approximately 3.5 wt%.
18. The cement composition of claim 15, wherein the superplasticizer includes a polycarboxylate ether.
19. The cement composition of claim 15, further including hydroxyethylcellulose in a concentration range of between approximately 0.05% bwoc and approximately 1.0% bwoc.

20. The cement composition of claim 15, wherein the 3DG carbons are surface functionalized with one or more of silicate compounds or nano-silica.

21. The cement composition of claim 15, wherein the SCM includes approximately 65 wt% metakaolin, approximately 32 wt% limestone, and approximately 3 wt% gypsum.

22. The cement composition of claim 15, wherein the SCM includes approximately 97 wt% of one or more of metakaolin or limestone, and approximately 3 wt% gypsum.

23. A cement composition including:
ordinary Portland cement;
a secondary cementitious material (SCM) including one or more of pyroclastic ash, slag ash, fly ash, metakaolin or limestone in an amount corresponding to up to approximately 70% replacement level of ordinary Portland cement; and
aggregates of carbon nanoparticles (3DG carbons) in amounts of between approximately 0.05% bwoc and approximately 2% bwoc, wherein the 3DG carbons include aggregates of carbon nanoparticles including graphene nanoplatelets, wherein the carbon nanoparticles are characterized by:

a plurality of porous concentric shells including graphene, wherein each shell encloses a porous carbon region; and

an interconnected porous network disposed in each carbon region and in fluid communication with contiguous carbon regions.

24. The cement composition of claim 23, wherein the SCM includes between approximately 50 wt% and approximately 70 wt% SiO_2 , between approximately 10 wt% and approximately 20 wt% Al_2O_3 , and less than approximately 10 wt% each of Fe_2O_3 and MgO .

25. The cement composition of claim 23, wherein the loss on ignition (LOI) of the SCM is less than approximately 10 wt%.

26. The cement composition of claim 23, wherein the 3DG carbons are characterized by a Raman spectroscopy signature having an I_D/I_G ratio between approximately 0.95 and approximately 1.05.

27. The cement composition of claim 23, wherein the size of the carbon nanoparticles is between approximately 20 nm and approximately 750 nm.
28. The cement composition of claim 23, wherein the size of the aggregates of carbon nanoparticles is between approximately 50 nm and approximately 1500 nm.
29. The cement composition of claim 23, wherein the size of the aggregates of carbon nanoparticles is greater than approximately 2 μm .
30. The cement composition of claim 23, wherein the 3DG carbons are surface oxidized with ozone.
31. The cement composition of claim 23, wherein the 3DG carbons are surface functionalized with one or more of silicate compounds or nano-silica.
32. The cement composition of claim 31, wherein the 3DG carbons surface functionalized with one or more of silicate compounds or nano-silica include between approximately 20 at. wt% and approximately 65 at. wt% Si, and between approximately 15 at. wt% and approximately 40 at. wt% O.
33. The cement composition of claim 31, wherein the O/Si ratio of the 3DG carbons functionalized with one or more of silicate compounds or nano-silica is between approximately 1.5 and approximately 3.
34. The cement composition of claim 23, wherein the 3DG carbons are surface functionalized with one or more of oxygen, nitrogen, silicon, sodium or potassium.
35. A method for regulating calcium-silicate-hydrate (CSH) nucleation and time-lapsed growth during the initial hydration of cement, the method including:
providing the cement composition of claim 20; and
mixing with water, wherein the water to cement ratio by weight is between approximately 0.3 and approximately 0.5.