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Recent Trends in Incorporating Graphene Coated Sand in Self-Sensing Cementitious Composites †

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Abstract: Self-sensing cementitious composites include the use of conductive materials which have important capabilities in monitoring structural health. Graphene has been widely used to modify cementitious composites to get self-sensing properties due to its unique electrical properties along with its exceptional specific surface area, high aspect ratio, and high strength and modulus. The development of a cost-effective graphene-based cement material with uniform dispersion of graphene in the cement matrix remains challenging. Graphene aggregation in the cement matrix is considered as a 'defect', undermining the reinforcing effect of graphene and potentially affecting the performance of cementitious composites. Rather than employing the traditional approach of directly incorporating graphene into the cement matrix in the development of smart sensing composites, researchers have used a more efficient approach via nano-surface engineering of the sand. This paper reviews the current state of research on graphene-coated sand, particularly the progress made in the recent years. The purpose of this review is to summarize the results of those recent experiments. When graphene-coated sand is added to the cementitious mix, the nano- and microscale properties of graphene–sand-incorporated cementitious composite are enhanced significantly, especially in terms of the fresh, piezoresistive, and mechanical properties and microstructures. However, more research is needed on graphene-coated sand-incorporated cementitious composite because it may provide a better reinforcement while also lowering the cost. Therefore, this review can encourage future researchers and civil engineers to develop functional graphene-based concrete for the next generation of smart infrastructure.

Keywords: graphene; coated sand; self-sensing cementitious composite

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1. Introduction

Self-sensing cementitious composites that combine structure and sensing functions have recently gained people's attention. This material can be created by adding conductive fillers into the cement matrix. By analyzing the matrix's voltage, currents, capacitances, and other signals, the stress, damage, and deformation can be detected in real time [1]. Developing a self-sensing cementitious composite provides a new method for structural health monitoring that effectively overcomes the shortcomings of traditional sensors. A change in resistivity and a reduction in sensing performance accuracy can result from metals and their oxides, which are easily affected by the external environment. Carbon-based fillers are said to be the ideal conductive fillers due to their superior durability, alkali resistance, and conductive performance [2]. Carbon nanostructures such as carbon nanotubes (both single- and multiwalled), carbon nanofibers (CNFs), and graphene have piqued the interest of many concrete researchers recently due to their superior mechanical, chemical, thermal, and electrical properties, as well as their performance as reinforcing materials [3]. Graphene-based nanomaterials have been broadly used in cementation composites due to their superior properties. Due to the diverse and rather sophisticated fabrication processes and structures, graphene-based nanomaterials can be classified in a variety of ways. Graphene, a single-layer carbon sheet, is a 2D nanomaterial and the basic structural unit of all graphene-based nanomaterials. It can be wrapped into 0D nanoparticles such as fullerenes and rolled into 1D nanotubes [4]. Table 1 shows the properties of 0D, 1D, and 2D graphene-based nanomaterials.

Table 1. Properties of 0D, 1D, and 2D graphene-based nanomaterials.

Materials		Mechanical Properties		Physical Properties				Electron Properties	Refs.
Dimension	Type	Modulus Elasticity	Tensile Strength	Aspect Ratio	SSA	Diameter/ Thickness	Density	Electron Conductivity	
0D	C_{60}	-	-	-	-	~1	1650	10^{-3}	[4]
	Carbon black (CB)	-	-	-	56.9	5–50	1700–1900	$\sim 10^3$	[4,5]
1D	Carbon nanotubes (CNTs)	950	11–63	1000–10,000	70–400	15–40	1330	10^6– 10^7	[4,6]
2D	Graphene nanoplatelet (GNP)	1000	~130	6000–600,000	2600	~0.08	2200	10^7–10^8	[4,6]
	Graphene oxide (GO)	23–42	~0.13	1500–45,000	700–1500	~0.67	1800	10^7–10^8	[4,6]

Directly introducing an aqueous solution of graphene oxide (GO) into the cement matrix makes the uniform dispersion of GO sheets in the matrix challenging [7]. Long-term ultrasonication treatment and strong acid functionalization have adverse impacts on graphene-based materials, which may induce structural flaws. With this said, the high cost and poor dispersion of graphene-based materials prevent further industrial deployment [7]. As a result, it is widely established that in situ fabricated materials exhibit improved dispersion, higher reinforcing efficiency, and reduced prices [7]. Graphene-coated sand is reportedly utilized in cementitious composites to overcome the uniform dispersion problem of graphene nanosheets in the matrix.

Graphene-coated sand is new to the construction industry, and prior researchers did not conduct many experimental trials. As a result, in-detail investigations need to be conducted. This article reviews the available literature on utilizing graphene-coated sand in cementitious composites. The remaining sections discuss the properties of self-sensing cementitious composites when graphene-coated sand is utilized to replace full volume of natural sand.

Characterization Techniques of Graphene

The current techniques adopted to evaluate the dispersion quality of graphene in the cement matrix are summarized in Table 2. As can be seen, a number of studies have reported the graphene dispersion quality in water using techniques such as zeta potential, scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy, X-ray diffraction (XRD), X-ray photoemission spectroscopy (XPS), atomic force microscopy (AFM), Fourier-transform infrared spectroscopy (FTIR), and elemental mapping. SEM equipped with an energy-dispersive spectrometer (EDS) has been used extensively to characterize the dispersion of CNMs in the cement matrix; however, due to the complexity of the hydration products, graphene is difficult to locate or even identify. SEM, on the other hand, is incapable of quantitatively characterizing CNM dispersion in the cement matrix, The comprehensive evaluation of CNM dispersion and distribution in the cement matrix is critical for the design and optimization of the CNM–cement interaction, effectively promoting CNM effectiveness [8]. According to Lu et al. [9], UV/Vis and Raman spectroscopy results revealed that the GO coverage on the surface of the sand is about 70%. According to Yao et al.'s [7] synthesis process of GC material, the critical process in dispersing the graphene is the conversion of glucose into graphene in cement material. Wrinkled nanosheets with a thickness of 1.1 nm measured by SEM and AFM were observed for graphene generated by glucose. The subsequent energy-dispersive X-ray spectroscopy (EDS) test revealed a clear carbon distribution. The C, O, Ca, and Si elements were found to be uniformly distributed throughout the GC material. Additional tests were performed using various characterization tools to confirm that the glucose was successfully transformed into graphene. Patterns of the GC material obtained by X-ray diffraction (XRD) revealed a new peak at 27°, representing the graphene flakes formed in the GC material, whereas the G band at 1578 cm^{-1} of the samples supported the formation of graphite in the 532 nm Raman spectrum. The sample exhibited a broad D-band centered at 1360 cm^{-1}, similar to nanometer-sized graphite particles and chemically modified graphene flakes, indicating the presence of disorder and the edges of the graphene domain as observed by high-resolution SEM. The presence of a 2G band (G and G′) on the aggregate surface indicated a high-quality graphene-coated surface [10]. X-ray photoemission spectroscopy (XPS) spectra were used to confirm the characteristic peak of graphene in GC material. As a result, elemental mapping or other complementary techniques must be used to confirm that the materials focused under SEM are indeed graphene. Table 2 shows the techniques adopted by a few researchers to evaluate the quality of the graphene suspension or cement matrix.

Table 2. Techniques adopted to evaluate the quality of the graphene suspension or cement matrix.

Methods	System	Description	Refs.
UV/Vis spectroscopy	Suspension	Beer–Lambert's law is applied to calculate the content of CNMs as a function of absorbance	[9]
Zeta potential		A higher zeta potential value indicates improved dispersion/coverage.	[9–12]
Scanning electron microscopy (SEM)	Suspension/cement matrix	Dispersion assessment based on direct observation of dimensions	[7,10,12]
Transmission electron microscopy (TEM)		Observation of graphene sample morphology	[12]
Raman spectroscopy		Based on point-count analysis	[7,10]
X-ray diffraction (XRD)		Differentiates between graphite and graphene samples	[7,12]
X-ray photoemission spectroscopy (XPS)		Employed to detect chemical species through a photoelectric effect under X-ray stimulation	[7,9,12]
Atomic force microscopy (AFM)		Employed to determine morphological features of graphene, such as layer thickness, number of layers, and lateral dimensions of a well-dispersed sample	[7]
Fourier-transform infrared spectroscopy (FTIR)		Employed to detect functional groups and to characterize graphene nanocomposites	[9,12]

2. Effects of Graphene-Coated Sand on Cementitious Composite

The addition of graphene-coated sand to the cementitious composite has a significant impact on both the fresh and the hardened properties of mortar. The nature of flow and consolidation is indicated by fresh properties, whereas service strength and durability are indicated by hardened properties. This section discusses the effects of graphene-coated sand on different properties of cementitious composites.

2.1. Effect on Flowability

The idea of employing conductive graphene-coated sand is to slightly improve flowability. When compared to the control specimen, the average flow diameter of the cementitious composite with graphene oxide-coated sand decreased by about 10.4%. The average flow diameter of cementitious composites containing reduced graphene oxide-coated fine aggregate (rGO@FAg) and graphene-coated fine aggregate (G@FAg), on the other hand, increased by about 4.3% and 8.7%, respectively. This could be due to the lower polar functionality of nanosheets, which indirectly increases the hydrophobicity of the coated fine aggregates, whereas the well-dispersed GO nanosheet has a high specific surface area (SSA), requiring a large amount of free water to wet its surface [11].

2.2. Effect on Mechanical Strength

2.2.1. Effect of Type of Graphene Used on the Compressive and Flexural Strength

It was reported that the addition of GO-coated sand resulted in an increase in its compressive and flexural strength when compared to plain mortar and mortar specimens incorporating reduced graphene oxide (rGO)-coated sand and graphene-coated sand [11]. However, another researcher obtained a different result, stating that graphene oxide cement paste with the addition of 0.05 wt.% GO (GOCP) had a slight decrease in compressive strength, while 3 wt.% carbon source before graphitization reaction (GCP3) had the highest compressive strength reading [7]. This could be due to the dispersion of nanomaterials in the cement matrix. However, Lu et al. [11] provided a different explanation, claiming that the hydrophobic nature of the rGO and graphene nanosheets weakens the bonds between the treated aggregate particles and the cement paste matrix. Table 3 summarizes the increase in compressive and flexural strength of cementitious composite incorporating graphene-coated sand.

Table 3. Increase in compressive and flexural strength of cementitious composite incorporating graphene-coated sand.

Specimens	Graphene Coated Fine Aggregate	Additions	Increase in Compressive Strength (%)	Increase in Flexural Strength (%)	Refs.
Cement Paste	Graphene	-	38.18	48.9	[7]
	Graphene Oxide		−0.75	6.95	
Mortar	Graphene	0.5 CF (6 & 10 mm)	16.9–26.6 (reduction)	-	[10]
Mortar	Graphene Oxide (GO)	-	33.4	10.4	[11]
	rGO		−5.3	-	
	Graphene		−7.5	-	
Cement Paste	Graphene Oxide	SF (3–7%)	8–15	1.5–14.3	[12]
	Graphene Oxide	MSF (3–7%)	6–15	4.4–12.8	
Mortar	Graphene Oxide	-	10–38	7–44	[9]

2.2.2. Effect of Carbon Fiber (CF) and Silica Fume (SF) on the Compressive and Flexural Strength

The use of graphene-coated fine aggregate resulted in a lower compressive strength reading when compared to the plain mixture. As a result, a low concentration of CF was added to boost the compressive strength reading. According to the results, graphene-coated sand with 0.1 wt.% 6 mm CF maintained compressive strength with no reduction, whereas increasing CF concentration and length could deteriorate the compressive strength reading [10].

Lu et al. [12] conducted a study on plain cementitious composite and GO-incorporated cementitious composite. It was determined that the GO-incorporated cementitious composite increased compressive strength when compared to the plain mix. Silica fume was used with GO-coated sand to improve compressive strength even further. This was supported by the concept that the hybridization of GO with SF could increase the locally available Ca cations during cement hydration even further. On the 28th day, the cementitious composite containing 5 wt.% GO-coated modified silica fume (5MSF@GO) had the highest compressive and flexural reading. Further increasing the concentration of SF reduced both strengths [12].

2.2.3. Effect of Hydration Rate on the Compressive and Flexural Strength

It was reported that the compressive strength and flexural strength of all specimens increased on the 28th day [9]. This is also evident in the results obtained by another researcher, who found that the results obtained on the 28th day provided a higher compressive and flexural reading than the results obtained on the third day [11]. As a result, as the hydration rate increases, so does the mechanical strength.

2.2.4. Effect of Graphene Dosage on the Compressive and Flexural Strength

According to Yao et al. [7], the compressive strength and flexural strength of the cement paste increase with the glucose/GO content. When compared to the other GCPs, the GCP-3 had the highest compressive and flexural reading. However, exceeding 3 wt.% could reduce both strengths.

2.3. Effect on Water Sorptivity

Most researchers obtained a similar result, whereby the control cementitious composite specimen has the highest water absorption, while the cementitious composite with graphene-coated sand with or without carbon fiber (CF) showed a lower water absorption compared to the control specimen. This could be due to the fact that graphene coating improves the hydrophobicity of fine aggregates [11]. Similarly, when either SF or MSF was added, the water sorptivity of cement composites decreased, which could be attributed to pore refinement in the cement composites due to the pozzolanic and filler effect of SF [12].

2.4. Effect on Electrical Resistivity

The plain mortar had the highest electrical resistivity, which agrees well with its non-conductive nature. However, Lu et al. [11] reported that mortar with graphene-coated sand had the highest electrical resistivity when compared to plain mortar. This could be because of the coated GO, which promotes the hydration of cement grains in the ITZ region and a denser microstructure. It should be noted that all mortar specimens portrayed an increasing trend in electrical resistivity with curing age. This could be due to the loss of free water. The electrical resistivity of mortar with graphene-coated sand (G@FAg) was 2–3 orders of magnitude higher when compared to the plain mix. It should be noted that the mortar incorporating G@FAg was very stable with curing age, implying that the graphene-coated fine aggregates had a greater influence on overall conductivity than changes in pore solution resistivity [10].

2.5. Effect on Piezoresistive Behavior

The fractional change in electrical resistivity (FCR) values for the mortar control mix and mortar with graphene oxide-coated sand (M-GO@FAg) demonstrated a highly disorganized distribution, indicating that these mortars are unsuitable for strain sensing. However, for each loading cycle, the FCR values for mortar with graphene-coated sand (M-G@FAg) decreased with compressive loading and then increased to the initial value upon unloading. M-G@FAg exhibited a much more consistent FCR trend in terms of the loading–unloading cycle without significant noise interference compared to the other mortars [11]. The FCR value of M-G@FAg could be further increased by adding CF to the mixture. With this said, the piezoresistive behaviors could be significantly improved by adding CF to the mix. In this case, the CF length dominated the concentration when the concentration was above 0.1 wt.%. This can be supported by the finding that the smart mortar containing G@FAg-0.5 CF-10 mm had outstanding self-sensing ability during 100 cycles of repeated compressive loading. Overall, the researchers preferred the mortar with G@FAg-0.1 CF-6 mm due to its good compressive strength, high conductivity, and high piezoresistivity [10].

2.6. Effect on Microstructure

According to Yao et al. [7], the mix with 3 wt.% graphene/glucose had the fewest micropores and cracks, which complies with the compressive and flexural strength tests [10]. Whereas the aggregation of graphene oxide (GO) sheets in cement paste incorporating graphene oxide (GOCP) formed a poor connection with cement matrix, leading to pores and cracks. Having said that, cement paste incorporating graphene (GCP) materials exhibited better anti-cracking behavior than GOCP and pure cement paste (CP). Due to the well-connected structure between graphene and cement matrix, an enhanced stress transport track in the cement matrix existed, whereas the poor connection with the hydration product restricted the stress transport in the GOCP matrix. Most studies claimed that adding graphene resulted in a denser structure by decreasing porosity and crack propagation. Lu et al. [12] studied the microstructure of a composite containing 0.04% GO with varying contents of silica fume (SF) and modified silica fume (MSF). They noted that the ideal candidate to refine the pore structure of the graphene nanoplatelet (GNP)-based cementation composite would constitute a suitable amount of SF or MSF. Large capillary pores were almost completely absent with the addition of 5 wt.% MSF at 0.04 wt.% GO. Instead, more mesopores were seen. According to Lu et al. [9], the M-GO@Sand sample had a denser microstructure than the M-GO-Sand sample. This refined microstructure may be a result of the well-dispersed GO's control over the composition and assembly of hydration products. It is interesting that crosslinked GO nanosheets were discovered because they tended to form linked clusters and halted microcracks from spreading. Similar research was conducted by Lu et al. [10], whereby the mortar incorporating G@FAg was compared to the plain mortar mix. Lu et al. [10] reported that the mortar containing G@FAg had a denser microstructure compared to the plain mix. This researcher then added CF to evenly enhance the microstructure of the mortar. The SEM images of cement paste incorporating glucose/GO and of cement mortar incorporating graphene-coated sand are shown in Figures 1 and 2, respectively.

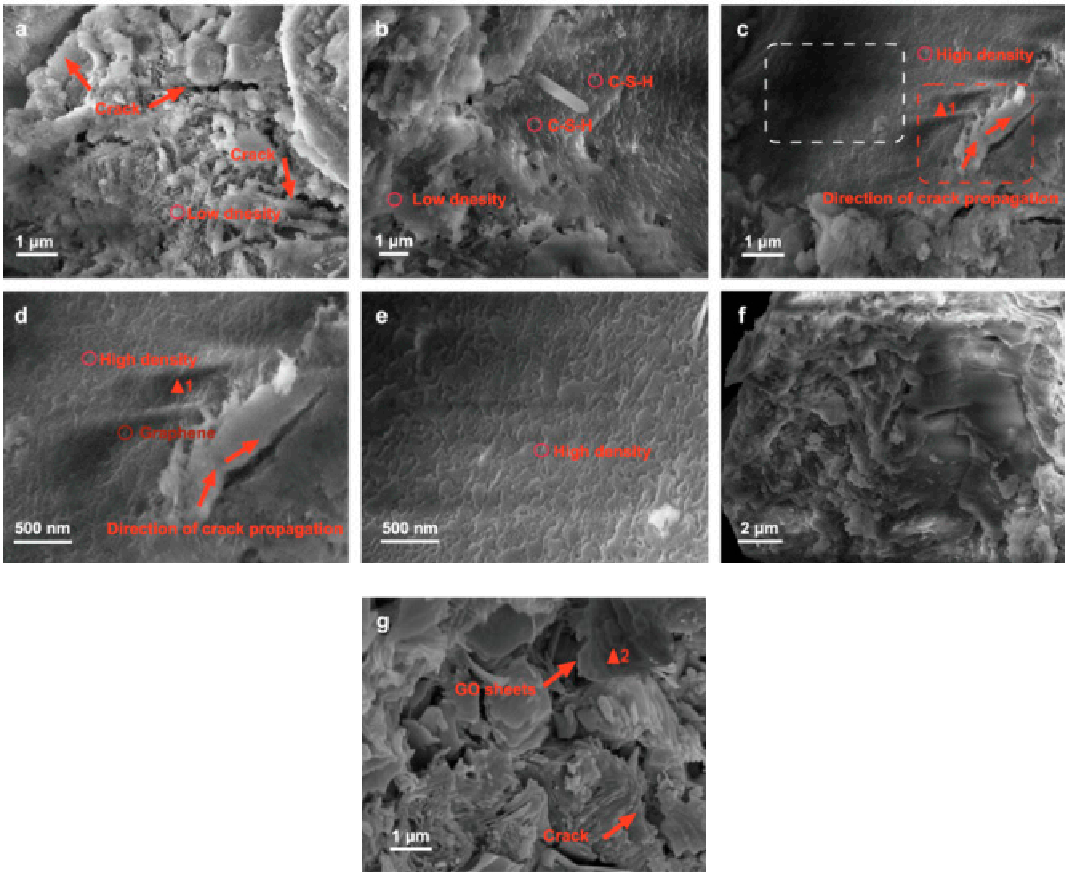

Figure 1. (**a**) CP; (**b**) GCP-1 paste; (**c**) GCP-3 paste; (**d**) local magnified images of (**c**) in the red dashed frame; (**e**) local magnification in calcium silicate hydrate (C–S–H) high-density region of GCP-3 sample; (**f**) GCP-6 paste; (**g**) GOCP. Reprinted/adapted with permission from Ref. [7]. Copyright © 2022 Elsevier, Yao Yao, Hu Liu, Zhenyu Zhang and Yan Zhuge.

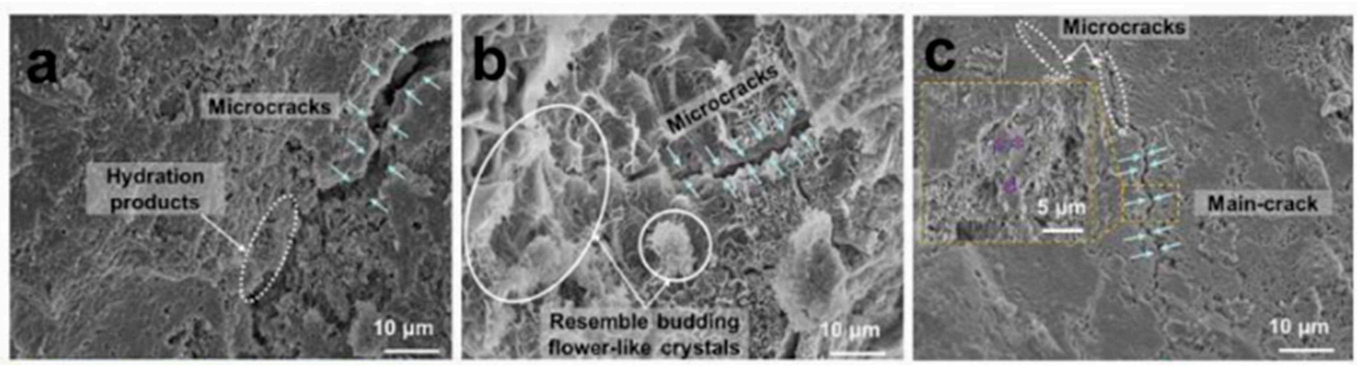

Figure 2. Representative SEM images of cement mortars: (**a**) M-Plain; (**b**) M-GO-Sand; (**c**) M-GO@Sand. Reprinted/adapted with permission from Ref. [9]. Copyright © 2022 Elsevier, Dong Lu and Xianming Shi.

3. Conclusions

This paper discussed the mechanical properties, water sorptivity, electrical resistivity, piezoresistivity, and microstructure of cementitious composite incorporating graphene-coated sand, as well as the improvements made to them. It was observed that the incorporation of graphene-coated sand in the cementitious matrix improved the mechanical behavior and water sorptivity. It also greatly influenced the electrical resistivity and piezoresistive behavior of the cementitious composites. Graphene-coated sand also helped to achieve a dense microstructure of the cementitious composites. This review may assist future researchers in discovering a better approach to improving the strength of self-sensing concrete at a lower cost.

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