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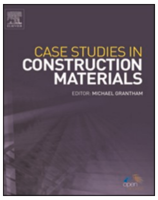

Short communication

Self-sensing cement-based sensors with superhydrophobic and self-cleaning capacities after silane-based surficial treatments

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ABSTRACT

A novel cement-based sensors was developed with integrated self-sensing superhydrophobicity, and self-cleaning functions in this paper. The synthesis was carried out by penetrating precast graphene nanoplate/cement-based sensors with silane/isopropanol solutions. The silane-treated cement-based sensors showed satisfactory stress/strain sensing performance with an average gauge factor of 141.8, and exhibited excellent hydrophobic behaviour with the highest water contact angle of 163° on the intact surface. The contact angle decreased to 148° and 142°, for the surface with scratches and for the inner part of sensors, respectively. The reduction was due to the spalling and less amount of silane particles within the scratches and the harder entry of silane to the inner part of sensor. The self-cleaning properties of silane-treated cement-based sensor were evaluated by the visual observation of removing efficiency of hydrophilic carbon black dust and lipophilic sauces after water rinsing. It was found that the silane-treated cement-based sensor showed excellent self-cleaning performance using hydrophilic carbon dust. Despite the removing efficiency decreased for the lipophilic sauces, the silane-treated cement-based sensors maintained much less stain than that of untreated ones on the surface. The related results will promote the synthesis and practical applications of multifunctional cement-based sensors for the application of intrisic structural health monitoring.

1. Introduction

Cement-based materials are the most widely used materials for producing infrastructures and civil architectures because of their low cost, high strengths, durability and serviceability. With the increasing demand for cutting green gas emissions and for intelligent, resilient and sustainable buildings and infrastructures, research focus has been gradually transformed from the traditional investigations on mechanical and durable properties into the development of smart, economical, and environmentally friendly construction materials. Consequently, various types of multifunctional cementitious materials, such as low carbon footprint cement [1,2], self-compacting concrete [3,4], self-healing and self-sensing concrete [5,6] and the superhydrophobic cementitious materials with self-cleaning ability [7,8], etc., have arisen rapidly.

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The development and research on smart cementitious composites with dual-functionalities, such as integrated self-sensing functionality and tensile ductility [9,10], integrated self-sensing and electromagnetic interference (EMI) shielding/absorbing properties [11,12], integrated self-sensing and self-heating properties [13,14], and integrated self-sensing and self-healing properties [15,16], have received growing attention in the recent year to fulfil the multifunctional requirements for next generation of the biomimetic, intelligent and resilient cement-based materials. However, rare investigations have attempted to integrate the self-sensing and self-cleaning capacities into the cementitious composite and to evaluate its synthetic performances.

In particular, the self-sensing and self-cleaning concrete enable the infrastructures and buildings to monitor and clean themselves automatically without additional sensors for structural health monitoring and workers for regular cleaning. Previous studies have shown the self-sensing performances of various cement-based sensors filled with different conductive fillers [17], manufactured in different steps [18], and measured in multiple stress and environmental conditions [19]. The low cost, easy manufacturing and installation process, high sensitivity and durability of cement-based sensors indicate their great application potential. Self-cleaning cementitious composites is a bionics design originating from the surface of the lotus leaf [20]. The hierarchical structures and micro papillae with hydrophobic nanofibers enable the lotus leaf to achieve the superhydrophobicity and self-cleaning property [21]. Superficial treatment with proper modifiers that reduce surface energy is one of the most practical strategies to improve surface hydrophobicity [22]. Research has proven that similar papillae can be created inside of the silane-treated cementitious composites, thus making the cementitious composites hydrophobic and possess self-cleaning capacity[23]. In addition to silane-based coating, superhydrophobic alumina coating, and photocatalytic superhydrophilic coating also have received increasing research interest to attain the excellent self-cleaning property [24,25].

In this study, silane-based hydrophobic coatings were applied on the surface of cement-based sensors to develop multifunctional cementitious composites with integrated superhydrophobicity, piezoresistivity and self-cleaning property. This approach improves the functionality of smart cementitious materials and promotes the practical application of cement-based sensors.

2. Experimental programme

The production of graphene nanoplate/cement-based sensors was conducted in the previous studies where detailed raw materials and manufacturing procedures can be found [26]. The content of graphene was 1.0% to the weight of binder, and the dispersion protocol was the combination of mechanical stirring and ultrasonication. Cement-based sensors were cast in a mould of 10 mm × 10 mm × 60 mm. The silane treatment is carried out when the cement-based sensor is hardened after 28 days of curing. As shown in Fig. 1 and Fig. 2, the trichloro-silane is firstly poured into the isopropanol solvent with mechanical stirring for dissolution, and the silane to isopropanol ratio is 4% by volume. Afterwards, the cleaned cement-based sensors are immersed in the silane/isopropanol solution. After 2 h, the sensors are taken out and moved to an oven for 4 h drying with the temperature of 50 °C. The immersion and followed drying procedures are conducted twice to ensure the sufficient entry of silane into cement-based sensors. As shown in Table 1, although the cost of prepared silane/isopropanol solution is relatively higher than the commercial product of the silane-based hydrophobic treatment on concrete, it is economically feasible since the mainstream application form of the cement-based sensors is small sensor elements embedded into large-scale structural elements [40,41] More significantly, isopropanol can reduce the viscosity of silane, which is responsible for the successful intrusion of silane to achieve the hydrophobic behaviour of the inner section in the cement-based sensors rather than only the surface [27,28].

To prepare the specimens for piezoresistivity-based self-sensing investigations, four copper meshes are embedded in the cementitious composites during casting as electrodes. Three compression cycles were applied on the cement-based sensors. The diagram of circuit connection for the piezoresistivity test can be found in reference [29]. The hydrophobicity is assessed through the water contact angle (CA) test with the deionized water as the testing liquid. The volume of each water drop is 0.2 μl, and the facility used is optical tensiometer Attension Theta. The self-cleaning performance is assessed using visual inspections of removal of carbon black dust and food stains, the removing efficiency before and after the sensor surfaces that were rinsed with deionized water are compared. The lipophilic sauces 1 and 2 are tomato and barbecue sauces, respectively. For each specimen, a total amount of deionized 10 ml water

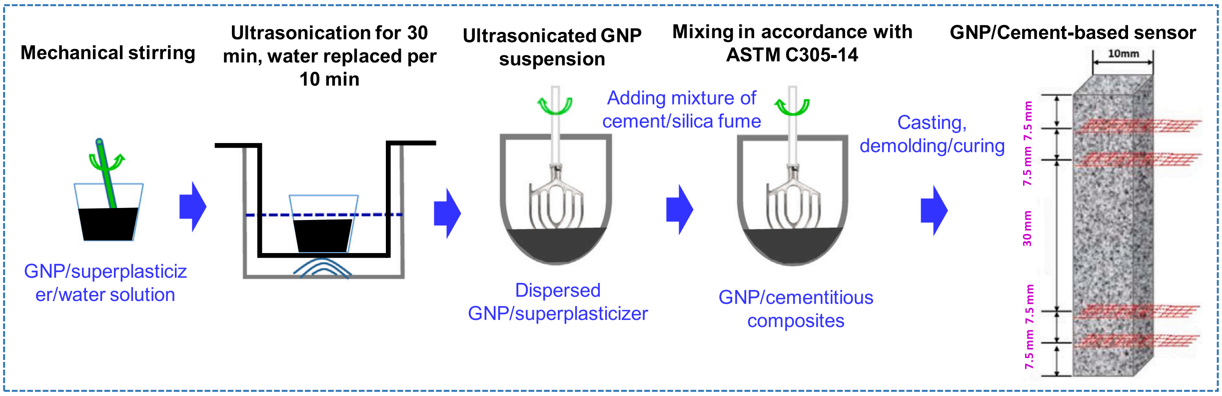


Fig. 1. Schematic diagram for the preparation procedures and specimen of graphene nanoplate /cement-based sensors.

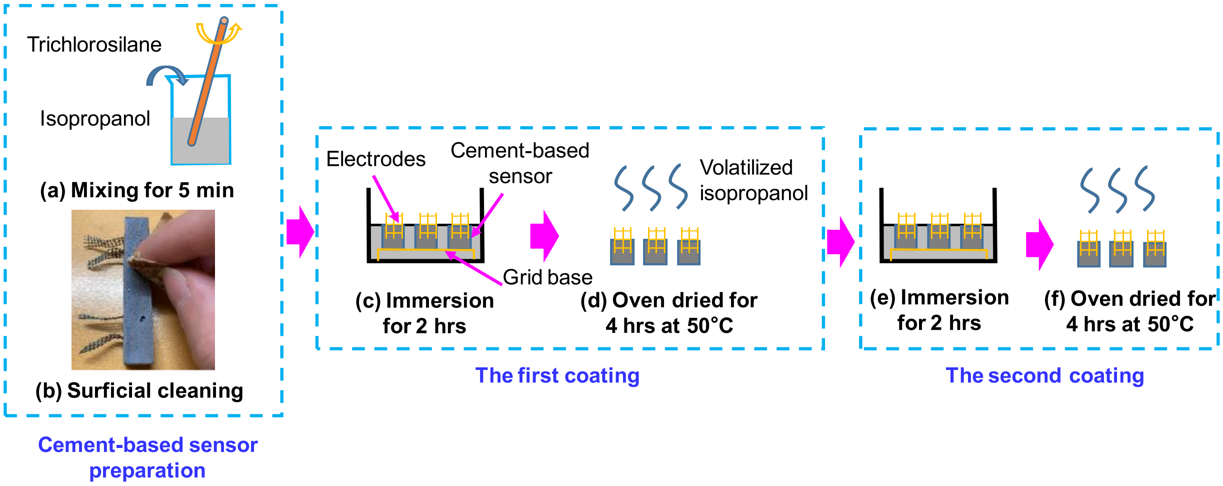


Fig. 2. Schematic diagram for the procedures of surficial enhancement on graphene nanoplate /cement-based sensors.

Table 1
Economic feasibility analysis of prepared silane/isopropanol solution for proposed superficial treatments.

Trichloro (1 H, 1 H, 2 H, 2 H-perfluorooctyl) silane	Price: A$159.00 per 10g^{0})
2-Propanol (Propan-2-ol, Isopropyl Alcohol, Iso-propyl Alcohol)	Price: A$18.50 per Liter^{1})
Prepared silane/isopropanol solution	Price: A$845.3 per Liter
Commercial silane-based hydrophobic treatment product for concrete	Price: A$49.45 per Liter^{2})

Note: reference website links:
0) https://www.sigmaaldrich.com/AU/en/product/aldrich/448931
1) https://asisscientific.com.au/shop/product/2-propanol-propan-2-ol-isopropyl-alcohol-iso-propyl-alcohol-ar-10-l/
2) https://komerco.com.au/collections/protective-coatings/products/sikagard-705

was spread on the surfaces using an injector. The self-cleaning performance of cement-based sensors without any treatment is compared to the experimental group after silane surficial enhancement.

3. Result and discussion

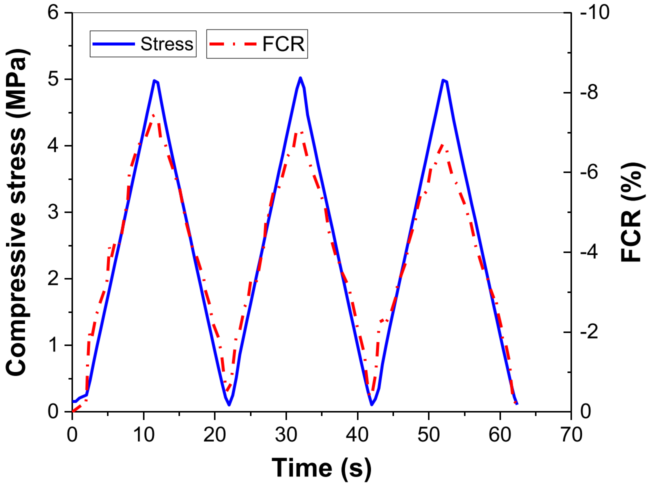
3.1. *Self-sensing performance*

Fig. 3(a) to (b) show fractional change of resistivity (FCR) of cement-based sensors as a function to compressive stress and strain, respectively. The average results of three duplicates were plotted. It was found that the compressive stress and strain had a linear correlation to FCR, which decreased as the stress or strain increased and recovered when the load was removed. Given the stress magnitude applied within the elastic range of cement-based sensors, the gauge factor can be obtained through the fitting curves between FCR and compressive strain. Gauge factor expressed as the FCR per unit strain is used to evaluate the sensing efficiency of piezoresistivity-based sensors. In this study, the graphene nanoplate/cement-based sensor after silane treatment achieved a gauge factor of 141.8, which was nearly 72 times higher than that of commercially available foil strain gauge. Table 2 summarizes the optimum stress sensitivity and gauge factor of GNP typed cement-based sensors reported in the available literature. It is seen that the developed hydrophobic cement-based sensor with silane-based surficial treatments exhibits competitive piezoresistive sensitivity under compressive loading, which is highly desirable.

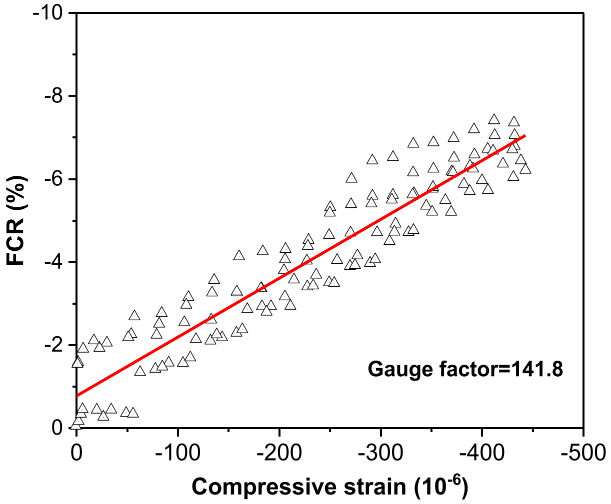
3.2. *Water contact angle*

Fig. 4(a) to (c) display water CA of cement-based sensors after silane treatment. The CA values of intact surface, destructed surface with scratches and the cross section of cement-based sensors are measured and compared. For the intact silane-treated surface shown in Fig. 4(a), the average CA reached the highest value of 163°. It demonstrates that the cement-based sensor had a superhydrophobic surface after immersion in silane/isopropanol solution owing to the invasion of hydrophobic silane. Previous studies have proposed the hydrophobic cementitious composites coupled with silane-based materials, but the CA values are usually lower than 150° because of the hydrophilic cement matrix [23,30]. The ultrahigh CA values obtained in this study are probably due to the additional filler of graphene nanoplate as conductive filler in cement-based sensor, given that the graphene nanoplate is beneficial for the hydrophobicity [29].

To simulate the situation of that concrete structures are damaged with man-made scratches, the silane treated cement-based



(a) Stress monitoring



(b) Strain monitoring

Fig. 3. Self-sensing performance of cement-based sensors after the silane treatment.

Table 2
Optimised piezoresistive sensitivities reported in existing studies on GNP typed cement-based sensors.

GNP content	Matrix type	Loading type	Stress range (MPa)	Stress sensitivity (%/MPa)	Strain range (με)	Gauge factor	Refs.
0.05 wt%	UHPC	Compression	0–20	1			[35]
7.5 wt%	Mortar	Compression	0–6.25		0–3300	110.7	[36]
10 wt%						90.8	
4.8 vol%	Mortar	Compression			400–2700	100	[37]
		Tension			0–100	500	
0.1 wt%	Mortar	Compression	0–18.75	0.7			[38]
5.0 vol%	Cement paste	Compression	0–20	0.78		156	[39]
3.0 wt%	Cement paste	Compression	0–10	3			[26]
1.0 wt%	Cement paste	Compression	0–5	1.4	0–425	141.8	This study

sensors were keyed with a sharp knife to create scratches on the surface, as shown in Fig. 4(b). The experimental results indicated a smaller CA value than that of intact surface, reaching approximately 148°. There are mainly two possible reasons responsible for the weakened hydrophobicity and reduced CA values. The first reason is the damaged micro papillae that reduce the surface energy of cementitious composites, and the second reason is the fall of hydrophobic silane and graphene nanoplate. In addition, as displayed in

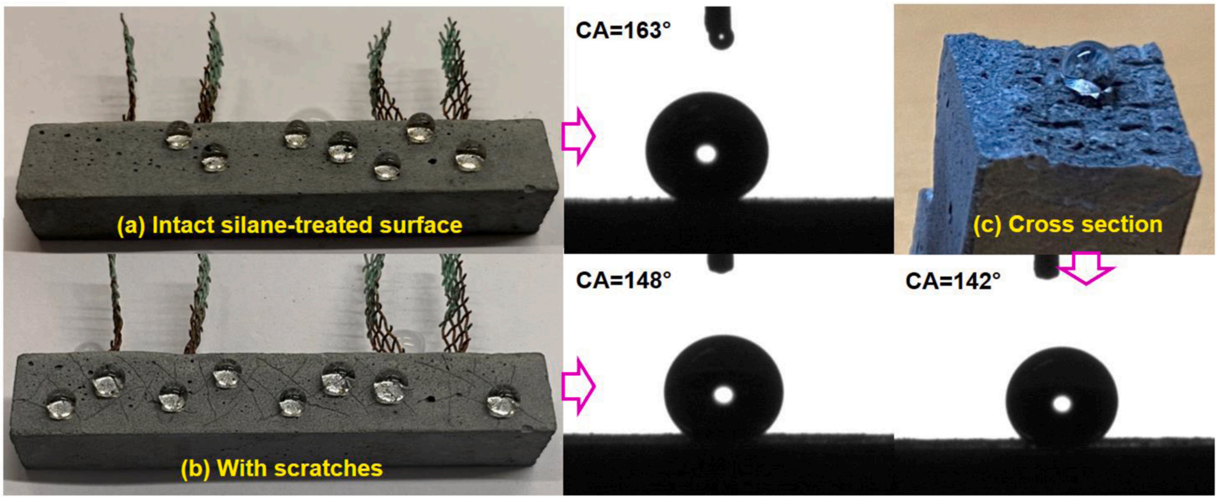


Fig. 4. Water contact angle of silane-treated cement-based sensor: (a) intact silane-treated surface; (b) with scratches; and (c) in the cross section.

Fig. 4(c), the contact angle test of cross section of cement-based sensors showed the smallest CA value of 142° compared to the CA values of surfaces. The results demonstrated that hydrophobicity was also achieved for the inner parts of cement-based sensors. This property can significantly enhance the water repellency of cement-based sensors and increase the serviceability of sensors by reducing the interference of electrical resistivity from water ingress [31–33]. In general, the hydrophobicity of internal cement-based sensors should be benefited from relatively small size and the two cycles of immersion/drying for silane treatment. In that circumstance, the silane/isopropanol solutions can be entered into inner porosity easily through capillary suction.

3.3. *Self-cleaning performance*

The carbon black dust and two lipophilic sauces with different stickiness are applied to observe the dust and food stains' removing efficiency by 10 ml deionized water, in order to assess the self-cleaning performance. Fig. 5(a) to (c) present the removing efficiency of cement-based sensors before and after the silane treatment. For the carbon dust sprinkled on the surface of cement-based sensors, the silane-treated sensor showed a very clean surface without leftover but the untreated sensor still had the residuals after the water drops rolling from the upper part of sensors. The experimental results are very similar to the previous studies, which found that the hydrophilic carbon dust was easily adhered and absorbed to the water drops [34]. Subsequently, the water drops removed the carbon dust for the silane-treated cement-based sensor. However, for the hydrophilic untreated cement-based sensor, water drops could penetrate into the cement matrix with carbon dust and that was why there left dark spots on the surface. As for the water drops removing efficiency regarding the lipophilic sauces, the experimental results showed the similar tendency of less residuals on the surface of cement-based sensors after silane treatment. In comparison to carbon dust, the sauces were more lipophilic rather than hydrophilic, and they could not completely adhere to the rolled water drops. Because the second sauce was stickier than the first one, it was found that the sauce with higher stickiness was much difficult to be removed, and tiny sauces still remained even for the silane-treated cement-based sensor. In addition, the results implied that the silane-based surficial treatment reduced the adhesion between cement matrix and lipophilic materials, such as sauces and enhanced the self-cleaning properties.

4. Conclusions

A novel trichloro-silane penetrated graphene nanoplate/cement-based sensor was developed in this study. This multifunctional sensor possessed integrated self-sensing, superhydrophobicity, and self-cleaning properties. It exhibited a high stress/strain sensing ability with a gauge factor of 141.8. The water contact angle of the intact sensor surfaces reached 163°, indicating an excellent hydrophobic behaviour. The self-cleaning performance of the sensor, assessed with visual adsorption of carbon dust and removal of lipophilic substances subjected to water rinsing, was much superior to the sensor without silane treatment, especially after performing hydrophilic cleaning of the carbon particles. Further researches will be conducted on the applications of this novel cement-based sensor for real structural health monitoring of building, pavement and bridges.

Declaration of Competing Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

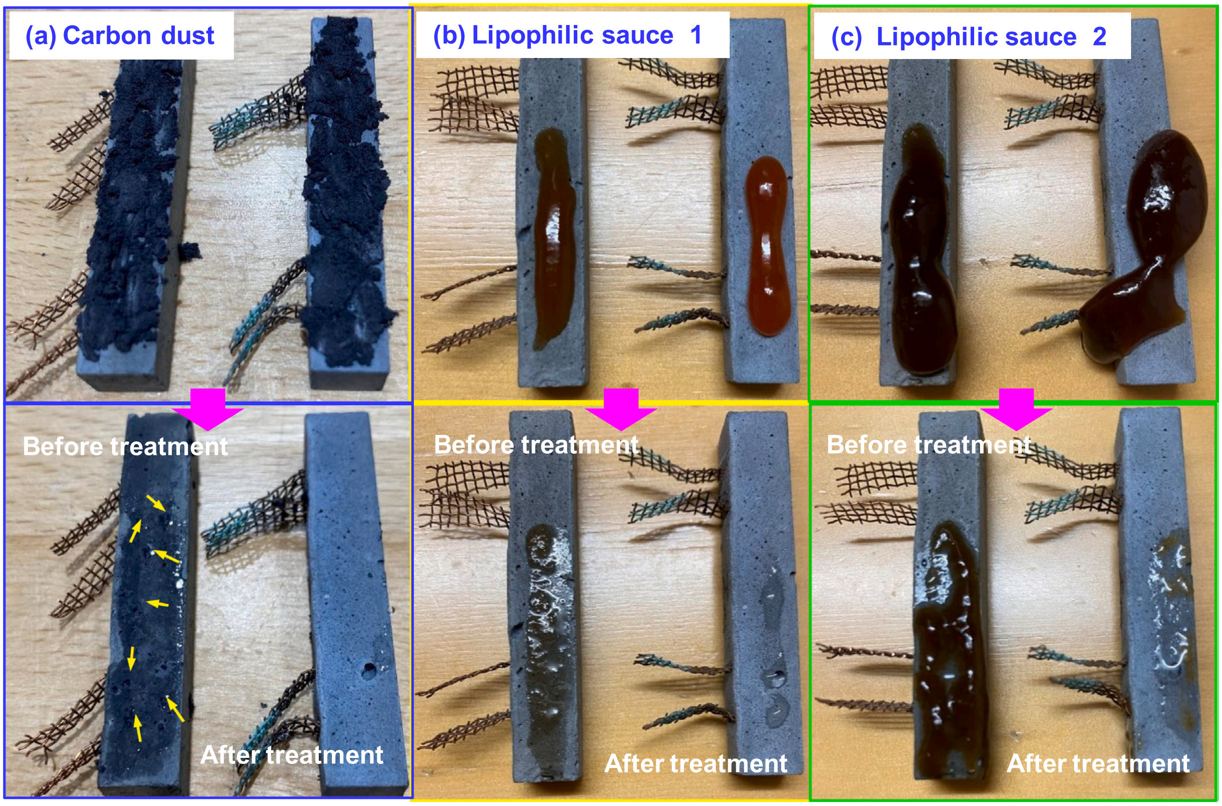


Fig. 5. Self-cleaning capacity of dust and lipophilic stain of cement-based sensors before/after silane treatment.

Data availability

Data will be made available on request.

Acknowledgements

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