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Influences of CNT Dispersion Methods, W/C Ratios, and Concrete Constituents on Piezoelectric Properties of CNT Modified Smart Cementitious Materials

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Abstract: In order to achieve a sound structure health monitoring purpose, carbon nanotubes (CNTs) are regarded as a promising candidate which can be added into cementitious materials to fabricate CNT modified smart concrete with self-sensing ability. This study investigated the influences of CNT dispersion method, water/cement (W/C) ratio, and concrete constituent on the piezoelectric properties of CNT modified cementitious materials. Three CNT dispersion methods (direct mixing, sodium dodecyl benzenesulfonate (NaDDBS) and carboxymethyl cellulose (CMC) surface treatment), three W/C ratios (0.4, 0.5, and 0.6), and three concrete constituent compositions (pure cement, cement/sand, and cement/sand/coarse aggregate) were considered. The experimental results showed that CNT modified cementitious materials with CMC surface treatment had valid and consistent piezoelectric responses to external loading. The piezoelectric sensitivity improved significantly as the increase of W/C ratio and reduced progressively as the addition of sand and coarse aggregates.

Keywords: smart concrete, piezoelectricity, carbon nanotubes, dispersion method, water-cement ratio, concrete constituent

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1. Introduction

As the most widely used construction materials, concrete has taken our civilization upwards for centuries. However, concrete structures may be subjected to various environmental threats including erosion, impact forces, and harsh weather conditions. Excessive exposure to such adverse environmental conditions could induce cracking and delamination of concrete, leading to potential long-term safety concerns. Thus, close monitoring of concrete structures in these environments are needed to prevent catastrophic failure [1, 2].

The most popular methods to inspect of concrete damages and deformations include visual inspection and the usage of attached or embedded sensors [3-5]. Although visual inspection is a cost-effective inspection method, it requires tremendous amounts of workload due to the large size and complexity of most civil infrastructures. In addition, the results of visual inspection are sometimes unreliable given that most of the concrete damages are occurred on the inaccessible parts of the structure [2, 6, 7]. For attached or embedded sensors, there are several types of sensing technologies available to monitor the conditions of concrete structures such as the resistance strain gauge, the shape memory alloy, and the fiber optical grating sensors. However, the attached or embedded sensors also have limitations such as challenges in compatibility with concrete and local measurements [2, 6, 8]. The needs for structural health assessment of civil infrastructures have necessitated research for the development of real-time and in situ monitoring techniques. Such kind of technique should allow the system to monitor its structural integrity while the infrastructure is in service, and the monitoring can be performed throughout the whole service life of the infrastructure.

Smart materials (e. g. smart cementitious materials) are intelligent systems with advanced properties such as shape memory or self-sensing [9, 10]. Smart cementitious materials are usually fabricated by adding functional fillers (biological materials, crystals, ceramics, polymers, nanomaterials, etc.) into the cement matrix [11, 12] to achieve the self-sensing purpose. The functional fillers usually take advantage of piezoelectric effect which is defined as the linear electromechanical interaction between the mechanical and electrical state, which electric charge is accumulated in response to the applied mechanical stress in a crystalline material with no inversion symmetry [13, 14]. With the addition of such functional fillers, the stress information of the cementitious material could be converted and monitored by the electrical signal measured from the matrix [15, 16]. Piezoelectric effect is a dynamic process because the stress is proportional to the electrical signal and the signal conversion is a reversible process [13]. The smart cementitious materials remain superior precision and high sensitivity even the material is under a high stress state [16]. Therefore, the development of smart cementitious materials with intrinsic piezoresistive or piezoelectric self-sensing capability is of great importance for monitoring concrete structures in real time [17].

Among various different types of functional fillers, carbon nanotube (CNT) is recognized as one of promising functional fillers in cementitious materials to achieve self-sensing properties [16, 18, 19]. The surface piezoelectric effect under a non-uniform strain was found in multi-walled CNTs using atomic force microscopy [20]. In addition, as CNTs have remarkably high aspect ratios (hundreds to several thousand) for large surface area to volume ratios, exceptional high tensile strength (30-50 GPa) and elasticity (1.0-1.5 TPa), the addition of CNTs has been investigated as an approach to enhance the mechanical properties of cementitious materials [21-24].

Previous studies showed that the challenge to achieve a satisfactory sensing property of the CNT modified smart concrete is the proper dispersion of CNTs in cementitious matrix. In another word, CNTs need to be well-dispersed in a cement matrix to form an extensive conductive network inside the concrete for a consistent sensing property [27]. However, CNTs tend to form into CNT clusters due to a considerable amount of Van der Waals force between them [25, 26]. To reduce the size of the CNT clusters for improving the dispersion, the most prevailing CNT dispersion method is the mechanical stirring method such as directly mixing and sonication [28]. The mechanical stirring approach is simple to apply, but it has been found insufficient to disperse CNTs uniformly in cement mortar. Therefore, CNT functionalization methods using various dispersing agents such as sodium dodecyl sulfate (SDS) and sodium dodecyl benzenesulfonate (NaDDBS) have been investigated to improve the CNT dispersion [27, 29]. A proper concentration of such dispersing agents may improve CNT dispersion [30, 31] while at the same time preserving or improving the physical and chemical properties of the cement mortar [32, 33]. However, the existing findings of surfactants on CNT dispersion modification vary significantly among different studies showing the lack of consistency [34]. Also, some dispersion agents may induce negative influences on cement hydration or void density [35, 36]. Recently, a different CNT surface modification method using carboxymethyl cellulose (CMC) has been investigated and showed promising effectiveness in improving CNT dispersion consistently while increasing the piezoelectric sensitivity in cement mortar [37]. However, there is no investigation yet on the effectiveness of this new surface modification in concrete which has sand and aggregate in addition to cement mortar.

In addition to the effectiveness of dispersion, a good self-sensing property of smart concrete is also influenced by a variety of other factors such as water/cement ratio and concrete constituent. The Water/Cement (W/C) ratio, a universal influential factor for most of the properties of cementitious materials, can change the deformation capacity of CNT modified cementitious materials and CNT dispersion in the cement-based matrix [32, 33]. Higher W/C ratios may have higher electrical resistance [38] or better CNT dispersion for CNTs modified cement mortar, thus, potentially a better piezoelectric sensitivity. Additionally, most of the existing studies for CNTs modified cementitious materials only investigated the influences of CNTs modifications in cement paste without sand or aggregates [37]. While in practice concrete always has fine and coarse aggregates in addition to cement and water. The influences of concrete constituents such as sand and aggregates on CNT modified smart concrete and the CNT dispersion effectiveness have not yet been investigated.

In this paper, the influences of dispersion method, W/C ratio, and concrete constituent on the piezoelectric response of CNT modified smart concrete are systematically investigated. Three different dispersion methods (direct mixing, NaDDBS, and CMC surface treatments), three W/C ratios (0.4, 0.5, and 0.6), and three concrete constituent compositions (pure cement, cement-sand, and cement-sand-coarse aggregate) were considered and experimentally tested. This paper may enrich the fundamental understanding of CNT modified smart cementitious materials with piezoelectric behavior for the purpose of self-sensing applications.

2. Materials and Methods

2.1. Materials

Since previous research showed that the multi-walled CNTs (MWCNTs) have been shown superior electrical conductivity compared to the single-walled CNTs, the multi-walled CNTs (supplied by Skyspring Nanomaterial Inc, USA) were adopted the functional fillers in cement. The concentration of CNTs throughout this study was selected to be 0.1% by the weight of cement since it was the reported optimal CNTs concentration for cementitious materials to obtain a considerable electrical performance [37]. For the dispersion agents, the NaDDBS and CMC were provided by Sigma-Aldrich Co, USA. According to specifications from the supplier, the used NaDDBS had an average molecular weight of 288.38 g/mol and a chemical formula of $CH_3(CH_2)_{11}OSO_3Na$. While the molecular weight of the used CMC was around 90,000 g/mol and its chemical formula was $CH_3(CH_2)_{11}C_6H_4SO_3Na$. The matrix material and aggregates were purchased from The Quikrete Companies. The matrix material was Type 1 Portland cement which met ASTM C387 for compressive strength requirements. According to the ASTM C33, all-purpose sand with a diameter range from 0.3 mm to 2.36 mm was used as the fine aggregate, and gravels with an approximate diameter of 9 mm were applied as the coarse aggregate. Due to the fact that this study focuses on the investigation of piezo-electric properties of cementitious materials, no superplasticizer additives were applied in this study to avoid additional influencing factors from potential interaction among the plasticizers, surfactants and CNTs.

Table 1. MWCNT properties

Parameters	Specifications
Purity	> 95 wt.%
Outside diameter	50-100 nm
Inside diameter	5-10 nm
Length	5-20 um
SSA	>60 m2/g
Ash	<1.5 wt%
Amorphous carbon	<3.0%

Electrical conductivity	>100 s/cm
Bulk density	0.28 g/cm^3
True density	~2.1 g/cm^3

2.2. CNT Dispersion Methods

CNT modified smart cementitious materials with three different dispersing methods, including mechanical stirring, surface treatments using NaDDBS and CMC were prepared. Regarding the mechanical stirring, direct mixing method was adopted in this study due to its low cost and ease of application [39, 40]. The Direct mixing did not involve any CNT treatment. 0.2 g CNTs were directly added to 120 mL of water while the solution was mixed with a stirring bar on the magnetism stirrer. The stirring speed was 1600 rpm. The CNT-water suspension attained homogenization after 15-minute stirring. Then, 200 g cement was added into the CNT-water suspension resulting in a 0.1% CNT concentration and 0.6 W/C ratio. Thus, it is worth noting that the water used for CNT dispersion was included in the W/C ratio. To investigate the influences of W/C ratio on sensing properties of CNT modified smart concrete, three W/C ratios including 0.4, 0.5, and 0.6 were considered in this study as they are the typical W/C ratios used in fields. The similar procedures were followed for 0.5 and 0.4 W/C ratios with the water amount being 100 ml and 80 ml respectively.

For NaDDBS surface treatment, a critical micelle concentration of NaDDBS in water, 1.4×10^{-2} mol/L (approximately equal to 0.4875% by weight), was taken as the input surfactant concentration [35]. 1.17g of NaDDBS was mixed with 120 mL of water using the magnetism stirrer for 15 minutes. While stirring, 0.2 g CNTs were added to the aqueous solution followed by 2-hour sonication to ensure the fully interaction between NaDDBS and CNTs. Then NaDDBS/CNTs solution was mixed with 200 g of cement. Previous study found that, air bubbles would appear in the cement paste [35] with NaDDBS addition. Therefore, 0.25% of defoamer (by volume) was utilized to decrease the air bubble in CNTs filled cement pastes. The defoamer was provided by Tributyl phosphate supplied by Sigma-Aldrich Co., USA.

For CMC surface treatment method, based on the previous investigation by the authors, 0.5% was believed to be the optimal CMC percentage for piezoelectric sensitivity of cement paste. Thus, 1.2 g of dry CMC was gently added into 120 mL of water, since CMC tends to clump in water owing to its high-water absorption and retention. The CMC solution was mixed on the magnetism stirrer for up to 30 minutes until CMC was free of clumps and completely dissolved into water. After mixing with 0.2 g CNTs, the CMC/CNT solution was transferred in a test tube with the volume of 50 ml and placed on a tube rotator for at least 72 hours rotating to make sure a proper coating of CMC on the CNTs. Then, 400 g of cement was added into the solution. The key dispersion procedures of NaDDBS and CMC surface treatments are shown in Figure 1.

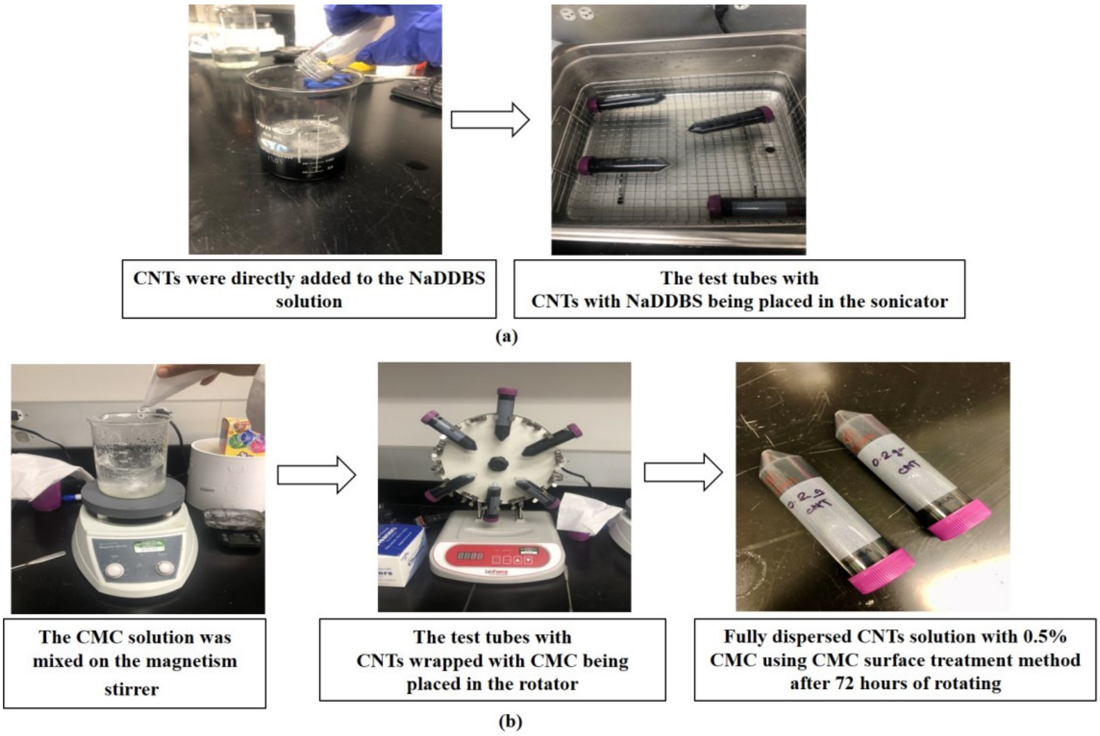
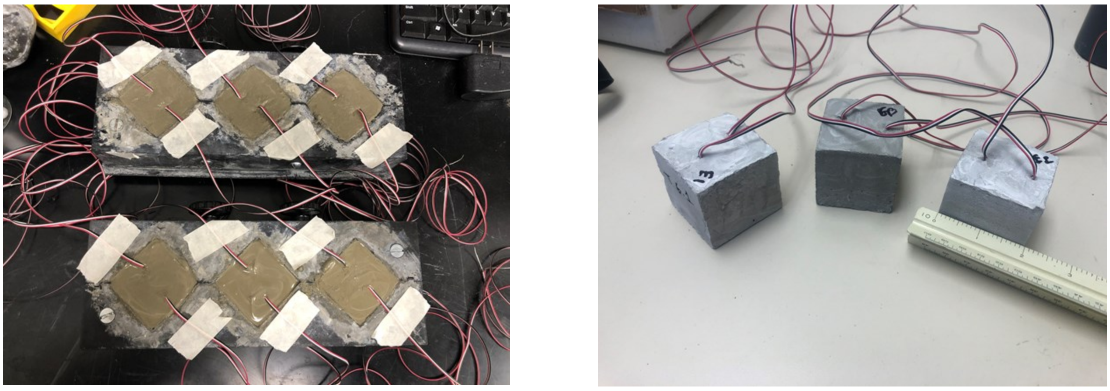


Figure 1. Key dispersion procedures: (a) NaDDBS surface treatment method.; (b) CMC surface treatment method

2.3. Samples Preparation

In addition, to investigate the influences of concrete constituents, three cementitious composites are studied including pure cement paste, cement mortar, and concrete with cement, sand, and coarse aggregate. For cement mortars, 400 g of sand was added into the 200 g cement pastes which were prepared in the last section, yielding a 1:2 design mix ratio of cement and sand. For concrete with cement, sand, and coarse aggregate, the well-prepared cement paste was mixed with 400 g of sand plus 600 g of coarse aggregate by hand using a trowel, resulting in a 1:2:3 design mix ratio of cement, sand, and coarse aggregates. After all the materials were thoroughly mixed, the pastes were placed into molds to make concrete cubes. The edge length of a concrete cube was 50.8 mm as shown in Figure 2(a), and the other sample configurations and manufacturing procedures are based on ASTM C109. The samples were cured in the molds for 24 hours at room temperature (22°C ± 2°C). An exception was that all the cement pastes and concrete samples with 0.5% CMC, needed 30 hours of sitting time in the molds to stay intact. The electrical wires were placed 12.7 mm deep and 12.7 mm apart from each other in each sample prior to the solidification of the concrete mixture. The samples were demolded and put into water for 7 days to cure followed by 10 days of air drying at room temperature. Figure 2(b) demonstrates a ready-mixed sample.



(a) (b)

Figure 2. Test samples: (a) The cubic molds for fabricating samples; (b) Samples embedded with electrical wires after curing.

Table 1 presents the testing matrix. For each testing group, three identical samples were fabricated to be statistically valid. Group A was used as a control group to confirm that the cement mortar without any functional fillers could not exhibit any piezoelectrical sensitivity. As no piezoelectrical effect is expected from either cement mortar or concrete without functional fillers, only three samples with W/C ratio of 0.6 were fabricated in the control group. As previous studies investigated on how the W/C ratio would influence the piezoelectrical effect on pure cement paste using direct mixing method [32, 41, 42] as indicated in the introduction, Group B (0.6 W/C), C (0.5 W/C), and D (0.4 W/C) were designed to investigate the influences of the W/C ratio for smart cement mortar using direct mixing method. If significant piezoelectrical effect can be found in these samples during the dynamic loading tests, more samples for the three different W/C ratios for smart concrete with aggregates will be further fabricated. Since CMC surface treatment method was a relatively new CNT dispersion method, there is a lack of related investigations regarding the piezoelectric effect of CNT modified smart cementitious materials. Thus, in this study, samples with three W/C ratios (0.6, 0.5 and 0.4) and two concrete constituents (pure cement and cement mortars) were prepared by CMC surface treatment method. Groups E to G and H to J were designed to investigate the influence of W/C ratio on CMC surfaced treated CNTs modified cement paste and cement mortar, respectively. The optimal W/C ratio from Group E to J was used to fabricate the sample Group K for CMC treated CNTs modified concrete with cement, sand, and aggregate to investigate the influences of course aggregate on the piezoelectrical effect. To investigate the influence from different dispersing method on the piezoelectrical effect, Groups L to N were fabricated as NaDDBS treated CNTs modified cement paste, cement mortar, and concrete with coarse aggregate.

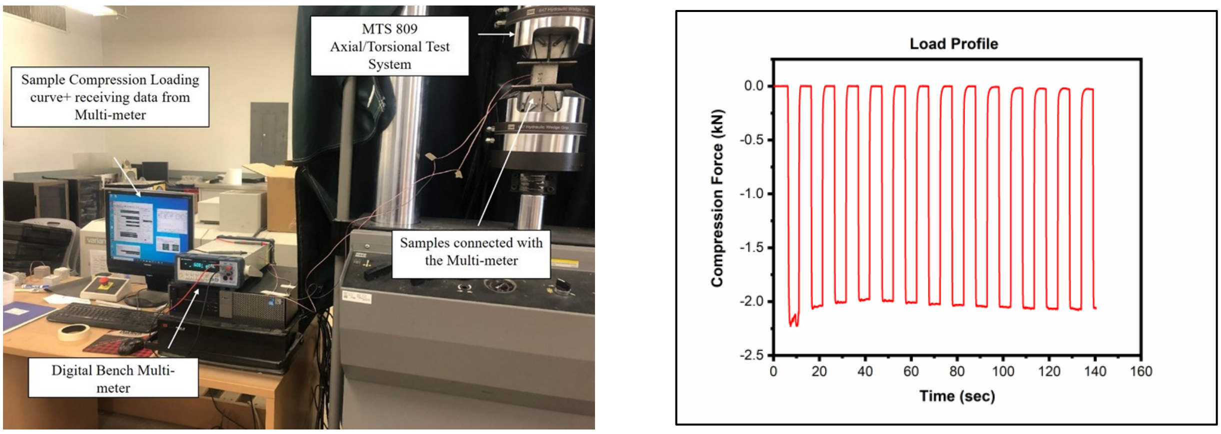
Table 2. Testing sample matrix

Dispersion Method	Group	Sample No.#	Description	W/C Ratio	Design Mix
None	A	3	Control (No CNTs and CMC)	0.6	1:2 Cement: Sand
Method #1 Direct Mixing	B	3	0.1% CNTs	0.6	1:2 Cement: Sand
	C	3	0.1% CNTs	0.5	1:2 Cement: Sand
	D	3	0.1% CNTs	0.4	1:2 Cement: Sand

Method #2 CMC Surface Treatment	E	3	0.1% CNTs + 0.5% CMC	0.6	Cement
	F	3	0.1% CNTs + 0.5% CMC	0.5	Cement
	G	3	0.1% CNTs + 0.5% CMC	0.4	Cement
	H	3	0.1% CNTs + 0.5% CMC	0.6	1:2 Cement: Sand
	I	3	0.1% CNTs + 0.5% CMC	0.5	1:2 Cement: Sand
	J	3	0.1% CNTs + 0.5% CMC	0.4	1:2 Cement: Sand
	K	3	0.1% CNTs + 0.5% CMC	Optimal W/C	1:2:3 cement: sand: coarse aggregate
Method #3 NaDDBS Surface Treatment	L	3	0.1% CNTs + 0.5% NaDDBS + 0.25% deformer	Optimal W/C	1:2 Cement: Sand
	M	3	0.1% CNTs + 0.5% NaDDBS + 0.25% deformer	Optimal W/C	1:2:3 cement: sand: coarse aggregate
	N	3	0.1% CNTs + 0.5% NaDDBS + 0.25% deformer	Optimal W/C	Cement

2.4. Experimental Setup

The prepared samples were assessed under dynamic loads to assess their piezoelectric sensing capacity. Figure 3(a) illustrates the experimental setup. Compressive loads were applied on each cement or concrete sample using MTS 809 Axial/Torsional Test Systems, Inc., USA. The piezoelectric responses were measured by a digital bench multi-meter (BK 5492B, B&K Precision Inc., USA). Samples were subjected to dynamic loading as shown in Figure 3(b) with an average load of 1,912 N and a range from 166 to 2,078N in 10-12 loading cycles. The responses are presented in μV (×10[6]) corresponding to the applied loading. The frequency of the loading was set to be 0.1 Hz. All the samples were tested at room temperature.



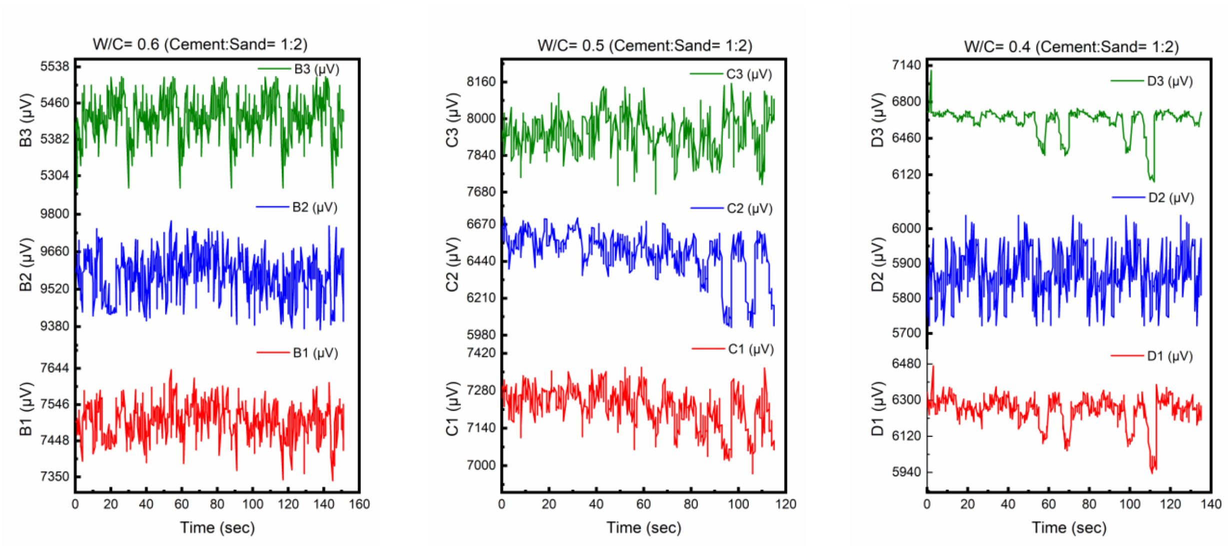
(a) (b)

Figure 3. (a) Laboratory setup for full experimental setup. (b) Dynamic loading curve

3. Results

3.1. Direct Mixing Method

Many previous studies investigating piezoelectric properties of CNT modified smart cementitious materials used pure cement as the matrix material [32, 41, 42]. Figure 4(a-c) presents the piezo electric responses (μV) from the samples of smart cement mortar using direct mixing method made with 0.6, 0.5 and 0.4 W/C ratios respectively. As shown in Figure 4, there was no resemblance in dynamic responses with stress levels of the cyclic loads. The piezoelectric response of cement mortars might change with external compressive load, but for every specific time, the value of the response did not show consistent sensing patterns to the corresponding compressive stress. As cement mortars with direct mixing failed to show fully functional piezoelectric effect for the sensing purpose, no further smart concrete with cement, sand, and aggregate were fabricated.

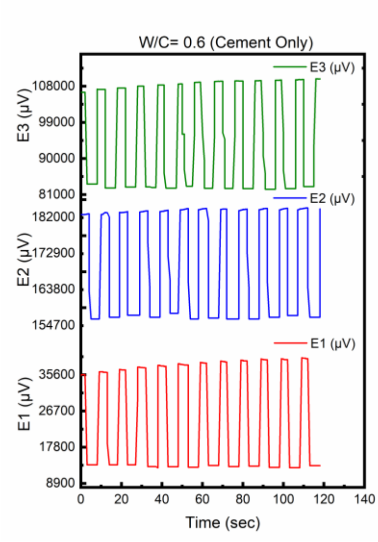


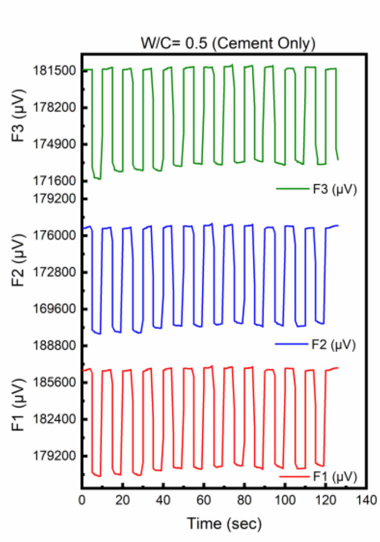
(a) (b) (c)

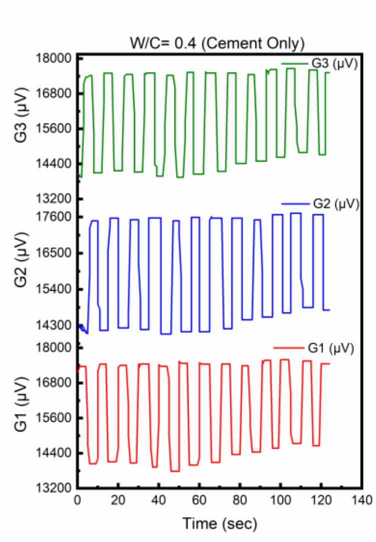
Figure 4. Piezoelectric responses for direct mixing method with different W/C ratios

3.2. CMC Surface Treatment Method

Figure 5(a-f) presents the piezoelectric responses (μV) of CNT modified smart cementitious materials for cement paste and cement mortar with CMC surface treatment method but different W/C ratios and concrete constituents. In each cyclic loading, the maximum piezoelectric response over maximum loading is defined as the piezoelectric sensitivity which is regarded as one of the most important parameters for piezoelectric properties of self -sensing smart materials. All the piezoelectric responses shared a similar changing pattern as the compressive stress with similar frequency, indicating a strong correlation between the variations of the dynamic responses and stress during each cyclic load. For each one-unit N change in the force, the average corresponding change in piezoelectric response was 12.95 μV/N, 4.34 μV/N, 1.61 μV/N in CNT modified pure cement with the W/C ratios of 0.6, 0.5, and 0.4, respectively. Similar pattern can be observed for the smart cement mortar as well. A W/C ratio of 0.6 was found to be the optimal W/C ratio. Thus, 0.6 W/C ratio was selected to fabricate the smart CMC treated CNTs modified concrete samples and the results are shown in Figure 6.


W/C= 0.6 (Cement Only)
E3 (μV)
E2 (μV)
E1 (μV)
108000
99000
90000
81000
182000
172900
163800
154700
35600
26700
17800
8900
0 20 40 60 80 100 120 140
Time (sec)

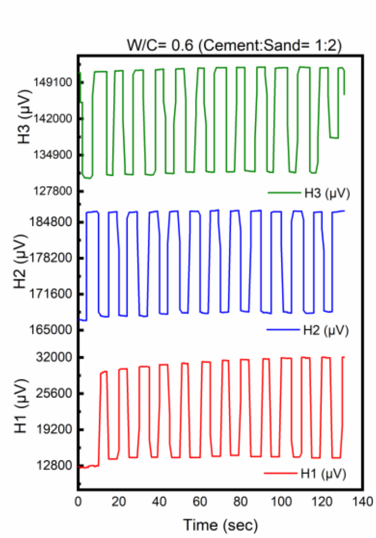

W/C= 0.5 (Cement Only)
F3 (μV)
F2 (μV)
F1 (μV)
181500
178200
174900
171600
179200
176000
172800
169600
188800
185600
182400
179200
0 20 40 60 80 100 120 140
Time (sec)

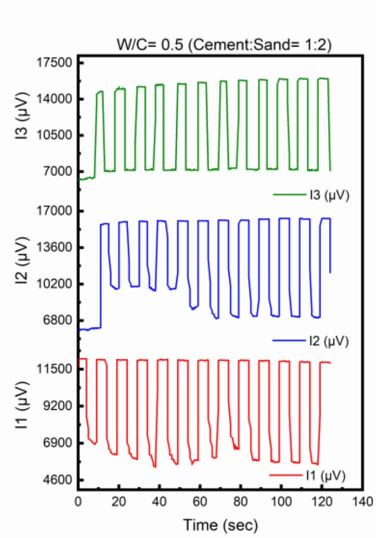

W/C= 0.4 (Cement Only)
G3 (μV)
G2 (μV)
G1 (μV)
18000
16800
15600
14400
13200
17600
16500
15400
14300
18000
16800
15600
14400
13200
0 20 40 60 80 100 120 140
Time (sec)

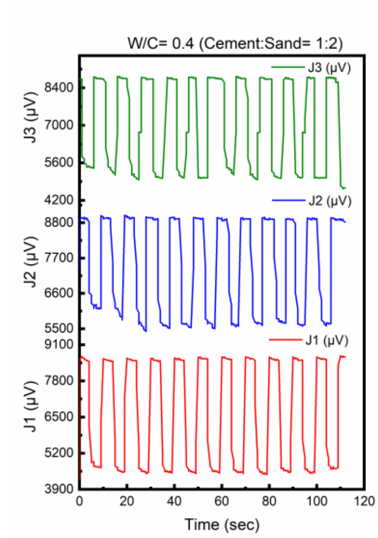
(a)

(b)

(c)


W/C= 0.6 (Cement:Sand= 1:2)
H3 (μV)
H2 (μV)
H1 (μV)
149100
142000
134900
127800
184800
178200
171600
165000
32000
25600
19200
12800
0 20 40 60 80 100 120 140
Time (sec)

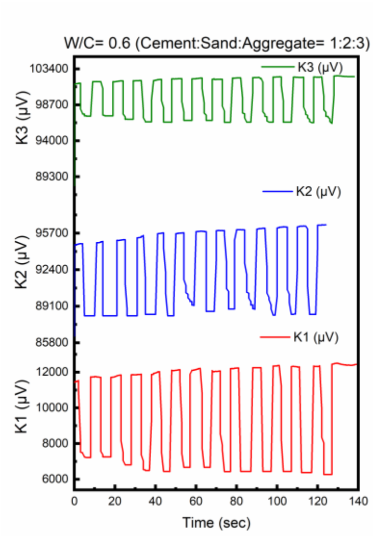

W/C= 0.5 (Cement:Sand= 1:2)
I3 (μV)
I2 (μV)
I1 (μV)
17500
14000
10500
7000
17000
13600
10200
6800
11500
9200
6900
4600
0 20 40 60 80 100 120 140
Time (sec)


W/C= 0.4 (Cement:Sand= 1:2)
J3 (μV)
J2 (μV)
J1 (μV)
8400
7000
5600
4200
8800
7700
6600
5500
9100
7800
6500
5200
3900
0 20 40 60 80 100 120
Time (sec)

(d)

(e)

(f)

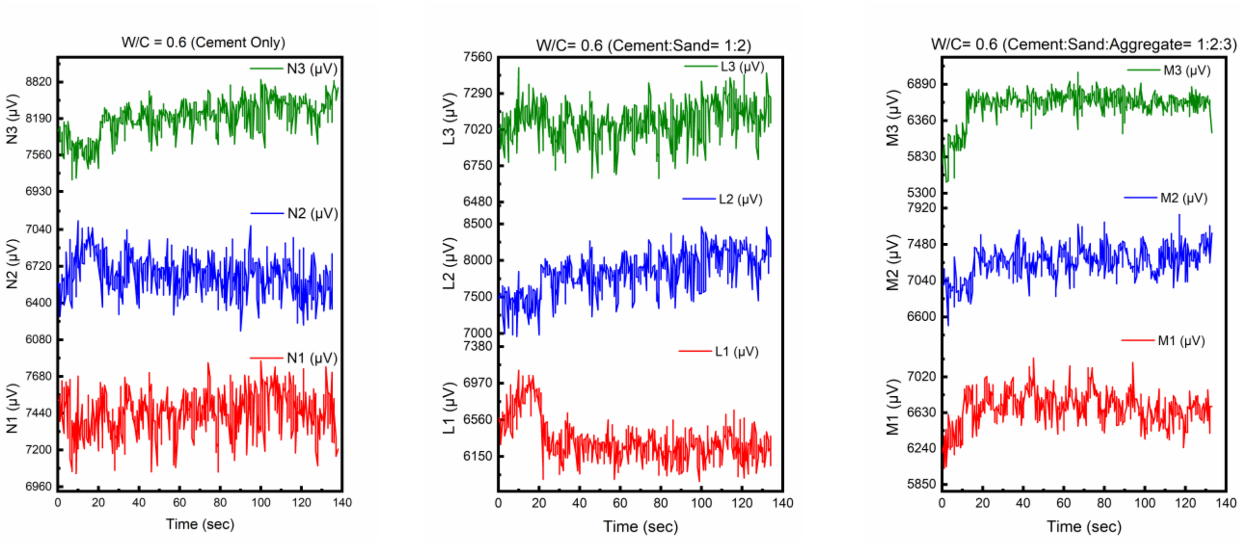

W/C= 0.6 (Cement:Sand:Aggregate= 1:2:3)
K3 (μV)
K2 (μV)
K1 (μV)
103400
98700
94000
89300
95700
92400
89100
85800
12000
10000
8000
6000
0 20 40 60 80 100 120 140
Time (sec)

(g)

Figure 5. Piezoelectric responses for CMC surface treatment method with different W/C ratios and concrete constituents.

3.3 NaDDBS Surface Treatment Method

NaDDBS surface treatment method has been proved effective in modifying CNT dispersion in cement for piezoelectric effect [37, 43]. Figure 6 (a-c) depicts the piezoelectric responses (μV) of pure cement, cement mortars and concrete with cement, sand and coarse aggregate prepared using NaDDBS surface treatment method with the optimal W/C ratio of 0.6 as determined from Figure 5. From Figure 5, the piezoelectric responses of concrete specimens with NaDDBS surface treatment method showed inconsistency with significant variation between the loading and unloading process for all three concrete constituent compositions. The dynamic responses were characterized by irregular fluctuations that more close to the pattern of random noise and did not show clear correlation to the changes of applied compressive stress. By comparing Figures 4, 5, and 6, it demonstrates that compared with direct mixing and NaDDBS surface treatement, the CMC surface treatment method can be an effective approach to disperse CNTs in smart cementitious materials to achieve potential self-sensing properties.



(a) (b) (c)

Figure 6. Piezoelectric responses for NaDDBS surface treatment method with different concrete constituents.

4. Discussion

4.1. Influences of Dispersion Methods

The results above preliminarily indicated the effectiveness among different dispersion methods. In order to further illustrate the influences of dispersion methods on the piezoelectric properties of CNT modified cementitious materials, comparisons were made among CNT modified cementitious materials with same testing conditions except dispersion method. Figure 7 shows the typical piezoelectric responses of CNT modified cement mortars with a constant W/C ratio of 0.6. The piezoelectric response of CNT modified cement mortars with CMC surface treatment followed a similar changing pattern under the dynamic loading. The piezoelectric response changed linearly with the dynamic loading and its value is proportional to the force levels in the consecutive cyclic loading. However, for the samples made with direct mixing and NaDDBS surface treatment methods, the piezoelectric responses kept almost unchanged regardless of loading variations similar to the control samples. The average piezoelectric sensitivity of CMC surface treatment was found to be 12.43 μV/N. In contrast, the sensitivities of both direct mixing and NaDDBS surface treatment were substantially lower. Interconnected CNTs inside the cement paste form an electric network which facilitates electron transfer [37]. The quality of the conductive network in cementitious materials is not dependent on a single factor. Matrix porosity and presence of aggregates may result in the discontinuation of the uninterrupted electron path, while the polarization effect may complicate the correlation between changes in electrical and mechanical conditions [44, 45]. With other factors being constant, a more uniform dispersion of CNTs may increase the probability of obtaining a more continuous conductive network. Thus, when sand was added into the CNT modified cementitious materials as find aggregates, CNT modified cement mortars with CMC surface treatment obtained a better piezoelectric property, while CNT modified cement mortars with direct mixing and NaDDBS surface treatment methods exhibited limited piezoelectricity. The effects of different dispersion methods on CNT dispersion could be found in a previously published paper by the authors [46], which indicated that the CMC showed smaller particles sizes and more uniform dispersion of CNTs compared to NaDDBS and direct mixing.

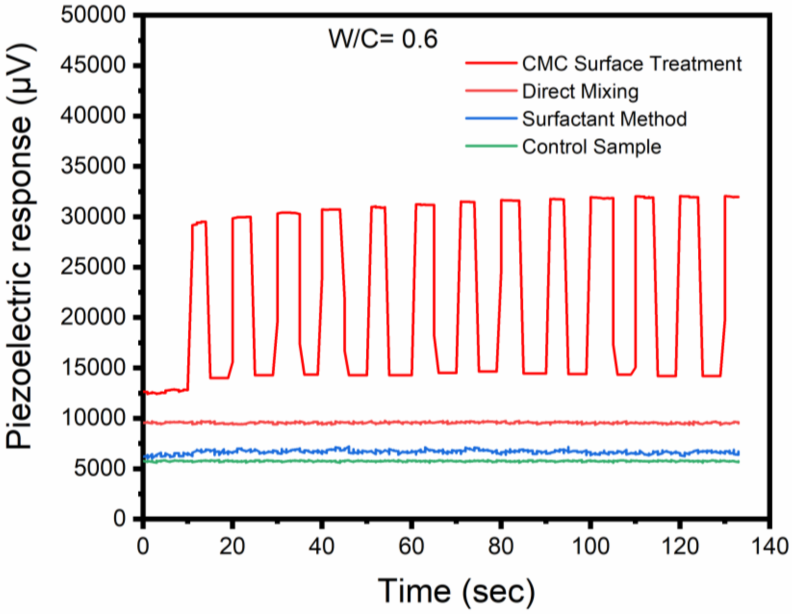


Figure 7. Comparisons of piezoelectric responses among the three dispersion methods with a constant W/C ratio of 0.6.

4.2. Influences of The Water Cement Ratios

According to the previous discussion, CNT modified smart cementitious materials with dispersion methods using direct mixing or NaDDBS surface treatment failed to perform a significant piezoelectricity. Therefore, the discussions regarding W/C ratios and concrete constituents were based on CNT modified smart cementitious materials with CMC surface treatment method only. Figure 8 shows average loading and unloading piezoelectric sensitivity of CNT modified pure cement paste with CMC surface treatment method but different W/C ratios. A higher piezoelectric sensitivity, provided it falls within a reasonable range and does not bring about excessive amount of irrelevant data, can be an indication of improved piezoelectricity and self-sensing capability. When the W/C ratio was 0.4 for the pure cement samples, the average loading and unloading piezoelectric sensitivities were 1.602 and 1.489 μV/N, respectively. As the W/C ratio increased to 0.5, the piezoelectric properties of both loading and unloading were increased to 4.369 and

4.028 μV/N, respectively, with the increments reaching around 190% compared to those with 0.4 W/C ratio. For the W/C ratio of 0.6, the increases of the loading and unloading sensitivities were as much as 7 times (12.950 and 11.950 μV/N) compared to the corresponding values of 0.4 W/C ratio. Increasing the W/C ratio showed significant increases in piezoelectric sensitivity of CNT modified pure cement pastes, which is consistent with previous research findings [46].

The similar tendency was also found samples as cement mortars. Figure 9 displays average loading and unloading piezoelectric sensitivities of CNT modified cement mortars among different water-cement ratios. With the W/C ratio of 0.4 for cement mortars with CMC surface treatment, the average loading and unloading piezoelectric sensitivities were 1.829 and 1.667 μV/N respectively. After the W/C ratio increased to 0.5, compared to CNT modified cement mortars with 0.4 W/C ratio, a dramatic increase (about 170%) was seen for both loading and unloading piezoelectric sensitivities, with the values being 3.754 and 3.445 μV/N respectively. When further elevating the W/C ratio to 0.6, piezoelectric sensitivities also tremendously rocketed up to 9.339 and 8.595 μV/N for loading and unloading, which were more than 5 times the values of 0.4 W/C ratio. The improvement in piezoelectric sensitivity of CNT modified cement mortars as a function of W/C ratio may be attributed to the same mechanism as pure cement.

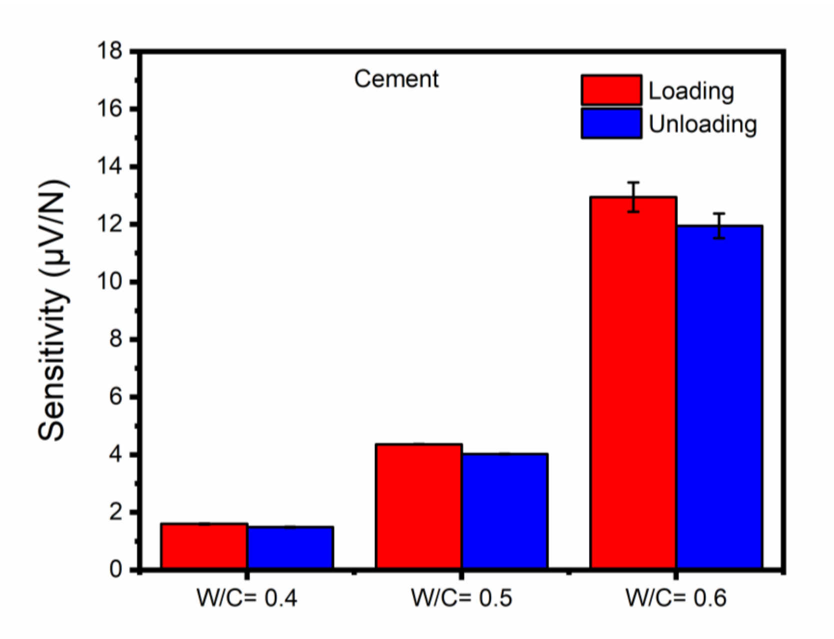


Figure 8. Average loading and unloading piezoelectric sensitivities of CNT modified pure cement paste with CMC surface treatment method but different water-cement ratios.

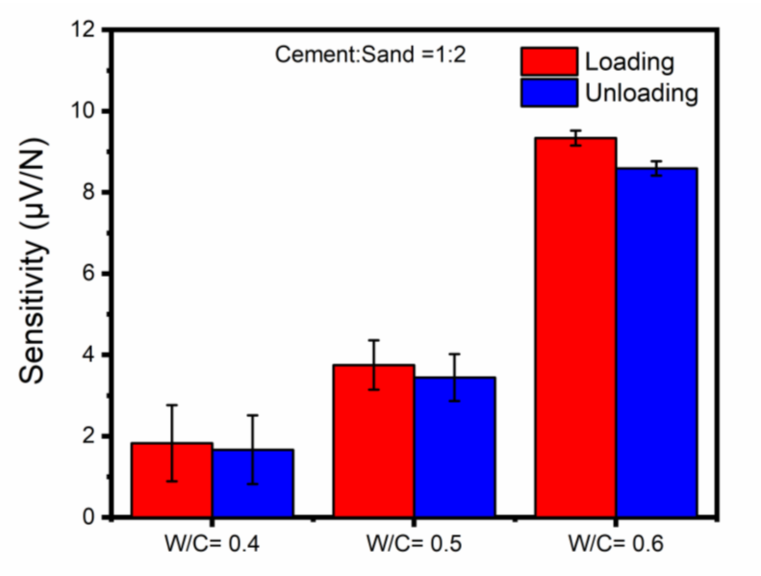


Figure 9. Average loading and unloading piezoelectric sensitivities of CNT modified cement mortars with CMC surface treatment method but different water-cement ratios.

4.3. Influences of Concrete Constituents

Figure 10 presents average loading and unloading piezoelectric sensitivities of CNT modified smart cementitious materials with the same W/C ratio of 0.6 but different concrete constituents. It was clearly shown in the figure that compared to CNT modified pure cement as the matrix material, the piezoelectric sensitivity reduced moderately when sand was added in the cement. The cement mortars attained loading and unloading piezo sensitivity of 9.34 μV/N and 8.59 μV/N, which were 27.87% and 28.12% lower than those of pure cement samples, respectively. After adding the coarse aggregates into the cement mortars, the sensitivities further declined progressively to 2.76 μV/N and 2.54 μV/N, with the decreasing increments being 78.68% and 78.74%, respectively. It is not surprising that the addition of fine and coarse aggregate had a negative effect on the piezoelectric properties of CNTs due to the interruption of continuous conductive network and the intrinsic high resistivity of aggregates. This influence was found to be highly substantial. The piezoelectric properties of CNT modified smart concrete were excessively limited compared to pure cement. Thus, when fabricating smart or self-sensing concrete in practical applications, the existence of fine and coarse aggregates cannot be ignored, and the influence of aggregates on the sensing performance of the concrete need to be considered. In addition, as expected, the sensitivities of loading were consistently slightly larger than those of unloading under all testing conditions, due to the occurrence of modest irreversible plastic deformations generated in the loading cycles.

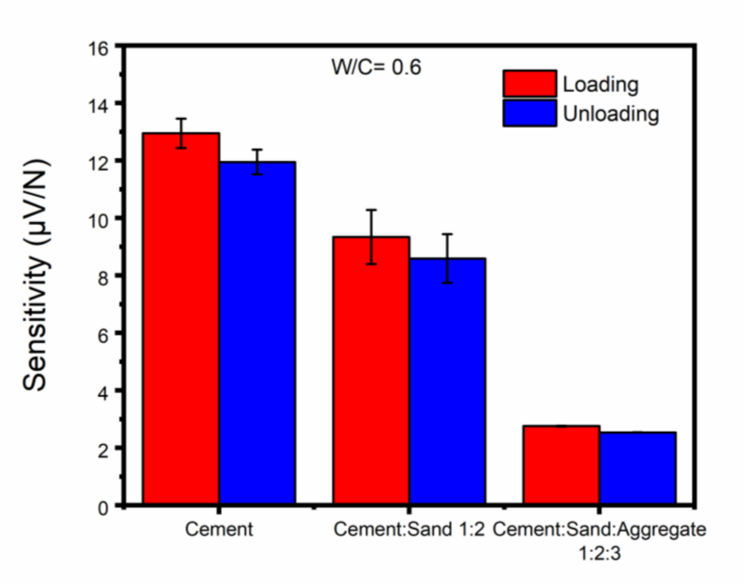


Figure 10. Average loading and unloading piezoelectric sensitivities of CNT modified cementitious materials with the same W/C ratio of 0.6 but different concrete constituents.

5. Conclusions and Future work

This study investigated the influences of CNT dispersion methods, W/C ratio, and concrete constituents on the piezoelectric sensing ability of CNT modified smart cementitious materials. The following conclusions can be drawn based on the findings from this study:

1. The comparison between three different dispersion methods showed that the CNT modified cementitious materials with CMC surface treatment showed functional and significant piezoelectric responses with better consistency. While direct mixing and NaDDBS surface treatment failed to perform an obvious piezoelectricity to CNT modified cementitious materials.
2. As the increase of W/C cement ratio, the piezoelectric sensitivities of both CNT modified cementitious materials with and without sand addition were improved significantly, which was consistent with previous research findings. Specifically, this study found that by increasing the W/C ratio from 0.4 to 0.6, the piezoelectric responses can potentially increase more than 8 times.
3. Adding aggregates significantly reduced the piezoelectric sensitivities of CNT modified cementitious materials. Especially, for CNT modified smart concrete with both fine and coarse aggregates, the sensing ability could decline to 78% of pure cement. When fabricating CNT modified smart concrete, the influences of aggregates should be considered.

The conclusion of this paper confirmed the importance of aggregates on the piezoelectric properties and self-sensing performance of CNT modified cementitious materials. Even with optimized dispersion method and W/C ratio, CNT modified concrete with sand and coarse aggregates ended up with a rather weak piezoelectric sensitivity. Thus, improving the piezoelectric sensitivity of CNT modified concrete still need further investigations.

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Author Contributions

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The authors declare no conflict of interest.

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