



The Study of Silica Fume Incorporated Calcium Silicate Nanocomposite for Mechanical Energy Harvesting Application

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ABSTRACT

In this work, the effect of the incorporation of silica fume nanoparticles (SiO_2) on dielectric properties and energy conversion efficiency of the calcium silicate based triboelectric nanogenerator (CS-based TENG) were investigated. SiO_2 nanoparticles with 0.1-0.5%wt concentrations were added to CS-material to form CS- SiO_2 nanocomposites which were then used to fabricate CS- SiO_2 TENG. It was found that the CS- SiO_2 0.2%wt nanocomposite had the highest dielectric constant (ϵ_r) of 66.5, which was over 3 times higher than that of the pristine CS material ($\epsilon_r = 21.3$). Under a vertical contact-separation operation mode, the fabricated TENG with CS- SiO_2 0.2%wt generated the highest output voltage and current of 110 V and 8.5 μA , respectively, which can deliver the highest power density of 182 mW/m^2 . The enhanced energy conversion performance of CS- SiO_2 0.2%wt TENG is accounted for the addition of SiO_2 nanoparticles that can promote the formation of CSH product and reduce air voids, resulting in the synergetic enhancement of dielectric constant and compressive strength of the CS- SiO_2 nanocomposite material.

Keywords: calcium silicate, silica fume, mechanical energy harvesting

1. INTRODUCTION

Many research efforts have been devoted to the development of green, renewable and sustainable energy sources. Mechanical energy is abundant in our living environment including human movement, vehicle motion, any kind of

vibrations, for example. Harvesting of these mechanical energies has now become one of the major challenges to serve the growing energy demands. Triboelectric nanogenerator (TENG) has emerged as a mechanical energy harvesting device

based on contact electrification and electrostatic induction which can offer high energy conversion efficiency, large power output, simple fabrication process and low cost [1,2].

Electrification effect can occur in any two surfaces that are brought into contact. The surface charges occurred during contact and separation events can induce the current in conductive electrodes to flow generating an alternating electrical current. The generated surface charges depend on the two triboelectric materials which can be considered from the triboelectric series by which materials are listed according to their affinities to electrons. The larger the difference in electron affinity of the two materials the higher generated electrostatic charges and hence larger output performance.

Contact electrification is a function of contact surface area, material with large surface exposed to mechanical energy would be therefore beneficial for generating high electrical output performance. Calcium silicate (CS) based composites including calcium silicate hydrate (CSH), tricalcium silicate (C_3S), dicalcium silicate (C_2S), and calcium hydroxide (CH) are the main hydration products of cement material which is known as a crucial component of constructions such as buildings and pavements. In addition, by virtue of being a low cost material and feasible to be composited with other materials, CS material is thus promising for the use as a triboelectric material.

It was reported that the generated electrical output is strongly dependent on the dielectric properties of the triboelectric materials[3,4]. CS-based materials have generally poor dielectric properties. The dielectric properties of composite can be enhanced by various ways such as filling with high dielectric constant materials[5,6] or with conductive[7,8] or semiconductor materials via interfacial polarization[9]. Silica fume is an amorphous form of silicon dioxide (SiO_2) with a very small particle size ranging from 100-200 nm in diameter. Silica fume can be used to enhance dielectric properties in lead zirconate titanate-

cement (PZT-cement) composite due to its nanosize that produced denser structure and its pozzolanic property that can further densify the structure of cement matrix[10]. Furthermore, due to the much finer particle size than cement and its pozzolanic activity[11], silica fume can reduce the pore space in concrete[12] which can be used as a filler to increase strength and durability of cement materials[13].

In this work, silica fume (SiO_2) nanoparticles was employed to incorporate in CS-based material to improve dielectric properties so as to enhance the energy conversion efficiency of CS-based TENG. The effect of SiO_2 concentration on dielectric properties and output voltage and current of the CS- SiO_2 TENGs were studied. Morphologies and crystal structures of the fabricated nanocomposites were also presented. The optimum working condition of the fabricated CS- SiO_2 TENGs was investigated to achieve the highest energy conversion performance.

2. MATERIALS AND METHODS

CS materials were fabricated from ordinary Portland cement type 1 (ASTM C150), Insee brand. SiO_2 nanoparticles (silica fume, Sigma-aldrich) were added to cement powders at 0.1, 0.2, 0.3, 0.4, and 0.5%wt. The mixtures were then mixed with deionized (DI) water with the water to cement (W/C) ratio of 0.5 and put into acrylic molds with the size of $4 \times 4 \times 1 \text{ cm}^3$. A stainless sheet was used as a current collector for a CS TENG. The specimens were kept in the molds for 24 h and then left in ambient temperature for 7 days. The output voltage and current were measured using an oscilloscope scope (RIGOL DS1054) and a digital multimeter (KEITHLEY DMM6500) under a vertical contact-separation mode TENG. The dielectric properties of specimens were probed using the KEYSIGHT E4990A impedance analyzer with frequencies ranging from $40 - 1.2 \times 10^8 \text{ Hz}$. The sample morphologies and crystal structures were investigated using a scanning electron microscope (LEO 1450VP SEM) and XRD

(EMPYREAN PANalytical X-ray diffractometer) at 2θ of 10° - 80° .

The prepared CS-SiO₂ nanocomposites with 0.1-0.5%wt SiO₂ were used as tribo-materials, 'tribo1', and polytetrafluoroethylene (PTFE) sheet

was used as a counter tribo material, 'tribo2', as depicted in Figure 1(a). The output voltage and current of the assembled TENGs were measured under vertical contact-separation mode at a frequency of 5 Hz and applied force of 10 N.

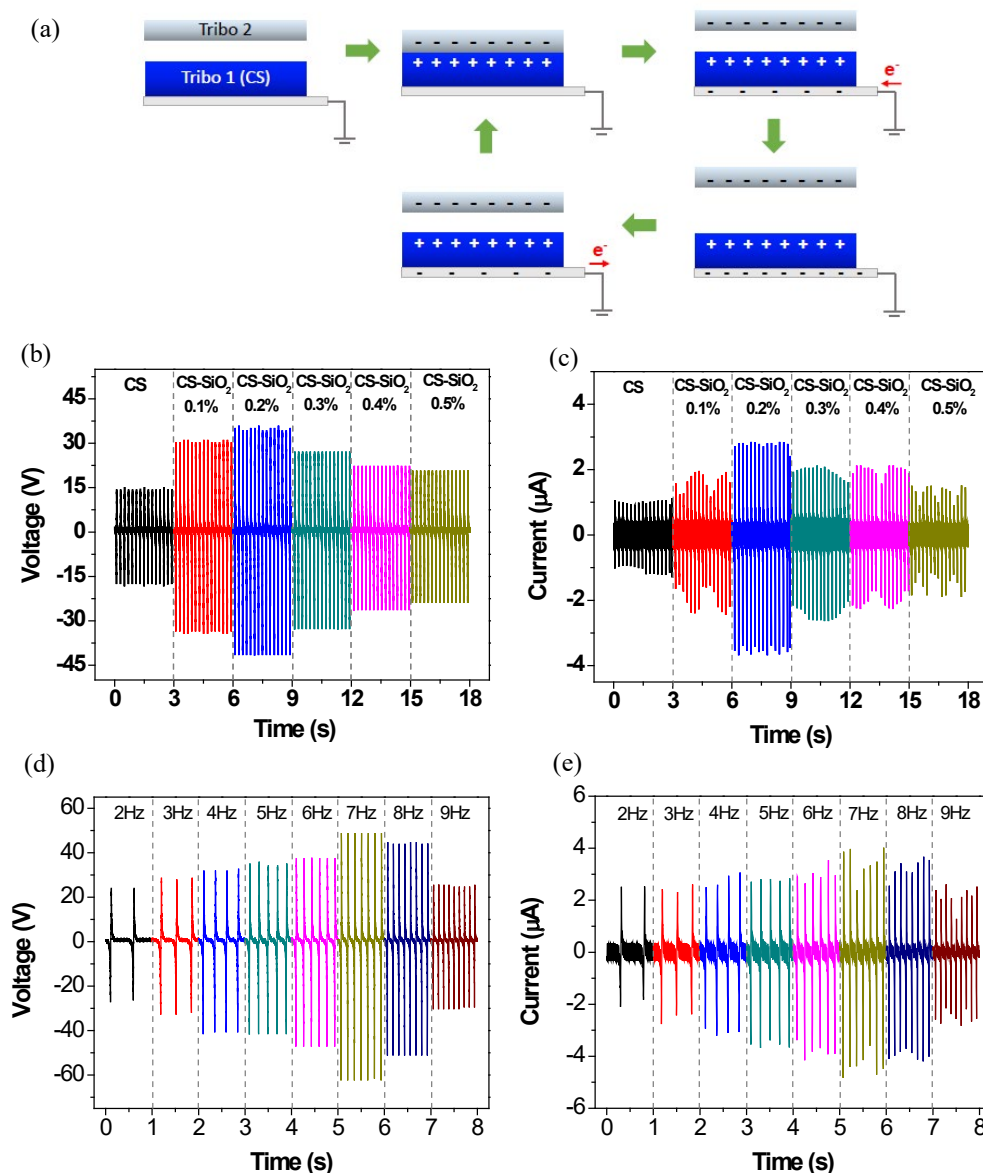


Figure 1. Schematic of the working mechanism of the fabricated CS-SiO₂ TENGs; tribo1 is CS-based materials and tribo2 is PTFE contact triboelectric material (a). Voltage (b) and current (c) outputs of the CS-SiO₂ TENGs at SiO₂ concentrations of 0.1-0.5%wt. Voltage (d) and current (e) outputs of the CS-SiO₂ 0.2%wt TENGs tested at frequencies ranging from 2-9 Hz.

3. RESULTS AND DISCUSSION

Working mechanism of the fabricated CS-SiO₂ TENG is explained in the schematic in Figure 1(a). According to electrification effect, when the surfaces of PTFE and CS-SiO₂ (tribo1 and tribo2, respectively) are in contact, they become electrically charged with different signs; PTFE has negative charges and CS-SiO₂ has positive charges. As the two surfaces are separated, the potential drop is created, which can drive electrons to flow from ground to the electrode and flow back to ground when the two surfaces are in contact again. This creates an alternative current (AC) output signal with the frequency of the mechanical agitation. The voltage and current outputs of the CS-SiO₂ TENG increased with the increasing amount of SiO₂ up to 0.2%wt and gradually dropped down at the higher SiO₂ concentration as shown in Figure 1(b) and (c) and their values are presented in Table 1. The highest electrical peak to peak

voltage and current of 77.1 V and 6.4 μ A were generated from the CS-SiO₂ 0.2%wt TENG. These outputs were over two times higher than those of the unmodified CS TENG which were 32 V and 2.1 μ A, respectively.

To study the optimum working condition of the fabricated CS-based TENGs, electrical outputs were measured from CS-SiO₂ 0.2%wt TENG under a vertical contact-separation with repeated movement at frequencies ranging from 2 - 9 Hz and the results are presented in Figure 1(d) and (e), and Table 1. It was found that the electrical outputs of CS-SiO₂ 0.2%wt TENG increased with increasing frequency and produced the highest peak to peak voltage of 110 V and current of 8.5 μ A at 7 Hz frequency. This is due to the retained triboelectric charges at high frequency that can effectively generate high voltage and consequently induce high charge transfer resulting in high outputs performance.

Table 1. The peak to peak voltage and current of CS TENG and CS-SiO₂ 0.1-0.5%wt TENG derived from Figure 1(b)-(e) and their dielectric constant and dielectric loss tangent values at 1 kHz.

Specimens	TENG Output At 5 Hz		Frequency (Hz)	TENG output		Dielectric Properties at 1 kHz	
	Voltage (V)	Current (μ A)		Voltage (V)	Current (μ A)	ϵ_r	Tan δ
CS	32.0	2.1				21.3	1.5
CS-SiO ₂ 0.1%wt	65.2	4.2				46.9	1.7
CS-SiO ₂ 0.2%wt	77.1	6.4	2	50.2	4.4	66.5	1.8
			3	59.4	5.1		
			4	72.5	6.1		
			5	77.1	6.4		
			6	84.3	7.3		
			7	110.0	8.5		
			8	95.8	7.7		
			9	54.6	5.2		
CS-SiO ₂ 0.3%wt	59.3	4.6				42.4	1.4
CS-SiO ₂ 0.4%wt	49.7	4.2				41.0	1.4
CS-SiO ₂ 0.5%wt	44.7	3.2				39.5	1.4

However, at the frequency of over 7 Hz, the electrical outputs were reduced which was due to the discharge of very high surface charge density at high frequency [14,15].

The power density generated by the fabricated CS-SiO₂ 0.2%wt TENG was investigated at various load resistances. The output voltage and current of CS-SiO₂ 0.2%wt TENG measured at the applied force of 10 N at 7 Hz frequency with the external load resistances ranging from 1 - 50 M Ω are presented in Figure 2(a) and Table 2. It is shown that the output current reduced whereas the output voltage increased with the increasing load resistance. The power density of the CS-SiO₂ 0.2%wt TENG at various load resistances derived from Figure 2(a) are presented in Figure 2(b). The highest delivered power density of CS-SiO₂ 0.2%wt TENG was 182 mW/m² at 10 M Ω load resistance. With this outputs performance, the fabricated CS-SiO₂ 0.2%wt TENG with the size of 4x4x1 cm³ can light up 36 green LEDs as shown in Figure 2(c).

The generated electrical outputs of the CS-SiO₂ TENGs are found to be dependent on their dielectric properties as evidenced by the dielectric constant (ϵ_r) and dielectric loss ($\tan \delta$) presented in Figure 3(a) and (b). From the dielectric constant of CS-SiO₂ nanocomposites at the frequency of 1 kHz as shown in Table 1, it was observed that the pristine CS material had the lowest dielectric constant of 21.3 with dielectric loss of 1.5 while the CS-SiO₂ materials with modulated dielectric properties were observed at various SiO₂ concentration. The CS-SiO₂ 0.2%wt sample had the highest dielectric constant of 66.5 and the highest dielectric loss of 1.8. However, the dielectric constant values were reduced with higher SiO₂ concentration which were 42.4, 41, and 39.5 in the CS-SiO₂ with 0.3, 0.4 and 0.5%wt, respectively, whereas their dielectric loss values decreased down to 1.4 and remained the same in the three samples. This suggests that the electrical outputs of the fabricated TENG depend on dielectric constant of CS-SiO₂ nanocomposites

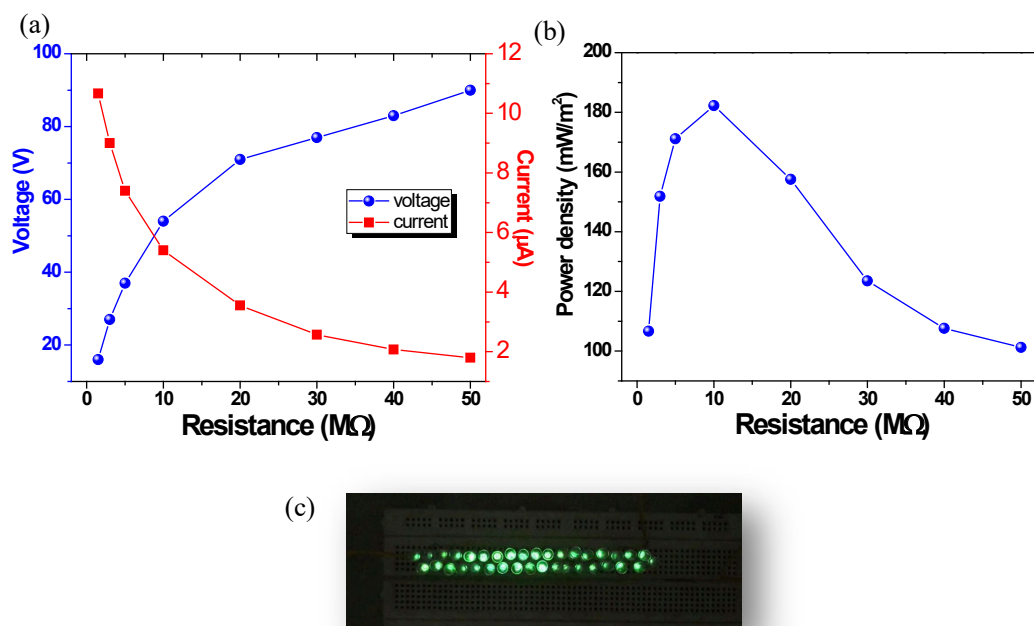


Figure 2. Voltage and current outputs at various load resistances (a), power density of the CS-SiO₂ 0.2%wt TENG (b), and the output from the 4x4x1 cm³ TENG can light up 36 LEDs (c).

Table 2. Voltage and current outputs, and power densities of the CS-SiO₂ 0.2%wt TENG at various load resistances derived from Figure 2.

Resistance (MΩ)	Voltage (V)	Current (μA)	Power (μW)	Power density (mW/m ²)
1	16	10.7	171	107
3	27	9.0	243	152
5	37	7.4	274	172
10	54	5.4	292	182
20	71	3.6	252	158
30	77	2.6	198	124
40	83	2.1	172	108
50	90	1.8	162	101

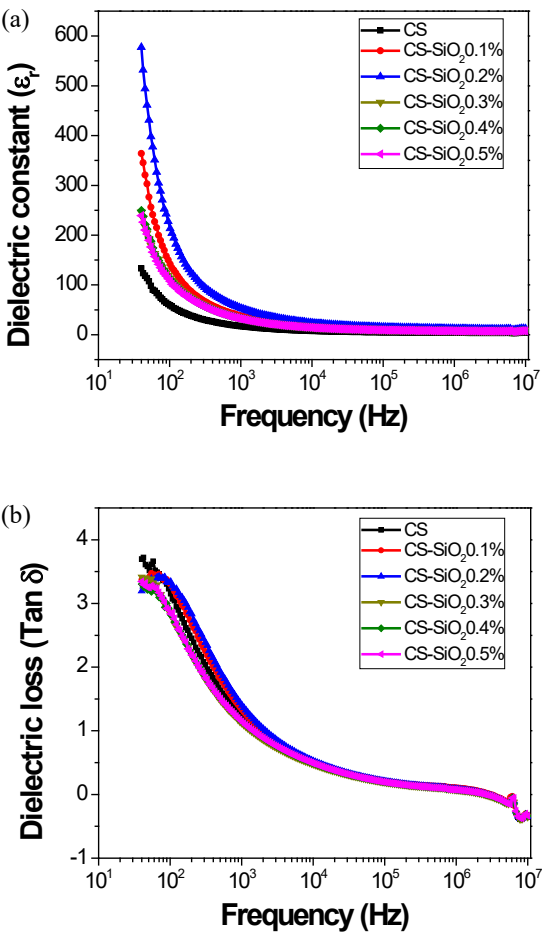


Figure 3. Dielectric constant (a) and dielectric loss of CS and CS-SiO₂ at 0.1-0.5%wt SiO₂ (b).

which can be enhanced over three folds by adding SiO_2 nanoparticles at 0.2%wt. The presence of SiO_2 nanoparticles can reduce air pore formation in CS composite resulting in the increased dielectric constant of nanocomposite, since SiO_2 has higher dielectric constant ($\epsilon_r = 3.9$ for silica fume) than that of air. However, the less dielectric constant of SiO_2 nanoparticle than that

of CS material diminished the overall dielectric constant of CS- SiO_2 nanocomposites at higher SiO_2 concentration (0.3-0.5%wt).

SEM images in Figure 4(a) and (b) reveal the morphologies of pristine CS and CS- SiO_2 0.2%wt samples. It is observed that the CS- SiO_2 0.2%wt nanocomposite had denser structure, which could be attributed to the reduction of air

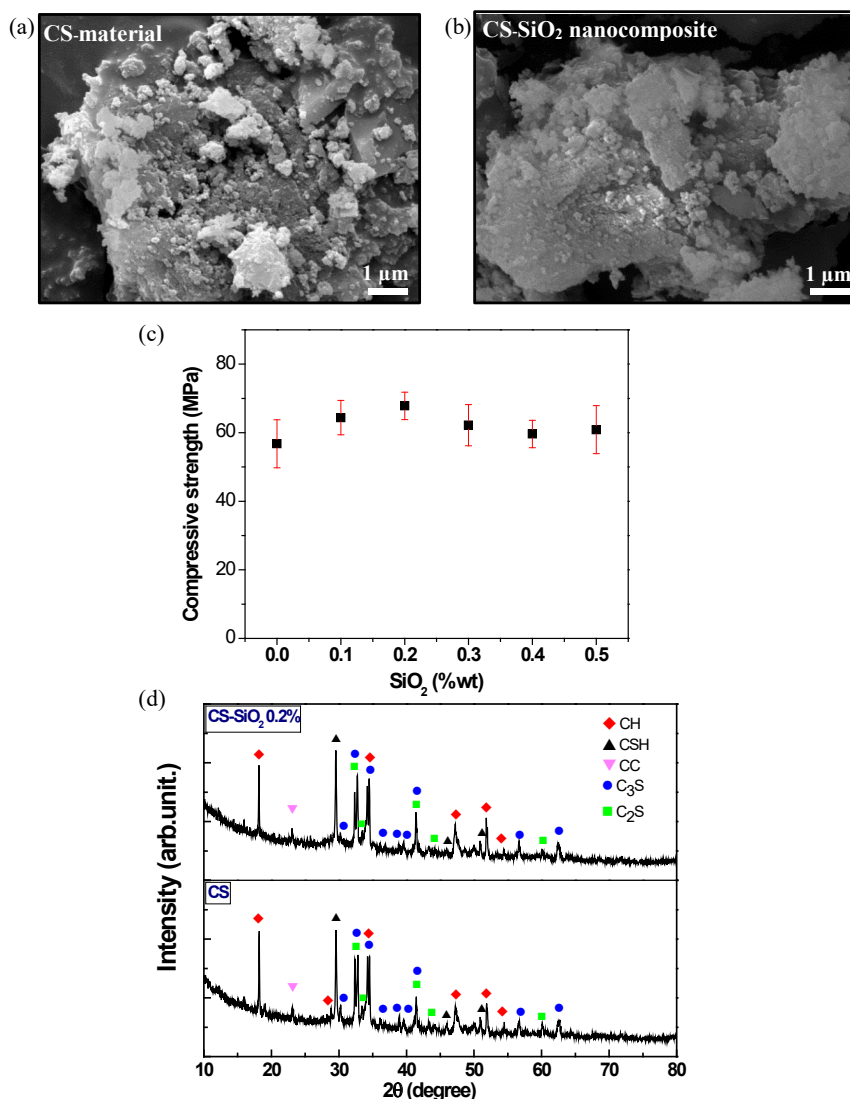


Figure 4. SEM images of the ordinary CS (a) and CS- SiO_2 0.2%wt nanocomposite (b). Compressive strength of the ordinary CS (c) and CS- SiO_2 0.1-0.5%wt nanocomposites and XRD patterns of the ordinary CS and CS- SiO_2 0.2%wt nanocomposite (d).

voids due to the filling of SiO₂ nanoparticles[16]. Furthermore, the high surface area of silica fume nanoparticles can provide nucleation site for the formation of CSH[17,18], which can consequently improve mechanical property of the CS-SiO₂[19]. Our results have presented that the fabricated CS-SiO₂ composite exhibited superior mechanical property over the ordinary CS material as revealed in compressive strength test in Figure 4c). The 60-day compressive strength of CS-SiO₂ 0.2%wt was 67 MPa which was 15% higher than that of the ordinary CS which was 58 MPa.

The strength mechanism is supported by microstructural analysis using XRD as presented in Figure 4(d). The XRD patterns of ordinary CS and CS-SiO₂ 0.2%wt nanocomposite exhibit identical XRD patterns in peak positions composing of the diffraction planes from calcium silicate hydrate (CSH), tricalcium silicate (C₃S), dicalcium silicate (C₂S) and calcium hydroxide (CH). This suggests that no new crystal phase formed after adding SiO₂. However, the peak intensity of the CSH in the CS-SiO₂ 0.2%wt sample is slightly higher than that of the pristine CS one, indicating that the formation of CSH was enhanced with the presence of SiO₂. The addition of SiO₂ can thus improve both TENG performance and compressive strength of the CS material.

4. CONCLUSIONS

CS-SiO₂ TENG was successfully fabricated and tested for energy conversion performance. The CS-SiO₂ TENG with the addition of SiO₂ at 0.2%wt generated the highest output voltage and current which were 110 V and 8.5 μ A, respectively. The maximum delivered power density of 182 mW/m² was achieved at the load resistance of 10 M Ω . The superior energy conversion performance of CS-SiO₂ 0.2%wt TENG is accounted for the improved dielectric properties due to the addition of SiO₂ nanoparticles which can promote the formation of CSH product and can consequently reduce air voids. This results in the synergetic enhancement

of dielectric constant and compressive strength of the CS-SiO₂ nanocomposite material.

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REFERENCES

- [1] Fan F.-R., Tian Z.-Q. and Lin Wang Z., *Nano Energ.*, 2012; **1**: 328. DOI:10.1016/j.nanoen.2012.01.004.
- [2] Wang S., Lin L. and Wang Z.L., *Nano Lett.*, 2012; **12**: 6339. DOI:10.1021/nl303573d.
- [3] Chen J., Guo, H., He X., Liu G., Xi Y., Shi H. and Hu C., *ACS Appl. Mater. Interf.*, 2016; **8**: 736. DOI:10.1021/acsami.5b09907.
- [4] Kim Y. J., Lee J., Park S., Park C., Park C., and Choi H.-J., *RSC Adv.*, 2017; **7**: 49368. DOI:10.1039/C7RA07274K.
- [5] Xie L., Huang X., Wu C. and Jiang P., *J. Mater. Chem.*, 2011; **21**: 5897. DOI:10.1039/C0JM04574H.
- [6] Kim P., Doss N. M., Tillotson J. P., Hotchkiss P. J., Pan M.-J., Marder S. R., Li J., Calame J. P. and Perry J.W., *ACS Nano*, 2009; **3**: 2581. DOI: 10.1021/nn9006412.
- [7] Huang X., Jiang P. and Xie L., *Appl. Phys. Lett.*, 2009; **95**: 242901. DOI:10.1063/1.3273368.

- [8] Zhao X., Zhao J., Cao J.-P., Wang X., Chen M. and Dang Z.-M., *J. Phys. Chem. B*, 2013; **117**: 2505. DOI: 10.1021/jp310021r.
- [9] Li J., Seok S.I., Chu B., Dogan F., Zhang Q. and Wang Q., *Adv. Mater.*, 2009; **21**: 217. DOI:10.1002/adma.200801106.
- [10] Chaipanich A., *Curr. Appl. Phys.*, 2007; **7**: 532. DOI:10.1016/j.cap.2006.10.016
- [11] Zhang X., Yang H., Yang Q., Du X., Li C., Cheng X., *Adv. Mech. Eng.*, 2019; **11(2)**: 1-9. DOI: 10.1177/1687814019828948.
- [12] Panjehpour M., Ali A.A.A. and Demirboga R., *Int. J. Sustain. Constr. Eng. Technol.*, 2011; **2(2)**: 1-7.
- [13] Toutanji H.A. and El-Korchi T., *Cem. Concr. Res.*, 1995; **25**: 1591. DOI: 10.1016/0008-8846(95)00152-3.
- [14] Wang S., Xie Y., Niu S., Lin L., Liu C., Zhou Y.S. and Wang Z.L., *Adv. Mater.*, 2014; **26**: 6720. DOI:10.1002/adma.201402491.
- [15] Wang J., Wu C., Dai Y., Zhao Z., Wang A., Zhang T. and Wang Z.L., *Nat. Commun.*, 2017; **8**: 88. DOI:10.1038/s41467-017-00131-4.
- [16] Naji Givi A., Abdul Rashid S., Aziz F.N.A. and Salleh M.A.M., *Compos. B-Eng.*, 2010; **41**: 673. DOI:10.1016/j.compositesb.2010.08.003.
- [17] Biricik H. and Sarier N., *Mater. Res.*, 2014; **17**: 570. DOI:10.1590/S1516-14392014005000054.
- [18] Wang L., Zheng D., Zhang S., Cui H. and Li D., *Nanomaterials (Basel)*, 2016; **6**: 241. DOI:10.3390/nano6120241.
- [19] Maddalena R., Hall C. and Hamilton A., *Thermochim. Acta*, 2019; **672**: 142. DOI:10.1016/j.tca.2018.09.003.