The growth of carbon nanotubes & carbon nanofibers on cement admixture particles

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***Abstract*—** *Carbon nanotubes (CNTs) and carbon nanofibers (CNFs) are beneficial reinforcement materials for high performance and multifunctional cement-based composites. However, it is difficult to uniformly disperse CNTs/CNFs in cement-based composite during the composite fabrication process due to CNTs/CNFs aggregation. The in situ growth of CNTs/CNFs on cement/mineral admixture provides a new method to solve this issue. This article summarizes the methods and theories of in situ growth of CNTs/CNFs on cement/mineral admixture, including chemical vapor deposition method and microwave irradiating conductive polymers method. Properties of the cement-based composites made from the CNTs/CNFs-grown cement/mineral admixture are presented. The issues about the in situ growth of CNTs/CNFs on cement/ mineral admixture that needed to be further studied are discussed.*

***Keywords*— Carbon nanotubes, Carbon nanofibers ,Cement-based composites ,Cement, Mineral admixture.**

I. INTRODUCTION

Cement-based material is a quasi-brittle material according to are weak. Under the effect of the load, temperature, humidity and other factors, the cement-based material is easy to crack and fracture. The traditional solution is mainly to use steel or millimeter/ micron fiber (such as steel fiber, carbon fiber, and polyvinyl alcohol fiber) to reinforce the cement-based materials. However, researchers recognized that micro-sized reinforced materials can only limit the expansion of internal microcracks of cement-based materials instead of preventing the microcracks from engendering. The addition of carbon nanotubes (CNTs) and carbon nanofibers (CNFs) can address the problems mentioned above. CNTs/CNFs can transfer the reinforcement and modification behavior on the cement-based materials from microscale to nanoscale. CNTs/CNFs possess better mechanical property, whose elastic modulus, tensile strength and ultimate deformation are respectively 10, 20 and 18 times that of microscale carbon fiber. The inter-laminar shear strength of the CNTs/CNFs and the epoxy resin layer is an order of magnitude higher than that of micro carbon fiber and the epoxy resin layer [1–3]. Li et al. firstly observed that the addition of 0.5 wt.% CNTs can respectively improve the flexural, compressive strength and the failure strain by 25%, 19% and 27%. Raki et al. reported that CNTs can improve the Vivtorinox hardness of the early hydration of cement-based material by 600%, the Young modulus by 227% and the flexural strength by 40% [2]. Veedu incorporated 0.02 wt.% CNTs into the cement-based materials to make its flexural and compressive strength increase by 30% and 100% [3]. Chaipanich et al. firstly used CNTs of 0.5% and 1% by weight in a fly ash cement system to produce carbon nanotubes-fly ash composites in the form of pastes and mortars and found that the use of carbon nanotubes results in higher strength of fly ash mortars [4]. Shah et al. only added 0.048–0.08 wt.% CNTs into cement-based materials to increase its flexural strength and elastic modulus by 8–40% and 15–55% [5,6]. Gay and Sanchez founded that the split tensile strength of the cement-based materials with the addition of 0.2 wt.% CNFs is 26% higher than that of the cement-based materials with fly ash [7]. Kumar et al. discussed the effect of multiwalled CNTs on strength characteristics of the hydrated Portland cement paste [8]. Gao et al. founded that the compressive strength of the CNFs reinforced concrete with the addition of 0.16 wt.% CNFs was 42.7% higher than that of ordinary concrete. Researches pointed out that CNTs/CNFs achieves enhancement effect by nucleation, increasing the amount of C–S–H gel of high hardness, improving pore structures, controlling nanoscale cracks, improving the early strain capacity and reducing autogenous shrinkage, etc. [1–3]. These mechanisms also would improve the durability of the cement-based materials. Han et al. have founded that the addition of CNTs could improve the transport properties of the cement mortar. In addition, due to the excellent electrical, thermal, electromagnetic properties of the CNTs/CNFs, it could make the cementbased materials possess electrical, thermal, electromagnetic and sensing properties, and then make the cement-based materials possess multi-functional properties [1,3].

However, CNTs/CNFs are easy to agglomerate due to its high specific surface energy. Therefore, effective dispersion methods are needed to disperse CNTs/CNFs into the cement-based materials in order to fully implement enhancement effect of CNTs/CNFs. To solve the problem, researchers carried on a lot of studies and obtained some effective methods, such as physical dispersion methods (including high-speed shear and ultrasonic dispersion), chemical dispersion methods (surface covalent bond modification with strong acid treatment or non-covalent bond modification with surfactants, etc.), and the combination of physical and chemical methods [1–3]. However, the above methods only can improve the dispersion effect to some extent. In addition, there exist some other disadvantages such as high energy consumption, decreasing aspect ratio, etc. [9–11]. Recently researchers put forward a new method to solve the dispersion problem of CNTs/CNFs, which is to make CNTs/CNFs and cement/mineral admixture a whole by

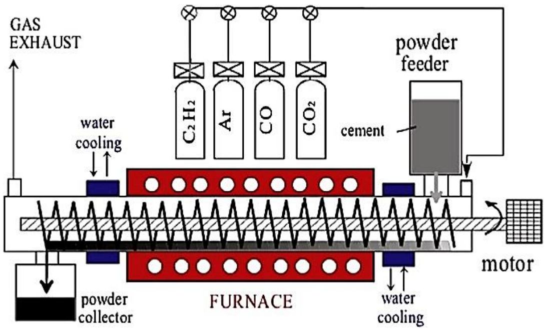

FIG. 1. SCHEMATIC REPRESENTATION OF EXPERIMENTAL SETUP WITH CONTINUOUS FEEDING OF CEMENT PARTICLES USING A SCREW FEEDER FOR THE CVD IN SITU CNTS/CNFS GROWTH [14].

in situ growing CNTs/CNFs on the cement/mineral admixture particles. This article summarizes the studies of in situ growth of CNTs/ CNFs on cement/mineral admixtures, including the methods and theories of in situ growth of CNTs/CNFs, and the properties of the cement-based materials prepared with the addition of the CNTs/ CNFs-grown cement/mineral admixture.

II. METHODS OF IN SITU GROWTH OF CNTS/CNFS ON CEMENT/MINERAL ADMIXTURE

The research on the in situ growth of CNTs/CNFs on the cement/mineral admixture mainly contains the in situ growth of CNTs/CNFs on cement, silica fume, clinker, fly ash, etc. The methods of in situ growth of CNTs/CNFs include chemical vapor deposition method and microwave irradiating conductive polymers method.

2.1 Chemical vapor deposition method

Chemical vapor deposition (CVD) method, also called hydrocarbon gas pyrolysis method, is making gaseous hydrocarbon passing through the template attached with the catalyst particles under the condition of high temperature, where the gaseous hydrocarbon decomposed to produce CNTs/CNFs.

Nasibulin et al. firstly employed CVD method to grow CNTs/CNFs on the surface of cement, in which cement with catalyst is heated to grow CNTs/CNFs in the carbon source gas environment. Because cement contains Fe_2O_3, SiO_2, MgO and Al_2O_3 etc. catalytically materials for the growth of CNTs/CNFs, no external catalyst is needed for the in situ growth of CNTs/CNFs. They proposed a set of reactor system (as shown in Fig. 1) which is able to continuously feed the matrix material. The detailed process is as following: (1) acetylene was used as the carbon source gas passing through the reactor; (2) Sulphate-resistant cement with 4% Fe_2O_3 was introduced into the quartz tube reactor with a powder feeder; (3) The temperature of the resistively heated furnace was kept in the range of 400–700 C; (4) At the end of the reactor system a powder collector was used to collect products. The experimental results indicated that no carbon precipitated on particles below 450 C;

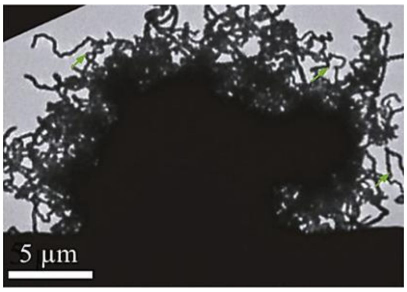

FIG. 2. TEM IMAGE OF COMPLETE COVERAGE OF THE CEMENT PARTICLES BY CNTS/CNFS [14].

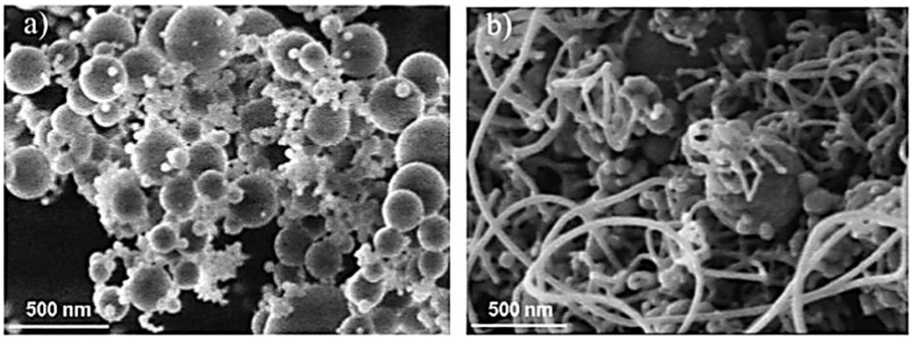

FIG. 3. SEM IMAGES OF (A) PRISTINE SILICA PARTICLES AND (B) CNTS GROWN ON THE SURFACE OF SILICA [12].

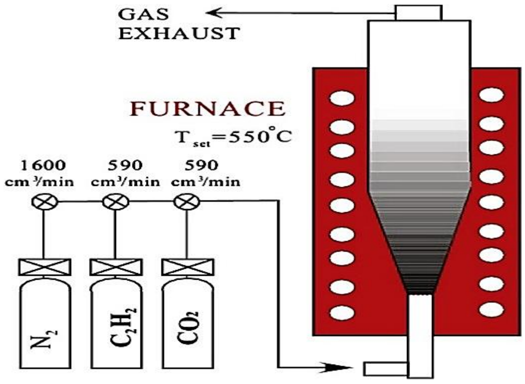

FIG. 4. SCHEMATIC PRESENTATION OF THE FLUIDIZED BED REACTOR USED FOR SYNTHESIS OF CNFS ON THE SURFACE OF CLINKER PARTICLES [17].

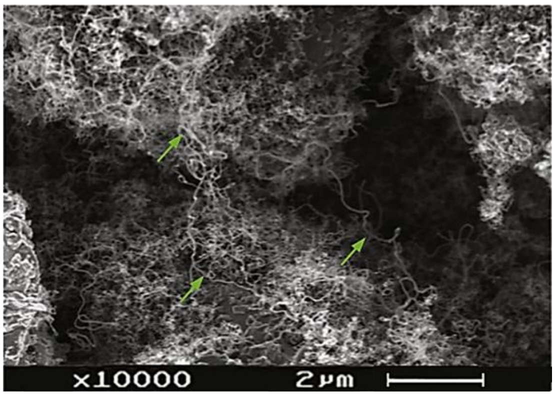

FIG. 5. SEM IMAGES OF CNFS GROWN ON CLINKER. [17].

CNFs with the diameter of about 30 nm and average length of 3 lm were grown on the surface of the cement particles in the temperature range from 550 C to 750 C; at higher temperatures the cement particles were completely covered by CNTs and CNFs (as shown in Fig. 2) [12–20].

Nasibulin et al. also tried CVD method to grow CNTs/CNFs on the silica fumes (as shown in Fig. 3). The experimental results indicate that on the surface of silica particles, CNFs with the diameters varied from 30 to 50 nm were observed at 550 C. Increasing temperature results in the growth of multiwalled CNTs with 5– 10 walls. The outer diameter of multiwalled CNTs varied from 10 to 15 nm at 600 C and from 12 nm to 20 nm at 750 C, respectively. The maximum length of the CNTs was found to be 15 lm [12]. Nasibulina et al. employed the fluidized bed reactor (as shown in Fig. 4) to grow CNFs directly on cement clinker particles by using CVD method. As seen from Fig. 5, CNFs were uniformly formed on the surface of the clinker particles with an average length about 10 lm. The growth time was varied from 6 to 30 min to optimize the growth conditions. The amount of the deposited CNFs on the surface of clinker particles depended on the growth time.

Thermogravimetric analysis (TGA) results showed that the concentration of CNFs on clinker particles was varied from 1% to 5%.

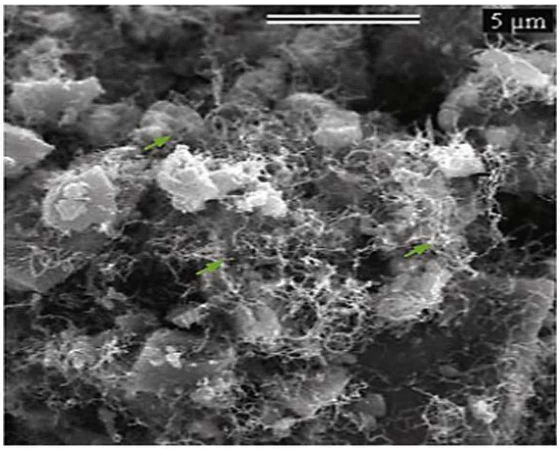

FIG. 6. SEM IMAGE OF CNTS GROWN ON CLINKER[21].

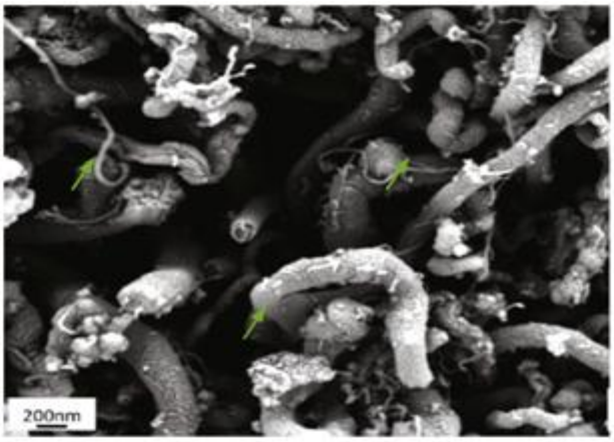

FIG. 7. SEM IMAGES OF CNTS AND CNFS GROWN ON FLY ASH[23].

TABLE 1
IN SITU GROWTH OF CNTS/CNFS ON CEMENT/MINERAL ADMIXTURES BY CVD METHOD

Substrate	Carbon source	Active agent/catalyst	Temperature (C)	Product	Productivity (%)	Researchers
Cement	C2H2	Fe	550–750	CNFs	–	Nasibulin et al. [12–18]
Silica fume		Fe		CNTs and CNFs		
Clinker	C2H2	Fe	550	CNFs	1–5%	Nasibulina et al. [17]
		Iron ore/red mud	–	CNTs	4.03–10.4%	Ludvig et al. [21]
Fly ash	C2H4	Fe (1.38–5%)	0–700	CNTs and CNFs	2.29–8.5%	Dunens et al. [23]

Ludvig et al. also employed CVD method to grow CNTs/CNFs directly on the cement clicker and silica fume [21,22], but they added iron ore and industrial byproducts such as converter dust, steel mill scale and red mud as extra catalysts. Their research showed that the clinker-CNTs composite contained high purity multiwalled CNTs (as shown in Fig. 6). TGA was performed to determine CNTs yield. A CNTs yield of 4.03% in mass of clinker-CNTs nanocomposite was obtained. Iron ore and industrial byproducts such as steel mill scale and red mud were added to the clinker in different proportions, which resulted in CNTs yield increase to 10.40% [21]. Silica fume produced CNTs and CNFs with a diameter of 30–60 nm [22].

Dunens et al. employed the fluidized bed CVD method for in situ CNTs/CNFs growth on fly ash (FA) and included Fe content as a catalyst support similar to many laboratory-developed catalysts for CNTs/CNFs synthesis. They impregnated the FA with iron nitrate to increase the Fe content to increase metal loading: $Fe(NO_3)_3 9H_2O$ was dissolved in ethanol and sonicated for 15 min prior to the addition of a weighed amount of sieved FA substrate in the appropriate proportions to result in catalysts with a total iron loading of either 2.5 or 5 wt%. The mixture was stirred and air-dried at 40 C for 15 h prior to calcinations in air at 800 C for 12 h. The results of the research showed that the 2.5 wt.% Fe loaded FA products contained 7.65 wt.% CNTs and CNFs, and the 5 wt.% Fe loaded FA products contained 8.25 wt.% CNTs and CNFs [23]. Fig. 7 shows the CNTs and CNFs grown on the surface of FA.

According to above-mentioned researches, in situ growth of CNTs/CNFs on the cement/mineral admixtures by CVD method is effected by substrate, carbon source, temperature and catalyst, which lead to the different products and different productivity. These research results are summarized in Table 1.

2.2 Microwave irradiating conductive polymer method

Microwave heating is rapid which could heat the materials to high temperature in a short time. Polypyrrole is a kind of conductive polymer with moderate conductivity and is able to absorb microwave irradiation very efficiently, so it could be used as the heating source for the growth of nanocarbons. Microwave poptube precursors, such as ferrocene powders, are physically mixed in the solid state with polypyrrole. Upon microwave irradiation of the conducting materials, they will be rapidly heated to reach the temperature above 1100 C, where the ferrocene could be decomposed to an iron catalyst and cyclopentadienyl that could serve as the carbon source, which could initiate ultrafast CNTs growth [24–26].

Liu and Zhang firstly used microwave irradiating conductive polymer method to initiate CNTs/CNFs in situ growth. Fig. 8 shows the preparation process they used: (1) PolypyrroleCl powder (PPyCl) was mixed with fly ash and ferrocene; (2) The mixture was put into the microwave oven to heat. The microwave initiated CNTs growth will take only 15–30 s under the microwave irradiation at room temperature in air. Fig. 9 shows that CNTs uniformly cover on the surface of the conducting PPyCl coated fly ash. The bulk four probe DC conductivity of CNTs coated fly ash is 0–0.87 lS/cm, a moderate enhancement in electrical conductivity compared to insulating bare fly ash. Compared to the CVD approach, the microwave irradiating conductive polymer method does not need any inert gas protection and additional feed stock gases [24–26].

III. THE PERFORMANCE OF THE CEMENT-BASED COMPOSITES PREPARED WITH THE CNTS/CNFS-GROWN CEMENT/MINERAL ADMIXTURE

Nasibulin et al. prepared cement pastes using the CNTs/CNFs grown cement and cured in water at 20 C for 7, 14 and 28 days, then tested their compressive strength, flexural strength and electrical resistance. Tables 2 and 3 show the results of the research. As shown in Table 2, the mechanical tests after 7 days curing in water showed that the paste prepared with the addition of CNTs/CNFs grown cement decreased compared to pastes produced from only the pristine sulphate-resistant (SR) cement. This might be explained by a lower degree of hydration of the modified cement in the initial curing processes. Table 3 shows the properties of pastes made from CNTs/CNFs-grown cement synthesized in different parameters (reaction temperature, carbon gas flow rate etc). It can be see from Table 3 that the CNTs/CNFs-grown cement can have compressive strength more than 2 times higher than that of paste prepared from the pristine cement. As for the electrical conductivity, Table 2 shows 70 times increase in the electrical conductivity could be obtained with CNTs/CNFs-grown cement [12–18].

Hlavácˇek et al. also prepared cement pastes with CNTs/CNFs grown cement (the water/binder ratio was set to 0.35 and the CNTs/CNFs paste ratio varied from 0.0 to 0.038), and tested the compressive strength and the fracture energy. The experimental results show a 25% increase in the compressive strength and a 14% of increase in the fracture energy when the addition of 3.5% CNTs/CNFs-grown cement [19,20].Ludvig et al. prepared cement pastes and cement mortar with CNTs/CNFs-grown clinker and tested the tensile, compressive and flexural strength. Results showed a 34.28% of increase in the tensile strength with a simple physical mixture containing 0.3% of CNTs/ CNFs on the cement clinker matrix of cement paste and 14.1% higher flexural strength and 88.3% higher compressive strength of cement mortar [21,22].

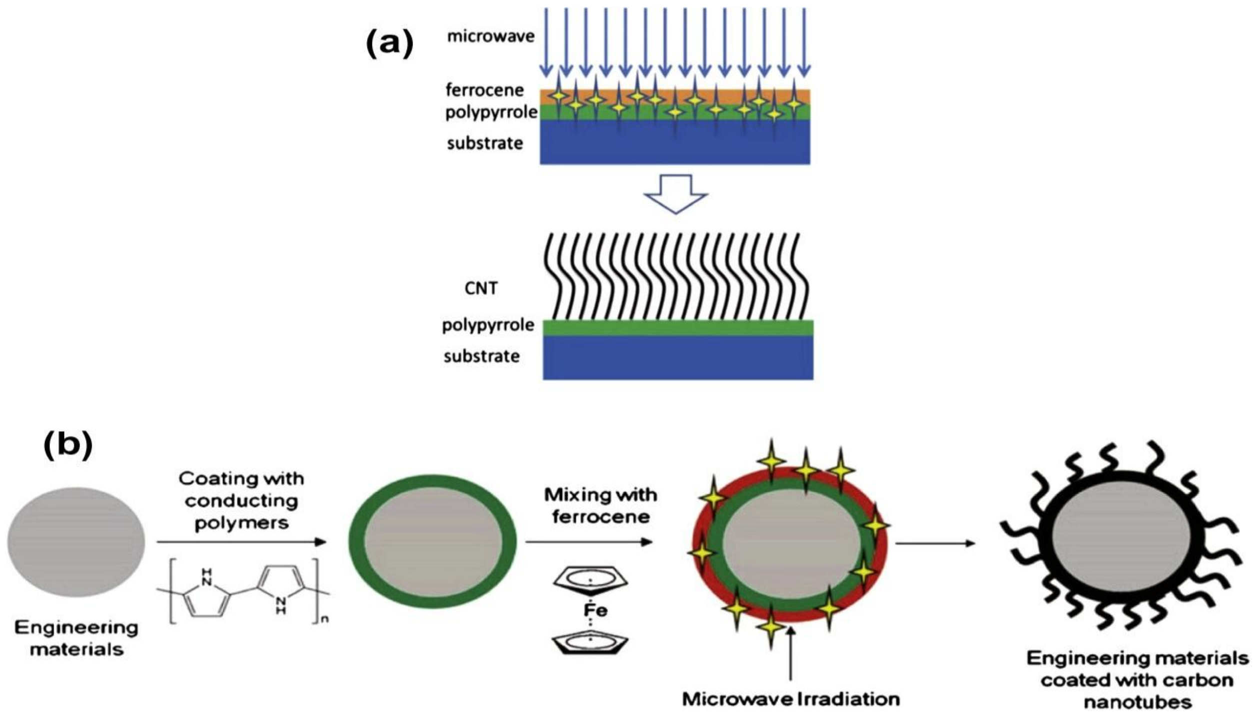

FIG. 8. (A) MICROWAVE INITIATED CNTS GROWTH ON CONDUCTIVE SURFACES AND (B) MICROWAVE INITIATED CNTS GROWTH ON ENGINEERING MATERIALS [24–26].

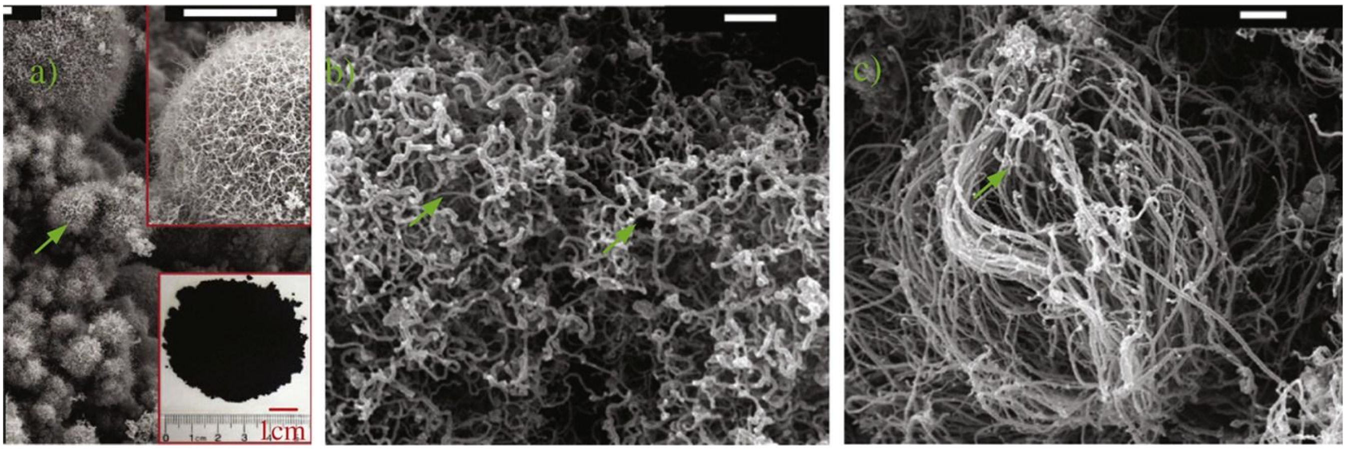

FIG. 9. (A) SEM IMAGES OF THE AS-PRODUCED CNTS ON FLY ASH, INSETS: (TOP) ZOOM-IN SEM IMAGE; (BOTTOM) DIGITAL PICTURE OF COATED FLY ASH (B AND C) SEM IMAGES OF CNTS COATED POLYPYRROLE COATED FLY ASH [24–26].

TABLE 2
PROPERTIES OF CEMENT PASTE (7 DAYS CURING IN WATER) PREPARED BY ADDING DIFFERENT SAMPLES OF CNTS/CNFS-GROWN SR CEMENT [14].

Cement grown CNTs/CNFs-additions(%)	Temperature(^oC)	C_2H_2(cm^3/min)	CO_2(cm^3/min)	Compressive strength (MPa)	Flexural strength (MPa)	Electrical resistivity(MX cm)	
						1 days after	2 months
0	0 –	–	–	49	16	3.8	9.7
5	5600	280	280	38	15	3.1	7.2
10	10600	280	280	36	12	2.8	5.9
30	30600	280	280	24	8.0	1.7	2.5

CNTs/CNFs-grown SR cement is using SR cement as matrix to grow CNTs/CNFs; electrical resistivity is tested after strength test

TABLE 3
MECHANICAL (AFTER 28 DAYS CURING IN WATER) AND ELECTRICAL (1 DAY AFTER MECHANICAL TESTING) PROPERTIES OF CEMENT PASTE PREPARED BY ADDING DIF FERENT SAMPLES OF CNTS/CNFS GROWN SR-CEMENT [14].

Cement grown CNTs/ CNFs addition (%)	Temperate (C)	C2H2 (cm^3/min)	CO_2 (cm^3/min)	CO (cm^3/min)	Compressive strength (MPa)	Electrical resistivity (MX cm)
0	–	–	–	–	25	9.7
100	550	860	0	177	22	0.23
100	575	660	660	0	55	1.3
100	500	500	500	0	40	1.7
100	525	660	660	0	56	4.0

CNTs/CNFs-grown SR cement is using SR cement as matrix to grow CNTs/CNFs; electrical resistivity is tested 1 day after strength test.

TABLE 4
THE PERFORMANCE OF THE CEMENT BASED COMPOSITES PREPARED WITH THE CNTS/CNFS-GROWN CEMENT OR CLINKER.

Type of cement basedv composites	CNTs/CNFs addition (%)	Performance	Researchers
Cement paste	0.4	2–3 times increase in the compressive strength, 40 times increase in the electrical conductivity	Nasibulin et al. [12–18]
Cement paste	3.5	25% increase in the compressive strength, 14% increase in the fracture energy	Hlavácˇek, Šmilauer [19]
Cement paste	0.3	34.28% increase in the tensile strength	Ludvig et al. [21]
Cement mortar	–	14.1% higher flexural strength and 88.3% higher compressive strength	Ludvig et al. [22]

As can be seen from the above results, there were varying degrees of improvement in the compressive strength, tensile strength, flexural strength, fracture energy and electrical resistivity of the cement-based composite prepared with CNTs/CNFs-grown cement or clinker, which are summarized as Table 4.

IV. FUTURE PERSPECTIVES

Besides the growing of CNTs/CNFs on the cement/mineral admixture, recently Nasibulin et al. employed the CVD method to grow CNTs/CNFs on the surface of sand and soil [16]. Hlavácˇek and Šmilauer prepared the mortar with the CNTs/CNFs grown sand showing a 25% of increase in the compressive strength and a little increase in the fracture energy. In addition, short fibers such as steel fiber, carbon fiber, polyvinyl alcohol fiber and polypropylene fiber are widely-used reinforced materials. There have been studies in grafting or growing CNTs/CNFs onto the CFs [27–29]. Due to the effect of multi-scale enhancement with the addition of nanoscale fibers together with microscale fibers, CNTs/CNFs-grown CFs or other fibers could be employed to reinforce or modify the cement-based materials.

The in situ growth of CNTs/CNFs on cement/mineral admixture is still a new research, which needs to be further studied on the following aspects:(1) The research of growing CNTs/CNFs on other mineral admixtures with CVD method and microwave irradiating conductive polymers method; (2) The research of simple and large-scale technology of in situ growth of CNTs/CNFs on cement/ mineral admixture; (3) The research of the influence of CNTs/ CNFs-grown cement/mineral admixture particles on the hydration heat, hydration degree, and the initial and final setting time of cement; (4) The mechanical performance, functional performance and durability of the cement-based materials made of CNTs/ CNFs-grown cement/mineral admixture and (5) The research of reinforcement or modification mechanism of the CNTs/CNFsgrown cement/mineral admixture to the cement-based materials.

V. CONCLUSION

This article summarized the technologies, theories, products, productivity of in situ growth of CNTs/CNFs on cement/mineral admixture and the properties of the cement based composites made of CNTs/CNFs-grown cement/mineral. The main methods of in situ growth of CNTs/CNFs on cement/mineral admixture are chemical vapor deposition method and microwave irradiating conductive polymers method. The productivity of the in situ growth of CNTs/CNFs can reach to 10.4%. Best results of the researches show 34.28% increase in the tensile strength of the cement-based composite prepared with the CNTs/CNFs-grown cement/mineral admixture, 2–3 times increase in the compressive strength, 14% increase in the fracture energy and 70 times increase in the electrical resistivity. The in situ growth of CNTs/CNFs on cement/mineral admixture provides a new method to add nanofiber to cement-based material, which may drive a new development of the field of multifunctional nanofiber reinforcing cement-based composites.

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