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A Review of Nanomaterials in Cement-Based Composite

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This paper reviews the development condition of nanomaterials used in concrete over years. The definitions of nanomaterial, nanotechnology, and nano-concrete are reviewed. The impacts of nanomaterials on cementitious material in the point of advantages and disadvantages are analyzed. Moreover, this paper analyzes and classifies the nanomaterials into the extra quality enhancement and modification to plain cementitious composite. Indeed, the outstanding properties of the embedded nanomaterials can be introduced to concrete such as the mechanical improvement, pore structure refinement, hydrate acceleration, and smartness modifying of self-cleaning, and/or self-sensing. Before the full potential of nanotechnology can be realized in concrete applications, various techniques have to be solved including proper dispersion, compatibility of the nanomaterials in cement, processing, manufacturing, safety, handling issues, scale-up, cost, the impact on the environment and human health.

Keywords : Nano materials, Cementitious material, Nanotechnology, Nano-concrete

1. INTRODUCTION

1.1 Background of concrete and cementitious composite

Concrete is the most abundant man-made construction material that ages over time. The properties of high strength, super durable and relatively low price make concrete become an indispensable material in modern construction field(Li et al. 2004; Alberti et al. 2017). Additionally, concrete contents multiple length scales and multi-phase, presenting as a heterogeneous material with nanostructure itself(Lin et al. 2016). Moreover, the properties of each scales are derived from those of the next smaller scale(Sanchez and Sobolev 2010; Jennings et al. 2008; Sanchez and Borwankar 2010), thus the changing and modifying the ingredients can also impact on both micro-behavior and macro-performance. Nowadays, High strength concrete(HSC), high performance concrete(HPC), green concrete and are no longer the new concepts in modern concrete science. Reviewing the development of the history of concrete, the social demands including the engineering and/or environmental aspect always force the development of concrete and cementitious materials.

To date, concrete with embedded nanomaterials is being demanded more and more in the construction field. Only tiny amount of nanomaterial can influence the performances of concrete so deeply. Unlike other reinforcing materials used in concrete, the nanomaterial can influence not only on general performance but also on the micro-structure of concrete. In this paper we are would like to review details clearly on fabrications and properties of nano-concrete. Since the importance of nanomaterial and nano-concrete, several items related to nanomaterial and nano-concrete were reviewed in this study.

1.2 Main approaches of nanotechnology

Guterrez(2005) reported that all materials can be transformed into nanoparticles and there are indeed various nanomaterials

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around the world. The success of nanoparticle fabrication is depended on the purity or basic chemical composition of parent materials. It has been reported widely that there are two main approaches for nanoparticles as "top-down" approach(Singh et al. 2017; Abdoli et al. 2011) and "bottom-up" approach(see Fig. 1)(Drexler et al. 1991; Jankowska et al. 2009).

The "top-down" approach is modifies the larger structures to nanoscale particles by mechanical attrition and etching techniques such as milling while maintaining their original properties. The advantages of the "top-down" approach are that it can be applied directly without any chemical or electronic devices(Norhasri et al. 2017) and appropriate for massive industries. However, the disadvantages of this method are the inconsistent in uniformity and quality between the parent products and the finals. Except for the inconsistent problem, the threshold value of the fineness should also be considered. Depending on the type of the mill and the material, the particle fineness increases with increasing grinding time but approaches a threshold of a certain value as the fine particles tend to agglomerate, therefore particles cannot be ground further without grinding aids.

Another approach is called "bottom-up" approach which was introduced by Drexler et al.(1991) The brief summarized of this approach is the nanomaterial to assemble or self-assemble

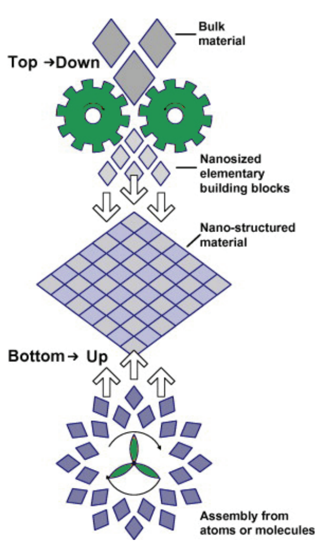

Fig. 1. Illustration of the "top-down" and "bottom-up" approaches in nanotechnology. Adapted from Sobolev and Gutiérrez 2005

from the level of atoms or molecules. For that reason, the "bottom-up" approach is also called "molecular nanotechnology" or "molecular manufacturing". By using the "bottom-up" approach, breakthroughs for nanostructural design and fabrication in material and manufacturing can be promised especially. Normally, most nanomaterials such as nano silica, nano alumina, nano clay which have been used in concrete are produced by using the bottom- up approach(Norhasri et al. 2017). While, depending on the process of the bottom- up approach, some disadvantages have been reported by Sobolev and Gutiérrez(2005). as expensive cost, expertise required in chemical applications and limits for laboratory only.

As a conclusion, selection of those two methods should be based on suitability, cost, and expertise of nano behavior(Norhasri et al. 2014; obolev and Gutiérrez 2005).

2. DEFINITION OF NANOTECHNOLOGY, NANOMATERIAL AND NANO-CONCRETE

2.1 Definition of nanotechnology

Nanotechnology was introduced by Feynman during his lecture "There's Plenty of Room at the Bottom" in the late 60's(Feynman 1960). Nanotechnology is commonly defined as the understanding, controlling, and structuring the matter on the order of nanometers, commonly restricted below 100nm, to create materials with fundamentally new properties and functions (NSTC. 2007). Nanotechnology has broad-reaching applications in the construction field. By applying nanotechnology in construction materials, the primary properties can be modified and improved. Moreover, concrete is a material with nanostructure, the nanoscale properties of concrete will directly influence the general properties such as strength properties, durability, and smartness. Awareness of nanotechnology is a far-reaching approach for introducing more appropriate cementitious materials to fill existing needs. It was also reported by Hanus et. al.(2013), that nanotechnology has the potential to reduce the environmental impact and energy intensity of structures, as well as improve safety and decrease costs associated with civil infrastructures.

2.2 Definition of nanomaterials

Nanomaterials and nanotechnology are being awareness rapidly in recent years. The nanomaterials and nanoparticles are defined as particles with scales ranging from 1 to 100nm in two or three dimensions(NSTC. 2007). As reported by several researchers(Björnström et al. 2004; Lin et al. 2008; Jo et al. 2007), the most significant properties of nanomaterials is the super high surface area to volume ratio, which can provide nanomaterials with the ability and potential for excellent chemical reactivity. To date, many new nanoparticles have been introduced to the cementitious system. Using nanomaterials and nanoparticles in concrete or other cementitious materials is an application of nanotechnology in construction material. The most commonly reported nanomaterials for cementitious composite research are nano-silica(nano-SiO_2), nano-titanium oxide(nano-TiO_2), nano carbon tubes(CNTs). Apart from that, nano-clay, nano-iron (nano-Fe_2O_3), nano-limestone(nano-$CaCO_3$), nano-alumina (nano-Al_2O_3), nano graphene or graphene oxide, nano boron nitride also have been reported. As basic awareness, the effects of nanomaterials on the performance of cementitious composite are reflected on the workability, rheological, mechanical properties, durability, early hydration kinetics and electrical properties.

Depending on the improvement and modification effect, the nanomaterials used in concrete can be classified into two groups, ① to accelerate the early hydration and refining the pore structure. Thus the matrix shows improvement of mechanical properties and durability. ; ② to improve the electronic performance and other performance related to smartness such as self-sensing, self-cleaning. Some metalic nanoparticles and carbon-based nanomaterials can improve the electrical properties of a cementitious matrix. Additionally, nanomaterials can also be classified based on the morphology configuration as zero-dimensional particles, one-dimensional fibers, and two-dimensional sheet. The detail and function of these nanoparticles will be discussed in the following sections.

2.3 Definition of nano concrete

Nano concrete is a concrete with nanomaterials less than 500nm(Norhasri et al. 2014). Being incorporated nanomaterials, structural efficiency, durability, and strength of cementitious composite can be improved and will thereby assist in improving the quality and durability of structures. The application of nanotechnology in concrete can reduce the emission of carbon dioxide associated with concrete production(Hanus et al. 2013). Moreover, nano concrete has higher resistance to corrosion and ambient environment, since the micro structures are improved. Although the application of concrete with embedded nanomaterials in a real construction project is still rare, the related researches are necessary. As a matter of fact, due to the enhancement of durability, nanoconcrete shows longer surviving time and lower the maintaining coast comparing with plan concrete. it will contribute to the total costs in a big picture. Apart from that, nano-concrete has special functions such as self-sensing and self-cleaning. Those functions are related to smartness, could be achieved by adding nanomaterials in a cementitious composite. It has to be pointed out that the concept of smart concrete is emerging recently. The smart concrete is a concrete containing a material that allows self-monitoring of strain and/or other properties(Ding et al. 2019), which is directly depending on the nano conductive materials, such as carbon nanotubes(CNTs), carbon nanofibers (CNFs), graphene and graphene oxide. The development of being smartness to the concrete and cementitious material is a big step for future construction material and infrastructures. Additionally, nanomaterials were introduced to cementitious composite as a reinforced material only if the nanomaterials were well dispersed. Nanomaterial holds a large surface area, leading to huge Van der Waals forces which will hold the nanomaterials together, consequently, leading to agglomerates (Konsta-Gdoutos et al. 2010).

Nanomaterials usually hold large aspect ratio and hence, generate larger Van der Waals force. In order to obtain a reasonable dispersion of nanoparticles in a cementitious matrix, some special mixing methods are necessary. Ultrasonication has been widely used for achieving a uniform dispersion of nanoparticles in an aqueous solution. It was reported by Chuah et al.(2014), low ultrasonic energies cannot offer uniform dispersion, whereas high ultrasonic energies will jeopardize the morphology properties. Therefore, the input energy of ultrasonication should be well controlled to avoid excessively fragmented nanomaterials. Another method for good dispersion is to lower the surface energy of nanomaterials. To lower the surface energy, one common approach is by involving chemical agent such as superplasticizer and dispersing agent to the mixture. Al-Rub et al.(2012) confirmed that the commercial high-range polycarboxylate based water-reducing can help to achieve a uniform dispersion of CNTs. The two method reviewed above can be classified by the physical method, which is by involving extra force or agent to modify the string process or the properties of the matrix. Beside physical methods, a chemical method was also reviewed. The approach of chemical method is to oxidize the CNTs, CNFs, and graphene by using an acid agent, making a hydrophilic property by adding functional groups on the surface of the nanoparticles. The treated CNTs can uniformly dispersed without any aggregation detected(Liu et al. 2018). However, the oxidation process may lower the mechanical performance of the nanomaterials. Even that, the mechanical performance of the cement matrix with those treated nanomaterial is still higher than a plan mixture.

3. NANOMATERIALS IN CONCRETE

3.1 Zero-dimensional nanomaterials

Shape or morphology is illustrated the physical properties and the surface condition of a material. The morphology properties of nanomaterials can influence the reinforcing effect of the cementitious matrix. As mentioned briefly in the above section, depending on the physical topography, the nanomaterials used in concrete can be classified into zero-dimensional particles, one-dimensional fibers, and two-dimensional sheet.

The zero-dimensional nanomaterials, also called nanoparticles, content two branches which are metal oxide nanoparticles and other nanoparticles. The metal oxide nanoparticles, such as nano alumina(nano-Al_2O_3)(Ismael et al. 2016), nano iron(nano-Fe_2O_3) (Ortega-Villar et al. 2019), nano titanium dioxide(nano-TiO_2) (Han et al. 2017), and nano silica(nano-SiO_2)(Björnström et al. 2004; Lin et al. 2008; Jo et al. 2007) react with $Ca(OH)_2$, increasing the amount of calcium silicate hydrate(C-S-H), leading to a more compact microstructure. thus the mixtures showed improvement of both mechanical properties and durability.

3.1.1 Nano-TiO_2

Nano-TiO_2 has a wide range of applications, from paint to sunscreen to food coloring(Vallee et al. 2005). For a construction field, nano titanium dioxide was documented mostly for the production of self-cleaning concrete. Another benefit of nano-TiO_2 content concrete was acted through understanding cleaning effect of pollutants by a photocatalytic reaction, such as NOx and other emissions from vehicles and industry(Ghafari et al. 2015; Lee et al. 2013; Vohra et al. 2003). Additionally, nano-TiO_2 as documented by Jayapalan et.al.(2009), can also accelerates the early hydration of Portland cement. This effect result in a enhancement of compressive and flexural strength(Meng et al. 2012; Haruehansapong et al. 2014; Nazari et al. 2010). Beside acceleration effect, the mechanism of enhancement could also be considered as the nano particles decrease the pore volume of a cementitious composite, thus result in improvement of the engineering properties. Moreover, nano-TiO_2 also has a positive effect on the enhancing the abrasion resistance of concrete(Li et al. 2007). However, it was also found that the loss of catalytic efficiency may happen due to the age-depended carbonation.

3.1.2 Nano-Al_2O_3

Nano-Al_2O_3 is another nano metalic particles used in concrete in order to modify the performance of common concrete. It controls the setting time of cement mixtures(Li et al. 2006). Nano-Al_2O_3 also has a positive effect on UHPC on speeding up the initial setting time and reducing segregation and flocculation(Li et al. 2006). Additionally, adding Nano-Al_2O_3 also result in increasing of compressive strength and the elastic modulus of the mortar(Li et al. 2006).

3.1.3 Nano-Fe_2O_3

Nano-Fe_2O_3 can provide concrete with self-sensing capability. Concrete with embedded Nano-Fe_2O_3 shows changing of the volume electric resistance with the applied load. Hence, concrete structures with nano-Fe_2O_3 could sense their own compressive stress. It offers concrete with a valuable stress-resistance in the load-bearing structures. Another positive effect is that nano-Fe_2O_3 can also improve the mechanical properties(Ortega-Villar et al. 2019). As reported by(Ortega-Villar et al. 2019), 5% of nano-Fe_2O_3 increase the modulus of elasticity up to 143%. However, nano-Fe_2O_3 has a limited effect on the compressive strength (Ortega-Villar et al. 2019).

3.1.4 Nano-SiO_2

Nano-SiO_2 is another well known and outstanding nanomaterial (see Fig. 2). The effective of nano-SiO_2 covered both fresh aspect and hardened aspect. Many modifications effect of nano-SiO_2 have been reported as increasing the workability(Jo et al. 2007), improvement of strength(Jo et al. 2007; Li et al. 2004; Ji 2005), enhancement of durability(Li et al. 2004; Ji 2005), acceleration of hydration, and refinement of the pore structure. The morphology properties of nano-SiO_2 are round shape, provides a ball bearing maneuver in cement particles and act as ultra-filler in concrete(Lin et al. 2008). The appropriate workability helps concrete to form a dense structure and results in durability and resistance to water penetration enhancement. Moreover, nano-SiO_2 not only act as a filler for a cementitious composite but also as an activator to promotes pozzolanic reaction(Li et al. 2007). 0.25% nano SiO_2 was observed to increase compressive strength at 28 days by as much as 10% and flexural strength by 25%(Li et al. 2006). Additionally nano-SiO_2 also act as a cement replacement material, as reported by Li et al.(2007), 20% to 30% of cement content can be reduced by introducing nano silica to a matrix. Other advantages of nano-silica reported as delaying the conversion of metastable hydrates of calcium aluminate cement and to maintain the long-term strength of CAC by forming strätlingite(Richardson et al. 2004).

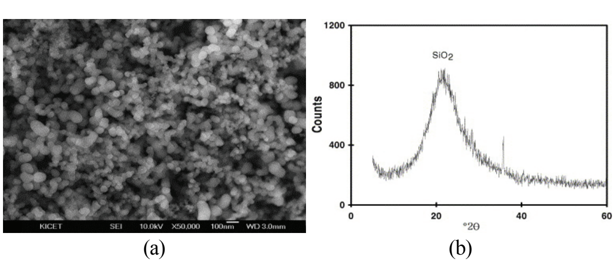

Fig. 2. Characteristics of nano-SiO_2 particles. Adaped from Jo et al.(2007)

3.1.5 Nano clay

Apart from metalic nanoparticles, nano clay, nano kaolin, and nano limestone(nano-$CaCO_3$) also have been reviewed.

Nano clay is the nanoparticle of layered mineral silicates (Norhasri et al. 2017). The most advantage of nano clay is to be considered as an inexpensive materials comparatively. Thus the nano clay concrete can be adaptable with adequate cost(Norhasri et al. 2017). The contribution of nano clay could be introduced as mechanical performance enhancement(Sobolev and Gutiérrez 2005; Kroyer et al. 2003; Lindgreen et al. 2008), resistance to chloride penetration enhancement, self-compacting properties of concrete, and also reducing shrinkage(Korb et al. 2009; Beaudoin et al. 2009; Skibsted et al. 2008). Like other nanoparticles, nano clay acts as a nucleation agent for C-S-H and modify the structure of C-S-H. It also was documented that clay materials can accelerate the cement hydration by increasing the degree of hydration for both alite and belite (Poulsen et al. 2009). However, clay particles are typically highly hydrophilic, the control of water requirements in clay-cement composite is important.

3.1.6 Nano kaolin

Nano kaolin can be classified into a by-product of kaolin (Norhasri et al. 2017). The chemical formula for kaolinite, which is the chemical name of nano kaolin, as used in mineralogy is $Al_2Si_2O_5(OH)_4$. After treatment or endothermic dehydration, kaolin will changes from crystal to amorphous stage(Cong and Kirkpatrick 1996) which is documented as metakaolin. Metakaolin is a pozzolanic material with high reactivity which performs similar reaction to silica fume. The refinement of microstructure due to the pozzolanic reaction can be promised, thus the enhancement of strength and durability were shown as consequences. Norhasri et.al.(2017) reported that 8%-10% compressive strength, 10%-15% flexural strength and tensile strength of cement mortar be enhanced compared to the plain OPC(Lindgreen et al. 2008).

3.1.7 Nano limestone

Nano limestone can accelerate the hydration of C_3S in 10 mass present. The formation of small fibrous C-S-H products around the nano-$CaCO_3$ was observed by scanning electron microscopy(SEM)(Cong and Kirkpatrick 1996).

As a conclusion, nanoparticles, including non-reactive and reactive nanoparticles, can act as nuclei for cement phases, further promoting cement hydration due to their high reactivity, as nanoreinforcement, and as filler, densifying the microstructure and the ITZ, thereby, resulting in porosity decrement. The most significant issue for all nanoparticles is effective dispersion(Li et al. 2004). Moreover, hydrate hybridization was reported as another issue for nanotechnology in concrete(Li et al. 2004). Modification of the structure of C-S-H at the nanoscale to creates hybrid, organic, cementitious nanocomposite has received attention due to the interest in more sustainable concrete structures(Richardson 1999; Korb et al. 2007; Nonat 2004). The interactions at interfaces between matrix and nanomaterials are key factors to optimize the benefits of those nanomaterials addition to concrete.

3.2 One-dimensional nanomaterials

One-dimensional fibers were reported such as carbon nanotubes and carbon nanofibers by several researchers. The one-dimensional nanomaterials used in concrete are potential candidates for application as nanoreinforcements in the cement matrix. Comparing to the conventional reinforced method, nano-reinforcement is to reinforces the matrix from the nanoscale to resistance to crack propagation, providing more efficiency affect. On the other hand, carbon nanotube and carbon nanofibers exhibit outstanding mechanical properties such as tensile strength in the range of GPa and moduli of elasticity in the range of TPa(Li et al. 2004). Apart from that, the electric and electromagnetic properties also are documented by Makar et al.(2005) and Li(2007), which make concrete has the properties of self-sensing and electromagnetic shielding.

3.2.1 Carbon nanotubes

Carbon nanotubes(CNTs) are a form of carbon which was first discovered in 1952 in Russia, and later re-discovered in Japan in 1991(Xie et al. 2005). CNTs include single-walled nanotubes(SWCNTs) and multi-walled nanotubes(MWCNTs)(see Fig. 3). The diameter of CNTs are on the scale of 1 to 100 nanometers with surface area typically in the range of 100,000 to 700,000m^2/kg(Kang et al. 2006). CNTs show outstanding mechanical properties with 1TPa Young's modulus and 63GPa tensile strength which are much higher than steel and carbon fibers. Besides that, CNTs also show high bonding force to the matrix, which also makes CNTs an appropriate nanoreinforcement material to cementitious composite. The modification affects to cementitious composite with CNTs can be summarized as a reduction in workability, hydration process acceleration, strength enhancement, microstructure refinement, durability improvement and smartness improvement.

Markar et al.(2005) reported that addition of 0.02% CNTs to cement pastes directly affected on the early hydration process. Marker et al. reported that the addition of 1w% and 2w% SWCNTs to cement can accelerate the hydration of C_3S and enhance the morphology of both the initial C_3A and the C_3S hydration products. The acceleration of hydration is due to the nucleating effect provided by the additional CNTs.

The workability reduction caused by embedded MWCNTs was reported by several researchers(Xu et al. 2015; Kim et al. 2012; Musso et al. 2009). The different dosage of functionalized MWCNTs with 9.5nm in diameter and 1.5㎛ in length to co-mixed with cement paste was evaluated. The result showed a reduction in the workability and the reduction increased with

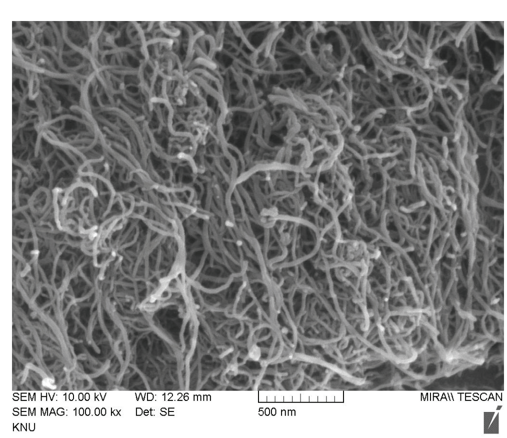

Fig. 3. Properties of MWCNT illustrated by SEM

increasing MWCNTs content.

The enhancement effects of mechanical properties by CNTs have been reported by many researchers. For the different cementitious composite, such as paste, mortar, and concrete, the mechanical properties improvement includes increasing in compressive strength, increasing in flexural strength, increasing in Young's modulus, increasing in fracture energy and toughness. The mechanical strength improvement due to the additional CNTs associated with pore structure improvement and also acted as nucleating agents for C-S-H. Using CNTs in UHPC was benefit on improvement of the flexibility of the composite (Musso et al. 2009). Flexibility provided by CNTs also increased the tension and compression abilities of UHPC thus the steel reinforcement can be reduced(Norhasri et al. 2017). However, the reduction in compressive strength could also happen due to the high concentration of CNTs caused agglomeration (Norhasri et al. 2017).

Apart from the mechanical properties improvement, CNTs can also improve the electrical conductivity. Concrete is listed at the border between insulators and poor semiconductors. The resistivity for saturated and dry concrete ranges between $10^6\Omega$ cm to $10^9\Omega$cm respectively(Kim et al. 2017). The electrical resistance reduction was reported by many researchers such as Konsta-Gdoutos et al.(2010). During the previous experiments, various dosages of CNTs were used ranged from 0.1% to 3%. Even the dosage and morphology properties are different from one to another experiment, the reduction on electrical resistance was observed in all the experiments. The reduction in electrical resistance could be explained as follow. After connected to the direct current voltage, the movement of ions in cement matrix leads to electrical polarization and consequently causes the increase of electrical resistance with time. While, when involved CNTs to cement matrix, the electrical polarization is decreased and electrical conductivity is increased. The concrete modified by embedded CNTs shows good electrical properties and could greatly contribute to the conductivity concrete. The conductive concrete with CNTs can be applied to a de-icing pavement and electromagnetic shielding structures(Nam et al. 2011).

The well electrically conductive properties can also make CNTs concrete to be a smart concrete with sensitivity. The electrical properties of CNTs concrete changes with stress/strain level, articulating a linear and reversible piezoresistive response even for a large strain of 3.4%(Li et al. 2007). The sensitive cementitious composites have the ability to sense tiny structural defects before they become significant, which could be used in monitoring the condition of structures. Civil infrastructures are generally a country's most expensive and crucial investment, with concrete as the most widely used construction material. With increasing service time, concrete structures trend to ages and deteriorates, consequently leads to substantial loss of structural integrity. As documented by Stallings et al.(1996), over 50% of all bridges in the USA were built before 1940. Structural health monitoring to them had largely been done manually by visual inspection. Examination of structures by visual inspection is expensive, time-consuming, insufficient, and labour-intensive. Moreover, the visual inspection can only confirm the damages which already showed on the surface of the structure. Comparing to the visual inspection method, self-monitoring can not only save the time and labor, but also can provide detailed insight into the surface of a structure, finding damages in a micro-scale and provide an array of real-time information.

Besides the mechanical performance improvement and electrical behavior modification, CNTs have also been demonstrated to help to establish antimicrobial surfaces of a concrete structure. The antimicrobial surface of structures have been reported much less than mechanical performance but has a crucial position in some special infrastructures including hospitals, childcare center, nursing homes(Ding et al. 2019). The antimicrobial surface can assist in minimizing the spread of disease and reducing the prevalence of illness and discomfort. The nanoparticles can interact with microbial cells directly, and have significant benefit over bounds of conventional chemical, photochemical or physical disinfection methods.

In summary, the concrete with embedded CNTs shows not only superb engineering properties but also electrical conductivity, sensitivity to stress, electromagnetic shielding effect, and antimicrobial ability. The application of CNTs concrete is mostly be blocked by the pricy of the nanomaterials. Recently the infrastructures built by concrete with CNTs is increasing. One can be expected the potential demanding of the smart concrete in the near future.

3.2.2 Carbon nanofibers

Carbon nanofibers(CNFs) has similar mechanical properties to CNTs. The application of CNTs to the concrete matrix can also help to stop the crack propagation by bridging effect. Although CNTs demonstrate to improve the interfacial interaction between the CNFs and the cement paste, no significant changes in compressive and splitting tensile strengths are observed. As a well electrical material, CNTs can also bring electrical conductivity and electromagnetic shielding effectiveness to concrete infrastructures. The biggest difference between CNTs and CNFs is that CNFs present numerous exposed edge planes along the surface that constitute potential sites for advantageous chemical or physical interaction(Sanchez and Sobolev 2010). Comparing to CNTs, CNFs also shows lower production cost, which is lower about one-hundredth times than MWCNTs(Norhasri et al. 2017).

It has to be emphasized that improvements of mechanical properties directly connect to the dispersion condition of the CNTs and CNFs. Since one-dimensional nanomaterials have larger aspect ratio than zero-dimensional nanomaterial. Therefore, the one-dimensional nanomaterials are harder to achieve the homogeneous dispersion, comparing to the zero-dimensional nanoparticles.

3.3 Two-dimensional nanomaterials

3.3.1 Graphene and graphene oxide

The two-dimensional nano-sheets were reported as graphene, graphene oxide and nano boron nitride. Graphene is a new-rising nanomaterial which consists of a one-atom-thick planar sheet comprising a sp2-bonded carbon structure with exceptionally high crystal and electronic quality(Vinayan 2016)(see Fig. 4). The graphene oxide, also carbon structure of one-atom-thick planar sheet, has various oxygen-containing groups. Those functional groups mainly are epoxides and hydroxyls on their basal planes, and carboxyls on the edges make graphene oxide high hydrophile. So graphene oxide can be treated as

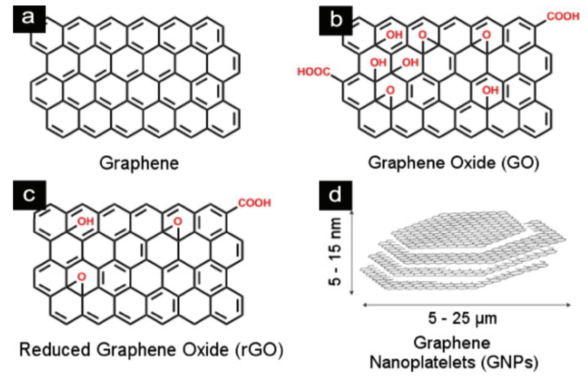

Fig. 4. Representation of (a) graphene, (b) graphene oxide (GO), (c) reduced graphene oxide (rGO) and (d) graphene nanoplatelets (GNPs). Adapted from Vinayan(2016)

the functionalized graphene through the oxidation process. It was demonstrated that because of those functional group graphene oxide can dispersion well in water. Consequently, graphene and graphene oxide can be candidated to enhance the mechanical properties of cement matrix. However, functionalization that functional groups are grafted may degrade the mechanical properties of graphene(Yang et al. 2011). Therefore, graphene oxide sheets has lower elastic modulus and tensile strength than graphene. It was documented by Chuah et al.(2014) that the mean modulus of GO sheets is 32GPa and the tensile strength is 130MPa.

As a nanomaterial, graphene and graphene oxide content the advantages of accelerating the hydration, enhance the mechanical performance, refine the microstructures in cement concrete matrix. As a electrical conductive material, adding graphene and/or graphene oxide to cement matrix could also help to lower the electrical resistivity, thus creating a conductive concrete. As a unique nanomaterial, Alkhateb et al.(2013) documented the reshaping of the morphology of C-S-H gels caused by the additional GOs. Samuel et al.(2014) also reported the positive effects of graphene oxide in the concrete. Except improving the mechanical performance, the graphene oxide due to the functional groups is desirable for homogeneous dispersion in cement. Agglomeration of nanomaterials is a common problem due to the strong van der Waal's attractive forces at the nanoscales. Those functional groups can help to disperse in the cement matrix, leading higher efficiency of reinforcement than other nanomaterials. Moreover, water molecules on GO constitute a water reservoir and water transport channels for further hydration of cement(Lin et al, 2016).

As an electrical conductive material, graphene and graphene oxide can also lower the electrical resistivity of concrete. It was also reported by Rhee et al.(2016). that the embedded graphene can bring a sense to a cement mortar(Rhee et al. 2016).

In summary, graphene and graphene oxide is a relatively new emerging nanomaterial especially to cementitious composite when comparing to other nanomaterials. The further evaluations and experiments including the mechanism of mechanical properties improvement, electrical modification ability, self-sensing performance are needed. Secondly, the functional group on the surface of graphene can be controlled by the oxidation process. In other words, graphene oxide is a functionalized material that can be designed by controlling the oxidation process according to the application.

3.3.2 Nano boron nitride

Nano boron nitride(nano-BN)(see Fig. 5) is an another two dimensional nano material which was reported in concrete research(Zhang et al. 2018). According to the published documents, nano-BN has layered structure with various properties, such as high mechanical strength, high thermal conductivity, excellent heat resistivity, lubricity, corrosion resistance, and volume stablility(Saggar et al. 2015; Li et al. 2015; Rafiee et al. 2013) As reported by M.A. Rafiee et al.(2013) the embedded nano-BN with dosage 1w% can increase the compressive strength and toughness of concrete mixtures to 64% and 200% respectively. In concrete research, nano-BN is a new material. According to the published documents, the fundamental propose to involve this material is to enhance the strength and durability, while the micro structures especially in the interface between the cement matrix and the nanoparticles are rarely been documented.

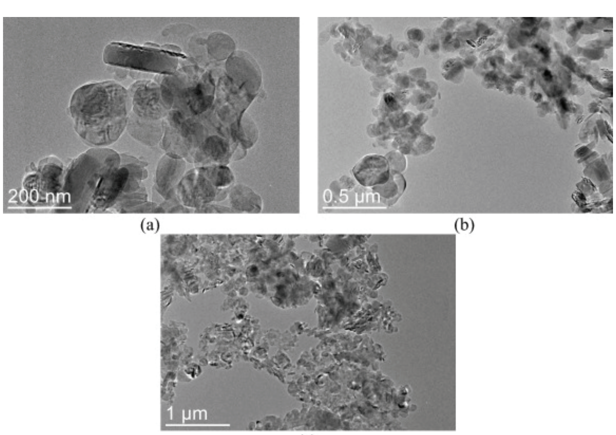

Fig. 5. TEM image of nano-BN: (a) 120nm; (b) 500nm; (c) 1μm. Adapted from Zhang(2018)

4. CONCLUSION

With the developing of technology and the maturing production method of nanomaterial, more nanomaterials will be introduced to cementitious composite. After reviewing the main nanomaterials for concrete and cementing materials, the conclusion can be summarized as below:

First of all, zero dimensional nanoparticles, the most widely used nanomaterial in cementitious composite, can be further divided into metallic particles and non-metallic particles. It is confirmed that the improvement of the mechanical properties of concrete by nanoparticles is due to the nucleation effect and filling effect. For some metallic particles, certain dosage can provide other properties beside mechanical properties such as electronic properties. Furthermore, some nanoparticles can enhance the mechanical properties of concrete for its pozzolanic effect, such as nano SiO_2, nano clay and nano kaolin. On the other hand, as the particles size decreased, the specific surface area increased. The large specific surface area of embedded nanoparticles can lead to easily formed agglomeration and uneven dispersion in the matrix. For this reason, there are drawbacks at the binding interface between the concrete matrix and nanoparticles. Therefore, the improving properties of mechanical properties are limited. Based on the above analysis, the research of nanoparticles for concrete application should focus on the mechanism of how the nano particles influence the cementitious matrix. Furthermore, the limitation of enhancing efficiency due to the ill dispersion should be well understood. Beside mentioned above, the cost of nano concrete is usually much higher than normal concrete, even though the dosage of nanoparticles is far less than other admixtures. But it is believed that the cost of nanoparticles will be decreased with developing nano technology and so application of nano material to cement concrete will be increasingly common.

Secondly, one dimensional fiber-like materials also been widely applied. The most mentioned one dimensional nanomaterial are carbon nano tube and carbon nano fiber. The enhancement of mechanical properties by fiber-like materials is due to the bounding effect. Furthermore, it has been confirmed that CNT can resistance to crack propagation to increase the mechanical properties and durability. On the other hand, as a nanomaterial, large specified surface area lead to strong self-attraction between the particles to be agglomerated. Therefore, the dosage to cement matrix should be limited. The mainly application of CNT and CNF is to enhance the mechanical properties and provide electrical properties.

Thirdly, two dimensional nanomaterials, such as graphene, graphene oxide, and born nitride, are new raising nanomaterials for concrete enhancement. Unlike zero dimensional nanoparticles and one dimensional nano fibers, graphene and graphene oxide not only enhance the mechanical properties but also reshape the morphology of C-S-H gels and altere the micro-structure of cement paste, due to the functional groups on the surface of graphene oxide. Furthermore, graphene and graphene oxide can also provide bridging effect to resist the crack propagation.

Finally, the distribution problem of nanomaterials in cementitious matrix is crucially. It is because all the improvement of engineering properties and other additional function such as electrically conductivity and self-sensing happened only when the nano-particles were evenly distributed. Unfortunately, the special mixing methods generally associate with cost increasement and some methods are not suitable for mass application. Thus a more general mixing method is necessary for massive application of nano-concrete.

By reviewing various nano materials through previous studies, to use nanomaterial in concrete is a crucial way to create new functional material by performance modification. Furthermore, the application of nano concrete can decrease the environmental impacts, which caused by ordinary cement production.

Conflict of interest

None.

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