NANOMATERIALS IN CONSTRUCTION: AN OVERVIEW

Huynh Van Tien[1*], **Giang Ngoc Ha**[1],
Vo Pham Phuong Trang[1], **Vu Bao Khanh**[2]
[1]*Ho Chi Minh City University of Food Industry*
[2]*Nguyen Tat Thanh University*
*Email: *tienhv@cntp.edu.vn*

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ABSTRACT

Nanomaterials (carbon nanotube, graphene, metal oxides) with scientifically interesting properties have attracted researchers around the globe to come into a pursuit of applying in construction industry. The potential applications might include mechanical improvement, energy saving, antimicrobial and self-cleaning surfaces. This mini-review first aims at presenting fundamental knowledge about nanomaterials such as history and definition, classification, and fabrication. The application of nanomaterials in construction industry is summarized in the later part. Many studies were performed to show benefits of nanomaterials once they are incorporated into conventional materials used in construction industry. However, safe design, production, reuse, and remanufacturing should be addressed to enhance the sustainability of both the nanotechnology and construction industry.

Keywords: Nanotechnology, construction, concrete, coating, nanomaterials.

1. INTRODUCTION

1.1. History

Nanotechnology might have been inspired by the lecture "There is plenty of room at the bottom" given by Richard Feynman in 1959. The speech was considered as sci-fiction at the time because he had mentioned the possibility of manipulating materials "atom by atom". By the invention of Scanning Tunneling Microscope and Atomic Force Microscope (AFM), the ability of imaging and fabrication at the nanoscale has come to the reality. The term "nanotechnology" was first used in 1974 by Norio Taniguchi. The term was applied in semiconductor processes which include processing of materials by changing one atom or one molecules. In 1981, Eric Drexler used the term "nanotechnology" again to describe a new ‘bottom-up” approach, instead of the “top-down” approach discussed earlier by Feynman and Taniguchi [1, 2].

The term *nano* which means dwarf in Greek is used as a prefix for any unit to indicate the meaning of a billionth of that unit. Figure 1 could give a good imagination and comparison of the scale of a nanometer. Generally, the sizes of nanomaterials are comparable to those of viruses, DNA, and proteins, while microparticles are comparable to cells, organelles, and larger physiological structures [3]. Despite the wide use of the word *nanotechnology*, the term has been misleading in many instances. This is because some of the technology deals with systems on the micrometer range and not on the nanometer range (1–100 nm) [4].

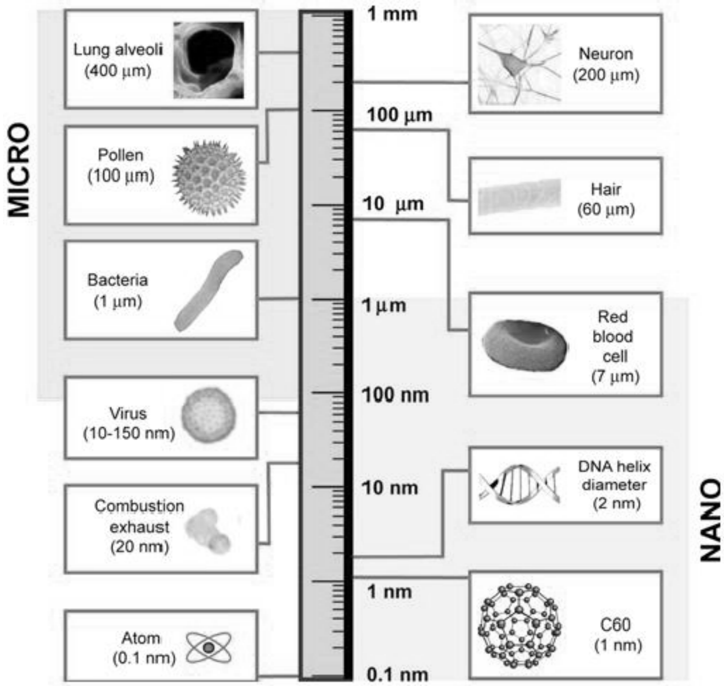

Figure 1. Logarithmical length scale showing size of nanomaterials compared to biological components and definition of 'nano' and 'micro' sizes [3]

1.2. Classification

Nanomaterials can be classified as zero-dimensional (0-D), one-dimensional (1-D), two-dimensional (2-D), and three-dimensional (3-D), which are illustrated in Figure 2. 0-D nanomaterials are materials wherein all the dimensions are measured within the nanoscale. The most representatives of 0-D nanomaterials are nanoparticles.

On the other hand, 1-D nanomaterials have one dimension that is outside the nanoscale. These nanomaterials include nanotubes, nanorods and nanowires. 2-D nanomaterials exhibit platelike shapes. Common examples of 2-D nanomaterials are nanofilm, nanolayers and nanocoatings. 3-D nanomaterials (bulk nanomaterials) are characterized by having three arbitrary dimensions above 100 nm. 3-D nanomaterials can contain dispersions of nanoparticles, bundles of nanowires, and nanotubes as well as multi-nanolayers [5].

1.3. Fabrication

Briefly, there are two typical approaches for fabrication of nanomaterials: the “top-down” and “bottom-up”. Figure 3 shows an example for the fabrication of graphene quantum dots (GQDs) using two above mentioned approaches [6]. In the “top-down” approach, nanomaterials are fabricated by disintegrating a bulk material into smaller fragment by external force until the desired nanosize is obtained. The nanomaterials using the “bottom-up’ approach are obtained by starting from the individual atoms or/and molecular. Those species are synthesized together by chemical reactions and/or self-assembly approach to form the final nanostructure. Because the “bottom-up” approach is driven mainly by the reduction of Gibbs free energy, nanostructures and nanomaterials produced are in a state closer to a thermodynamic equilibrium state. Therefore, the “bottom-up” approach promises a better chance to obtain nanostructures with less defect, more homogeneous chemical composition and better short and long range ordering. In contrast, the “top-down” approach introduces internal stress, in addition to surface defect and contamination [7].

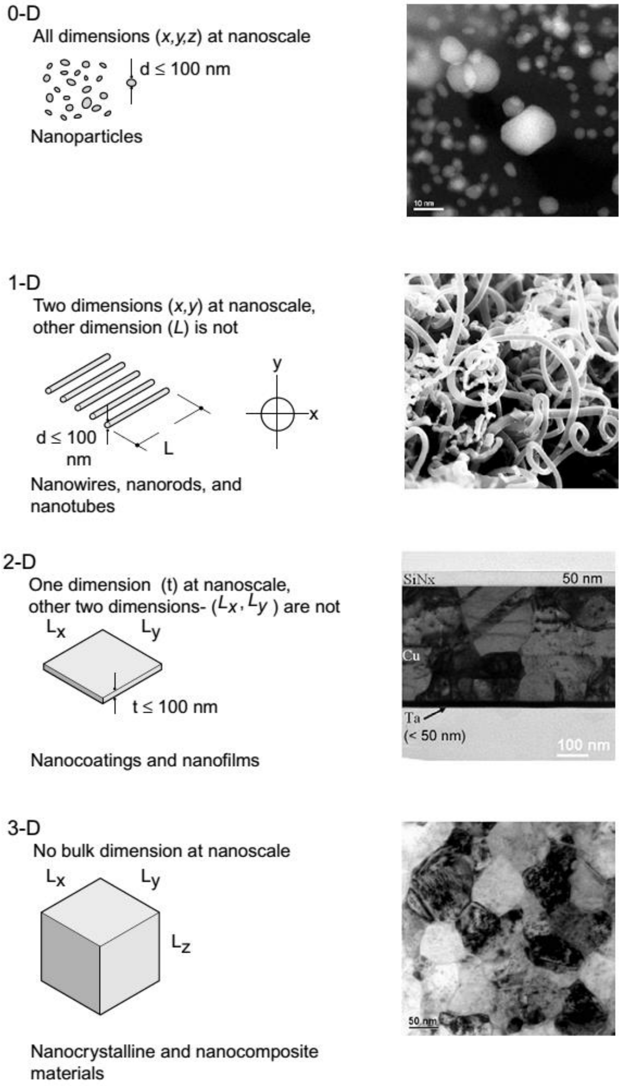

Figure 2. Classification of nanomaterials according to 0-D, 1-D, 2-D, and 3-D [5]

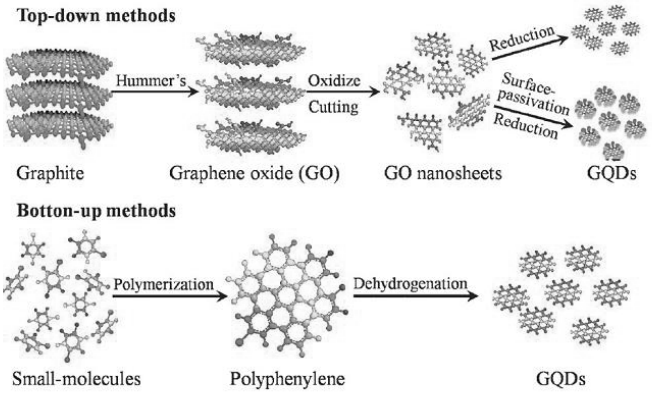

Figure 3. Schematic diagram of the "top-down" and "bottom-up" approaches for synthesizing graphene quantum dots (GQDs) [6]

2. NANOMATERIALS IN THE CONSTRUCTION INDUSTRY

Materials used in construction industry can be reinforced by a variety of nanomaterials in order to have superior structural properties, functional paints, and coatings, and high-resolution sensing/actuating devices. The selected current and potential nanomaterials applied in construction are listed in Table 1, and Table 2 is an overview of typical nanomaterials offered at the market for actual use in the European construction industry in 2009 [8].

Table 1. Nanomaterials actually applied in construction materials [8]

Material	Functionality introduced	Nanoparticle	Type of introduction
Concrete	Self-cleaning surface (photo-catalytic) Increased durability	TiO_2	Surface layer
	Ultra-strong concrete Corrosion reduction	SiO_2 (silica fume)	Mixed in matrix, filler to improve material strength
Insulation material	Improved insulating properties against heath, cold, fire or a combination thereof	Nanoporous material	Aerogel, often SiO_2 or carbon based
Coatings	Photo-catalytic, self-cleaning, hydrophobic properties	TiO_2, ZnO, SiO_2	Additive in the coating
	Anti-bacterial	TiO_2, ZnO and Ag	Additive in the coating
	Scratch resistance	SiO_2, Aluminium oxide	Additive in the coating
	Easy-to-clean surfaces	Carbon fluorine polymers	Additive in the coating
	Fire retardant	TiO_2, SiO_2 and nano-clays	Additive in the coating
	UV-protection of wood	TiO_2, ZnO, CeO_2	Additive in the coating
	Decolourisation of wood by tannin	Nano-clays	Additive in the coating
Glass	IR-reflection	Tungsten oxide	Surface coating
	Non-reflective glass	Nanoporous surface SiO_2	Surface structure; surface coating
	Fire or heat protection	Metal oxides SiO_2	Surface coating; transparent silica gel inter-layer between two glass panels
	Easy-to-clean properties	Ag, SiO_2, carbon fluorine polymers	Surface coating
	Photo-catalytic self-cleaning properties	TiO_2	Surface coating
Infrastructure	UV active air pollution reduction on asphalt, road pavement blocks, sound barriers and tunnels	TiO_2	Surface coating

Table 2. Examples of nanomaterials used in construction industry [9]

Nanomaterials	Architecture/construction materials	Expected benefits
Carbon nanotubes	Concrete	Mechanical durability; crack prevention
	Ceramics	Enhanced mechanical and thermal properties
	NEMS/MEMS	Real-time structural health monitoring
	Solar cell	Effective electron mediation
SiO_2 nanoparticles	Concrete	Reinforcement in mechanical strength
	Ceramics	Coolant; light transmission; fire resistant
	Windows	Flame-proofing; anti-reflection
TiO_2 nanoparticles	Cement	Rapid hydration; increased degree of hydration; self-cleaning
	Windows	Superhydrophilicity; anti-fogging; fouling-resistance
	Solar cell	Non-utility electricity generation
Fe_2O_3 nanoparticles	Concrete	Increased compressive strength; abrasion-resistant
Cu nanoparticles	Steel	Weldability; corrosion resistance; formability
Ag nanoparticles	Coating/painting	Biocidal activity

2.1. Metal oxide nanoparticles

Nanoparticles based on metal oxide are among the most popular nanomaterials. Therefore, as can be observed in table 1 and 2, the nanotechnolgy in construction industry was dominated by the application of inorganic metal-based materials.

De-icers such as $CaCl_2$ and $MgCl_2$ can penetrate through nano- or micropores which concrete develops because of cement hydration, react with concrete to weaken the structure. Silica (SiO_2) and iron oxide (Fe_2O_3) can be utilized as fillers to pack the pores and reinforce concrete; therefore, they can prevent concrete from weakening issue as abovementioned [9- 11]. Incorporating of these nanoparticles in fly ash as a cement replacement also enhanced the mechanical properties of concrete [11]. Silica nanoparticles coating on windows control exterior light as antireflective material, and this contributes to energy conservation [12, 13].

TiO_2 absorbed UV fraction in sunlight to create reactive sites which have capability to remove bacterial and dirt on windows. Therefore, coating TiO_2 on parts outside of a building can possibly play a role as an antifouling agent to fabricate the self-cleaning surfaces. Hydrophobic dust is difficult to accumulate on a highly hydrophilic window surfaces created by photoinduced species.

Green and sustainable energy in construction are other possible applications as the outside surfaces (roofs and windows) are coated with dye-sensitized TiO2 solar cells to produce electricity [9].

Figure 4 shows a building exterior wall. It is very obvious to distinguish which side of the wall has been treated with paint containing TiO_2 (Bio Pro Coatings). The left side of the wall (treated in August, 1999) is “self-cleaning” and does not collect grime which has discolored the untreated right side of the wall.

Figure 4. Treating the surface with the coating does not change the appearance of the surface; however, the self-cleaning phenomenon will result in the surface staying clean for 3 years or more [Bio Pro Coatings]

2.2. Carbon-based nanomaterials

Carbon is among the most abundant elements on earth. Organic materials are constructed from chains of carbon atoms connected by covalent bonds. With the same number of carbon atom, hundreds of chemical compound might be formed. In addition to the abundance of the source, the carbon-based materials are considered to be less toxic than others which are based on inorganic metal. Therefore, nanomaterials fabricated from carbon-based sources have been attracted much attention from many research groups recently.

2.2.1. Carbon nanotube (CNT)

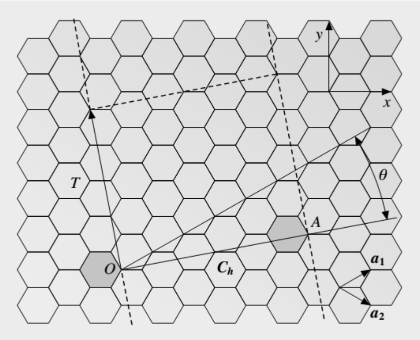

Figure 5. Sketch of the way to make a single-wall carbon nanotube, starting from a graphene sheet [15]

There are two types of CNT: single wall CNT (SWCNT) and multi wall CNT (MWSNT). It is relatively simple to imagine a SWCNT. It is enough to consider a perfect graphene sheet (2-D) and to roll it into a cylinder, as illustrated in Figure 5, making sure that the hexagonal rings placed in contact join coherently. The tips of the tube are sealed by two caps, and each cap is a hemi-fullerene of the appropriate diameter. SWCNTs have three different structures that are shown in Figure 6. The high-resolution transmission electron (HRTEM) images of SWCNT are also provided in Figure 7.

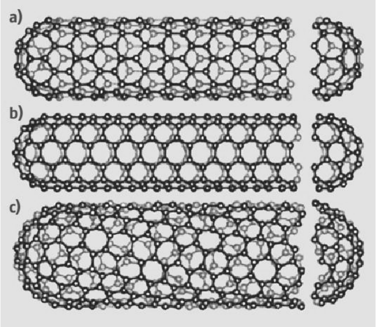

Figure 6. Sketches of three different SWNT structures that are examples of (a) a zigzag-type nanotube, (b) an armchair-type nanotube, (c) a helical nanotube [16]

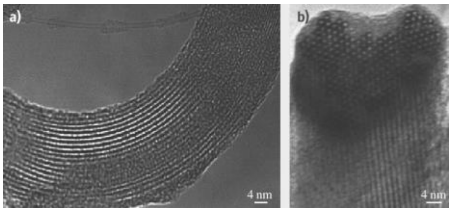

Figure 7. HRTEM images of a SWCNT rope. (a) Longitudinal view. An isolated single SWCNT also appears at the top of the image. (b) Cross-sectional view [17]

The cross-sectional view image allows us to recognize the individual SWCNT in the SWCNT rope. The easiest way to construct MWCNT is the use of a model of Russian-doll. SWCNT with regularly increasing diameters are coaxially arranged into a multiwall nanotube. The HRTEM image of MWCNT is shown in Figure 8. CNT has excellent mechanical properties and therefore make it the suitable candidate for the improvement of the volume stability of cement-based materials. Young's modulus (MWCNT) on the order of 270-950 GPa and tensile strength of 11-63 GPa were obtained [18]. CNTs, a representation for polymeric chemical admixtures, can greatly enhance the mechanical durability by gluing concrete mixtures (cementitious agents, concrete aggregates) and prevent crack propagation. The use of CNTs as crack bridging agents into nondecorative ceramics can improve their mechanical strength and thermal properties, as well as reduce their fragility. Moreover, CNTs are also part of devices that are implanted in construction structures for real-time monitoring for damage and health of materials (cracking, corrosion, wear, and stress) and for environmental conditions (smoke, temperature, and moisture) [9].

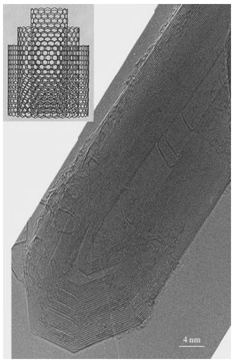

Figure 8. HRTEM image of a MWCNT. The insert shows a sketch of the Russian doll model [19]

The addition of small amount of CNT in cementitious materials results in a significant improvement of their mechanical properties. For example, with the addition of 0.5 wt% MWCNT into cement matrix, the flexural strength and compressive strength increased in 25 and 19%, respectively [20]. The similar result was also observed once the CNT or tungsten di-sulfide nanotube incorporated into cement [21]. It is worth mentioning that one of the major challenges towards achieving this goal is an effective dispersion of the as-produced aggregated nanotubes in a matrix. The use of sonication or/and dispersant (surfactants) can facilitate the integration of individual nanotubes in cement paste matrix.

Conducting nano-indentation on CNT-added cement pastes revealed that the use of highly dispersed small amount (0.05 wt%) of MWCNT can increase the amount of high stiffness C-S-H and decrease the porosity (Figure 9). The alteration of the nano-structure results in an improvement of the volume stability of cement-based materials at very early age. As can be seen in Figure 9, the autogenous shrinkage of cement paste was reduced by about 25 %, and this could be ascribed to the reduction of the capillary stresses induced by the reduction of the porosity (Figure 10) [22, 23].

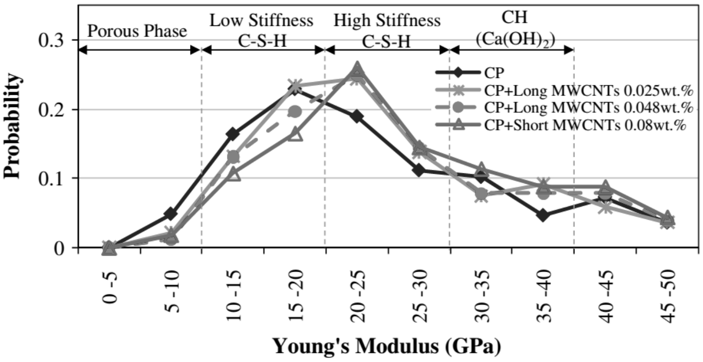

Figure 9. Probability pots of the Young's modulus of 28 days cement paste (CP) and cement paste reinforced with 0.025 wt% long, 0.048 wt% long and 0.08 wt% short MWCNTs [22]

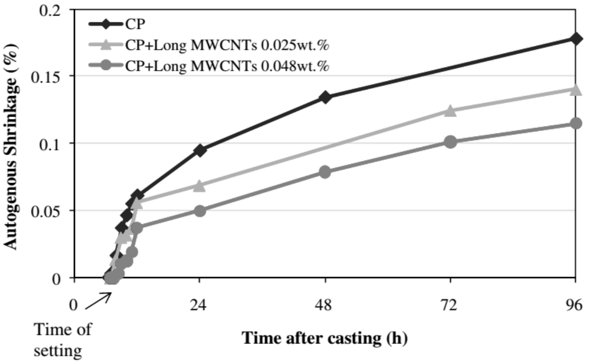

Figure 10. Autogenous shrinkage of cement paste and cement paste reinforced with 0.025 wt% and 0.048 wt% long MWCNTs [22]

It was also established that the introduction of oxygen-containing functional groups to the surface of CNTs leads to an increase in early strength of cementitious composite compared with the composite containing pure CNTs [24]. The early work has also demonstrated that the best observed performance included a 50% increase in compressive strength in a MWCNT sample [25], over 600% improvement in Vicker's hardness at early ages of hydration in a SWCNT sample [26] and a 227% increase in Young's modulus for a MWCNT sample [11].

2.2.2. Graphene

Graphene is a flat monolayer of carbon atoms, tightly packed into a two-dimensional honeycomb lattice, which is shown in Figure 11. This material has received much attention due to its unique properties such as high surface area, high mechanical strength, easy functionalization, excellent conductivity, and possible mass production. The atomic resolution scanning tunneling microscopy (STM) image of Graphene layer is also given in Figure 12.

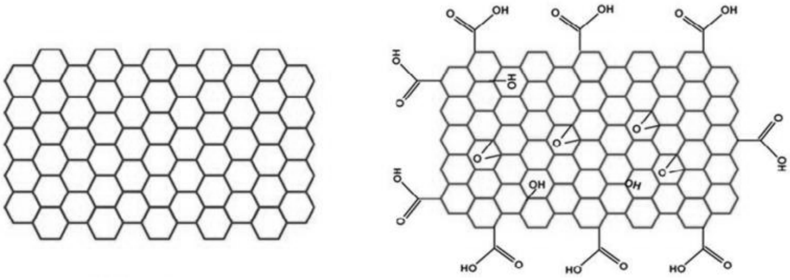

Figure 11. Structure of graphene (left) and graphene oxide (right) [27].

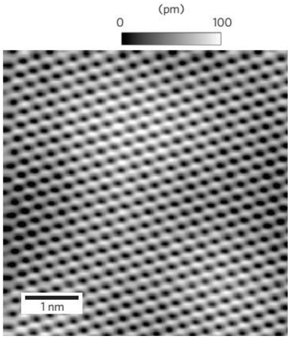

Figure 12. Topographic STM images
of the multilayer epitaxial graphene sample grown on SiC [28].

By the oxidation of graphite using strong oxidizing agents, oxygenated functionalities are introduced in the graphite structure which not only expand the layer separation, but also makes the material hydrophilic (meaning that they can be dispersed in water). This property enables the graphite oxide to be exfoliated in water using sonication, ultimately producing single or few layer graphene, known as graphene oxide (GO). The main difference between graphite oxide and graphene oxide is the number of layers. Graphite oxide is a multilayer system while in a graphene oxide, dispersion a few layers flakes and monolayer flakes can be found. Compared with CNT, graphene oxide is readily dispersible in water, using moderate sonication. Because of its high specific surface area, it exhibits very low percolation threshold and therefore significantly limit the addition level required.

Graphene and graphene oxide have superior elastic modulus and tensile strength; however, the use of graphene oxide (GO) in cement-based materials has not been widely explored [29]. Compelling mechanical properties, such as elastic modulus of ~1 TPa and tensile strength of ~100 GPa [30], make graphene materials attractive as nanoreinforcements for cement composites. Once GO incorporated in cement pastes and mortar with low amount (below 0.05 wt%), it enhances the flexural strength of the matrix [29]. The incorporation of 0.05 wt% of graphene nanoplatelets in mortar and cement also resulted in an increase in compressive strength of mortar, and flexural strength and elastic stiffness of cement paste, of 28%, 39%, and 109%, respectively [31]. The typical enhancement was presented in Figure 13.

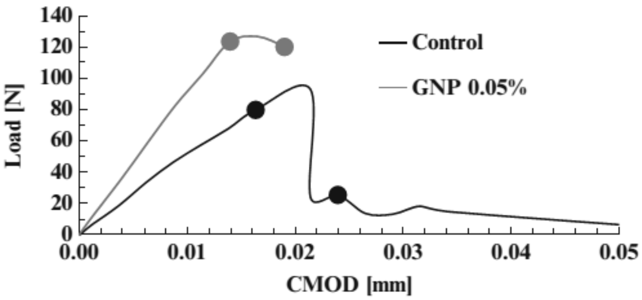

Figure 13. Representative load-CMOD curves from cement paste notch beam tests [31].

Effect of GO nanosheets on properties of cement composites was investigated to estimate the nanomaterial capibility in construction industry. The work has indicated an evidence of significant increase in tensile, flexural, compressive strength (78.6, 60.7 and 38.9%, respectively) of cement composites by adding 0.03 wt% of GO [32].

3. CONCLUDING REMARKS AND PERSPECTIVES FOR THE FUTURE

The properties of conventional materials in construction can be tuned by nano-engineering via incorporating of nanomaterials. This incorporation enhances not only mechanical performance but also durability (low electricity, self-cleaning and self-healing) of the resulting composite materials. High percentage of all energy used is consumed by commercial buildings and residential houses. Therefore, application of nanomaterials in construction industry should be considered in a broader perspective for both improving material properties and conserving energy.

Because nanomaterials as new materials have been recently designed and brought into use, understanding and knowledge of their toxicity are important. Therefore, advanced analytical techniques should be among high priorities for detection and characterization of nanomaterials releasing from or incorporating into construction materials. Safe design, production, reusing, and remanufacturing will enhance the sustainability of both the nanotechnology and construction industry [9].

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TÓM TẮT

TỔNG QUAN VỀ VẬT LIỆU NANO TRONG XÂY DỰNG

Huỳnh Văn Tiến[1*], Giang Ngọc Hà[1],
Võ Phạm Phương Trang[1], Vũ Bảo Khánh[2]
[1]*Trường Đại học Công nghiệp Thực phẩm TP.HCM*
[2] *Trường Đại học Nguyễn Tất Thành*
*Email: *tienhv@cntp.edu.vn*

Vật liệu nano (carbon nanotube, graphene, oxit kim loại) với những tính chất khoa học thú vị đã thu hút các nhà nghiên cứu trên toàn cầu theo đuổi việc ứng dụng chúng trong công nghiệp xây dựng. Những ứng dụng tiềm tàng bao gồm cải thiện tính chất cơ lý, tiết kiệm năng lượng, bề mặt kháng vi khuẩn và tự làm sạch. Nội dung bài báo này trước tiên trình bày tổng quan kiến thức cơ bản về vật liệu nano như lịch sử hình thành, định nghĩa, phân loại và chế tạo vật liệu nano. Các ứng dụng nổi bật của vật liệu nano trong công nghiệp xây dựng sẽ được tổng hợp trong phần sau đó. Nhiều nghiên cứu được tiến hành để thể hiện được ích lợi vượt trội của vật liệu nano một khi chúng được thêm vào trong những vật liệu truyền thống trong công nghiệp xây dựng. Tuy nhiên, thiết kế an toàn, sản xuất, khả năng tái sử dụng và tái sản xuất cũng được hướng đến để cải thiện tính chất bền vững của cả công nghệ nano lẫn công nghiệp xây dựng.

Từ khóa: Công nghệ nano, xây dựng, bê tông, lớp phủ, vật liệu nano.