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NANO CONSTRUCTION MATERIALS: REVIEW

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Abstract. This review paper addresses the current developments regarding use of nano-materials in construction industry. In this report, primarily, the significance of nanotechnology for construction industry is emphasized. Secondarily, the introduction and application of important nano building products are presented. Some prominent world construction projects using nanotechnology are also documented. Along with benefits, some serious health risks are also associated with the use of nano technology. These risks should be known and remedied so that the nano building products could be fully exploited for the benefit of the mankind.

1. INTRODUCTION

The voyage of nanotechnology starts from the lecture of famous Nobel Laureate Richard Feyman in 1959 at the California Institute of Technology saying, “There is plenty of room at the bottom” [1]. During the past few decades, nanotechnology brought revolution in the world. Nanotechnology is the branch of material science dealing with nano particles. Nano particle is defined as the one that has at least one of its dimensions in nanometers or 10^{-9} m. It is the study of materials at nano scale. The properties of the particles have been observed to drastically change when they are milled to nano size [2]. A copper wire bends due to the movement of its atoms at about 50 nm scale. Copper particles smaller than 50 nm are super hard materials that do not display the same malleability and ductility as those above 50 nm [3]. Gold nano particles have much lower melting point (300 °C) than the bulk gold (1064 °C) [4]. Thus this fact has been well-established that the properties of the particles change as they approach to nano size. Knowing that, the scientists and engineers worked on its application in various fields like chemistry, physics, electronics, medicines, and many others.

Building materials are an important subject in civil engineering. The important building materials include concrete, steel, stones, bricks, plastics, timber, glass and many metals [5]. Stone and timber are considered to be the oldest materials, used by the early humans to build shelters against the natural calamities and the beasts. Like every other species, the construction materials also passed through an evolutionary process and today we see concrete and steel as the modern giants in construction industry. As the technology grew, newer and smart materials were developed by the engineers and researchers all over the world and this process continues even today. Use of nano technology and nano materials in civil engineering is a recent initiative, which emerged at the end of the last century. The use of this technology solved many problems of the construction industry: thanks to the higher strength and lower density of the nano-materials.

Concrete is the most widely used material in the world. It is estimated that its annual production is about 20 billion tons higher than any other material on this planet earth [6,7]. It is considered to be the backbone of civil engineering. An ordinary con-

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crete is a mixture of cement, sand, gravel and water. Additives and admixtures are also sometimes added to achieve some special properties, which are not possible to attain with an ordinary concrete [8]. Apart from cement, all the other ingredients of concrete are easily available natural materials. Even cement is also an easily available industrial material. When the concrete fresh matrix is allowed to cure appropriately, it hardens and gains considerable strength equal to or even more than the stone. That is why it is also known as man-made rock and this is the secret of its tremendous popularity [5].

Many supplementary cementitious materials are also sometimes added in concrete, also known as additives. Among these silica fumes are very important materials. This industrial byproduct is obtained from an electric arc furnace process. In this process, the reduction of high purity quartz at high temperatures produces silica vapors. These silica vapors are condensed at low temperature to minute particles known as silica fumes. The addition of silica fumes in concrete makes it denser, enhances its bond quality and increases its resistance against chemicals [9].

Steel is an iron-carbon alloy. But not every iron-carbon alloy is steel. Steel is defined as an iron-carbon alloy having carbon content up to 1.7 % [10]. In addition to carbon, some other elements like manganese, copper, silicon, nickel and molybdenum are also present in minor quantities [11]. Apart from iron, the other alloying elements are intended to increase strength, hardness and corrosion resistance of steel.

Paints or coatings are frequently used in construction to protect the surface from harmful weathering effects. Additionally, they also provide beauty to the surface. Paints are composed of base, vehicle or binder, solvent or thinner, drier and coloring pigments. Various materials are used to make paint [12]. As an example, lead or aluminium are used as base; resins are used as vehicle or binder; oil or water are used to adjust the viscosity; lead or cobalt are used as drier. In the presence of so many useful materials, the question arises, as what the nanotechnology is going to offer in addition? The answer lies in the same well-known statement of Richard Feyman that there is plenty of room in the bottom.

2. SIGNIFICANCE OF NANOTECHNOLOGY IN CONSTRUCTION

Before the invention of graphene, steel was considered to be the strongest construction material. ASTM A36 steel has density of 7.85 g/cm^{-3}, yield strength of 250 MPa and an ultimate strength of 400-550 MPa [13]. Fortunately, graphene has now superseded steel. Graphene is the thinnest material ever invented, consisting of only a mono layer of carbon atoms. In grapheme, the atoms are arranged in a hexagonal pattern. It weighs only 0.77 g/m^2 [14]. At the moment, the graphene is being used in the form of carbon nanotubes, abbreviated as CNTs or carbon nanofibers abbreviated as CNFs. CNTs are made by arranging the graphene atomic scale wire mesh in the cylindrical shape. Additionally, CNFs are also being fabricated by arranging the graphitic carbon atoms in the form of plates placed one over the other. But the characteristics of graphene are just not limited to its light weight. It is almost 100 times stronger than steel of the same thickness; even better than copper in heat and electricity conduction, and has exceptional optical and mechanical properties [14].

In construction materials, civil engineers are ever interested in density and strength. Unfortunately, higher strength is also associated with higher density, which increases the dead weight of the structure. Graphene has tremendous potential to be the future backbone of civil engineering due to its lower density and excellent strength.

The importance of nanotechnology is not just limited to graphene, CNTs and CNFs. Another series of research is also going on to use the construction materials themselves in nanometers. People are introducing nanocement in market. One step forward in this regard is Bodome group of Austria, who have introduced their nanocement on commercial scale [15,16]. Most commonly, the present commercial cement particle varies in size from 1 to 100 micrometers [17]. It is believed that finer particles (nano) have larger surface area per unit volume, which is very important in cement and concrete technology. Large surface area of binder results in higher early and final strength due to faster and more effective hydration reactions [8,18].

Several new cement composites are also being developed by incorporating in them titania (TiO_2), silica (SiO_2), clay, and alumina (Al_2O_3) particles of nano sizes [2]. Similarly, nano paints are being developed that significantly boost the resistance of the paints and coatings against the aggressive environments. Paints containing nano titania and CNTs have found to be very effective against the industrial pollutants and car exhausts [19]. Knowing the importance of nano technology for civil engineering, the important nano materials for construction industry developed during the past few years are discussed in the following paragraphs.

3. OUTSTANDING NANO MATERIALS FOR CONSTRUCTION INDUSTRY

3.1. Nano silica

As discussed above, micro silica fumes are added in concrete to fill in the voids, decrease the concrete alkalinity, and increases its resistance against the chemical attack. Cement and water undergo chemical reactions known as hydration reactions: A cement particle is composed of four chemical compounds namely, Tricalcium sulfide (C_3S), Dicalcium sulfide (C_2S), Tricalcium Aluminate (C_3A), and Tetracalcium Alumino-ferrite (C_4AF) [8]. The hydrations of the first two compounds with water lead to the formation of calcium-silicate-hydrate (CSH) gel and calcium hydroxide (CH) also known as Portlandite as shown in the following reactions:

$$C_3S + H_2O \rightarrow CSH + Ca(OH)_2 + Heat\uparrow, \quad (1)$$

$$C_2S + H_2O \rightarrow CSH + Ca(OH)_2 + Heat\uparrow. \quad (2)$$

The CSH gel is a strong bond and forms strong connection between the concrete particles. On the other hand, Portlandite is a soluble product and leaches out in water. It is a weak link between the concrete particles. The addition of silica particles in concrete mix converts the weak CH into stronger CSH. Silica fumes refine the properties of concrete by two means: its fine size fills the voids between cement particles and the voids between cement particles and aggregates; and secondly they react pozzolanically with CH to produce CSH gel, increasing the binding quality and decreasing the capillary porosity of concrete [20]. Thus it is well established that silica fumes increase the strength of concrete and produce a denser and more homogeneous matrix. This effect of silica fume has been proved by electron microscopy measurements [21].

Silica fumes as discussed above are micro particles. It was believed that the nano silica particles will be more effective if used in lieu of micro silica fumes. Different research groups during the past decade added nano silica particles in concrete and published their experimental data. Kim et al. [22] have reported up to 70% increase of concrete compressive strength by incorporating nano-silica particles. Yang [23] mixed 0.75% nano silica particles by mass of cement and reported 7.5% increase in bending tensile strength of concrete. Quercia et al. [24] mixed 3.8% nano silica particles by mass of cement and reported 21.5% increase in splitting cylinder tensile strength of concrete at 28 days and 13% increase in compressive strength at 91 days; one interesting information, which they reported was that while the reference concrete showed no improvement of compressive strength beyond 28 days, the nano silica concrete increased its strength by 15% from 28 to 91 days. Said et al. [25] have reported significant improvement in concrete having nano-silica vis-à-vis strength development, refinement of pore structure and densification of interfacial transition zone. They attributed all this to the large surface area of nano-silica particles. Based on the above discussion, the evolution of concrete from mm size to nano meter is shown diagrammatically in Fig. 1.

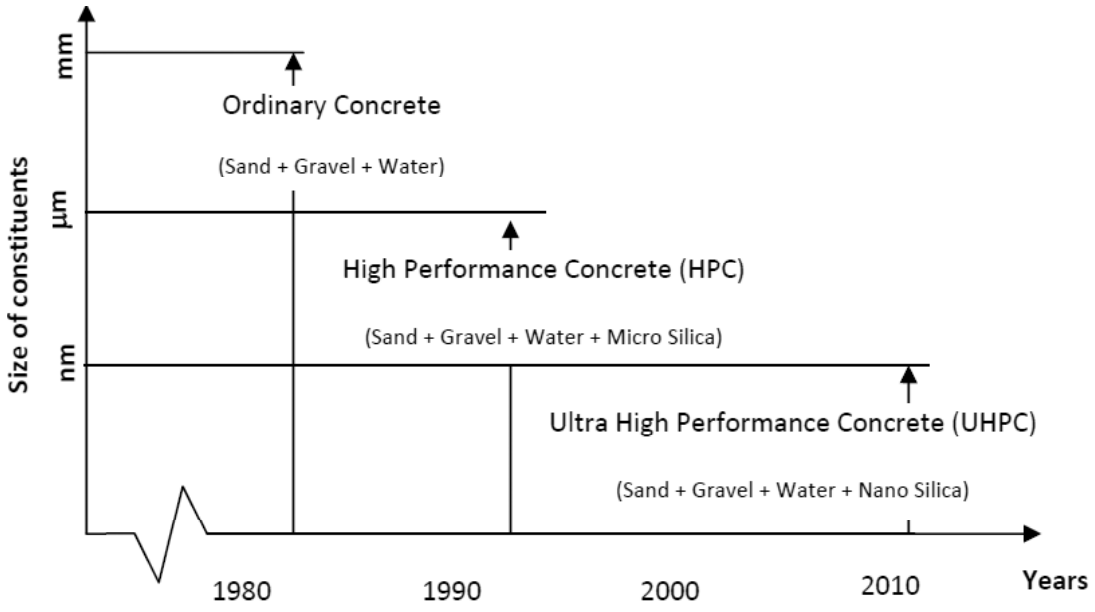

Fig. 1. Evolution of concrete from millimeter to nanometer era.

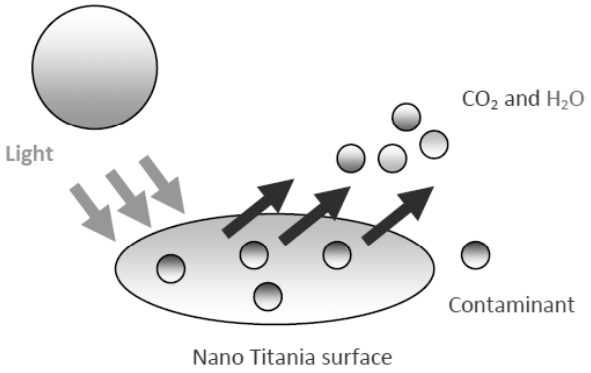

Fig. 2. Mechanism of nano titania photocatalysis.

3.2. Nano titania

Titania also known as titanium oxide, is a naturally occurring oxide of titanium, having chemical formula TiO_2. Since 1921 it is being used as pigment in paints and coatings for providing whiteness, brightness and opacity [26,27]. Titanium dioxide has excellent ultraviolet (UV) resistant qualities and is used as sunscreen in cosmetics [28,29]. The USA Food and Drug Association (FDA) has declared micro and macro titania safe for use in food, drugs and cosmetics [30]. Some recent studies however, suggest titanium dioxide nanoparticles as toxic [30,31].

Since the past decade, nano titania particles are being produced in abundance. Nano titania particles have found to be stable, anticorrosive and possess photocatalytic properties [32]. Many researchers have credited this photocatalytic activity of titania particles to their high surface area [33]. Nano-layers of titania are being put on the glass of windows so that they are self-cleaning. It has also been proved that nano-titania containing paints are easy to clean and have much larger design life [32].

Apart from paints, nano titania particles have also been added in concrete [33]. The manufactured concrete is named as self cleaning concrete or photocatalytic concrete. Another famous name is smog-eating concrete. This concrete is also known as Green Concrete due to its self cleaning properties. The applications of nano photocatalytic concrete also include environmental pollution cleansing and self-disinfecting [34,35]. The advantage of using solar light and rainwater as driving force has opened a new domain for environmentally friendly building materials. TiO_2 disintegrates organic pollutants into harmless CO_2 and water, in the presence of light. Products of reaction are easily removed by rain or simple rinsing. Buildings stay cleaner and more beautiful. The mechanism of reaction is shown in Fig. 2.

Photocatalytic concrete made headlines for the first time in 2007, when an Italian company Italcementi made photocatalytic concrete at commercial scale [35]. The details of the buildings constructed with nano titania concrete can be seen on websites [36,37].

One major disadvantage of using TiO_2 is that UV light is required to activate the photocatalysis and initiate the killing of the bacteria and viruses. In recent years, visible light absorbing photocatalysts with $Ag/AgBr/TiO_2$ has proved to be more successful at killing the germs [38,39].

3.3 Carbon nano tubes

At present, CNTs are considered to be the strongest materials. In the following Table 1, the strengths and densities of the common construction materials are shown.

In comparison to the above mentioned materials, a carbon nanotube has a modulus of elasticity of 1.8 TetraPascal, a tensile strength of 63 GPa and a density of 1.4 $g\text{-}cm^{-3}$ [44,45]. Thus a carbon nanotube has strength 120 times that of steel and is a much lighter material. Algae and barnacles cannot adhere to paints containing Carbon nano tubes (CNT). Thus CNT containing paints might successfully be applied in boats and ships. Similarly, because of the high strength of CNTs, paints with much larger hardness and scratch resistance have been made. The nano paint used on the Forth Bridge constructed in Scotland is claimed to need repainting after 25 years [46,47]. Forth Bridge has been designated as worlds heritage by UNESCO. The painting of the Forth bridge was often considered as a task that had never ended since it opened in 1890. The latest repainting with nano-paint has made it possible to repaint it after a period of 25 years [48].

CNTs can be incorporated in modern suspension bridges and cable-stayed bridges. Modern suspension bridges consist of roadways and cables made of thousands of individual steel wires of 0.1 inch thickness. The CNTs having strength hundreds of times of that of steel can be employed in ropes of suspension bridges [49].

Apart from paints, CNTs are also being incorporated in concrete. A very useful study in this regard was carried out by Konsta-Gdoutos et al. [50]. Through scanning electron microscopy (SEM), they have proved that the CNTs fill the pore spaces in concrete more effectively. The authors claim that CNTs can make concrete impenetrable to water and salts, thus greatly enhancing the durability of con-

Table 1. Characteristics of construction materials.

Material	Modulus of elasticity (GPa)	Ultimate Tensile Strength (MPa)	Density ($g.cm^{-3}$)
Ordinary Concrete [8,18]	25	2-5	2.4
Steel A36 [40]	200	550	7.8
Limestone [41]	15-55	5-8	2.7
Aluminium [42]	70	40-50	2.7
Glass Window [5]	50-90	70	2.6
Timber [43]	16	1-10 (Perpendicular to grain)	0.54-0.7

crete. Li et al. [51] have reported that adding 0.05% CNTs in foam concrete results in lower density, increased compressive strength, lower thermal conductivity, lower average pore diameter, and more homogeneous pore wall structure. However, the dispersion of CNTs in concrete matrix is highly complicated due to extremely high surface area of the nanoparticles and due to Van der Waals forces [52]. In the absence of proper dispersion techniques, the CNTs make agglomerates and thus their effectiveness could be lost [53]. In another study carried-out by Konsta-Gdoutos et al. [54], it is reported that CNTs can be effectively dispersed in concrete mixing water by using ultrasonic energy and a surfactant. Another point of view in this regard is presented by Nasibulin et al. [55]. They propose a new approach to attach CNTs directly on the surface of cement particles in concrete matrix, named as cement hybrid material or CMH. Nasibulin et al. have claimed that the CHM has two times the compressive strength, and 40 times the electrical conductivity of the hardened paste without CNTs.

3.4. Carbon nanofibers

Carbon nanofibers (CNFs), are grapheme layers arranged as stacked cones, cups or plates [56,57]. It is again reiterated here that graphene layers wrapped into perfect cylinders are called carbon nanotubes. Based on the work done by Mullapudi et al. [58], an optimum concentration of CNFs was determined for use in concrete, which not only improves its compressive strength as well as electrical properties. CNF are considered to be superior over CNTs because their stacked structure has exposed edges having more increased surface area and better bonding characteristics [59]. CNFs can comparatively be easily produced and hence cost much less than CNTs. Hence CNFs are more attractive than CNT for construction materials.

Deicing salts are spread in snowy areas to melt down the ice on roads. But this salt is responsible for corrosion of reinforcing steel bars embedded in concrete. Following that electrical resistive deicing system came into being. Carbon nano fibers have proved to possess high electrical conductivity, high heating capacity at low voltage and resistant to corrosion [60]. As such, CNF is thought as the heating element in electrical deicing systems. This suggestion first came into headlines through Chang et al. [61], and they put the idea of CNF-reinforced concrete also known as self-heating concrete.

Self-heating concrete is a thermally conductive concrete integrated with a resistive carbon nanofiber (CNF) paper. The CNF paper is connected to an electric grid, which converts electrical energy into heat. The heat is transferred to the surface and consequently, the snow gets melted, as shown in Fig. 3. The de-icing system eliminates the use of heavy machinery and de-icing salt for removal of snow from roads. Based on the study of Chang et al., a physico-finite element model was prepared to assess the performance of the proposed system [62]. They claim that the proposed system can be very effective for roadway deicing. However, the system needs to be evaluated in field to validate its effectiveness.

3.5. Nano food additives for concrete

Corrosion of steel embedded in reinforced concrete is a hot issue in civil engineering [63,64,65]. Billions of dollars are spent each other to rehabilitate the structures affected by chloride-induced-corrosion. At National Institute of Standards and Technology (NIST) USA concretes incorporated with nano food additives are being developed [66]. The technique has been named as VERDiCT (Viscosity Enhancers Reducing Diffusion in Concrete Technology). It is believed that with nano additives in con-

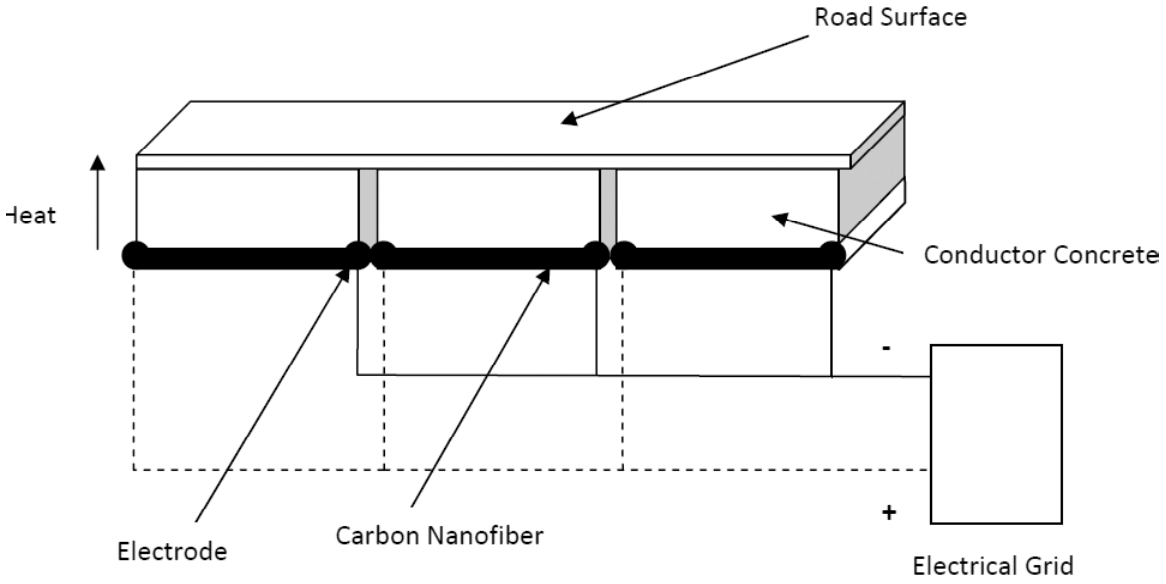

Fig. 3. Mechanism of self heating concrete.

crete porous solution, the viscosity of the concrete pore solution can be enhanced, which will slow down the ingress of destructive species causing steel rusting.

3.6. Nano-layered oils in fibers reinforced concrete

Fiber-reinforced is focused type of concrete in which short discrete fibers of synthetic or natural fibers are incorporated. The important fibers used are steel, poplypropyelene, glass and carbon [66]. Engineered Cementitious Composites (ECC) are also a fiber reinforced concrete. Also known as bendable or flexible concrete, ECC is the invention of Dr. Victor Lee of the university of Michigan in USA [67]. It is another revolution in concrete technology made possible through the use of nanotechnology. Conventional concrete is highly rigid and brittle and has a strain capacity of only 0.1%. ECC is a special type of fiber reinforced concrete in which nano-slicked fibers are used, which make the concrete to have a strain capacity of more than 3%. This concrete has been claimed to bend like metal [67].

4. RISKS ASSOCIATED WITH NANOPARTICLES

Apart from benefits, there are certain serious risks associated with the exposure to nano particles. Nano particles are very fine in size; hence they are highly airborne and waterborne. The situation can become serious when such nano particles are also of toxic nature [68,69]. Similarly, as discussed above, nanotitania particles might be of toxic nature as reported by USA health department. It is necessary to address the health issues related to nano technology before its application because every engineering and technology is meant for the benefit of the human society.

5. CONCLUSIONS

1. Nanotechnology has tremendous potentials in construction industry. The examples are germ-free laboratories and hospitals, waterproof buildings, urban environmental protection.
2. The important developments made in concrete technology are ultra high strength concrete, photocatalytic concrete, self-heating concrete, bendable concrete and concrete containing CNTs.
3. Nano Silica Concrete incorporates nano silica instead of micro silica particles or well known silica fumes. This concrete results in higher initial and final compressive strengths, higher workability, and lower permeability. Additionally, higher tensile strength and segregation resistance are also achieved. The new concrete is named as Ultra High Strength Concrete. The advantages of this concrete are numerous: the column sections in buildings can be reduced. The amount of steel reinforcement in concrete can also be reduced. And in highways and railway tunnels, thinner tunnel segments can be constructed leading to a great saving in excavations [70].
4. It is a well known fact that nano TiO_2 on UV irradiation can be used as an effective way to reduce the contaminants and enhance environmental safety.

5. Photocatalytic concrete is a green material. With this concrete, structures looking new for decades can be constructed. Inside hospitals and laboratories, the spread of germs can be minimized and urban air quality can be improved.
6. Various contaminants like algae and barnacles cannot cling to CNT-containing nano paints, which can increase the time saving in repainting massive marine structures.
7. Serious health issues related to the use of nano materials must be well understood and remedies are mandatory.
8. The investigation for various applications of nanotechnology to build up novel building materials continues. It is by now obvious that the science of the very small is creating big changes, with various economic benefits to the construction industry.

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