Part G

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Nanomaterial 29. Nanomaterials in Civil Engineering

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Manufactured nanomaterials (MNMs) with unique physical and chemical properties have attracted a great deal of attention as key materials to underpin future scientific and technological advancements. Applications of MNMs can also provide breakthroughs in the construction industry by reinforcing mechanical properties, decreasing vulnerability to chemical corrosion and accidental damage, and providing supplementary functions such as anti-biofouling and hydrophilicity. With the enhancement of material performance and functionality, use of MNMs enables (partial) nonutility generation, low carbon emission, and self-assessment of structural health to increase the sustainability of buildings and infrastructures. On the other hand, recent research into the safety of MNMs has raised concerns about their adverse biological and environmental effects. There is a high probability that MNMs used in construction will have hazardous effects on human and ecological receptors, considering that MNMs incorporated into construction materials would be released via multiple exposure routes during their entire lifecycle (manufacturing, construction, demolition, and recycling/disposal). Consequently, to responsibly utilize the potential benefits of nanotechnology in construction, multidisciplinary efforts are required to develop proactive strategies to mitigate the environmental release of MNMs and guidelines to manage their environmental risks throughout construction-related activities.

Nanotechnology, as a new industrial revolution, has brought myriad opportunities to a variety of scientific, engineering, and technology sectors. The *bottom-up* synthetic strategy in the transitional zone between atom and molecule creates nanodimensional materials with novel physical and chemical properties, offer-

ing great potential for diverse applications including (photo)catalysts, electronic and electrochemical materials, energy conversion and storage devices, mechanical composites, and optical instruments [29.1–5].

The incorporation of various manufactured nanomaterials (MNMs) into the matrices of conventional

Fig. 29.1a,b Annual number of research articles published in the subject areas of (**a**) MNM-containing concrete/cement and (**b**) MNM-containing steel. The literature search was performed at the Scopus website using the keywords "Nano" and "Cement" or "Concrete" (**a**) and "Nano" and "Steel" and "Strength" or "Corrosion" (**b**)

construction materials leads to drastic advancement in vital characteristics including mechanical strength, fatigue and damage resistance, durability, and lightness [29.6–9]. MNMs as additives improve cohesive and tensile strength, flexibility, forgability, and weldability to enable facile construction and processing operations [29.8, 10]. MNMs incorporated into construction materials add new auxiliary functions such as photo-induced pollution control, antimicrobial activity, and heat- and sound-absorbing capacity [29.11–13]. Use of MNMs contributes to increased energy efficiency in commercial and residential buildings (e.g., highly insulating materials and energy-generating coatings) [29.14, 15]. Coatings of MNMs provide corrosion resistance, fire retardation, and water repulsion to protect construction materials from weathering, aging, and contamination, eventually promoting their long-term serviceability [29.8, 16, 17]. MNMs embedded in construction materials are also applied in sensing and monitoring functions to assess construction safety and structural health [29.18, 19].

Contrary to the general perspective on the promising applications of nanotechnology, technical viability has been relatively less explored in the construction industry, which is attributed to:

- 1. Lack of informative research to ensure the potential benefits and identify the functionalities,
- 2. Uncertainties associated with nanoscale materials' longevity and environmental health and safety,
- 3. Conservative nature of construction industry, leading to limited adoption of new technology, and
- 4. Economical feasibility.

Nevertheless, use of MNMs in the construction industry is expected to increase rapidly, as shown by the increasing number of research articles published on the subject of *nanoconstruction* in Fig. 29.1 because of:

- 1. Recent advancement in harnessing unique nanoscale properties,
- 2. Rapid expansion of commercial interest in nanoenabled products,
- 3. Several research projects underway to assess and control potential hazards associated with engineered nanomaterials (NMs),
- 4. High performance and versatility of MNMs imparted at low additive ratios, and
- 5. Decreasing cost of base NMs due to their mass production.

In particular, despite the benefits of incorporating MNMs into construction materials, it is highly probable that concerns about their potential to become harmful environmental contaminants after their unwanted discharge limit their utility [29.20–22]. This underscores the need for assessment, standard protocols, and regulatory guidelines to address the environmental health and safety issues associated with manufacturing, transportation, use, and disposal of construction materials and products containing MNMs.

29.1 Applications of MNMs in Construction

The unique properties of MNMs can be exploited in construction for a variety of applications that encompass reinforced structural materials, low-maintenance and ecofriendly materials, multifunctional paints and coatings, renewable energy generation systems, and intelligent sensor/actuator devices (Table 29.1). The current and potential applications of MNMs in construction are described below, and some selected examples for MNMs used in construction and related MNMcontaining products are illustrated in Figs. 29.2 and 29.3.

29.1.1 Concrete and Cement

Concrete is one of the most common manmade materials in the world. Conventional concrete is relatively strong in compression because fine and coarse aggregates such as sand and natural gravel in concrete efficiently carry the compressive load. However, traditional concrete has heterogeneous micro- and mesoporous structures through the random packing of concrete mixture of aggregates, cement, and water. Thus, it is weak in tension and flexure due to the complex internal pore

structure of the concrete. There are several possible explanations for the improvement of mechanical properties by MNMs [29.7]. Firstly, nanosized materials fill the cement pores and serve as packing materials in concrete. Secondly, nanoparticles (NPs) promote cement hydration through tight binding with the cement hydrate. Finally, NMs efficiently inhibit the growth of large crystals (e.g., $Ca(OH)_{2}$).

NPs have been applied to improve compressive strength during the past decade. Research into SiO₂, $TiO₂$ or Fe₂O₃ NPs used as a concrete additive material has shown that these nanosized particles serve **Fig. 29.2a–h** Examples of MNMs used in the construction industry. (a) SiO₂ nanoparticles (source: Los Alamos National Laboratory); (b) Fe₂O₃ nanoparticles (courtesy of Dr. Changha Lee, Ulsan National Institute of Science and Technology); (c) TiO₂ nanoparticles; (**d**) Ag nanoparticles (source: US Environmental Protection Agency); (**e**) carbon nanotubes (source: National Cancer Institute); (**f**) CdSe quantum dots (source: Lawrence Berkeley National Laboratory); (g) BaTiO₃ nanoparticles (source: The National Academy of Sciences of Ukraine); (**h**) Cu nanoparticles (courtesy of Dr. Changha Lee, Ulsan National Institute of Science and Technology)

as a filling agent to increase the strength of the concrete and improve its abrasion resistance [29.23–25]. Addition of silica NPs as a part of the mixture also enhances the durability of the concrete by blocking water penetration. $SiO₂$ NPs can control the degradation of $(CaO) \cdot (SiO₂) \cdot (H₂O)$, which is the product of the cement hydration process, by blocking water entry into the pores [29.8]. In addition, the weight of concrete would be reduced by using silica fume. Hematite $(Fe₂O₃)$ NPs can be used as a monitoring material to quantify the stress levels by measuring section electrical resistance as well as a packing material [29.8]. Research into

Fig. 29.3a–d MNM-containing construction products and their applications. (**a**) Concrete (source: US Department of Transportation Federal Highway Administration); (**b**) window glass (source: NBNL); (**c**) rooftop solar panel (source: US Department of Energy); (**d**) bridge (source: MCEER, the State University of New York Buffalo)

carbon-encapsulated nickel NPs incorporated into concrete also demonstrated an increase in the compressive strength of the cement due to the intense antiparallel ordering caused by a magnetic dipole interaction [29.7].

 $TiO₂$ NPs have other supplementary functions when applied to cement/concrete, such as sterilizing and self-cleaning, as well as filling the pores [29.26]. $TiO₂$ as an ultraviolet (UV)-responsive photocatalyst yields reactive oxygen species (ROS) under light irradiation, resulting in destruction of volatile organic compounds, NO_x , and bacterial membranes. Due to the UV-activated hydrophilic conversion, rain droplets attracted to an outdoor surface containing nano- $TiO₂$ particles form a water layer which can wash away airborne pollutants, as airborne pollutants trapped in a TiO₂ particle matrix undergo further oxidative degradation under sunlight illumination. Since $TiO₂$ particles form a white pigment, nano- $TiO₂$ -added concrete has the additional advantage that it can retain whiteness during the lifetime of the concrete. Incorporation of nano- $TiO₂$ into concrete has already been commercialized in the construction industry. The Jubilee Church in Rome was constructed from precast nano-TiO₂integrated concrete panels, which is sometimes called *white concrete* [29.8]. Prior to the Jubilee Church, nano- $TiO₂$ was incorporated into road surfaces, and it was found that the NO_x concentration was significantly decreased near the constructed road [29.8].

 $CaCO₃$ NPs have also been suggested as supplementary materials for addition to cement. Strength development during the initial period of cement hydration is significantly improved when nano-CaCO₃ is added [29.9]. The mechanism behind the improved cement hydration rate by nano- $CaCO₃$ needs to be further investigated, but the difference in the impact on hydration between micro-CaCO₃ and nano-CaCO₃ provides evidence that the size of the calcium carbonate particles plays a significant role in the hydration process. Another possible use of calcium carbonate as a biosealant in concrete is being studied [29.8]. Anaerobic microorganisms are incorporated into concrete mixing water, and subsequently excrete calcium carbonate, which fills the cement pores and results in improved compressive strength. Similarly, self-healing concrete in which microcapsules containing healing agents and catalysts are embedded is being investigated to solve crack problems of concrete [29.51]. When cracks form in the concrete, the capsules would be ruptured. The released healing agent then contacts the catalyst, and the crack will be filled through polymerization.

Traditionally, steel has been incorporated in conventional concrete as a *reinforcement bar* (rebar) in order to strengthen the concrete in tension and flexure, but the process of placing steel bars and introducing wet concrete is time consuming and expensive. Cracking due to rebar corrosion or freeze–thaw cycles is also an issue for steel-reinforced concrete. Glass, plastic, or steel fibers have sometimes been added to produce reinforced concrete. These materials can either replace the steel rebars entirely or be added to concrete already reinforced by steel bars. Concrete reinforced with fibers, for example, carbon graphite fiber, which is a corrosion-proof and very high strength-to-weight material, is less expensive and has still higher tensile strength. Nanosized fibers were recently studied as an alternative reinforcing material for concrete. Reinforced concrete was produced by introducing nano- and microsized carbon fibers [carbon nanotubes (CNTs)] and centimeter-sized carbon graphite fibers, exhibiting improved mechanical properties [29.6, 52]. Incorporation of CNTs is expected to show advantages over traditional fibers in reinforced concrete due to their distinct structural properties. CNTs are known as the strongest and stiffest materials in terms of tensile strength and elastic modulus, respectively. Therefore, they would improve the mechanical properties of the concrete. Also, the small size of CNTs should make them fill the cement pores and interrupt crack formation and growth at very early stages. On the other hand, the high aspect ratio of CNTs would play a role in preventing crack propagation, because higher energy would be required to propagate the crack around the nanotubes. In addition, CNTs can be chemically functionalized to interact with adjacent cement component. A recent study demonstrated that CNTs in concrete act as a nucleus to bind tightly with cement hydrate (C-S-H) around functionalized nanotubes [29.53].

In spite of their many advantages, there are economic and technical limitations to the use of CNTs in reinforced concrete. The cost of CNTs is still high and not competitive with other fiber materials. Furthermore, CNTs tend to form aggregates due to van der Waals forces, thus additional processes are required to achieve uniform distribution of individual tubes. Another issue with CNTs is weak bonding between the nanotubes and the cement matrix. Several research studies have been conducted to tackle these problems by functionalizing the nanotubes or through the use of surfactants and sonication to achieve uniform dispersion [29.27].

29.1.2 Steel

Steel has served as a reinforcement material in concrete or as a structural component in bridges, highways, or buildings by itself. In addition to its corrosion resistance, steel is also selected based on properties such as strength or weldability. Welding is one of the steel fabrication processes and creates a sector called the *heat-affected zone* (HAZ) adjacent to welds. The material properties of the HAZ are altered by heat-intensive cutting or welding processes, thus the HAZ and welds are brittle and can fail easily when a sudden dynamic load (e.g., seismic load) is applied. Addition of nanosized particles such as magnesium and calcium improves the weld toughness of steel as well as decreasing the size of the HAZ to $1/5$ of that of conventional welded steel [29.8]. Not only improvement of toughness at welded joints, but also cost-saving due to the decreased material requirement to meet allowable limits is also expected when research currently underway is completed.

High-strength steel experiences delayed fracture problems, in which the steel material becomes brittle and fractures following exposure to hydrogen when strong tension is applied. Vanadium and molybdenum NPs have been incorporated to reduce the effects of hydrogen embrittlement and, therefore, to improve the delayed fracture problem of high-strength steel materials, especially high-strength bolts [29.8].

Many efforts have been made to improve the corrosion resistance of steel using nanotechnology, but very few products are available in the construction market. One of them is MMFX2 steel, which has a distinct nanostructure. A laminated lath structure resembling plywood in MMFX2 makes the steel corrosion resistant by hindering microgalvanic cell formation. In addition, according to the manufacturer, the unique features of the product provide improved strength, ductility, and toughness compared with conventional steel products. MMFX2 steel is currently used in many construction sites including bridges, parking structures, buildings, and highways. The Federal Highway Administration, the US Navy, and the American Iron and Steel Institute developed high-performance steel for bridges in 1990s. This new steel has higher fracture toughness, improved weldability, and better corrosion resistance than conventional steel by incorporating copper NPs, which are known to reduce the surface roughness of steel [29.10]. Another steel product available in the commercial market, but not for construction applications, is Sandvik Nanoflex. Although the manufacturer does not provide detailed information about the product, it is reported that very hard NPs are incorporated in the Sandvik Nanoflex steel matrix. Therefore, Sandvik Nanoflex has good corrosion and wear resistance and high modulus of elasticity.

Several ongoing research efforts focus on production of nanoscale fabricated metals, which are stronger than conventional steel or titanium. Such metals would be fabricated by weaving the material to produce ultrafine lattice structures or refining the cementite phase of steel to nanosize to produce cables [29.8]. The expected properties of such products are improved strength and reduced weight, and one of their applications could be as a structural component of suspension bridges.

29.1.3 Plastic

Multi-walled CNTs as a proxy for carbon black show improved performance as a filler material, drastically increasing the mechanical strength and electric and thermal conductivity of plastic composites [29.27, 28]. CNTs incorporated into plastics also function as a flame retardant to enable rapid heat dissipation, preventing the possible release of hazardous gasses under fire [29.29]. Addition of nanoscale ceramic materials (e.g., nanoclays) to the polymer matrices creates lightweight nanocomposite plastics with high compressive strength [29.30]. Wood–plastic composites produced by manipulating fiber-to-fiber bonding at the nanoscale, which require much less maintenance and have a long service life because of their high rot resistance, gain improved mechanical properties through modifications using carbon nanofibers and nanoclays [29.31].

29.1.4 Window Glass

Incorporation of MNMs into glass matrices allows the production of windows to control the passage of light and heat through the walls of buildings. Such applications can increase energy efficiency by reducing heat loss to conserve building heating energy (e.g., lowemissivity glass) and by blocking solar heat to curtail energy consumption for air-conditioning and ventilation (e.g., heat absorbing and solar control glass). Due to its strong visible and infrared absorption, nanosized tungsten oxide (WO_3) improves the heat reflectivity of a window to simultaneously reflect in-room heat back inside and mitigate solar heat gain through the window, and further enables variable light transmission [29.32]. Window glass containing lanthanum hexaboride (LaB₆) NPs that selectively capture the heating wavelengths from 750 to 1300 nm secures sufficient natural daylight while maintaining uniform room temperature in hot weather seasons by transmitting visible light and blocking unwanted infrared light from the solar spectrum [29.11]. Nanostructured indium tin oxide (ITO) (or indium antimony oxide) film also creates highly transparent infrared-absorbing coatings on window glass, being commercialized under the product name AdNano ITO [29.11, 54]. Ultrafine $TiO₂$, ZnO, and $TiO₂/CeO₂$ uniformly cast on glass surfaces produce UV-reflecting windows by filtering out the UV fraction of sunlight without significantly decreasing visible light transmittance $[29.8, 14, 33, 34]$. In this case, rutile $TiO₂$ NPs with low photoactivity are in common use to avoid unwanted photocatalyzed destruction of surrounding matrices, as ZnO NPs are surface-modified with silica to facilitate homogeneous dispersion on the surface [29.14].

Light transmittance through the window can be controlled by photochromic coatings or layers that reversibly change their inherent color in response to incident light [29.55]. Photochromic films formed of MNMs including metal NPs, hybrid metal/metal oxide NPs, and quantum dots (QDs) can produce *smart windows* that react to light conditions, controlling the intensity of incident light, being translucent in the visible region to brighten interior spaces, or being reflective in the infrared region to retard thermal transfer [29.35, 36, 56–58]. Photochromic films containing platinum, palladium, or gold NPs exhibit coloration/color fading characteristics under light irradiation [29.57]. Dark-blue color rapidly develops on TiO2 films in combination with phosphotungstic acid $(H_3PW_{12}O_{40})$ under UV irradiation and disappears in the presence of oxygen as an electron acceptor in the dark condition, as $MoO₃$ or $WO₃$ films coated with gold or platinum also undergo reversible UV-induced coloration on the window [29.35, 36]. In particular, $TiO₂$ film loaded with silver NPs on the window enables repeatable multicolor photochromism in which the initial brownish-grey color rapidly changes to the color of the excitation wavelength under irradiation by monochromatic visible light [29.58]. In addition to the photosensitive smart window, thermochromic glass that includes polymeric layers doped with various transition metals (e.g., Fe, Co) or metal/metal oxide nanocomposites (e.g., $Au/VO₂$) also modifies the transmission and reflection properties, adapting to the surrounding temperature to create a nonelectrically activated window to regulate daylight depending on the background thermal conditions [29.59, 60].

Antireflective coating of silica NPs causes microand nanoroughness on the glass surface, reducing the magnitude of visible light reflected and offering a clear view from inside to outside [29.14]. Vertically oriented pure rutile $TiO₂$ nanorods on glass substrate also form an antireflective coating [29.61]. Note that 20% of the incident light is reflected at the $TiO₂$ –air interface, while the reflection at the uncoated glass–air interface is as low as 4% . Alternating layers of $SiO₂$ and $TiO₂$ NPs that exhibit a large refractive index contrast significantly improve light transmission through the window [29.14, 62].

Deposition of nano-TiO₂ on window glass offers a self-cleaning function under irradiation by sunlight or indoor light, because $TiO₂$ can photosensitize production of ROS such as OH radicals, valence-band holes, and relevant efficient oxidation of organic substrates [29.2, 63]. The photocatalyzed reactions initiating on nanosized $TiO₂$ -coated glass lead to photooxidation of hydrocarbons and photokilling of pathogenic microorganisms attached to the window and from the surrounding atmosphere [29.37, 64]. In particular, metal or nonmetal doping allows $TiO₂$ NPs to utilize visible light for photocatalytic ROS generation. Photoinduced hydrophilic conversion occurring on a TiO₂ surface, which makes water spread out over the surface rather than remain as droplets, mitigates accumulation of hydrophobic dirt, as the increased density of surface hydroxyl groups under exposure to UV light enables antifogging and stain-proofing actions of the TiO₂-modified window [29.65, 66]. Such a photo-driven process for surface hydrophilization can be kinetically accelerated on TiO₂-based composite layers (e.g., TiO₂/WO₃ or TiO₂/SiO₂) [29.67, 68].

Inclusion of metal-oxide NPs can improve the mechanical strength, thermal stability, and chemical durability of window glass. Incorporation of aluminum nanopowders enhances the mechanical strength, microhardness, and chemical resistance of glass without significantly changing its optical properties [29.38], as silica NPs make windows highly scratch and wear resistant [29.14]. Nanoscale silica layers sandwiched between two glass panels form fire-protective window glass in which silica NPs swell, converting to mechanically reinforced and opaque forms in the event of a fire [29.8].

29.1.5 Coatings

Coatings utilizing MNMs are expected to impart diverse supplementary functionalities to construction-related

surfaces and produce the desired protective and resistant surfaces on existing construction materials. Use of MNMs for thermal insulation leads to energy conservation and carbon emission reduction through efficient heat management. Due to the large surface-to-volume ratio and high porosity, nanoporous silica as an insulator enables significant air entrapment within a layer of minimal thickness, thereby effectively hindering heat transfer across the layer [29.14, 20]. Aerogels or nanofoams of metal oxides (e.g., silica and alumina) that contain nanoscale pores primarily filled with air (> 90%) can be employed for ultrathin and lightweight insulating coatings (relative to conventional insulating layers of polystyrene or cellulose) [29.14, 20]. Threedimensional and highly branched networks of $SiO₂$, TiO2, or carbon NPs show exceptional insulative performance because nanosized cells, pores, and particles within the unique nanostructures produce substantially limited pathways for thermal conduction (through the interconnected NPs) and thermal energy transport (through the enclosed air molecules) [29.8, 14, 20].

Metallic NPs (e.g., silver and gold) produce antimicrobial coatings on diverse construction materials including cement/concrete, steel, plastic, and glass [29.14, 39–41]. The antimicrobial activity of silver NPs embedded in paint leads to efficient inactivation and sterilization of pathogenic microbes on the substrate surface [29.12]. Silver or gold NPs dispersed in polymer matrices form antibacterial metal/polymer nanocomposite coatings, hindering microbial adhesion on the substrate material [29.40, 41]. Thin films of metaloxide-based semiconductor NPs (e.g., TiO₂ and ZnO) on pavements, walls, and roofs function as antifouling and self-cleaning coatings under solar irradiation to depollute airborne contaminants, protect construction products from stains and dirt, and inhibit growth of bacteria and mold on the surface [29.42, 69]. Micro- and nanopatterning reduce the surface energy and associated adhesion [29.70], offering water-repellant surfaces for construction products and making them less susceptible to dirt accumulation.

Thin films of ceramic NPs (e.g., $SiO₂$), which are highly resistant to oxidation, can function as physical barrier layers to protect metallic construction materials against corrosion $[29.16]$. TiO₂ NPs surface-modified with fluoroalkylsilane form hydrophobic coatings on the surface of stainless steel to prevent moisture-induced corrosion [29.17], as photogenerated conduction-band electrons are transferred from $TiO₂$ coatings to the corroding metals, providing corrosion resistance properties under solar irradiation [29.71].

Ultrafine metal-oxide particles (e.g., $SiO₂$, ZnO , and Al_2O_3 NPs) can serve as nanofillers for polymer-based coatings, thereby preventing infiltration of oxygen, water, and corrosive chemicals through the voids and cracks present in the polymer matrices [29.43]. Polymer encapsulation of nanosized Zn or $Fe₂O₃$ as anodic-type corrosion inhibitors leads to prolonged anticorrosion performance on the coated steel [29.43]. In particular, composite materials having metal-oxide core (e.g., $CeO₂$, $SiO₂$, $TiO₂$, and $ZrO₂$ NPs) with polymer shell responsive to an electric or mechanical trigger can produce *smart* corrosion-proof coatings by acting as nanoreservoirs to store organic corrosion inhibitors and release the entrapped reagents when external signals are applied [29.16]. In addition to corrosion resistance, nanosized SiO_2 , TiO_2 , and Sb_2O_3 as nonflammable fillers or additives reduce the thermal transfer rate, and improve the existing fire-resistant properties of polymer coatings or decorative paints [29.44, 45].

Flexible solar panels that utilize silicon-based photovoltaic or dye-sensitized $TiO₂$ solar cells are being integrated into roofing membranes and mounted on windows, converting solar energy to generate electric power available for homes and buildings. The solar energy coating as a partial nonutility power producer achieves improved efficiency of renewable energy generation through the incorporation of semiconductor QDs (e.g., CdSe and InAs) [29.15] and carbon-based NMs (e.g., C_{60} and CNTs) [29.46].

29.1.6 Lighting

A light-emitting diode (LED) employs inorganic semiconductor NPs (e.g., GaN, ZeSe, and GaAsP) with different band-gaps and produces various colors of light as a result of electroluminescence [29.48, 49]. LED devices are rapidly replacing conventional fluorescent and incandescent light bulbs because LEDs require low electric energy for lighting, provide long service life, and guarantee safe end-of-life management (i. e., no release of toxic metals).

29.1.7 Sensors

Nano- and microelectromechanical systems (NEMS and MEMS) can be applied as miniaturized implantable devices to allow real-time in situ monitoring and accurate assessment of the health status of construction materials/structures (e.g., cracking and stress) and environmental conditions (e.g., temperature, humidity, and pressure) [29.72]. In addition to nondestructive evalu-

ation, NEMS and MEMS can also enable an effective strategy for quality management in cement/concrete construction by in situ observation of the cement hydration process, cement/concrete hardening, and strength development [29.73]. Piezoelectric materials such as $BaTiO₃$ and $PbTiO₃$ that can convert mechanical force and stress to an electric charge create *intelligent aggregates* or *smart aggregates* that can be embedded into concrete blocks to monitor initial concrete strength and structural health [29.18]. Uniform dispersion of piezoelectric ceramic NPs into the polymer matrices forms sensor coatings to detect crack initiation and development and track the structural response to impact damage [29.74]. CNT/polyelectrolyte thin films fabricated by the layer-by-layer (LBL) method cause a change in electrical resistance in response to mechanical stress (i. e., piezoresistive characteristics), suggesting potential application as a highresolution strain-sensing system in concrete structures [29.50].

29.2 Environmental Release of MNMs Used in Construction

With the projected rapid increase in MNM use for construction materials, the possible release into the environment and associated human exposure have become areas of growing concern [29.75–80] (Fig. 29.4). Although numerous studies have reported toxicological impacts of NMs, a knowledge gap still remains with respect to the environmental risk of NMs associated with their exposure pathways for the potential receptors (ecosystems and human beings). In particular, while a limited body of literature has focused on the environmental fate, behavior, exposure, and toxic effects of MNMs as raw materials prior to further processes toward an end-product [29.76, 77, 80–82], there are few safety and health considerations and lifecycle studies regarding MNMs incorporated into construction products and the resultant MNM wastes generated during construction activities. The identification of possible sources, environmental release scenarios, and exposure routes of MNMs used in construction is critical in assessment of their overall environmental hazard and risk,

and development of countermeasures. Therefore, the possible exposure scenarios via multiple routes for environmental discharge of MNMs used in construction are considered herein based on previous published studies and typical construction practices.

29.2.1 Construction Material Manufacturing

It is highly probable that the manufacturing stage will be the major source for environmental release of MNMs during the whole lifecycle of NM-containing construction products. MNMs that are not properly bound or incorporated into the basic materials such as concrete, steel, glass, etc. can directly disperse into the surrounding environment. During specific manufacturing processes including coating, molding, compounding, and incorporation, unintentional emission of MNMs into the atmosphere can occur as the primary pathway for environmental discharge, resulting in possible exposure of manufacturing workers via inhalation; For

Fig. 29.4 Primary pathways into the environment and corresponding exposure routes to humans expected during the lifecycle of MNMs used in construction (*A* for air; *S.W* for surface water; *S.G.W* for soil and groundwater; *H* for human)

example, airborne NPs could be blown away during weighing of raw materials, and the aerosol type of fullerenes and CNTs could be emitted while treating carbon NMs in a sonicator for better dispersion in liquid media [29.83]. The risk assessment worksheet on the DuPont Light Stabilizer reported that nano-TiO₂ particles could be released during the packaging process over the acceptable level [29.84]. Sepiolite nanoclay used as a filler material in construction nanocomposites would be likely released into the air during early manufacturing processes of mining and transporting [29.85]. In closed manufacturing facilities, indoor air control using ventilation systems, dust collectors, and personal protective equipment such as masks, coveralls, and gloves locally mitigate exposure of workers to MNMs released from manufacturing and related processes.

29.2.2 Structural Applications

MNMs could be released into the environment from buildings and associated infrastructures constructed with nanorelated materials. Use of NM-containing construction products makes individuals and communities in commercial and residential buildings more susceptible to exposure to MNMs [29.31]; For instance, they could be exposed to MNMs incorporated into wallpapers, glasses, paints, etc. through inhalation, dermal contact, or accidental digestion. Wear and abrasion of such structures by accidents (e.g., fire, car crash or earthquake) or weather (e.g., rainfall, snow, and wind) can cause immediate or gradual weathering of MNMs from basic construction materials, increasing the potential for adverse effects on environment and human health. TiO₂ NPs used in exterior paints of building facades as a whitening pigment have been found in building runoff after rainfall [29.79]. MNMs suspended in runoff could be deposited on the topsoil in the surrounding area, and could be delivered to ecological receptors including plants, soil invertebrates, and soil microbes. MNMs released from structures could be transported through sewerage systems to enter adjacent surface waters, posing an immediate threat to aquatic habitats and deteriorating drinking-water quality. Also, MNMs could possibly infiltrate into the subsurface in significant quantities to reach and contaminate groundwater.

29.2.3 Structural Demolition

Partial or complete demolition of structures containing MNMs would also result in personal exposure to and environmental discharge of MNMs. Pulling down buildings and infrastructures proceeds in a relatively less controlled way, whether it is achieved by nonexplosive (using bulldozers, cranes, or hydraulic excavators) or explosive (or implosive) demolition practices. Consequently, it would be difficult to protect workers from the possible uptake of nano- and ultrafine particles and control their emission to the atmosphere during demolition activities. In addition to particulate emissions, water sprinkled on demolition waste to reduce dust levels could cause dissolution and suspension of MNMs and their subsequent transport to the aquatic environment. Demolition debris could emit hazardous wastes when NM-related components are not separated or eliminated beforehand. Proactive steps by trained specialists should be taken to preferentially dispose of NM-containing products such as windows, coatings/paintings, and sensor devices prior to the overall demolition operation.

29.2.4 Construction Waste Disposal

In general, construction (and demolition) wastes are transported to designated landfills equipped with engineered liner systems and leachate treatment facilities. However, environmental exposure to MNMs and associated adverse health effects would potentially arise if construction wastes containing MNMs are not properly treated and disposed of, e.g., dumped in shallow unlined pits or piled up in the open air. Furthermore, there is a high likelihood that construction debris, if disposed of with MNMs not encapsulated within sound structures, would discharge MNMs in the presence of prolonged exposure to rainfall or wind; For example, concrete debris exhibits high vulnerability to wind- or rainfallinduced erosion on the cleaved surfaces, which could lead to detachment of MNMs from NM-concrete debris in construction wastes and associated environmental release of free MNMs. Once MNMs in free particulate form are leached out from construction wastes, they would enter environmental media through various pathways. While MNMs initially undergo dispersion in air or in solution or suspension in runoff, it is highly probable that most MNMs released into the environment would penetrate into the subsurface and eventually reach groundwater aquifers. Despite limited mobility in soil (relative to air and aqueous media), CNTs and TiO2 NPs could migrate significant distances through porous media (soil and groundwater) in the presence of dissolved organic matter in the pore water [29.81, 86].

For the overall risk assessment, further research should focus on the fate, behavior, and transport of MNMs in multiple environmental media [e.g., air, groundwater, sediment, (surface and subsurface) soil, or surface

water] and environmental transformation processes for MNMs and associated modifications of their chemical structures, reactivity, mobility, bioavailability, and toxicity.

29.3 Potential Adverse Biological Impacts and Toxicity Mechanisms

The development of MNMs for the construction industry may produce unintentional environmental and human health impacts as a result of their unique chemical, biological, catalytic, and photoactive properties. Toxicological studies of these materials have shown that MNMs display a wide variety of toxicity mechanisms to organisms at every trophic level [29.87]

(Fig. 29.5). Therefore, release from nanoenabled construction materials and structures could pose a risk to microorganisms (which provide valuable ecosystem services including primary productivity, nutrient cycling, and waste degradation) and higher organisms. These toxic responses include cell wall disruption (e.g., single-walled nanotubes, SWNTs), DNA/RNA damage

(e.g., multi-walled nanotubes MWNT), direct cell membrane oxidation (e.g., nC_{60}), dissolution of toxic metal components (e.g., QDs), and ROS-induced oxidative stress (e.g., $TiO₂$) (Table 29.2).

29.3.1 TiO2

TiO2 NPs possess unique photocatalytic properties as UV light or sunlight irradiation of particles produces ROS, which can cause inflammation, cytotoxicity, and DNA damage in mammalian cells [29.88–98]. In addition, slight variations in $TiO₂$ morphology affect their uptake through cell membranes by stimulation of phagocytosis, and encourage endogenous ROS generation as an immune response within the cell matrix [29.94, 99]. Compared with their bulk counterparts, they exhibit differential toxicity [29.100]; for example, in one study, nano-TiO₂ displayed greater induction of apoptosis and white blood cell generation [29.101].

TiO2 elicits similar ROS-derived toxicity in unicellular microorganisms. Solar irradiation enables the antimicrobial activity of $TiO₂$ towards various bacteria, including *Escherichia coli*, *Micrococcus luteus*, and *Bacillus subtilis*, and fungi, such as *Aspergillus niger* [29.13, 102, 103]. Membrane damage and particle adhesion are implicated as other mechanisms of toxicity $[29.104]$. Additionally, nano-TiO₂ appears to have a synergistic effect with other co-contaminants; For example, nano-TiO₂ toxicity and metal bioaccumulation were increased in the marine invertebrate *Daphnia magna* after simultaneous exposure with copper [29.105], and in carp species after simultaneously exposure with cadmium [29.106].

29.3.2 Quantum Dots

QDs contain toxic heavy metals such as cadmium, lead, and zinc in core/shell configurations [29.107] and have been recognized as among the most toxic materials [29.108]. The release of core metals has been accepted as the predominant mechanism of QDs' toxicity towards mammalian cells [29.109–114] and bacteria [29.115, 116]. In human cells, toxicity can manifest as ROS damage to organelles and release of inflammation signaling proteins [29.117, 118]. In whole-organism toxicity trials, mice displayed particle accumulation in the spleen, liver, and kidneys [29.119], while microorganisms, such as bacteria and algae, experience growth inhibition, cytotoxicity via lipid peroxidation, oxidative stress, and cellular particle uptake [29.115, 116, 120].

Toxicity, however, is not solely the result of metal ion release; some coating materials themselves may also be toxic [29.95, 117, 121]; For example, intact QDs can impair calcium influx and exocytotic mechanisms in murine brain cells [29.122]. It was also observed that eukaryotic cells experience oxidative stress, nucleic acid damage, and cytotoxicity resulting from internalization or membrane association with QDs [29.118, 119, 123]. Furthermore, gene expression studies in algae show that QDs elicit different responses compared with exposure to their respective ions [29.124].

29.3.3 Carbon Nanotubes

CNTs (SWNTs and MWNTs) pose a potential hazard [29.125] because they exert acute toxicity through ROS generation, inflammation, cell cycle arrest, and increased apoptosis in human and mammalian cells [29.126–128]. Trails of human cells exposed to chronically low doses show accumulation within cells and no adaptive protective mechanism development [29.129]. Extensive testing of whole organisms has been performed for CNTs. In rodent toxicity experiments, exposure through inhalation resulted in pulmonary toxicity such as inflammation, fibrosis, and epithelioid granulomas [29.125,130]. In contrast, exposure through oral dosing resulted in increased weight gain, morphological changes to the liver, and increases in lipid hydroperoxide [29.131].

Both SWNTs and MWNTs can also exhibit antimicrobial properties. Recent studies have shown CNTs to inhibit bacterial processes in river water, activated sludge, and wastewater effluent, which are likely sinks for CNTs released into the environment [29.132, 133]. The mechanism of microbial toxicity of SWNTs appears to be direct damage to cell walls [29.133, 134], while MWNTs cause toxicity via oxidative stress [29.135, 136]. The antimicrobial properties appear to also be related to aggregate size [29.137] and interactions with bacterial extracellular polymeric substances (EPS) [29.132].

29.3.4 C₆₀ Fullerene

 C_{60} water-stable aggregates (referred to as nC_{60}) [29.138]) display toxicity to human and mammalian cells ranging from lipid peroxidation to necrosis and inflammatory responses [29.138–152]. Meta-analysis of rodent lung exposure data suggests that levels as low as the mg/m³ range can elicit a toxic response in mammalian cells $[29.153, 154]$. nC₆₀ aggregates dis-

play broad antimicrobial activity independent of the preparation method, i. e., solvent mediated, sonication, or prolonged stirring in water [29.145,147,155]. Recent studies confirmed that nC_{60} toxicity to bacteria was due to direct oxidation of the cell upon direct contact rather than by ROS-dependent oxidative stress [29.146, 156]. Oxidative stress exerted by nC_{60} leads to lipid peroxidation, which is also responsible for cytotoxicity in eukaryotic organisms $[29.141, 151, 157]$. C₆₀ derivatives such as fullerol and carboxyfullerene, designed to enhance their aqueous availability, are capable of puncturing the cell membrane [29.158] and behaving as oxidizing agents in biological systems [29.159].

29.3.5 SiO₂

The effect of silica NPs on human and mammalian cells has been studied extensively because of their extensive use in biomedical and industrial applications [29.154, 163, 166–170, 176, 177]. Exposure to nanosized SiO2 triggers lipid peroxidation and membrane damage to human lung cancer cells [29.178], induces tumor necrosis genes in rats [29.170], and exerts carcinogenic activity [29.179]. While microbial toxicity occurs at higher doses as compared with mammalian cells [29.154, 180], nanosized silica causes toxicity via ROS generation [29.154] and impedes cell division in unicellular algae [29.163]. While the exact mechanism of toxicity is unclear, it has been related to size and relative surface area, where particles with greater surface area were more toxic to both mammalian [29.181, 182] and algal cells [29.183]. Regarding toxicity to microorganisms, studies suggest that toxicity is related to direct attachment and interaction of the particles [29.164, 165, 183].

29.3.6 Copper/Copper Oxide

Cu and CuO NPs induce oxidative stress, which can result in membrane, protein, and DNA damage in bacteria, algae, yeasts, mice, and human cells [29.91, 97, 160, 171, 184]. Oxidative toxicity results from ROS generation by copper ions via Fenton or Haber–Weiss reactions [29.185]. Furthermore, Cu NPs can exert toxicity over a range of lethal and nonlethal doses; For example, studies in mice showed that low, subtoxic doses of Cu NPs elicited the same cell stresses characteristic of higher doses [29.173]. While Cu NP toxicity is primarily linked to the bioavailability of free ions in the exposure media [29.161, 172], recent studies have found that ions cannot explain the total toxicity, and unique nanoproperties may also contribute to toxicity [29.162].

29.4 Mitigation of Environmental and Health Impacts

The most pressing challenges facing the construction industry community in using nanoenabled construction materials include manufacturing of safe materials without significant modifications of their unique desired properties, applications of NM-containing materials with minimal hazard during their service life, and recycling and disposal to reduce waste materials and prevent soil and groundwater contamination. Thus, it is important to discern the chemical compositions, structures, and associated properties of NMs that are essential for their characteristic toxicological activities and environmental behaviors. Such investigation provides basic information for the design of safer products under consideration of exposure control (e.g., protective coatings and magnetic composites) and adoption of greener substitutes for toxic MNMs. The assessment of exposure routes, environmental fate, and transport for MNMs used in construction, with development of analytical methodologies to trace MNMs in multimedia, should be critical in controlling environmental pollution related to construction activities and establishing the strategy

for waste management (e.g., separation/collection, recycle/reuse, and disposal).

29.4.1 Manufacturing

Chemical structure–activity relationships that elucidate which specific properties of MNMs are critically associated with their environmental behavior and toxicological activity are urgently required. In the absence of empirical data on various MNMs, these will provide a foundation to develop strategies to mitigate hazards and assess exposure scenarios and pathways. Physicochemical and structural properties associated with MNMs affect their fate, behavior, and transformation in environmental matrices (e.g., adsorption/desorption, aggregation, chemical redox reaction, deposition, or dissolution), which will directly bear on bioavailability, bioaccumulation, and toxicity [29.186].

Structure–activity relationships, with research into the toxicity mechanisms of MNMs, can offer basic design concepts for environmentally safe nanocomposites;

For instance, encapsulation in polymer resins or surface functionalization hinders direct contact of carbon-based NMs (e.g., fullerene and SWNTs) as a key step in damage to bacterial cells, significantly diminishing their antimicrobial activity. Durable coating with inorganic film renders metal oxides (e.g., CuO and $Fe₃O₄$) and QDs resistant to weathering. Also, the predictive relationships may suggest the urgent need to remove potential toxic components from MNMs and switch to alternative materials.

Development of MNMs with easy degradation or recovery in response to specific environmental conditions may minimize environmental hazards in the event of accidental release during transportation, construction, or demolition. Incorporation of MNMs in pH- or temperature-responsive polymers can cause rapid hydrophobic conversion and resultant precipitation after their release into an aquatic environment, as encapsulation by nanomagnetite enables facile magnetic separation. Versatile MNMs can cover multiple functions to replace several MNMs without significant loss of functionalities (e.g., $TiO₂$ NPs as white pigment and $TiO₂$ coatings for light-transmittance control, self-cleaning, and superhydrophilicity), eventually decreasing the quantity of MNMs used in construction. Efforts to improve manufacturing processes should be initiated to increase production yields of NM-based construction products and highly promote their desirable properties with minimal generation of nanoscale wastes.

29.4.2 Application

In-depth studies should be carried out on the vulnerability of MNMs to redox reactions, corrosion and passivation, and photochemical and biological transformations encountered during the lifetime of nanoenabled products. The physical, chemical, and/or biological conversions may lead to modifications of MNMs' properties associated with their adverse biological effects and environmental mobility. Thus, it is important to identify the effects of physicochemical environmental parameters such as pH, salinity, and natural organic matter, and biological media compositions/metabolisms on the reactivity, distribution, bioavailability, and toxicity of MNMs.

Off-site fabrication, preassembly, and modularization of construction components containing MNMs in well-controlled conditions can minimize unwanted personal and environmental exposure. The effective longevity and projected life expectancy of MNMcontaining construction products under conditions encountered should be considered for sustainable applications, based on laboratory and field studies to predict their resistance to aging, abrasion, chemical corrosion, cracking, and weathering. Leaching tests should be done to assess the possibility that MNMs incorporated into construction materials (e.g., $TiO₂$ in self-cleaning exterior and pavements, QDs in photovoltaic cells, and CNTs in concrete) may undergo separation from the matrices in some damaging conditions (e.g., fire, water, wind, and flood), dispersing into the surrounding atmosphere or entering stormwater runoff.

29.4.3 Recycling/Disposal

Recycling of MNM-containing construction materials, which aims to reduce the consumption of raw MNMs and minimize MNM-containing wastes, requires various prerequisite steps, including the development of efficient strategies to extract and collect MNMs from complex matrices (with minimal modification of the pristine properties), characterization of spent MNMs and evaluation of their capacity for reactivation, and assessment of the applicability of the reclaimed MNMs in terms of their original functionalities.

Since collective efforts are still underway to establish regulatory frameworks to specifically address MNM disposal, there should be special considerations for safe MNM waste disposal and recycling procedures. In an effort to prevent potential secondary contamination through landfill clay liners to the underlying aquifer, barrier reinforcement will be recommended to prevent infiltration of NM leachate and resultant groundwater pollution. Product labeling to identify and trace MNMs and relevant guidelines are needed to ecoresponsibly dispose of and recycle waste products that include MNMs and waste MNMs themselves. Following disposal, appropriate interception and remediation approaches may need to be developed depending on the MNM source, release dynamics, and disposal scenario.

29.5 Conclusions

Due to the potential for enhancement in material properties and functionalities, application of nanotechnology in construction is expected to create intelligent materials and systems, present opportunities for energy savings, and enable environmentally responsible products, buildings, and construction activities. Smart, nanoenabled products can detect and respond to changes in indoor environmental conditions, providing useradapted control of key environmental parameters, e.g., dimming light and altering temperature and humidity. Nanosensor assemblies embedded in buildings and infrastructures can remotely monitor and assess their structural health and vulnerability. Self-healing materials, which are still in early stages of development, are capable of autonomous crack management to recover original mechanical properties (e.g., preventing crack development through slow release of a bonding agent from polymer capillaries embedded in the concrete matrices).

Use of MNMs for thermal insulation (e.g., $SiO₂$) NPs and aerogel) and light transmittance control (e.g., WO₃ NPs) can significantly contribute to energy conservation, considering that energy consumption by commercial buildings and residential houses (including heating, lighting, and air ventilation) accounts for approximately 40% of all energy used in the USA. Incorporation of MNMs such as fullerenes, CNTs, and graphenes [29.46, 47] advances energy conversion and storage systems including hydrocarbon-based fuel cells, thermo- and photovoltaic cells, batteries, and capacitors. Solar light activation of $TiO₂$ to generate ROS enables pollution-controlling and self-cleaning coatings, reducing energy associated with maintenance for surface-treated pavements, windows, and walls [29.26, 61,64]. Due to the improved resistance to abrasion, corrosion, fire, and fatigue, MNM-containing construction materials could possibly outperform conventional materials in terms of durability and longevity, indirectly reducing energy consumed to repair, restore, and replace damaged materials.

Applications of MNMs as alternatives to toxic components prevent environmental hazards through the potential discharge and exposure during manufacturing, transporting, construction and renovation, and disposal. The opportunities for material replacement include silver and iron oxide NPs for cadmium, cobalt, and lead as pigment in paint [29.12], silica NPs for poly-

chlorinated biphenyl (PCB) insulators $[29.14]$, TiO₂ NPs for perfluorochemicals as stain repellents [29.17], and CNTs for halogenated flame retardants [29.29]. QD-based light-emitting diodes (LEDs) [29.48, 49] and CNT- or ZnO nanowire-based sensors and actuators [29.187, 188] possibly mitigate hazards associated with accidental release of mercury used in fluorescent lamp bulbs, pressure gages, thermometers, and switches. MNM-containing products enable buildings and infrastructures to capture or exploit natural heat and light (e.g., heat-absorbing windows, solar panels, and energy coatings) [29.11, 32], eventually reducing carbon emissions associated with heating and ventilation. Use of MNMs allows structural materials to be lighter and thinner without a significant loss of the desirable properties, mitigating wasteful use of raw materials and enabling resource-efficient production in construction.

As there are growing concerns that use of MNMs for the development of new construction products could increase possible environmental risk, it is critical to understand their potential mobility, properties, and impacts in and across air, water, soil, and biota. Analytical methodologies to detect and monitor MNMs (separate from or incorporated into construction materials) at environmentally relevant concentrations within complex environmental media and characterize their chemical and morphological features remain underdeveloped. Assessment of long-term global exposure to MNMs used in construction needs to be conducted, as the current focus of the potential adverse health effects is confined to manufacturing and construction workers. Considering that constructed infrastructure coexists with the natural environment, ecodesign strategies to enhance the environmental compatibility of materials and environmentally responsible lifecycle management of MNMs to minimize their unwanted environmental impacts also need to be prioritized. Overall, despite the current expectations regarding the promising opportunities of MNMs in construction, there are immediate concerns among the academic and industrial communities about the negative environmental implications. This highlights the need to encourage proactive research including green design and manufacturing, use and disposal practices, and recycling and reclamation strategies to ensure the ecoresponsibility and sustainability of both the nanotechnology and construction industries.

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