SYNTHESIS AND DISPERSION MECHANISM OF NANOMATERIALS IN CEMENT-BASED COMPOSITES: A STATE-OF-THE-ART REVIEW

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Abstract- Nanomaterials have emerged as a promising avenue for enhancing the reinforcement of cementitious materials, revolutionizing the concrete industry. Incorporating nanoparticles into concrete has shown significant improvements in mechanical performance, including increased strength and resilience. This paper provides a comprehensive overview of recent studies on the synthesis and dispersion of nanomaterials in cementitious materials, encompassing graphene oxide, graphene, nano-titanium oxide, CNTs, nano-alumina, nano-clay, nano-kaolin, nano-silica, and nano-ferric oxide. The findings highlight the advancements in nanomaterial integration and their profound impact on concrete properties. Additionally, the review identifies the challenges associated with nanoparticle dispersion and discusses techniques such as ultrasonication and the use of surfactants to improve dispersion in cement composites, thereby enhancing mechanical and photocatalytic properties.

Keywords- Nanomaterials, Synthesis, Dispersion mechanism, Cementitious composites

1 Introduction

Nanomaterials have revolutionized the concrete industry, offering immense potential to enhance reinforcement in cementitious materials [1]. Incorporating innovative nanoparticles and fibers into concrete has resulted in significant improvements in mechanical performance, increasing strength and resilience. Nanomaterials such as nano-silica, nano-clay, carbon nanofibers, carbon nanotubes (CNTs), nano-titanium dioxide, graphene oxide, and nano-graphite platelets have been successfully employed to reinforce cementitious composites [2]–[7]. These nanomaterials have led to the development of cementitious composites with exceptional properties, including energy absorption and resistance to crack propagation. Challenges arise from agglomeration due to van der Waals forces, impacting the workability of cement; however, nanoparticles can fill voids, resulting in a dense microstructure and adding self-cleaning and air-purifying properties [8], [9].

Researchers have extensively investigated the integration of nanomaterials with cement-based composites to enhance their structural performance. Jamal et al. [10] studied the effect of synthesized nanomaterials such as nano-silica, nano alumina, graphene oxide, and carbon nanotube on the mechanical performance of concrete and found that the strength properties were significantly improved. Further, they recommended the dosages of nano-silica (1-4%), nano alumina (1-3%), graphene oxide (0.05-0.1%), and carbon nanotube (0.1-0.5%) for practical applications in the concrete industry. Similarly, Du et al. [11] found that the synergistic performance of nano-silica and nano-iron oxide significantly improved concrete performance and used the ultrasonication technique for uniform dispersion of nanomaterials. Nano-silica accelerates cement hydration and acts as a nucleation seed for calcium-silicate-hydrate (C-S-H), improving mechanical performance, workability, and durability [8], [9]. Nano-alumina enhances mechanical strength, with a small amount significantly increasing compressive resistance [12]. Nano-Fe_2O_3 has also shown promise in enhancing compressive strength at optimal dosages [13]. TiO_2 nanoparticles enhance the photocatalytic properties of concrete, enabling pollutant degradation [14]. Graphene family nanoparticles improve structural strength, robustness, and self-sensing capabilities [15], [16]. Carbon nanotubes offer low electrical resistance and self-sensing abilities, enabling strain detection for structural health monitoring systems [17], [18]. The overall performance of nanomaterials in cement-based composites primarily depends on their production techniques along with their homogenous and uniform dispersion within the matrix.

This review focuses on recent studies exploring the synthesis and dispersion of nanomaterials, including graphene oxide, graphene, nano-titanium oxide, CNTs, nano-alumina, nano-clay, nano-kaolin, nano-silica, and nano-ferric oxide, in cementitious materials. The condensed content provides a comprehensive overview of advancements in nanomaterial integration and their impact on concrete properties.

2 Comprehensive Examination of Research Endeavor

2.1 Synthesis of Nanomaterials

The synthesis of nanomaterials has been a dynamic field of research and development since the inception of nano-engineering in the 1960s. Nanoparticles have a greater impact on fillers compared to micro-based materials due to their smaller size, as stated by Gutierrez et al. [19]. According to their study, any substance can be converted into nanoparticles. The production process of nanoparticles significantly affects the integrity and composition of the base materials, and two methods have been established as shown in Figure 1 [18], [20]. One approach is the top-to-down method [21], while the other is the bottom-to-up method [22]. The choice of methodology depends on factors such as suitability, cost-effectiveness, and comprehension of nano behaviour [23]. Milling is a commonly employed top-to-down method, and the choice of milling technique is based on the accessibility and feasibility of the equipment required, as it allows for instant modifications exempt from the imperative of additional chemical or electromechanical equipment. The top-to-down method entails scaling down macro structures to the nanoscale while retaining their characteristics and molecular structural arrangement [24]. This is achieved through etching and mechanical attrition processes to reduce bulk materials into nanoparticles. Many large industries utilize this technique as it enables the production of affordable nanoparticles in large quantities and is simple to sustain due to the use of electromechanical equipment with minimal chemical modifications. The contemporary method in nanomanufacturing is a different name utilized for the top-to-down method. Even so, this approach may result in inconsistent or variable uniformity and quality of the final nanoparticles. Though, the characteristics of nanoparticles can be improved through modification of milling processes including the number and types of balls employed, milling speed, and types of jars used [21], [25]. Numerous nanoparticles, including nanograins, nanoalloys, nano quasicrystal line materials, and nanocomposites, have been produced via high-energy ball milling. This method was initially developed in 1970 by John Benjamin for obtaining oxides nanoparticles using superalloys. He used it to modify and reinforced an alloy product for elevated-temperature applications [26]. The distortion and shaping of particles during milling are influenced by factors such as plastic deformation, fracture, and cold welding. Additionally, milling involves mixing particles or components to develop new degrees in material structure. The resulting nanoparticles from the milling process often exhibit flake-like shapes, although enhancements may be made based on the choice of balls and milling method. Nonetheless, in the field of concrete, the predominant means of producing nanomaterials, including nano silica, nano clay, and nano alumina, involve bottom-up synthesis methods. The bottom-to-up techniques involve the production of materials at the molecular level, through fabrication or self-fabrication processes. It is additionally recognized as molecular manufacturing or molecular nanotechnology, encompassing applications such as chemical formulations and synthesis [26]. The bottom-up technique in chemical synthesis offers precise control and design of nanoparticles in terms of their size and shape. Unlike top-down techniques, this method results in more uniform and well-organized nanoparticle structures, with atoms or molecules arranged in an orderly and crystalline manner. Various methods such as chemical reactivity, optical absorption, and electronic conductivity can be employed in this technique [18], [27]. Notably, the bottom-up technique also allows for significant modifications in surface energies and morphologies, enabling size reduction and precise creation of surface atoms. This versatile technique finds broad applications, including enhancing catalytic capability, sensing capabilities, and developing innovative pigments and paints with self-healing and self-cleaning properties. However, it should be acknowledged that the bottom-up technique is primarily applicable in laboratory settings and may entail high operational costs, require specialized knowledge in chemical applications, and have limited applicability in certain contexts [28], [29]. Despite these limitations, the bottom-up technique remains highly effective in producing nanoparticles for cutting-edge biotechnology and electronic components applications, showcasing its potential for advanced nanomaterial manufacturing. Thus, it is evident that there are two viable techniques, with the bottom-up technique offering precise control and design capabilities, for manufacturing nanomaterials to create novel cement-based composites.

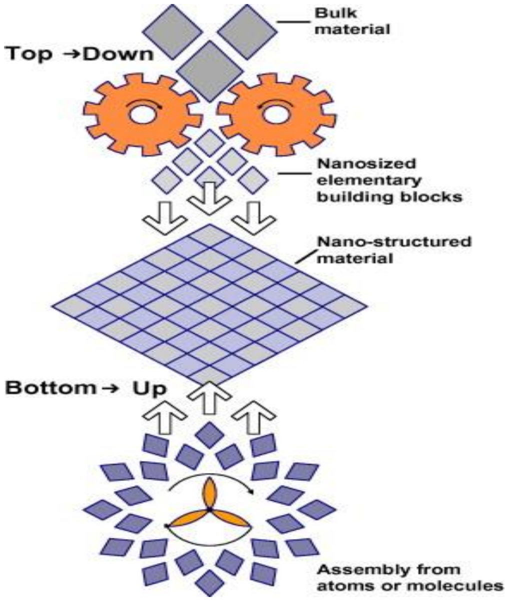

Figure 1. Nanomaterial production: top-down vs. bottom-up techniques [18]

2.2 *Dispersion Mechanisms of Nanomaterials*

Nanomaterials, characterized by their ultrafine particulates, high compaction, and greater surface area, are prone to agglomeration due to the strong van der Waals forces that affect their dispersion within cementitious composites [15]. Achieving adequate dispersion of nanoparticles is crucial for maximizing the capability of these additives and enhancing the performance of cementitious materials, but it remains a significant challenge in the field of cement composites [30]. Despite the importance of quantifying the extent of nanomaterial dispersion in cement matrices, there is currently no universally accepted technique for this purpose. Most research relies on indirect methods that evaluate the mechanical properties of cement composites to assess whether agglomeration has occurred. This is because non-uniform distributed nano additives in the matrix can form clumps, or flocs due to attractive electrostatic attraction, leading to detrimental effects on the mechanical characteristics of cement composites. For instance, achieving homogeneous dispersion of hydrophobic carbon nanotubes (CNT) in cement composites is particularly challenging [31], [32]. Rocha and Ludvig [32], found that CNT agglomeration and a decrease in the improved mechanical performance of cementitious material could happen if the CNT dosage in the matrix exceeds 0.05 weight percent (wt%). In their research, CNT was dispersed in a non-aqueous isopropanol medium using ultrasonication for 2 hours, without undergoing surface treatment to improve its dispersibility.

Covalent and non-covalent techniques are commonly utilized to functionalize carbon nanotubes (CNTs) to promote their dispersion and prevent aggregation [31], [33]. Chemical functionalization entails introducing functional groups onto the surface of CNTs, consequently enhancing their binding capacity to the cement matrix and improving their dispersion in cement composites. However, some researchers have noted that this approach may also weaken the mechanical properties of CNTs, thereby potentially compromising the performance of the composites [34]. As a result, non-covalent functionalization techniques that involve the use of other nanomaterials in combination with CNTs or surface treatments with surfactants, such as superplasticizers, have gained popularity [34]–[36]. For instance, Meng et al. [29] reported that incorporating polycarboxylate ether superplasticizer as a surfactant can enhance the dispersion of multi-walled CNTs (MWCNTs) and reduce their tendency to agglomerate in water. The dispersion process of MWCNTs with the addition of cyclodextrin-modified polycarboxylate superplasticizer, demonstrates a twin phenomenon of electrostatic repulsion and steric hindrance, preventing aggregation of CNTs. Additionally, Stynoski et al. [33] found that the dispersion stability of CNTs was significantly improved after functionalization with nano silica.

In the realm of cement composites, superplasticizers are commonly employed as dispersants for nanomaterials, as reported in various studies [37], [38]. Perez-Nicolas et al. [37] investigated the zeta potential of nano-additives distribution and found that limited water-reducing agents (based on naphthalene) revealed effective dispersion of nano-TiO_2 when mechanically stirred for 20 minutes in water. The zeta potential analysis revealed that the amalgamation of this water-reducing agent and nano-TiO_2 resulted in the most negative value, indicating strong electrostatic repulsion. Furthermore, Qian et al. [38] studied the compatibility of nano clay with polycarboxylate ether superplasticizer and determined that there was an optimal dosage of polycarboxylate ether for a fixed amount of nano clay, which facilitated favourable dispersion in cement paste and prevented agglomeration. Specifically, a mixture of 0.2 wt% polycarboxylate ether and 0.5 wt% nano clay resulted in notable advancements in both the thixotropy and yield stress properties of the cement matrix. Ultrasonication is a distinct technique commonly employed to improve the uniform distribution of nano-additives in cement composites, often in conjunction with the use of a superplasticizer as a surfactant [38], [39] [15]. Ahmad and Qureshi [15] utilized a natural surfactant, namely acacia gum (AG), for the dispersion of nano graphite platelets (NGPs) as shown in Figure 2. They maintained a constant quantity of NGPs while varying the amount of AG, with NGPs to AG ratios ranging from 1:0 to 1:1 in intervals of 0.2 as depicted in Table 1.

Table 1: Variation of NGPs to AG ratios for dispersion [13]

Sample Type	**NGPs: AG**
S1	1:0
S2	1:0.2
S3	1:0.4
S4	1:0.6
S5	1:0.8
S6	1:1

Each ratio of NGPs to AG was subjected to mechanical sonication for 45 minutes to achieve a dispersion solution, followed by characterization using ultraviolet-visible (UV-Vis) spectroscopy. The optimal dosage was found to be an NGPs/AG ratio of 0.6:1, based on the maximum light absorbance observed during UV-Vis spectroscopy. To assess the photocatalytic properties of various cement samples, Yousefi et al. [39] studied the dispersal of nano-TiO_2 in cement mixtures, comparing the impact of manual stirring and sonication. Their findings revealed that without ultrasonication, significant agglomeration of nano-TiO_2 occurred. Furthermore, ultrasonic dispersion of the nano-TiO_2 improved the photocatalytic capabilities of the cement samples.

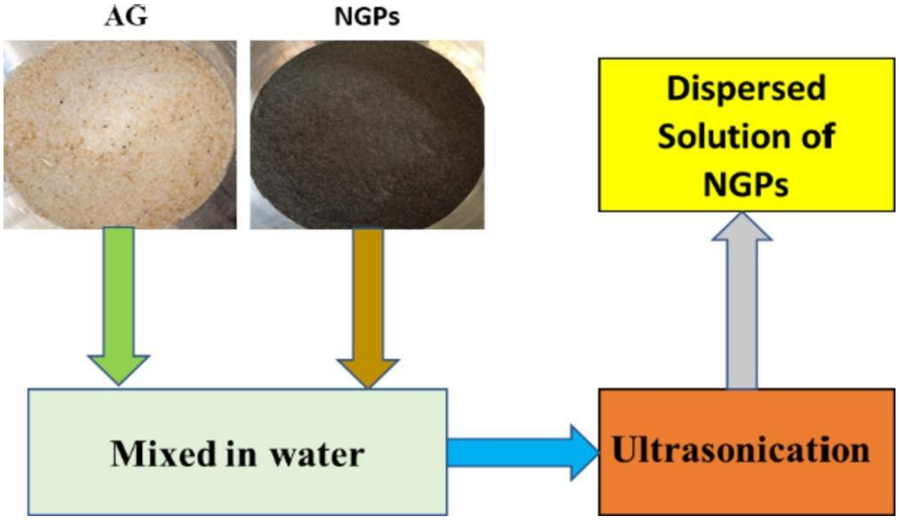

Figure 2: Dispersion of NGPs with acacia gum (AG) as a natural surfactant followed by 45 minutes of ultrasonication [13]

3 Conclusions

Nanomaterials have revolutionized the material's world by reinforcing the matrix of the composite at the nano level, thereby introducing enhanced mechanical and durability resilience in cement-based composites. The effectiveness of nanomaterials primarily depends on their production techniques and dispersion mechanisms. The following conclusions were drawn based on the review of the literature:

1 Nanoparticles can be synthesized using top-to-down and bottom-to-up methods. The top-to-down method enables large-scale production but lacks precise control and design capabilities. On the other hand, the bottom-to-up technique offers precise control and design but may have higher costs and limited applicability. Both methods have their advantages and are used in different contexts, with the top-to-down method being more common in industries and the bottom-to-up technique more prevalent in laboratory settings.
2 The effectiveness of nanomaterials in mitigating the degradation of cementitious composites largely depends upon the dispersion of nanomaterials in CBMs. Surfactant use, ultrasonic application, and functionalization of nanomaterials are frequently used applied methods to disperse nanomaterials.
3 Achieving proper dispersion of nanoparticles in cementitious materials is challenging due to agglomeration and quantifying nanomaterial dispersion lacks a universally accepted technique. Future, research work might be recommended to be carried out to establish an innovative approach for uniform and homogeneous dispersion of nanomaterials.

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