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Biomimetic superhydrophobic surface of concrete: Topographic and chemical modification assembly by direct spray

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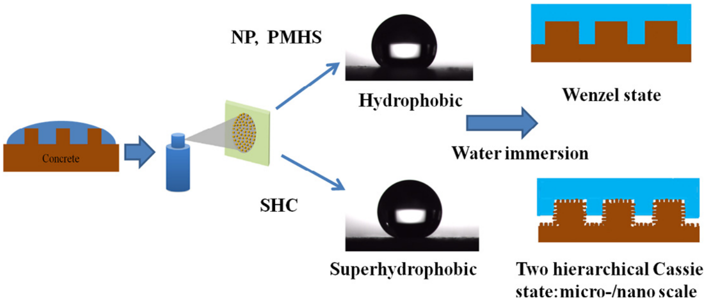
HIGHLIGHTS

- A superhydrophobic concrete was fabricated by a direct spraying method.
- Microstructure and surface chemical properties was simultaneously modified.
- A hierarchical surface was induced by the agglomeration and reaction of NS and PMHS.

GRAPHICAL ABSTRACT



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ABSTRACT

Concrete is an inherently multi-scale hydrophilic composite. Superhydrophobic surfaces have not been created solely by using chemical modification to reduce surface energy. A superhydrophobic concrete surface was fabricated by direct spraying nano-silica gel functionalized by low surface-energy surfactants to simultaneously modify the inherent multi-scale microstructure and surface chemical properties. The newly modified microstructures were characterized by scanning electron microscopy (SEM) and digital holographic microscopy (DHM) to facilitate an understanding of the effects of micro- and nanoscale topological features on the super-wetting properties. The superhydrophobic and self-breathing properties of the modified surface were confirmed by its large contact angle ($CA = 162° \pm 3°$), small slide angle ($SA = 5° \pm 1°$) and carbonation depth measurements. The chemical bonding between hydrophobic functional group grafted with nano-silica and cement hydration products, as well as the interface hydration of nano-silica in an alkaline environment, are estimated by Fourier transform infrared spectroscopy (FT-IR) and X-ray diffraction (XRD).

1. Introduction

Concrete is now the largest and most widely used building material in the world, and is the most-consumed resource by humans besides water. Due to the chemical components and morphology of hydration productions, such as $Ca(OH)_2$ and C-S-H gel [1,2], Concrete is a porous hydrophilic material [3,4], and water ingress and aggressive ion transport in its porous microstructure are two key issues that influence its durability. In each of these processes, water acts as a transport medium for aggressive ions such as CO_2, chloride, and sulfate ions, or is itself a reactant in a degradation reaction, such as in alkali–silica reactions or freeze-thaw deterioration [4]. Therefore, the most effective way to increase the durability and prolong the service life of a concrete structure is to prevent water transmission in it.

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Superhydrophobic materials have received more attention because of their advantages in various self-cleaning and anti-icing applications [5,6]. Natural organisms have inspired the design of superhydrophobic materials. Hydrophobic materials commonly exist on the surfaces of anti-wetting plants and animals. For example, plant cuticles are generally covered by epicuticular wax or other substances mainly consisting of straight-chain aliphatic hydrocarbons with different substituted functional groups. These chemical shields effectively decrease free surface energy [7–9]. In addition to their chemical composition, surface structure is also a key factor in surface wetting conditions. Lotus leaves exhibit low adhesion, superhydrophobicity, and self-cleaning properties (Lotus effect, Fig. 1d), due to randomly distributed micro-papillae covered by branch-like nano-structures that create the micro- and nanoscale hierarchical roughness [10,11].

Until now, superhydrophobic concrete surfaces have been created by applying to them siloxane-based emulsions with either an integrated micro-texture [12] or with embedded hierarchical structure [13,14]. In these methods, a fresh microroughness was produced during mixing, and thus, they cannot be applied to existing structures. A top-down multilayered coating method has also been used to create superhydrophobic concrete. In this method, a water repellent layer was built on a pre-sprayed binding layer made of epoxy [15]. In these studies, the morphology and surface chemistry were modified separately. Some specific processes remain complicated and not practically applicable. Furthermore, precoating substrate materials are usually airtight, resulting in a high risk for swelling and flaking. Therefore, the development of simple, cost-effective, breathable, and scalable superhydrophobic surfaces would facilitate applications requiring enhanced durability in civil engineering.

The contact angle (CA, θ) is often used to quantify the wetting condition of a water droplet on a solid surface. The wetting state can be hydrophilic ($\theta > 90^\circ$) or hydrophobic ($\theta < 90^\circ$). Additionally, the wetting state can be categorized as superhydrophilic ($\theta < 10^\circ$) and superhydrophobic ($\theta > 150^\circ$ and slide angle, SA $< 10^\circ$) [16]. The CA can be calculated using Young's equation [17] with the assumption that the solid surface is glazed, chemically homogeneous, and undissolved. However, in most realistic cases, solid surfaces are inevitably coarse and chemically heterogeneous. Hydrophobic wetting states on coarse surfaces usually present two different modes, as shown in Fig. 1b and 1c. For the mode in Fig. 1b, water has completely infiltrated the rough grooves, which is called homogeneous wetting and can be described by the Wenzel model [18,19]. In Fig. 1c, when air is trapped between the water droplets and surface, the mode is termed heterogeneous wetting, which can be described by the Cassie model [20]. Typically, surfaces described by the Wenzel model are 'sticky' in that water droplets tend to adhere better than a flat counterpart, while those following the Cassie–Baxter model are 'slippery' in that water droplets tend to roll off more easily than a flat equivalent [21,22].

Overall, previous studies have shown success in fabricating superhydrophobic surfaces with two types of techniques: creating sufficient roughness on the hydrophobic surfaces, and modifying a rough surface with molecules of low free energy. Concrete is an inherently multi-scale and multi-phase composite [4], and a one of its remarkable features is that its constituents and pore structure span several orders of magnitude from nanometer to micrometer scales. This feature may be of special interest for creating biomimetic super-wetting surfaces. However, until now, superhydrophobic properties have not been realized on concrete surfaces solely by chemical modification of surfaces with low surface energies. Therefore, the physical and chemical modification of concrete surfaces must be further studied.

Given this context, we present a simple technique to fabricate superhydrophobic concrete by directly spraying chemically-modified nanoparticle suspensions to simultaneously modify the original physical hierarchical microstructure and chemical properties of a concrete surface. Wetting ability was characterized by water contact angle (WCA) and sliding angle (SA) tests. The newly modified microstructure was characterized by scanning electron microscopy (SEM) and digital holographic microscopy (DHM). Interface chemical reactions were characterized by Fourier transform infrared spectroscopy (FT-IR) and X-ray diffraction (XRD). Mechanical soundness and self-breathing were evaluated by cyclic tape-peeling and carbonation tests, respectively.

2. Experimental section

2.1. Materials

N-propyltrimethoxysilane (NP) and polymethyl-hydrogen siloxane oil (PMHS) obtained from Perfectly Advanced Material of Chemical Inc., were used as low surface energy surfactants, and acidic Ludox colloidal silica nanoparticles (NS, 25 wt% SiO_2 suspension in water, pH = 4.0), with an average particle size of 70 nm, were obtained from Nanjing HT.nano Co., Ltd., to induce the micro-roughness. Deionized water (DI water) was employed as the dispersive solvent. A Chinese standard graded 52.5 P II-type Portland cement was used. Standard sand with a maximum particle diameter of 4.75 mm was mixed with tap water to produce mortar and form concrete specimens.

2.2. Fabrication of SHC coating, cement paste and mortar

To prepare the superhydrophobic coating (SHC), acidic Ludox was first mixed with DI water and stirred for 30 min at 25 ± 2 °C, using a magnetic stirrer in an oil bath. Then, the NP was added to the solution and stirred for 5 h. PMHS was then added and the solution was stirred for another 3 h. The produced solution was diluted (5 wt%) with DI water and then spread on the mortar surface. The final coating formed via self-assembly during the natural drying process.

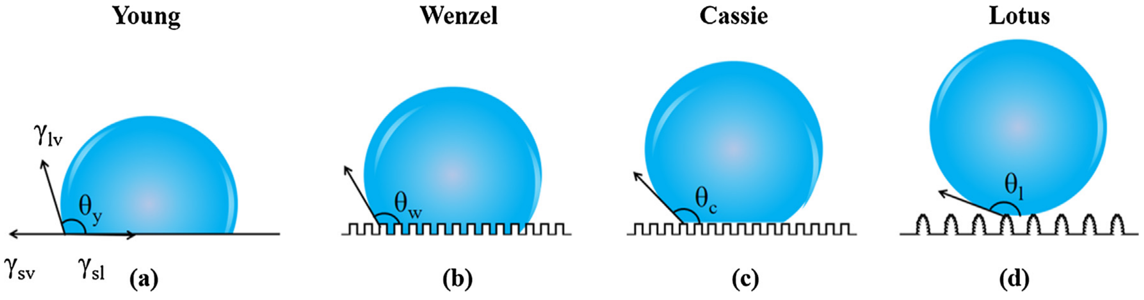

Fig. 1. (a) Liquid droplet on a smooth surface. (b) liquid droplet in the Wenzel state. (c) liquid droplet in the Cassie state. (d) Lotus effect.