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Nano-materials enhanced protectants for natural stone surfaces

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Abstract: Natural stones undergo wet weathering, bowing and dissolution and suffer irrevocable degradation. Self-cleaning is an effective approach to stone protecting. Herein, nanomaterial enhanced protectants for Marble, Qingshi and Hedishi was developed. Inherent microscale cracks and holes exist on the polished natural stone surfaces. When modified by commercial protectant, 101S, the surfaces showed hydrophobic but not superhydrophobic. Superhydrophobicity was achieved through modification by 101S emulsions containing Al₂O₃ and SiO₂ nano-powder. Meanwhile, the cracks and holes were reserved. The principle of the protectants prepared in this work is permeation and consolidation on the stone surfaces as well as the inner surfaces of the cracks and holes. The reservation of the micro cracks and holes on the stone surfaces is important since the breathability of the stones is remained. The superhydrophobic surfaces showed good thermal stability below 250 °C.

Keywords: Natural stone, nanomaterial enhanced protectant, hierarchical structure, superhydrophobicity

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Introduction

Natural stones are one of the earliest materials employed by human beings for architecture, sculpture, decoration and so forth due to the high earth-abundance, robustness and harmless. Stones undergo wet weathering, bowing and dissolution and suffer irrevocable degradation [1, 2]. In ambient environment, rain has a pH value that can vary from 5.6 in normal conditions where the acidity results from ambient CO₂, to 4.5 in areas polluted by SO₂ and NO_x [3]. The dissolution rate of salts such as calcite and magnesite increases with the decreasing of the pH level [4]. The invading of water and acidic species through the micro cracks and holes on the stone surfaces is one of the most harmful factors due to the crystallization-dissolution cycles of the soluble salts in the stones which induce tensions inside the porous matrix, thus accelerating its decay [3, 4].

Two strategies have been employed in the field of stone conservation, *i.e.* surface protection and consolidation [5-11]. The consolidation treatment is aimed at limiting the stone decohesion due to decay patterns, and for this reason it penetrates deeply in the material's porosity network [12-15]. For the surface protection strategy, the treatment acts on the cortical portion of the material on which it is applied and surface water-repellent treatments had been considered [16-18]. Treatments of coating totally-enclosed films of paraffin, acrylic, acryl-siliconic, epoxy resin and fluorinated polymers on stone surfaces had been generally adopted [19-27]. Although these films can effectively isolate the pollution sources, the breathability of the stones is greatly weakened due to the blocking of the gas channels existed on the stone surfaces. As a consequence, moistures inside stones will experience cycles of crystallization, melting, thawing which also accelerate the decay of the stones with the variation of the air temperature. Especially in heavily salt-laden cases, simple application of water

repellent can even increase the deterioration rate of the treated stones, leading eventually to flake, scale, and cracking [28]. Moreover, the durability of this kind of films is limited due to the relatively weak adhesion between the films and the stone substrates. Hence, protectants combine water repellence, breathability maintaining and adhesion is in need.

Self-cleaning construction provides another approach to natural stones protection due to the great water repellence and breathability maintaining possibility [16, 18]. Self-cleaning (or superhydrophobicity) can be obtained by a combination of surface micro- and nano-structures and low-surface-energy chemicals derivatization [29, 30]. In the surface pattern strategy, inherent micro roughness existed on the polished natural stone surfaces, and addition of nanoscale materials in protectants is effective for nanoscale roughness construction. Manoudis *et al.* added silica nanoparticles in a commercial protectant of polyalkylsiloxane and water static contact angle (SCA) of 160° on Marble surfaces was obtained [12]. Tang *et al.* prepared Marble protectants by adding nano CaCO_3 nanoparticles in copolymer of epoxy and acrylate [31]. Marble protectants had been prepared by Zhang *et al.* using nanoscale CaCO_3 nanoparticles [32, 33]. Performances of robustness, abrasion, contamination resistance, weathering resistance, and durability of natural stones protected by nano materials enhanced protectants (NMEPs) have been greatly improved. Meanwhile the antibacterial and antifungus properties were improved as well.

In present work, an approach to NMEPs was developed, and the corresponding protect films were formed by permeating and consolidating on stone surfaces as well as the inner surfaces of the micro cracks and holes underneath natural stone surfaces. Al_2O_3 and SiO_2 nano-powder were added in a commercial water resistant coating, 101S, to prepare protectants. Protectant films were formed by a dip-coating on natural

Marble, Qingshi and Hedishi stone surfaces as well as the inner surfaces of cracks beneath the stone surfaces of several micrometers through permeating and consolidating. Water resistance of the stone surfaces was greatly improved without sacrificing the breathability of the stones. Superhydrophobicity was achieved with water SCA of bigger than 150° and hysteresis angles (HAs) less than 20° . The superhydrophobic surfaces showed good thermal stability below 250°C .

Experimental

Materials and sample preparation

Bulk natural stones of Marble, Qingshi and Hedishi stone were obtained from local area of Dali prefecture, Yunnan province, China. Commercial water resistant coating, 101S, was obtained from Solmont Technology (Shenzhen) Co., Ltd. Al_2O_3 (99.9%, 30 nm) and SiO_2 (99.5%, 15 nm) nano-powders were obtained from Shanghai Macklin Biochemical Technology Co., Ltd and Shanghai Aladdin Bio-Chem Technology Co., Ltd, respectively.

Bulk natural stones were first cut into $50\text{ mm} \times 15\text{ mm} \times 10\text{ mm}$ coupons. Double faces of each coupon were primary polished by 400[#] grinding wheels and pasted on a glass slide by UV curing adhesive. Natural stone surface samples were prepared by sequentially polishing the coupons by 1200[#] grinding wheels and polishing cloth followed by a 15 min ultrasonic washing in ethanol and DI water ($18.2\text{ M}\Omega$, MilliQ) respectively to remove native oxide and contaminations. The samples were dried in a drying box for 24 h under 40°C followed by a 1.5 min uv-ozone cleaning prior to treatment.

Nano-powders were heated under 100°C on a heating plate for 1 h to eliminate moistures prior to use. The 101S emulsions was obtained by adding a certain amount

of nano-power followed by a 5 periods alternated ultrasonic dispersion under 28 KHz and 40 KHz for 5 min and a magnetic tiring for 2.5 h, respectively. The cleaned natural stone surface samples were immersed into the 101S emulsion for 14 h and dried at 40 °C for 24 h. The preparation diagram of the samples is shown in Fig. 1.

Figure 1 Schematic diagram of the preparation and modification of the natural stone surfaces by nano-powder enhanced 101S hydrophobic agent

Surface characterization

X-ray diffraction (XRD, EMPYREAN, PANalytical, NL with Cu K_α radiation, $\lambda=1.5406$ Å) was employed to analyze the components of the natural stones. Natural stone surfaces were characterized with water contact angle measurements, scanning electron microscopy (SEM). Readers are referred to the literature for the detailed procedures [34, 35]. The thermal stability of the superhydrophobic stone surfaces was evaluated by tests of annealing detailed in the following section.

Results and discussion

XRD patterns of the three natural stones are shown in Fig. S1 and corresponding main components of the stones are summarized in Table S1 of the supporting information appendix (SI Appendix). The dominant component of Marble is CaCO_3 , while that of

Qingshi and Hedishi is SiO₂.

Water repellence of 101S

Water contact angles on glass and stone surfaces before and after modification by 101S were summarized in Table 1. In order to evaluate water resistance of 101S, and to minimize the affection of surface roughness, water wettability of blank and 101S coated glass surfaces were surveyed. Water SCA of 62.6° was obtained on hydrophilic blank glass surface. It increased to 118° after coated with 101S, while the hysteric angle (HA) is 24.9°. The water repellence component of 101S is perfluoroalkylpolyether (PFPE) in which –CF₂ and –CF₃ are the water-repellent functional groups. The result agrees with the maximum contact angle of 120° what can be obtained on a flat surface derived by groups of –CF₂ and –CF₃.³⁶

Table 1 Water contact angles on glass and natural stone surfaces before and after 101S modification

Surface	Blank		With 101S modification		
	SCA (°)	SCA (°)	ACA (°)	RCA (°)	HA (°)
Glass	62.6	118.0	128.0	103.1	24.9
Marble	53.0	139.3	148.0	114.0	34.1
Qingshi	38.3	137.0	141.0	93.6	47.3
Hedishi	47.0	133.6	137.9	111.0	26.9

All polished stone surfaces are hydrophilic with water static contact angles of 53°, 38° and 47°, respectively. After modified by 101S, the SCAs increase to 139°, 137° and 134°, meanwhile the HAs are 34°, 47° and 27°, respectively. Numerous microscale holes and cracks existed on and beneath the natural stone surfaces. Surface tension of 101S is 14 mN/m (at 20 °C). It can easily permeate into the micro cracks and holes and consolidate on the inner surfaces of these cracks and holes as well as on the stone surfaces. Microscale roughness enhanced the water repellence. However, it

has some discrepancy with superhydrophobicity which requires water SCA exceeds 150° and the sliding angle is less than 5° (or the HA is less than 20°). Superhydrophobicity of stone surfaces cannot be achieved by 101S modification means it can only be achieved by a combination of low-surface-energy chemicals and surface micro- and nano-structures.

Surface wettability

Wettability of stone surfaces modified by Al_2O_3 nano-powder added 101S. The concentrations of the Al_2O_3 nano-powder added in 101S are 0.1 mg/mL, 0.5 mg/mL, 1 mg/mL, 1.5 mg/mL and 2 mg/mL. Figure 2a-c shows variation of water SCAs, advancing contact angles (ACAs) and receding contact angles (RCAs) on the modified stone surfaces with the concentration of the Al_2O_3 nano-powder. For modified Marble surfaces (Fig. 2a), when 0.1 mg/mL was added into 101S, water SCA is 166.5° , significantly increased compared with that of 139.3° obtained on the surface modified by nanomaterial-free 101S. Meanwhile, the HA decreases from 34.1° to 11.2° . The SCA continuously increases to the maximum value of 171.2° with the concentration to 1.5 mg/mL. When the concentration of Al_2O_3 nano-powder reaches to 2.0 mg/mL, the SCA decreases to 166.8° . For the HA, the minimum value obtained when the concentration of Al_2O_3 nano-powder is 0.5 mg/mL, it increases to 14.6° with the concentration of Al_2O_3 nano-powder to 1.5 mg/mL, and then decreases to 12.1° . On the modified Qinshi surfaces, the SCA reaches to 166.8° when 0.1 mg/mL Al_2O_3 nano-powder was added to 101S. The SCA first decreases and then increases with the concentration of Al_2O_3 nano-powder thereafter. The maximum SCA of 169.2° was obtained when the concentration of Al_2O_3 nano-powder is 1.5 mg/mL. The HA varies in the range of 11.3° to 14.6° with the concentration of Al_2O_3 nano-powder.

The modified Hedishi surfaces present excellent water repellence when 0.5 mg/mL Al_2O_3 nano-powder was added in 101S, and SCA of 170.3° was obtained in this case; meanwhile, the HA is 16.8° , slightly bigger than those obtain on Marble and Qingshi surfaces. The SCA and HA decrease with the concentration of Al_2O_3 nano-powder in the range of 0.5 mg/mL to 2.0 mg/mL. Superhydrophobicity was achieved in all cases.

The optimal SCAs and corresponding concentration of Al_2O_3 nano-powder are summarized in Figure 2d. The optimal SCA on modified Qingshi surface is relatively smaller and the corresponding concentration of Al_2O_3 nano-powder is bigger than those of modified Marble and Hedishi surfaces. The result is related to the difference of the surface pattern between Qingshi and Marble (and Hedishi) which will be detailed later.

Figure 2 Variations of water contact angles on (a) Marble, (b) Qingshi and (c) Hedishi surfaces modified by the as-prepared protectants with the concentration of Al_2O_3 nano-powder, and the optimal water SCAs on stone surfaces corresponding to

concentration of Al_2O_3 nano-powder (d)

Wettability of stone surfaces modified by SiO_2 nano-powder added 101S. Nano SiO_2 powder was used as another additive to 101S. Variations of water contact angles as a function of the concentration of SiO_2 nano-powder are shown in Figure 3a-c. Water repellence of the modified Marble surface was significantly improved when 0.1 mg/mL SiO_2 nano-powder was added into 101S, *i.e.* the SCA increased from 139.3° in the SiO_2 free case to 166.7° , while the HA decreased from 34.1° to 11.2° , presenting superhydrophobicity. Superhydrophobicity was maintained in the concentration range of SiO_2 nano-powder of 0.5 mg/mL to 2 mg/mL with a slightly increase of the HA (Fig. 3a). For the Qingshi surfaces, the variations of the SCA and ACA are similar to those on Marble surfaces. However, the RCA is relatively small in the SiO_2 nano-powder concentration cases ranging from 0.1 mg/mL to 0.5 mg/mL. Superhydrophobicity was achieved when the concentration reaches to 1.0 mg/mL. The variation of the water contact angle on modified Hedishi surfaces is similar with that on Marble surfaces. In the whole concentration range of SiO_2 nano-powder surveyed in this work, superhydrophobicity is well maintained.

The optimal SCAs and corresponding concentration of SiO_2 nano-powder are summarized in Figure 3d. Similar to the surfaces modified by Al_2O_3 nano-powder added 101S, the optimal SCA on modified Qingshi surface is relatively smaller and the corresponding concentration of SiO_2 nano-powder is bigger than those of the modified Marble and Hedishi surfaces. We suggest that the result is induced by the different pattern of the Qingshi surface from those of Marble and Hedishi surfaces.

Figure 3 Variations of water contact angles on (a) Marble, (b) Qingshi and (c) Hedishi surfaces modified by the as-prepared protectants with the concentration of SiO_2 nano-powder, and the optimal water SCAs on stone surfaces corresponding to concentration of SiO_2 nano-powder (d)

It is demonstrated that water repellence of the surveyed stone surfaces was significantly improved by addition of Al_2O_3 and SiO_2 nano-powder in 101S and superhydrophobicity was achieved in all the cases except for Qingshi surfaces in which superhydrophobicity was achieved only the concentration of SiO_2 nano-powder exceeds 1.0 mg/mL. Numerous micro holes and cracks existed on and beneath the natural stone surfaces. 101S emulsion permeated into the holes and cracks and consolidated on the inner surfaces to form a layer of water resistant film. The addition of Al_2O_3 and SiO_2 nano-powder provides nanoscale roughness on the surfaces. Hence, superhydrophobicity was achieved by functions of the 101S and the nanoscale roughness together with the inherent microscale roughness on the stone surfaces.

Mechanism of the water repellence

Figure 4 shows SEM images of Marble surfaces and profiles before and after modified by the as-prepared protectants. Nonuniform micro cracks and holes exist on the polished blank Marble surface. The width of the cracks as well as the diameter of the holes is in the range of several hundred nanometers, and the length of cracks is mainly several micrometers (Fig. 4a). The depth of these cracks and holes is ranging from nanometers to micrometers (Fig. 4b). The micro cracks and holes almost maintain unchanged after 101S modification (Fig. 4c-d). During the modification by 101S, the liquid state protectant stay on the Marble surface and permeated into the cracks and holes, and protective film formed after solidification of the 101S. The morphology of the Marble surfaces didn't change when covered by the protective film. That is why the SCA increased from 53° to 139.3° instead of 118° which obtained on the 101S covered smooth glass surface. In other word, the microscale roughness on the Marble surface enhanced the water repellence. However, the corresponding hysteric angle of 34.1° is relatively big, much below the standard of superhydrophobicity. Hence, only microscale roughness on the Marble surface is fall short of the structural request of the superhydrophobicity.

When 2 mg/mL Al_2O_3 nano-powder was added into 101S, nanoscale embossments dispersed on the microscale pattern of the Marble surfaces (Fig. 4e-f). Thus, micro-nano structure was constructed. The micro-nano roughness and the low surface energy of 101S provide an approach to superhydrophobicity. The cracks and holes were maintained except a little size decrease after modification. It is important because stones will breathe through the cracks and holes in ambient environment, *i.e.* air and moistures outer and inner the stones can exchange through these cracks and holes and the possible breakdown of the stones induced by ambient temperature will

be decreased.

The present of 0.5 mg/mL SiO₂ nano-powder addition is similar to that of Al₂O₃ nano-powder except a little difference of the morphology, *i.e.* the size of the embossments are bigger than that induce by Al₂O₃ nano-powder. The cracks and holes were also maintained (Fig. 4g-h).

SEM images of Qingshi and Hedishi surfaces are shown in Figure S2 and S3 of the SI Appendix. The morphology of Hedishi surfaces is similar to that of Marbles while the morphology of the Qingshi surfaces presents step-like or fish scale like morphology, and cracks and holes are not distinct. The unique morphology is the reason of the difference request of the nano-powder concentration to superhydrophobicity from that of Marble and Qingshi.

Figure 4 SEM images of blank (a&b), and modified by 101S (c&d), 101S emulsion contain 1.5 mg/mL Al_2O_3 nano-powder (e&f), and 0.5 mg/mL SiO_2 nano-powder (g&h) Marble surfaces and profiles, respectively

Based on the models of Wenzel and Cassie [37-40] and the morphology of the stone surfaces above-mentioned, a conclusion that Cassie state of water droplets stay on the superhydrophobic stone surfaces can be drawn. The corresponding fractions of

the solid in contact with the liquid droplet are summarized in Figure 5. The average fraction is about 5%, which is a receivable value of droplets in Cassie-Baxter state when contact with a solid surface [34, 35, 41]. The micro/nanoscale hierarchical structures can trap a large amount of air, which can prevent the penetration of water into the grooves and bestow superhydrophobicity of the surfaces.

Figure 5 Fractions of the modified stone surfaces in contact with water droplets calculated based on the Cassie model

Thermal stability of the superhydrophobic surfaces

In order to survey the thermal stability of the as-prepared superhydrophobic surfaces, samples of Marble, Qingshi and Hedishi surfaces modified by 101S containing 1.5 mg/mL, 0.5 mg/mL and 2 mg/mL Al₂O₃, and 1.5 mg/mL, 1 mg/mL and 2 mg/mL SiO₂ nano-powder were annealed at 100, 150, 200, 250 and 300 °C for 15 min on a hot plate in air, respectively. After natural cooled to room temperature, the samples were subjected to water contact angle measurements.

Figure 6 shows water CAs of the control (without annealing) and the annealed surfaces. The ACAs and SCAs of the samples maintained almost unchanged below 250 °C and decreased sharply when the temperature is higher than 250 °C. The RCAs experienced a period of increase below 200 °C and then decrease thereafter. The

bigger RCAs rose in the period of 150 – 200 °C. The surfaces became hydrophilic when annealed at 300 °C, a reflection of decomposition of the 101S. The results agree with the thermal stability of surfaces modified by fluorinated low surface tension chemicals, indicating the good thermal stability of the as-prepared superhydrophobic surfaces [34-36].

Figure 6 Variation of water CAs as a function of temperature of the as-prepared superhydrophobic surfaces of Marble, Qingshi and Hedishi surfaces modified with 101S emulsion containing 1.5 mg/mL, 0.5 mg/mL and 2 mg/mL Al₂O₃ (a-c), and 1.5 mg/mL, 1 mg/mL and 2 mg/mL SiO₂ nano-powder (d-f), respectively.

Conclusions

Inherent microscale cracks and holes exist on the polished natural Marble, Qingshi and Hedishi surfaces. When modified by commercial protectant, 101S, the surfaces showed hydrophobic but not superhydrophobic. Superhydrophobicity of the natural stone surfaces was achieved through modification by 101S emulsions containing Al₂O₃ and SiO₂ nano-powder. Meanwhile, the cracks and holes were reserved.

The nano-powder provided nanoscale embossments on the inherent microscale structures on the natural stone surfaces to construct micro-nano hierarchical roughness

which is the structural base of the superhydrophobicity. The principle of the protectants prepared in this work is permeation and consolidation on the stone surfaces as well as the inner surfaces of the cracks and holes. The reservation of the micro cracks and holes on the stone surfaces is important since the breathability of the stones can be remained. The superhydrophobic surfaces showed good thermal stability below 250 °C and damaged with the annealing temperature elevation thereafter.

Nano-powder addition into water repellence protectants or nano enhancement of repellence protectants provides an easy and effective approach to self-cleaning (superhydrophobicity) of natural stone surfaces which will provide an avenue to industrial production for stone surface protection.

Abbreviations

SCA: Static contact angle; ACA: Advancing contact angle; RCA: Receding contact angle; HA: Hysteresis angle; NMEPs: Nano materials enhanced protectants; SEM: Scanning electron microscopy; XRD: X-ray diffraction

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Authors' contributions

ZX and ZQ: Methodology, Data curation, Original draft preparation. ZQ and B: Visualization, Investigation. DQ and RH: Supervision. YM: Validation, Writing-Reviewing and Editing. All authors read and approved the final manuscript.

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Availability of data and materials

The datasets used and analyzed during the current study are available from the corresponding author on reasonable request.

Competing interests

The authors declare that they have no competing interests.

Ethics approval and consent to participate

Not applicable.

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Supporting Information

Nano-materials enhanced protectants for natural stone surfaces

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Section 1. Components of natural Marbel, Qingshi and Hedishi stones

Figure S1 XRD patterns of the natural Marble, Qingshi and Hedishi stone samples

The dominant component of Marble is CaCO_3 , while that of Qingshi and Hedishi is SiO_2 . The corresponding locations of the components are summarized in Table S1.

Table S1 Dominant components of natural Marbel, Qingshi and Hedishi stone samples and the corresponding locations in XRD patterns.

Stone	component	Location (2θ)
Marble	CaCO_3	23.05, 29.40, 35.97, 39.41, 43.16, 47.11, 48.503, 60.67, 65.61
	$\text{CaMg}_3(\text{CO}_3)_4$	23.12, 29.50, 36.06, 39.52, 43.27, 47.25, 47.70
	$\text{Cu}_2\text{FeGeS}_4$	29.15, 48.30, 48.65, 57.42
Qingshi	SiO_2	20.83, 26.59, 36.50, 39.37, 40.23, 42.39, 50.03, 55.17, 59.86, 68.20
	AlPO_4	20.76, 26.43, 36.37, 39.06, 40.71, 59.61, 67.23
	C	26.55, 44.57, 54.54
Hedishi	SiO_2	20.86, 26.64, 36.54, 39.46, 40.29, 42.45, 45.788, 50.13, 54.87, 59.95, 65.78
	SiS_2	20.79, 26.51, 36.50, 39.49, 42.40, 50.08, 54.935, 60.02, 68.42

Section 2. SEM images of Qingshi and Hedishi surfaces before and after modification.

Figure S2 SEM images of blank (a&b), and modified by 101S (c&d), 101S emulsion contain 2.0 mg/mL Al_2O_3 nano-powder (e&f), and 2.0 mg/mL SiO_2 nano-powder (g&h) Qingshi surfaces and profiles, respectively.

Figure S3 SEM images of blank (a&b), and modified by 101S (c&d), 101S emulsion contain 0.5 mg/mL Al_2O_3 nano-powder (e&f), and 1.0 mg/mL SiO_2 nano-powder (g&h) Hedishi surfaces and profiles, respectively.

The morphology of Hedishi surfaces is similar to that of Marbles with nonuniform micro cracks and holes while the morphology of the Qingshi surfaces presents step-like or fish scale like morphology, and cracks and holes are not distinct compared with those of Marble and Hedishi stones.

Figures

Figure 1

Schematic diagram of the preparation and modification of the natural stone surfaces by nano powder enhanced 101S hydrophobic agent

Figure 2

Variations of water contact angles on (a) Marble, (b) Qingshi and (c) Hedishi surfaces modified by the as prepared protectants with the concentration of Al_2O_3 nano powder, and the optimal water SCA on stone surfaces corresponding to concentration of Al_2O_3 nano-powder (d)

Figure 3

Variations of water contact angles on (a) Marble, (b) Qingshi and (c) Hedishi surfaces modified by the as prepared protectants with the concentration of SiO₂ nano powder, and the optimal water SCA on stone surfaces corresponding to concentration of SiO₂ nano powder (d)

Figure 4

SEM images of blank (a) and modified by 101S (c, d), 101S emulsion contain 1.5 mg/mL Al_2O_3 nano powder (e, f), and 0.5 mg/mL SiO_2 nano powder (g) Marble surfaces and profiles, respectively

Figure 5

Fractions of the modified stone surfaces in contact with water droplets calculated based on the Cassie model

Figure 6

Variation of water CAs as a function of temperature of the as prepared superhydrophobic surfaces of Marble , Qingshi and Hedishi surface s modified with 101S emulsion containing 1.5 mg/mL 0.5 mg/mL

and 2 mg/mL Al₂O₃ (a c)c), and 1.5 mg/mL 1 mg/mL and 2 mg/mL SiO₂ nano powder (d f), respectively.

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