

# Silicone/Silica Nanocomposites as Culture-Stone Protective Materials

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**ABSTRACT:** The water absorption ratio of the cement-based material culture stone was reduced obviously by the addition of composite additives of silica AS-40 with a nanoparticle size, hydroxyl polysiloxane emulsion, and water-based methyltrimethoxysilane (MTMS); its surface exhibited hydrophobicity and a certain acid resistance. Furthermore, both of the culture stones treated by two hybrid coatings prepared from the sol-gel reaction of tetraethoxysilane (TEOS) with MTMS and TEOS with MTMS and octyltrimethoxysilane (OTMS), respectively, showed excellent water repellence, long-term contamination resistance, and good acid resistance;

particularly, the culture stone treated by the coating from the OTMS precursor displayed better surface hydrophobicity. On the other hand, both the water-based additives and the two hybrid coatings were characterized by Fourier transform infrared spectroscopy and transmission electron microscopy. The sol-gel reaction coatings of TEOS with MTMS and OTMS were also characterized by <sup>29</sup>Si-NMR. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: E282–E291, 2012

**Key words:** additives; coatings; nanocomposites; silicas; silicones

## INTRODUCTION

Cement and concrete have been widely used in the construction and building fields. Culture stone, with its classical appearance, has been used as an indoor finishing material and is a cement product. It is known that water is one of the key factors responsible for the weathering and durability of building materials. Because of the high porosity and high water absorption of cement-based materials, many efforts toward the improvement of the water repellence and durability of cement composites with additives during the mixing process of cement and other components or with coating materials on hardened cement-based materials have been reported.<sup>1</sup> Silica fume (mean particle size = 0.1–0.2 μm) is a common additive for producing high-performance, cement-based materials with excellent strength and abrasion resistance and lower water permeability and dry shrinkage.<sup>2,3</sup> Further investigation has shown that the surface treatment of silica fume with silane as an additive can similarly enhance the workability, tensile strength, and compressive strength of cement-based materials.<sup>4</sup> However, silica fume has been known to be pozzolanic, and its addition weakens the workability of the cement mix.<sup>5</sup> To improve

the properties of cement-based materials, smaller size nanosilica particles as solid additives have been introduced into systems and have proven to be effective in increasing the mechanical properties, weathering resistance, and durability against Ca leaching.<sup>6,7</sup> However, there have been few reports on organic-inorganic nanocomposites produced from silica sol, a water dispersion of nano-SiO<sub>2</sub> particles pretreated by water-based silicone, which is used as a liquid additive of cement-based materials.

On the other hand, the protective surface treatment of stones by polymeric resins can prevent the direct contact of water or any pollutants, notably reduce the water absorption, and therefore, significantly enhance the durability of stone materials. Because organic-inorganic nanocomposites combine the advantages of polymers and inorganic nanoparticles, many of their applications have been reported. *In situ* polymerization by the sol-gel method may be the most desirable method for preparing nanocomposites because the nature of polymer precursors, especially the structure of organic silicone, can vary in a wide range to meet certain requirements. Organic silicone is one material that has a low surface tension, water repellence, anticorrosion and weathering resistance, and so on and has been used as a coating on porous materials, such as concrete and stone. It can penetrate into the pores of materials to form an impervious layer on the surface and, thus, lead to excellent resistance to environmental attack.<sup>8–13</sup>

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In this research, the performance of a cement-based material with the addition of composite additives of silica sol, water-based methyltrimethoxysilane (MTMS), and a hydroxyl polysiloxane emulsion during the mixing process was investigated. To alleviate the complex interaction between the multiple ingredients in the cement-based material and to correctly evaluate the effects of the additives on the cement composites, in this study, only cement and sand were configured as cement-based material components, and the effects of the other aggregates and other functional additives on them are not discussed. The suitable composition of the three water-based materials was determined by the compressive strength and water absorption ratio of the cement-based materials; these were measured by corresponding methods. Also, because of the advantage of the surface treatment, which was designed to prevent the direct contact of water, acid rain, or other pollutants from the surface of the cement-based material, the culture stone after curing for 28 days was treated by silicone hybrid coatings from the sol-gel reaction of tetraethoxysilane (TEOS) with the silane precursor MTMS, TEOS with MTMS, and octyltrimethoxysilane (OTMS), respectively. The water-repelling, contamination-resistance, and acid-resistance properties of the untreated culture stone or culture stone treated by these silicone hybrid coatings were investigated. The nanocomposite additives and silicone hybrid materials were characterized by Fourier transform infrared (FTIR) spectroscopy, transmission electron microscopy (TEM), scanning electron microscopy (SEM), and  $^{29}\text{Si}$ -NMR.

## EXPERIMENTAL

### Materials

Four major ingredients of cement mortar were used in this study: (1) type I cement complying with Chinese standards GB2015-1980 and GB2016-1980, (2) 99% fine quartz sand passed through an 80-sieve mesh, (3) distilled water, and (4) additives from a composite of water-based silica sol (LUDOX AS-40, pH 9.2,  $[\text{SiO}_2] = 40$  wt %) (GRACE Davison, Columbia, MD, USA), hydroxyl polysiloxane emulsion (Lanxing Co., Jiangxi Province China), or MTMS (Lanxing Co., Jiangxi Province, China).

Three silane precursors, TEOS (CP, Lanxing Co.), MTMS, and OTMS (Dow Corning, Corporation, Midland Site, Michigan, USA), were used as major reagents for the surface treatment of the cement-based materials by the sol-gel method, in which the reaction was catalyzed by dibutyltin dilaurate (DBTDL; Dow Corning Corporation, Midland Site, Michigan, USA) or tetrabutyl titanate  $[\text{Ti}(\text{OC}_4\text{H}_9)_4]$ ; Sigma-Aldrich Corporation, St. Louis, Missouri].

### Preparation of water-based additives of the cement-based material

A transparent, water-based MTMS solution was prepared by the mixture of the MTMS precursor (100 g), distilled water (100 g), and glacial acetic acid (2 g) with stirring for 60 min at room temperature. The composite additive sample (AH) was prepared by the addition of a hydroxyl polysiloxane emulsion to silica sol AS-40, and sample (AHM) was prepared by the addition of a mixture of water-based MTMS and hydroxyl polysiloxane emulsion to silica sol AS-40 at room temperature with stirring for 3 min.

### Preparation of the cement mortar and culture stone

Before they were mixed with the water-based additives, the solid raw materials, cement and fine quartz (cement/fine quartz sand = 1/1 w/w), were first blended inside plastic bags to achieve better homogeneity. Three blends with water/cement ratios of 0.40, 0.46, and 0.50 were used to mix the cement composites, whose performance was carefully examined. From the results, the optimum water/cement ratio was then determined to be 0.46. The control sample (A-0) without any additives was composed of cement, sand, and water at a ratio of 100/100/46. Later, different kinds of additives, silica sol AS-40, hydroxyl polysiloxane emulsion, and water-based MTMS, and three various dosages of 0.2, 0.4, and 0.8 wt % cement, respectively, were added to the cement paste, and we carefully examined the setting and strength of the cement mortar. Finally, the dosages of AS-40, hydroxyl polysiloxane emulsion, and water-based MTMS were fixed at 0.2–0.4, 0.2–0.8, and 0–0.6 wt % of the cement, respectively. The added dosages were calculated by the solid weight of silica sol, the nonvolatile matter weight of the hydroxyl polysiloxane emulsion, and the weight of the MTMS precursor, respectively.

The two composite additives, AH and AHM, were added to the cement paste, in which the final proportion of cement to sand to water was 100/100/46, and the mixing proportion of the silica/hydroxyl polysiloxane/MTMS is shown in Table I; the cement weight was fixed at 100. The dosages of AS-40 were fixed at the two points 0.2 and 0.4 wt % of cement, whereas the dosage of hydroxyl polysiloxane emulsion was gradually increased from 0.2 to 0.8% until the total dosages of AS-40 and hydroxyl polysiloxane emulsion in the composite additive AH reached 1.0 wt % of cement. In the composite additive AHM, the dosage of AS-40 was also fixed at 0.2 or 0.4 wt % of cement, but the total dosage of AHM was fixed at 1.0 wt % of cement with increasing dosages of hydroxyl polysiloxane emulsion and water-based MTMS for convenient comparison with the properties of mortar with the composite additive.

**TABLE I**  
**Compositions of the Composite Additives**

Designation	Silica sol/hydroxyl polysiloxane/MTMS (by mass)
A-0 (control)	0/0/0
AH-22	0.2/0.2/0
AH-24	0.2/0.4/0
AH-28	0.2/0.8/0
AH-42	0.4/0.2/0
AH-46	0.4/0.6/0
AHM-226	0.2/0.2/0.6
AHM-244	0.2/0.4/0.4
AHM-262	0.2/0.6/0.2
AHM-424	0.4/0.2/0.4
AHM-433	0.4/0.3/0.3
AHM-442	0.4/0.4/0.2

Cement weight, 100.

The total weight of water included the weight of water in the water-based additives and in other forms. Then, the cement pastes were subjected to a conserved box at  $25 \pm 2^\circ\text{C}$  and  $90 \pm 5\%$  relative humidity; they were demolded after 48 h and subjected continuously for 1 or 26 days to  $25 \pm 2$  or  $80 \pm 5\%$  relative humidity. The compressive strength and water absorption ratio of the hardened cement mortars were tested with corresponding measurement methods.

The culture stones were manufactured in the same way as cement mortar. The composition of the solid mixture was as follows: cement/sand/expanded perlite/pigment = 100/100/50/5. The cement pastes were mixed with constant quantities of a high-performance water-reducing agent (solid dosage = 0.10 wt % of cement), ethene–vinyl acetate polymer emulsion (solid dosage = 0.50 wt % of cement), and composite additive AHM and a constant total amount of water; this was necessary to achieve the right workability and, later, for casting into a silicone rubber mold.

All of the cement-based samples were compared with the control sample A-0.

### Measurement methods

The compressive strength of the cement mortar was tested according to GB/T 17671-1999 (equivalent to ISO 679) issued by the Chinese General Bureau of

Building Materials. The water absorption ratio of the mortar was tested according to Japanese standard JIS A6203.

Two acidic solutions, hydrochloric acid solution (10%, v/v) and acidic rain, which was rapidly simulated by a mixed sulfuric–nitric (1 : 1) acid solution (10%, v/v), were designed to investigate the acid resistance of the mortar. The acid-resistance tests were performed according to the following procedures. The cement products were placed inside plastic containing deionized water, hydrochloric acid solution, and sulfuric–nitric acid solution, respectively. The samples were immersed in these solutions for 24 h and then removed and washed with clean water. After they were dried at room temperature, the samples were analyzed by observation of their surface changes.

Water drops (10  $\mu\text{L}$  each) were deposited on the surfaces with the coatings, and the static water contact angles were measured at  $25^\circ\text{C}$  with an AST Products Optima XE goniometer (Billerica, USA).

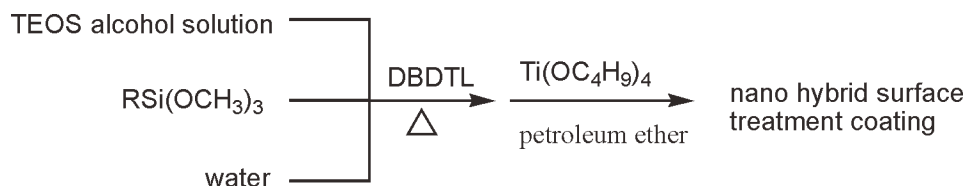
### Preparation of the surface-treatment agents

#### Preparation of sample (TE-MT) solution

To a 250-mL, four-necked, round-bottom flask fitted with an auto stirrer and a fluxing assembly, 66 g of a TEOS (5.2 g, 0.025 mol) alcohol solution, 34 g of MTMS (0.25 mol), 9.0 g of water (0.5 mol), and 0.05 g of DBTDL were added. Then, the mixture was heated and kept at  $70^\circ\text{C}$  under stirring for 2 h. Solvent petroleum ether (91 g) was then added. After cooling, a surface-treatment agent TE–MT (200 g) was obtained.

#### Preparation of the sample (TE-MT-OT) solution

To a 500-mL, four-necked, round-bottom flask fitted with an auto stirrer and a fluxing assembly, 66 g of a TEOS (5.2 g, 0.025 mol) alcohol solution, 34.0 g of MTMS (0.25 mol), 34.0 g of OTMS, 9.0 g of water (0.5 mol), and 0.10 g of DBTDL were added. Then, the mixture was heated and kept at  $70^\circ\text{C}$  under stirring for 4 h. After cooling, the surface-treatment agent TE–MT–OT was obtained by the addition of 1.0 g of  $\text{Ti}(\text{OC}_4\text{H}_9)_4$  and the addition of solvent petroleum ether to the total solution weight (400 g, Fig. 1).



**Figure 1** Preparation of the surface-treatment agent.

### Surface treatment of the cement-based materials

The cement mortar and culture stone samples after a total of 28 days of maintenance in the box were brushed with the surface-treatment agent at a dosage of 0.030 g of solution/cm<sup>2</sup> of area. Then, they were dried naturally at room temperature for 24 h.

## RESULTS AND DISCUSSION

### Waterproofing additives

Compositions of the water-based additives

Culture stone is made from cement, sand, light-mass aggregate expanded perlite, pigments, functional additives, and water. The interactions among these functional additives, water, pigment, cement, sand, and other aggregate are very complex. To easily confirm the optimum composition of the new water-based nanocomposite, we first chose the active material Portland cement, sand, and waterproofing additives as the study subject.

The three materials silica sol, hydroxyl polysiloxane emulsion, and water-based MTMS had different effects on the cement particle hydration, crystallization, and microstructure of the cement composite and changed the two major indices, mechanical strength and water absorption, of the hardened cement mortar. Primal setting and strength experiments showed that the silica sol AS-40 had a setting-enhancing effect on the cement paste under the low dosage range 0.2–0.4 wt % of cement, whereas the other two materials, hydroxyl polysiloxane emulsion and water-based MTMS, presented the opposite property of retarding the effect and greatly decreased the early strength of the mortar. When the dosage of nanosilica was increased to 0.8%, the cement paste was set quickly and was unworkable after 20 min of mixing. Because nanosilica (SiO<sub>2</sub>) particles have a pozzolanic reaction between Ca(OH)<sub>2</sub> and SiO<sub>2</sub> to form calcium silicate in an alkaline environment, the added dosage of nanosilica was fixed in the range 0.2–0.4 wt % of cement.

Table II lists the results of the two main indices of mortars and shows that the mortars presented excellent properties with the composite technique. The control mortar A-0, without any additives, had a high water absorption ratio of 10.1%, whereas the mortars with the AH and AHM additives had low water absorption ratio ranges of 2.0–4.6 and 1.3–1.9%, respectively. Both the composite additives AH and AHM remarkably decreased the water adsorption ratio with similar strengths as the control mortar. On one hand, the pozzolanic effect of nanosilica might have offset the retarding effect of silicone and led to the early, 3-day compressive strengths of mortars with AH or AHM additives nearing the control

**TABLE II**  
Compressive Strength and Water Absorption Ratio of Cement Mortar with Composite Additives

Additive	Compressive strength (MPa)		24-h water absorption ratio (%)
	3 days	28 days	
A-0	19.5	34.3	10.1
AH-22	22.3	35.6	4.6
AH-24	21.4	33.8	3.7
AH-28	18.3	31.5	2.2
AH-42	24.5	34.7	2.5
AH-46	21.9	33.2	2.0
AHM-226	20.7	32.1	1.5
AHM-244	21.5	36.2	1.3
AHM-262	20.9	33.4	1.4
AHM-424	23.5	33.9	1.9
AHM-433	21.6	32.5	1.7
AHM-442	20.8	34.2	1.8

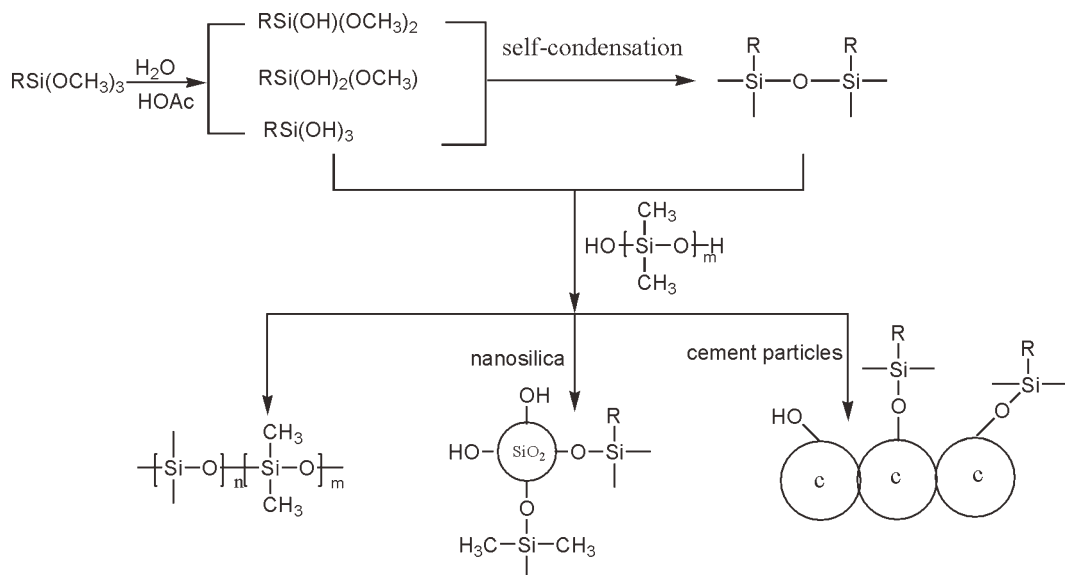
mortar. On the other hand, the packing effect of nanosilica particles in silica sol acted as a filler to fill in the interstitial spaces inside the skeleton of the hardened microstructure of the cement mortar to increase its density and the strength.

Table II also shows that the integral properties of the mortars with AHM additive were better than those of the mortars with the AH additives. At a total additive dosage of 1.0 wt % of cement, the water absorption ratios in the AHM series were lower than the lowest value of 2.0% in the AH series. The mechanism shown in Figure 2 may explain the results of the decrease in the water absorption ratios of the hardened cement mortar. Under the catalyst of acetic acid, MTMS with three active groups of —OCH<sub>3</sub> was hydrolyzed to three monomers, CH<sub>3</sub>Si(OCH<sub>3</sub>)<sub>2</sub>(OH), CH<sub>3</sub>Si(OCH<sub>3</sub>)(OH)<sub>2</sub>, and CH<sub>3</sub>Si(OH)<sub>3</sub>, to become a transparent solution. Later further gradual polycondensation among these products occurred, and MTMS became a hydrophobic polymer.<sup>14</sup> Also, the monomers could react with the hydroxyl groups of hydroxyl polysiloxane or hydroxyl groups on the surface of the nanosilica particles or cement particles. Both the polycondensation polymer and surface modification reaction on the particles greatly improved the waterproofing properties of the whole mortar. Table II shows that the additive AHM-244, which had a proportion of nanosilica to hydroxyl polysiloxane to MTMS of 0.2/0.4/0.4 wt % of cement, was an optimum additive.

### TEM and IR characterization of the composite additives

Figure 3(a) shows the TEM of the water-based MTMS diluted by alcohol. It clearly shows that the white spheres had an average size of 320 nm. The example of the water-based composite additive





**Figure 2** Alkyltrimethoxysilane hydrolysis, condensation, or reaction with nanosilica or cement particles (HOAc = acetic acid).

AHM-244 shown in Figure 3(b) shows clear mono-dispersed nanospheres (size = 20 nm).

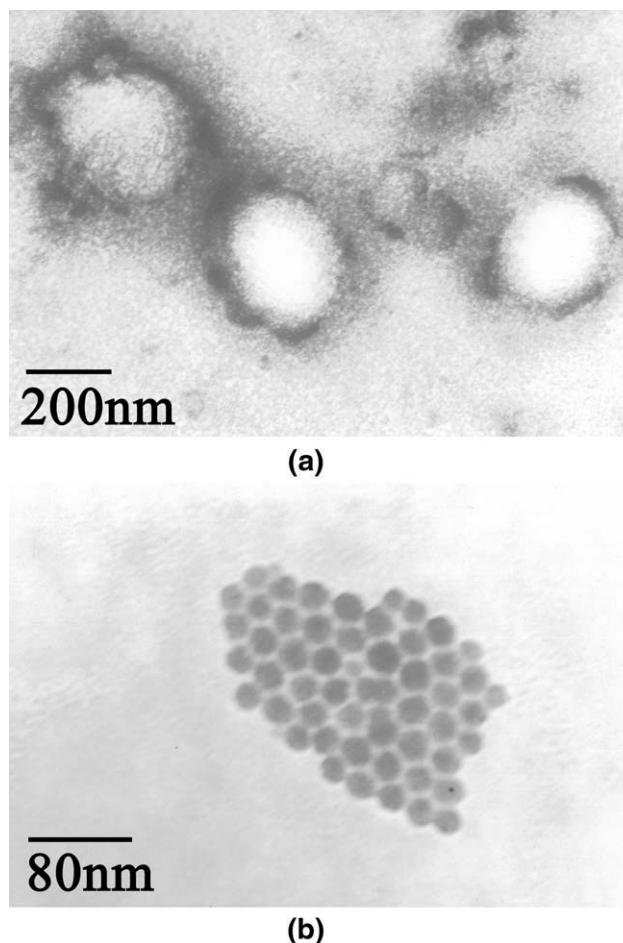
The solids obtained from water-based MTMS, AHM-244, and AS-40, after heating at  $110^\circ\text{C}$  for 3 h, were examined by FTIR spectroscopy, as shown in Figure 4. In the absorption domain of the IR spectra ranging from  $1000$  to  $1200\text{ cm}^{-1}$ , two broad absorptions culminating at  $1029$  and  $1133\text{ cm}^{-1}$ , clearly due to  $\text{Si}-\text{O}-\text{Si}$  stretching, were observed, shown in Figure 4(a), and presented the MTMS hydrolysis polymer. The solid from AHM-244 or AS-40 in Figure 4(b) only appeared to be a single broad absorption because of the presence of superimposed signals of inorganic  $\text{SiO}_2$  in silica sol. In the peak ranging from  $3200$  to  $3600\text{ cm}^{-1}$ , all of the solids appeared to have a broad absorption due to the  $\text{O}-\text{H}$  stretching in  $\text{Si}-\text{O}-\text{H}$ . However, in the spectra of the MTMS hydrolysis polymer and AHM-244 appeared narrow peaks,  $2919$  and  $2968\text{ cm}^{-1}$ , which belonged to the  $\text{C}-\text{H}$  stretching peak. These results of  $\text{Si}-\text{O}-\text{H}$  groups existing in the three water-based materials were consistent with those in Figure 2.

### Nanohybrid surface-treatment agents

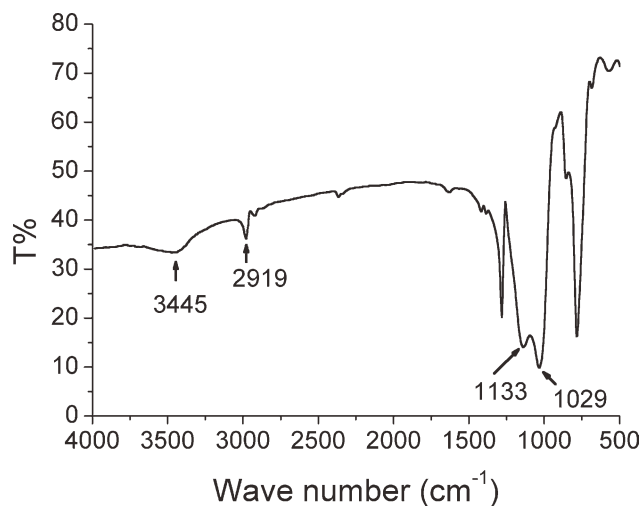
#### TEM and IR characterization

Although we added the waterproofing composite additive AHM-244, the cement mortars could still adsorb water to a certain degree. During the maintenance of cement-based materials, some inorganic salts can be introduced into the surface with the movement of water molecules. It is clear that the culture stone, with the porous lightweight aggregate expanded perlite, had a higher porosity and bigger water absorption ratio. Water repellence provided only by waterproofing additives might be not enough

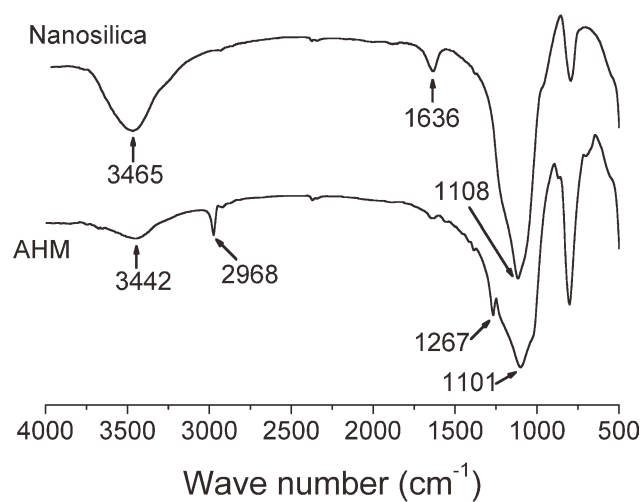
to protect the stone from the attack of UV rays in sunlight,  $\text{CO}_2$ , water, or acid rain outdoors. We designed two new hydrophobic surface-treatment agents



**Figure 3** TEM images of (a) water-based MTMS diluted by alcohol ( $\text{OsO}_4$ ) and (b) composite additive AHM244.



(a)



(b)

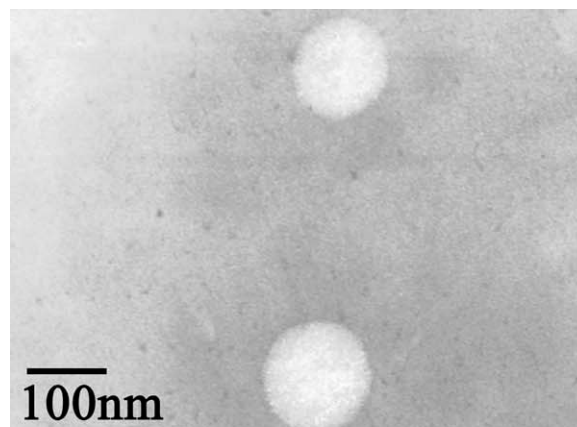
**Figure 4** FTIR spectra of the (a) MTMS hydrolysis polymer and (b) nanosilica and composite additive AHM244.

containing functional silane or polysiloxane, which had good weathering resistance and durability with nanostructures by the sol-gel method. The preparation of the surface-treatment agents is shown in Figure 1.

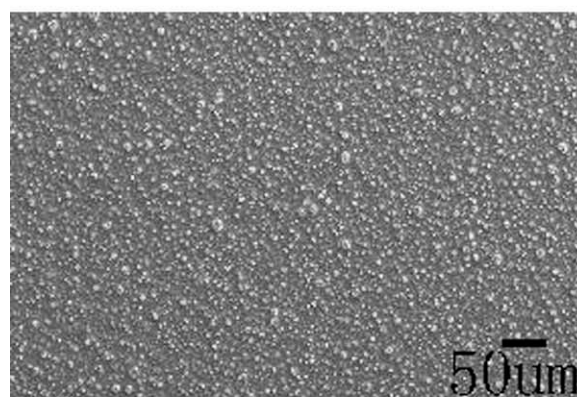
In the preparation of the TE-MT and TE-MT-OT solutions under the catalysis of DBTDL, the groups  $-\text{OC}_2\text{H}_5$  and  $-\text{OCH}_3$  easily hydrolyzed to become  $-\text{OH}$  groups, and they further polymerized and grew to become nanosize polymer particles, which were observed by TEM (Fig. 5). Figure 5(a) clearly shows sparse sphere nanoparticles (mean size = 130 nm) in the TE-MT solution, whereas Figure 5(c) shows smaller nanoparticles (mean size = 70 nm) in the TE-MT-OT solution. This was the result of the long-chain octyl's stereo hindrance to become bigger or to aggregate. Figure 5(b) shows the SEM of the film of the TE-MT solution dipping on the copper after TE-MT aging for 15 days. It is clear that the

surface of the film was tough and full of different big micrometer size particles because of the nanosize particles with Si-OH groups further aggregating or gelation with the removal of solvent, which isolated the hybrid nanoparticles.

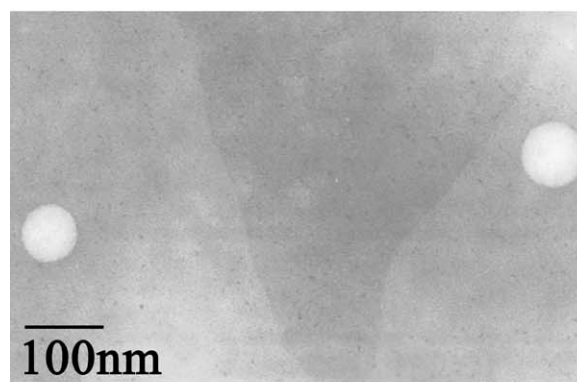
Figure 6 shows the two different IR spectra of the TEOS sol-gel reaction with MTMS and the TEOS sol-gel reaction with MTMS and OTMS. In the peak from 1000 to 1200  $\text{cm}^{-1}$  belonging to Si-O-Si



(a)



(b)



(c)

**Figure 5** Electron microscopy of the hybrid coatings: (a) TEM of TE-MT ( $\text{OsO}_4$ ), (b) SEM of the film of TE-MT, and (c) TEM of TE-MT-OT ( $\text{OsO}_4$ ).

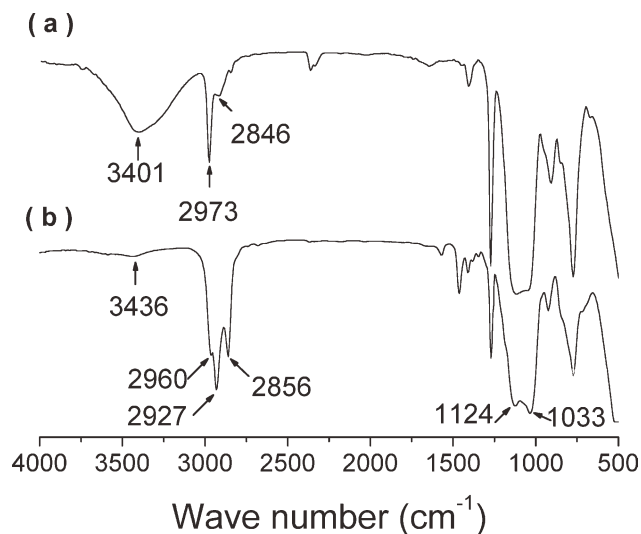


Figure 6 FTIR spectra of (a) TE-MT and (b) TE-MT-OT.

stretching, TE-MT-OT showed clear two broad absorption peaks at 1033 and 1124  $\text{cm}^{-1}$ , whereas TE-MT did not show two clear absorptions. This might have been due to the full reaction of the OCH<sub>3</sub> groups in TE-MT and the partial reaction in TE-MT-OT due to the stereo hindrance of long-chain alkyl octyl in the OTMS precursor.<sup>15</sup> In addition, TE-MT had a broad peak at 3401  $\text{cm}^{-1}$  (O-H stretching) and narrow peaks at 2973 and 2846  $\text{cm}^{-1}$  (C-H stretching). TE-MT-OT had a weaker broad peak at 3436  $\text{cm}^{-1}$  (O-H stretching), attributed to Si-OH from the partial hydrolysis of RSi(OCH<sub>3</sub>)<sub>3</sub>, and complicated stronger narrow peaks at 2960, 2927, and 2856  $\text{cm}^{-1}$  (C-H stretching) due to the several different C-H bonds in octyl.

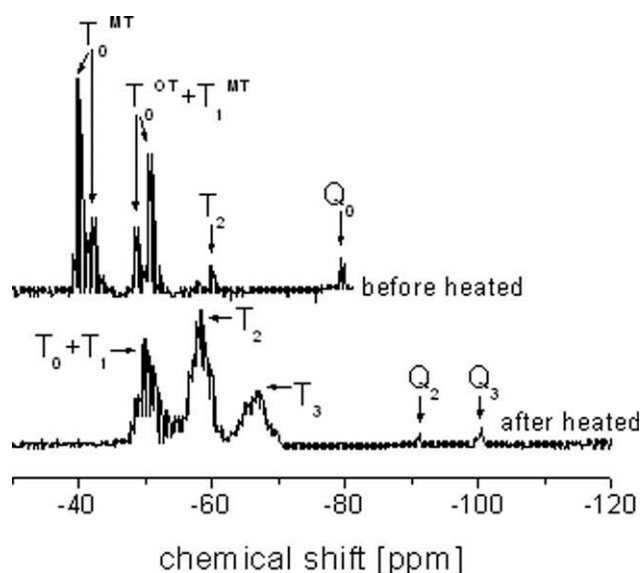


Figure 7 <sup>29</sup>Si-NMR of TE-MT-OT before heating and after heating during preparation.

### <sup>29</sup>Si-NMR of TE-MT-OT

Because of the liquid state of the mixture of TEOS, MTMS, and OTMS before heating at 70°C during the preparation of TE-MT-OT, the spectrum of <sup>29</sup>Si-NMR of TE-MT-OT before heating was recorded on an MSL 400 Bruker spectrometer with tetramethylsilane (TMS; Sigma-Aldrich Corporation, St. Louis, Missouri, USA) as an external reference and CDCl<sub>3</sub> (Sigma-Aldrich Corporation, St. Louis, Missouri, USA) as a solvent. The solid-state <sup>29</sup>Si-NMR of TE-MT-OT after heating was carried out with a Bruker MSL 500 spectrometer. The results are shown in Figure 7.

For several trialkoxysilane and tetraalkoxysilane entities, namely, T<sub>0</sub> [(R'O)<sub>3</sub>SiR], T<sub>1</sub> [(R'O)<sub>2</sub>Si(OSi)R], T<sub>2</sub> [R'OSi(OSi)<sub>2</sub>R], T<sub>3</sub> [Si(OSi)<sub>3</sub>R], Q<sub>0</sub> [(R'O)<sub>4</sub>Si], Q<sub>1</sub> [(R'O)<sub>3</sub>Si(OSi)], Q<sub>2</sub> [(R'O)<sub>2</sub>Si(OSi)<sub>2</sub>], Q<sub>3</sub> [R'OSi(OSi)<sub>3</sub>], and Q<sub>4</sub> [Si(OSi)<sub>4</sub>], we could distinguish resonance signals at -37 to -44 ppm (T<sub>0</sub>), -48 to -52 ppm (T<sub>1</sub>), -56 to -62 ppm (T<sub>2</sub>), -64 to -70 ppm (T<sub>3</sub>), -72 to -82 ppm (Q<sub>0</sub>), -82 to -89 ppm (Q<sub>1</sub>), -92 to -96 ppm (Q<sub>2</sub>), -100 to -104 ppm (Q<sub>3</sub>), and -110 ppm (Q<sub>4</sub>).<sup>16,17</sup> The transition from Si-OR' to the corresponding silanol Si-OH gave a shift to lower fields. Figure 7 shows that there were several groups of peaks: T<sub>0</sub>, T<sub>1</sub>, T<sub>2</sub>, T<sub>3</sub>, Q<sub>0</sub>, Q<sub>2</sub>, and Q<sub>3</sub>. The groups of peaks in <sup>29</sup>Si-NMR of TE-MT-OT before and after heating during the preparation of TE-MT-OT are listed in Table III.

The condensation degree of MTMS was 100% and became the T<sub>1</sub>, T<sub>2</sub> (-52.7 and -54.5 ppm), and T<sub>3</sub> (-64.8, -66.5, and -67.4 ppm) structures; this resulted from the disappearance of the T<sub>0</sub> peaks (-39.6, -40.8, -41.9, and -43.0 ppm) of MTMS, which might have included partly hydrolyzed MTMS silanol Si-OH in the mixture of the three silanes before heating. The peaks at -48.4, -49.7, -50.4, and -51.6 ppm were ascribed to the T<sub>0</sub> structure of OTMS before heating, and they nearly kept the same chemical shifts (-48.3, -49.5, -50.8, and -51.5 ppm) after heating. The peak at -59.6 ppm might have been due to further condensation of the

TABLE III  
Chemical Shift of Groups of the Peaks in <sup>29</sup>Si-NMR of TE-MT-OT

Group of peaks	Chemical shift (ppm)	
	Before heating	After heating
T <sub>0</sub>	-39.6, -40.8, -41.9, -43.0;	-(MTMS); -48.3, -49.5, -48.4, -49.7, -50.4, -51.6
T <sub>1</sub>	—	-52.7, -54.5
T <sub>2</sub>	-59.6	-56.6, -57.9, -59.1
T <sub>3</sub>	—	-64.8, -66.5, -67.4
Q <sub>0</sub>	-79.0, -79.8	—
Q <sub>2</sub>	—	-91.2
Q <sub>3</sub>	—	-100.5



**TABLE IV**  
Waterproofing Properties of the Surface-Treated and Untreated Cement Products

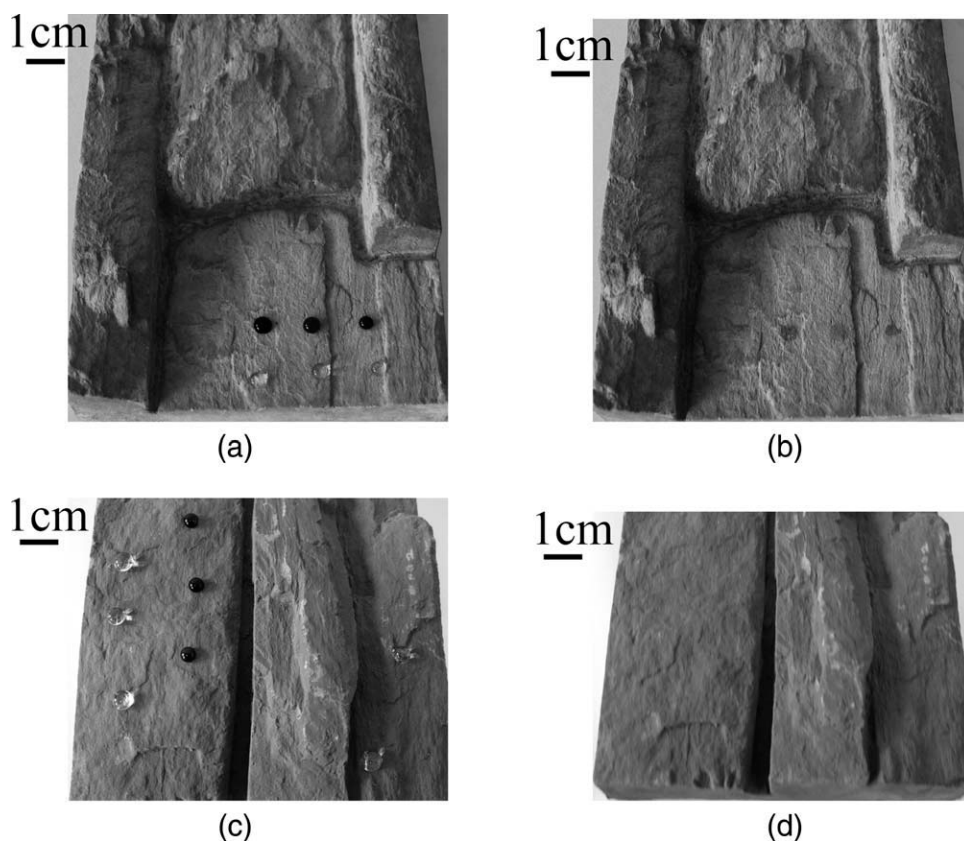
Sample	AHM-244 (%)	Surface treatment agent	Static water contact angle (°)	24-h water absorption ratio (%)
Mortar	0	0	0	10.1
	0	TE-MT	98	2.7
	0	TE-MT-OT	119	1.2
	1.0	0	101	1.3
Culture stone	0	0	0	15.6
	1.0	0	98	4.3
	1.0	TE-MT	111	1.5
	1.0	TE-MT-OT	126	0.85

partly hydrolyzed MTMS before heating to the  $T_2$  structure. The condensation degree of OTMS was found to be about 20% in the  $T_1$  or  $T_2$  structure by analysis of the areas of all of the peaks of  $T_0$ ,  $T_1$ ,  $T_2$ , and  $T_3$  before and after heating. TEOS ( $Q_0$ :  $-79.0$  and  $-79.8$  ppm) reacted 100% with water molecules to become the  $Q_2$  ( $-91.2$  ppm) and  $Q_3$  ( $-100.5$  ppm) structures.

Culture stone properties after the surface treatment

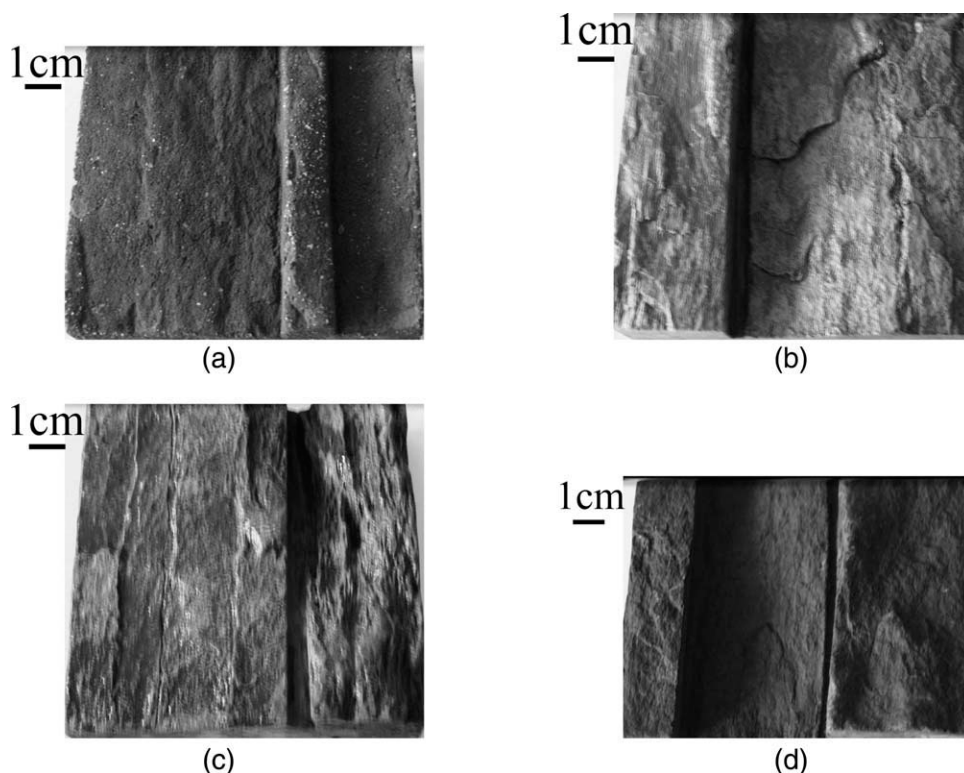
Hydrophobic polymer surface treatment has been reported to be used in the conservation of stone.<sup>18,19</sup>

These polymers, including organic silicone resin, fluoro-containing polymers, and epoxy nanosilica hybrids, directly prevent the contact of water with the substrate and significantly enhance the durability of the substrate. Silicone has been used widely as a building material because of its excellent properties and low price. Table IV shows the waterproofing properties results of the cement mortars and culture stones treated and untreated with alkyltrimethoxysilane sol-gel reaction products. The water absorption ratio of the culture stone only with 1.0% AHM-244 evidently decreased from 15.6% without additives to 4.3%. After surface treatment, especially by TE-MT-OT solution, both mortars and culture



**Figure 8** Hydrophobicity and contamination resistance effect of the culture stone (a,b) untreated, (c,d) treated by TE-MT-OT, (a) with water and ink droplet remaining for 1 h, (b) after washing and cleaning, (c) with water and ink droplet remaining for 1 h, and (d) after washing and cleaning.





**Figure 9** Appearance of the treated or untreated stones after immersion in acid solution: (a) untreated, (b,c) treated by TE-MT, (d) treated by TE-MT-OT, (a,b,d) immersion in hydrochloric acid solution (10% v/v) for 24 h, and (c) immersion in sulfuric-nitric (1 : 1) acid solution (10%, v/v) for 24 h.

stones had remarkably reduced water absorption ratios.

In the experimental water contact angle measurement, it was observed that the water droplet spread out rapidly on the surface of the untreated mortar without any additives and soon wholly wetted the surface, which had a  $0^\circ$  static water contact angle, which was opposite of the water contact angles of the mortars treated by TE-MT and TE-MT-OT solution, which reached  $98^\circ$  and  $119^\circ$  (Table IV), respectively. This was ascribed to the hydrophobic long-chain octyl and rough porous surface according the theory of Cassie's rough surface wetting model.

The untreated culture stones with 1.0% water-based additive AHM-244 displayed a high water contact angle of  $98^\circ$ , and a spherical water droplet could be observed in a short time on the stones' surface [Fig. 8(a)], resulting from some hydrophobic siloxane or polysiloxane molecules moving to the surface during the stone's making process. After treatment by TE-MT or TE-MT-OT [Fig. 8(c)] solution for 24 h, the culture stone exhibited excellent hydrophobicity, which resulted from the static water contact angles of the rough stone surfaces being  $111^\circ$  and  $126^\circ$  (Table IV), respectively.

Figure 8 also shows the contamination resistance of the culture stones with the additive AHM-244.

The untreated stone could only prevent short-term contact contamination of pollutants, such as blue, black, or red ink; this resulted in the stone surface keeping no marks of ink staying the surface for 5 min after washing and cleaning, whereas the untreated stone surface kept some marks of ink staying for 1 h after washing and cleaning [Fig. 8(b)]. However, the stone surface treated by TE-MT-OT solution did not leave any trace of ink staying for 1 h after washing and cleaning [Fig. 8(d)].

#### Acid resistance

It has been proven that water and carbon dioxide ( $\text{CO}_2$ ), especially acidic rain in the external environmental, have a great influence on the durability of alkaline mortars. We designed two acidic solutions, hydrochloric acid solution (10% v/v) and acidic rain, which was rapidly simulated by a mix of sulfuric and nitric (1 : 1) acid (10% v/v), to investigate the acid resistance of the mortars.

The alkaline, cement-based material without any protection gave out lots of bubbles and was soon destroyed after immersion in the two acidic solutions. This was the result of reaction between the strong proton acid and carbonates or  $\text{Ca}(\text{OH})_2$  close to the acidic solutions to give out  $\text{CO}_2$  gas and water-soluble salts. However, Figure 9(a) shows

that the untreated culture stone with the additive AHM-244 showed some degree of resistance to the hydrochloric acid solution (10%, v/v) after 24 h of immersion; this resulted from some big stomata and fine cracking on the stone surface. Through surface treatment with TE-MT or TE-MT-OT solution, the stones shown in Figure 9(b-d) had excellent acidic resistance, resulting in no remarkable changes on the surfaces after immersion in the two acidic solutions for 24 h.

### CONCLUSIONS

In this study, we exploited two protection methods of the cement-based material culture stone, which is used as an indoor finishing material. One method was the use of a water-based silicone/silica nanocomposite additive, and the other was surface treatment by a silicone nanohybrid solution. The results show that with the addition of the nanocomposite additives of the three materials, water-based nanosilica sol AS-40, hydroxyl polysiloxane emulsion, and water-based MTMS, the cement-based material showed a greatly decreased water absorption ratio and a similar compressive strength as the control sample without any additives, and the water contact angle increased remarkably from 0 to over 98°. After surface treatment by the two nanohybrid solutions from the *in situ* sol-gel polymerization of TEOS with MTMS or TEOS with MTMS and OTMS by the addition of some water in an alcohol solvent under the catalysis of DBTDL at 70°C, the culture stones showed excellent water repellence, contamination resistance, and acid resistance.

Therefore, we concluded that the culture stones with the two protection methods exhibited good waterproofing and durability for outdoor use.

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