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Development of Micro–Nano Biomineralized Protective Layers for Conservation of Stone Artifacts

Han-Chung Wu,* Wu-Shan Chu, Chin-Wen Chung, Wei-Fang Yu, and Jhih-Yan Yu

Conservation and Research Center, Cheng Shiu University, Kaohsiung 833301, Taiwan

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In this study, we explored the development of protective structural layers for stone cultural relics using biomineralization techniques. Our objective was to formulate protective materials with excellent acid resistance, stain resistance, and hydrophobic properties to serve as a functional material platform for sensing applications. The results showed that a protective layer with self-cleaning properties can be developed through biomineralization, effectively reducing the adhesion of contaminants. Quantitatively, the biomineralized coating exhibited superior performance, achieving contact angles as high as 149.28°, particularly on sandstone and basalt. Additionally, we included a comparative analysis with commercial materials. Experimental findings revealed that the protective coating developed in this study exhibits the highest drying speed and superior hydrophobicity. Importantly, the developed layer provides a stable interface that is compatible with integrated sensor systems for the long-term, smart monitoring of stone heritage degradation. Overall, the feasibility of using biomineralization techniques for protective coatings is high, showing significant potential for smart conservation in outdoor stone cultural relics.

1. Introduction

In this study, we focused on the protection and restoration of stone cultural heritage artifacts in Taiwanese temples. Inspired by biomineralization mechanisms, we aimed to develop a stone surface protective layer with acid resistance, pollution resistance, and hydrophobicity. Stone artifacts in Taiwanese temples, characterized by their solid texture and exquisite carvings, bear contemporary artistic and cultural meanings such as commemorations and records, deeply reflecting early societal values and religious beliefs. However, exposure to high temperature and humidity environments makes these stones vulnerable to long-term erosion by moisture, acid rain, salts, bird droppings, and vegetation, resulting in surface weathering, flaking, and pollutant adsorption and penetration. These processes induce chemical chain reactions that cause cracking and discoloration, leading to deterioration.(1–4) Furthermore, in the evolving field of heritage conservation, there is an increasing demand for the integration of sensors and related

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*Corresponding author: e-mail: ogskipg@gmail.com
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technologies to enable the active, real-time monitoring of environmental stressors. Establishing a stable material interface is crucial for ensuring the data accuracy and long-term durability of such sensing applications when applied to porous and weathered stone surfaces.

Field investigations have identified natural calcium oxalate–calcium phosphate films that form protective layers on stone surfaces. Both domestic and international researchers have chemically synthesized biomimetic mineral films with preliminary success,(5–7) demonstrating promising potential for stone heritage protection. Biomineralization-inspired coatings have been shown to improve surface hardness, reduce porosity, and impart hydrophobicity, contributing to enhanced durability under environmental stress.(8,9)

On the basis of this, we adopted a biomineralization strategy in this study to systematically investigate the formation mechanisms and performance of protective layers under various conditions. Importantly, the biomineralized layer developed in this study is designed not only as a barrier but also as a functional substrate compatible with integrated sensing devices. By optimizing surface hydrophobicity and chemical stability through a biomineralization strategy, this layer provides a robust platform for future smart monitoring systems, effectively bridging the gap between material-based protection and sensor-aided preservation technologies. Additionally, we analyzed the degradation and decomposition behaviors of common pollutants affecting stone artifacts and identified key controlling parameters. Ultimately, the developed protective layer is expected to effectively retard deterioration processes and preserve the historical value and cultural heritage of these artifacts.(10,11)

2. Materials and Methods

2.1 Sample materials

Stone materials commonly found in Taiwanese cultural artifacts were selected as samples, including granite, sandstone, basalt, and Guanyin stone (andesite), for the preparation and testing of the protective layers.

2.2 Sample pretreatment

Stone samples were first cleaned with deionized water to remove surface dust and dirt, then subjected to ultrasonic cleaning in three cycles of 30 min each. To eliminate organic impurities and potential interfering substances, the samples were soaked in a 1:1 (v/v) mixture of anhydrous ethanol and acetone for 30 min, followed by natural air drying.

2.3 Protective layer preparation

1. Organic pretreatment layer: Dried samples were immersed in 3–5% cetyltrimethylammonium bromide (CTAB) solution for 30 min to form a preliminary organic protective layer.
2. Nanoscale inorganic structural layer: A beaker containing 25 mL of sodium fluorosilicate (Na_2SiF_6) solution was prepared, followed by the sequential addition of ethanol, tetraethyl

orthosilicate (TEOS), and glycerol. After magnetic stirring for 10 min, samples were fully immersed. Deionized water and ammonia were slowly added to induce a sol–gel reaction. Treated samples were sealed with polyethylene film and left at room temperature for 7 days. Subsequently, samples were rinsed with deionized water and air-dried naturally. The resulting protective layers were transparent and stable, without affecting the stone's original color and texture.

2.4 Control materials

For comparison with commercial products widely used in cultural heritage restoration, two commercial protective agents were selected:

- Hong Brand Nano Stone Protector: This is a nanoscale silicone resin-based product that penetrates and cures within stone pores, forming a water-repellent surface layer.
- Akemi K: This is a modified alkylalkoxysilane oligomer that polymerizes upon water vapor absorption to form a polysiloxane water barrier within the substrate pores, maintaining gas permeability and non-yellowing properties.These commercial products were applied on sample surfaces according to manufacturer instructions and cured at room temperature for 24 h before performance testing alongside the newly developed protective layers.

2.5 Protective layer performance testing

To evaluate the practical performance of the developed and commercial protective layers as functional interfaces for heritage monitoring, tests were conducted on granite, sandstone, basalt, and andesite samples under uniform procedures. To ensure scientific reproducibility and account for material variability, all experiments were conducted in triplicate (n = 3), and data are presented as the mean value standard deviation.

- Stain resistance: Pure blue ink was dropped on sample surfaces and allowed to stand for 1 min, then rinsed with deionized water. Residual stain intensity was graded to assess anti-pollution capability. While current evaluation relies on visual inspection, we recognize its limitations; thus, future research will incorporate instrumental color shift analysis using the Commission Internationale de l'Éclairage L*a*b* (CIELAB) color space (ΔE^*) and microscopic imaging to provide a more objective quantification of residue.
- Acid resistance: HCl was dropped on sample surfaces using a Pasteur pipette, and bubbling was observed for 2–3 min to evaluate acid corrosion resistance. In this test, we evaluated the chemical stability of the biomineralized layer when used as a protective substrate for integrated sensors in acidic environments. Beyond observing surface bubbling, the integrity of the layer's surface tension was monitored to ensure its reliable performance as a sensing platform.
- Hydrophobicity: Quantitative contact angle measurements were performed using the sessile drop method; larger contact angles indicate higher water repellency. This metric is critical for assessing the material's ability to shield sensitive electronic sensor components from moisture interference. The performance was quantified across a range from 92.27 to 149.28° to provide a precise scientific benchmark.

Four groups, namely, the biomineralized protective layer developed herein, Hong Brand Nano Stone Protector, Akemi K, and untreated controls, were tested to compare performance across the three tests.

3. Results and Discussion

3.1 Development of surface protective material

The biomineralized surface protective material was prepared using TEOS and CTAB. The solution was colorless, transparent, and highly water-soluble. Fourier transform infrared (FTIR) spectroscopy analysis (Figs. 1 and 2) showed that the spectrum of this material closely resembles that of the commercial Hong Brand Nano Stone Protector. The latter exhibited two additional peaks at 2952 and 1073 cm^{-1}, indicating minor compositional differences that provide reference points for subsequent performance comparisons.

3.2 Stain resistance testing

In this study, we evaluated the stain resistance of granite, sandstone, basalt, and Guanyin stone samples by applying drops of pure blue ink onto their surfaces. The results were compared

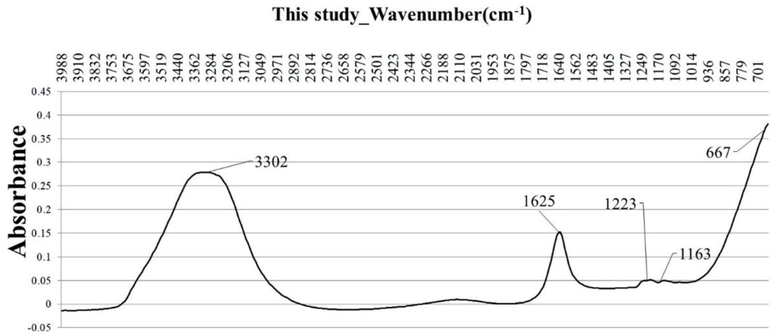

Fig. 1. Spectrum of the surface protective material developed in this study.

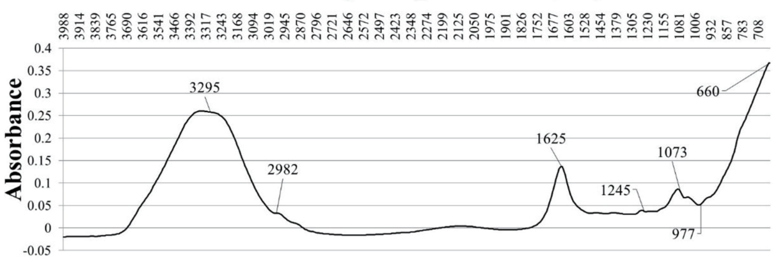

Fig. 2. Spectrum of the Hong Brand surface protective material.

against two commercial protective agents, Hong Brand and Akemi K, by observing the residual stain after rinsing with deionized water. The protective material developed in this study demonstrated the highest stain resistance on granite, sandstone, and Guanyin stone, showing minimal ink residue. For basalt samples, Akemi K exhibited the highest performance, followed by the developed material. The ability of the biomineralized layer to prevent pollutant adhesion is critical for maintaining the functional integrity of optical and chemical sensors mounted on stone surfaces, as it ensures that sensing windows remain clear of contaminants.

While the current ratings (excellent, good, and fair) are based on visual inspection, we acknowledge the need for increased objectivity. To enhance scientific rigor, future work will incorporate instrumental colorimetry using the CIELAB color space to quantify total color difference (ΔE^*), thereby replacing subjective grading with standardized metrics. The results are summarized in Table 1.

3.3 Acid resistance testing

Acid resistance was assessed by dropping HCl on the surfaces of stone samples and observing the formation of bubbles as an indicator of acid corrosion. The three protective materials effectively resisted acid attack across all stone types, with almost no bubbling observed. This chemical stability demonstrates that the biomineralized coating can serve as a robust protective substrate for electronic sensing components in environments prone to acid rain, preventing corrosive damage to sensor circuitry.

However, Akemi K showed some instability in maintaining the water droplet form on sandstone, basalt, and Guanyin stone samples within 1–2 min after acid application, suggesting possible effects on surface tension properties. The consistency of the developed material under acidic stress is vital for ensuring that integrated monitoring systems can acquire reliable data over long durations without interface degradation. The results are shown in Table 2.

Table 1
Results of visual inspection for stain resistance.

Protective material	Granite	Sandstone	Basalt	Guanyin stone
This study	Excellent	Excellent	Excellent	Excellent
Hong brand	Good	Good	Good	Good
Akemi K	Good	Fair	Good	Good

[*] Rating scale: Excellent > Good > Fair.

Table 2
Results of acid resistance testing based on surface observation.

Protective material	Granite	Sandstone	Basalt	Guanyin stone
This study	Good	Good	Good	Good
Hong brand	Good	Good	Good	Good
Akemi K	Good	Good	Good	Good

Table 3
Measured contact angles across stone samples.

Material	Granite	Sandstone	Basalt	Guanyin stone
This study	96.96° ± 2.0° (Excellent)	149.28° ± 5.5° (Superhydrophobic, Excellent)	136.80° ± 4.5° (Superhydrophobic, Excellent)	115.67° ± 3.5° (Hydrophobic, Excellent)
Hong brand	75.52° ± 2.5° (Hydrophilic, Good)	111.75° ± 4.0° (Hydrophobic, Good)	83.43° ± 2.5° (Hydrophilic, Good)	88.35° ± 3.0° (Hydrophilic, Good)
Akemi K	92.27° ± 2.0° (Hydrophobic, Good)	75.62° ± 4.5° (Hydrophilic, Fair)	81.42° ± 2.5° (Hydrophilic, Good)	93.49° ± 3.0° (Hydrophobic, Good)

*Hydrophilic: < 90°, Hydrophobic: 90°–150°, Superhydrophobic: > 150°.

3.4 Hydrophobicity testing

The hydrophobicity of the protective materials was evaluated by measuring contact angles using the sessile drop method. Quantitatively, the material developed in this study exhibited superior performance, with contact angles ranging from 92.27 to 149.28°. Notably, the sandstone and basalt samples displayed contact angles as high as 149.28 and 136.8°, respectively, indicating superhydrophobic characteristics. The results are shown in Table 3.

Such high hydrophobicity is essential for "smart conservation" applications, as it provides a water-repellent interface that protects sensitive sensing elements from moisture-induced noise or electrical failure. In comparison, the Hong Brand product showed only moderate performance, whereas Akemi K demonstrated significant instability across most stone types. These quantitative results underscore the potential of the developed biomineralized layer as a high-performance related material for sensor integration in stone heritage monitoring.

4. Conclusion

The experimental results of this study demonstrated that the effectiveness of surface protective materials is significantly affected by the porosity of the underlying stone substrates, which affects their resistance to environmental stressors. Among the evaluated parameters, quantitative contact angle measurements exhibited the most pronounced variation, with the developed biomineralized layer achieving superior hydrophobicity ranging from 92.27 to 149.28°. This high performance, particularly on high-porosity sandstone and basalt, underscores the material's potential as a functional interface for sensors and related technologies. By providing a stable, water-repellent, and acid-resistant barrier, this layer serves as a robust substrate that protects integrated sensing devices from environmental noise and corrosive damage, thereby ensuring the reliability of long-term heritage monitoring data.

The findings highlight the potential of biomimetic approaches in the development of protective coatings for cultural heritage conservation. Specifically, the use of biomineralization provides a promising, substrate-adaptive strategy that enhances surface protection without compromising the material's aesthetic or physical integrity. To address the limitations of subjective visual grading identified in this study, future work will transition to objective scientific metrics, including instrumental CIELAB color shift analysis and microscopic imaging to quantify surface changes with higher precision. Furthermore, research will be expanded to consider biological weathering mechanisms, such as biofilm formation, to develop a more comprehensive sensing and protection framework. This proposed strategy offers a sustainable and adaptable framework for advancing conservation science, effectively bridging material science with intelligent sensing applications in heritage preservation.

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