

# A crude protective film on historic stones and its artificial preparation through biomimetic synthesis

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## Abstract

A biomimetic film has been found on the surface of the historic stone buildings and monuments. The stone inscriptions under the film are preserved so well that has not been damaged for more than 1000 years. Samples of the crude film have been analyzed by XRD, FTIR, PLM, EDA, SEM and TEM. The results show that it consists mainly of calcium oxalate monohydrate. On the basis of the existence of the organism debris, it is concluded that the film should be a product of biomineralization. According to this hypothesis, a similar film has been prepared on the stone surface through biomimetic synthesis in our laboratory. The preliminary analysis shows that the artificial protective film functions well.

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**Keywords:** Protective film; Biomineralization; Biomimetic synthesis; Surface; Substrate; Stone conservation

## 1. Introduction

Historic stones are a sort of important cultural remains, which have been of great value in science, art and history. However, due to the corrosion of the stone materials, the further preservation of historic stones is endangered. People should take effective measures to minimize damage from environmental factors and slow down the ageing process of stones. Many measures have been adopted. Among them, coating treatments on stones is regarded as an effective and convenient method to retard corrosion [1,2]. But there are no completely satisfying materials until now, which are extremely convenient to be used to protect stones that function well. The characteristics of an ideal stone treatment mainly should include compatibility, reversibility and longevity [3].

Solid paraffin, one of most popular materials used in early time, can prevent rock surface from being damaged to some extent, but it cannot penetrate into the underlying stone to form an enduring protection. Meanwhile, wax is easy to absorb dust and become yellow, which makes the arts lose their original

appearance [4]. The inorganic protective materials were extensively used to mitigation of stone weathering before the 19th century. In their early application, inorganic protective materials had fine protective effects on stones. Unfortunately, many late instances have shown that inorganic protective materials could bring new salts whose crystal stresses are important weathering factors [5]. Organic polymers, other protective materials for conservation of rock art, which have been used since some decades, can be applied easily and show excellent effects within first years, but their efficient longevity does not meet with protector's desire. Besides, the contrast between hydrophilic stones and hydrophobic organic protective coatings could aggravate the damage of the stone surface layer caused by stress [6]. Therefore, it is an urgent task to explore new protective materials and methods, which is receiving growing attention and becoming a focus of research in many fields.

Investigating rock arts of the Double Tower in Lingyin Temple (Hangzhou, China), we find that although the tower has suffered from natural weathering, microbial destruction and erosion of acid rain for a long period, some stone inscriptions on its surfaces are preserved well. Being carefully observed, a crude film which is compact and translucent on the stone surface is there. Under the film, a few of sword marks carved about 1000 years ago are still dimly seen.

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The film on the Double Tower was sampled and analyzed by various instruments. The analysis results show that the film is a category of crude  $\text{CaC}_2\text{O}_4$  film. On the basis of analysis results, the forming mechanism of the film has been considered that it should be a biomimetic film. Moreover, inspired by the forming mechanism, the artificial conservation film of  $\text{CaC}_2\text{O}_4$  has been prepared through biomimetic synthesis.

## 2. Experimental

### 2.1. Research on the crude conservation film

#### 2.1.1. Samples of the crude conservation film

The Double Tower in Lingyin Temple was built about A.D. 960. An intact part of inscriptions was selected for sampling (see Fig. 1). The dust on the sample site surface was first blown off, and then a piece of film, about  $1\text{ cm}^2$  in size, was scraped off from the cleared place by a sterile scalpel for subsequent studying.

#### 2.1.2. Analyses on the crude conservation film

The samples were analyzed by various instruments. X-ray analyses were performed using a Philips PW1380 X-ray Diffractometer (XRD) (Germany). Fourier transform infrared (FTIR) spectra of samples were recorded over the range from  $4000$  to  $400\text{ cm}^{-1}$  on a Nicolet 170SX FTIR spectrometer (U.S.A.) with KBr disc method. Micrographs were taken with a Nikon 55165 polarized light microscope (PLM) (Japan), a Philips CM200 transmission electron microscope (TEM) (Germany) and a Hitachi S-570 scanning electronic microscope (SEM) (Japan). Chemical composition was determined with a PV9900 energy dispersive X-ray spectrometer accessory (EDAX) (Japan). All auxiliary materials used in the process of analyzing were of analytical grade.

### 2.2. Artificial preparation and characterization of the protective film

#### 2.2.1. Experimental materials and methods

White marble at the size of  $5\text{ cm} \times 5\text{ cm} \times 2\text{ cm}$  was selected as sample stone, which was not weathered. Chondroitin sulfate

(chemical formula:  $(\text{C}_{14}\text{H}_{21}\text{NO}_{15}\text{S})_n$ , abbreviated formula: CHS or CS) from bovine,  $\geq 95.0\%$  assay was commercially available. Pure chemicals including calcium chloride C.P. Grade,  $\geq 96.0\%$  assay and potassium oxalate A.R. Grade,  $\geq 99.8\%$  assay were used for this study. All water solvents were freshly distilled before use.

Sample stones were washed by flowing water and cleaned by distilled water, then soaked in alcohol for 12 h. The stock solutions of Ca ( $\text{CaCl}_2$ ) and Ox ( $\text{K}_2\text{C}_2\text{O}_4$ ) reactants were made up to concentration of  $0.11\%$  m/m. Equal volume stock solutions of Ca and Ox were added very slowly in enough water solvents to prepare the supersaturated solution of  $\text{CaC}_2\text{O}_4$ . Initial supersaturation (Si) for the crystallization was defined as the initial ionic product to the solubility product of calcium oxalate ( $=[\text{Ca}^{2+}]_i [\text{C}_2\text{O}_4^{2-}]_i / K_{\text{sp}}$ )<sup>1/2</sup>. Herein, the value of  $K_{\text{sp}}$  was used as the solubility product of COM ( $2.32 \times 10^{-9}\text{ M}^2$ ) [7]. The supersaturated solution of  $\text{CaC}_2\text{O}_4$  was then filtered to remove undesirable nucleus of crystallization. The CS solution was made up to concentration of  $0.30\%$  m/m, stirring thoroughly. The CS solution was dripped on the cleaned stone and dribbled naturally. After the film forming thoroughly, the supersaturated solution of  $\text{CaC}_2\text{O}_4$  was dripped on it and dribbled naturally too. The crystallization of calcium oxalate was induced by CS to form film at room temperature. Operating repeatedly, the film became thicker and thicker.

#### 2.2.2. Characterization of sample

For characterizing the structure and microtopography of the artificial film, X-ray diffraction (XRD) and atomic force microscopy (AFM) analyses was carried out. XRD patterns were recorded using a Bruker AXS D8 ADVANCE diffractometer. AFM images were recorded using a CSPM-2003 scanning probe microscope system made in Guangzhou Being Nano-instruments Co., Ltd.

The acid resistance of specimens was tested referring to the national trade standard for natural stone protectant of China, JC/T973-2005. The exact initial mass of the sample stones were taken down as  $m_0$  (g) at first. The samples were treated as the following process in succession: soaked in  $1\%$  (v/v)  $\text{H}_2\text{SO}_4$  for

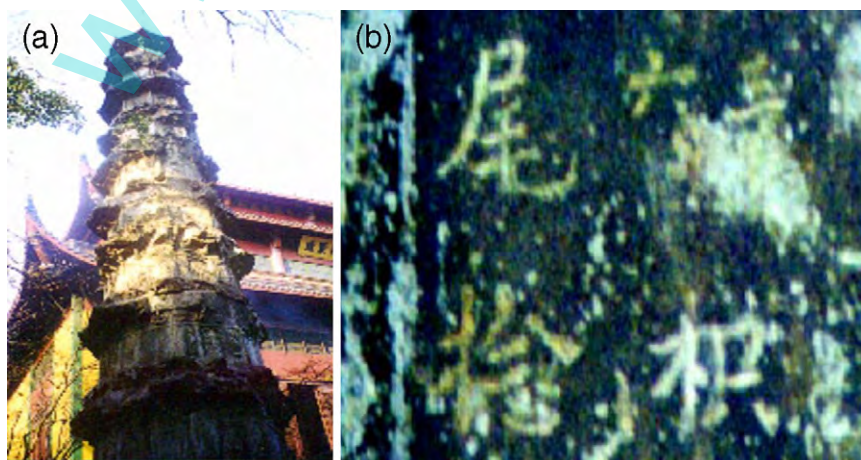


Fig. 1. Sampling site: (a) the Double Tower in Lingyin Temple, Hangzhou; (b) the inscriptions on the base of Double Tower.

48 h, taken out from the solution, washed lightly to remove soluble fractions on the stone surface, dried again at  $60 \pm 2^\circ\text{C}$  for 24 h and taken out from the oven and cooled down to room temperature in the drier. The terminal mass was taken down as  $m_1$  (g). The rate of mass loss of sample stones  $\Delta m$  (%) was calculated as the following equation:

$$\Delta m = \frac{m_1 - m_0}{m_0} \times 100$$

The above was a decay cycle, then operating repeatedly.

The soiling resistance of specimens was tested referring to the national trade standard for natural stone protectant of China, JC/T973-2005. The blue-black ink was mixed with water to prepare a series of standard solutions. The volume ratio of ink to water is: (i) 1 to 4, (ii) 2 to 3, (iii) 3 to 2, (iv) 4 to 1, (v) 5 to 0. A drop of pure ink was dripped in the stone surface, and the standard solutions were dripped respectively on five blocks of untreated stones. After 1 min, the ink spots were washed with flowing fresh water. After drying, the specimen was compared with the standard specimens to ascertain the rate of soiling resistance according to the shade of spot color.

### 3. Results and discussions

#### 3.1. Composition and structure of the crude conservation film

##### 3.1.1. FTIR analyses

FTIR analyses revealed the main composition of the crude film. For comparison, a standard sample of pure calcium oxalate monohydrate was analyzed together with the sample of the crude film. FTIR spectra are shown in Fig. 2. Spectrum A refers to the crude film and Spectrum B is the standard sample. By comparison, the characteristic infrared absorbance peaks of  $-\text{OH}$  (between  $3400$  and  $3450\text{ cm}^{-1}$ ) and  $\text{COO}^-$  (between  $1625$  and  $1320\text{ cm}^{-1}$ ) have been found, which indicates the existence of calcium oxalate [8]. In addition, there are the other absorbance peaks in Spectrum A which should be of calcium sulphate and calcium carbonate, because calcium sulphate and calcium carbonate are the primary ingredients of stone. Sulphate is characterized by the presence of absorbance peaks

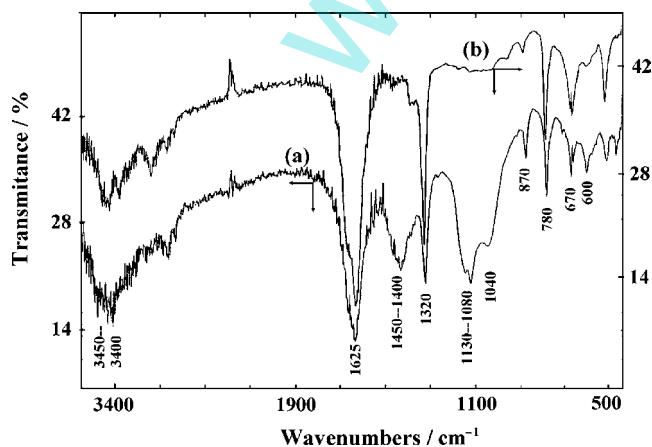


Fig. 2. FTIR spectra: (a) crude protective film; (b) standard (whewellite).

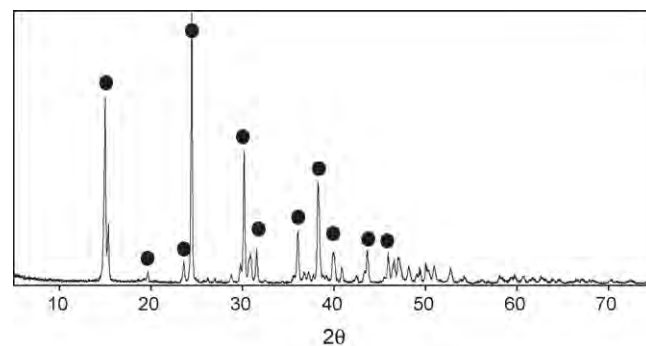


Fig. 3. XRD spectrum of the crude protective film.

around  $1150\text{--}1040\text{ cm}^{-1}$  (strong) and  $650\text{--}575\text{ cm}^{-1}$  (middle). Carbonate can be diagnosed by the presence of absorbance peaks around  $1425$ ,  $874$  (middle) and  $712\text{ cm}^{-1}$  (middle).

##### 3.1.2. XRD analyses

XRD analyses of the natural conservation film are shown in Fig. 3. A series of characteristic diffraction peaks ( $15.04$ ,  $24.41$ ,  $30.13$ ,  $31.51$ ,  $36.02$ ,  $38.28$ , etc. at  $2\theta$ ) of whewellite, i.e. calcium oxalate monohydrate, can be found. Associated with the analysis results of FTIR, it can be concluded that the main composition of the natural conservation film is calcium oxalate monohydrate, which plays a key role in stone conservation though its content in the surface layer of rock is poor.

##### 3.1.3. Surface microtopography analyses

Fig. 4 is a PLM image of a representative grain of the crude protective film, whose magnification is 500 times. The PLM image reveals that the film thickness is about  $5\text{--}15\text{ }\mu\text{m}$  and it can be divided into three parts. The surface layer is dust black; the intermediate layer is brown yellow and translucent; the inner layer, or bottom layer, is comparatively transparent. There is no extremely evident boundary between the protective film and the stone matrix.

Further studied was carried out by SEM at a magnification of 2000 and 5000 and TEM at a magnification of 100,000. The results show that three parts of the film have their own characteristics.

Fig. 5(b) is a SEM image at a magnification of 5000 of the surface layer. In order to observe further, TEM analyses have also been carried out and a TEM image at a magnification of

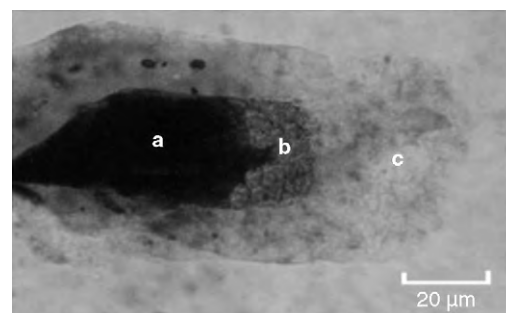


Fig. 4. PLM image of the crude protective film: (a) surface layer; (b) intermediate layer; (c) inner layer.

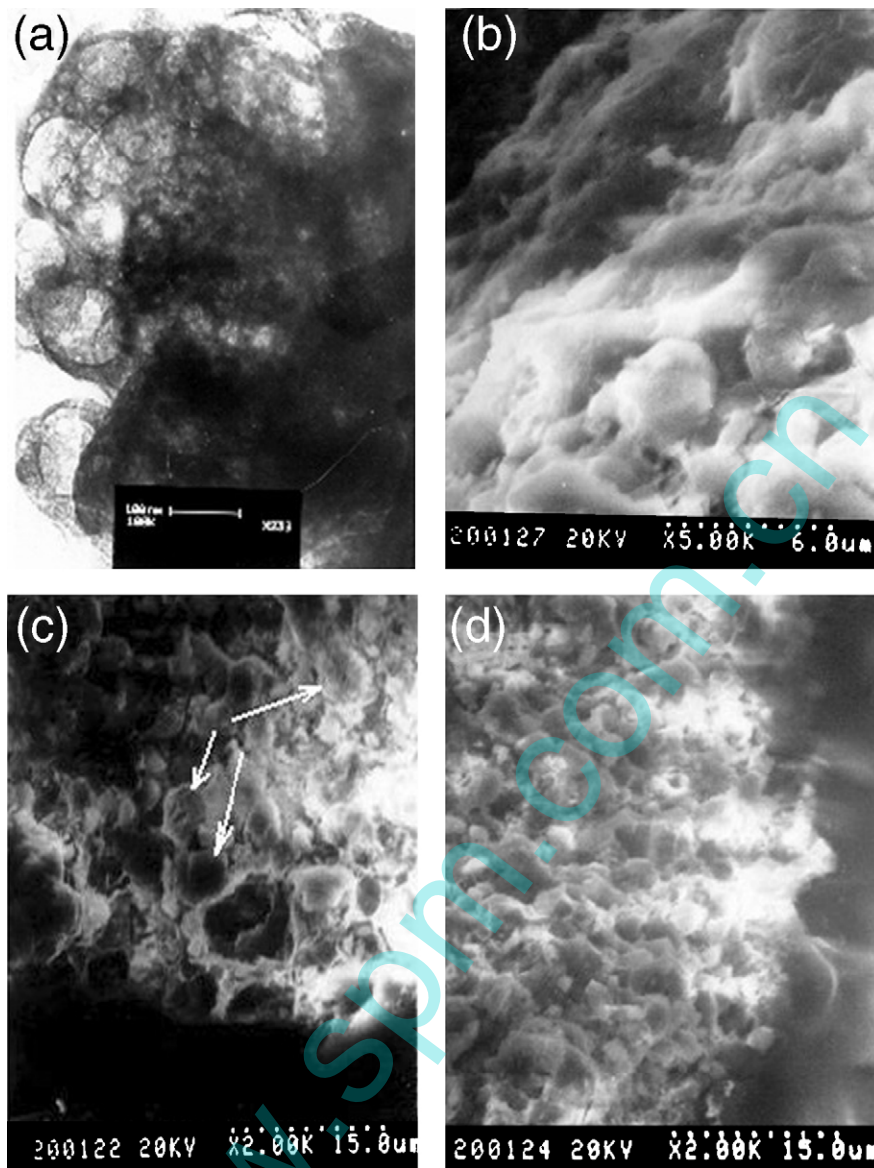


Fig. 5. Microtopography of the crude conservation film: (a) TEM image of the surface layer; SEM images: of (b) surface layer; (c) intermediate layer; (d) inner layer.

100,000 is shown in Fig. 5(a). A lot of microbial mycelia remains over the outside of rock can be found; it reveals a big fungal colonization that have ever been existing on the rock surface. Moreover, a few of crystal grains are there. When the fungi died because of aversive environmental conditions, their remains left over the rock surface. The remains of fungi absorb dust from the air and make the rock surface soiling. As a result, the appearance of rock become dust black.

Fig. 5(c) is a SEM image at a magnification of 2000 of the intermediate layer, which shows that there is a great decrease in the number of debris of microbial mycelia. In contrast with it, many crystal grains arrayed closely are found in the layer. The crystal grains form elliptical or spherical shape. Taken into consideration the FTIR and XRD analyses, it can be drawn that the crystal grains should be of whewellite and this section should be the main body of the crude protective film, which form a translucent film on the rock surface.

Fig. 5(d) is a SEM image at a magnification of 2000 of the inner layer. The inner layer is a conjunctive layer between the film and the underlying rock. The image shows that the figure of crystal grains of calcite, main mineral ingredients of rock, has been transformed in comparison with their original figure. The edges and angles of crystal grains become round and blunt instead of acute and sharp presumably because of microbial secretion effect. However, the size of crystal grains is almost the same as the origin (4–5  $\mu\text{m}$ ).

#### 3.1.4. EDAX analyses

EDAX analyses of each layer of the crude protective film are provided in Table 1. It can be found easily that the content of phosphorus in the film decrease from the surface layer to the inner layer, due to the microbial remains. In fact, the phosphorus is one of most important and necessary elements in the cell of microorganisms. It is especially important and remarkable that

Table 1  
EDA analyses on the composition (%) of parts A–C of the crude protective film

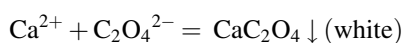
	Surface layer	Intermediate layer	Inner layer
Phosphorus	4.76	2.51	0.14
Sulfur	2.70	1.77	0.00
Silicon	1.66	1.82	6.13
Calcium	90.90	93.90	93.60

there are not any records on protective man-made treatments on the Double Tower. It can be suggested that the formation of the crude protective film has a close relationship with the microbial existence. On the contrary, there is an increase in the content of silicon in the film from the surface to the inner layer, because it is an elemental ingredient of rock, so the more the film is close to the underlying rock, the more the content of silicon in the film increase. Furthermore, there is also a decrease in the content of sulfur in the film from the surface to the inner layer, caused by biological metabolism that need participation of sulfur, or due to air pollution sulfur deposition on the rock surface.

Summing up all the above analyses, the main composition of natural protective film on the rock surface is calcium oxalate monohydrate. Microorganisms act an important part in the process of film formation. The solubility of monohydrate calcium oxalate dissolved in water is lower than that of calcium carbonate. Especially being dissolved in acidic water, the solubility of monohydrate calcium oxalate is an order of magnitude lower than that of calcium carbonate. Moreover, crystal grains of calcium oxalate are regular and dense because of participation of microbes. As shown in the PLM and SEM images, there is no evident interface between the protective film and the rock substrate, and compositional analyses reveal that the protective film is composed of calcic inorganic compounds as the rock substrate; so the film and rock adhere fast to each other and the rock is not damaged easily by stresses. The crude protective film of  $\text{CaC}_2\text{O}_4$  has protected historic stones well for a long time because of its low solubility.

### 3.2. Formation mechanism of the crude film

It can be concluded that the crude protective film of calcium oxalate should be the products resulting from biomineralization because of the presence of microbial remains. Rock surfaces can provide to microorganism nutrition with mineral elements, composing the rock, and organic substances attaching to rock surfaces. It is also well known that the fertility and diffusibility of microorganisms is very high. In fact, when microorganisms come to the surfaces of rock by wind and floating dust, they will propagate rapidly as long as the local environments, e.g. humidity, temperature and acidity, are fit for them. When microorganisms colonize the surface of calciferous rock, they secrete organic acid to erode the rock in order get mineral matter [9,10]. Among these organic acids, oxalic acid is the unique one that can react with calcium ion to form stable precipitate [11]:



The above reaction can be carried out successfully because of the solubility of calcium oxalate that is smaller than that of calcium carbonate. The formation of calcium oxalate from biochemical action has also been verified by a study carried out by Monte [12]. She cultured marble specimens with a fungal strain of the genus *Sporotrichum* isolated from the Pisa Tower. After 8 months' incubation, an orange-brown film of calcium oxalate was formed.

The crystalline form of calcium oxalate often has two types, e.g. whewellite (calcium oxalate monohydrate) and weddellite (calcium oxalate dihydrate). The crystalline form of the crude protective film on the rock surface, which is thin, regular, compact and crescent, is mainly of whewellite [13]. Sometimes, however, the film composed of weddellite, which is irregular, incompact and green in appearance, can be found in the other places. It might relate to circumstances surrounding the rock.

When the living environments of microorganisms are very dry, they are almost in a dormant state, at which they make great efforts to avoid water loss and energy consumption for maintaining their life. Meanwhile, microorganisms only secrete a little quantity of oxalic acid to form compact whewellite layer, and the layer covers the rock surface as full as possible for avoiding water evaporation from the interior of rock, as is hypothesized; and thus the microorganisms can only develop along the edge. In course of time, a compact biomineralized film of calcium oxalate monohydrate was formed on the rock surface. Although it is an instinctive response of microorganisms to their living environment, it is beyond conception that the biomineralized film of whewellite unexpectedly protects the rock surface well [14]. On the contrary, when the living environment is extremely wet, the microorganisms metabolize vigorously and secrete a great amount of organic acid in order to get enough mineral elements to grow as better as possible. The excess oxalic acid, leads to formation of weddellite, which can absorb and store more water. The fast microorganism growth results in a calcium oxalate film incompact, irregular and permeable. As soon as the humidity become decreasing, weddellite will convert into whewellite because calcium oxalate dihydrate is an unstable crystalline form [15]. Of course, also the presence of minor elements could influence the development of one of the crystal phases. In any case farther researches are need.

### 3.3. Characterization of the artificial protective film

The investigation of the crude protective film gives us an inspiration. A new film for historic stone conservation can be obtained by imitation of the crude film's growing. As in the above discussion about the formation mechanism of the crude film, the calcium oxalate film is a product resulting from biomineralization.

Biomineralization is a natural approach to advanced materials synthesis, by which minerals are synthesized by living organisms [16,17]. The process of biomineralization includes four main steps: organic molecular preorganization, interfacial recognition, growing guidance and cellular processing. Nature's way of

processing is an invaluable guide to developing new synthetic processes that can produce useful film with similar designs. The first key aspect is the self-assembly of organic materials, which contain anionic functional groups, on the substrate to perform a function as template. Second, the nucleation and growth of inorganic materials is controlled in specific sites by the orienting and shaping action of the assembled organic template, and finally, inorganic minerals of higher order structures are consequently prepared [18].

The key requirement for successful film formation by biomimetic synthesis is to promote the formation of the inorganic phase on the substrate directly (that is, heterogeneous nucleation) and prevent the homogeneous nucleation of particles in the solution, which can be carried out by surface chemical modification, such as surface functionalization, just like organic macromolecules secreted by cells in the process of biomineralization. Therefore, organic macromolecules act an important part in the process of natural and artificial biomineralization because they can provide some anionic functional groups as functional templates. These anionic functional groups include sulfonic group ( $-\text{SO}_3\text{H}$ ) and carboxy group ( $-\text{COOH}$ ) of acidic polysaccharide, carboxy group of protein, phosphate group of phosphatide, etc. [18,19].

In our investigation, chondroitin sulfate is selected as an organic macromolecule template. It is a category of principal acidic mucopolysaccharide in the ground substance of mammalian tissues and cartilage. The schematic diagram of CS' structure is shown in Fig. 6. At first, surfaces of stone substrates are functionalized to adhibit functional groups. Functionalized stones are then soaked in supersaturated solution. Coordination bonds are formed between the functional groups ( $-\text{SO}_3\text{H}$ ,  $-\text{COOH}$ ) of CS and calcium ions, by which the chelate complex of  $\text{Ca}^{2+}$ -CS is formed and free  $\text{Ca}^{2+}$  is transmuted into combined  $\text{Ca}^{2+}$ . As a consequent result, the concentration of  $\text{Ca}^{2+}$  about fundamental chain of CS become increasing; on the other hand, the concentration of  $\text{Ca}^{2+}$  in other region become decreasing. The required supersaturation for precipitation of  $\text{CaC}_2\text{O}_4$  crystals occur only on the fundamental chain of CS, and  $\text{CaC}_2\text{O}_4$  crystals grow only in desired specific sites. Consequently, growth and aggregation of  $\text{CaC}_2\text{O}_4$  crystals are under the guidance of interaction between mineral ions and organic molecules.

XRD analyses were operated at 40 kV and 40 mA and Cu K $\alpha$  radiation (1.5406 Å). The diffraction spectra were recorded

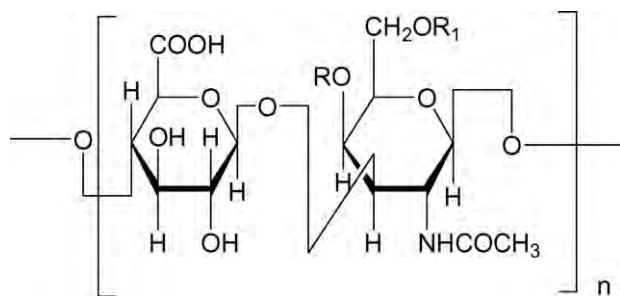


Fig. 6. Structural schematic diagram of CS. CSA:  $\text{R}-\text{SO}_3\text{H}_3$ ,  $\text{R}_1-\text{H}$ ; CSC:  $\text{R}-\text{H}$ ,  $\text{R}_1-\text{SO}_3\text{H}_3$ .

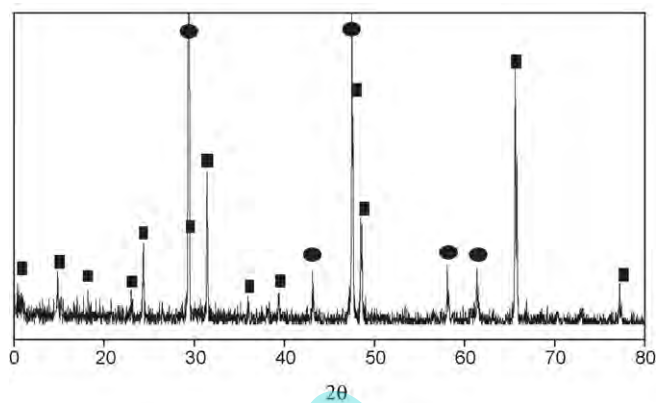


Fig. 7. XRD image of the artificial protective film on the stone sample: (■) whewellite; (●) calcite.

over the range  $10-80^\circ$  at  $0.02^\circ$  intervals in  $2\theta$ . A scanning speed of  $0.2^\circ/\text{s}$  was used. As shown in Fig. 7, a series of characteristic diffraction peaks of whewellite, which indicates the chief composition of the film is calcium oxalate monohydrate, can be found. The results of XRD also show the characteristic diffraction peaks of calcite, i.e. calcium carbonate, which are the peaks of the stone substrate. The discovery of the diffraction peaks of calcium carbonate illustrates that the film may be extremely thin on the stone surface.

AFM images were recorded in Fig. 8. The scanning probe needlepoint is of silicon nitride. The horizontal definition is 0.26 nm and the vertical definition is 0.01 nm. The imaging mode is contacting mode. The scanning size is  $28\ \mu\text{m} \times 28\ \mu\text{m}$  and the image pixel is  $512 \times 512$ . The scanned specimen size was  $1\ \text{cm}^2$ . They were cut off from the same block of stone sized  $5\ \text{cm}^2$  and treated as showed in Section 2.2.1. AFM images show that the biomimetic materials of calcium oxalate have grown on the stone surface to form, at the beginning, isolated structures. With the process repeating, the islands of calcium oxalate start to grow toward all sides to be a union and become thicker and thicker. Sample stone with a film of nine layers are almost entirely covered.

Fig. 8(d) is an image of a scanned specimen cut off straight from a bigger block of stone coated for nine times. It clearly reveals that the stone substrate is covered by the thin film with a peninsula form, which is more than 120 nm thick. But there is a blank zone uncovered. There presumably was the same film at the beginning, but it was removed by water during cutting stone for preparing the scanned specimen; or it is might be the surface deficiencies during the film process which can be overcome by improving the growth conditions of the film. Although the specimen had been gone through flushing of the flowing water, cutting of the cutter and scanning of the probe, the film can still adhere firmly to the stone substrate, which implies a good adhesive ability of the film on the stone surface.

The obtained value of efficacy to resist to acid was shown in Fig. 9. The results of the corrosion curve show that the corrosion curve slope of the blank is bigger than that of the treated stone, which reveals that the artificial protective film

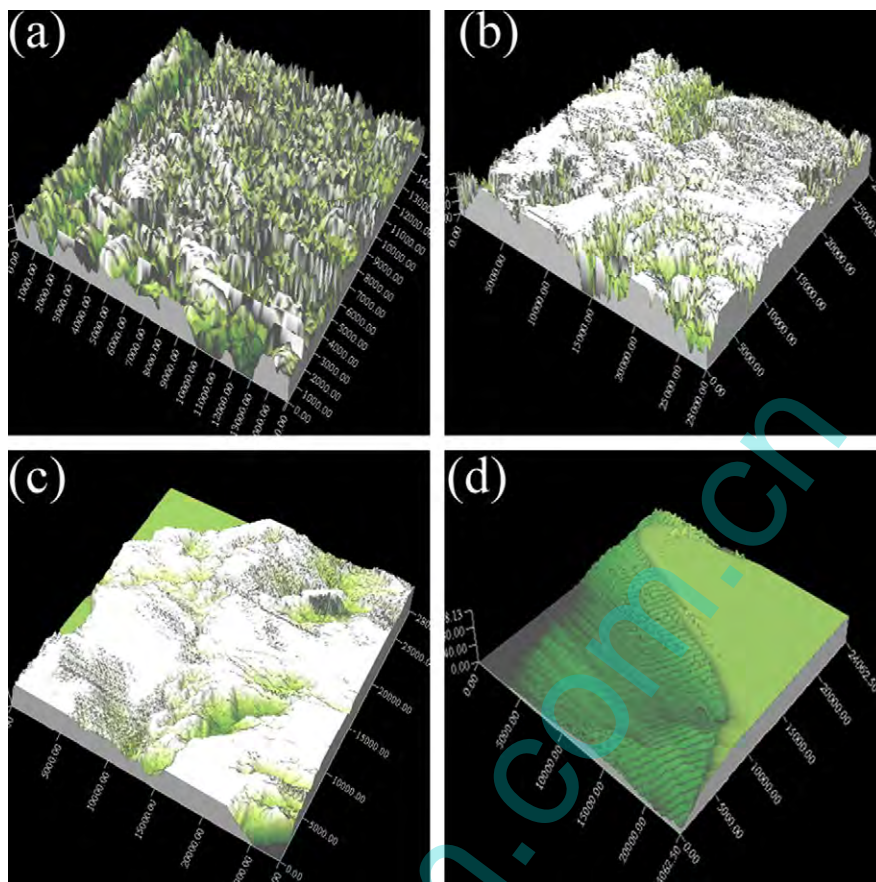


Fig. 8. AFM images of the artificial protective films. The layer number of film: (a) 0 (blank); (b) 1; (c) and (d) 9.

prepared by biomimetic synthesis can play a role in stone conservation. In addition, when the sulfuric acid solution, pH 0.8, was dropped on the coated sample stone, any visible phenomena occur; on the contrary, a large quantity of air bubbles, rises on the untreated stone showing corrosion phenomena.

The obtained value in soiling resistance measurements show that the soiling resistance of protected stone has been improved to grade II from grade V of unprotected stone.

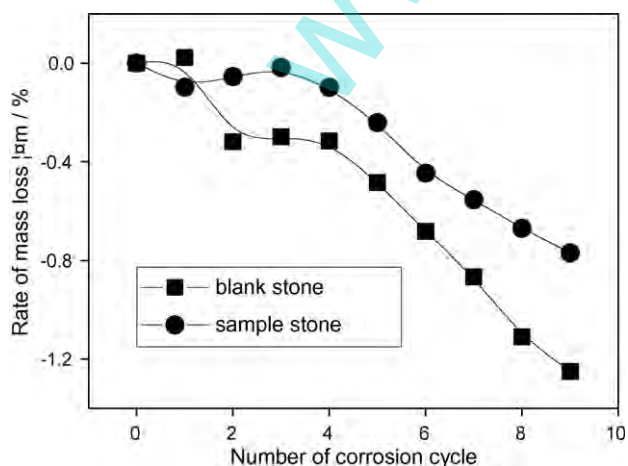


Fig. 9. Curve of acidic erosion.

#### 4. Conclusions

A crude protective film sampled from Double Tower at Lingyin Temple, working as a protective layer for the inscriptions on historic stone for nearly thousand years, has been analyzed by some instruments. The obtained results show that it consists mainly of calcium oxalate monohydrate and the film should be a product of biomineralization.

On the basis of the formation mechanism of the crude film, the artificial film of calcium oxalate monohydrated for stone conservation has been prepared through biomimetic synthesis. The raw materials are inexpensive and the synthesis pathway is simple. Moreover, the efficacy to resist acid of the treated stone has been proved to be well. The film material itself, calcium oxalate, is well compatible with the stone substrate. The most noteworthy advantage is that the biomimetic synthesis can be going under mild physiochemical conditions, being an important characteristic required for stone conservation. Therefore, the biomimetic synthesis should have great potentialities in applied protective methods and should represent a new prospective in stone conservation.

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