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Biomimetic fluorapatite films for conservation of historic calcareous stones

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Fluorapatite protective films were prepared on marble substrates using a biomimetic method. By mimicking the mineralization mechanism of enamel, phosphorus and fluorine were introduced on the surface of the marble substrate. In the presence of a biological template, namely collagen, an integrated fluorapatite film was produced and the marble substrate was entirely covered. The prepared fluorapatite films were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), and energy dispersive X-ray (EDX) spectroscopy. The performances of the fluorapatite films were evaluated by color changes, capillary water absorption, and acid resistance tests. The results revealed that the fluorapatite films had good compatibility with the marble substrate; the physical properties such as color and capillary water adsorption of the marble substrates were unchanged. The fluorapatite films also had good acid resistance and were stable even in heavy acid rain.

biomimetic, fluorapatite film, conservation, calcareous stones

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Calcareous stone is the most widely used material in historic statues and monuments. Because these stones are carbonates, historic relics exposed to the open air are vulnerable to weathering erosion. The extensive use of fossil fuels has been causing serious atmospheric pollution since the Industrial Revolution. Large quantities of air pollutants such as sulfur dioxide [1], carbon dioxide [2], and nitric oxide [3] released during the combustion of coal and oil have led to accelerated deterioration of calcareous stone relics [4].

Various precautions have been proposed for the conservation of historic calcareous stones. Coatings of synthetic polymers such as acrylics, epoxides, and organosilicon compounds have been extensively used in the conservation of historic stones in the past [5–7]. Surfactants such as oleates and organic phosphates [8] have also been explored for the conservation of calcareous stones. These organic protective materials work to a certain extent, but they have inherent disadvantages such as short lifetimes [9,10], poor compatibility with the stones, and they cause color changes of [11] the stones. Also, stone relics treated with organic materials can be attacked by microorganisms which feed on the protective organic materials [12]. Natural calcium oxalate films were found to be good for the protection of carbonate stones [13]. However, mimetic synthesis of the calcium oxalate films was unsatisfactory. The synthesized calcium oxalate on the carbonate substrate was usually present as isolated crystal particles rather than as a continuous film, and the adhesion between the crystal particles and the carbonate stone substrate was limited [14].

We recently studied the consolidation of weathered historic calcareous stones using hydroxyapatite, and the results were satisfactory [15]. In this paper, a fluorapatite protective film was prepared on the marble substrate by a biomimetic method. The strategy was to mimic the growth of

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tooth enamel. This involved introducing phosphorus and fluorine on the surface of the carbonate stone, and then letting them remineralize in the presence of collagen, which is a bioactive material used for bone restoration [16]. During the remineralization process, a compact and continuous fluorapatite film with good adhesion was produced. The protective performances of the prepared fluorapatite films were satisfactory. The films were able to protect calcareous stones from attack by heavy acid rain.

1 Experimental

1.1 Sample preparation

Absorbent cotton was immersed in a solution of ammonium phosphate (0.0–5.0 g/L), ammonium fluoride (0.0–0.6 g/L), and Type I collagen (0.0–0.1 g/L). The final mixtures were packed onto white marble specimens (2.5 cm × 2.5 cm × 0.5 cm) by pressing for 48 h. In the experiments, the molar ratio of ammonium phosphate to ammonium fluoride was fixed at 3∶1. After pressing, the specimens were washed with deionized water and dried in an oven at 60°C for 24 h. Absorbent cotton, ammonium phosphate, ammonium fluoride (Sinopharm Chemical Reagent Co., Ltd, China) and Type I collagen (Elastin Products Company, Inc., USA) were used without purification.

1.2 Characterization

The morphologies of the marble samples were observed by scanning electron microscopy (SEM, FEI SIRION-100). An electron diffraction spectrometer (EDS) attached to the SEM was used to determine the compositions of the marble samples. The crystal structures of the marble samples before and after biomimetic treatment were investigated by X-ray diffractometry (XRD, AXS D8 ADVANCE).

Color changes of the specimens were evaluated using a reflectance spectrophotometer (Concise Apparatus Co. Ltd, Shanghai, China). The reference material was an untreated marble.

The capillary water absorptions of the specimens were determined according to GB/T17146-1997 [17].

The acid resistances of the stone samples were judged according to the acidity changes of the sulfuric acid solution used for immersion tests on the stone samples.

2 Results and discussion

2.1 Biomimetic treatment of white marble

SEM results for the marble samples are presented in Figure 1. Figure 1a shows the SEM image of white marble. Figure 1b and c shows the SEM images of the marble samples treated with a mineralization solution (5.0 g/L of ammonium phosphate and 0.6 g/L of ammonium fluoride) in the absence and presence of Type I collagen.

In the absence of collagen, a film is produced on the surface of the marble substrate. However, the film is of poor quality. There are many cracks and film failure can also be observed (Figure 1b). In the presence of collagen (0.1 g/L), the quality of the film (Figure 1c) is greatly improved. Cracks and film failure are no longer observed. This indicates good adhesion between the film and the marble substrate. Energy dispersive (EDX) spectroscopy and XRD were used to confirm the composition of the film. The EDX results (Figure 2) indicate that the film is composed of calcium, phosphorus, oxygen, and fluorine. In the XRD spectrum of the film (Figure 3), the characteristic diffraction peaks of fluorapatite (d = 3.4478 Å, 2.7878 Å, 2.7137 Å, 2.6527 Å, 1.9271 Å, and 1.8378 Å) can be easily distinguished. The characteristic diffraction peaks of calcite (d = 3.0437 Å, 2.4954 Å, 2.2829 Å, 2.0906 Å, 1.9271 Å, and 1.8733 Å) can also be detected. X-rays can penetrate the thin fluorapatite film and detect the calcite in the marble substrate. These results show that the composition of the film is fluorapatite.

Generally, organic macromolecules such as soluble collagens can be used as templates to crystallize inorganic compounds, especially hydroxyapatite [18]. After treatment with the mineralization solution, calcium ions are dissolved out of the calcium carbonate matrix of the marble substrate. In the presence of collagen, these calcium ions absorb at active sites such as carboxyl groups [19] on the surfaces of the calcium carbonate matrix, react with phosphate and fluoride ions, and precipitate again as fluorapatite. Collagen can therefore promote the direct formation of a fluorapatite phase on the marble substrate [20], and this helps to improve the adhesive strength between the fluorapatite film and the marble substrate.

To prepare the fluorapatite film, the molar ratio of ammonium phosphate to ammonium fluoride in the mineralization solution was fixed at 3∶1. The results show that the concentration of the mineralization solution strongly affects the development of the fluorapatite film. At low concentrations (less than 2.0 g/L of ammonium phosphate), only part of the marble substrate is covered by the film (Figure 1d).

As the solution concentration increases, the fluorapatite film gradually becomes more extensive, and the marble substrate becomes completely covered (Figure 1e). SEM images of the film at higher magnification show that the fluorapatite film is coral-like, and very regular and homogenized (Figure 1f, g). However, when there is more than 5.0 g/L of ammonium phosphate in the solution, the thickness of the film ceases to grow (Table 1). The SEM image of a cross-section (Figure 1h) reveals that the maximum thickness of the fluorapatite film is ~60 μm. After cutting and flushing treatment, the film still adheres firmly to the marble substrate, implying good compatibility with the marble substrate.

The fluorapatite film is essentially formed by a metasomatic

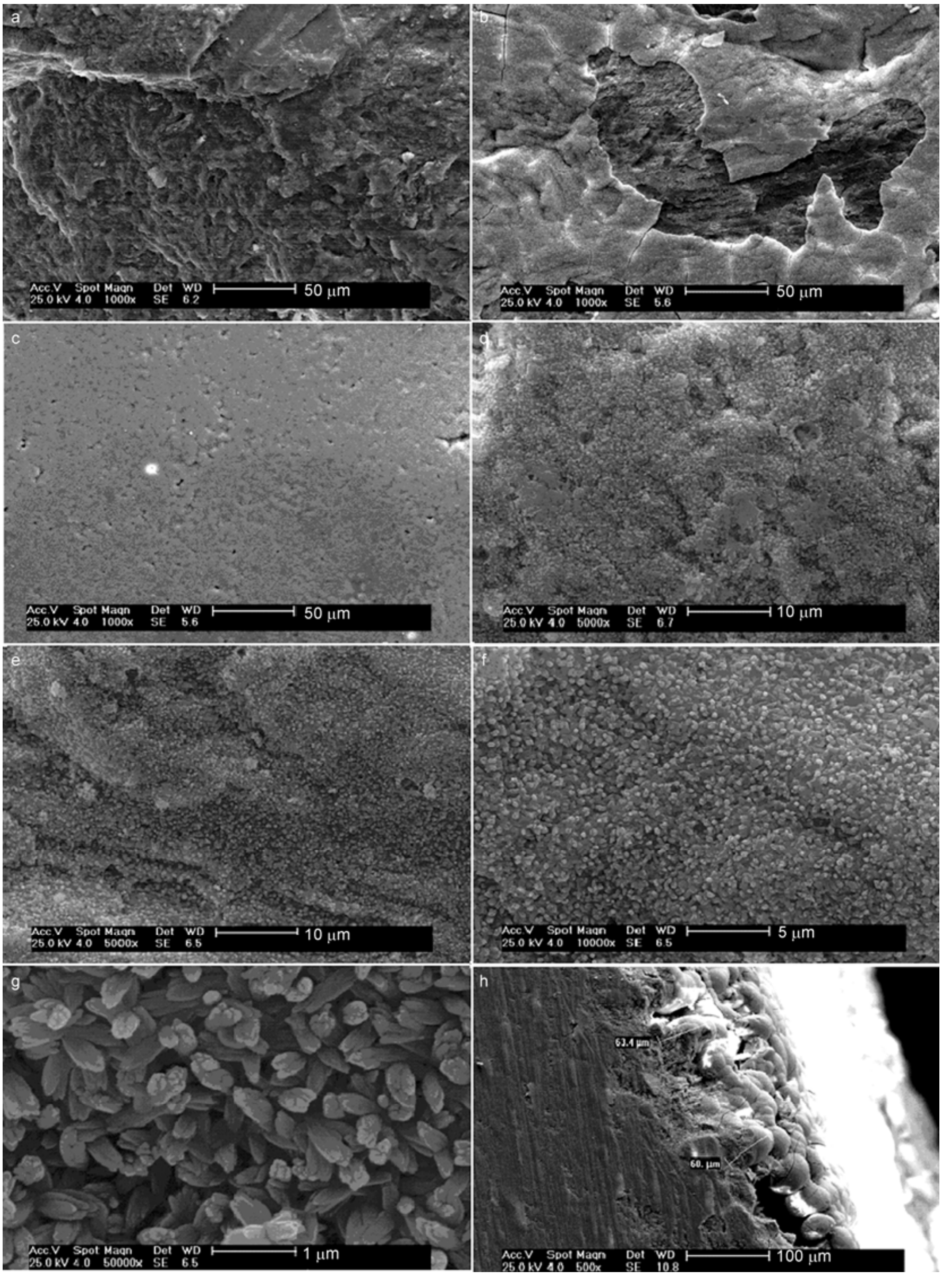

Figure 1 SEM images of the marble specimens. a, Marble substrate; b, marble treated with a mineralization solution containing 5.0 g/L of ammonium phosphate and 0.6 g/L of ammonium fluoride; c, e, f, g, marble treated with a mineralization solution containing 5.0 g/L of ammonium phosphate, 0.6 g/L of ammonium fluoride, and 0.1 g/L of collagen; d, marble treated with a mineralization solution containing 2.5 g/L of ammonium phosphate and 0.3 g/L of ammonium fluoride; h, cross-section of the marble treated with a mineralization solution containing 5.0 g/L of ammonium phosphate, 0.6 g/L of ammonium fluoride, and 0.1 g/L of collagen.

reaction between the mineralization solution and the marble substrate:

$$14H^+ + 6PO_4^{3-} + 10CaCO_3 + 2F^- \rightarrow Ca_{10}(PO_4)_6F_2 + 10CO_2 + 7H_2O \quad (1)$$

The metasomatic reaction takes place mainly on the surface of the marble substrate and the growth of the fluorapatite film is not unlimited. This is because the solubility of fluorapatite ($K_{sp} = 7.8 \times 10^{-122}$) is much lower than that of calcite ($K_{sp} = 4.5 \times 10^{-9}$). The produced fluorapatite film

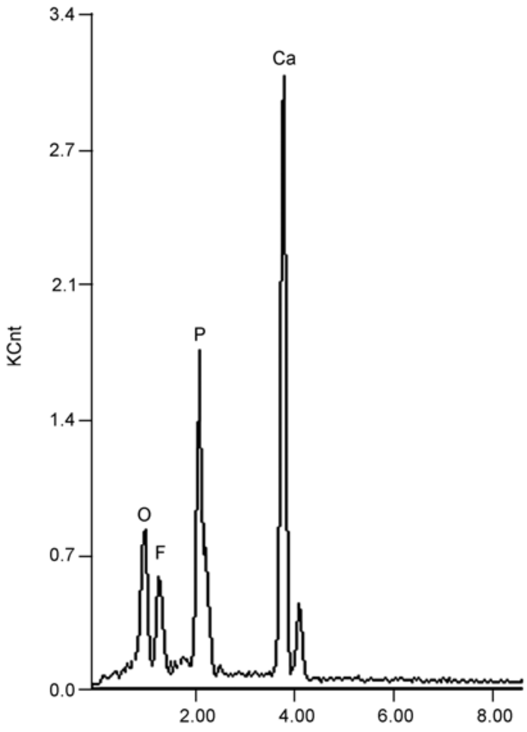

Figure 2 EDX results for the newly-formed film.

covers the surface of the marble substrate and blocks the dissolution of calcium carbonate. As the calcium cations are consumed, the metasomatic reaction and development of the fluorapatite film will finally stop.

To sum up, the optimal mineralization solution for preparing a fluorapatite film on the marble substrate is composed of 5.0 g/L of ammonium phosphate, 0.6 g/L of ammonium fluoride, and 0.1 g/L of Type I collagen.

2.2 Assessment of the fluorapatite film

(1) Capillary water absorption. The results of capillary water absorption for the marble specimens are listed in Table 2. The capillary water absorption of the marble specimen was almost unaffected by the biomimetic treatment. This indicates that the biomimetic treatment is a suitable conservation procedure because it does not alter the capillary water absorption and retains the "breathing function" of the marble substrate [21].

(2) Color changes. The color changes of the marble specimens before and after biomimetic treatment are reported in Table 2. For the treated marble specimens, the overall color variation is ~2.12. The color changes in two neighboring surfaces cannot be detected by visual observation if ΔE^* is less than 2. Almost no visual changes could be observed for white marble samples treated using the biomimetic method and the original states of the calcareous relics could be maintained.

(3) Acid resistance of the treated marble. The untreated marble has low acid tolerance (pH 5.5). The treated marble, however, has better acid tolerance (pH 4.0, equivalent to heavy acid rain). This is attributed to the low solubility, good adhesiveness, and anti-acid performance of the fluorapatite film. The solubility of fluorapatite in water is much lower than that of calcite. Fluorapatite and marble are both

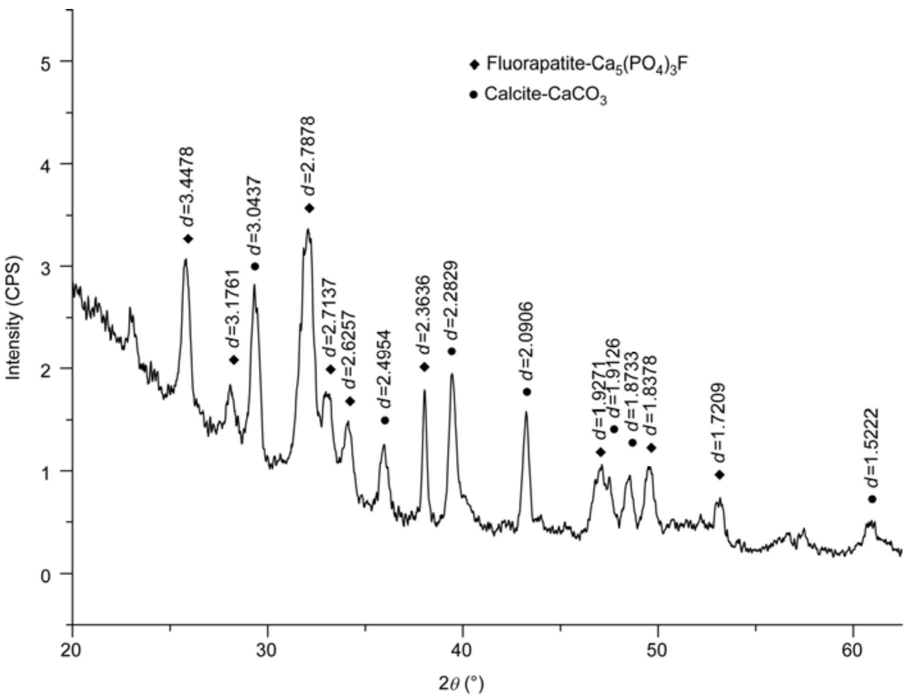

Figure 3 XRD results for the newly-formed film.

Table 1 Thickness evolution of the fluorapatite film

Concentration of mineralization solution (g/L)	3.0	4.0	5.0	6.0
Thickness of the fluorapatite film (μm)	25±5	55±8	60±5	60±7

Table 2 Performances of the fluorapatite films

	Color alteration				Capillary water adsorption (%)	Acid resistance (pH)
	*L**	*a**	*b**	*E**		
Untreated white marble	86.77	−132.9	3.39	0	0.078	>5.5
Treated white marble	88.29	−134.3	2.72	2.13	0.077	>4.0
	88.29	−134.3	2.77	2.14	0.075	>4.0
	88.28	−134.3	2.71	2.09	0.076	>4.0

calcic inorganic compounds. Because of the good compatibility between the physicochemical properties of the fluorapatite film and those of marble, the film can adhere firmly to the marble substrate. Compared with calcite, fluorapatite is insensitive to acid [22]. Fluorapatite can therefore act as a protective film and prevent erosion of calcareous relics by acid rain.

3 Conclusion

Fluorapatite films were prepared on marble substrates using a biomimetic method. The prepared fluorapatite films had good acid resistance and compatibility with the marble substrates. In addition, after the biomimetic treatment, the physical properties such as color and capillary water absorption of the marble substrate were unchanged. These positive results show that fluorapatite films are suitable protective materials for historic calcareous stones.

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1 Toniolo L, Zerbi C M, Bugini R. Black layers on historical architecture. Environ Sci Pollut Res, 2009, 16: 218–226
2 Ge Y, Jie D M, Guo J X, et al. Response of phytoliths in Leymus chinensis to the simulation of elevated global CO_2 concentrations in Songnen Grassland, China. Chin Sci Bull, 2010, 32: 3703–3708
3 Zhang Y H, Xie S D. Choice of control of sulfur and/or nitrogen deposition based on critical loads. Chin Sci Bull, 2010, 55: 493–498
4 Bonazza A, Messina P, Sabbioni C, et al. Mapping the impact of climate change on surface recession of carbonate buildings in Europe. Sci Total Environ, 2009, 407: 2039–2050
5 Tsakalof A, Manoudis P, Karapanagotis I, et al. Assessment of synthetic polymeric coatings for the protection and preservation of stone monuments. J Cult Herit, 2007, 8: 69–72
6 Zielecka M, Bujnowska E. Silicone containing polymer matrices as protective coatings: Properties and applications. Prog Org Coat, 2006, 55: 160–167
7 Manoudis P, Papadopoulou S, Karapanagiotis I, et al. Polymer silica nanoparticles composite films as protective coatings for stone-based monuments. J Phys Conf Ser, 2007, 81: 1361–1365
8 Spanos N, Kanellopoulou D G, Koutsoukos P G. The interaction of diphosphonates with calcitic surfaces: Understanding the inhibition activity in marble dissolution. Langmuir, 2006, 22: 2074–2081
9 Cappitelli F, Sorlini C. Microorganisms attack synthetic polymers in items representing our cultural heritage. Appl Environ Microbiol, 2008, 74: 564–569
10 Liu F C, Hao Y S, Wang Z Y, et al. Flaking and degradation of polyurethane coatings after 2 years of outdoor exposure in Lhasa. Chin Sci Bull, 2010, 55: 650–655
11 Grassi S, Favaro M, Tomasin P, et al. Nanocontainer aqueous systems for removing polymeric materials from marble surfaces: A new and promising tool in cultural heritage conservation. J Cult Herit, 2009, 10: 347–355
12 Cappitelli F, Principi P, Pedrazzani R, et al. Bacterial and fungal deterioration of the Milan Cathedral marble treated with protective synthetic resins. Sci Total Environ, 2007, 385: 172–181
13 Ramazzi L, Andreotti A, Bonaduce I, et al. Analytical investigation of calcium oxalate films on marble monuments. Talanta, 2004, 63: 967–977
14 Liu Q, Zhang B J. Syntheses of a novel nanomaterial for conservation of historic stones inspired by nature. Mater Lett, 2007, 61: 4976–4979
15 Yang F W, Liu Y, Zhang B J, et al. Biomimic conservation of weathered calcareous stones by apatite. New J Chem, 2011, 35: 887–892
16 Visser R, Arrabal P M, Becerra J, et al. The effect of an rhBMP-2 absorbable collagen sponge-targeted system on bone formation *in vivo*. Biomaterials, 2009, 30: 2032–2037
17 Test methods for capillary water absorption of building materials (GB/T 17146-1997)
18 Boanini E, Bigi A. Biomimetic synthesis of carbonated hydroxyapatite thin films. Thin Solid Films, 2006, 497: 53–57
19 Ruoslathi E, Yamaguchi Y. Proteoglycans as modulators of growth factor activities. Cell, 1991, 64: 867–869
20 Elena V, Rosseeva E V, Buder J, et al. Synthesis, characterization, and morphogenesis of carbonated fluorapatite-gelatine nanocomposites: A complex biomimetic approach toward the mineralization of hard tissues. Chem Mater, 2008, 20: 6003–6013
21 Mosquera M J, de los Santos D M, Montes A, et al. Superhydrophobic composite films produced on various substrates. Langmuir, 2008, 24: 2772–2778
22 Antar K, Jemal M. Kinetics and thermodynamics of the attack of fluorapatite by a mixture of sulfuric and phosphoric acids at 55°C. Thermochim Acta, 2007, 452: 71–75