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# Study of TiO<sub>2</sub>-Modified Sol Coating Material in the Protection of Stone-Built Cultural Heritage

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**Abstract:** Coating materials can effectively protect stone-built cultural heritage and, as such, research into coating materials has gained comprehensive attention from researchers. The aim of this work is to prepare a TiO<sub>2</sub>-modified sol coating material (TSCM) and study its protective effects on stone-built cultural heritage. TSCM and pure TiO<sub>2</sub> sol (p-sol, unmodified; for comparison) were applied evenly over the entire surface of stone samples. The prepared stone samples included untreated stone, stone treated with pure sol, and stone treated with TSCM. The protective effects of TSCM were evaluated by water absorption, water vapor permeability, acid resistance, and weather resistance experiments. The results show that stone treated with TSCM has excellent water absorption and water vapor permeability, strong acid resistance, and good weather resistance, compared with untreated stone or stone treated with p-sol. The acid resistance of stone treated by TSCM was 1.75 times higher than that treated with traditional coating materials. The weather resistance cycle number of stone treated by TSCM was four times higher than that treated with organic protective materials. These findings are expected to provide useful suggestions for the protection of stone-built cultural heritage.

**Keywords:** stone-built cultural heritage protection; TiO<sub>2</sub>-modified sol; coating material; weather resistance; acid corrosion resistance

## 1. Introduction

The information recorded by stone-built cultural heritage is very valuable in the study of a country's history. Thus, the protection of stone-built cultural heritage has attracted the attention of researchers in various fields. Stone-built cultural heritage exposed to weather conditions can be damaged by acid rain corrosion [1–4], industrial pollution [5,6], microbial erosion [7,8], and soluble salt crystallization [9]. Coating stone is an effective way to protect stone-built cultural relics from damage [10]. The coating materials can be divided into two categories: organic and inorganic [11]. Organic coating materials have demonstrated excellent hydrophobicity, weather resistance, acid resistance, and salt corrosion resistance [12–14]; however, they can easily turn yellow, age, and show other negative effects on cultural heritage, thus reducing the protection timespan [15]. Inorganic coating materials have good compatibility with stone, improving its permeability, aging resistance, and service life [16], but may form a hard shell on the surface of the stone, which can easily damage or destroy its surface [17].

Research into new coating materials has become an urgent task in protecting stone-built cultural heritage. Nano-TiO<sub>2</sub> has shown potential applicability, owing to its good stability, non-toxicity, and low price [18–20]. In 1992, Skoulikidis proposed the possibility of using TiO<sub>2</sub> as a protective stone coating by establishing a model [21]. Many studies have used TiO<sub>2</sub> nanoparticles dispersed in aqueous phase

or added to acrylic polymers [22–24], but they could be easily removed from the coating surface owing to weak bonding [25–27]. In order to avoid the loss of TiO<sub>2</sub> nanoparticles, some researchers have proposed to composite TiO<sub>2</sub> nanoparticles into a SiO<sub>2</sub>-sol [28], which can enhance its photocatalytic activity when applied to a building. To the best of our knowledge, there have been no scientific studies about compositing TiO<sub>2</sub> nanoparticles into a TiO<sub>2</sub>-sol for the protection of stone-built cultural heritage. More importantly, the method presented in the work of [28] provides us with valuable suggestions about the protection of stone-built cultural heritage. Hence, it is necessary to investigate a modified TiO<sub>2</sub>-sol with significant protective effect on stone-built cultural heritage.

The aim of this paper is to prepare a TiO<sub>2</sub>-modified sol coating material (TSCM) that is capable of protecting stone-built cultural heritage. Analyses of the composition and microscopic morphology of TSCM were conducted using X-ray diffraction (XRD) and scanning electron microscopy (SEM). Some experiments were conducted to evaluate the protective effects of TSCM, in terms of wettability, weather resistance, and acid resistance. The results suggest that TSCM has excellent water absorption, water vapor permeability, acid resistance, and weather resistance. The study, therefore, provides a new method for the protection of stone-built cultural heritage.

## 2. Materials and Methods

### 2.1. Materials

All chemicals used in this study were analytical reagents (purity greater than 99.7%), including tetrabutyl titanate (TBT; Aladdin, Waukesha, WI, USA), ethanol (ethanol; Aladdin), acetic acid (CH<sub>3</sub>COOH; Aladdin), acetylacetone (HACAC; Aladdin), and anatase TiO<sub>2</sub> nanoparticles (75 nm; Ze Chang Titanium Industry, Kunming, China).

Sandstone and marble (purchased from Guizhou province, China) were used in this study to evaluate the protective effects of TSCM, as the composition in sandstone minerals is relatively loose and its weather resistance is poor. Sandstone was selected to characterize the weather resistance and wettability before and after coating treatment. As the main component of marble is CaCO<sub>3</sub>, it is easily corroded by acids, whereas the acid resistance of sandstone is strong and cannot be observed obviously. Marble was thus selected to characterize the acid resistance before and after the coating treatment. Sandstone is mainly composed of silica (98.5%), and marble is mainly composed of calcium carbonate (99.5%). All the stone samples were cut into dimensions of 5 cm × 5 cm × 3 cm.

### 2.2. Preparation of TSCM

The preparation process of TSCM is as follows: 5 mL of TBT was added slowly to ethanol solution, stirring for 10 min (solution A). Then, 4 mL of acetic acid and 10 mL of hydrolysis inhibitor were added to the ethanol solution, stirring for 10 min (solution B). After that, solution A was transferred to solution B at a fixed flow rate of 3 mL/min, followed by stirring for 30 min, and the mixture was placed in a water bath at 40 °C with stirring for 2 h. Next, the mixture was aged at room temperature for two days. The result was transparent pure TiO<sub>2</sub>-sol (p-sol). Finally, TSCM was prepared by evenly mixing an appropriate amount of TiO<sub>2</sub> nanoparticles and p-sol.

### 2.3. Coating Method

The stone samples were washed and then placed into a drying oven (105 °C) for 24 h. Then, p-sol and TSCM were applied by brushing onto the surfaces of the samples. The stones treated by p-sol and TSCM were placed at room temperature for 48 h.

The number of stone samples is shown in Table 1. The coating materials covered the entire surface of the treated samples.

**Table 1.** Numbers of stone samples. TSCM, TiO<sub>2</sub>-modified sol coating material.

Sample Number	Stone Type	Coatings
1#	Sandstone	Untreated
2#		Treated with p-sol
3#		Treated with TSCM
4#	Marble	Untreated
5#		Treated with p-sol
6#		Treated with TSCM

#### 2.4. Characterization of Stone Samples

X-ray diffraction (XRD) (Rigaku, D/Max-3B, Tokyo, Japan) was used to analyze the p-sol and TSCM. Scanning electron microscopy (SEM) (FEI, Nova Nano SEM 450, Hillsboro, OR, USA) was conducted to analyze the micro-morphology of the stone samples.

#### 2.5. Protective Performance of TSCM

The experiments of water absorption, water vapor permeability, acid resistance, and weather resistance were operated according to the Chinese National Industry Standard JC/T 973-2005 [21,29,30].

##### 2.5.1. Test of Stone Appearance

The change of sandstone appearance was evaluated by the color difference. The color difference was measured by a fluorescent whiteness meter (XINRUI, Shanghai, China). The CIE  $L^*a^*b^*$  color space was used and color changes were evaluated by total color difference ( $\Delta E^*$ ) [31,32]. The total color difference ( $\Delta E^*$ ) between the untreated sample and treated sample was calculated using the following:

$$\Delta E^* = \sqrt{(L^* - L_0^*)^2 + (a^* - a_0^*)^2 + (b^* - b_0^*)^2} \quad (1)$$

where  $L_0^*$ ,  $a_0^*$ , and  $b_0^*$  are the CIE  $L^*a^*b^*$  co-ordinates of the untreated sample; and  $L^*$ ,  $a^*$ , and  $b^*$  are the co-ordinates of the treated sample.

##### 2.5.2. Test of Water Absorption

The water absorption of sandstone samples was defined as the change in weight after immersion in distilled water for 48 h. In detail, the stone samples were washed and placed into a drying oven at 105 °C for 24 h, and then cooled at room temperature. The weight was recorded as  $M_0$  (g). The samples were then immersed in distilled water for 48 h. After that, the samples were taken out and their weight was recorded as  $M_1$  (g). The water absorption  $\Delta M$  (%) was calculated as follows [33]:

$$\Delta M = \frac{M_1 - M_0}{M_0} \times 100\% \quad (2)$$

Each time the above calculation was performed, it was counted as one cycle. The experiment was repeated many times.

##### 2.5.3. Test of Water Vapor Permeability

A small amount of water was put into a triangular glass. Sandstone samples were put on top of the glass and the seam was sealed with glass glue. Then, the initial weight  $M_0$  (g) was recorded and the system was kept at room temperature for 24 h. The final weight was recorded as  $M_1$  (g). The water vapor permeability of a sample was then calculated by the following formula [29]:

$$\Delta M = M_0 - M_1 \quad (3)$$

Each time the above calculation was performed, it was counted as one cycle. The experiment was repeated many times.

#### 2.5.4. Test of Acid Resistance

The acid resistance of marble was preliminarily judged according to the occurrence of bubbles rising when a small amount of  $H_2SO_4$  solution was dripped onto its surface. Then, further experimental evaluation was carried out: the initial weights of marble samples were recorded as  $M_0$  (g), following which they were immersed in 1% (V/V)  $H_2SO_4$  solution for 24 h and then dried at 60 °C for 6 h. The final weight was recorded as  $M_1$  (g), and the acid resistance  $\Delta M$  (%) was calculated by the Equation (2) [21].

Each time the above calculation was performed, it was counted as one cycle. The experiment was repeated many times.

#### 2.5.5. Test of Weather Resistance

The initial weights of sandstone samples were recorded as  $M_0$  (g). Then, the samples were immersed in 0.5 M  $Na_2SO_4$  solution for 12 h, dried for 6 h at 60 °C and frozen for 4 h at −30 °C, and finally dried at 60 °C for 4 h. The final weight was recorded as  $M_1$  (g). The weather resistance (that is, mass change rate) of stone was calculated by the Equation (2) [33].

Each time the above calculation was performed, it was counted as one cycle. The experiment was repeated many times.

### 3. Results and Discussion

#### 3.1. Effect of Layer Numbers and Amount of $TiO_2$ Nanoparticles on Appearance

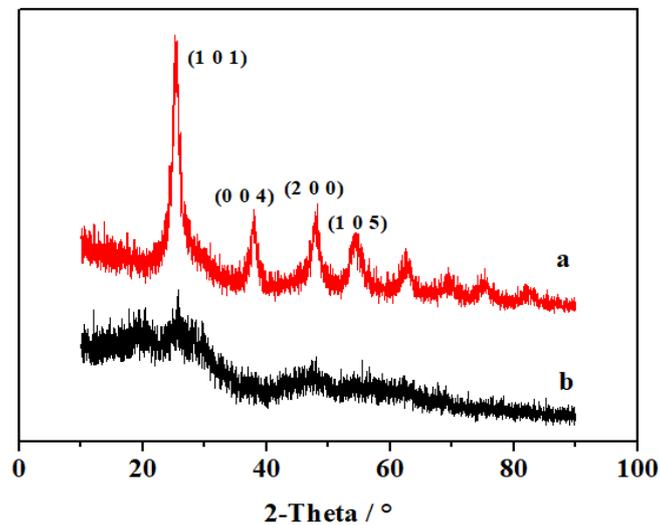
Pinho reported that the additive amount of  $TiO_2$  nanoparticles has an important effect on the transparency of TSCM; too much resulted in reduced transparency, while too little resulted in a poor protective effect [28]. Quagliarini and Munafò have proven that a multilayer coating can improve the protection effect [22,34,35], while Liu proved that a high number of layers could reduce the adhesion between stone and coating [21]. In order to ensure the appearance of the stone remained unchanged, the color difference should meet the condition that  $\Delta E^* < 5$  [36]. As shown in Table 1, the addition of  $TiO_2$  nanoparticles and the layer numbers had an important impact on color difference. The color difference of stone samples increased obviously with the increase of layer numbers and  $TiO_2$  nanoparticles. On the basis of the experimental results shown in Table 2, we can draw the conclusion that the optimal amount of  $TiO_2$  nanoparticles is 0.05 g/100 mL, with a layer number of 4.

**Table 2.** Effect of amount of  $TiO_2$  nanoparticles and the layer numbers on color difference.

$TiO_2$ Nanoparticles Addition/100 mL	Layer Numbers	$\Delta E^*$	$TiO_2$ Nanoparticles Addition/100 mL	Layer Numbers	$\Delta E^*$	$TiO_2$ Nanoparticles Addition/100mL	Layer Numbers	$\Delta E^*$
1 g/100 mL	1	3.17	0.05 g/100 mL	1	1.12	0.005 g/100 mL	1	0.95
	2	5.87		2	2.46		2	1.21
	3	8.98		3	3.70		3	2.03
	4	11.31		4	4.13		4	3.52
	5	13.46		5	4.98		5	4.00
0.5 g/100 mL	1	3.01	0.03 g/100 mL	1	0.98			
	2	4.18		2	1.11			
	3	6.59		3	2.61			
	4	8.51		4	3.75			
	5	11.09		5	4.53			
0.1 g/100 mL	1	1.32	0.01 g/100mL	1	1.00			
	2	3.00		2	1.71			
	3	4.89		3	2.87			
	4	6.43		4	3.55			
	5	8.12		5	4.01			

### 3.2. X-ray Diffractometer Analysis

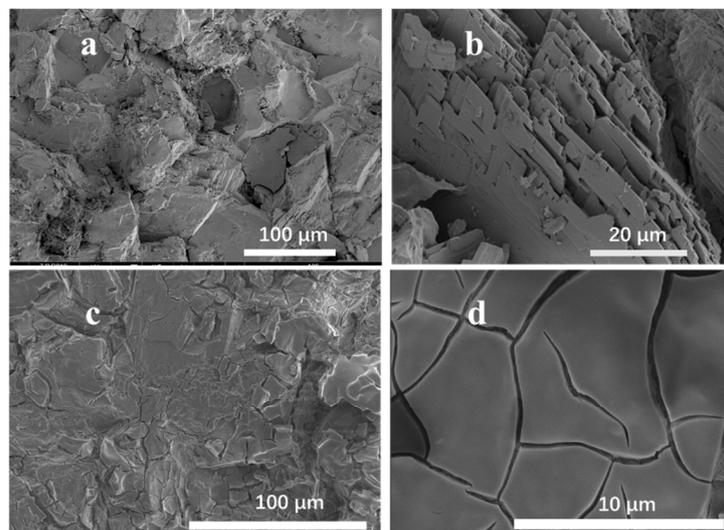
As shown in Figure 1b, transparent p-sol had no characteristic peak, indicating that the p-sol was amorphous. However, Figure 1a shows that TSCM had characteristic peaks at  $25.305^\circ$ ,  $37.799^\circ$ ,  $48.038^\circ$ , and  $53.892^\circ$ , which related to the diffraction surfaces of anatase: (1 0 1), (0 0 4), (2 0 0), and (1 0 5), respectively.



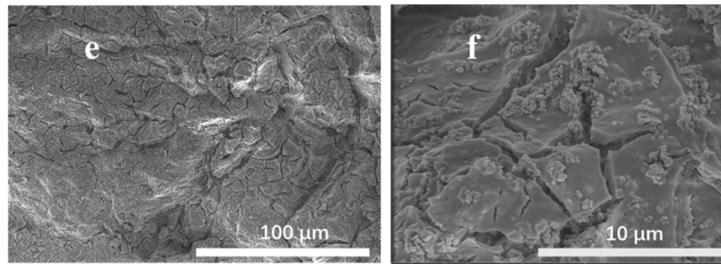
**Figure 1.** X-ray diffraction (XRD) spectra of TiO<sub>2</sub>-modified sol coating material (TSCM) (a) and p-sol (b).

### 3.3. Scanning Electron Microscopic Analysis

The micro-morphology of sandstone before and after coating treatment is discussed in this section. Figure 2 shows SEM images of samples 1<sup>#</sup>, 2<sup>#</sup>, and 3<sup>#</sup>. Sample 1<sup>#</sup> (without coating material) had a rough surface (see Figure 2a,b), where the higher roughness is the result of the surface pores [37,38]. Compared with sample 1<sup>#</sup>, samples 2<sup>#</sup> and 3<sup>#</sup> had a smoother surface and less porosity (see Figure 2c,e) [28]. It can be seen from Figure 2f that TiO<sub>2</sub> nanoparticles were embedded in the TSCM. The nanoparticles increased the contact area between the stone and external environment, as compared with Figure 2d. Furthermore, the many tiny cracks improved the “breathing” of the stone; similar results have been reported in the literature [39]. Hence, TSCM has a potential advantage over p-sol and organic protective agents [21].



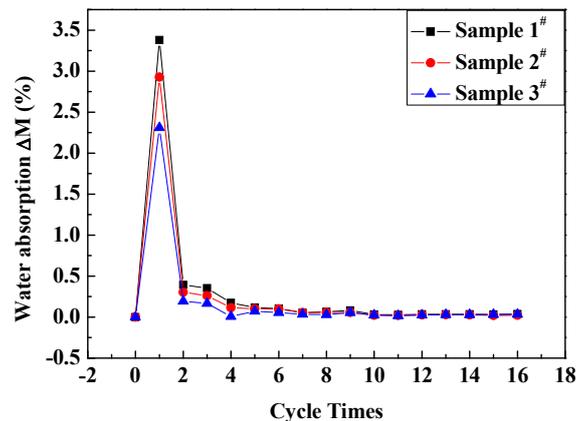
**Figure 2.** Cont.



**Figure 2.** Scanning electron microscopy (SEM) images of sample 1<sup>#</sup> (a) 100 um, (b) 20 um; sample 2<sup>#</sup> (c) 100 um, (d) 10 um; and sample 3<sup>#</sup> (e) 100 um, (f) 10 um.

### 3.4. Water Absorption

Water absorption is an important parameter in evaluating protective performance. Figure 3 presents the relationship between water absorption and the number of cycles. With an increasing number of cycles, water absorption increased sharply, and then decreased slowly. The water absorption in the different samples was almost equal when the number of cycles was greater than 5. Because the stone begins to absorb water quickly, the water absorption increases. When the water absorption is close to saturation, the water absorption rate decreases. The water absorption of sample 1<sup>#</sup> was the largest, while that of sample 3<sup>#</sup> was the smallest [40], indicating that the TSCM has made the sandstone samples more compact and less permeable to water. Low water absorption can protect the samples against the erosion of water and a soluble salt or base.



**Figure 3.** Water absorption curves.

### 3.5. Water Vapor Permeability

It is important to consider the change of water vapor permeability before and after stone treatment. A coating material does not completely seal a stone surface, as blocking the ability to pass water vapor in and out of the stone may lead to the condensation of internal water, or even accelerate the deterioration of the stone [39,41]. Figure 4 shows the water vapor permeabilities of the untreated and treated sandstone samples. The permeability of the treated sandstone sample was close to that of the untreated sample and the trends of the three curves were similar. This suggests that TSCM is a suitable protective measure; it does not dramatically alter the water vapor permeability and the “breathe function” of origin materials is retained.

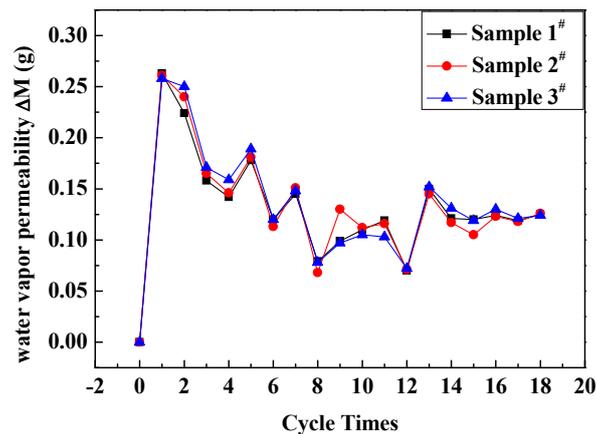


Figure 4. Water vapor permeability results.

### 3.6. Acid Resistance

The acid resistance of the samples was preliminarily judged by observing the formation of  $\text{CO}_2$  bubbles when  $\text{H}_2\text{SO}_4$  solutions with different pH values were dropped onto the sample surface. For sample 4<sup>#</sup>,  $\text{CO}_2$  bubbles were formed at pH = 1.5 [21]; for sample 5<sup>#</sup>, they formed at pH = 0.5–0.8; and for sample 6<sup>#</sup>, they formed at pH = −0.6, indicating that TSCM had stronger acid resistance.

A more detailed experiment of acid resistance was also carried out in this study; the results are shown in Figure 5. The acid resistance of sample 6<sup>#</sup> was the largest, and that of sample 4<sup>#</sup> was the smallest. Acid resistance represents the loss of sample weight due to acid corrosion and, so, smaller acid resistance values represent samples with weak acid resistance. Hence, the results showed that the coating materials prevented corrosion by acids; moreover, they showed that TSCM had better acid resistance.

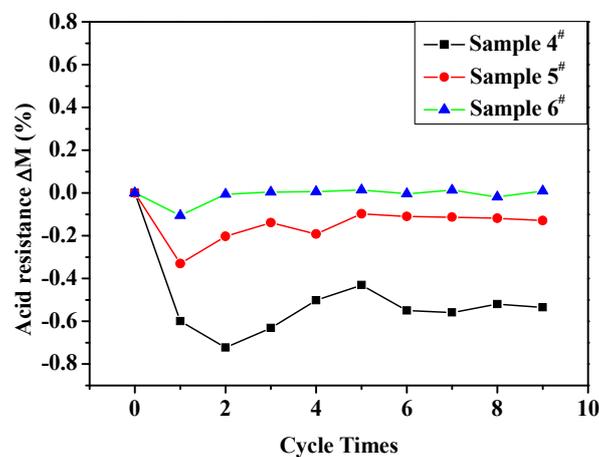


Figure 5. Acid resistance curves.

### 3.7. Weather Resistance

The experimental results of weather resistance are presented in Figures 6–8. Figure 6 shows photographs of samples 1<sup>#</sup>, 2<sup>#</sup>, and 3<sup>#</sup> after eight cycles; bubbles can be seen on the surface of sample 1<sup>#</sup>, while samples 2<sup>#</sup> and 3<sup>#</sup> did not change significantly. Figure 7 shows photographs of samples 1<sup>#</sup>, 2<sup>#</sup>, and 3<sup>#</sup> after 14 cycles; it can be seen that sample 1<sup>#</sup> was seriously damaged on multiple sides. Figure 7c shows that sample 2<sup>#</sup> was slightly damaged, but Figure 7d shows that sample 3<sup>#</sup> was almost undamaged. The relationship of the mass change rate of samples with the number of cycles is presented in Figure 8. The mass of the samples increased with cycles, owing to the immersion of samples in salt solution. However, from the sixth cycle onward, the mass of samples decreased with cycles, as the

samples were corroded. Furthermore, the mass of coated samples had a smaller change, especially for stone treated by TSCM. It has to be emphasized that the human eye could not observe the obvious change of samples on the macro scale, but the sample started to change at the micro scale when the number of cycles was 6. The results indicate that TSCM had good weather resistance.

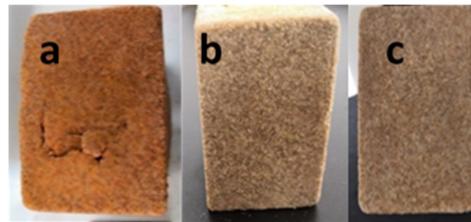


Figure 6. Three stone samples after eight cycles: (a) sample 1<sup>#</sup>, (b) sample 2<sup>#</sup>, and (c) sample 3<sup>#</sup>.

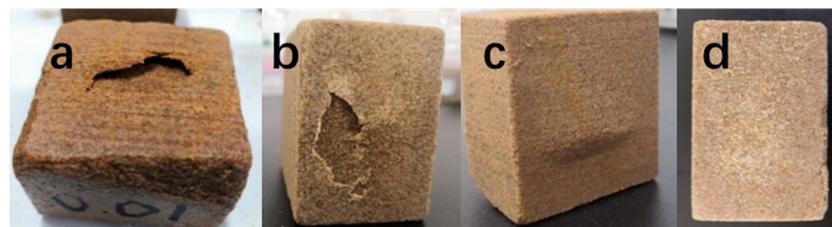


Figure 7. Three stone samples after 14 cycles: (a,b) sample 1<sup>#</sup>, (c) sample 2<sup>#</sup>, and (d) sample 3<sup>#</sup>.

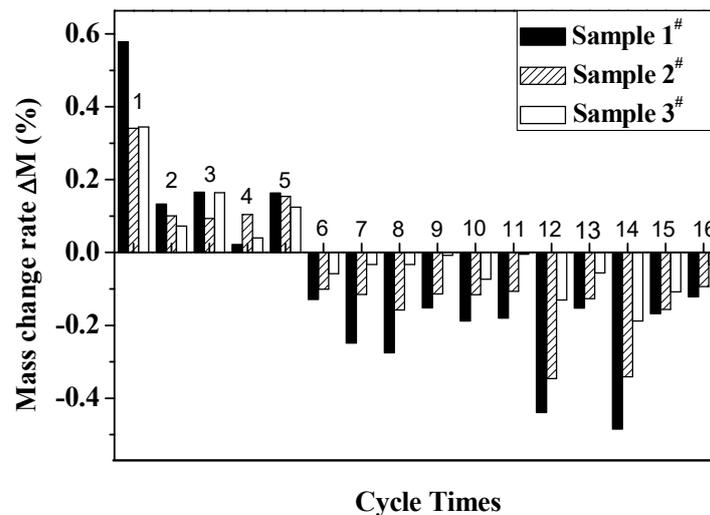


Figure 8. The relationship of mass change rate of samples with the number of cycles.

Table 3 presents a comparison of the protective effect results of coating materials between those found in this paper and in other studies. The acid resistance of stone treated by TSCM was 1.75 times higher than that treated with traditional coating materials. The cycle number in the weather resistance experiment was four times larger than that found for a silicone material.

Table 3. Comparison of protection performance between this work and other literatures.

Stone	Type of Product Applied	Corrosion Cycle (Weather Resistance)	Acid Resistance pH	References
Sandstone	polymerized siloxane	4	–	[38]
Marble	TiO <sub>2</sub> pure-sol	–	0.5–0.8	[21]
Marble	TSCM	–	–0.6	Present work
Sandstone	TSCM	16	<–0.6	Present work

#### 4. Conclusions

TiO<sub>2</sub>-modified sol coating material (TSCM) was designed using an innovative and simple synthesis route. It was shown to not affect the appearance of stone-built cultural heritage when the amount of TiO<sub>2</sub> nanoparticles was 0.05 g/100 mL and the number of layers of TSCM was 4. The protective effects of TSCM were tested by water absorption, water vapor permeability, acid resistance, and weather resistance experiments. The results confirmed that TSCM has a significant protective effect on stone-built cultural heritage: the water absorption of stone treated by TSCM was excellent; the acid resistance of stone treated with TSCM was 1.75 times higher than that treated with traditional coating materials; and the weather resistance cycle number of stone treated by TSCM was four times higher than that treated with organic protective materials. Therefore, TSCM has good potential application value in the protection of stone-built cultural heritage.

**Author Contributions:** H.S. and Q.L. conceived and designed the experiments; H.S. performed the experiments; M.Y. analyzed and discussed optical properties of the paints; M.L. performed the microstructural analysis; H.S. wrote the paper. All authors have read and agreed to the published version of the manuscript.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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