Research Article

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The study of rod-shaped TiO₂ composite material in the protection of stone cultural relics

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Abstract: TiO₂ has many advantages, such as UV resistance, thermal stability, and antibacterial; the attention toward TiO₂ composite materials (TCMs) is rapidly increasing in the protection of stone culture relics. An innovative rod-shaped TCM was synthesized in this study. The structure and morphology of TCM were studied by X-ray diffraction and scanning electron microscopy. The acid resistance, weather resistance, hydrophilicity, and photocatalytic performance of TCM had been investigated. The experimental results indicated that TCM has good protection effects. The stone sample treated with TCM has stronger acid resistance and weather resistance, better hydrophilicity, and more excellent photocatalytic activity compared with the untreated stone. More importantly, the stone treated with TCM has better acid resistance and weather resistance than that treated with normal shaped TiO₂ materials of the previous study. This work describes an effective way to protect stone cultural relics.

Keyword: stone cultural relic protection, rod-shaped TiO₂ composite material, acid resistance, weather resistance, photocatalytic degradation of pollutants

1 Introduction

China has a long history, and the information recorded in stone cultural relics promotes Chinese historical

research, such as statues, stone carvings, and buildings [1]. Most stone cultural relics are often exposed outdoors, and they are easily damaged by acid rain, wind erosion, salt crystallization, and other factors [2].

The damage of the stone cultural relics can be effectively reduced by coating protective materials [3–5]. Traditional coating materials have some disadvantages [6–8], such as acrylic polymers and silicone have the poor compatibility with the surface of stone [9], although they have good water resistance and reinforcement performance [10,11]. Many researchers pay attention to the research of new protective materials [12].

Due to their excellent stability [13,14], chemical resistance [15], antibacterial activity [16], non-toxicity, and low price [17,18], TiO₂ has potential application in the protection of stone cultural relics. Graziani et al. found that TiO₂ nanoparticles aqueous solution can well prevent the growth of microalgae on the surface of clay brick [16]. Quagliarini et al. also proved that the water suspension based on TiO₂ nanoparticles can protect limestone from the damage caused by microalgae [19]. Pinho et al. proved that the TiO₂ nanoparticles can be easily removed from TiO₂ nanoparticles aqueous materials coated on the surface of clay brick or limestone [20]. Dispersion of TiO₂ nanoparticles into organic materials can prevent the loss of TiO₂ nanoparticles, but it has one drawback that only a fraction of TiO₂ nanoparticles are exposed to the surface of the organic materials, which results in a decrease in the protection performance [21]. In addition, the high viscosity of TiO₂ nanoparticles organic material leads to uneven coating [22]. Pinho and Mosquera proposed to disperse the TiO₂ nanoparticles into the SiO₂ sol, and TiO₂–SiO₂ nanocomposites can overcome the above shortcomings and has good protection performance [23]. The research of Pinho aimed at the protection of buildings, and we also have studied the TiO₂-modified sol coating material in the protection of stone-built cultural heritage. However, to the best of our knowledge, the research on compositing TiO₂ nanoparticles into TiO₂ sol in stone cultural relics is very limited.

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Moreover, it is worth to study the protective properties of rod-shaped TiO₂ nanocomposite materials.

The main purpose of this work was to prepare an innovative rod-shaped TiO₂ composite material (TCM) through compounding rod-shaped TiO₂ nanoparticles into TiO₂ sol. The composition and microscopic morphology of TCM were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The protection performance of TCM, such as acid resistance, weather resistance, hydrophilicity, and photocatalytic activity, was evaluated. The results show that TCM has excellent protection performance in stone cultural relics.

2 Materials and methods

2.1 Synthesis of TCM

The TiO₂ sol solution (TSS) was prepared by the sol–gel method at low temperature, and the prepared sol solution was transparent with good stability. The specific operation is as follows: 5 mL of tetrabutyl titanate was added to the ethanol solution and stirred for 10 min (named solution A). Then, 4 mL of acetic acid and 10 mL of hydrolysis inhibitor were added to the ethanol solution and stirred for 10 min (named 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 2 days. The transparent pure TSS was prepared.

Normal shaped TiO₂ nanoparticles with an average particle size of 1 µm were purchased from Ze Chang Titanium Industry (Yunnan Province), and rod-shaped TiO₂ nanoparticles were prepared by the hydrothermal method. The TCM was synthesized as follows: the rod-shaped TiO₂ nanoparticles were added to the TSS at the optimal ratio of 0.05 g/100 mL (the value of optimal ratio was obtained through multiple experiments [24]), followed by stirring with a magnetic stirrer for 2 h and high-power ultrasonic agitation for 1 h. Last, TCM was prepared after allowed to stand for 1 h.

2.2 Preparation of stone samples

Most stone cultural relics are made up of marble or sandstone, so natural marble and sandstone are used to

Table 1: Classification and name of stone samples

Stone classification	Sample name	Coatings
Sandstone	A	Untreated
	B	Treated with TSS
	C	Treated with TCM
Marble	D	Untreated
	E	Treated with TSS
	F	Treated with TCM

evaluate the protective properties of TCM. Sandstone can well evaluate the weather resistance of the TCM, while marble can characterize the acid resistance. The components of the stone were analyzed by XRD; 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 the dimension of 5 cm × 5 cm × 3 cm. After all stone were washed and dried to constant weight, TCM and TSS were applied to the stone surface with a small brush.

The amount of TCM depends on the coating number of layers. The layer numbers are determined by two parameters: the total color difference (ΔE^*) of the stone samples and the amount of TiO₂ nanoparticles added. The total color difference (ΔE^*) should be less than 5, and the optimal layer number is 4 [24]. The classification and name of the stone samples are shown in Table 1.

2.3 Characterization of stone samples

The TCM, TSS, and rod-shaped TiO₂ nanoparticles were characterized by XRD, a D/max-2300 diffractometer (Rigaku, Tokyo, Japan) with Cu K α 1 radiation ($\lambda = 1.54056 \text{ \AA}$), operating at 35 kV and at angles ranging from 10° to 90° (2θ). The surface morphology of the stone samples was characterized by SEM (FEI, Hillsboro, America) with an FEI Sirion instrument, which has a field emission filament working at 5 kV. The instrument has a resolution of 1.5 nm and is equipped with a through lens detector operating in an ultra-high resolution mode.

2.4 Protection performance of TCM

The hydrophilicity of the stone samples was elevated by contact angle, while the JC2000A surface tension/contact angle meter (Leao, Shanghai, China) was used to measure the contact angle of the sandstone sample surface [25,26].

The photocatalytic performance of the stone samples was reflected by total color difference (ΔE^*). The specific operation is as follows: 100 $\mu\text{mol/L}$ methylene blue (MB) ethanol solution was prepared. Then, the MB ethanol solution was sprayed evenly on the surface of the sandstone samples (0.5 mL MB ethanol solution was evenly applied to the 2,200 mm^2 of the sandstone surface), then the ultraviolet light of 365 nm was used to irradiate the stone samples in an airtight box [27]. The CIE $L^* a^* b^*$ color space was used [28,29], and the value of $L^* a^* b^*$ was measured by the fluorescent whiteness meter (Xinrui, Shanghai, China). Finally, the ΔE^* is calculated according to the following equation:

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

where L_0^* , a_0^* , and b_0^* are the CIE $L^* a^* b^*$ coordinates of the sample before irradiation and L^* , a^* , and b^* are the coordinates of the sample after irradiation.

The initial weight of the marble samples were recorded as M_0 (g). First, the marble samples were immersed in 1% v/v H_2SO_4 solution for 24 h. Second, the marble samples were dried at 60°C for 6 h. Finally, the weight of the dried marble samples was recorded as M_1 (g). The acid resistance of the marble samples was calculated as follows:

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

The above experimental process is named as one cycle time.

The initial weight of the sandstone samples was recorded as M_0 (g). First, the sandstone samples were immersed in 0.5 mol/L Na_2SO_4 solution for 24 h, then dried for 6 h at 60°C. Second, the samples were frozen for 4 h at -30°C. Finally, the sandstone samples were dried at 60°C for 4 h. The weight of the dried samples was recorded as M_1 (g). The weather resistance of the sandstone samples was calculated by Eq. 2 [30], and the above experimental process is named as one cycle time.

3 Results and discussion

3.1 XRD analysis

The XRD of TCM, TSS, and rod-shaped TiO_2 nanoparticles are reported in Figure 1, which demonstrates that three samples show the diffraction patterns of anatase TiO_2 . The pattern of TSS indicated that it is amorphous

Figure 1: X-ray diffraction (XRD) spectra of (a) TCM, (b) TiO_2 nanoparticles, and (c) TSS.

from curve c, and rod-shaped TiO_2 nanoparticles is anatase from curve b. With the addition of anatase rod-shaped TiO_2 nanoparticles, the characteristic peak of TCM is strengthened from curve a, which verifies that the added rod-shaped TiO_2 nanoparticles are embedded in the TiO_2 sol, and similar results were reported in a previous study [31].

3.2 SEM analysis

Figure 2 shows the SEM images of the rod-shaped TiO_2 nanoparticles and samples A, B, and C. Figure 2a shows that the TiO_2 nanoparticles is rod-shaped. Figure 2b shows that sample A is untreated sandstone and has a rough surface [32,33]. Figure 2c presents that sample B has a smoother surface compared with sample A (Figure 2b) [23]. Figure 2d shows that sample C also has smooth surface, and the rod-shaped TiO_2 nanoparticles perfectly exposed on the surface of the TCM. Compared with Figure 2c, there are fewer cracks on the surface of TCM. Figure 2e and f shows TCM at 40 and 5 μm scales. It can be seen that rod-shaped TiO_2 nanoparticles are embedded in the TiO_2 sol, and it can be inferred that the rod-shaped TiO_2 nanoparticles increase the wear resistance and tensile strength of TCM.

3.3 Hydrophilicity

As shown in Figure 3, the contact angle of stone samples A, B, and C was 110.5° (Figures 3a), 42.5° (Figure 3b),

Figure 2: Scanning electron microscopy (SEM) images of (a) TiO_2 nanoparticles, (b) sample A, (c) sample B, and (d–f) sample C.

Figure 3: Contact angle of (a) sample A, (b) sample B, and (c) sample C.

and 0° (Figure 3c), respectively. The contact angle does not change with 2 min, indicating that the external light source does not affect the test. The smaller the contact angle, the stronger the hydrophilicity. Superhydrophilicity indicates that water diffuses rapidly. The blank stone sample is hydrophobic. After treatment with TCM, the stone samples change into superhydrophilic, because of the addition of the rod-shaped TiO_2 nanoparticles. Similar reports can be found in the literature [34]. Hence, we can draw a conclusion that dust can be easily removed from the surface of the stone samples treated with TCM.

3.4 Acid resistance

The acid resistance of the samples can be judged by the formation of CO_2 bubbles when H_2SO_4 solutions of different pH values were dropped on the surface of the stone samples [1]. The results were as follows: pH = 1.5 for sample D [15], pH = 0.5–0.8 for sample E, and pH less than –0.6 for sample F. Hence, the TCM has stronger acid resistance than TSS.

To further evaluate the acid resistance of stone samples, a more detailed acid corrosion experiment was carried out. Figure 4 shows the acid resistance of stone samples D, E, and F. The acid resistance of sample F is the highest, and sample D is the lowest. It can also be seen that the acid resistance of the treated samples was greater than that of the untreated sample. Acid resistance refers to the weight loss of the stone samples in the acid corrosion process. According to the study of Liu *et al.*, the higher the value of acid resistance, the stronger the acid corrosion resistance [35]. In comparison, the acid resistance of sample C was more significant, indicating that TCM has a strong corrosion resistance,

Figure 4: The acid resistance of the blank stone sample (D), stone sample treated with TSS (E), and stone sample treated with TCM (F).

that is because rod-shaped TiO_2 nanoparticles compounded in TiO_2 -sol can improve acid resistance of TCM. Moreover, the acid resistance of TCM is stronger than that of normal shaped TiO_2 nanoparticles composite material previously studied [24]. The acid resistance of TCM meets protective requirements of stone cultural relics.

3.5 Weather resistance

The experimental results of weather resistance are presented in Figure 5. Figure 5a–c represents the appearance photograph of samples A, B, and C after eight cycle times, respectively. There was hard shell on the surface of sample A, while the samples B and C did not change significantly.

Figure 5: Three stone samples after eight cycles: (a) sample A, (b) sample B, and (c) sample C; three stone samples after 14 cycles: (d) sample A, (e) sample B, and (f) sample C.

Figure 5d–f represents the appearance photograph of samples A, B, and C after 14 cycle times, respectively. Sample A was seriously damaged on multiple sides, and sample B was slightly damaged, but sample C was obviously undamaged. In brief, the untreated stone samples would be easily damaged (Figure 5a and d), and the stone samples treated with TSS would be moderately damaged (Figure 5b and e), while TCM has the best protection effect on the stone samples (Figure 5c and f).

The relationship of weight change rate of stone samples with cycle times is presented in Figure 6. In the first six cycle times, the weight of the stone samples increased with the number of cycle times, because the stone sample was immersed in the salt solution and salt seeps into the stone samples after the water evaporates. The weight of the stone samples decreases after the seventh cycle time, showing that the stone samples were obviously corroded. It is necessary to emphasize that the weight of the stone samples treated with TCM changed with increase in cycle time, indicating that the stone samples treated with TCM were slight damaged, which is difficult to be observed in Figure 5c and f. In short, the weight change rate of sample C was least, indicating that TCM can protect the stone samples from the damage caused by environmental factors. And the weather resistance of TCM is more excellent than that of normal shaped TiO_2 nanoparticle composite material previously studied [24].

3.6 Photocatalytic degradation of pollutants

Photocatalytic degradation of pollutants represents the self-cleaning ability of coating material, and it can be

Figure 6: The relationship of weight change rate of samples with cycle times: (A) blank stone sample, (B) stone sample treated with TSS, and (C) stone sample treated with TCM.

judged by the value of ΔE^* . MB ethanol solution was sprayed on the stone surface, the whiteness of the stone samples decrease, and the value of their $\Delta E^* < 0$. When these samples were irradiated under UV light, the value of their ΔE^* increased, showing the photocatalytic degradation of MB [23,29]. Figure 7 shows the relationship of the ΔE^* with time under UV light. It can be seen that there are almost no degradation of MB on the surface of sample A with increase in the irradiation time. MB on the surface of samples B and sample C rapidly degrades with increase in the irradiation time from the first 5 h of irradiation, followed by a stable value with irradiation time increasing from 6 to 12 h. In addition, degradation rate and degradation amount of TCM are greater than those of TSS. That is because rod-shaped TiO_2 nanoparticles can enhance photocatalytic

Figure 7: The ΔE^* of blank stone sample (A), stone sample treated with TSS (B), and stone sample treated with TCM (C).

degradation of MB. Therefore, TCM has the significant ability of photocatalytic degradation of pollutants.

4 Conclusions

TCM was synthesized by compounding rod-shaped TiO_2 nanoparticles into TiO_2 sol. The XRD proved that the TCM system is anatase phase, and the characteristic peaks of TCM are strengthened due to the addition of rod-shaped TiO_2 nanoparticles. The SEM showed that the rod-shaped TiO_2 nanoparticles are perfectly embedded in the TCM and can increase the wear resistance and tensile strength of TCM. The stone sample treated with TCM has superhydrophilicity, showing that TCM help to clean the stains on the stone surface. The acid resistance of the stone sample treated with TCM was strongest compared with that of the untreated stone and the stone treated with TSS. The weather resistance experiment shows that TCM can effectively prevent stone samples from being damaged by the external environment. In addition, TCM has significant ability of photocatalytic degradation of pollutants. TCM can effectively protect stone cultural relics and has potential application value in the field of cultural relic protection.

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