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Study on the stability of antibacterial silver-carried zirconium phosphate

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ABSTRACT

The stability of antibacterial silver-carried zirconium phosphate (AgZrP) was investigated using thermoanalysis (TG/DSC), X-ray diffraction (XRD), UV light irradiation and water soaking methods. The weight loss of AgZrP was no more than 5.0 mass% at the heat treating temperature of 1100°C, and the onset temperature of decomposition for the crystal structure of AgZrP appeared 1096.9°C. The whiteness of the sample treated at 900°C (4# sample) was 86.4% after exposed to UV light for 24h, and its MIC against *E.coli* and *S.aureus* was 100 mg.l^{-1} and 150 mg.l^{-1} respectively. Moreover, the percentage of release Ag^+ in 4# sample was only 6.1 mass% and the MIC against *E.coli* and *S.*aureus still remained 220 mg.l^{-1} and 280 mg.l^{-1} respectively after soaking in water for 10 days. Therefore, AgZrP possessed excellent thermal stability, light permanency and water resistance.

KEYWORDS

AgZrP;
Thermal stability;
Light permanency;
Water resistance;
Antibacterial activity.

1. INTRODUCTION

Viruses and bacteria have become the primary courses to imperil human health in the world. Since the horrific of "SARS" aroused the antibacterial consciousness of people, the research of the antibacterial fields became hot. Inorganic antibacterial agents were a relatively new field and have attracted a lot of scientists' attention since 1990s. Compared to organic antibacterial agents, inorganic antibacterial agents possessed so many outstanding properties, such as long-lasting effects, broad-spectrum antibiosis and better heat resistance, that they can be used in the manufacture of antibacterial materials and product[1-5].

AgZrP was recently emerging as various commercial products due to its relatively good light permanency among silver-carried antibacterial agents[6-9], but the application of AgZrP was still affected by the stability. Up to now, there are the study was especially focused on the preparation and antibacterial activity of AgZrP. However, to the best of our knowledge, there have been few reports on studying its stability, which is very important for the applications. In this paper, the thermal stability, light permanency and water resistance were evaluated.

2. EXPERIMENTAL

Sodium zirconium phosphate (carrier) was supplied by Guangzhou Kinte Co., Ltd. (Guangzhou, China). The carrier was dispersed in deionized water to obtain a suspension of 10.0 mass% (mass fraction) and added into a 1 L reaction kettle, then stirred, and an amount of $AgNO_3$ (AR) supplied by Guangzhou Chemical Re-

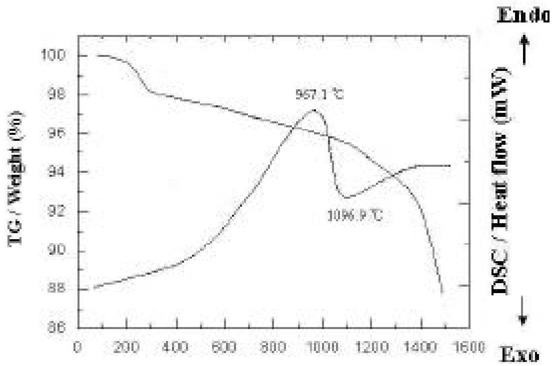

Figure 1: TG/DSC curves of AgZrP

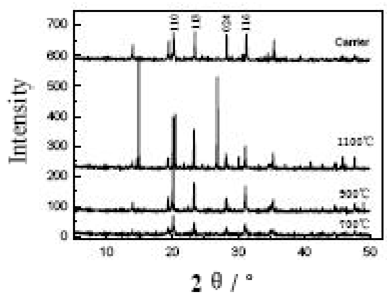

Figure 2: XRD patterns of the carrier and the AgZrP treated at different temperatures

agent Factory (Guangzhou, China) was added (final concentration 0.7 mass%). The reaction was controlled at 60°C for 3 h. The Ag-exchanged sample was filtered and washed with deionized water. The washed sample was dried at 105^{0}C for 12h, and then treated at different temperature in calcining furnace. The final product of AgZrP was obtained after being smashed and sifted through 300-mesh sieve, and the Ag content in AgZrP was about 9.5 mass%.

Thermoanalysis method (TG/DSC) was conducted with a thermal analyzer (NETZSCH STA449C) under N_2 flow, and the temperature range of the measurement was 25-1500^{0}C, the scanning rate 20°C/min. The crystal structure of AgZrP was characterized with a RAD-C X-ray diffractometer (40 kV, 40 mA, Cu Kα, λ=0.1541nm). Their components were analyzed by EDX using SEM equipped with an Oxford ISIS-300 energy-dispersive X-ray detector, and their silver content can also be determined.

The MIC of antibacterial particles was measured by two-fold diluting method[10,11], and the bacteria of *Escherichia coli* (*E.coli*, ATCC25922*)*, *Staphylococcus aureus* (*S.aureus*, ATCC6538*)* were selected as indicators. The UV irradiation tests were carried out at the light source of high-voltage mercuric lamp (365nm) and the interval of 30 cm, and the whiteness and antibacterial activity of AgZrP irradiated different times were tested. The slow release of Ag^+ in AgZrP was carried out by the process that the 0.1 g sample was soaked in 20ml distilled water in a polypropylene bottle at 37^{0}C, after 1-10 days of rotation, the Ag^+ concentration in water was measured by an 180-80 atomic absoption spectrophotometer (Hitachi).

3. RESULTS AND DISCUSSION

3.1 Thermal stability

Figure 1 showed the TG/DSC curves of AgZrP as a function of temperature, as measured under an air atmosphere. The DSC curve of AgZrP exhibited an endotherm at 967.1^{0}C, corresponding to its melting point, and an exotherm at 1096.9^{0}C which was assigned to the change of its crystal structure. As shown in the TG curve, the weight loss of AgZrP generally identified with two regions below 1500^{0}C. Free (absorbed) water involved between 200 and 300^{0}C, and the onset temperature of decomposition for the crystal structure of AgZrP appeared about 1100^{0}C, which accorded with the study result of DSC, but the weight loss of AgZrP was no more than 5.0 mass% at 1100^{0}C. This result suggested that AgZrP possessed excellent thermal stability.

The changes of crystal structure for AgZrP at different heat treating temperature were studied by XRD. XRD patterns of carrier and the AgZrP treated at 700, 900 and 1100^{0}C in the air for 3h were showed in figure 2. Both of the carrier and the AgZrP treated at different temperatures showed seven diffraction peaks respectively, which were consistent with the earlier determined patterns of sodium zirconium phosphate with hexagonal crystal system[12,13]. Compared with the four strong diffraction peaks of carrier 2θ values of 20.24° (d_{110} =0.439 nm), 23.47° (d_{113}=0.379 nm), 28.22° (d_{024} =0.316 nm) and 31.23° (d_{116}=0.286 nm), the AgZrP treated at different temperatures also displayed four diffraction peaks with a small enhancement in crystal space distance. For example, the AgZrP treated at 900 °C displayed the diffraction peaks at 2θ values of 20.17° (d_{110}=0.440 nm), 23.34° (d_{113}=0.381 nm), 28.16°

(d_{024}=0.317 nm) and 31.10° (d_{116}=0.287 nm). When the treating temperature raised to 1100°C, new peaks resulting from the growth of a new phase of zirconium phosphate crystal appeared at 14.9°, 20.5°and 26.8°. As a result, the crystal structure of AgZrP was not obviously affected by the heat treating temperature of less than 1100°C.

3.2 Light permanency

Effect of heat treatment temperature on whiteness (exposed to 365 nm UV light for 24h), Ag content and antibacterial activity of AgZrP was also evaluated, as shown in TABLE 1. Increasing the heat treating temperature, the whiteness became high, but the antibacterial activity decreased because of the increased MIC against *E.coli* and *S.aureus*. When the heat treating temperature was 900^0C, its whiteness was 86.4%, and the MIC against *E.coli* and *S.aureus* was 100 $mg.l^{-1}$ and 150 $mg.l^{-1}$ respectively. This indiacated that AgZrP treadet at 900^0C possessed excellent light permanency and antibacterial activity. Raising the heat treating temperature to 1100^0C, its whiteness increased to 90.6%, but the antibacterial activity decreased greatly, because the MIC against *E.coli* and *S.aureus* rised to 500 $mg.l^{-1}$ and 700 $mg.l^{-1}$. In addition, the Ag content in AgZrP was not obviously affected by the heat treatment below 1100^0C.

Effect of UV irradiation time on antibactreial activity of $4^{\#}$ sample (treated at 900^0C) was estimated as shown in TABLE 2. With the extension of UV irradiation time, the whiteness decreased and the antibacetrial activity became worse. These results can be explained that when AgZrP was exposed to UV lamp, some ionic silver was reduced to metallic silver, and the metallic silver content in AgZrP enhanced with the increase of UV irradiation time. Unfortunately, its color became deep, and the antibacterial activity declined. When the UV irradiation time was 48h, its whiteness decreased from 91.3% to 82.7%, and the MIC against *E.coli* and *S.aureus* increased from 100 $mg.l^{-1}$, 150 $mg.l^{-1}$ to 250 $mg.l^{-1}$ and 320 $mg.l^{-1}$ respectively. Therefore, $4^{\#}$ sample still remained good light permanency and antibacterial activity after exposed to UV light for 24h.

3.3 Water resistance

Figure 3 showed the percentage of release Ag^+ in $4^{\#}$ sample soaking in deionized water for different time at 37^0C. In the first 8 d, the release Ag^+ linearly increased with the lapse of soaking time. If the soaking time more, the rate of release Ag^+ slowed down. Surprisedly, the percentage of release Ag^+ was only 6.1 mass% after soaking 10 d. The antibacterial activity of $4^{\#}$ sample soaking in deionized water for different time at 37^0C was also estimated as shown in TABLE 3. The MIC against *E.coli* and *S.aureus* became high with the lapse of soaking time, but it still showed good antibacterial activity against *E.coli* and *S.aureus* with the MIC of 220 $mg.l^{-1}$ and 280 $mg.l^{-1}$ respectively after soaking 10 d. The results indicated that $4^{\#}$ sample showed excellent water-resistance.

TABLE 1: Effect of heat treatment temperature on whiteness, Ag content and antibacterial activity of AgZrP

Samples	T/^{0}C	Ag content /mass%	Whiteness* /%	MIC / $\mu g.l^{-1}$ E.coli	MIC / $\mu g.l^{-1}$ S.aureus
1	Untreatment	9.5	73.9	10	25
2	500	9.5	80.2	25	50
3	700	9.5	82.5	25	50
4	900	9.5	86.4	100	150
5	1100	9.3	90.6	500	700

*Exposed to 365 nm UV light for 24h

TABLE 2: Effect of UV irradiation time on whiteness and antibacterial activity of $4^{\#}$ sample

		Irradiation time (h)				
		0	12	24	36	48
Whiteness (%)		91.3	88.9	86.4	84.1	82.7
MIC	*E.coli*	100	150	200	220	250
($mg.l^{-1}$)	*S.aureus*	150	200	250	280	320

TABLE 3: Effect of soaking time on antibacterial activity of 4 sample

		Soaking time (d)					
		0	2	4	6	8	10
MIC	*E.coli*	100	120	150	160	200	220
($mg.l^{-1}$)	*S.aureus*	150	160	200	250	260	280

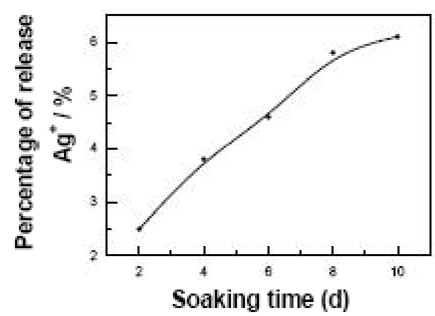

Figure 3: The percentage of release Ag^+ in 4 sample soaking in deionized water for different time

4. CONCLUSION

The thermal stability, light permanency and water resistance of AgZrP were evaluated in the paper. The weight loss of AgZrP was no more than 5.0 mass% at the heat treating temperature of 1100^0C, and the onset temperature of decomposition for the crystal structure of AgZrP appeared 1096.9^0C. The whiteness of $4^{\#}$ sample treated at 900^0C was 86.4% after exposed to UV light for 24h, and the MIC against *E.coli* and *S.aureus* were 100 $mg.l^{-1}$ and 150 $mg.l^{-1}$ respectively. Moreover, the percentage of release Ag^+ in $4^{\#}$ sample was only 6.1 mass% and the MIC against *E.coli* and *S.aureus* still remained 220 $mg.l^{-1}$ and 280 $mg.l^{-1}$ respectively after soaking in deionized water for 10 d. The results indicated that AgZrP possessed excellent thermal stability, light permanency and water resistance, and the study will be favorable to extend the applied fields of AgZrP.

5. ACKNOWLEDGMENTS

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