Preparation and characterisation of copper inorganic antibacterial material containing holmium

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A new inorganic antibacterial material was synthesised by the sol–gel method using copper ion as antibacterial ion, holmium nitrate as additive and white carbon black as carrier. The structure and properties of the inorganic antibacterial material were characterised by inductively coupled plasma atomic emission spectroscopy, Fourier transform infrared spectroscopy (FT-IR), scanning electron microscope (SEM) techniques, energy dispersive spectrum (EDS) analysis, X-ray diffraction (XRD) and antibacterial experiments (Escherichia coli as experimental bacteria). The result showed that the bacteriostasis rate of this new material was higher than that of the general Cu antibacterial white carbon black (without containing holmium); the bacteriostasis rate was over 90%. The form of the inorganic antibacterial material was investigated by XRD. The difference between the new inorganic antibacterial material and white carbon black was studied by FT-IR. Scanning electron microscopy and EDS were used to detect the holmium ion in the material.

Keywords: Antibacterial material, Copper, Holmium, White carbon black

This paper is part of a special issue on antimicrobial materials

Introduction

Antibacterial materials have become a hot research topic because of its important role on people’s health. Antibacterial materials can be divided into inorganic, organic and natural antibacterial materials.\textsuperscript{1,2} Organic antibacterial materials maintain the highest bacteriostasis rate, but have bad thermal stability, could easily cause second pollution and are toxic. Natural antibacterial materials are non-toxic and do not cause second pollution; however, they are thermally unstable and have narrow antibacterial scope. Inorganic antibacterial materials can overcome these disadvantages and can thus have broad application in different fields.\textsuperscript{3–5} The antibacterial ions in inorganic antibacterial materials are important. Many metal ions have antibacterial property, such as Ag\textsuperscript{+}, Cu\textsuperscript{2+}, Zn\textsuperscript{2+}, Ni\textsuperscript{3+}, Hg\textsuperscript{2+}, Pb\textsuperscript{2+}, Bi\textsuperscript{3+}, Cr\textsuperscript{3+} and Sn\textsuperscript{2+}; among which, Ag\textsuperscript{+}, Cu\textsuperscript{2+} and Zn\textsuperscript{2+} have been widely used.\textsuperscript{6–10} Silver ion has a high bacteriostasis rate; however, silver is expensive, easily oxidised and changes in colour. The bacteriostasis rate of copper ions is higher than zinc ions but lower than silver ions. Copper ions do not change colour during the application process.

Recently, many researchers have pointed out that rare earth elements can improve antibacterial efficiency.\textsuperscript{10–13} Given their special electronic configuration, rare earth elements have unique physical and chemical properties and good antibacterial effects. Holmium ions have been added into antibacterial materials, and the result showed that the new inorganic material had better antibacterial property than the general Cu inorganic antibacterial materials.\textsuperscript{14–16}

In this work, copper ion was selected as antibacterial ion, holmium nitrate as additive and white carbon black carrier to prepare a new inorganic antibacterial material. The new inorganic antibacterial material was characterised by scanning electron microscope (SEM), energy dispersive spectrum (EDS) analysis, X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) and antibacterial experiment. The factors influencing the load rate in the new inorganic antibacterial material were also studied.

Experimental

Material preparation

A certain amount of sodium bicarbonate (Analysis reagent, Aladdin) and sodium silicate (Analysis reagent, Aladdin) was preheated and added into the reactor. The mixture was stirred by an agitator with an agitation speed of 300–500 rev min\textsuperscript{−1}. After 15 min, the revolving speed was adjusted to 200–300 rev min\textsuperscript{−1}, and the remanent sodium silicate and sodium bicarbonate were then added into the reactor. After 30 min, nitric acid was added into the system to adjust the pH to 3. A quantitative amount of precipitator was then added into the reactor. After 30 min, holmium nitrate (Analysis
reagent, Alfa Aesar) solution was added into the system and mixed. After 2 min, copper sulphate (analysis reagent, Aladdin) solution was placed into the reactor. The reaction was stopped after 1 h. The mixture was then treated by a suction filter machine. The filtered materials were placed into the drying oven, wherein the temperature was maintained at 120°C for 2 h. The Cu–Ho antibacterial white carbon black was synthesised.

Characterisations

**Inductively coupled plasma atomic emission spectroscopy**

The Cu²⁺ content in the material was determined by the inductively coupled plasma atomic emission spectroscopy (ICAP6300, Thermo Fisher Scientific Company in American). A series of copper standard solutions were prepared and were measured to obtain the standard curve. The sample was then measured to determine the copper ion concentration from the standard curve.

**Fourier transform infrared spectroscopy**

To study the influence of Cu and Ho on the structure of white carbon black, FT-IR (TENSOR37) was used to detect the structures of white carbon black and Cu–Ho antibacterial white carbon black. The FT-IR machine was produced by BRUKER Company, Germany.

**Scanning electron microscopy and EDS analysis**

The holmium ion of the new material was detected by SEM (XL30ESEM-TMR) and EDS (phoenix-OIM).

**X-ray diffraction**

Cu–Ho antibacterial white carbon black was characterised by XRD (D/max-2200) (Rigaku Corporation, Japan).

**Tests of antibacterial activity**

Exactly 10 mL of sterilised NaCl was placed into a Triangle flask, and then 0·1 g of Cu–Ho antibacterial white carbon black and a hectolambda of *Escherichia coli* microbial concentration were added. All the operations were carried out in a laminar flow. Afterward, the Triangle flask was placed into the oscillator. After shaking for 1·5 h at 37°C in the oscillator, the hectolambda of the mixture liquid was transferred into petri dishes, and then poured into culture medium. The mixture was spread evenly on the surface of culture medium, and the petri dishes were kept in an incubator at constant temperature (37°C) for 24 h. Colony forming units could be observed by the naked eyes. The bacteriostasis rate of the Cu–Ho antibacterial white carbon black can be calculated by the ratio with blank test. The blank test was treated in the same way. The process of adding 0·1 g of Cu–Ho antibacterial white carbon black into the Triangle flask was removed.

**Results and discussion**

In this paper, inductively coupled plasma atomic emission spectroscopy was used to monitor the load rate of copper ions in the Cu–Ho antibacterial white carbon black. The load rate was investigated as a function of copper ion concentration, reaction time and holmium ion concentration.

**Influence of copper ion concentrations on load rate**

The concentration of copper sulphate is one of the main factors affecting the load rate of the copper ions on the new inorganic antibacterial material. The relationship between the copper sulphate concentration and load rate was studied. The concentrations of copper sulphate were 0·005, 0·01, 0·03, 0·05, 0·07 and 0·09 mol L⁻¹ respectively (holmium nitrate was maintained at 0·005 mol L⁻¹ and the reaction time was 1 h); the result is shown in Fig. 1.

![Graph 1: Relationship between copper ion concentration and load rate](image1)

![Graph 2: Relationship between reaction time and load rate](image2)

![Graph 3: Relationship between concentration of holmium ion and load rate](image3)
The load rate of copper ions increased with the reaction time up to 1-5 h. No significant change on the load rate of copper ions was observed when the reaction time exceeded 1-5 h. This result may be due to the fact that the copper ion loaded to the white carbon black was saturate when the reaction time reached 1-5 h. The copper ions had same positive electricity; thus, the copper ions excluded each other and the load rate was less varied when the reaction time increased. Thus, 1-5 h was the optimum reaction time in this study.

**Influence of holmium ion concentration on load rate**

The concentration of holmium ions may influence the load rate of copper ions. The relationship between holmium ion concentration and load rate was studied. The concentrations of holmium nitrate were 0·001, 0·003, 0·005, 0·007 and 0·009 mol L⁻¹ (copper sulphate concentrations, 0·05 mol L⁻¹; reaction time was 1 h). The result is shown in Fig. 3.

**Scanning electron microscopy and EDS analysis**

The SEM image and EDS analysis are shown in Figs. 4 and 5 respectively. Figure 5a and b corresponds to points 1 and 2 of Fig. 4 respectively. Figure 4 shows that the Cu–Ho antibacterial white carbon black was in amorphous state. Holmium ion and white carbon black were observed in Fig. 5b, confirming the existence of holmium ions in the Cu–Ho antibacterial white carbon black.

**Fourier transform infrared spectroscopy**

The FT-IR spectra of the samples were obtained at 25°C through FT-IR (WQF-2000) at an interval of 4 Image (SEM) of Cu–Ho antibacterial white carbon black

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**Figure 1** shows that the load rate of copper increased with the concentration of the copper sulphate when the copper concentration was <0·05 mol L⁻¹. The load rate was kept at a relatively high level and increased slowly when the copper ion concentration was >0·05 mol L⁻¹. Thus, a concentration of copper sulphate at 0·05 mol L⁻¹ would be the optimum reaction concentration.

**Influence of reaction time on load rate**

Reaction time is another important factor that affects the load rate of copper ions. The relationship between reaction time and load rate was studied; the result is shown in Fig. 2.

**Table:**

<table>
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<tr>
<th>Element</th>
<th>Wt%</th>
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<td>69.23</td>
</tr>
<tr>
<td>SiK</td>
<td>43.83</td>
<td>30.77</td>
</tr>
<tr>
<td>Matrix</td>
<td>Correction</td>
<td>ZAF</td>
</tr>
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</table>

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(a) a analysis (EDS) of point 1 in Fig. 4; b EDS analysis of point 2 in Fig. 4

5 Analysis (EDS) of Cu–Ho antibacterial white carbon black
The structural groups of the Cu–Ho antibacterial white carbon black and pure white carbon black were studied. Figure 6 shows the FT-IR spectra of white carbon black and the Cu–Ho antibacterial white carbon black. Figure 6 indicates that the absorption peaks of Cu–Ho antibacterial white carbon black were almost at the same location compared with white carbon black, indicating that the copper ions and holmium ions almost had no effect on the white carbon black. Thus, Cu–Ho antibacterial white carbon black can be used instead of pure white carbon black. Furthermore, Cu–Ho antibacterial white carbon black has antibacterial property.

**X-ray diffraction**

The XRD images of the Cu–Ho antibacterial white carbon black and pure white carbon black are shown in Fig. 7, indicating that the two materials were amorphous. The two pictures in the figure only had small difference; hence, the additive did change the state.

Every instrument has its lowest detectable limit. In the material, the absorption peak of the copper ions and the
Holmium ions could not be detected, which may be due to their low concentration.

**Antibacterial effect**

Figure 8 shows the bacteriostasis rates of the white carbon black containing holmium ions, white carbon black containing copper ion and Cu–Ho antibacterial white carbon black. The four figures showed that copper ions and holmium ions have antibacterial property to a certain degree. The antibacterial property of the Cu–Ho antibacterial white carbon black was the best one, and its bacteriostasis rate can reach 98.32%. This outstanding performance may be due to the fact that Cu–Ho antibacterial white carbon black can release more free hydroxyl radicals that kill bacteria efficiently. Thus, the Cu–Ho antibacterial white carbon black can be used similar to Ag antibacterial white carbon black in the antibacterial field.

**Conclusions**

In this new inorganic antibacterial material, the carrier, white carbon black, was prepared by the sol–gel method, and the Cu–Ho antibacterial white carbon black was synthesised by adhering holmium nitrate and copper sulphate on the white carbon black under certain conditions. In this study, we investigated the influence of the copper sulphate and holmium nitrate concentrations...
and the reaction time to load rate of the copper ions. The results showed that the load rate of copper ions reached a high level when the concentration of copper sulphate was 0.05 mol L\(^{-1}\), the concentration of holmium nitrate was 0.005 mol L\(^{-1}\) and the reaction time was 1.5 h. The FT-IR spectra analysis showed that the additives had little effect to pure white carbon black. Thus, the material can replace pure white carbon black. The antibacterial rates of the Cu–Ho antibacterial white carbon black exceeded 90%. The SEM image and EDS analysis showed the holmium ions in the material. The XRD analysis showed that the material was amorphous.

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Reference

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