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MOFs with enhanced photothermal and photocatalytic effects for rapid sterilization

Short title: Light-responsive MOFs for rapid sterilization

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ABSTRACT

Background: Antibiotics commonly used to treat bacterial infections in clinical practice can lead to the creation of drug-resistant bacteria, which are more difficult to eradicate. Therefore, there is an urgent need to develop a new antibacterial agent and antibacterial means that will not make bacteria resistant to resistance.

Methods: We synthesized MoO42-/PCN-222 composites using a simple hydrothermal and electrostatic adsorption methods. We characterized the successful synthesis of the

material by field emission scanning electron microscopy (FE-SEM) and X-ray diffraction (XRD). Then we tested the photocatalytic and photothermal properties of the materials, and finally we evaluated the antibacterial properties of the materials against Staphylococcus aureus by the spread plate method.

Results: The results showed that MoO42+/PCN-222 composite had excellent antibacterial properties, and 20MoO42+/PCN-222 could kill 94.05% of Staphylococcus aureus under 660 nm light irradiation for 10 minutes.

Conclusions: In this article, we synthesized MoO42-/PCN-222 composites by a simple hydrothermal and electrostatic bonding method. The material has excellent photocatalytic and photothermal effects, so the composite material has excellent killing effect on S. aureus. We believe this work can provide new insights for the application of PCN-222 based materials.

Keywords: MOF; Antibacterial; Bacterial infection; Phototherapy

INTRODUCTION

Since the discovery of penicillin by Alexander Flemming in 1923, antibiotics have been considered a panacea for bacterial infections.[1] But the massive use of antibiotics has led to the emergence of drug-resistant bacteria, which seriously threaten the health of humans, animals and the environment.[2] In terms of human health, its impact is mainly felt in areas such as surgery, transplantation and infection treatment.[3] In the United States, at least 2 million people are infected with drug-resistant bacteria each year, and at least 230 million people die from these infections each year, according to an analysis of data from the Centers for Disease Control and Prevention (CDC).[4] Therefore, in order to solve the problem of bacterial resistance, people have to seek antibiotics that can replace antibiotics. At present, with the development of nanomaterials, it has been found that nanomaterials can bind and destroy the bacterial membrane of bacteria, resulting in leakage or combination of cell contents with cell contents, which causes oxidative stress, electrolyte imbalance and enzyme inhibition and other phenomena of bacteria, resulting in bacterial death.[5] Many nanomaterials have been used for antibacterial treatment, such as toxic metal ions (Ag^{+}, Zn^{2+}, Bi^{3+}, Cu^{2+}, etc.),[6]

positively charged organic compounds (quaternary ammonium salts, antimicrobial peptides, etc.) and compounds with nanometer enzyme properties (ferric oxide, gold nanoparticles, manganese dioxide, etc.).[7–8] However, the above-mentioned antibacterial methods generally take a long time to achieve a good antibacterial effect, so there is an urgent need to develop safe and time-consuming antibacterial methods.

At present, the methods widely used for rapid sterilization are photocatalysis and photothermal sterilization. Photothermal sterilization refers to a method of using light to irradiate a photothermal agent to generate local high heat to kill bacteria.[9] Photocatalytic sterilization refers to the use of light to irradiate photocatalytic materials to generate active oxygen for sterilization.[9] But usually, a single antibacterial method cannot achieve a good antibacterial effect in a short time, Therefore, it is currently popular to combine the two antibacterial methods of photothermal and photocatalysis to achieve a good sterilization result. At present, many materials have been used for photothermal and photocatalytic synergistic antibacterial research, such as copper sulfide, molybdenum sulfide and metal organic framework materials.[10–12]

In conclusion, to achieve a good antibacterial effect, we constructed MoO_4^{2-}/PCN-222 composites. PCN-222 metal-organic framework (MOF) is composed of Zr ion and porphyrin organic ligands, so PCN-222 has excellent photocatalytic effect. After loading MoO_4^{2+}, the MoO_4^{2-}/PCN-222 composite has a good photothermal and photocatalytic effect. The antibacterial results showed that 20MoO_4^{2-}PCN-222 composites could kill 94.2% of *Staphylococcus aureus* within 10 minutes under 660 nm red light irradiation.

EXPERIMENTAL PROCEDURE

The synthesis of PCN-222

Dissolving 10 mg $ZrCl_4$, 250 mg benzoic acid and 200 μL H_2O in 2 mL N,N-dimethylformamide (DMF) nder magnetic agitation for 5 minutes. Then, 10 mg tetrakis (4-carboxylphenyl) porphyrin (TCPP) as added to the solution and stirred magnetically at room temperature for 10 minutes. The resulting homogeneous solution was transferred to a 50 mL teflon-lined stainless steel autoclave and then heated at 120 ºC

for 24 hours. The products were separated by centrifugation and further purified with ethanol several times.

The synthesis of MoO_4^{2-}/PCN-222 composite

20 mg PCN-222 was dispersed in 10 mL deionized water, and then 10 mg and 20 mg sodium molybbolybate dihydrate were added, stirred for 12 hours, and then the products were centrifuged, washed and dried to obtain $10MoO_4^{2+}$/PCN-222 and $20MoO_4^{2+}$/PCN-222 composites, respectively.

Materials characterization

The morphology of the material was observed by field emission scanning electron microscope (FE-SEM JSM7100F, JEOL, Japan). The phase composition of the material was determined by X-ray diffraction (XRD, D8A25, Bruker, Germany).

Reactive oxygen detection

1, 3-diphenyliso-benzofuran (DPBF) dye is used as reactive oxygen detection reagent. The material was mixed evenly with DPBF solution, and then the peak drop of DPBF at around 420 nm was detected under the light condition of 660 nm. The drop of DPBF was measured with a microplate tester every 20 seconds.

Photothermal detection

To evaluate the photothermal effect of materials, different materials were dispersed in 96-well plates containing 200 μL water, and each well was exposed to 660 nm light for 10 minutes. The temperature was recorded every 2 minutes.

RESULTS AND DISCUSSION

We synthesized MoO_4^{2-}/PCN-222 composites by simple hydrothermal and electrostatic adsorption methods. The morphology of the material was observed by field emission scanning electron microscopy (FE-SEM). As shown in Figure 1a, PCN-222 exhibited two kinds of morphologies, mainly composed of nanorods and small cubes. After

loading MoO_4^{2-} ions, the morphology of MoO_4^{2-}/PCN-222 composites were the same as that of pure PCN-222, indicating that MoO_4^{2+} ions did not affect the morphology of PCN-222. At the same time, in order to know whether the MoO_4^{2-} ions were successfully loaded, we performed the EDS detection on the $20MoO_4^{2-}$/PCN-222 composite material. It could be seen from Figure 1c-h that in addition to C, N, O and Zr elements originally contained in PCN-222, Mo element also appeared, indicating that MoO_4^{2+} was successfully loaded in PCN-222.

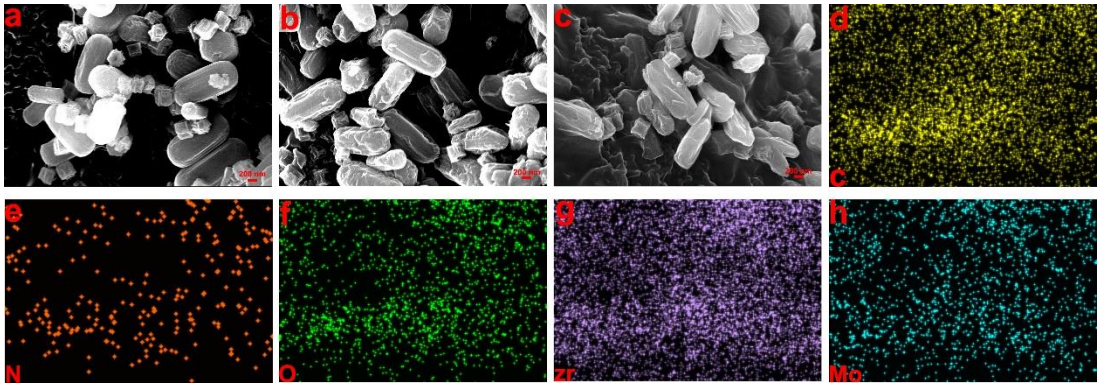

Figure 1. The FE-SEM images of (a) PCN-222, (b) $10MoO_4^{2-}$/PCN-222 and (c) $20MoO_4^{2-}$/PCN-222. The EDS data of $20MoO_4^{2-}$/PCN-222 of (d) C element, (e) N element, (f) O element, (g) Zr element and (h) Mo element.

In order to further understand the phase composition of the material, we did the XRD test of the material. As shown in Figure 2, the XRD peaks of PCN-222 were consistent with the previous literature, indicating the successful synthesis of PCN-222.[13] After loading MoO_4^{2-}, the peak intensity of PCN-222 decreased, but the main characteristic peaks did not change, indicating that in the process of synthesizing MoO_4^{2-}/PCN-222 composites, water molecules might have an effect on the crystal form of PCN-222.

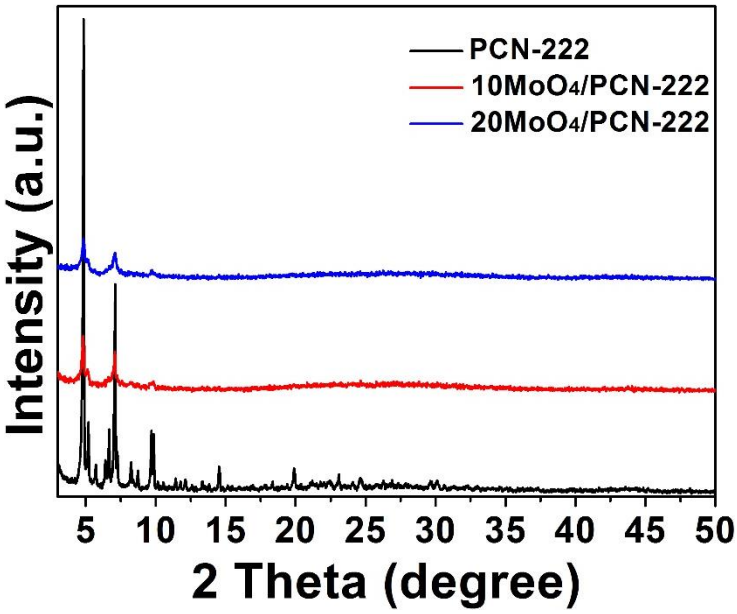

Figure 2. The XRD pattern of materials.

As shown in Figure 3a, the absorption intensity of MoO_4^{2-}/PCN-222 composite material in the visible light region was significantly enhanced compared with that of PCN-222, indicating that the load of MoO_4^{2-} could effectively increase the absorption capacity of PCN-222 to visible light. In addition, the forbidden band width of the material was calculated by plotting the transformed value of the Kubelka-Munk function and the photon energy (eV).[14] According to Figure 3b, the estimated band gaps of PCN-222, $10MoO_4^{2-}$/PCN-222, $20MoO_4^{2-}$/PCN-222 were 1.78, 1.61 and 1.59 eV, respectively. It showed that the forbidden band width of PCN-222 was significantly reduced after MoO_4^{2-} was loaded, indicating that the photocatalytic efficiency of the composite material was significantly enhanced. The heating temperature curve of the sample was shown in Figure 3c, the temperature of $10MoO_4^{2-}$/PCN-222, $20MoO_4^{2-}$/PCN-222 composites was significantly higher than that of PCN-222. And after 6 minutes of irradiation, the temperature of the $10MoO_4^{2-}$/PCN-222 and $20MoO_4^{2-}$/PCN-222 composite material rose to 52.3 ℃ and 54.3 ℃, respectively. In contrast, the temperature of the PCN-222 group was only 49.7 ℃, indicating that the loading of MoO_4^{2-} could significantly improve the photothermal conversion efficiency of PCN-222.

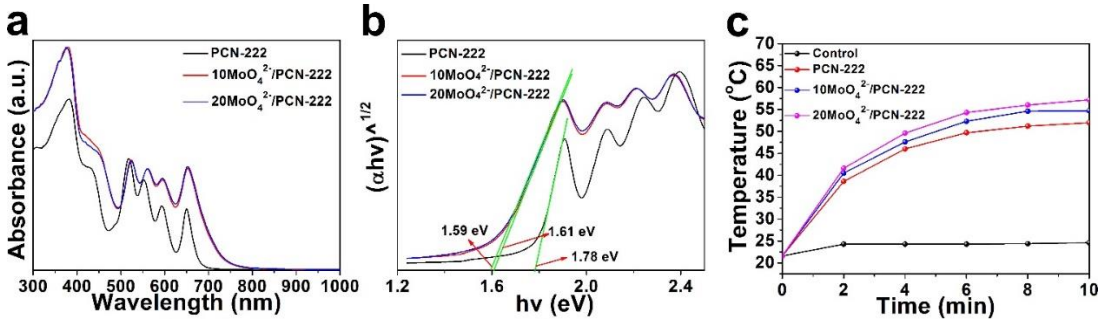

Figure 3. (a) UV–vis-NIR diffuse reflectance spectra (DRS) of materials. (b) The corresponding Kubelka−Munk function plots derived from DRS. (c) The photothermal heating curves of samples.

1,3-Diphenylisobenzofuran (DPBF) acts as an $^1O_2$ trap, reacting rapidly with $^1O_2$ to form a product with a reduced absorption intensity centered at 420 nm.[15] For the control group, the change in the absorption peak of the DPBF solution after 80 s of illumination was negligible (Figure 4a), indicating that DPBF was very stable and was not affected by illumination. In contrast, the absorption intensities of the DPBF solutions of the PCN-222 and MoO_4^{2-}/PCN-222 composite groups gradually decreased under light irradiation (Figure 4b–d), indicating that the generation of $^1O_2$ was significant. At the same time, according to the comparison curve, the active oxygen yield of MoO_4^{2-}/PCN-222 composite material was higher than that of PCN-222, indicating that after MoO_4^{2-} ions were loaded, MoO_4^{2-} enhanced the separation and transfer rates of photogenerated electron-air pairs in PCN-222. All in all, the MoO_4^{2-}/PCN-222 composite exhibited excellent photocatalytic effects.

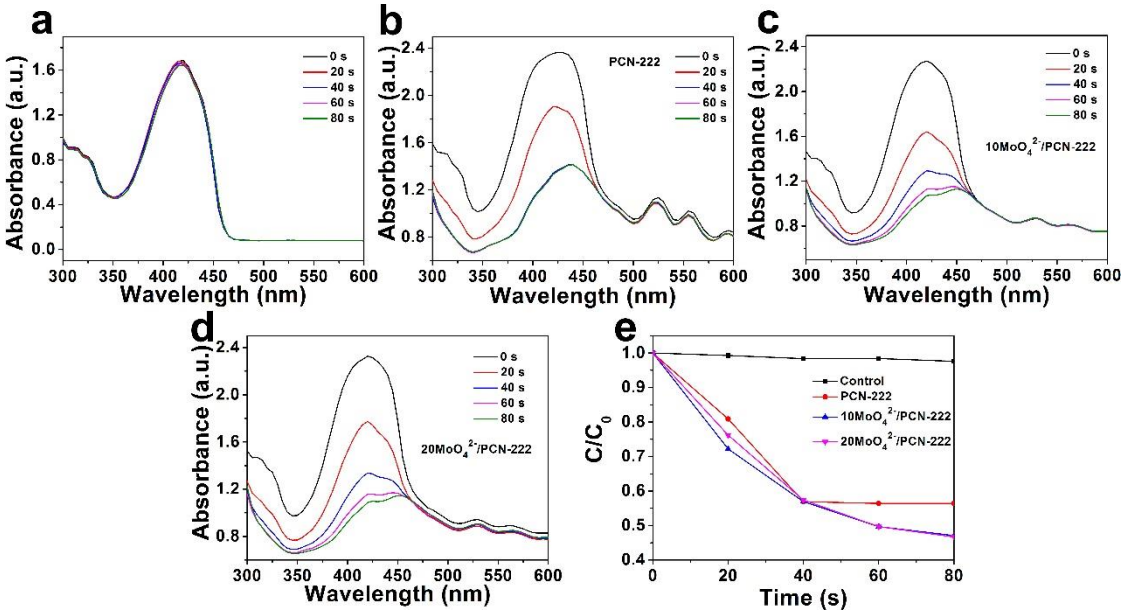

Figure 4. The decay of DPBF for the detection of $^1O_2$ in (a) Control, (b) PCN-222, (C) $10MoO_4^{2-}$/PCN-222, (d) $20MoO_4^{2-}$/PCN-222. (e) The corresponding contrast curve of DPBF decline.

We evaluated the antibacterial ability of the material against *Staphylococcus aureus* (*S. aureus*) using the spread plate method. As shown in Figure 5, after being irradiated with 660 nm light for 10 min, the bacterial colonies of PCN-222, $10MoO_4^{2-}$/PCN-222 and $20MoO_4^{2-}$/PCN-222 groups showed different degrees of decline, and the antibacterial effects against *S. aureus* were 21.89%, 94.2% and 94.05%, respectively (Figure 5). The antibacterial results showed that the antibacterial rate of the MoO_4^{2-}/PCN-222 composite was much higher than that of PCN-222d alone, indicating that the loading of MoO_4^{2-} significantly enhanced the antibacterial effect of PCN-222.

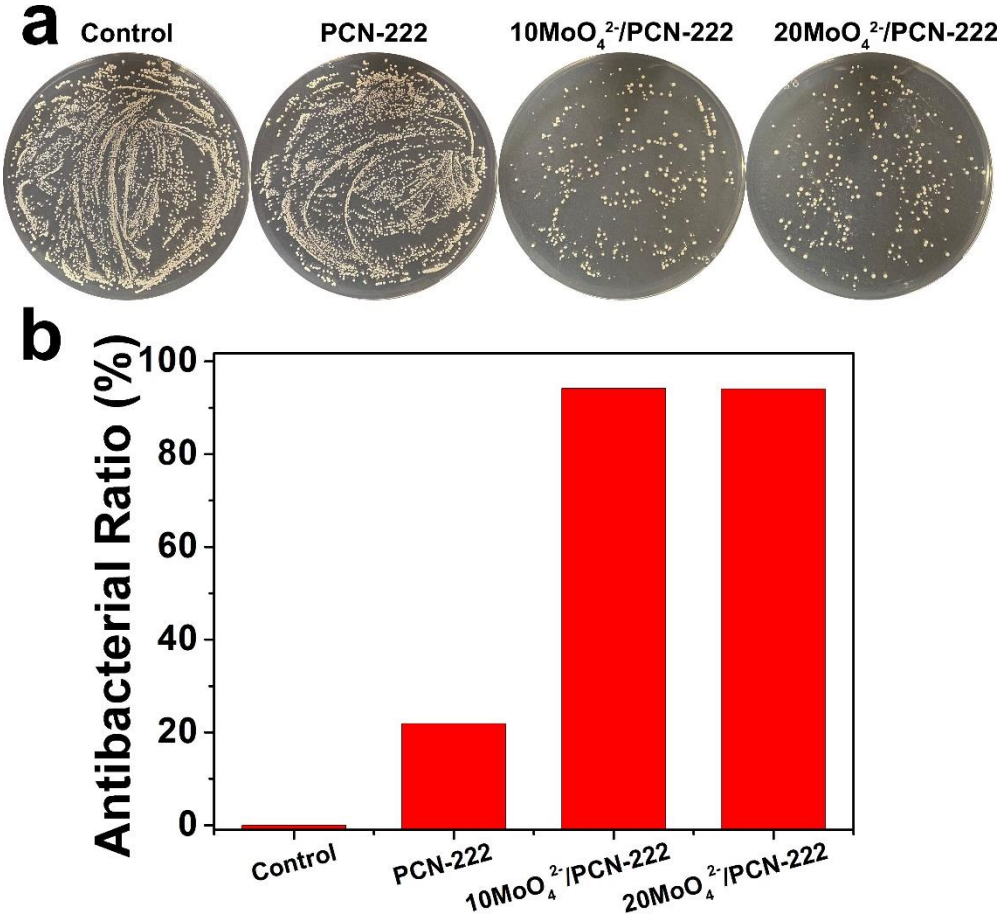

Figure 5. (a) Spread plate results of *S. aureus* eradication in different samples after irradiation with 660 nm light for 10 min and (b) The corresponding antibacterial ratio of different samples.

CONCLUSION

In this article, we synthesized MoO_4^{2-}/PCN-222 composites by a simple hydrothermal and electrostatic bonding method. The material has excellent photocatalytic and photothermal effects, so the composite material has excellent killing effect on *S. aureus*. We believe this work can provide new insights for the application of PCN-222 based materials.

Conflict of Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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