Preparation and Antibacterial Properties of SA/Nano-Cu_2O Gel by In-stitu Method

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Abstract. Preparation of gel of nano-Cu_2O by in stiu reduction method in sodium alginate (SA) solution. The In-situ method is relation to the addition of nano-powder method, without dispersant, coupling agent can prepare SA/nano-Cu_2O gel, it is a green preparation method. To explore the impact of various factors on the reaction, therefore the optimum condition of the preparation of Cu_2O gel in usual atmospheric pressure is determined. The structure and morphology of the Cu_2O in the gel was investigated by FT-IR and SEM and the bacterial-resistance properties were tested. The results of this study show that the Cu_2O particles in the SA gel are essentially sphere and uniform grading. The gel had excellent bacteriostatic activity towards escherichia coli and staphylococcus aureus. Because gel SA/nano-Cu_2O does not contain other dispersant and coupling agent, the composition is single, the security is higher, and the stability is good, so this gel in the medical antibacterial material and the antimicrobial textile domain will have a more broad application prospects.

1 Introduction

Antimicrobial material is a new type of functional material which has the function of killing or inhibiting microorganisms, and it has been widely used in various fields. Inorganic antibacterial agent is one of the important branches[1-2].

Mainly includes four categories: sliver based antimicrobial agents, copper based antibacterial agent, TiO_2 based photocatalytic antibacterial agent and ZnO based metal oxide antibacterial agent[3-5]. Sliver based antimicrobial agents are the most widely studied and used in the present. It has excellent antibacterial properties, and even kill bacteria at low concentration. Sliver based antimicrobial active ingredients are mainly Ag^+, and Ag is expensive, as a broad-spectrum antimicrobial agents, the cost is too high, is not conducive to the use of a wide range[6]. Copper as a relatively cheap material, not only a wide range of sources, low cost, and has the same excellent antibacterial properties as sliver, copper based antibacterial material will also become one of the important inorganic antibacterial materials[7-8]. Cu_2O belong to eight cubic crystal system in the Fig 1. How to prepare with good water solubility, stability, antimicrobial cuprous oxide antibacterial materials will be the emphasis and difficulty of this paper.

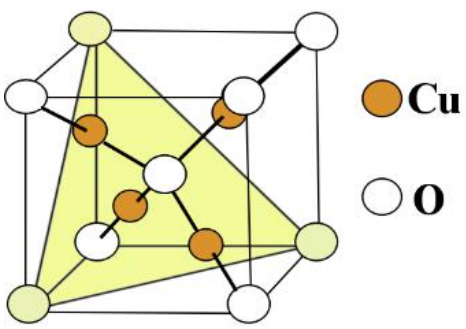

Fig. 1. Unit cell structure of Cu_2O

2 Experimental

2.1 Materials. Sodium alginate (SA) was supplied by Jiejing Seaweed Co., Ltd. Shandong Province, P. R. China. Anhydrous cupric sulfate was purchased from Fukai chemical limited liability company. Ascorbic acid was supplied by Sinopharm Chemical Reagent Co., Ltd. All other reagents were of analytical grade.

2.2 Preparation of SA/nano-Cu_2O gel.

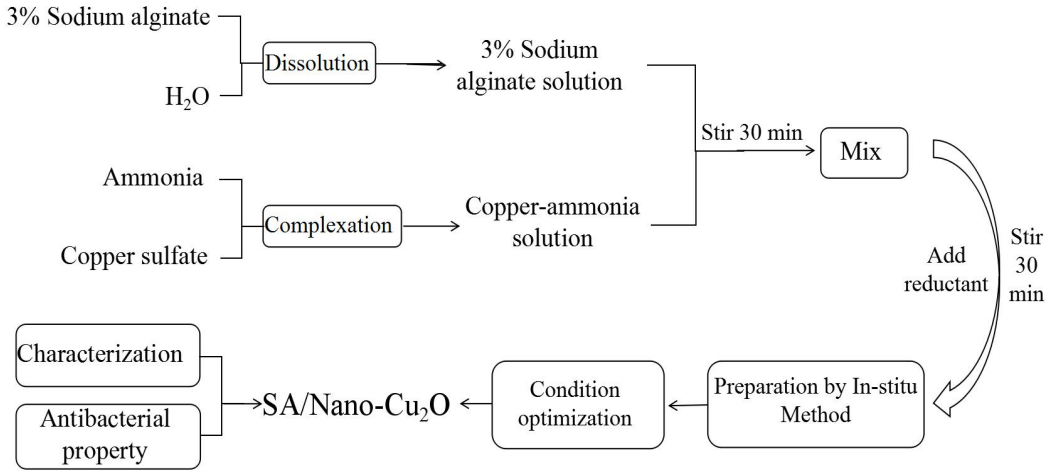

Fig. 2. Preparation flowchart

2.2 The single factor experiment.

Study on the optimal reductant. Weighing exactly 0.4g SA and 40mL de-ionised water and transferring them into a three mouth flask, set a certain temperature, and dissolved with stirring. Add a certain cuprammonium solution, stirring 30min. The experiments were carried out using three kinds of experiment, one is to restore with the sodium borohydride solution, the second is to restore with the glucose solution, the third is to restore with the ascorbic acid solution, continue to stir 30min, to get the corresponding gel, respectively. Discussed and recorded.

Study on the optimal dosage of reductant. Weighing exactly 0.4g SA and 40mL de-ionised water and transferring them into a three mouth flask, set a certain temperature, and dissolved with stirring. Add a certain cuprammonium solution, stirring 30min. The different amounts of 7mL, 9mL, 11mL, 13mL ascorbic acid solution of 0.5mol/L were added to the solution, respectively. Continue to stir 30min. Experiments were carried out respectively. Carry out the antibacterial experiments and record at the end of the experiments.

Study on the optimal temperature of experiment. Weighing exactly 0.4g SA and 40mL de-ionised water and transferring them into a three mouth flask, set the temperature at the 40℃, 60℃, 70℃, 80℃, respectively and stirring and dissolve to the experiment. Add a certain cuprammonium solution, stirring 30min. The optimum dosage of reductant solution was added. Continue to stir 30min. Experiments were carried out respectively. Carry out the antibacterial experiments and record at the end of the experiments.

Study on the optimal dosage of cuprammonium solution. Weighing exactly 0.4g SA and 40mL de-ionised water and transferring them into a three mouth flask, set the optimal temperature, and dissolved with stirring. Preparation of cuprammonium solution: take 0.5mol/L 3mL of copper sulfate in the centrifuge tube, by drops of ammonia until blue precipitation disappeared, into a colorless settled solution. The different amounts of 0.5mL, 1mL, 1.5mL, 2mL curprammonium solution were added to the solution, respectively. Stirring 30min. The optimum dosage of reductant solution was added. Continue to stir 30min. Experiments were carried out respectively. Carry out the antibacterial experiments and record at the end of the experiments.

2.4 Characterization and test.

Infrared spectrometry. The gel preparation under the optimum conditions and it was centrifuged and filtered. The obtained cuprous oxide powders are washed 2-3 times with the anhydrous ethanol and put it into vacuum oven to dry. Using potass bromide tabletting method for IR test of Cu_2O

powder after drying. Take 0.5mg drying of cuprous oxide powders and a small amount of potassium bromide powders grinding evenly, 20MPa press 3 to 5 minutes, in 500~3500cm^{-1} wavelength range scanning.

The SEM images of Cu_2O powders. The gel preparation under the optimum conditions and it was centrifuged and filtered. The obtained cuprous oxide powders are washed 2-3 times with the anhydrous ethanol and put it into vacuum oven to dry. SEM observation: use the TM3000 scanning elecrton microscope to observe the surface morphology and particle size of the Cu_2O poeders after drying.

3 Results and discussion

3.1 The results and discussion of single factor experiment.

The effect of kinds of reductant. Three different kinds of reducing agents were used in the experiment and the results of the experiments were as follows. Compared with the other two kinds of reducing agents, the reduction of ascorbic acid is moderate and the experimental conditions are relatively simple, the experimental results are better than the other two kinds of reducing agent. Therefore, this experiment used ascorbic acid as a reducing agent.

Table 1 The effects of different kinds of reductant on the result of the experiment

Reductant	Volume	Concentration	Temperature	Phenomena	conclusion
sodium borohydride	1 mL	1 mol/L	25 ℃	The solution changed from blue to black	The reducibility of sodium borohydride is too strong, the copper ion is oxidized to pure copper.
glucose	1 mL	1 mol/L	80 ℃	The solution changed from blue to yellow	The reducibility of glucose is weak and it has a high requirement for experimental environment and conditions.
ascorbic acid	10 mL	0.01 mol/L	25 ℃	The solution changed from bule to erythrine	The reducibility of ascorbic acid is moderate, and the experimental conditions are relatively simple.

Effect of dosage of reductant on antibacterial property. a, b, c and d represent the samples with an addition of 0.5mol/L ascorbic acid at 7mL, 9mL, 11mL and 13mL, respectively. As can be seen from the antibacterial experiment pictures (show in Fig. 3.), if other factors remain unchanged, the best antibacterial effect can be achieved when the additive amount of ascorbic acid reaches 9mL.

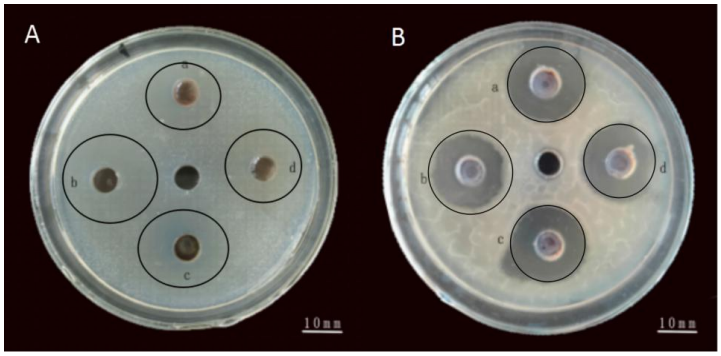

Fig. 3. The antibacterial property contrast of different dosage of reductant: A escherichia coli B staphylococcus aureus

Effect of temperature of experiment on antibacterial property. a, b, c and d represent the samples with the temperature of experiment at 40℃, 60℃, 70℃ and 80℃, respectively. As can be seen from the antibacterial experiment pictures (show in Fig. 4.), if other factors remain unchanged, the best antibacterial effect can be achieved when the temperature of experiment at 70℃.

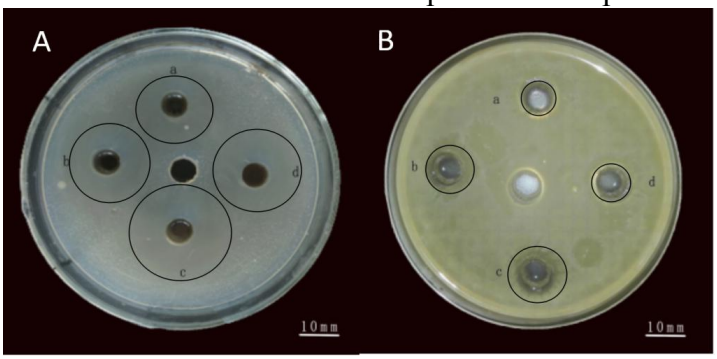

Fig. 4. The antibacterial property contrast of different temperature of experiment: A escherichia coli B staphylococcus aureus

Effect of dosage of cuprammonium solution on antibacterial property. a, b, c and d represent the samples with an addition of cuprammonium at 0.5mL, 1.0mL, 1.5mL and 2.0mL, respectively. As can be seen from the antibacterial experiment pictures (show in Fig. 5.), if other factors remain unchanged, the best antibacterial effect can be achieved when the additive amount of cuprammonium solution reaches 9mL.

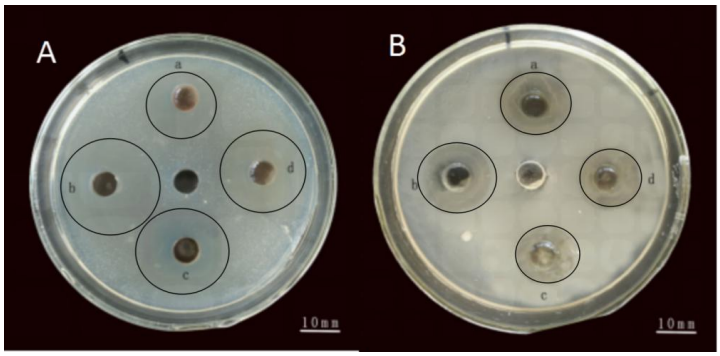

Fig. 5. The antibacterial property contrast of different dosage of cuprammonium solution: A escherichia coli B staphylococcus aureus

3.2 Characterization test results and discussion.

IR analysis. IR spectra is made for synthesized Cu_2O and purchased Cu_2O. It is quite matched. The results are as in Fig. 6. Characteristic vibration absorption of Cu(I)-O is at 628cm^{-1}. Synthesis Cu_2O for their synthesis of Cu_2O, buy Cu_2O for the market to buy the Cu_2O. It can be seen from the infrared image that the peaks of the two are basically the same, except for the special vibration absorption of Cu_2O, and the two curves are absorption peaks of water at approximately 1630 cm^{-1} and 3440 cm^{-1}.

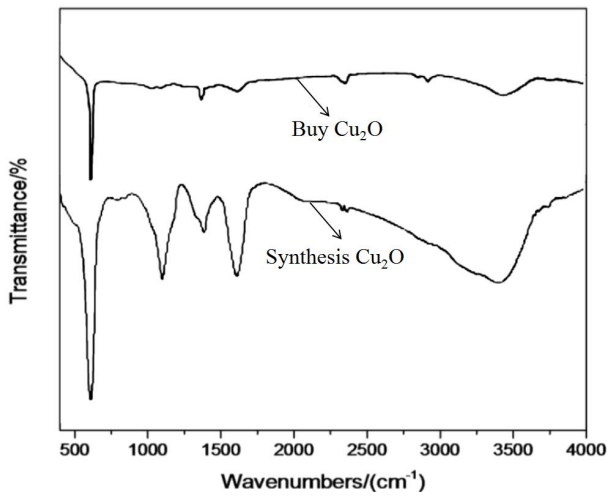

Fig. 6. IR spectra of the synthesis Cu_2O and the buy Cu_2O

SEM morphological analysis. As shown in the Fig. 7., the SEM of Cu_2O was prepared under the optimal conditions, view from the figure, the prepared sample Cu_2O is in ball shape with quite plump particles and even distribution. The particle diameter is about 500nm, and it had been up to nano material. It indicates that the preparation process still has improvement space.

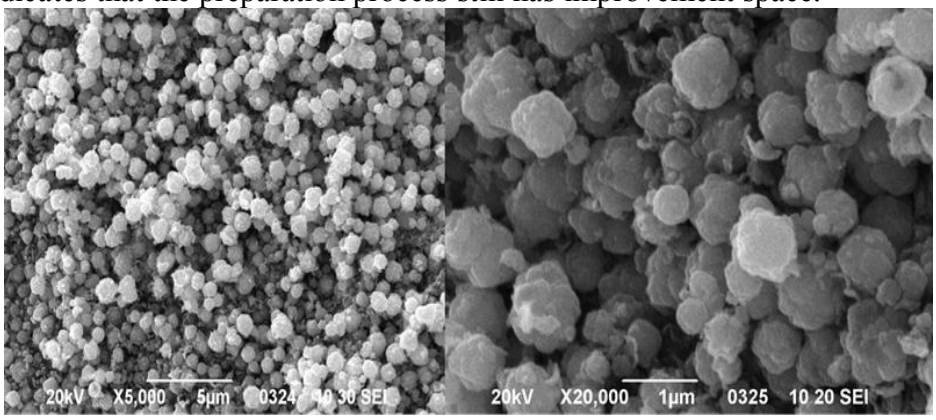

Fig. 7. SEM images of the Cu_2O

4 Conclusions

This experiment by in situ reduction method introduced nano-Cu_2O particles in the SA gel, the optimum condition is determined by single factor experiment. The result show: Under 70℃, the reductant is 9mL 0.5mol/L. Add 1mL 0.5mol/L cuprammonium solution in the 3% SA solution, after reacting for 30min, Cu_2O particles in the prepared SA nano-Cu_2O gel are even and have high purity. Furthermore, they have significant antibacterial action for both scherichia coli and staphylococcus aureus.

References

[1] Y. Dong, Y. Li, Wang C, et al. Preparation of cuprous oxide particles of different crystallinity[J]. Journal of Colloid and Interface Science, 2001, 243(1): 85-89.

[2] L. Gragnaniello, S. Agnoli, G. Parteder, et al. Cobalt oxide nanolayers on Pd (100): The thickne ss-dependent structural evolution[J]. Surface Science, 2010, 604(21): 2002-2011.

[3] M. Schmid, M. Shishkin, G. Kresse, et al. Oxygen-deficient line defects in an ultrathin aluminum oxide film[J]. Physical review letters, 2006, 97(4): 046101.

[4] D. Zherebetskyy, L.W. Wang. In‐Gap States in Electronic Structure of Nonpolar Surfaces of Insulating Metal Oxides[J]. Advanced Materials Interfaces, 2014, 1(8).

[5] Y. Konishi, T. Nomura, D. Satoh. Solvothermal preparation of cuprous oxide fine particles by hydrolysis of copper (II) carboxylate in two-phase liquid-liquid system[J]. Industrial & engineering chemistry research, 2004, 43(9): 2088-2092.

[6] M. Yin, C.K. Wu, Y. Lou, et al. Copper oxide nanocrystals[J]. Journal of the American Chemical Society, 2005, 127(26): 9506-9511.

[7] N. Prakash, S. Latha, P.N. Sudha, N.G. Renganathan: Environ. Sci. Pollut. Res. Vol. 20 (2013), p. 925-938

[8] M.V. Subbaiah, Y. Vijaya, A.S. Reddy, G. Yuvaraja, A. Krishnaiah, Desalination Vol. 276 (2011), p. 310-316