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Synthesis and characterization of silver-incorporated calcium phosphate antibacterial nanocomposites for mask filtration material

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ABSTRACT

Mask filtration materials play an important role in biological protective masks. Masks with active antibacterial functions can cutting off the transmission of pathogenic bacteria to protect population health. Porous calcium phosphate (CaP) has good biocompatibility and with high specific surface area, porous CaP shows excellent air filtration performance. However, CaP usually exhibits poor antibacterial activities. In this paper, the porous silver-incorporated calcium phosphates were studied as a mask filtration material. CaP powders composed of various Ag concentrations (1.0, 2.0, 3.0, 4.0 and 5.0 wt%) were prepared, characterized and evaluated for antibacterial functions. Environmental aerosol particles filtration test results indicated that the Ag—CaP mask filtration materials can effectively filter aerosol particles in the environment. The filtration efficiency of Ag—CaP mask filtration materials for PM10, PM2.5 and PM1.0 were 96%, 91% and 85%, respectively. The antibacterial experiments revealed that the Ag—CaP mask filtration materials showed super antibacterial effect. The filtration efficiency of staphylococcus aureus aerosol was above 96%. Synthesis of nanosized Ag—CaP as an antibacterial agent is of potential importance in active anti-bacterial bioprotective masks.

1. Introduction

In recent years, the infection rate of major infectious diseases such as AIDS, tuberculosis and viral hepatitis is still high in worldwide, especially the outbreak of influenza (H1N1) has brought greater threats and impacts to people's health and safety [1–3]. Respiratory infectious diseases can be transmitted through air and droplets, which can easily cause concentrated infection of large population. Cutting off the transmission of pathogenic bacteria is an effective means to protect population health [4–6]. Public Health experts strongly recommended that people wear masks in case of a flu outbreak. In the case of an influenza outbreak, many countries are stockpiling bioprotective masks as a non-drug intervention to control the spread of the virus [7–9]. The growing demand for biological protective masks, which have been developed as a result of the worldwide outbreak of swine flu, as a results, novel mask filtration material are also boosting demand [10–12].

Calcium phosphates (CaP) are extensively used as biomaterials because it is biocompatible and shown no toxic for human [13–16]. Therefore, the synthetic forms of these calcium phosphates are widely used in bone tissue engineering and other biological products [17–21]. However, CaP usually exhibits poor antibacterial activities. Long-term application of CaP products can be affected by the presence of various bacterial infections resulting in serious problems. Porous calcium phosphate has good biocompatibility and air filtration performance [22–25]. When this material is used in masks as the filtration material, its active sterilization function is of vital importance. As antibacterial filtering masks material, the mask material needs both good filtration function and antibacterial function at the same time. Therefore, antibacterial filtering masks material needs design porous structure with hierarchical pores. On the one hand, it can better guarantee respiration and circulation; on the other hand, it can create a better anti-bacterial microenvironment.

Biological protective masks are used to protect people under biological pollution environments [4,6,26]. Masks can be divided into passive biological protective mouth cover and active anti-bacterial bioprotective mask according to their functions. Passive biological

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protective mouth cover is a kind of protective mask widely used at present. It is mainly filtered by physical filtration airborne particulate matter or harmful pathogens [27]. The material usually has high filtration efficiency [28]. Active anti-bacterial bioprotective mask indicates that a mask has an ability of active antibacterial functions. Some antibacterial ingredients were added into mask filtration materials [29]. In order to realize the active antibacterial functions, the use of antimicrobial agents, including metal ions (Ag+, Cu2+ and Zn2+) in mask filtration materials is of great interesting [30–32]. Among various ions, silver ions have long been recognized to have strong inhibitory and bactericidal effects as well as abroad range of antimicrobial activities [33–38].

In order to develop protective masks with better protective performance, better response to the outbreak of respiratory infectious diseases such as influenza, and protect the health and safety of residents, this paper studied the silver-incorporated calcium phosphates mask filtration materials. Synthesis of nanosized particles of silver-incorporated calcium phosphates (Ag—CaP) as an antibacterial agent is of potential importance in active anti-bacterial bioprotective mask filtration materials. In this study, CaP powders composed of various Ag concentrations (1.0, 2.0, 3.0, 4.0 and 5.0 wt%) were prepared, characterized and examined for antibacterial activity. The current research proposes a favorable use of such antibacterial nanocomposites for mask filtration material.

2. Materials and methods

2.1. Synthesis and characterization of Ag—CaP antibacterial nanocomposites

Silver-incorporated calcium phosphates (Ag—CaP) powder with particle size of 50–100 nm was synthesized by a wet chemical method in our laboratory through the chemical reaction between $Ca(NO_3)_2$, $AgNO_3$ and $(NH_4)_2HPO_4$ under alkaline conditions. Calcium phosphates was consisted as biphase calcium phosphate (HA/β-TCP = 30:70), and the silver contents varied from 0.5 to 5.0 wt%. Wet-chemical precipitation method for synthesis of Ag—CaP was expressed as following equations:

$$(10\text{-}x)\ Ca^{2+} + xAg^{+} + 6PO_4^{3-} + 2OH^{-} \rightarrow Ca_{10\text{-}x}Ag_x(PO_4)_6(OH)_2 \quad (1)$$

$$5Ca(NO_3)_2 + 3(NH_4)_2HPO_4 + 4NH_4OH \rightarrow Ca_5(OH)(PO_4)_3 + 10(NH_4)NO_3 + 3H_2O \quad (2)$$

$Ca(NO_3)_2$ and $(NH_4)_2HPO_4$ were used as the calcium and phosphate sources, and the $AgNO_3$ was used as the silver source, respectively. The amount of the reactants was calculated based on the calcium + silver: phosphorus molar ratio according to the design of Ag wt% (Table 1). One kilogram of $Ca(NO_3)_2$ was first dissolved in 6000 ml deionized water, and it is added to 5–25 g $AgNO_3$ in this solution under stirring conditions. 0.5 kilogram of $(NH_4)_2HPO_4$ was dissolved in 2000 ml deionized water. Before the reaction, 30 ml and 200 ml ammonium hydroxide were added into the calcium and phosphate solutions. the phosphate solution was pumped to the calcium solution in a reaction tank through a micro pump with a speed of 0.9 rpm. The reaction was continued for 20 min under vigorous stirring conditions. pH was kept at 8 by using ammonium hydroxide. The resultant solution was aged to two days at room temperature, and then filtered. The product was washed with methanol to remove the residual impurities. The final product was dried at 90 °C in oven for 12 h and then annealed at 300 °C for 24 h inside a muffle furnace. The product was white to greyish powder (as shown in Fig. 1). The porous structures of the Ag—CaP materials were fabricated by H_2O_2 foaming method. Porous Ag—CaP were sintered at 1200 °C to obtain mask filtration materials.

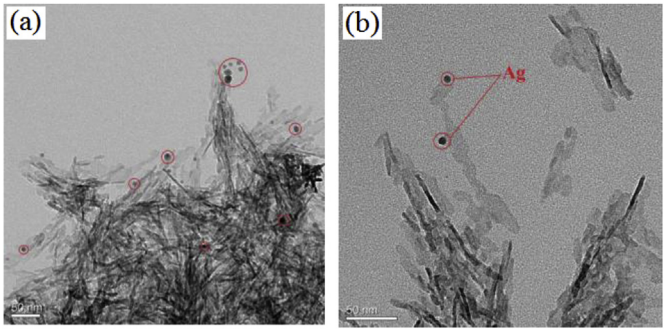

Fig. 1. Morphological characteristics of synthetic Ag—CaP nanoparticles (TEM).

The size and morphology of Ag—CaP powders were analyzed by transmission electron microscope (TEM; HITACHI H600-IV, Japan). For TEM analysis, the powder sample was ultrasonically dispersed in ethanol to form a dilute suspension, and then a few drops were deposited on the carbon-coated copper grids. The X-ray diffraction pattern was recorded for the as synthesized Ag—CaP powder particles by using a Philips X'Pert 1 X-ray diffractometer (Philips X'Pert, XRD, Netherlands) with CuKa radiation at a current of 20 mA and voltage 30 kV. Scans were performed with 2θ values from 20° to 60° at a rate of 0.05°/sec. The obtained peaks were compared with standard references in the JCPDS file available in the software for HAp (09-0432) and β-TCP (09-0169).

2.2. Structural and morphological characterization of Ag—CaP mask filtration materials

Scanning electron microscope (SEM, JSE-5900LV, Japan) was used for scaffolds microstructure characterization. The scaffolds were sputter coated with gold. The porosity of the scaffolds was measured using the mercury intrusion method [39], and three replicates were used. Phase composition of the scaffold were analyzed using XRD (Philips X'Pert 1 X-ray diffractometer, Netherlands) with CuKa radiation at a current of 20 mA and voltage 30 kV. Scans were performed with 2θ values from 20° to 60° at a rate of 0.05°/sec. The obtained peaks were compared with standard references in the JCPDS file available in the software for HA (09-0432) and β-TCP (09-0169). The linear shrinkage was calculated by measuring the length, width and height of scaffolds before and after sintering treatment using a sliding caliper.

Table 1
The detailed information of the reagents and products in the chemical reaction process of Ag—CaP.

Sample ID	Dissolved in 6000 ml deionized water				Theoretical value: (Ca + Ag)/P	Calculation Ag Wt%	Test Ag Wt%
	$Ca(NO_3)_2$	$\cdot 4H_2O$(g)	$AgNO_3$	(g)			
#0	2000		0		1.610	0%	0%
#1	1995		5		1.610	1%	0.86%
#2	1990		10		1.609	2%	1.75%
#3	1985		15		1.609	3%	2.52%
#4	1980		20		1.609	4%	3.57%
#5	1975		25		1.609	5%	4.48%