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Carbon sphere influence on textural properties and bioactivity of mesoporous bioactive glass/hydroxyapatite nanocomposite

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Abstract

Mesoporous bioactive glass/hydroxyapatite nanocomposite (MBG-HA) synthesis was conducted through evaporation-induced self-assembly (EISA) method followed by in situ carbonization, with non-ionic block co-polymer as mesoporous template and glucose-derived carbon sphere as co-template. The mixture of different carbon sphere contents into a glass network in the $CaO–SiO_2–P_2O_5$ system tailored the structural, morphological, and textural properties of MBG–HAs. Based on the preliminary results, the carbon sphere content and textural and structural parameters of as synthesized MBG–HAs showed a negative trend. The MBG–HA 0.5 with additional low carbon sphere content, showed a high surface area and large pore volume. The inclusion of HA nanoparticles inside the channels strongly influenced the high carbon sphere content of the MBG–HA8 mesoporous structure. For in vitro bioactivity tests, MBG–HAs with higher textural parameters possessed a faster apatite phase formation kinetics following the sequence MBG–HA0.5 > MBG–HA2 > MBG–HA5 > MBG–HA8.

Keywords: A. Sol–gel processes; B. Nanocomposite; D. Apatite; D. Glass

1. Introduction

Since the discovery of 45S5 bioglass by Hench in 1971, various bioactive glasses (BGs) and glass ceramics (BGCs) have been investigated as bone-repair and bone-substitute biomaterials. These bioactive materials can generate an amorphous calcium phosphate layer (ACP) or hydroxyapatite (HA)-type material when exposed to physiological solutions, which is their ability to strongly integrate with live bone [1–5]. Both the chemical composition and textural features of these bioactive materials are important in HA growth. As a result, significant progress has been achieved in the development of improved BGs and the assessment of their bioactive properties [6–11]. In 1991, Li et al. [9] exploited a sol–gel technique to prepare a new family of BGs with improved bioactivity compared with the conventional melt-quenching procedures. The sol–gel method enabled the preparation of glasses at low synthesis temperature and expanded the SiO_2 content in the bioactive composition range by up to 90 mol% [10,11]. Moreover, the method simplified the glass composition and particularly avoided the addition of sodium oxide.

Mesoporous materials have gained attention as potential biomaterials in bone tissue regeneration and drug delivery systems. Currently, studies on mesoporous materials for bone tissue regeneration are conducted by several groups [12–21]. Vallet-Regí [12–14] systematically investigated the in vitro bioactivity of different mesoporous material types, such as MCM-48, SBA-15, MCM-41, and ordered mesoporous bioactive glasses (MBGs), allowing their use in biomedical engineering for tissue regeneration. Zhao et al. prepared a multicomponent MBG ($CaO–SiO_2–P_2O_5$) through the evaporation-induced self-assembly (EISA) method [15–17]. Xia and Chang prepared MBG (M58s)

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using a two-step acid-catalyzed self-assembly (TSACSA) method followed by hydrothermal treatment [19–21]. This strategy highlighted the incorporation of structure-directing agents in obtaining successful structures with tunable pore size and internal pore architecture. This method resulted in new-generation MBGs in the ternary $CaO–SiO_2–P_2O_5$ system exhibiting superior bioactivity in vitro, which is attributed to their outstanding surface area and porosity values. These characteristics certainly made BGs highly relevant for drug carriers and bone tissue regeneration.

In mesoscopic scale, MBGs exhibit well-ordered pore arrangement due to the incorporation of a mesoporous template. However, for MBG materials, they exist in an amorphous state due to the amorphous nature of bioglass walls. Processes were explored to prepare mesoporous bioceramics with improved crystalline property similar to the microcrystalline technology-prepared BGCs [22–25]. This progress in MBG modification has fueled research interest to obtain nanocrystalline bioceramics while maintaining the mesostructure. The rapid development of nanotechnology allows advancements in designing a novel silica mesoporous/apatite nanocomposite, where HA nanocrystals are dispersed in noncrystalline silica matrices [26–29]. Furthermore, this nano-sized HA, similar to bone mineral component, has been studied extensively for bone tissue regeneration because of its bioactivity, exceptional biocompatibility, and osteoconductivity. Therefore, an MBG–HA nanocomposite design where the amorphous MBG and nanocrystalline HA combination is dispersed will broaden the functionality beyond the pure material [30,31]. A possible method in preparing bioglass-apatite composite was explored using carbon sphere as the co-template. The role of hydrophilic carbon sphere favored the localized enrichment of calcium ions and facilitated HA nanocrystal formation [30]. However, few studies report the synthesis of this material and consider the influence of carbon sphere content on the mesostructure physiochemical properties and its subsequent in vitro bioactivity. The relation of textural properties (i.e., related to pore volume and size) and apatite nucleation rate are considerably interesting in determining the final properties required for biomedical applications.

The current study demonstrated the MBG–HA nanocomposites in $85SiO_2–10CaO–5P_2O_5$ ternary system through the EISA method followed by in situ carbonization, with non-ionic triblock co-polymer ($EO_{20}PO_{70}EO_{20}$, P123) as template and glucose-derived carbon sphere as co-template. Different from previous reports, the dried gel was initially carbonized for 3 h at 350 °C under Ar atmosphere to stabilize the mesostructure network, and then calcined for 8 h at 700 °C under ambient air to remove the organic template. The effects of carbon sphere content on HA nanoparticle formation in the nanocomposite was studied. Subsequent variation in textural properties, with the addition of carbon sphere content, was observed to expound their influence on the bioactive behavior.

2. Experimental section

2.1. Preparation of carbon sphere

The carbon spheres were prepared by the hydrothermal process described in the literature [32]. Briefly, 8 g glucose were dissolved in water (40 ml) to form a clear solution, which was transferred into a 40 ml teflon-sealed autoclave at 160 °C for 20 h. The black products were collected by centrifugation at 8000 rpm for 10 min, then washed with distilled water and ethanol three times, respectively, and dried at 80 °C for 12 h.

2.2. Synthesis of MBG–HA nanocomposites

According to the method reported by López-Noriega et al. [14], the MBG–HA nanocomposites in the $85SiO_2–10CaO–5P_2O_5$ system were carried out with 4 g of P123, 1 mL of 0.5 N HCl, and 60 g of ethanol. The mixture was stirring at 40 °C in water bath until the solution became clear. Accordingly, 7.4 g of tetraethyl orthosilicate (TEOS), 0.68 g of trithyl phosphate (TEP), 0.98 g of $Ca(NO_3)\cdot 4\,H_2O$ (CaNT), carbon spheres (C) with CaNT at a definite ratio were added into solution. After stirring at 40 °C after 72 h, the resulting sols were cast in Petri dishes (9 cm diameter) to undergo the EISA method at 40 °C. The gelation process occurred after 3 days, and the gels were aged for 7 days in the Petri dishes at 40 °C. Finally, the dried gels were first carbonized at 350 °C under Ar atmosphere for 3 h, and afterwards calcined at 700 °C in air for 8 h. The heating rate for the calcination was controlled at 1 °C/min. According to the weight percent of carbon spheres to the total amount of CaNT, the obtained MBG–HAs with different amount of carbon spheres were denoted as MBG–HA0.5, MBG–HA2, MBG–HA5 and MBG–HA8, respectively (Table 1).

Table 1
Chemical compositions and structural parameters of MBG–HAs with different carbon sphere contents.

Sample	CaNT/(g)	C/(g)	C/CaNT weight ratio	BET surface area/m^2g^{-1}	Pore volume/$cm^3\,g^{-1}$	Pore size/nm
MBG–HA0.5	0.98	0.49	0.5:1	426.1	0.583	5.4
MBG–HA2	0.98	1.96	2:1	376.0	0.539	5.2
MBG–HA5	0.98	4.90	5:1	352.8	0.462	4.9
MBG–HA8	0.98	7.84	8:1	315.2	0.403	4.8