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Facile synthesis and in vitro bioactivity of radial mesoporous bioactive glasses

Yudong Wang, Tianshun Liao, Miao Shi, Cong Liu, Xiaofeng Chen *

School of Materials Science and Engineering, South China University of Technology, Guangzhou 510641, PR China
National Engineering Research Center for Tissue Restoration and Reconstruction, Guangzhou 510006, PR China

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ABSTRACT

This paper reports a facile method for fabricating radial mesoporous bioactive glasses (RMBGs) using Hexadecyl trimethyl ammonium bromide (CTAB) micelle as the reaction center. The radial structure was formed with the extension of precursor dissolved in the hydrophobic solvent (cyclohexane) which gathered in the internal part of the CTAB micelle. The morphology, structure and in vitro bioactivity of RMBGs were investigated by various methods. The results indicate that the CTAB micelle could restrict the precursor-dissolved cyclohexane and was in favor of preparing the RMBGs with radial mesoporous structure, high specific surface area and good apatite-forming ability. The obtained RMBGs with the novel structure and properties may have potential application in drug delivery and hard tissue regeneration.

1. Introduction

Bioactive glasses (BGs) have shown a great prospect in bone and dental tissue regeneration because of their good bioactive, resorbable, osteogenesis and dentinogenesis properties [1–3]. Previous studies have suggested that the bone-bonding ability of BGs was the result of the formation of a hydroxycarbonate apatite layer on the surface when contacting the simulated body fluid (SBF) [4–6].

These years, lots of studies have been focused on the sol-gel bioactive glasses combined with the soft template technology and fabricated many kinds of bioactive glasses with different morphology and structure [7–10]. Previous studies have shown that regular spherical BGs possessed improved physicochemical and biological properties compared to the irregular BGs, exhibiting their potential applications in bone tissue regeneration and drug release systems [6,11]. However, for the aspect of drug delivery, the common bioactive glasses particles were still facing the problem of low drug-loaded capacity [10,12–14]; novel BGs particles with higher specific surface area and newly mesoporous structure were needed to improve the drug-loaded capacity.

Here, we utilized the CTAB micelle as the reaction center and the extension of precursor located in the interior of the micelle contributed to the radial mesoporous structure of the novel bioactive glasses particles. The radial mesoporous structure which could be adjusted by changing the Ca concentration contributed to the high specific surface area and good apatite-forming activity; most of all, possessed a great possibility for higher drug-loaded capacity [15–17].

2. Experimental

Materials: Tetraethyl orthosilicate (TEOS), triethylphosphate (TEP), calcium nitrate tetrahydrate (CN), ethanol absolute (EtOH) and ammonia solution (25 wt% NH_3 in water) were purchased from Guangzhou Chemical Reagent Factory. Hexadecyl trimethyl ammonium bromide (CTAB) and cyclohexane were supplied by Aladdin (Shanghai, PR China). All chemical reagents above were analytical grade. Deionized water was obtained from a water purification system (Milipore S.A.S, France).

Preparation of RMBGs: RMBGs were prepared utilizing the CTAB micelle as the reaction center. 0.6 g CTAB were added to a mixture of 62.5 ml deionized water and 37.5 ml ethanol at 35 °C to form the CTAB micelle. 1.35 ml TEOS dissolved in 18 ml cyclohexane was dropped into the solution above. Thereafter, 0.5 ml ammonia solution was added into the solution to initiate the reaction to promote TEOS hydrolysis. Then the mixture was stirring for 20 min and 0.103 ml TEP and a certain amount of CN were sequentially added to the mixture in every 30 min. After 3 h, the solution gradually turned opaque due to the formation of a white precipitate and

* Corresponding author at: School of Materials Science and Engineering, South China University of Technology, Guangzhou 510641, PR China.
E-mail address: chenxf@scut.edu.cn (X. Chen).

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the white precipitate were collected by filtration, rinsed with ethanol and deionized water, and dried at room temperature for 24 h. Finally the RMBGs were obtained after removing organics and nitrates by calcination at 650 °C for 3 h. Besides, CN amount of 0.286 g, 0.531 g and 0.858 g were used for comparison and the corresponding RMBGs were denoted RMBGs-1, RMBGs-2 and RMBGs-3 respectively.

Characterization: The samples' morphologies, microstructure and particle size distribution were determined using transmission electron microscopy (TEM, JEM-2100F, JEOL, Japan) and Zetasizer nano-ZS (Marvin, England). Specific surface area was measured using the multipoint Brumauer–Emmett–Teller(BET) N^2 absorption technique at 77.3 K. The pore size and pore size distributions were calculated by the Barrett–Joyner–Halenda (BJH) method using desorption isotherm branch.

The in vitro bioactivity of the obtained RMBGs was tested by immersing in SBF (Na^+ 142.0, K^+ 5.0, Mg^{2+} 1.5, Ca^{2+} 2.5, Cl^- 147.8, HCO^{3-} 4.2, HPO_4^{2-} 1.0 and SO_4^{2-} 0.5 mmol L^{-1}) at a concentration of 1 mg/ml at 37 °C to monitor the formation of HA on the surface of the sample [18]. Once removed from the incubation, the solids were taken out, washed with deionized water, dried in air and characterized using scanning electron microscopy (SEM, MERLIN Compact, Carl Zeiss, Germany), Fourier transform infrared spectroscopy (FT-IR, Nexus, Nicolet Co., USA) and powder X-ray diffraction (XRD, X'pert PRO, Panalytical, Netherlands) with Cu K_a (1.548 Å).

3. Results and discussion

Fig. 1 shows representative TEM images and the particles size distributions of the samples prepared under different CN amount of 0.286 g, 0.531 g and 0.858 g. TEM images indicated that all the samples exhibited regularly spherical morphology and favorable dispersibility (Fig. 1A–C). TEM images in high magnification of RMBGs-1, RMBGs-2 and RMBGs-3 showed the radial structure of samples and the microstructure and particles size could be changed by adjusting the CN amount (Fig. 1D–F). RMBGs-1 showed the radial structure clearly and this microstructure turned indistinct with Ca concentration increased. Besides, the average particles diameters of RMBGs were 339 nm (RMBGs-1), 354 nm (RMBGs-2), 836 nm (RMBGs-3) and all samples exhibited relatively narrow particle size distribution as shown in Fig. 1G–I.

The specific surface area and pore structure of the RMBGs samples were obtained by N_2 absorption-desorption isotherm. As shown in Fig. 2A, all samples exhibited type IV isotherm patterns with H3-type hysteresis loop associated with slot-shape mesopore according to IUPAC classification [19]. The specific surface areas of RMBGs-1, RMBGs-2 and RMBGs-3 are 986.353 $m^2 g^{-1}$, 847.289 $m^2 g^{-1}$ and 750.141 $m^2 g^{-1}$ respectively, which is much higher than the reported BG microsphere in the literature [8,11]. As shown in Fig. 2B, the pore structure of samples exhibited a narrow mesoporous size distribution. The average pore diameters of RMBGs-1, RMBGs-2 and RMBGs-3 are 3.927 nm, 5.101 nm and 5.132 nm, respectively.

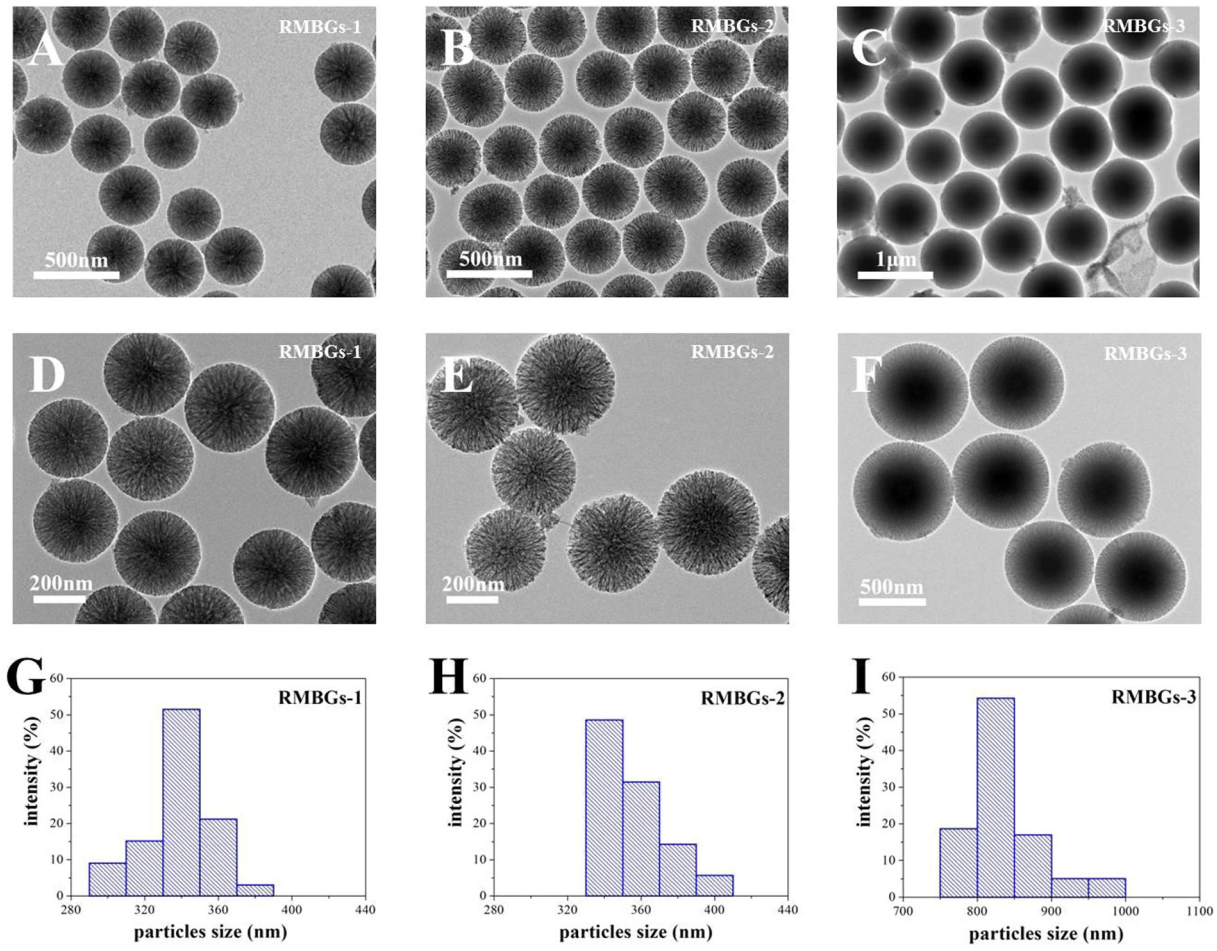

Fig. 1. TEM images and particle size distribution of RMBGs.