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Persistent luminescent particles containing bioactive glasses: Prospect toward tracking in-vivo implant mineralization using biophotonic ceramics

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ABSTRACT

In this paper, we demonstrate that persistent luminescent bodies can be obtained by carefully choosing the sintering temperatures and duration. A borosilicate and a phosphate glasses were sintered into bodies with persistent luminescent (PeL) $SrAl_2O_4:Eu^{2+},Dy^{3+}$ microparticles which have a green emission up to tens of hours after ceasing irradiation. When sintered at high temperature for a short time or at lower temperature for a longer time, a decrease in the PeL from the bodies was observed and was related to the glasses crystallization. A decrease in the PeL from the bodies was also observed after immersion in simulated body fluid and was related to the mineralization of the sintered bodies. Therefore, we clearly show that by tracking the changes in the PeL overtime, these PeL bodies have a real potential application as biophotonic sensors to track dissolution and mineralization of the implant in the body.

1. Introduction

In 1969, L.L. Hench discovered 45S5 (Bioglass®), a new biomaterial that degrades within the body leading to the precipitation of a hydroxycarbonated apatite layer at its surface [1]. Not only the bioactive glasses support the cell attachment but they also stimulate more bone regeneration than any other ceramics [2]. From all developed bioactive glasses, the most commonly used glasses are 45S5 (Bioglass®) and S53P4 (BonAlive®) although they possess two major drawbacks.

Their first drawback is their high tendency toward crystallization [3–5]. Both 45S5 (Bioglass®) and S53P3 (BonAlive®) crystallize from the surface at high rate [5]. The crystallization kinetic inhibits the drawing of these glasses into fibers or the sintering of particles into porous scaffolds without simultaneous crystallization [5–7]. While the crystallization was found to suppress the bioactivity of the phosphate glasses [8], it did not suppress it in silicate bioactive glass [7,9]. As suggested in [10], the composition of the crystals as well as the crystal density play an important role in the resulting bioactivity of the glass-ceramic as it is crucial to determine the ability of the crystal to dissolve in aqueous medium and to quantify the remaining glassy phase. Despite the bioactivity being maintained, the presence of crystals may also lead to difficulties in predicting the final bioactivity of the obtained glass-ceramic. Indeed, the ion released from the glass-ceramic will differ from the original glass composition and will be dependent on the manufacturing reproducibility. Therefore new glasses have been developed with tailored thermal properties enabling sintering without crystallization. The 13–93, borosilicate and borophosphate glasses are examples of bioactive glasses with optimum thermal properties for hot forming [11,12].

The second drawback of Bioglass® and BonAlive® lies in the difficulties in imaging them in-vivo. Bioactive glasses are typically radio-transparent and therefore cannot be detected easily and unambiguously radiographically [13]. In bone cements and bone implants, radio-opacity is crucial in order to allow an easy follow-up of the dissolution and resorption after implantation. In bone cements, taken as an example, radio-opacity is achieved by adding radio-opaque agents such as zirconia (ZrO_2), barium sulfate ($BaSO_4$) or iodine-based molecules [14]. However, the risk associated to radiography remains, i.e. exposure to radiation, and therefore alternative solutions should be found to reduce the use of radiography during follow-ups.

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As mentioned in [15], the use of optical imaging, in which photons are the information carriers, is becoming a rapidly growing field for applications in pharmacology, molecular and cellular biology as well as diagnostics. In the recent years, the use of persistent luminescent particles has been investigated as optical probes to image vascularization, tumors and grafted cells [16]. Persistent luminescence (PeL) or afterglow is a form of emission which continues after the removal of the irradiation source [17]. This source can be for example visible light, UV radiation or X-rays. Maldiney et al. demonstrated highly sensitive in-vivo detection by using near infrared nanoparticles [16].

The first persistent luminescent crystals in glass were formed in glassy materials by the "frozen sorbet" method [18]. Later, Massera et al. demonstrated the feasibility to incorporate PeL microparticles (MPs) in phosphate-based bioactive glasses during the glass melting [19–21]. While the PeL of the MPs could be maintained, it appeared clear that the melting process should be fully controlled for the MPs to survive during glass processing. It should be pointed out that this melting process could not be used to prepare PeL silicate glasses due to the high glass melting temperature at which the MPs are not thermally stable.

Here, we report on the processing of PeL borosilicate and phosphate bioactive bodies obtained by sintering glass particles with PEL MPs such as $SrAl_2O_4:Eu^{2+},Dy^{3+}$. The impact of sintering temperature on the PeL of the MPs is discussed and correlated to the particles degradation as evidenced by SEM/EDX. The sintered bodies were immersed in simulated body fluid (SBF). The dissolution of the glass and of the MPs was assessed by ICP-OES. The change in the MPs morphology and composition and in the PeL was investigated as a function of the immersion time in SBF.

2. Experimental

The silicate glass with the composition $26.93SiO_2$-$26.93B_2O_3$-$22.66Na_2O$-$1.72P_2O_5$-21.77CaO (in mol%) (referred as B50) was melted using SiO_2 (99.4% pure quartz), and analytical grades of Na_2CO_3, H_3BO_3, $CaCO_3$, and $CaHPO_4.2H_2O$. The glass was melted in a Pt crucible at 1250 °C for 1 h.

The phosphate glass with composition $50P_2O_5$-40CaO-$10Na_2O$ (in mol%) (referred as PCa) was prepared using standard melting method in platinum crucible. $NaPO_3$, $CaCO_3$ and $(NH_4)_2HPO_4$ were used as raw materials. $Ca(PO_3)_2$ precursor was first independently prepared using slow heating rate up to 900 °C. The precursors were mixed in a Pt crucible and melted at 1000 °C for 30 min.

After quenching, the B50 and PCa glasses were then annealed at 40 °C below their respective T_g (510 °C for B50 glass and 454 °C for PCa glass) to remove any residual stress.

The glasses were then crushed and sieved to particles with a size ranging from 125 to 250 µm. This particle size was chosen in order to minimize the risk of crystallization: decreasing the particles size increases the surface area to volume ratio, subsequently favoring crystallization [22]. The glass particles were then mixed with 3 wt% of $SrAl_2O_4:Eu^{2+}$, Dy^{3+} microparticles (MPs) and then sintered without any pressure from 30 min to 1 h at temperature ranging from 600 to 675 °C, for the B50 glass and from 515 to 595 °C for the PCa glass. The bodies were processed by loosely placing glass particles into a stainless steel mold, and shaking to obtain particles rearrangement.

The obtained bodies were analyzed using XRD. The XRD analysis was carried out on the powder samples with the Panalytical EMPYREAN multipurpose X-Ray Diffractometer using iron filtered cobalt K-Alpha radiation. The scaffolds were crushed into powder and the powder was gently pressed into the sample holder. The spectra were obtained using the Bragg-Brentano geometry and by rotating the sample holder around the Phi-axis at a constant speed of 16 revolutions per minute during the scan.

The microparticles composition and morphology were studied using a (SEM/EDX) Zeiss ULTRAplus scanning electron microscope (SEM) and INCA Energy 350 energy dispersive X-ray analyser (EDX).

The photoluminescence (PL) and persistent luminescence (PeL) properties of the $SrAl_2O_4:Eu^{2+},Dy^{3+}$ containing bodies were measured at room temperature, on powder, using a Varian Cary Eclipse Fluorescence Spectrophotometer equipped with a Hamamatsu R928 photomultiplier (PMT). The photoluminescence (PL) (λ_{exc}: 266 nm, Nd:YAG pulse laser, 8 ns, TII Lotis) was measured at room temperature using a CCD camera (Avantes, AvaSpec-2048 × 14). For PeL measurements, the samples were irradiated for 5 min at room temperature with a compact UV lamp (UVGL-25, 4 W, λexc: 254 nm). The PeL spectrum was then measured 1 min after ceasing the irradiation using a data collection time of 4 s for the whole spectrum.

The in-vitro testing was performed in simulated body fluid (SBF), following the SBF preparation protocol proposed by Kokubo [23]. The pH was adjusted to 7.4 at 37 °C. The PCa and B50 bodies were immersed in SBF solution for 1, 3, 4, 5 and 7 days at 37 °C in incubating shaker (100 RPM). The diameter and weight of each scaffold were measured to ensure that the volume to surface ratio remains constant, which was achieved by using 10 ml of SBF per every 100 mg of bodies in all the experiments. After every immersion, the pH was measured and 1 ml of the immersion solution was diluted in 9 ml of 1 M HNO_3 solution. At each time point, the pH of the solution was recorded and the diluted solution was analyzed using ICP-OES (ICP-OES 5110, Agilent technology). The element studied and the wavelength analyzed in ICP were P (253.561 nm), Sr (216.596 nm), Si (250.690 nm), Ca (422.673 nm), B (249.772 nm) and Al (396.153 nm).

3. Results

Fig. 1a and c presents the photographs of the sintered MPs-containing B50 and PCa glasses, respectively, in daylight. The B50 glasses were sintered at 600 °C for 30 min (1), 600 °C for 1 h (2), 600 °C for 1 h (3) and 675 °C for 1 h (4) while the PCa glasses were sintered at 515 °C for 30 min (1), 535 °C for 30 min (2), 535 °C for 1 h (3), 555 °C for 30 min (4) and 595 °C for 30 min (5). The sintering temperatures were chosen based on previous thermal analysis performed on the borosilicate [12] and phosphate [24] glasses. All MPs-containing borosilicate sintered glasses were found to be mechanically stable and to maintain PeL after stopping irradiation (Fig. 1b). The height of the sintered borosilicate glass was found to decrease with increasing sintering duration and temperature pertaining to the increased viscous flow. However, as seen in Fig. 1d, an increase in the sintering temperature from 515 to 535 °C clearly leads to a decrease in intensity of the PeL of the sintered PCa glass. Note that the PCa sintered glass body heat treated at 515 °C for 30 min could not be handled without crumbling.

Fig. 2 presents the conventional luminescence spectra of the sintered glasses. In all spectra one band at ~400 nm and one at ~525 nm are visible which can be associated to the $4f^65d^1 \rightarrow 4f^7$ emission from Eu^{2+} located in two different cation sites in the $SrAl_2O_4$ structure according to [25]. A decrease in the intensity of the emission bands can be observed with increasing sintering duration and temperature (Fig. 2a and b).

Fig. 3 presents the PeL spectra of the sintered glasses. As seen in [17], the persistent luminescence spectra of the glasses exhibit two broad bands with a maximum at 410 and 490 nm. As for conventional luminescence, these bands are attributed to the $4f^65d^1 \rightarrow 4f^7$ transitions

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