ELECTRONIC SUPPLEMENTARY INFORMATION

Bioactive glass-gelatin hybrids : building scaffolds with enhanced calcium incorporation and controlled porosity for bone regeneration

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Figure S1. SEM image of a macroporous class-I hybrid scaffold (30wt.% SiO₂-CaO/70 wt.%

gelatin) with pore size larger than 700 µm and large interconnections.



Figure S2. Experimental $\{^{1}H\}^{-29}$ Si CP MAS spectra (black lines) of the class-I hybrids scaffold with 50 wt.% SiO₂–CaO / 50 wt.% gelatin and their fits (red lines). The individual Qⁿ resonances are shown below the experimental spectra. All spectra were recorded at a magnetic field of 9.4 T with a spinning frequency of 6 kHz and a recycle delay of 1s. The ¹H and ²⁹Si nutation frequencies were of 62 and 48 kHz during the CP time, respectively. ¹H SPINAL decoupling¹ was applied during acquisition. The The CP durations are (a) 0.25, (b) 0.5, (c) 1.0, (d) 2.5, (e) 5.0, (f) 7.5, (g) 10.0 and (h) 12.5 ms.



Figure S3. Experimental $\{^{1}H\}$ - ^{29}Si CP MAS spectra (black lines) of the class-II hybrids scaffold with 50 wt.% SiO₂-CaO / 50 wt.% gelatin and their fits (red lines). The individual Qⁿ resonances are shown below the experimental spectra. Experimental conditions were the same as those in figure S2.



Figure S4. Variation of the individual Qⁿ and T^{n 29}Si resonance as a function of the CP duration for (a) class-I and (b) class-II hybrid scaffolds with 50 wt.% SiO₂–CaO / 50 wt.% gelatin. The curves correspond to fits of the data points using the expression $I(t) = I_0(1 - T_{SiH}/T_{1\rho}^H)^{-1} [exp[m](-t/T_{1\rho}^H) - exp[m](-t/T_{SiH})], \text{ where } T_{SiH} \text{ is the CP time constant and } T_{1\rho}^H \text{ is the } ^1\text{H spin-lock longitudinal relaxation constant. }^2$

Table S1. Isotropic chemical shifts, linewidths and relative intensities of the Qⁿ and Tⁿ resonances in class-I and class-II bioactive glass/gelatin hybrids (50 wt.% BG / 50 wt.% gelatin). The isotropic chemical shifts (δ_{ISO}) and full widths at half maximum (fwhm) were determined from fits of the ²⁹Si CP MAS spectra recorded at different CP times. The CP time constant (T_{SiH}) and the ¹H spin-lock longitudinal relaxation constant ($T_{1\rho}^{H}$) were determined from the variation the intensity of the individual resonances as a function of the CP duration. The relative intensities of the Qⁿ and Tⁿ resonances were obtained from fits of the quantitative MAS spectra.

	Unit	$\delta_{\rm ISO}$	Fwhm	T _{SiH}	$T_{1\rho}^{H}$	I (%)
_		(ppm)	(ppm)	(ms)	(ms)	
Class-I	Q ⁴	-109.3(3)	8.6(5)	25(5)	1.9(1)	33(4)
	Q^{3}_{H}	-100.1(3)	7.6(4)	16(1)	0.7(1)	31(4)
	Q ³ Ca	-94.7(4)	8.2(5)	15(3)	1.2(2)	19(5)
	Q^2_{2H}	89.3(4)	8.0(4)	10(1)	0.6(1)	12(5)
	Q ² _{H/Ca}	-83.7(5)	7.0(5)	6(1)	1.0(2)	5(4)
Class-II	Q ⁴	-109.4(3)	8.0(5)	18(2)	2.0(1)	26(3)
	Q^{3}_{H}	-100.2(3)	7.6(4)	12(1)	0.8(1)	27(3)
	Q ³ Ca	-94.6(4)	8.1(5)	14(2)	1.3(1)	16(5)
	Q^2_{2H}	89.3(4)	7.9(4)	9(1)	0.7(1)	11(5)
	Q ² _{H/Ca}	-83.7(5)	7.0(5)	6(1)	1.0(1)	4(3)
	T ³	-66.0(2)	7.8(2)	7(1)	1.1(1)	12(2)
	T^2_H	-56.8(3)	6.4(4)	6(1)	0.8(1)	4(2)

Figure S5: TGA thermograms of type B gelatin and of pure SiO₂-CaO sol-gel bioactive glass. The glass was synthesized via the same sol-gel route described in the manuscript using calcium ethoxide as a calcium precursor, and the gel was dried at 60°C for 24h.









Fig. S6 TEM images of different cross-sections of class II hybrid scaffolds (30wt.% SiO₂– CaO/70 wt.% gelatin) at various magnifications after 3 days immersion in SBF, a) x 9,600, b) x 16,500 magnifications, c) corresponding Selected Area Electron Diffraction pattern showing

the presence of hydroxyapatite nanocrystals (the 11 most intense reflections characteristic of the HA hexagonal structure are indicated). The SAED pattern is characteristics of hexagonal-HA (space group P 63/m) nanocrystals smaller than 500 nm.⁴ The first ring belongs to the (002) planes with $d_{002} = 0.34$ nm, the second one to (012) planes ($d_{012} = 0.32$ nm), the strong and broad third ring is formed by several reflections, namely (211), (112) and (030) with interplanar spacings ranging from 0.27 to 0.28 nm.^{4, 5} Other reflections are (022) ($d_{022} = 0.26$ nm), (130) ($d_{130} = 0.23$ nm), (222) ($d_{022} = 0.19$ nm). The seventh ring has two contributions from (132) and (213) planes ($d_{213} = 0.18$ nm, $d_{132} = 0.19$ nm). Finally the eighth ring corresponds to (004) ($d_{004} = 0.17$ nm).^{4, 6-8}.



Figure S7. Example of macroscopic shapes allowed for the BG/gelatin hybrid scaffolds. The ruler is graduated in cm.

	Class I	Class II	BG nominal	
	hybrid	hybrid	composition	
SiO ₂	73.1	75.5	75	
CaO	26.9	24.5	25	

Table S2. Inorganic compositions (wt.%) of BG hybrid scaffolds (30wt.% SiO2–CaO/70wt.% gelatin) measured by SEM-EDS.



Figure S8. Pulse sequence used for the ²⁹Si homonuclear dipolar double quantum-single quantum correlation MAS experiment. ²⁹Si longitudinal magnetization was first created by a ¹H-²⁹Si CP bock followed by a ²⁹Si 90° pulse. ²⁹Si double quantum (DQ) coherences were then excited and reconverted after an evolution period t_1 using the BaBa-xy16 dipolar recoupling sequence. ⁹A z-filter delay was applied before the final 90° read pulse. ¹H CW decoupling (with a nutation frequency of 60 kHz) was applied during both the DQ excitation/reconversion periods. ¹H SPINAL-64¹ decoupling (with a nutation frequency of 50 kHz) was applied during the t_1 evolution period and signal acquisition. The t_1 increment was synchronized with the rotor period. The DQ excitation and reconversion periods were both set to 4 ms corresponding to 24 rotor periods. The phases of the DQ excitation block and of of the final 90° pulse were cycled by step of 90° to select the desired coherence pathway. Quadrature detection in the indirect dimension was achieved using the States method.¹⁰

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