

Supplementary Information

Effect of particle size, crystal phase and crystallinity on the reactivity of tricalcium phosphate cements for bone reconstruction

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Transmission electron microscopy of XRD-amorphous TCP nanoparticles

Transmission electron microscopy (TEM) confirmed the formation of spherically-shaped nanoparticles by flame spray synthesis of calcium and phosphate containing precursors. Corresponding electron diffraction pattern (Fig. S1, inset) only showed diffuse signals as expected for amorphous materials.

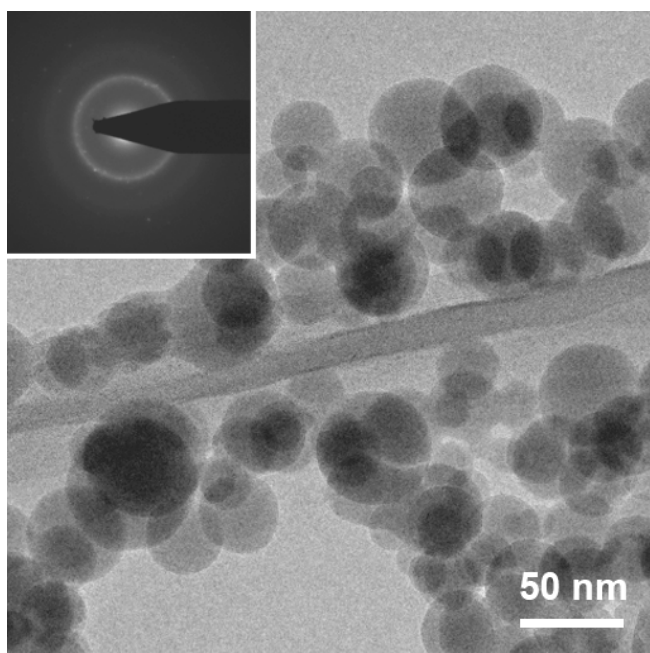


Fig. S1 TEM image of amorphous TCP particles (a-40nm) confirming the formation of spherically shaped nanoparticles. The particle size is in full agreement with the mass-mean primary particle size calculated from nitrogen adsorption (BET measurements).

Differential scanning calorimetry of amorphous TCP

Thermoanalysis of amorphous TCP using calibrated differential scanning calorimetry (DSC, Fig. S2) showed the presence of two exothermic events. X-ray diffraction patterns of samples removed at 700 or 900°C (after 30 min of calcination) allowed identification of the two events as crystallization of amorphous TCP to α -TCP (614°C) and subsequent crystallization of α - to β -TCP at 920°C.

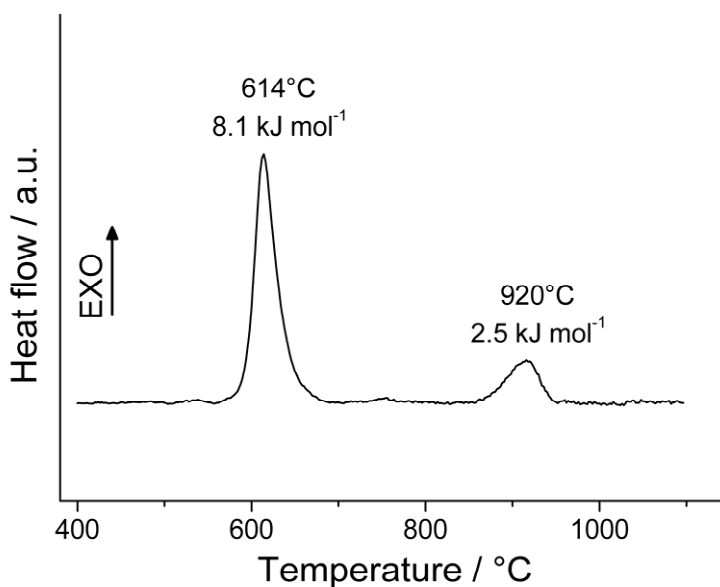


Fig. S2 Two exothermic events occurred during thermal analysis of amorphous TCP nanoparticles: Crystallization of amorphous to α -TCP at 614°C (energy release of 8.1 kJ mol⁻¹) and conversion of α - to β -TCP at 920°C (2.5 kJ mol⁻¹).

Particle size distributions of all used materials

Particle size distributions of all investigated materials were collected on an X-ray disk centrifuge (XDC, Brookhaven Instruments, Holtsville, NY, USA) or using a laser scattering particle size distribution analyzer (LA-300, Horiba, Kyoto, Japan).

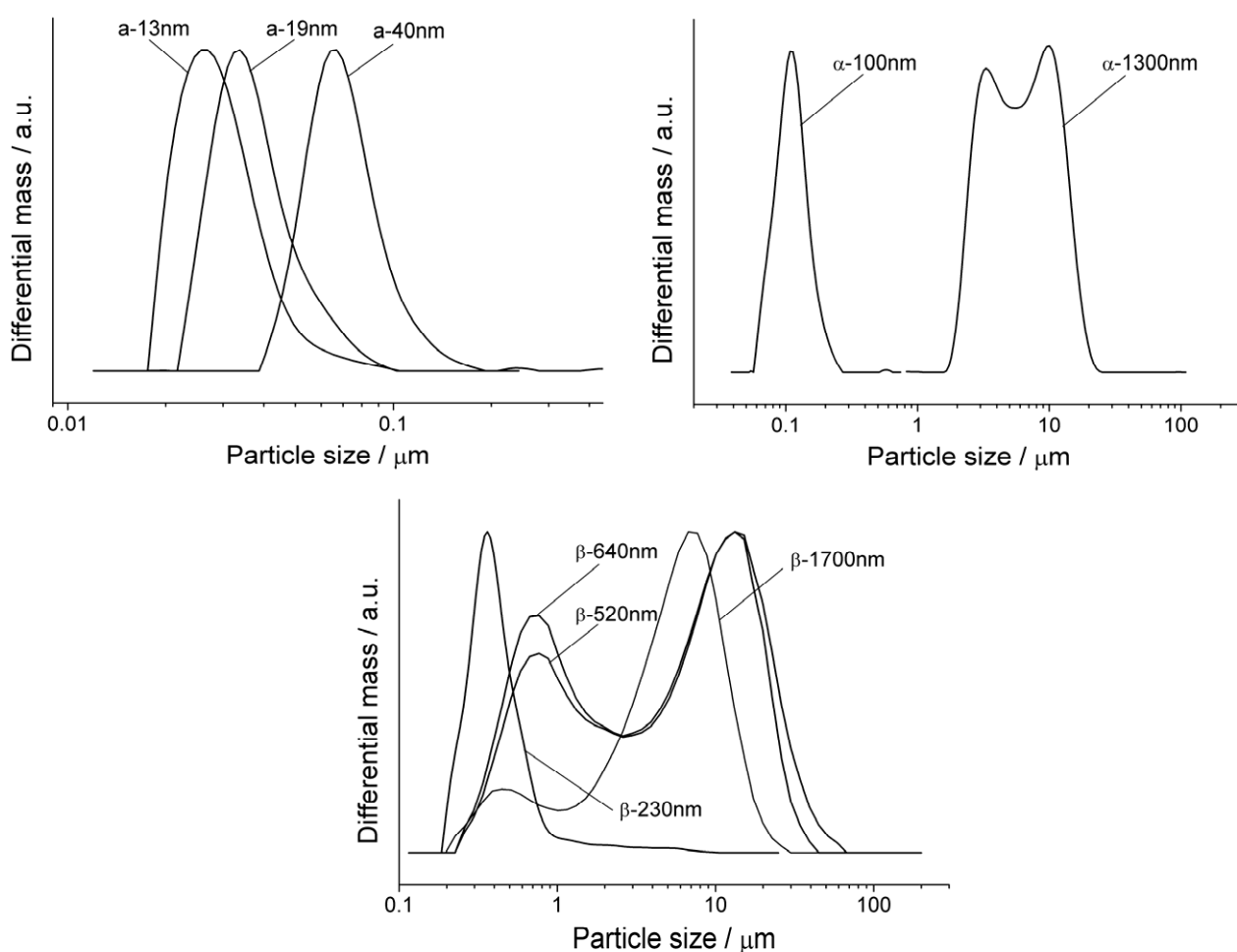


Fig. S3 Particle size distributions of all investigated materials. The amorphous TCP nanoparticles displayed monomodal, narrow sized distributions (top left). The nanoparticle-derived TCP samples α -100nm and β -230nm showed similar, monomodal particle size distributions while crystalline TCP prepared by solid state reactions displayed bimodal distributions.

Details on the calculation of reaction kinetics

Dissolution depth

Under the assumption, that the surface specific dissolution rate of solid particles with a given volumetric particle size distribution and a total initial particle volume (V_{init}) is independent of the individual particle size, a dissolution depth δ' can be introduced:

$$\delta' = R - r_c$$

where R is the initial particle radius and r_c is the radius of the unreacted core. In a dimensionless representation where $\delta = \delta'/R$ this can be rewritten to:

$$\delta = 1 - \frac{r_c}{R}$$

For each dissolution depth δ a new particle size distribution can be calculated, where each initial particle size is reduced by δ . By calculating the total volume of the new particle size distribution assuming spherical particles ($V(\delta)$), the conversion ($\alpha = 1 - V(\delta)/V_{init}$) can be evaluated as a function of δ .

Therefore, the dissolution depth can be calculated as a function of the conversion using the initial volumetric particle size distribution:

$$\alpha(\delta) = 1 - \frac{V(\delta)}{V_{init}} \Rightarrow \delta = f(\alpha)$$

Assuming, that the cumulative energy release is proportional to the amount of material reacted, the calorimetric data can be used to give the conversion (α) as a function of time:

$$\alpha(t) = g(t)$$

By combining the two, the evolution of the dissolution depth can be followed over time:

$$\delta = f(g(t))$$

Comparison with core-shell models

In order to compare the experimental data (δ) with core-shell models, a total reaction time τ and an initial particle size R has to be chosen. In this case, τ was chosen at the point where 99% of the total energy was released and R was chosen as the largest particle size of the particle size distribution contributing to the total volume to more than 0.5%.

It has to be added, that when comparing the experimental data with the diffusion limiting core-shell models (Fig 5a), the assumption of a particle size independent dissolution rate is violated. Nonetheless

there is a good agreement between the experimental data and the model which can be attributed to the narrowness of the particle size distribution of the flame derived TCP.

Reaction models

Liquid film diffusion control (Fig 4a)

In this case it is assumed that the reaction progress is limited by the diffusion of a reactive compound from the surface of the TCP particle to the bulk liquid phase. It is further assumed that this diffusion step can be described by a mass transfer type of equation.¹

Shell layer diffusion control (Fig 4b)

The reaction of the core (TCP) results in the formation of a layer (CDHA) which covers the core in a shell type configuration. In this scenario it is assumed that the diffusion of the reactive compound through the formed CDHA layer limits the rate of the overall reaction.²

Chemical reaction control (Fig 4c)

If the chemical reaction is slow in comparison to mass transport the assumption can be made that solely the rate of the chemical reaction (dissolution or precipitation kinetics) limits the formation of the product (CDHA).^{3,4}

References

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