



# Temperature-dependent morphology changes of noble metal tricalcium phosphate-nanocomposites

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## Abstract

Calcium phosphates, functionalized with nano-sized metal particles, are a promising material class for the treatment of bone defects. However, a sintering process is required in principle to achieve sufficient strength of calcium phosphate scaffolds. In this work laser-generated nano-sized silver, gold and platinum particles were adsorbed on micro-sized  $\beta$ -tricalcium phosphate particles and further heat treated at temperatures between 600 and 1200 °C. Gold and platinum nanoparticles underwent exponential growth starting at about 600 °C, while sintering of  $\beta$ -tricalcium phosphate started at 800 °C. We hypothesise that this phenomenon is caused by a heat-induced evaporation and growth process where the decrease of the particle number is directly correlated with the size increase. The silver nanoparticles on the other hand formed a new phase with the calcium phosphate ( $\text{AgCa}_{10}(\text{PO}_4)_7$ ) during the heat treatments and could not be observed within the ceramic scaffold anymore. Addressing the lack of information in nanoparticle-combined calcium phosphate scaffolds, this study contributes to the further modification of bone replacement materials with biologically relevant functions and molecules.

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## 1. Introduction

Calcium phosphates are an important class of materials in regenerative bone therapy. Many studies proved that calcium phosphates exhibit excellent properties regarding osteoconductivity [1,2] and cell-mediated bioresorption [3,4]. Especially tricalcium phosphate and hydroxyapatite are used as bone grafts, because of their bioactivity and chemical similarity to the mineral component of natural bone tissue [5]. Nevertheless pure calcium phosphate materials alone lack the same good properties regarding osteoinduction compared to autologous bone [6–8]. One way to enhance the osteoinduction of a material is the addition of agents like drugs, growth factors [9] or nano-sized particles [10]. Especially nano-sized particles made from noble metals exhibit various effects on cells and tissues. For example gold nanoparticles have been found to stimulate the differentiation of mesenchymal stem cells into

osteoblasts [11] and suppress the formation of reactive oxygen species [12]. Platinum nanoparticles also have been found to decrease the formation of reactive oxygen species [13]. Furthermore they hamper the formation of osteoclasts and thereby can slow down the post-menopausal osteoporosis [14]. Besides, silver nanoparticles have been observed to act as an antibiotic agent due to their known  $\text{Ag}^+$  release [15] for instance on catheters [16].

Metal nanoparticles tend to aggregate in a dried state without proper stabilisation; conventional dispersion techniques like sonication, stirring or mixing are often not suitable for further material processing [17,18]. One approach for the prevention of metal nanoparticle aggregation is their immobilising adsorption on a bulk support such as micrometre-sized supporting particles, resulting in supported nanoparticles with a homogenous dispersion on the microphase surface. Various techniques have been proposed to generate and adsorb nanoparticles on microparticles, like chemical [19] or sonochemical reduction [20,21], flame pyrolysis [22,23], or precipitation methods [24]. The adsorption efficiency of colloidal metal nanoparticles on inorganic microparticles is however limited by surfactants or ligands on the

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surface of the nanoparticles, which are often needed in conventional generation methods for the improvement of colloidal stability. In contrast to conventional methods, the generation of colloidal metal nanoparticles, using pulsed laser ablation in liquid (PLAL) [25,26] enables the generation of pure nanoparticles out of metals in various liquids like water [27] and organic solvents [28] or directly in monomers [29] without any additional chemical substances. Surface modifications of laser-generated nanoparticles have also been reported, using coordinating ligands, biomolecules or stabilisation agents [30–33] directly during the ablation process. The adsorption of laser-generated nanoparticles on microparticles was also demonstrated for a variety of metal nanoparticles like gold, silver or platinum using microparticle supports like barium sulphate, titanium dioxide or calcium phosphate [34]. Ligand coverage of laser-generated metal nanoparticles has a pronounced effect on the adsorption efficiency. At low ligand concentration, a nearly complete nanoparticle adsorption was recorded, however, almost complete prevention of adsorption was observed at high ligand concentrations [34].

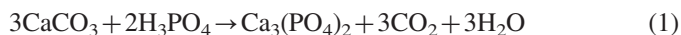
Nanocomposites, made of metal nanoparticles embedded in an inorganic ceramic matrix, are promising materials for applications as regenerative bone replacements. Yet, the physical and chemical properties of nanoparticles depend on their size and shape [35]. Therefore thermal heat treatments, which are in general necessary for a ceramic process (sintering), could strongly affect the nanoparticles. Diffusion, grain boundary movement, vaporisation and condensation occur during the sintering of ceramics, whose driving forces relate to the minimisation of surface and interfacial energies [36]. We hypothesised that these processes would influence the size and distribution of noble metal nanoparticles, adsorbed on calcium phosphates, during high temperature treatments.

In this work, the structural changes during sintering of laser-generated metal nanoparticles adsorbed on  $\beta$ -tricalcium phosphate microparticles at various temperatures were analysed. The behaviour of gold, silver, and platinum nanoparticles was investigated regarding particle size and dispersion within  $\beta$ -tricalcium phosphate. Element and phase composition analyses as well as experiments to determine the hardness of the sintered nanocomposites were performed and correlated to the structural changes of the adsorbed noble metal particles.

## 2. Experimental section

### 2.1. Synthesis of $\beta$ -tricalcium phosphate microparticles

$\beta$ -tricalcium phosphate granulate was synthesised in three steps. The first step was a wet chemical reaction between  $\text{CaCO}_3$  and  $\text{H}_3\text{PO}_4$  (pro analysi, Applichem).



Subsequently the material, acquired from the reaction, was heat treated to obtain the desired  $\beta$ -tricalcium phosphate phase. In the final step,  $\beta$ -tricalcium phosphate was suspended in demineralised water and granulated using the spray drying technique. For the chemical reaction (1) 600.36 g  $\text{CaCO}_3$  was

mixed with 660.40 g of demineralised water. The suspension was left for 30 min on a roll bench for homogenisation. According to Eq. (1) 653.06 g of 60 wt% phosphoric acid solution was poured with constant stirring into the  $\text{CaCO}_3$  suspension to adjust the calcium to phosphorus ratio to 1.5, which is the same ratio as in pure tricalcium phosphate. The mixture was kept for 12 h to react and outgas. Grinding balls of  $\text{ZrO}_2$  (diameter 2 cm) were given into the suspension and the mixture was left for 2 h on a roll bench. The suspension was heated for 30 min at 85 °C in a water bath and then again homogenised for 2 h on the roll bench. Afterwards the mixture was dried in a drying chamber at 150 °C and subsequently heated up to 1000 °C for 2 h in a furnace. The obtained  $\beta$ -tricalcium phosphate material was suspended in demineralised water and milled in an agitator ball mill using 1 mm  $\text{ZrO}_2$  grinding balls. The suspension was spray dried (B 290, Büchi,) to obtain  $\beta$ -tricalcium phosphate granulate. The granulate was analysed by X-ray diffraction (D8 Advance, Bruker AXS) to confirm the phase purity of the  $\beta$ -tricalcium phosphate.

### 2.2. Nanoparticle generation and adsorption on calcium phosphate

Metal nanoparticles were manufactured by pulsed laser ablation of solid targets (gold, platinum, and silver; foils of 1 mm thickness; 99.9% purity; Goodfellow) in aqueous sodium citrate solutions. A high power Q-switched Nd:YAG slab laser (Edgewave HD40I, EdgeWave GmbH) emitting at a central wavelength of 1064 nm (pulse duration 7 ns, pulse energy 45 mJ and repetition rate 1 kHz) was used for pulsed laser ablation. The laser beam was guided horizontally by a laser scanner (Scanlab, HurryScan II-14) with a fixed spiral scan pattern (diameter 5 mm, interline distance 50  $\mu\text{m}$ ) and an applied scan speed of 1 m/s on the target surface. The laser beam was focused through a telecentric f-theta lens (Sill Optics) with a focal length of 56 mm. The ablation was carried out in a self-constructed ablation chamber, with an overall reservoir of 40 ml volume, at room temperature and atmospheric pressure [37]. During ablation, the fluid circulated with a constant volume flow provided by a motor driven stirrer. The targets were fixed inside the chamber, parallel to a laser entrance quartz-window (at a distance of 5 mm) and perpendicular to the focused laser beam [37]. The manufactured nanoparticle mass was determined by differential weighing of the solid target with a microbalance (Sartorius M3P) before and after ablation.

The adsorption of colloidal noble metal nanoparticles on  $\beta$ -tricalcium phosphate microparticles was analysed using different concentrations of aqueous solution of sodium citrate as nanoparticle stabiliser (concentration 0–5 mmol/L, Sigma-Aldrich). Therefore a dedicated amount of  $\beta$ -tricalcium phosphate powder was dispersed in water using sonication and added to the aqueous colloidal nanoparticle solution. Afterwards, the suspension was allowed to separate by sedimentation. The sediment containing the microparticle-supported nanoparticles was separated by decantation and dried for

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