

Embryonic States of Fluorapatite-Gelatine-Nanocomposites and Their Intrinsic Electric Field Driven Morphogenesis

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The biomimetic system fluorapatite-gelatine bears strong resemblance to the biosystem hydroxyapatite-collagen which plays a decisive role in the human body as functional material in the form of bone and teeth. The morphogenesis of fluorapatite-gelatine nanocomposites offers the advantage of revealing a concise sequence of growth developments, whereas bone and teeth are formed by much more complex processes with involvement of cell activities in living system. In former investigation we already showed that on the μm -scale the biomimetic composite (containing about 2-3 wt.-% protein) starts its shape development with a hexagonal prismatic seed which transforms via growing dumbbell states to a slightly notched sphere [1]. In this work we are interested in the nanoscaled embryonic precursor state of the hexagonal prismatic seed. Starting from the molecular level, we especially examined the role of intrinsic electric fields directing the morphogenesis [2,3].

By means of TEM investigations the development of fluorapatite-gelatine composites is revealed starting from molecular dimensions up to the formation of mesoscaled (elongated) hexagonal prisms. The composite nature of the aggregates on all states of development is proved by IR spectroscopy and chemical analyses. The initial states are characterised by triple-helical fibre protein bundles which are mineralised step by step forming and fixing nano-platelets of fluorapatite in a mosaic-arrangement. After being fully mineralised the bundles form elongated composite nanoboards. In the next step of the growth process the boards aggregate to bundles of boards which are in a more or less parallel alignment with respect to each other (Fig. 1). By adding up more and more composite nano-boards a critical size is reached and an electric field is developed which takes over control and directs the further development of the aggregates (Fig. 2). This kind of electric field directed growth of the elongated polar nanoboards additionally leads to the formation and inclusion of bent protein nanofibrils into the growing composite aggregate. By this, cone like nanofibril structures develop along the long axis of the aggregates accompanied by more perfect parallel alignment of the composite boards within the aggregates. The further shape development is characterised by adding composite nanoboards especially in order to increase the 3rd dimension in volume. This thickening process preferably takes place in the middle part of the elongated aggregates and finally proceeds to their basal ends until a perfect hexagonal prismatic seed is formed which then is ready for further shape development on the μm -scale (via dumbbell state to a notched sphere).

1. R. Kniep, P. Simon, in *Top. Curr. Chem.: Biomineralisation I, II* (Ed.: K. Naka), Springer, Heidelberg, **I** (2007) p73-125.
2. R. Kniep, P. Simon, *Angew. Chem. Int. Ed.* **47** (2008) p1405.
3. P. Simon, E. Rosseeva, J. Buder, W.G. Carrillo-Cabrera, R. Kniep, *Adv. Funct. Mater.*, submitted.
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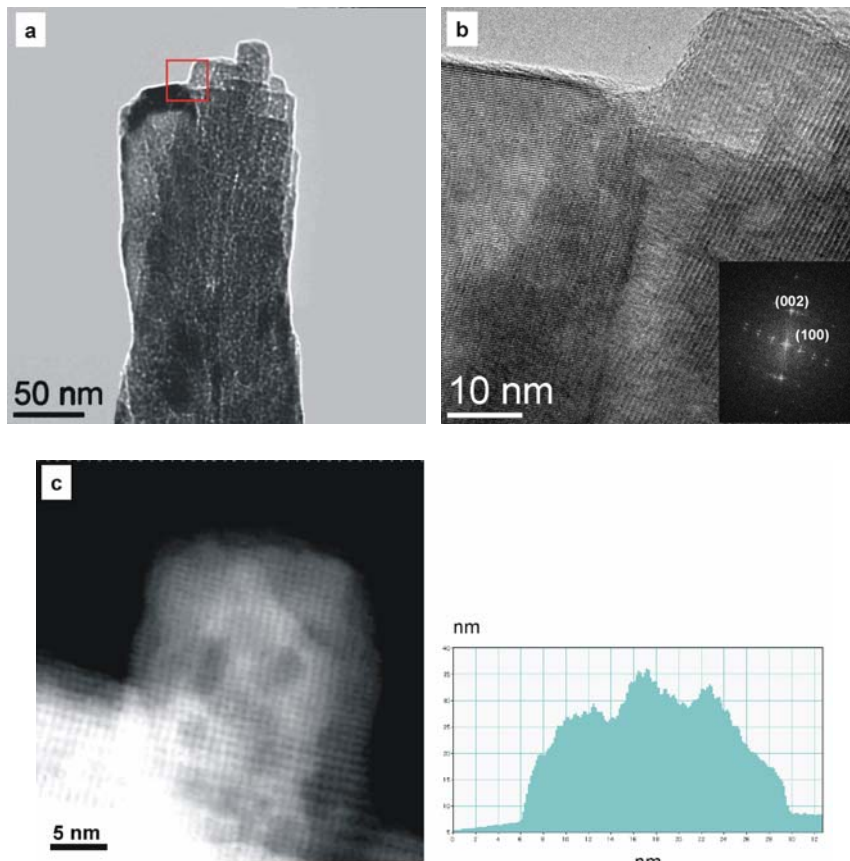


Figure 1. (a) Overview TEM image of a shelf shaped nanocomposite. The aggregate is formed of single nano-boards, which are in parallel alignment with respect to each other. (b) The orientational mismatch of $\sim 20^\circ$ of the different boards is revealed in the HR-TEM image. (c) Electron phase image retrieved from the electron hologram showing the presence of nano pores (dark, roundish structures) caused by built-in proteins superimposed with the crystal lattice planes of fluorapatite. The horizontal phase profile (bottom right) indicates a thickness of about 35 nm and a width of 25 nm of the nanoboards.

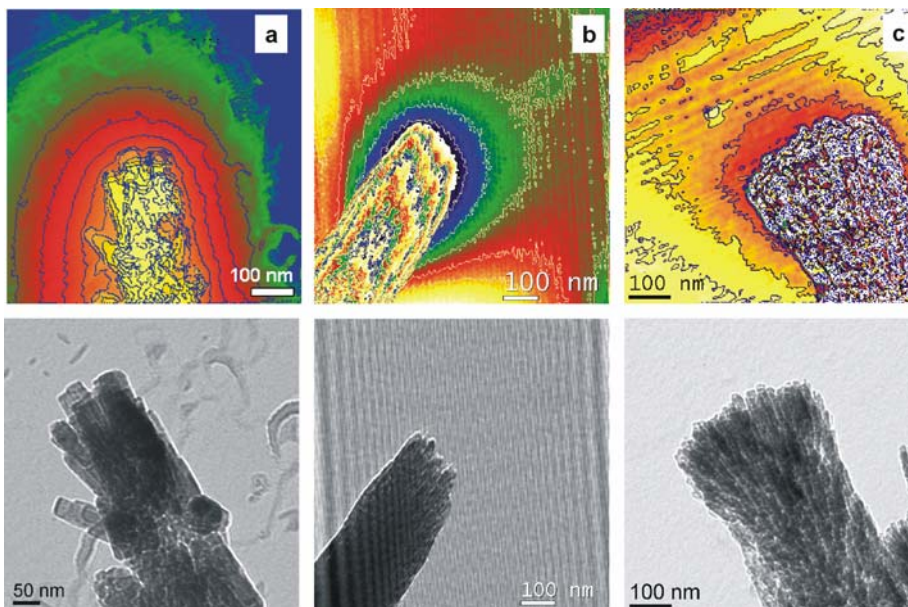


Figure 2. (a,b,c) Electron holography of the platy nanoscale embryonic composites showing the development of intrinsic electric fields along the aggregates' growth.