CryoTEM in materials science: Studying biomimetic mineralization

Nico A.J.M. Sommerdijk

Laboratory of Materials and Interface Chemistry and Soft MatterCryo_TEM Research Unit, Eindhoven University of Technology, Eindhoven, The Netherlands, N.Sommerdijk@tue.nl

N.Sommerdijk@tue.nl
Keywords:bioinspired materials, electron tomography, calcium phosphate

The often astonishing materials properties of crystalline biominerals are generally related to the hierarchical assembly of specifically interacting organic and inorganic components. A yet unfulfilled dream of many scientists is to synthesize new materials with similar advanced properties applying Nature's biomimeralization strategies.[1] For the design of such biomimetic hybrid materials with predetermined structure and properties it is essential to understand the factors that dictate their formation.

The *in situ* study of the development of mineral formation can make an important contribution to the understanding of the processes involved in bio(mimetic) mineralization.[2] It is however not a trivial matter to obtain morphological and structural information of such systems in their native hydrated state. We and others recently have presented the possibility to use cryoTEM as a method to investigate the early stages of mineral formation without removing the developing particles from their aqueous environment. [3, 4]

Using dedicated tools including a vitrification robot with attached glovebox also makes it possible to investigate mineral formation at interfaces,[5] while cryo-electron tomography allows us to investigate template-mineral interactions in 3D.[4,6,7] Moreover, we combine cryo-TEM imaging with more materials science oriented techniques such as cryo-STEM/EDX and low dose selected area electron diffraction to combine morphology with structural and chemical information.

We will discuss the biomimetic formation of calcium phosphate using templates from both synthetic and biological origin. Our investigations revealed that crystallization preceded by an amorphous phase, which itself is formed through the assembly and aggregation of nanometer building blocks termed "pre-nucleation clusters" [6,7]. They also show the role of the templating surfaces and matrices in these processes. Using high resolution cryoTEM in combination with several other in-situ techniques we demonstrate in detail the structure of these "clusters" and their role in the formation of the subsequent amorphous and crystalline phases.

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