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The effects of immobilized carboxylic-functional groups on the dynamics of phase transformation from amorphous to octacalcium phosphate†

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Abstract

The influence of carboxylic-functional-groups (-COOH) on the phase transformation from amorphous calcium phosphate (ACP) to octacalcium phosphate (OCP) was investigated. 11-Mercaptoundecanoic acid, a carboxylic thiol, was immobilized on gold nanoparticles via covalent bond formation. Time-resolved static light scattering measurements indicated that a structural-reconstruction-type phase transformation occurred with or without the presence of -COOH on the nanoparticles. When it dispersed in calcium phosphate solutions, these nanoparticles inhibited the phase transformation dynamics and also changed the reaction path, forming HPO_4-OH-layer-deficient OCP at pH 6.5 an intermediate phase, which did not show the typical OCP X-ray diffraction (XRD) peak at $2\theta = 4.7°$. This phase was not observed in the reference solution containing gold nanoparticles without bound -COOH. The HPO_4-OH-layer-deficient OCP transformed to conventional OCP gradually, as revealed by XRD, nuclear magnetic resonance, and Raman analyses. Thus, the immobilized -COOH appeared to behave as a negative catalyst, resulting in the formation of the intermediate phase. Such a mechanism partially clarifies complex biomineralization processes, for example teeth enamel and dentin formation, in vivo.

Keywords: Biomineralization, calcium phosphate, phase transformation, early tooth formation, intermediate phase