Electronic supplementary information

Step-by-step from amorphous phosphate to nano-structured calcium hydroxyapatite: monitoring by solid-state ^{1}H and ^{31}P NMR and spin dynamics

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1. Details of synthesis

Synthesis I. Producing the sample containing AMP, the Zn^{2+} ions were introduced as an inhibitor of hydroxyapatite crystallization. Calcium hydrogen phosphate dihydrate ($CaHPO_4 \cdot 2H_2O$, 99.1 %, Eurochemicals) and zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$, ≥ 99.5%, Roth) were used as starting materials. All chemicals were used as received without additional purification. In a typical synthesis, certain amounts of $CaHPO_4 \cdot 2H_2O$ and $Zn(CH_3COO)_2$ corresponding to Ca-to-Zn molar ratios of 9 were dissolved in a mixture of 100 ml of distilled water and 13 ml of 1 M phosphoric acid (H_3PO_4, 75 %, Roth). Total concentration of metal ions in the reaction mixture was 0.065 M. Temperature of the obtained solution was set to 75 °C and the mixture was stirred for 1 h. Next, under constant mixing on a magnetic stirrer, concentrated ammonia solution (NH_4OH, 25 %, Roth) was added in order to adjust the pH to 5.6. The increase of the pH value of the reaction medium resulted in instantaneous formation of white precipitates, which were instantly filtered and dried without aging in the reaction mixture.[5]

Synthesis II. The composite sample containing AMP and nano-CaHA was synthesized by wet precipitation method using calcium nitrate tetrahydrate ($Ca(NO_3)_2{\cdot}4H_2O$, ≥ 99 %, Roth) and diammonium hydrogen phosphate ($(NH_4)_2HPO_4$, ≥ 98 %, Roth) as starting materials. For the synthesis an appropriate amount of $Ca(NO_3)_2{\cdot}4H_2O$ was dissolved in deionized water resulting in 0.75 M solution. Next, concentrated ammonia solution (NH_4OH, 25 %) was added to the above solution in order to adjust pH to 10. In parallel 0.5 M $(NH_4)_2HPO_4$ solution in deionized water was prepared. Next, under constant stirring on magnetic stirrer, the prepared solutions were mixed together resulting in the instant formation of white precipitates. The obtained precipitates were stirred in the reaction mixture for 10 minutes, afterwards vacuum filtered and washed with deionized water and dried at 50 °C overnight in the oven.[6]

Synthesis III. The high-crystalline nano-CaHA sample was obtained by the sol−gel process. Calcium acetate monohydrate, $Ca(CH_3COO)_2{\cdot}H_2O$, and ammonium hydrogen phosphate, $(NH_4)_2HPO_4$, were selected as Ca and P sources, respectively, in Ca/P mole ratio 1.67. The mixture of calcium acetate and ammonium hydrogen phosphate was stirred at 60 - 65 °C for 1 h. The tartaric acid was selected as complexing agent. Obtained mixture was vigorously stirred for 12 h at 60 - 65 °C in a beaker covered with a watch glass. After evaporation of solvent, the transparent white gels were obtained. The gels were dried in an oven for 10 h at 110 °C. The obtained powders were grinded in agate mortar and heated to 800 °C for 5 h and repeatedly two times at 1000 °C for 5 h.

2. DFT

2.1 Atomic coordinates used in the calculations of hexagonal CaHA with ´up´ and ´down´ configurations of hydroxyl groups.

OH up

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O	6.32775	3.36822	8.59875
O	3.09626	12.95463	12.03825

O	9.17709	9.15875	15.47775
O	6.32775	3.36822	15.47775
O	8.05516	11.9573	1.71975
O	1.36884	4.36555	18.91725
O	1.36884	4.36555	5.15925
O	8.05516	11.9573	8.59875
O	1.36884	4.36555	12.03825
O	8.05516	11.9573	15.47775
O	2.0238	2.10483	0.48291
O	7.4002	14.21801	20.1541
O	7.4002	14.21801	3.92241
O	2.0238	2.10483	2.95659
O	2.0238	2.10483	7.36191
O	7.4002	14.21801	13.2751
O	7.4002	14.21801	10.80141
O	2.0238	2.10483	16.71459
O	2.0238	2.10483	14.24091
O	7.4002	14.21801	6.39609
O	7.4002	14.21801	17.68041
O	2.0238	2.10483	9.83559
O	1.87726	8.86167	0.48291
O	7.54674	7.46117	20.1541
O	0.81093	13.51777	0.48291
O	8.61307	2.80508	20.1541
O	7.54674	7.46117	3.92241
O	1.87726	8.86167	2.95659
O	8.61307	2.80508	3.92241
O	0.81093	13.51777	2.95659
O	1.87726	8.86167	7.36191
O	7.54674	7.46117	13.2751
O	0.81093	13.51777	7.36191
O	8.61307	2.80508	13.2751
O	7.54674	7.46117	10.80141
O	1.87726	8.86167	16.71459
O	8.61307	2.80508	10.80141
O	0.81093	13.51777	16.71459
O	1.87726	8.86167	14.24091
O	7.54674	7.46117	6.39609
O	0.81093	13.51777	14.24091
O	8.61307	2.80508	6.39609
O	7.54674	7.46117	17.68041
O	1.87726	8.86167	9.83559
O	8.61307	2.80508	17.68041
O	0.81093	13.51777	9.83559
O	11.30126	8.86167	0.48291
O	-1.87726	7.46117	20.1541
O	5.52294	5.35634	0.48291
O	3.90107	10.9665	20.1541
O	-1.87726	7.46117	3.92241
O	11.30126	8.86167	2.95659

O	3.90107	10.9665	3.92241
O	5.52294	5.35634	2.95659
O	11.30126	8.86167	7.36191
O	-1.87726	7.46117	13.2751
O	5.52294	5.35634	7.36191
O	3.90107	10.9665	13.2751
O	-1.87726	7.46117	10.80141
O	11.30126	8.86167	16.71459
O	3.90107	10.9665	10.80141
O	5.52294	5.35634	16.71459
O	11.30126	8.86167	14.24091
O	-1.87726	7.46117	6.39609
O	5.52294	5.35634	14.24091
O	3.90107	10.9665	6.39609
O	-1.87726	7.46117	17.68041
O	11.30126	8.86167	9.83559
O	3.90107	10.9665	17.68041
O	5.52294	5.35634	9.83559
O	6.7358	10.26625	0.48291
O	2.6882	6.05659	20.1541
O	2.6882	6.05659	3.92241
O	6.7358	10.26625	2.95659
O	6.7358	10.26625	7.36191
O	2.6882	6.05659	13.2751
O	2.6882	6.05659	10.80141
O	6.7358	10.26625	16.71459
O	6.7358	10.26625	14.24091
O	2.6882	6.05659	6.39609
O	2.6882	6.05659	17.68041
O	6.7358	10.26625	9.83559
O	4.712	8.16142	1.3414
O	4.712	8.16142	4.7809
O	4.712	8.16142	8.2204
O	4.712	8.16142	11.65991
O	4.712	8.16142	15.09941
O	4.712	8.16142	18.53891
H	4.712	8.16142	0.41824
H	4.712	8.16142	3.85774
H	4.712	8.16142	7.29724
H	4.712	8.16142	10.73674
H	4.712	8.16142	14.17624
H	4.712	8.16142	17.61574

2.2 The calculated ^{1}H and ^{31}P isotropic shielding constants of H_3PO_4, $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-}moieties (in ppm); geometry optimization by B3LYP/cc-pVTZ, NMR -by PBE1PBE/cc-pVTZ

	^{31}P	^{1}H
H_3PO_4	322.5	28.39
$H_2PO_4^-$	321.1	30.13
HPO_4^{2-}	303.6	30.94
PO_4^{3-}	291.9	-