

SUPPLEMENTARY MATERIAL

Article: Morphology control of hydroxyapatite as a potential reinforcement for orthopedic biomaterials: The hydrothermal process.

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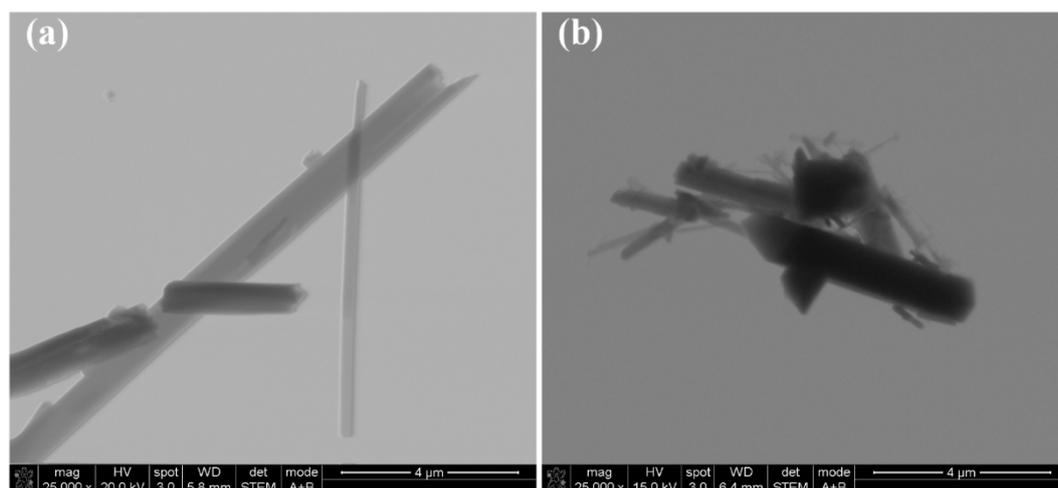


Figure S1. STEM images of products obtained in hydrothermal synthesis (200 °C, 20 bar, 5 h) for (a) whiskers Ca^{2+} ion concentration 0.05 mol/dm³, and (b) hexagonal rods Ca^{2+} ion concentration 0.2 mol/dm³.

The STEM images of whiskers and hexagonal rods obtained during 5 hours of synthesis are shown in Figure S1. It is possible to observe that whiskers and hexagonal rods are characterized by smooth surface and clear contours.

Table S1. IR bands assignments for hydroxyapatites under investigation (vw-very weak, w-weak, sh-shoulder) [52,53].

| Band assignment | Ca ²⁺ concentration (mol/dm ³) and reaction time | | | | | | |
|---|---|-----------|-----------|-----------|-----------|-------------|----------------|
| | 5h | | | | | 1h | |
| | 0.025 | 0.05 | 0.1 | 0.15 | 0.2 | 0.05 | 0.2 |
| OH surface | 3571 | 3571 | 3571 | 3570 | 3570 | 3571 | 3571 |
| water | 3415 | 3408 | 3468/3402 | 3468/3400 | 3467/3408 | 3397 | 3467/3413 |
| CH ₃ ,CH ₂ | 2971/2933/2882w | 2972/2932 | 2971/2929 | 2971/2927 | 2970/2924 | 2970/2928 | 2970/2931/2881 |
| Overtone CO ₃ ²⁻ and ν ₃ /ν ₁ PO ₄ | 2002/1988 | 2002/1989 | 2002/1989 | 2002/1989 | 2002/1988 | 2002/1990 | 2002/1988 |
| Water O-H | 1631 | 1631 | 1630 w | 1635vw | 1630 | 1630 | 1630 |
| P=O str. | 1210/1143 | 1210 sh | ~1210 vw | – | – | 1206/1143sh | 1143sh |
| ν ₃ asym. PO ₄ ³⁻ | 1105/1090 | 1109/1092 | 1093 | 1092 | 1093 | 1098 | 1093 |
| ν ₃ asym. PO ₄ ³⁻ ideal crystal | 1031 | 1031 | 1046/1020 | 1047/1023 | 1048/1023 | 1031 | 1048/1026 |
| asym. str. P-O | 963 | 962 | 961 | 961 | 961 | 963 | 962 |
| CO ₃ ²⁻ | 872 | 872 | 876 | 878 | ~878sh | 867* | 876 |
| P ₂ O ₇ ⁴⁻ | 729w | 729vw | 733vw | 726vw | 726vw | 730vw | 731vw |
| str. OH ⁻ labile PO ₄ ³⁻ | 634 | 635 | 633 | 633 | 633 | 634 | 633 |
| 603+562+473 ν ₄ str. PO ₄ ³⁻ | 603 | 602 | 603 | 603 | 603 | 603 | 603 |
| | 563 | 563 | 563 | 562 | 562 | 562 | 562 |
| | 473 | 473 | 473 | 473 | 473 | 473 | 473 |
| H ₂ PO ₄ ⁻ , or P ₂ O ₇ ⁴⁻ | 427 | ~427vw | ~427vw | – | ~427vw | ~429vw | 425 |

Table S2. Effect of the synthesis temperature and the pressure on the lattice parameters of the phases present in the synthesized powders (reaction conditions: Ca^{2+} 0.05 mol/dm³, 200°C, 5 h, 250 rpm).

| temperatur e (°C) | pressure (bar) | phase composition | COD | system | space group | crystal lattice parameters | | | |
|----------------------|-------------------|----------------------|--------------|-----------|-------------|----------------------------|----------|----------|-------------------------|
| | | | | | | a (Å) | b (Å) | c (Å) | V* (Å ³) |
| 200 | 20 | HAp | 9002214 [50] | hexagonal | P 63/m | 9.43940 | 9.43940 | 6.88610 | 531.36 |
| 170 | 10 | HAp | 9011092 [49] | hexagonal | P 63/m | 9.42400 | 9.42400 | 6.87900 | 529.09 |
| 150 | 6 | HAp | 9011092 [49] | hexagonal | P 63/m | 9.42400 | 9.42400 | 6.87900 | 529.09 |
| 130 | 4 | HAp | 9001233 [48] | hexagonal | P 63/m | 9.41660 | 9.41660 | 6.87450 | 527.91 |
| 110 | 2 | HAp | 9001233 [48] | hexagonal | P 63/m | 9.41660 | 9.41660 | 6.87450 | 527.91 |
| | | D CPA | 9007619 [51] | triclinic | P1 | 6.91 | 6.627 | 6.99800 | 309.28 |

*cell volume.

Table S3. Effect of the stirring rate on the lattice parameters of the phases present in the synthesized powders (reaction conditions: Ca^{2+} 0.05 mol/dm³, 200 °C, 5 h, 20 bar).

| Stirring rate (rpm) | phase composition | COD | crystal lattice parameters | | |
|------------------------|-------------------|--------------|-------------------------------|----------|-------------------------|
| | | | a=b (Å) | c (Å) | V* (Å ³) |
| 1000 | HAp | 9001233 [48] | 9.41660 | 6.87450 | 527.91 |
| 750 | HAp | 9001233 [48] | 9.41660 | 6.87450 | 527.91 |
| 250 | HAp | 9011092 [49] | 9.42400 | 6.87900 | 529.09 |
| 125 | HAp | 9011092 [49] | 9.42400 | 6.87900 | 529.09 |
| 62.5 | HAp | 9002214 [50] | 9.43940 | 6.88610 | 531.36 |
| 0 | HAp | 9002214 [50] | 9.43940 | 6.88610 | 531.36 |

*cell volume.