Supporting Information

Silk fibroin directs the formation monetite nanocrystals and their

assembly into hierarchical composites

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Figure S1. XRD patterns of SF film before (FA) and after immersion in diH_2O (wet) and after freeze drying (dry).



Figure S2. SEM images of samples obtained in the calcium phosphate precursor solution with a calcium concentration of 0.84 M.



Figure S3. (A, B) SEM images of the sample obtained in the precursor solution after removal of the silk film and (C) the corresponding XRD pattern.



Figure S4. (A, B) SEM images of the silk film treated with ethanol vapor after freeze drying; (C) XRD patterns of SF film before (FA) immersion in diH₂O and after immersion in diH₂O followed with ethanol vapor treatment (wet) and after freeze drying (dry).



Figure S5. SEM images of the sample after mineralization for 4 h (A, B) and 24 h (C, D) in the presence of ethanol treated silk film.



Figure S6. (A) SEM image and (B) the corresponding EDS spectrum and (C) EDS mapping of the sample after pretreatment in precursor solution for 7 days.



Figure S7. XRD patterns of the samples before mineralization (0 h) and after mineralization for 4 h and 24 h.



Figure S8. Raman spectrum of the silk film (blank) and samples after mineralization for 0 h, 4 h and 24 h.



Figure S9. SEM images of the samples collected during the mineralization process. (A-B) shows that presence of humps within the crystals. Part of the crystal surface become smooth, as indicated by arrows.



Figure S10. Consecutive TEM images (A-E) with increasing magnification for a sample collected during the mineralization process. (F) Zoomed out TEM images of the sample after beam damage.



Figure S11. pH changes of the precursor solution during mineralization.



Figure S12. (A) XRD pattern of silk film without pretreatment in calcium phosphate solution and mineralized for 2 h, and silk film treated with calcium phosphate solution for 1 day and 3 days before mineralization. (B) XRD pattern of silk film without pretreatment in calcium phosphate solution and silk film treated with calcium phosphate solution for 1 day and 3 days mineralized for 24 h.



Figure S13. (A) pH change of the precursor solution before mineralization; (B) the amount changes of Ca and P ratio with time in precursor solution before mineralization.