

Electronic Supplementary Information

A physicochemical process for fabricating submicrometre calcium iron phosphate spheres

Maki Nakamura,^{*a} Ayako Oyane,^a Ikuko Sakamaki,^a Yoshie Ishikawa,^a Yoshiki Shimizu,^a Kenji Koga,^a Kenji Kawaguchi^a and Naoto Koshizaki^{a,b}

^a Nanosystem Research Institute, National Institute of Advanced Industrial Science and Technology, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8562, Japan. E-mail: ma-ki-nakamura@aist.go.jp

^b Graduate School of Engineering, Hokkaido University, Kita 13, Nishi 8, Kita-ku, Sapporo, Hokkaido 060-8628, Japan.

Experimental

Pulsed laser irradiation to the reaction mixture

Aqueous CaCl₂ (200 mM), K₂HPO₄·3H₂O (200 mM) and FeCl₃·6H₂O (200 mM) were used as the calcium, phosphate and ferric ion source solutions, respectively. The final calcium, phosphate and ferric ion concentrations of each reaction mixture (4 mL) were 16.7 mM, 10.0 mM and 0–10.0 mM, respectively. After preparing the reaction mixture in a glass vessel with stirring, pulsed laser irradiation was immediately performed using the output of the third harmonic (355 nm) or the second harmonic (532 nm) of an Nd:YAG laser (Quanta-Ray LAB-150-30, Spectra-Physics) operated at 30 Hz with a fluence of 67–200 mJ/pulse/cm² (output power of 1–3 W). The laser beam possessed an output diameter of 8 mm and was irradiated without focusing.

After irradiation for various periods up to 30 min, the product was collected by centrifugation (6,000 rpm, 10 min), washed twice with ultrapure water and dispersed again in ultrapure water. The solution was centrifuged three times at 500 rpm for 5 min, and the

collected sediment was classified as Group L. Furthermore, the supernatant was centrifuged three times at 1,000 rpm for 10 min, and the collected sediment was classified as Group S.

Analysis of the products

The morphology, composition and crystalline structure of the resulting sediments were examined using a scanning electron microscope (SEM; XL30, FEI), an energy dispersive X-ray spectrometer (EDX; Genesis2000, EDAX) and a thin-film X-ray diffractometer (XRD; M18X, MAC Science) with CuK α X-rays by depositing and drying small spots of sediment on a silicon substrate. The particle size in ultrapure water was measured by dynamic light scattering (DLS) with a particle size analyser (Zetasizer Nano-ZS, Malvern). The contents of Ca, P and Fe contained in the spheres were determined as follows. First, the spheres were dried under reduced pressure and dissolved in 1 M HCl solution. After dilution with water, the quantities of Ca, P and Fe in these solutions were measured using inductively coupled plasma-atomic emission spectrometry (ICP-AES; ULTIMA2, Horiba). The absorption spectrum of the precipitates initially formed in the reaction mixture was obtained using a UV-VIS-NIR spectrophotometer (SolidSpec-3700DUV, Shimadzu).

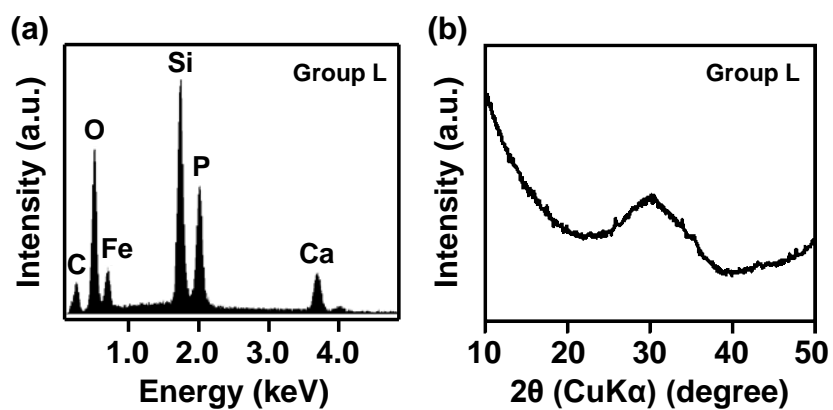


Fig. S1 EDX spectrum (a) and XRD pattern (b) of the spheres in Group L obtained by pulsed laser irradiation to the CaP reaction mixture supplemented with ferric ions under basal conditions.

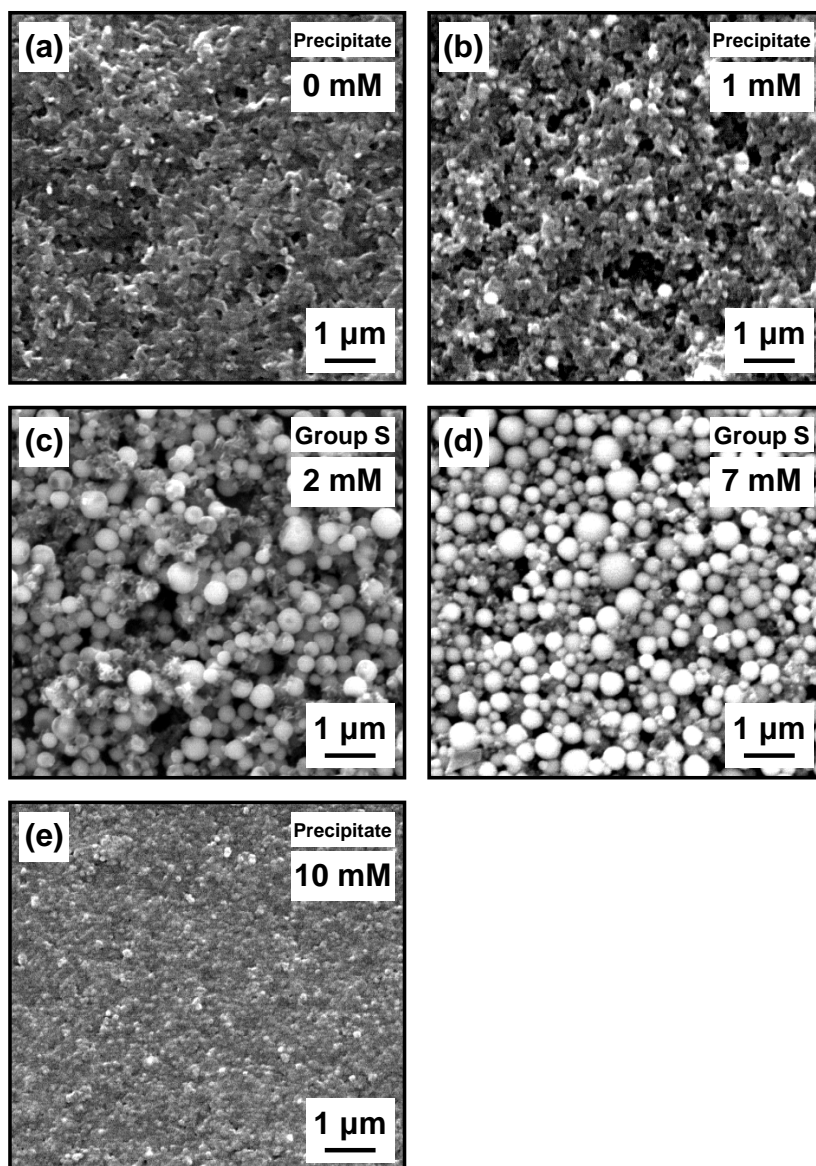


Figure S2. SEM images of the as-collected precipitates (a, b and e) and spheres in Group S (c and d) obtained by pulsed laser irradiation to the CaP reaction mixture supplemented with various concentrations of ferric ion [0 (a), 1.0 (b), 2.0 (c), 7.0 (d), 10.0 (e) mM].

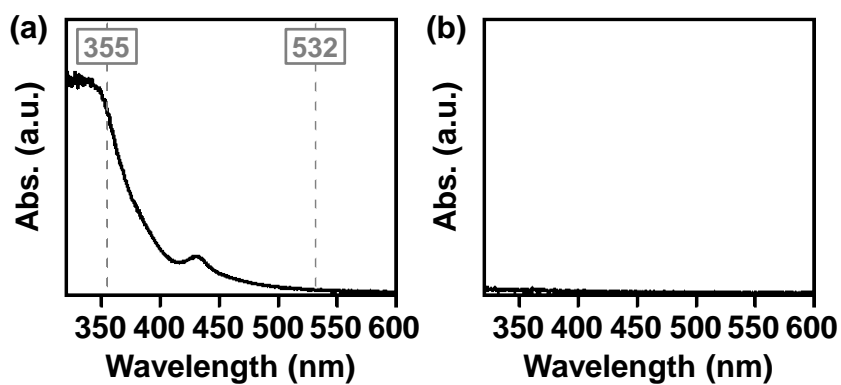


Figure S3. UV-VIS absorption spectra of the precipitates initially formed in the reaction mixture with 5.0 mM ferric ions (a) and without ferric ions (b) before laser irradiation.

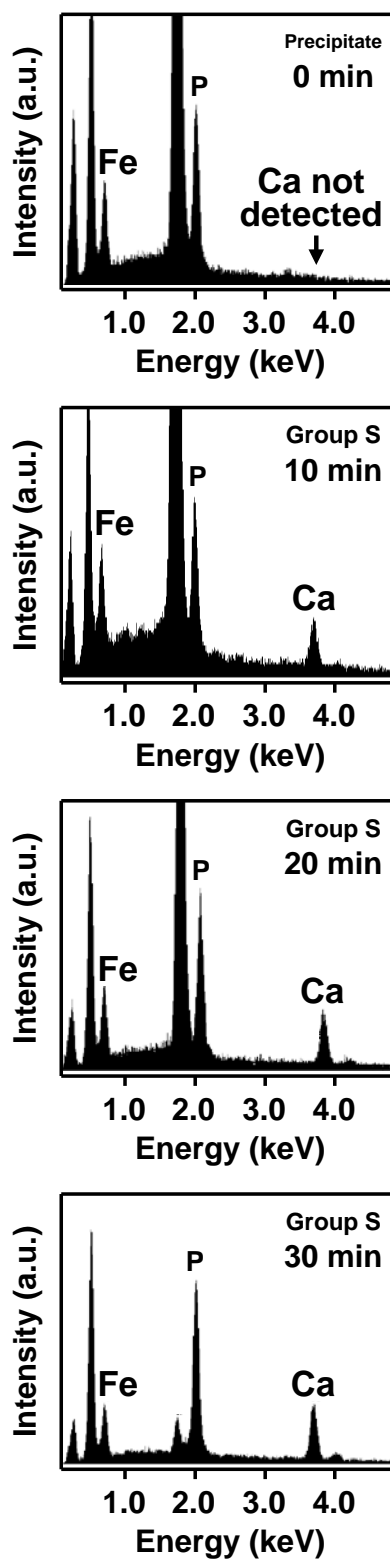


Figure S4. EDX spectra of the as-collected precipitates (irradiation time: 0 min) and spheres in Group S (irradiation time: 10, 20 and 30 min) obtained by pulsed laser irradiation for various time periods (0–30 min).