

Electronic Supplementary Information

Laser-assisted one-pot fabrication of calcium phosphate-based submicrospheres with internally crystallized magnetite nanoparticles through chemical precipitation

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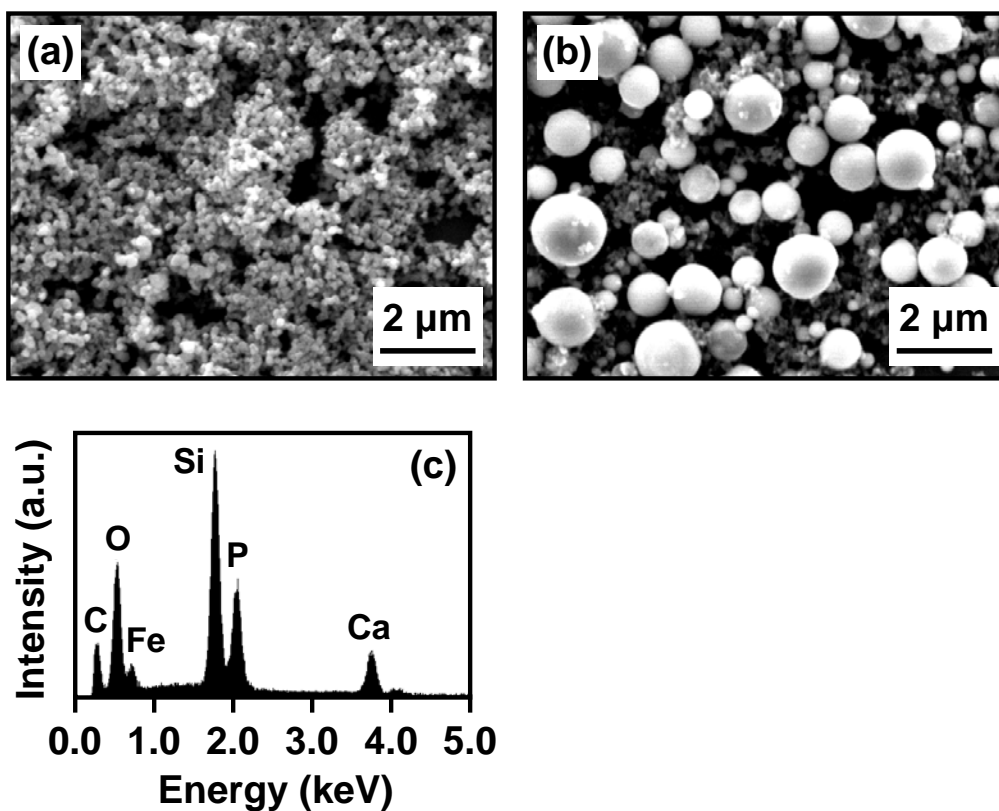


Fig. S1 (a) SEM image of the precipitates initially formed in the reaction mixture with a 5.0 mM concentration of ferrous ions prior to laser irradiation. (b) SEM image of the precipitates after laser irradiation to the reaction mixture with a 5.0 mM concentration of ferrous ions (before centrifugation). (c) EDX spectrum of (a).

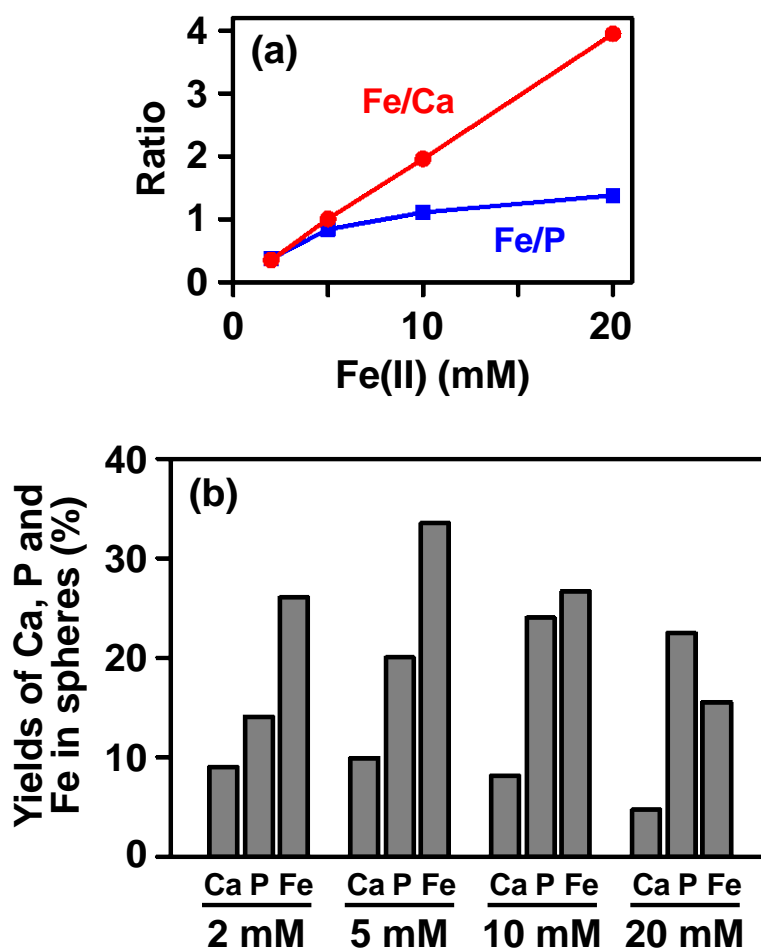


Fig. S2 (a) The elemental ratios of Fe/P and Fe/Ca of the spheres (Groups S+L) with respect to the ferrous ion concentration, as determined by ICP-AES. (b) The yields of Ca, P, and Fe in spheres (Groups S+L). The yields were defined in each elements (Ca, P, and Fe) as a proportion of elemental contents in the spheres to the total elemental contents added to the reaction mixture (Ca: 16.7 mM, P: 10 mM, Fe: 2.0–20.0 mM in 4mL of reaction mixtures).

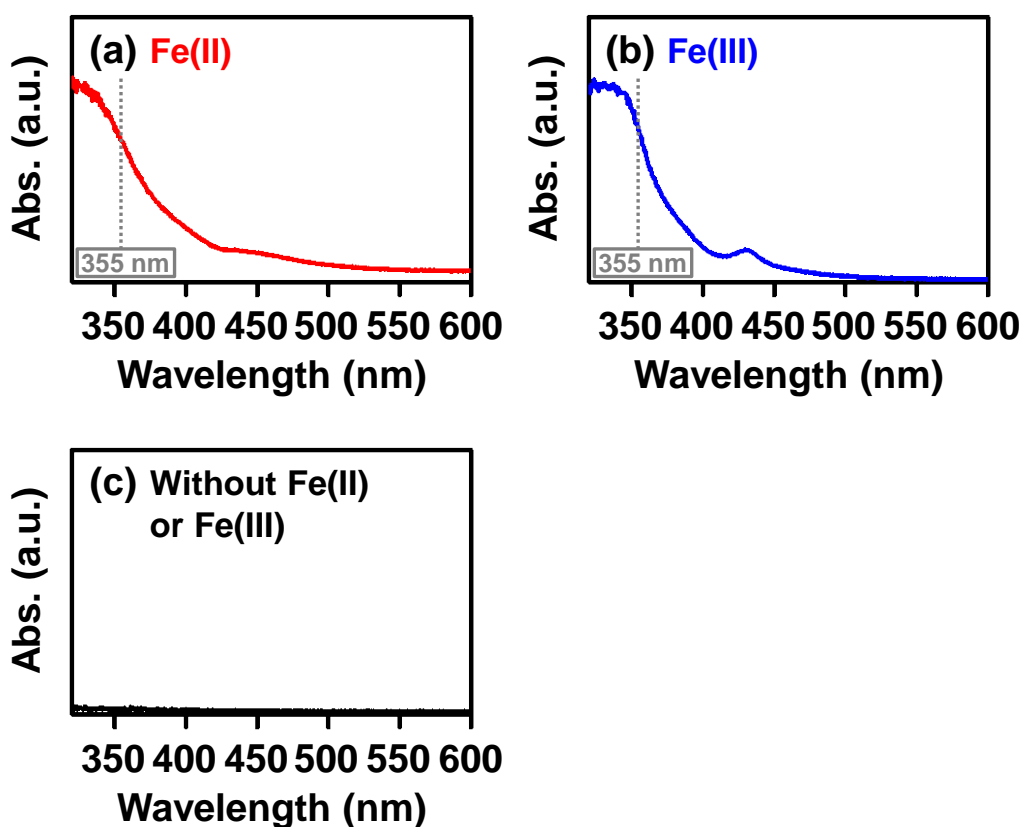


Fig. S3 UV-Vis absorption spectra of the precipitates initially formed in the reaction mixture with a 5.0 mM concentration of ferrous (Fe(II)) ions (a), a 5.0 mM concentration of ferric (Fe(III)) ions (b), and without ferrous or ferric ions (c), prior to laser irradiation. Diffuse reflection measurements using an integrating sphere were performed. The precipitates were mounted on a reference material, pressed BaSO₄ powders, for the measurements.

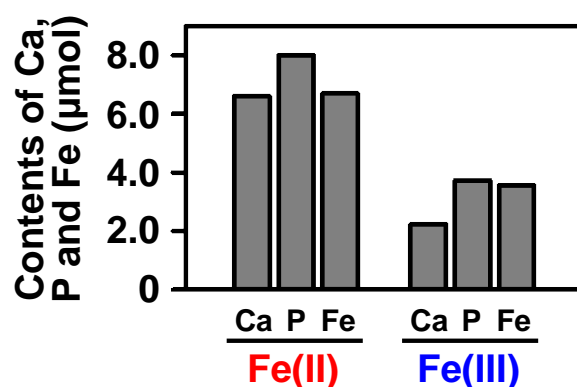


Fig. S4 Ca, P, and Fe contents of the spheres (Groups S+L) obtained in the system with a 5.0 mM concentration of ferrous (Fe(II)) ions and a 5.0 mM concentration of ferric (Fe(III)) ions under equivalent irradiation conditions (200 mJ/pulse/cm², 30 min), as determined by ICP-AES.

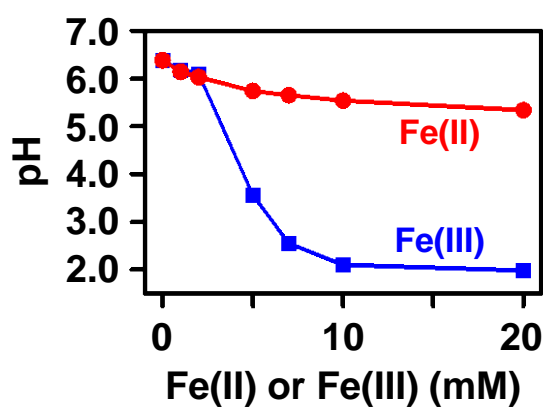


Fig. S5 The pH values of the as-prepared reaction mixtures with respect to the ferrous (Fe(II)) and ferric (Fe(III)) ion concentration.

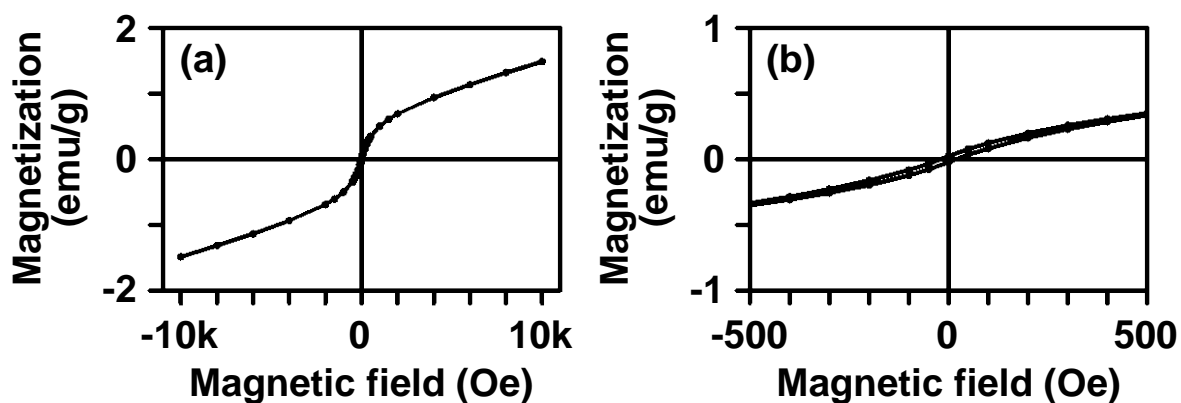


Fig. S6 (a) Magnetization curve at 300 K for the amorphous calcium iron phosphate spheres (Groups S+L) fabricated from the CaP reaction mixture with a 20.0 mM concentration of ferrous ions without added NaOH. (b) The same data as (a) magnified around the origin.

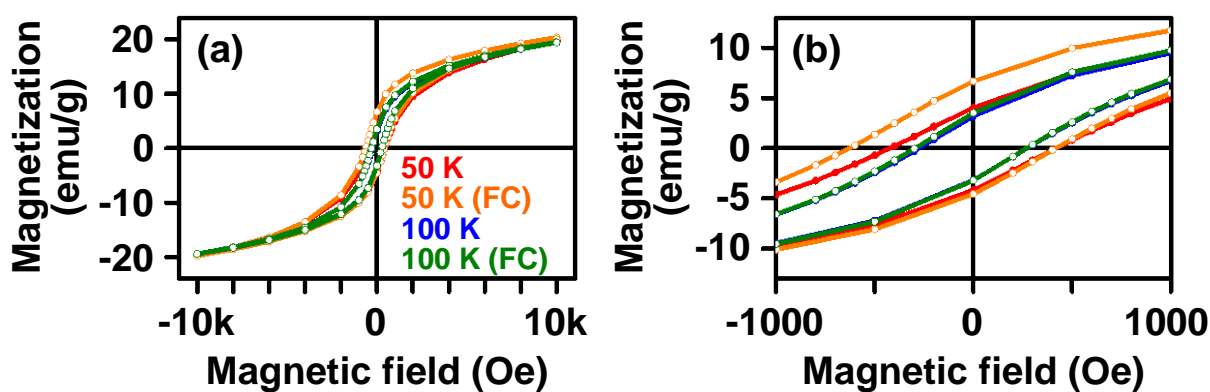


Fig. S7 (a) Magnetization curves at 50 and 100 K for CaP-based magnetic spheres: normal curves (zero field cooled) and FC (10 kOe field cooled) curves. (b) The same data as (a) magnified around the origin.

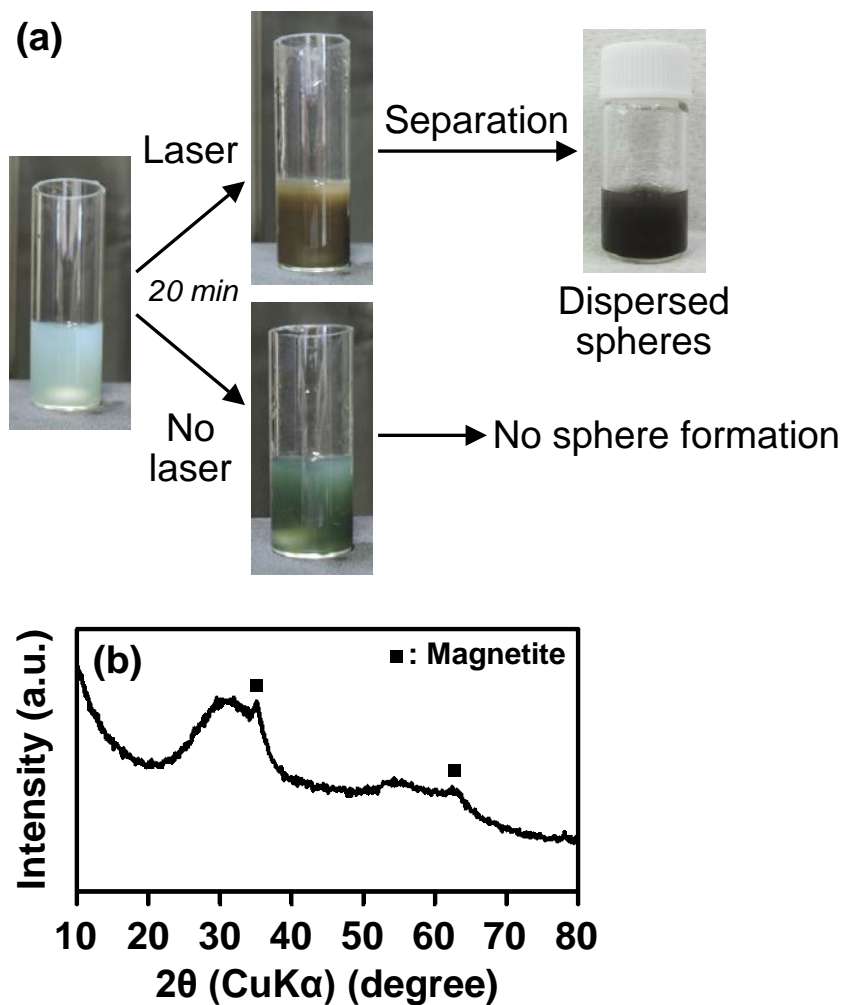


Fig. S8 (a) Photos of the reaction solution at each step of the process, one of which was processed with stirring alone for 20 min (i.e., no laser irradiation). The CaP reaction mixture supplemented with a 20.0 mM concentration of ferrous ions and a 25.0 mM concentration of NaOH was used. (b) XRD pattern of the as-collected precipitates formed in the reaction mixture stirred without laser irradiation.

Table S1. Effect of irradiation time, laser fluence, and concentration of the light-absorbing agents on sphere formation (results of SEM observations)

(a) Effect of irradiation time (200 mJ/pulse/cm², Fe(II) or Fe (III): 5 mM)

Irradiation time (min)	0	5	10	15	20	30
Ferrous ion: Fe(II)	×	×	S	S+L	S+L	S+L
Ferric ion: Fe(III) ^a	×	×	S	S	S+L	S+L

(b) Effect of laser fluence (30 min, Fe(II) or Fe (III): 5 mM)

Laser fluence (mJ/pulse/cm ²)	67	133	200
Ferrous ion: Fe(II)	×	S	S+L
Ferric ion: Fe(III) ^a	×	S	S+L

(c) Effect of ferrous or ferric ion concentration (200 mJ/pulse/cm², 30 min)

Concentration (mM)	0	1.0	2.0	5.0	7.0	10.0	20.0
Ferrous ion: Fe(II) ^b	×	×	S	S+L	- ^c	S+L	S+L
Ferric ion: Fe(III) ^a	×	×	S	S+L	S	×	- ^c

^a From ref. 8.

^b From Table 1.

^c Data not obtained.

×: spheres were scarcely observed in either Group S or L (the majority consisted of irregularly shaped precipitates).

S and L: a sphere assemblage without irregularly shaped precipitates was observed in Groups S and L, respectively.