Electronic Supplementary Information

A physicochemical process for fabricating submicrometer hollow fluorescent spheres of Tb^{3+}-incorporated calcium phosphate

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Experimental

Preparation of CaP-1. Carbon nanopowders (0.3 g, Aldrich) and HAp nanopowders (1.5 g, Taihei Chemical Industrial Co., Ltd.) were mixed by mechanical milling in a planetary ball mill (Fritsch, type P-6) at 600 rpm (20 *g*) for 10 min. The obtained mixed powder was **CaP-1**.

Preparation of CaP-2. Powders of **CaP-1** (0.005 g) were dispersed into 4 mL of ethanol in a glass vessel. After ultrasonication, pulsed laser irradiation was immediately performed using the output of the third harmonic (355 nm) of a Nd:YAG laser (Quanta-Ray LAB-150-30, Spectra-Physics) operated at 30 Hz with a fluence of 200 mJ/pulse/cm^2 (an output power of 3 W), with stirring the dispersion. The laser beam possessed an output diameter of 8 mm and was irradiated without focusing. After irradiation for 20 min, the product was collected by centrifugation (6000 rpm (3700 *g*), 10 min), washed with ultrapure water, and dispersed in ultrapure water. The solution was centrifuged three times at 1000 rpm (103 *g*) for 10 min, and the collected supernatant was

centrifuged at 2000 rpm (410 *g*) for 10 min. The collected sediment was **CaP-2**.

Preparation of CaP-3. Carbon nanopowders (0.00083 g) and HAp nanopowders (0.00417 g) were dispersed into 4 mL of ethanol in a glass vessel. After ultrasonication, pulsed laser irradiation and centrifugation were performed in a similar manner to the procedure for **CaP-2**. The collected sediment was **CaP-3**.

Preparation of CaP-4. Powders of **CaP-1** (0.005 g) were dispersed into a 4-mL ethanol solution of terbium nitrate hexahydrate (5 mM) in a glass vessel. After ultrasonication, pulsed laser irradiation and centrifugation were immediately performed in a similar manner to the procedure for **CaP-2**. The collected sediment was **CaP-4**.

Preparation of CaP-5. Powders of **CaP-1** (0.005 g) were dispersed into a 4-mL ethanol solution of terbium nitrate hexahydrate (5 mM) in a glass vessel. After ultrasonication, the dispersion was stirred for 20 min without laser irradiation. The product was collected by centrifugation (6000 rpm (3700 *g*), 10 min), washed with ultrapure water, and collected again. The collected sediment was **CaP-5**.

Characterization. The obtained samples were mounted on a silicon substrate, and the morphology, chemical composition, and crystalline structure were examined by scanning electron microscopy (SEM; XL30, FEI), energy dispersive X-ray spectroscopy (EDX; Genesis2000, EDAX), X-ray diffractometry (XRD; M18X, MAC Science) with CuKα X-rays, and X-ray photoelectron spectroscopy (XPS; Axis Nova, Kratos). The micro and crystalline structure of the samples mounted on a thin carbon-coated copper grid were investigated by transmission electron microscopy and diffraction (TEM and TED; JEM-2010, JEOL). The fluorescence spectrum of **CaP-4** dispersed in distilled water was obtained by spectrofluorophotometer (RF-5300PC, Shimadzu).

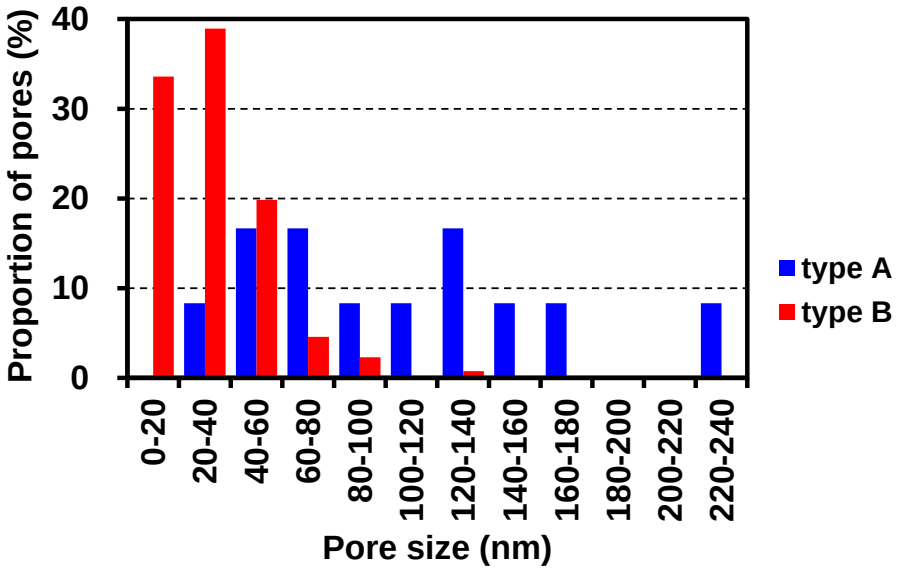

Fig. S1 Pore size (hollow diameter) distribution of single-hollow spheres (type A) and multi-hollow spheres (type B). Pore sizes were measured on TEM images for total 12 single-hollow spheres (type A) and 38 multi-hollow spheres (type B).

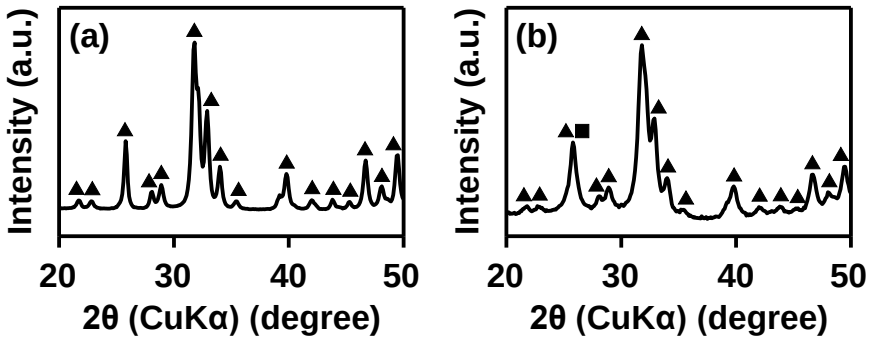

Fig. S2 XRD analysis of (a) raw HAp and (b) **CaP-1**. ▲: HAp, ■: graphite.

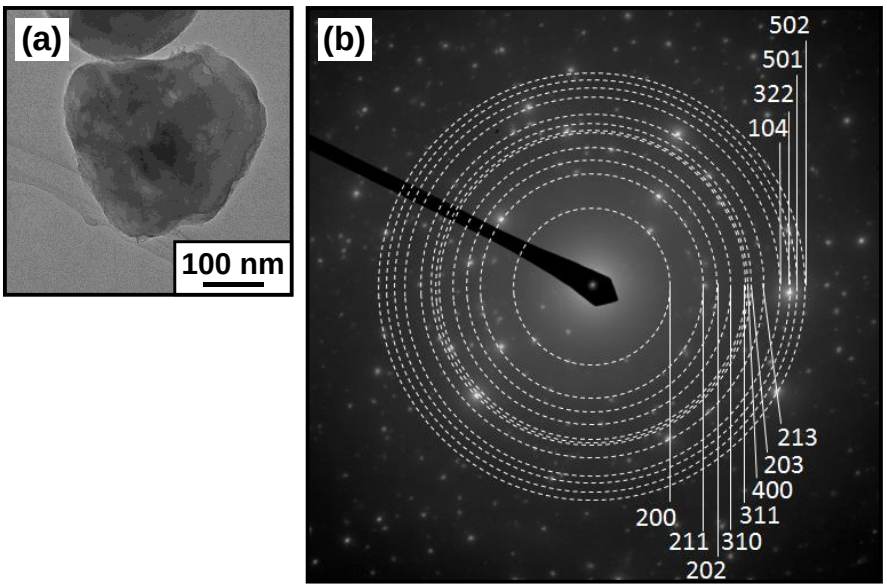

Fig. S3 (a) TEM and (b) TED images of inadequately spheroidized agglomerates observed as a residual dross in **CaP-2**. Most of the discrete spots in TED were indexed as the planes of HAp.

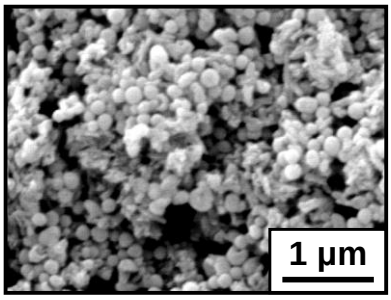

Fig. S4 SEM image of **CaP-3**.

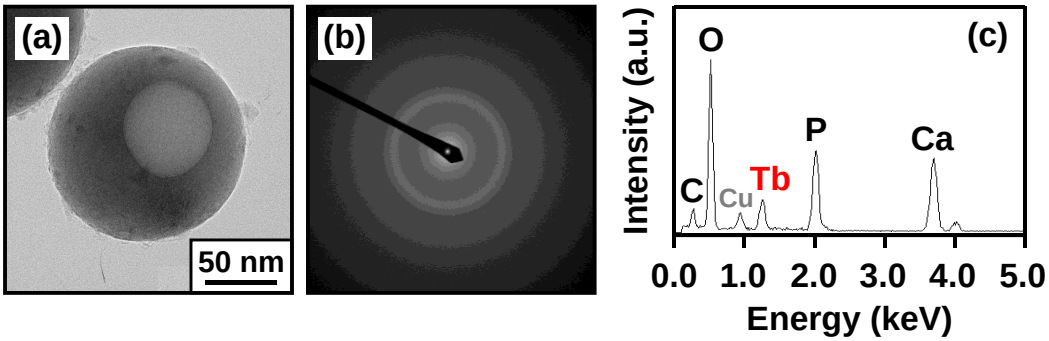

Fig. S5 (a) TEM and (b) TED images and (c) TEM–EDX spectrum of a sphere in **CaP-4**. The peak of Cu was derived from a copper grid for TEM observation.

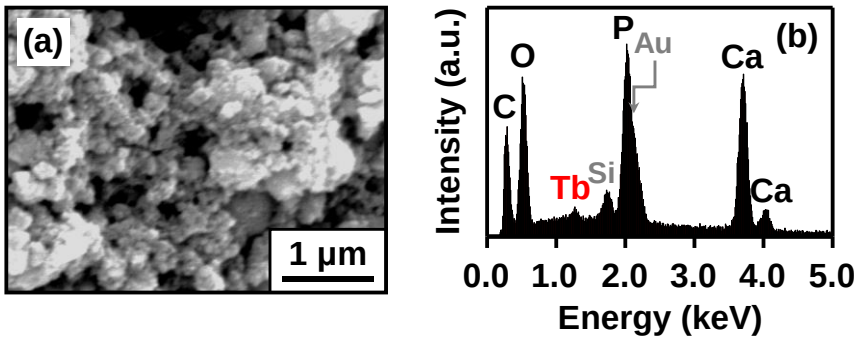

Fig. S6 (a) SEM image and (b) SEM–EDX spectrum of **CaP-5**.

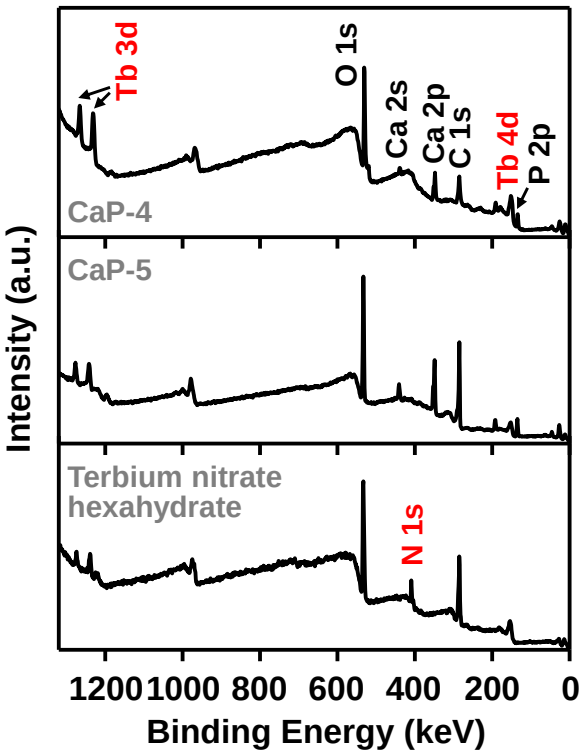

Fig. S7 XPS spectra of **CaP-4**, **CaP-5**, and terbium nitrate hexahydrate.