

Electronic Supplementary Information (ESI)

Self-organized formation of seven-rod bundle morphology for lanthanum Prussian blue analog microcrystals via a precipitation process

Fumiyuki Shiba,* Ren Nagata, and Yusuke Okawa

Department of Materials Science, Chiba University
1-33 Yayoicho, Inageku, Chiba 263-8522, Japan

*E-mail: shiba@faculty.chiba-u.jp

Evaluation for the elemental composition of the microcrystals

The elemental composition of the microcrystal was evaluated by atomic absorption spectrometry (AAS) for K^+ and Fe (of $[Fe(CN)_6]^{4-}$) and by colorimetry for La^{3+} . Accurately weighed KLa-HCF powder (25 mg) was dissolved to 2.5 mL of 1 mol/L HNO_3 and adjusted to 25 mL with distilled water using a volumetric flask (*test solution A*; for K^+ determination). The test solution A was further diluted with distilled water (HNO_3 concentration was adjusted to 0.1 mol/L): 2.5 mL of the test solution A was diluted to 50 mL with distilled water as *test solution B* for La^{3+} determination: 10 mL of the test solution B was further diluted to 20 mL as *test solution C* for $[Fe(CN)_6]^{4-}$ determination. (The test solutions B and C also contained 0.1 mol/L HNO_3 .)

Standard solutions for K^+ and La^{3+} determinations were prepared by diluting the commercially available standard solutions (1000 mg/L). Those for Fe were prepared by accurately dissolving $K_3[Fe(CN)_6]$ powder (and diluting) to take into account the interference due to the coordination of CN to Fe on the AAS measurement. All the standard solutions also contained 0.1 mol/L HNO_3 .

The AAS determination for K and Fe was conducted by Varian SpectrA55 with the acetylene/air flame. The absorption lines employed were $\lambda = 404.4$ nm and 248.3 nm for K and Fe, respectively.

On the colorimetry for La^{3+} , xylenol orange (XO) was used as the coloring agent in the presence of cetylpyridinium chloride (CPC).¹ Into each 20 mL volumetric flask that contains a certain amount of La^{3+} solution (standard solution or test solution B), 1 mL of XO aqueous solution (1 mmol/L), 2 mL of CPC aqueous solution (0.01 mol/L, also contains methanol in 20%), 4 mL of tris(hydroxymethyl)aminomethane buffer solution (0.25 mol/L, pH 8.65 adjusted by HCl) were introduced. Then distilled water was added

to adjust the volume to 20 mL. Absorbance at 630 nm was measured using a Shimadzu MultiSpec-1500 spectrophotometer.

The molar concentrations of the ionic component (K^+ , La^{3+} , and $[Fe(CN)_6]^{4-}$) in the test solution A were determined from the AAS and colorimetric results with the respective dilution ratio to identify their compositional ratio. The number of hydrated water molecules was calculated by the difference between the weight of the KLa-HCF powder dissolved in the test solution A and the total mass of the ionic components expected from the evaluated molar concentrations.

Angles of the side faces to the *c*-axis

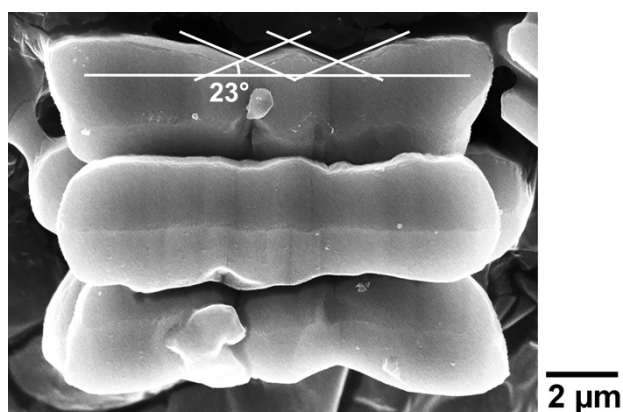


Fig. S1 FE-SEM observation from the corner direction of a rod's hexagon to evaluate the angles of side faces to the *c*-axis. Those around the concaves are about 23°, which is close to 27° for the $\{10\bar{1}1\}$ plane.

Effect of the reaction time on the morphology

The microcrystals at different times are shown in Fig. S2, where they are from the single batch of dispersion sampled at 1, 4, 12, and 30 min of preparation. The

preparation condition was the same as the procedure described in the experimental section in the main text (55°C). The images are virtually the same, suggesting the formation of KLa-HCF is completed within 1 min, and the morphology and size are maintained for at least 30 min.

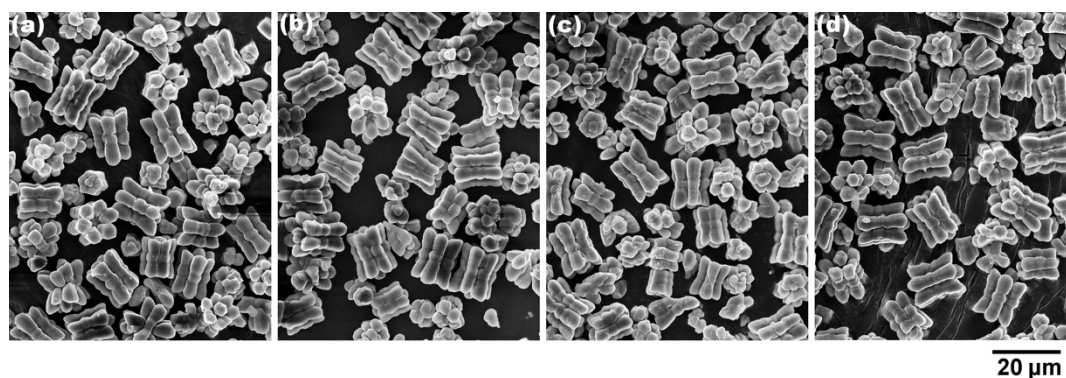


Fig. S2 FE-SEM images of KLa-HCF microcrystals sampled at (a) 1 min, (b) 4 min, (c) 12 min, and (d) 30 min from the ascorbic acid addition (reaction temperature 55°C).

Reference

1. M. Otomo and Y. Wakamatsu, *Bunseki Kagaku*, 1968, **17**, 764.