

Supporting Information

Wide-area multilayered self-assembly of fluorapatite nanorods vertically oriented on a substrate as a non-classical crystal growth

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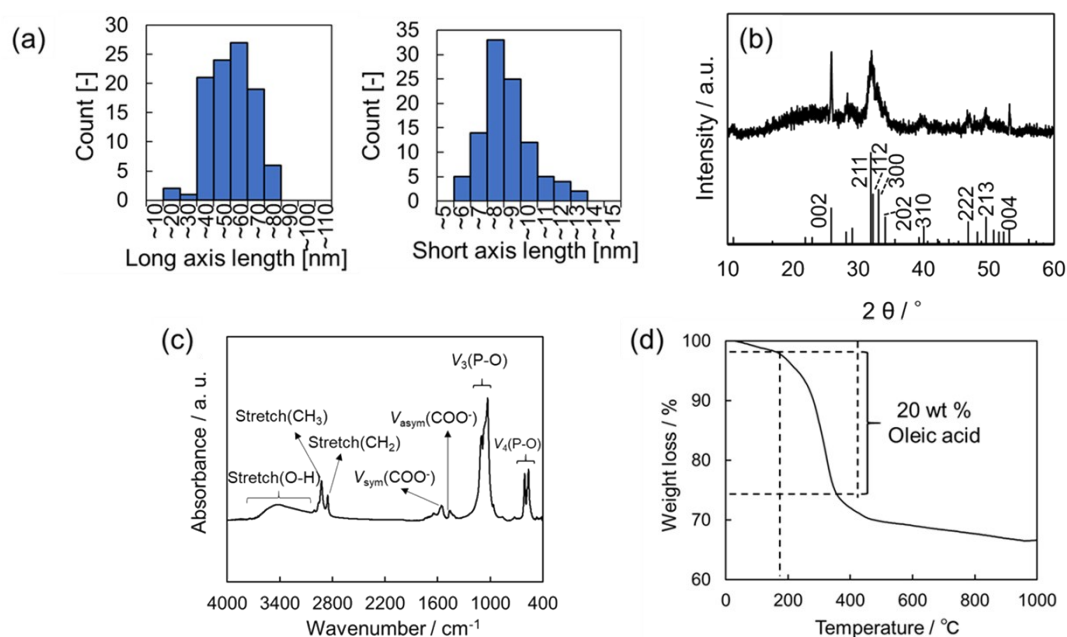


Fig. S1 Characterization of FA nanorods. (a) Histograms of length and width of nanorods estimated from TEM images ($n=100$), (b) a typical XRD pattern, (c) an FTIR spectrum, and (d) a TG curve for nanorods.

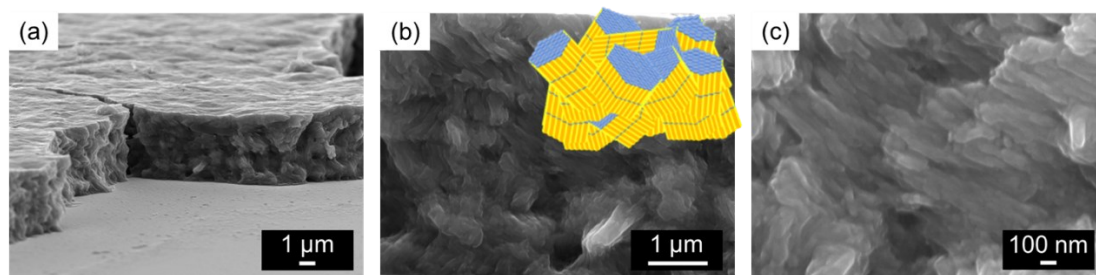


Fig. S2 SEM and schematic images of nanorod assembly prepared from the toluene dispersion. The concentration of FA nanorods was 2.8 g/dm^3 . (b, c) Enlarged images of the cross section of the film shown in (a). A typical domain in which FA nanorods are arranged in the same direction is shown in (c).

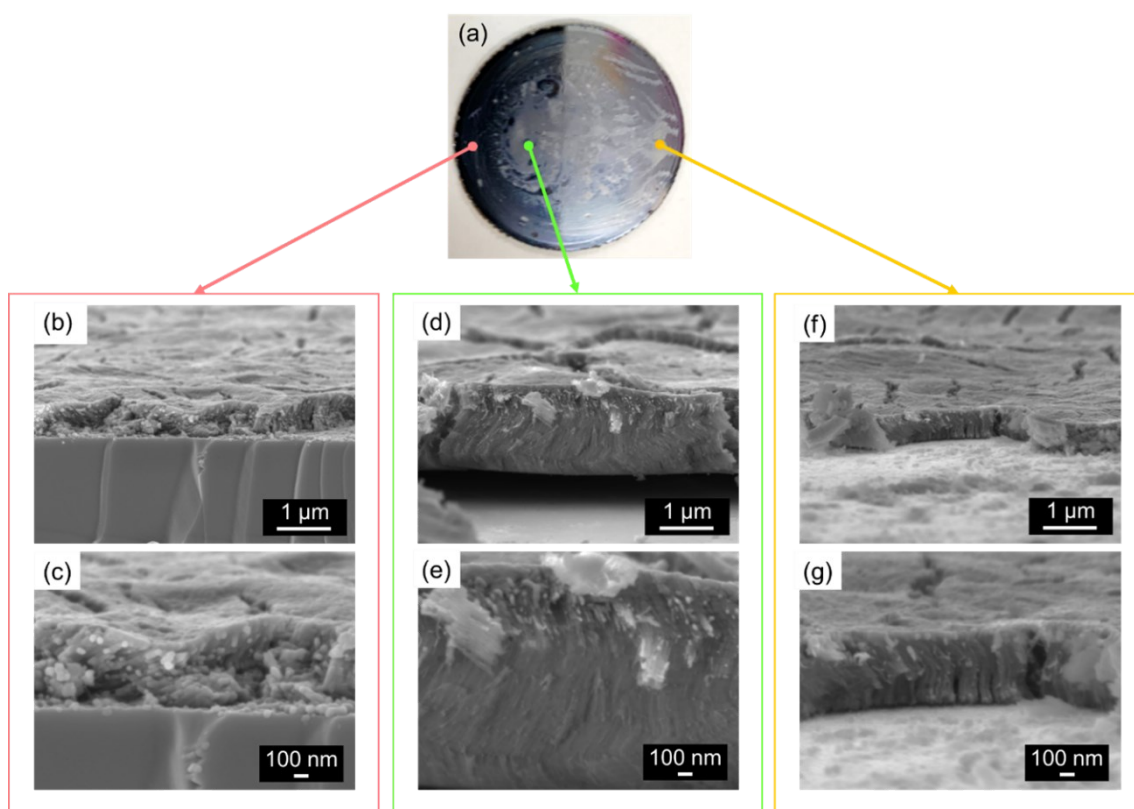


Fig. S3 Photographic (a) and SEM (b–g) images of nanorod assembly prepared from the hexane dispersion on various parts of a discoidal substrate. (c, e, g) Enlarged images of the cross sections shown in (b), (d), and (f), respectively. An inhomogeneous film consisting of FA nanorods was produced on the discoidal substrate. We observed vertical (d–g) and tilted (b, c) arrangements of FA nanorods in the film.

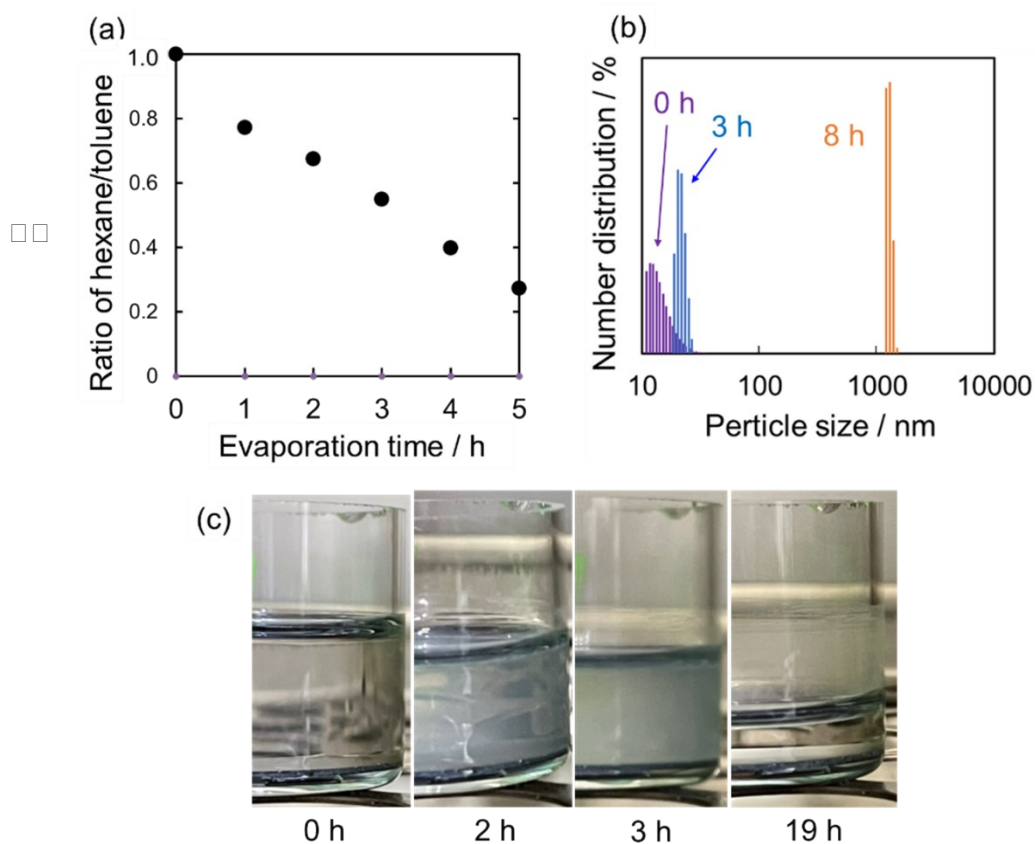


Fig. S4 The variation of the volume ratio of hexane/toluene in the mixture as a function of the evaporation time (a), the cluster size variation with the evaporation (b), and photo images of turbidity of the dispersion with the evaporation (c). The hexane/toluene ratio and the size distribution were estimated using the gas chromatography and DLS methods, respectively. The aggregation of the nanorods is suggested to proceed due to a gradual increase in the polarity with the selective evaporation of hexane according to the variation of the size distribution and an increase in turbidity of the dispersion. A clear liquid was obtained after the evaporation for 19 h. This suggests that the film deposition occurred before the liquid phase evaporated completely on the substrate.

When the initial ratio was smaller than 1:1, the agglomeration of nanorods immediately occurred. Thus, the steady deposition of the nanorods on a substrate was difficult in the dispersion. When the initial ratio was larger than 1:1, the dispersion state was not changed with a decrease in the hexane ratio to the standard value. Finally, we obtained the same structures of assembled nanorods from mixtures at the hexane-toluene ratios larger than 1:1.

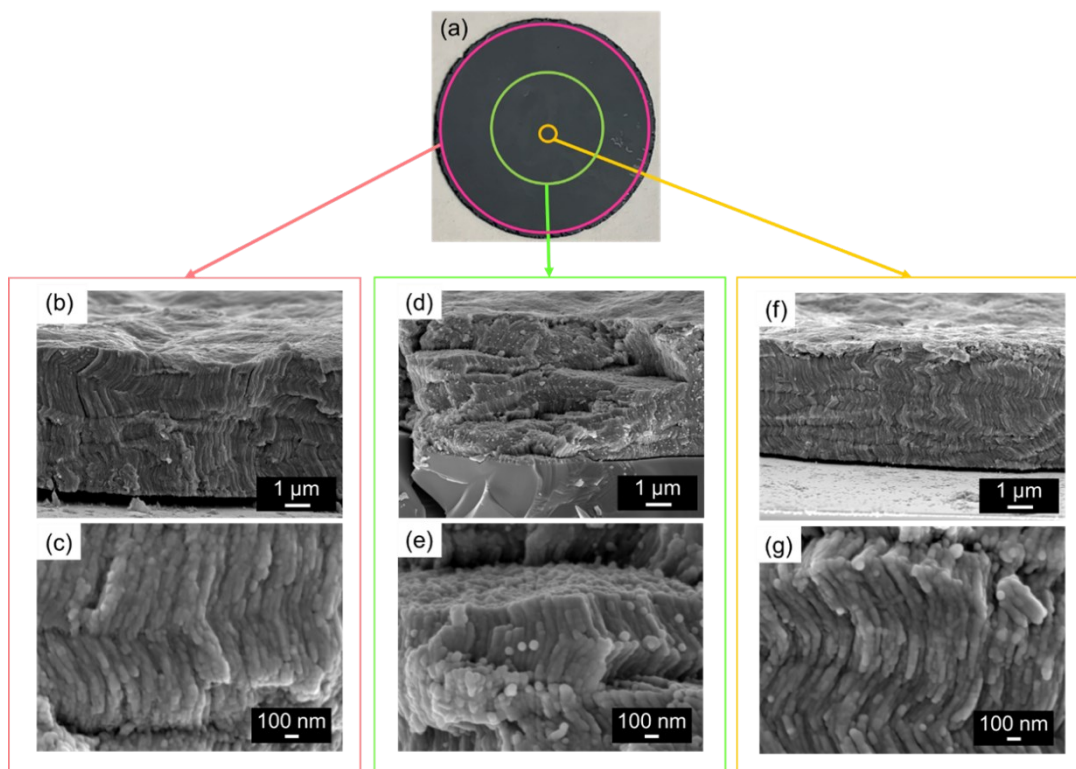


Fig. S5 Photographic (a) and SEM (b–g) images of nanorod assembly prepared from the toluene-hexane dispersion. dispersion on various parts of a discoidal substrate. (c, e, g) Enlarged images of the cross sections shown in (b), (d), and (f), respectively. Micrometer-thick films were homogeneously covered on a millimeter-scale area of the substrate. Here the multilayered accumulation of standing-up FA nanorods were found to produce the films. The fractured horizontal surfaces were partially observed at an incisal edge of the films (d).

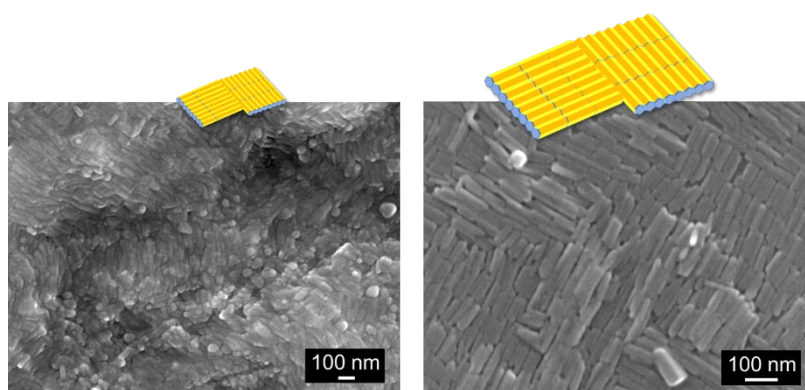


Fig. S6 SEM and schematic images of the top surface consisting of horizontal FA nanorods on the film.

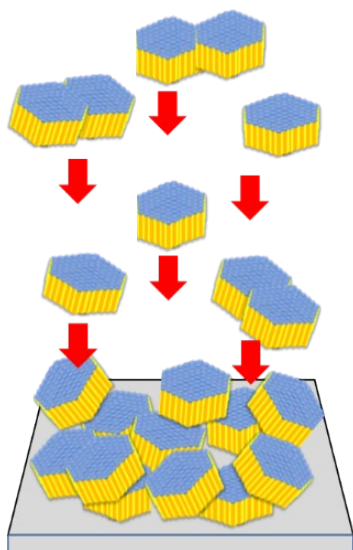


Fig. S7 Schematic illustration of a random accumulation process of FA nanorods. The clusters are stacked randomly through rapid sedimentation in toluene.

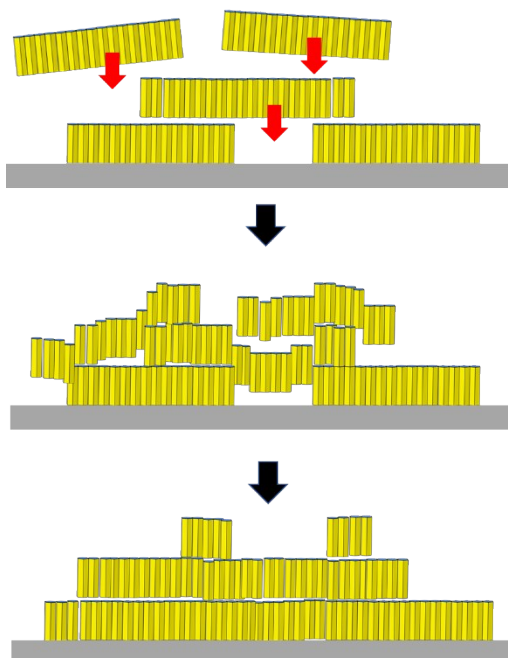


Fig. S8 Schematic illustration of the filling process of voids in multilayered accumulation by the sliding down of upper clusters.

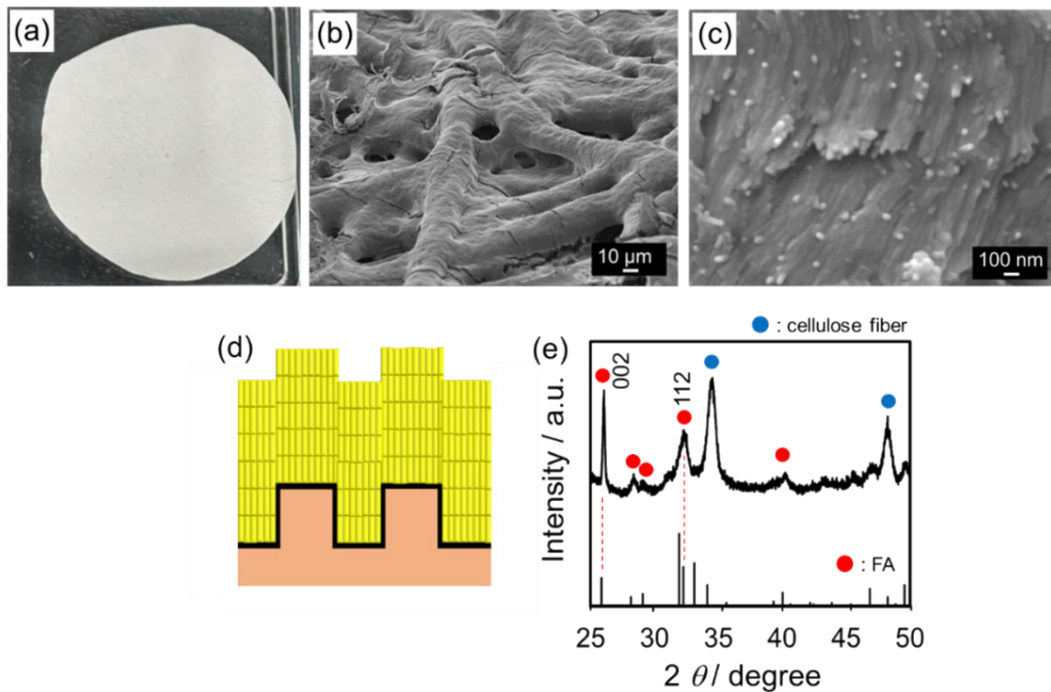


Fig. S9 Photographic (a) and SEM (b, c) images, schematic illustration (d), and a typical XRD pattern (e) of nanorod assembly prepared on a filter paper from the toluene-hexane dispersion. The surface (b) and the cross section (c, d) of the nanorod assembly.