Supporting Information

In situ preparation of hydroxyapatite in lamellar liquid crystals for joint lubrication and drug delivery

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Polarized optical microscopy (POM)

A small amount of sample was placed between two washed slides and left to rest at a constant temperature for 10 min. The photographs of the sample birefringence were observed and recorded by a polarizing light microscope (DMLP, Leica, Germany).

Small angle X-ray scattering (SAXS) measurements

The phase structure and lattice parameters were determined by SAXS. The sample was sealed in a cuvette and measured by a NanoSTAR small-angle X-ray scatterometer (Bruker, Germany), which produces copper Kα X-rays (nickel-tungsten baffle filter) with a wavelength of 1.542 Å from an X-ray generator (PW3830). The approximate distance between the sample and detector was 277.0 mm, and the sample was exposed for 10 minutes.

Rheological measurements

The rheological properties of the HAP/LLCs were evaluated on a Haake RheoStress 600 rheometer (Germany) with a cone-plate sensing system (Ti; diameter 35 mm; cone angle: 1°), maintained at a constant temperature (25 ± 1 °C) using a HAAKE DC10 circulating water bath. The samples were first tested by fixing the oscillation frequency at 1.0 Hz and stress sweeping in the range of 0.01-1000 Pa shear stress. Subsequently, the shear stress of 1 Pa was selected in the linear viscoelastic region, and the shear frequency was set to 0.01 - 100 Hz for the frequency sweep. The viscosity of the samples was tested by steady-state shear in CR mode. The structural recovery properties of HAP/LLCs were measured continuously in steps at high shear rates of 100 s^{-1} and low shear rates of 0.1 s^{-1}.

X-ray photoelectron spectrometer (XPS) analysis

After the friction test, the test discs were ultrasonically cleaned with petroleum ether and acetone. The chemical state of the characteristic elements on the abrasion surface was analyzed by the X-ray photoelectron spectrometer (XPS, ESCALAB250Xi, ThermoFisher Scientific), and the Al-Kα excitation source was selected with a binding energy of 29.35 eV and a binding energy measurement accuracy of ± 0.3 eV. The C1s binding energy of 284.8 eV was used as the internal standard.

Drug release study

The drug release study was performed by the dialysis membrane diffusion method. 0.5 g of the drug-loaded HAP/LLCs with a loading capacity of 20 mg g^{-1} was placed in a dialysis bag (3500, 44 mm), which was then closed and immersed in 50 mL of pH = 7.0 PBS solution in a water bath (25 ± 1 °C). A certain amount of dialysate was taken from outside the bag and supplemented with an equal amount of fresh PBS solution at regular intervals. The absorbance *A* was measured by UV 2500 spectrophotometer, and its cumulative drug release was calculated until *A* remained constant, which was considered as reaching diffusion equilibrium.

For the drug released measurement during friction, the friction pair was first placed in a dialysis bag and then fixed to the bottom fixture, and a PVC plastic spacer was placed between the fixture and the dialysis bag to prevent the bag from breaking during friction. 0.5 g of the drug-loaded HAP/LLCs with a loading capacity of 20 mg g^{-1} was added to the slider. Finally, 50 mL of pH = 7.0 PBS solution was added. The drug released during friction was tested at room temperature (25 °C) with different loads and frequencies. A certain amount of dialysate was taken from the outside of the dialysis bag and supplemented with an equal amount of fresh PBS solution at certain time intervals for12 h. The absorbance *A* was measured by UV 2500 UV spectrophotometer, and the cumulative drug release was calculated.

***In vitro* cell cytotoxicity**

The HAP/LLCs and the drug-loaded HAP/LLCs were pretreated using the extraction method. 1.0 g of HAP/LLCs and 1.0 g of drug-loaded HAP/LLCs with a concentration of 20 mg g^{-1} of ibuprofen were placed in 5 mL of sterile standard 1×PBS for 24 h, fully infiltrated. Then the corresponding extracts were extracted and diluted sequentially to 20, 10 mg mL^{-1} (high concentration) and 0.5, 0.1, 0.05 mg mL^{-1} (low concentration). Human-derived hepatocytes (L02) were selected, and the corresponding extracts were subjected to in vitro cytotoxicity studies using the MTT method. The cell suspension was diluted and inoculated into 96 plates at a density of 5000 cells per well, incubated in an incubator at 37°C for 24 h. Different concentrations of the extract were added to

each well; the medium containing MTT was added at 24 h and 48 h, respectively, and continued in the incubator for 4 h. The supernatant was aspirated, added 100 μL of DMSO to each well and shaken well. The absorbance value A of each well was measured at OD 570 nm by the enzyme-linked immunoassay instrument and calculated the cell viability.

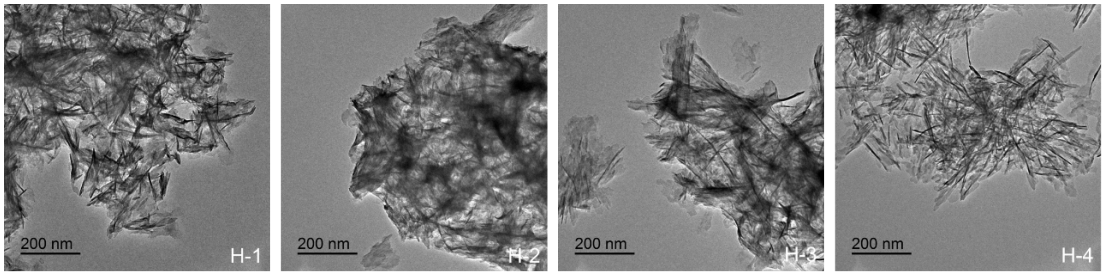

Fig. S1. TEM images of HAP

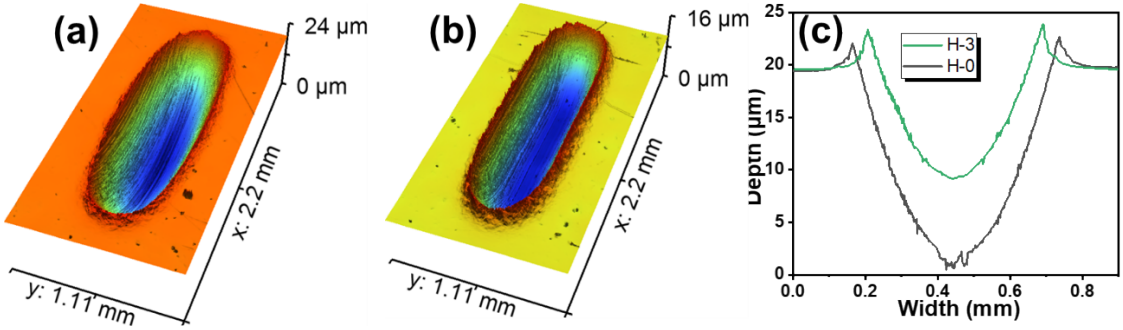

Fig. S2. (a, b) Optical microscopy images of the worn surfaces and (c) wear depth curves of the HAP/LLCs. (load, 30 N; frequency, 2 Hz; duration, 30 min; temperature, 25 °C).

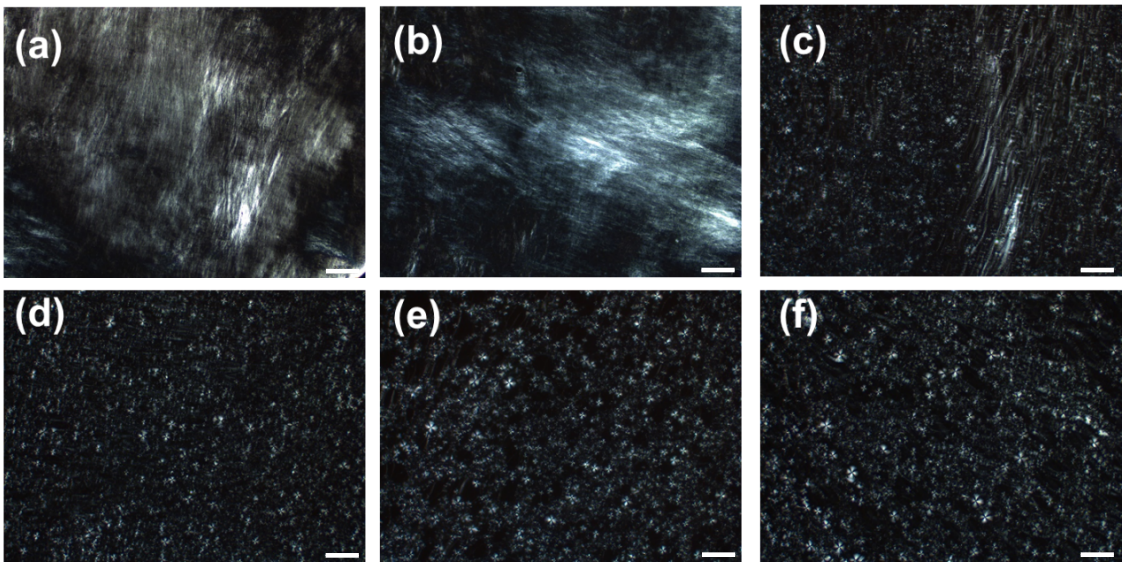

Fig. S3. POM images of the HAP/LLCs (per gram) loaded with different concentrations of ibuprofen; H-3, Tween 85: Tween 80: H_2O = 0.56: 0.14: 0.3. (a) 10 mg; (b) 20 mg; (c) 30 mg; (d) 40 mg; (e) 45 mg; (f) 50 mg. Scale bar = 50 μm.

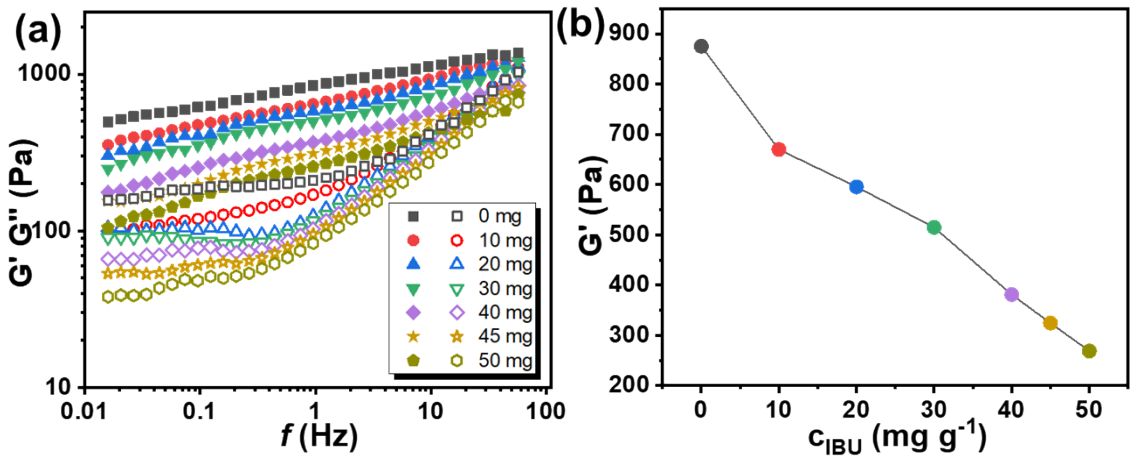

Fig. S4. (a) Frequency sweep curves of the HAP/LLCs (per gram) loaded with different concentrations of ibuprofen, H-3, Tween 85: Tween 80: H_2O = 0.56: 0.14: 0.3; (b) The elastic modulus G' of the drug-loaded HAP/LLCs varied with the concentration of ibuprofen; 1 Pa; 1 Hz.

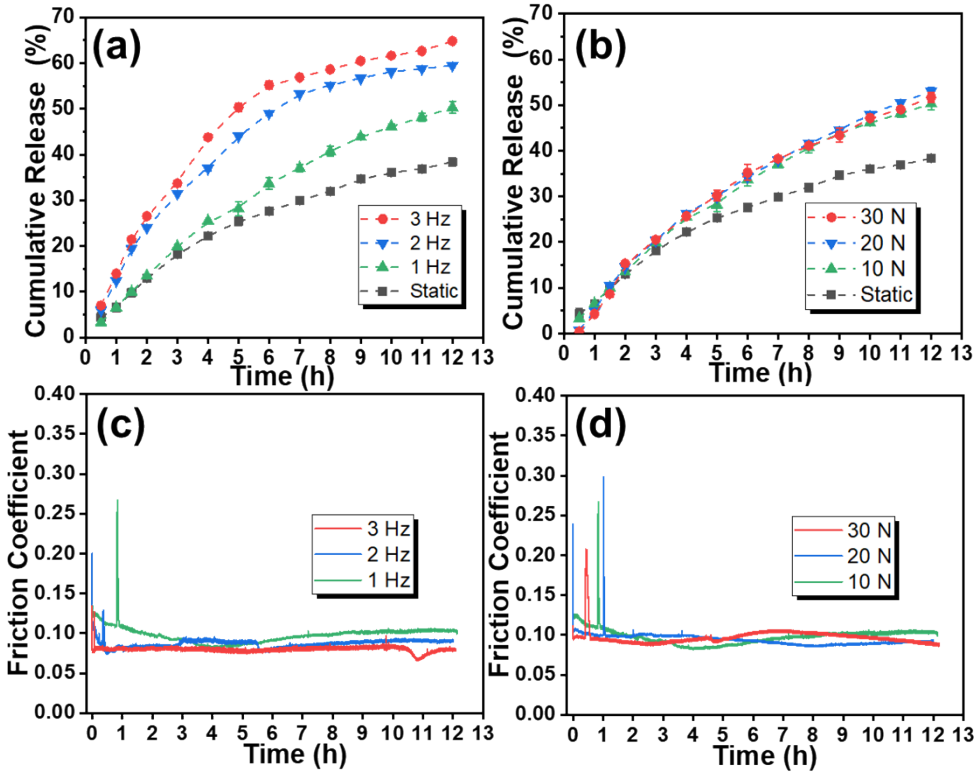

Fig. S5. Cumulative release profiles of ibuprofen at (a) different frequencies, constant load, 10 N; (b) different loads, constant frequency, 1 Hz; friction coefficient curves with time of the drug-loaded HAP/LLCs (S3) at (c) different frequencies, constant load, 10 N; (d) different loads, constant frequency, 1 Hz; Tween 85: Tween 80: H_2O = 0.56: 0.14: 0.3.

Table S1. The cumulative release of ibuprofen at 12 h

	S7	**S8**	**S9**	**S10**
static	24.7%	28.4%	38.4%	49.6%
10 N; 1 Hz	39.0%	45.7%	50.2%	58.1%

Table S2. Cumulative release of ibuprofen at different frequencies (12 h)

	LLCs	**HAP/LLCs**
10 N; 1 Hz	45.6%	50.2%
10 N; 2 Hz	56.8%	59.5%
10 N; 3 Hz	60.9%	64.8%

Table S3. Cumulative release of ibuprofen under different loads (12 h)

	LLCs	**HAP/LLCs**
10 N; 1 Hz	**45.6%**	**50.2%**
20 N; 1 Hz	**43.4%**	**53.1%**
30 N; 1 Hz	**41.7%**	**51.7%**

LLCs: Tween 85/Tween 80/H_2O lamellar liquid crystals.

HAP/LLCs: HAP/Tween 85/Tween 80/H_2O lamellar liquid crystals, HAP: 3.0 mM.