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Collagen fibers with tuned wetting properties for dual separation of oil-in-water and water-in-oil emulsion

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Experimental section

Materials

Collagen fibers (CFs) were provided by the National Engineering Research Center of Clean Technology in Leather Industry (China), which were prepared from cattle hides. Kerosene was obtained from Tianjin Hengxin Chemical Reagents Factory (China). Pump oil was purchased from Tongyi Petroleum Chemical Co., Ltd (China). Titanium sulfate ($Ti(SO_4)_2$) was provided by Sinopharm Chemical Reagent Co., Ltd (China). Zirconium sulfate tetrahydrate ($Zr(SO_4)_2{\cdot}4H_20$), ferric sulfate ($Fe_2(SO_4)_3{\cdot}XH_2O$), sodium dodecylbenzene sulfonate (SDBS), span80, olive oil and petroleum ether were analytical grade.

CFs-Zr fabrication[1]

15 g of CFs was immersed in 200 mL of deionized water at room temperature for 24 h. Then, 200 mL of $Zr(SO_4)_2$ solution (0.25 mol L^{-1}) was added in the above mixture, followed by adjusting the pH to 1.8-2.0, with constant stirring at 30°C for 4.0 h. After this, the pH of the resultant mixture was adjusted to 4.0-4.5 within 2.0 h, and kept constant stirring at 40°C for 4.0 h. Subsequently, the obtained intermediates were filtrated, fully rinsed with deionized water and ethanol, dried, and then the CFs-Zr was obtained. A series of composites, denoted as CFs-Zr_1, CFs-Zr_2, CFs-Zr_3 and CFs-Zr_4, respectively, were also synthesized according to the above procedure except that the concentrations of $Zr(SO_4)_2$ solutions were 0.05, 0.1, 0.15 and 0.2 mol L^{-1}, respectively. In addition, the preparation procedures of CFs-Fe and CFs-Ti were

similar to those of CFs-Zr except that $Fe_2(SO_4)_3$ (0.25 mol L^{-1}) and $Ti(SO_4)_2$ (0.25 mol L^{-1}) solutions were used for the preparation of CFs-Fe and CFs-Ti, respectively.

Emulsion preparation

Three types of O/W nanoemulsions were prepared by adding dodecane, olive oil or pump oil into the SDBS solution (0.1 mg mL^{-1}) in the ratio of 1:100 (v/v) under vigorous stirring at 3000 rpm, followed by stirring at 3000 rpm for 1.0 h. Three types of W/O nanoemulsions were also obtained by dropping deionized water into n-dodecane (kerosene or petroleum ether) containing span 80 (3.0 g L^{-1}) in the ratio of 3:200 (v/v) under vigorous stirring at 3000 rpm, followed by stirring at 3000 rpm for 1.0 h. The detailed constituents of above emulsions were given in Table S1.

Table S1 The constituents of the O/W nanoemulsions (NE1-NE3) and W/O nanoemulsions (NE4-NE6).

	NE1	NE2	NE3	NE4	NE5	NE6
SDBS (g)	0.05	0.05	0.05	0	0	0
Span80 (g)	0	0	0	1.5	1.5	1.5
Deionized water (mL)	500	500	500	7.5	7.5	7.5
Dodecane (mL)	5.0	0	0	500	0	0
Olive oil (mL)	0	5.0	0	0	0	0
Pump oil (mL)	0	0	5.0	0	0	0
Kerosene (mL)	0	0	0	0	500	0
Petroleum ether (mL)	0	0	0	0	0	500

Emulsion separation

Emulsion separation was performed on a column separation apparatus, which was consisted of a feeding beaker, filtrate collector, peristaltic pump, plastic tubes and separation column (10.0 mm of inner diameter). 1.5 g of the CFs-Zr was packed into the column and the emulsion was then pumped into the column. The filtrates were collected and analyzed subsequently. The separation flux was calculated as $V/(t{\cdot}S)$, where t is the separation time, V and S are the volume of collected filtrate and the inner cross-section area of column, respectively. The used CFs-Zr was washed with ethanol and dried, and then reused for the next cycle of separation.

Characterization

The surface morphology and element composition of the samples were characterized by Field-emission Scanning Electron Microscopy (FESEM, Nova Nanosem 450, USA) equipped with X-ray energy dispersive spectroscopy (EDS). X-ray photoelectron spectroscopy (XPS, Thermo Scientific, Escalab250Xi, USA) was used for further analyzing the chemical composition of CFs and CFs-Zr. Fourier transform infrared (FTIR, Thermo Scientific Nicolet IS10) was used to identify the functional groups of CFs and CFs-Zr. All the contact angles were measured on a contact angle goniometer (Krüss, DSA30, Germany) and the volume of liquid in the measurements was 3.0 µL. The droplet size distribution of emulsions and filtrates was analyzed by dynamic light scattering (DLS) (Brook haven, NanoBrook, America). The oil content in filtrates of O/W emulsion was determined by an infrared photometer oil content analyzer (Oil 460, Beijing Chinainvent Instrument Co., Ltd) after extracted by C_2Cl_4. COD tester (HACH DRB200) was conducted to measure the organic content in filtrates. Water content of W/O emulsions and the corresponding filtrates was determined by a Coulometric Karl Fischer titrator (Wo Ye technology, S-300, China). The water-absorbing behaviors of CFs-Zr was observed using a stereomicroscope (Leica, M205 C, Germany).

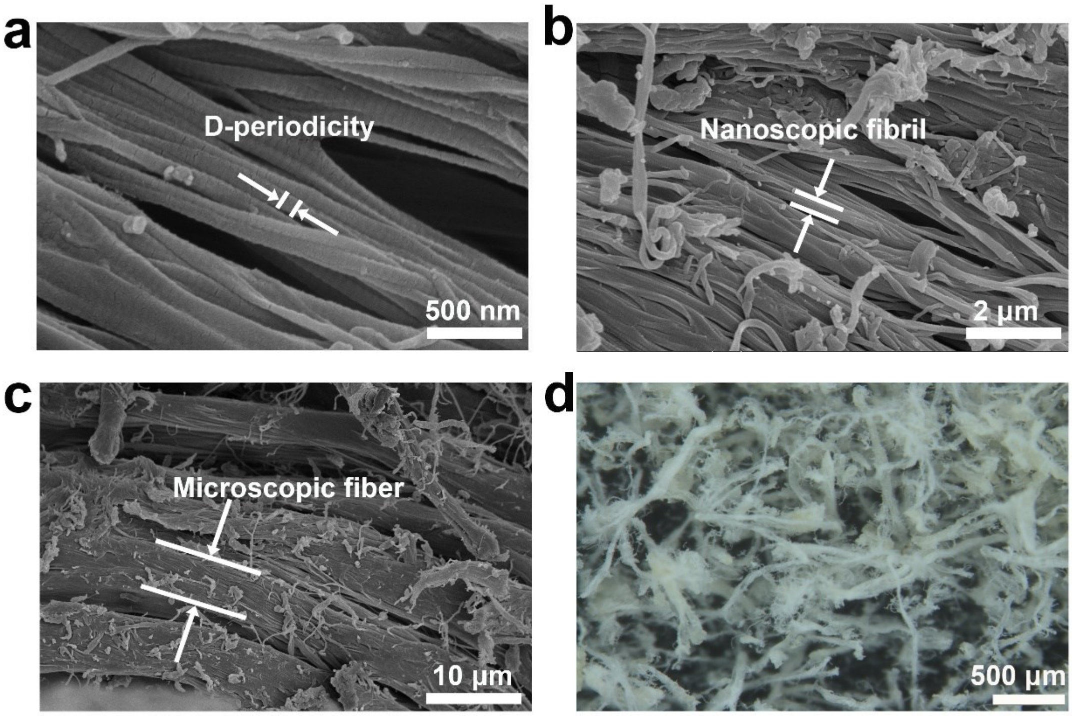

Fig. S1 FESEM images of CFs showing the D-periodicity ~67 nm (a), nanoscopic fibrils (b) and microscopic fibrils (c), optical microscopy image of CFs showing the 3D fibrous network (d).

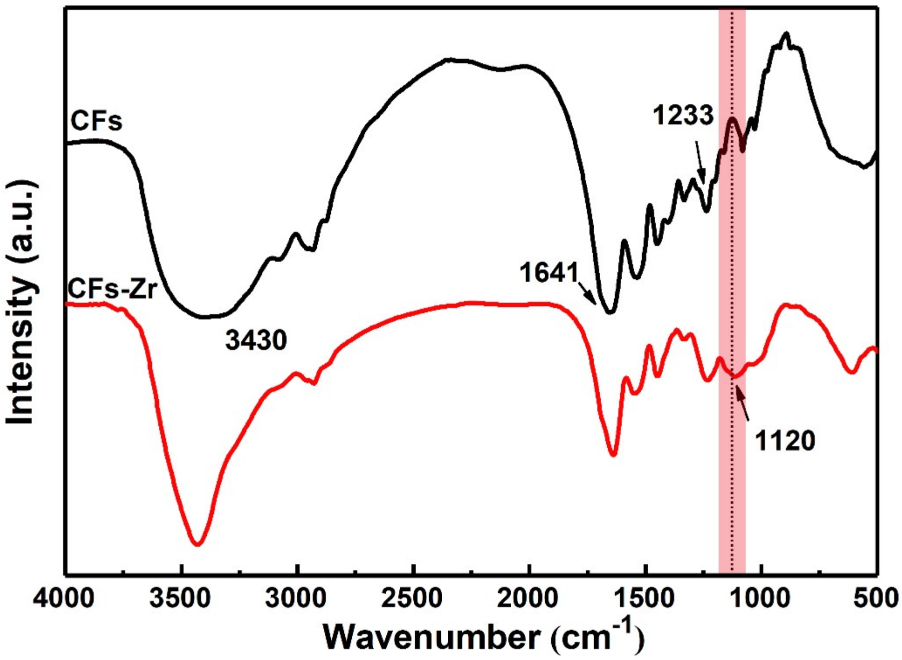

Fig. S2 FTIR spectra of the CFs and CFs-Zr.

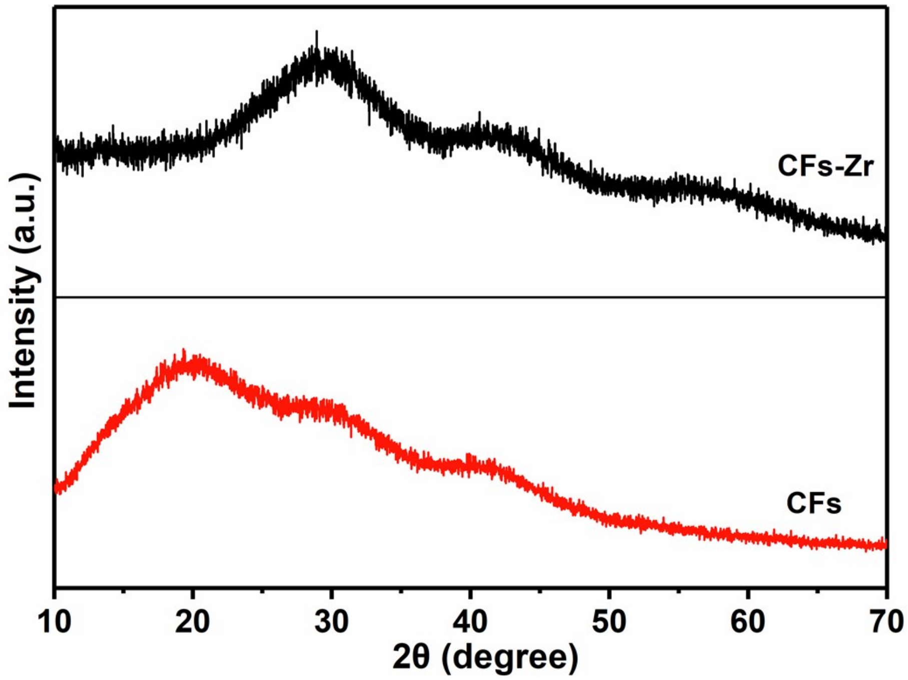

Fig. S3 XRD patterns of the CFs-Zr and CFs.

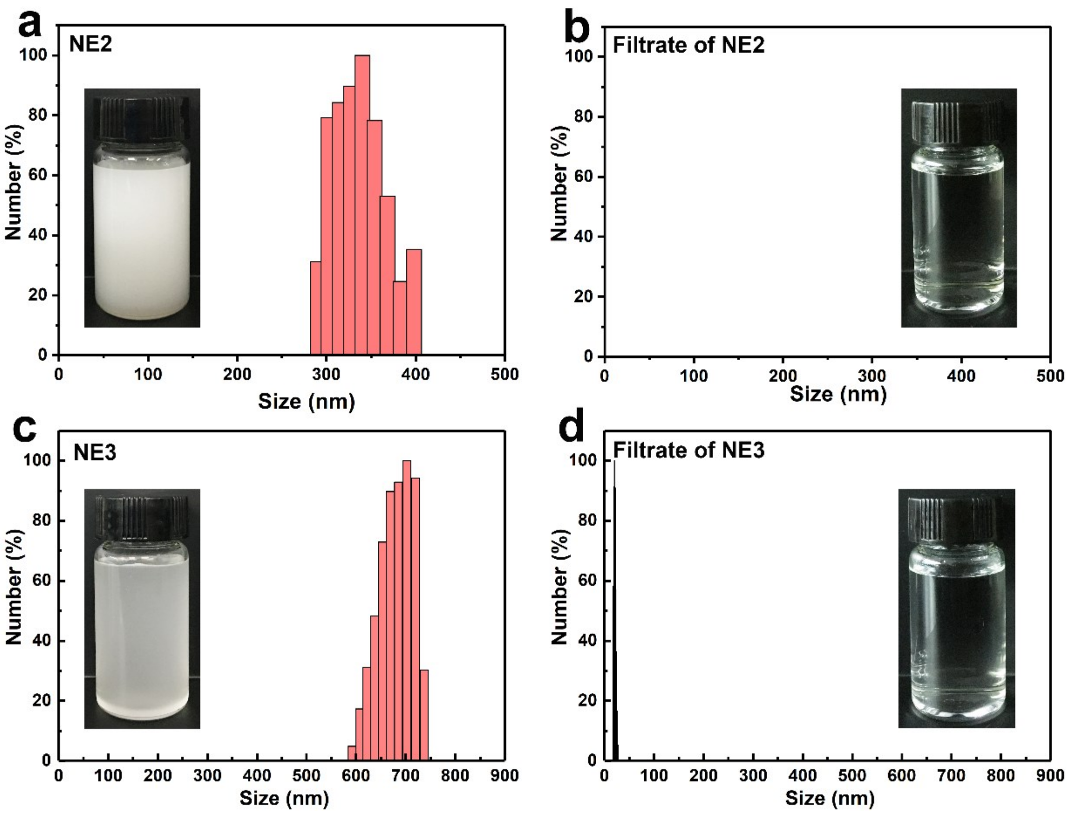

Fig. S4 DLS curves of NE2 before (a) and after (b) the separation by the CFs-Zr, DLS curves of NE3 before (c) and after (d) the separation by the CFs-Zr. The insets in a and b show the digital photographs of NE2 and the filtrate of NE2, respectively. The insets in c and d show the digital photographs of NE3 and the filtrate of NE3, respectively.

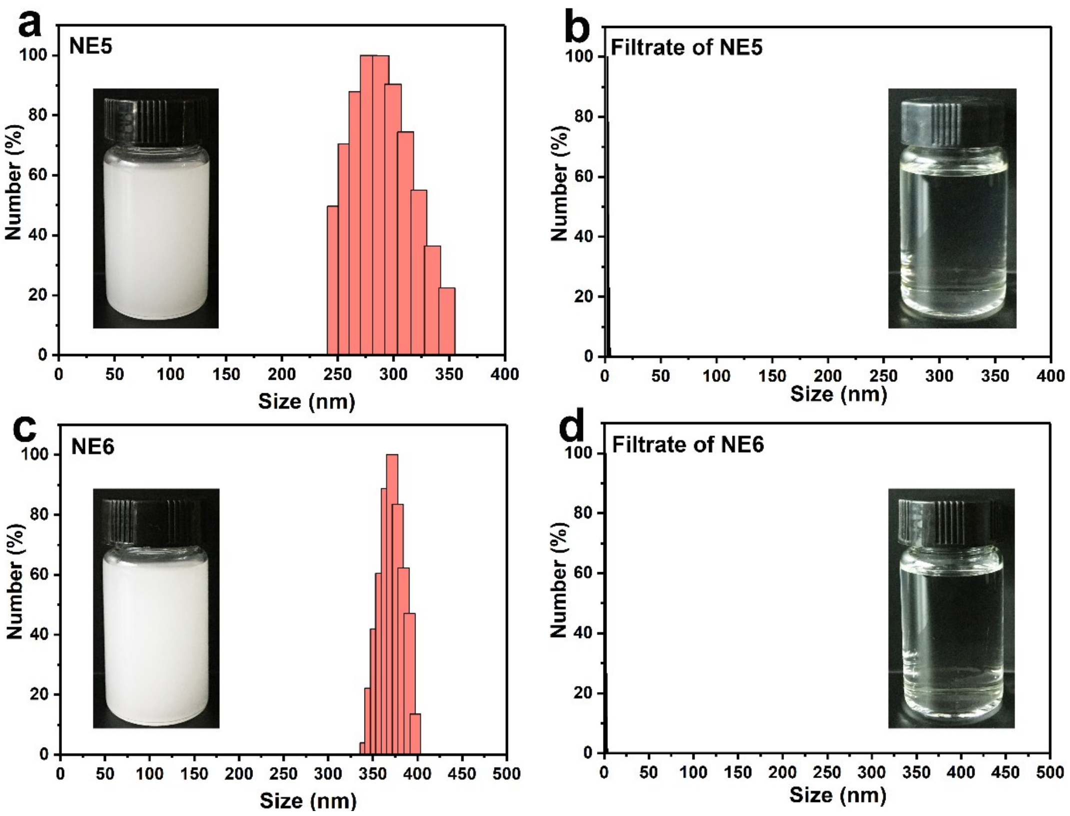

Fig. S5 DLS curves of NE5 before (a) and after (b) the separation by the CFs-Zr, DLS curves of NE6 before (c) and after (d) the separation by the CFs-Zr. The insets in a and b show the digital photographs of NE5 and the filtrate of NE5, respectively. The insets in c and d show the digital photographs of NE6 and the filtrate of NE6, respectively

Table S2 Comparison of separation performances between the CFs-Zr and other dual separation materials.

Materials	O/W emulsion	W/O emulsion	Separation condition	Reference
	Separation efficiency	**Separation efficiency**		
Janus graphene oxide sponges	100%	99.2%	Changing the flow direction of emulsions	2
Janus ceramic membrane	95%	99%	Changing-over the membrane	3
Janus cellulose membrane	>96.0%	>96.5%	Changing-over the membrane	4
3D hollow porous rape pollens	≤99.12%	>98.85%	Switching the wettability by the calcination and steam modification	5
Copolymer/SiO_2 coated filter paper	>99%	>99%	Switching the wettability by treating with acidic solution	6
PNIPAAm modified nylon membrane	>98%	>97.8%	Switching the wettability by the stimulation with thermo	7
Dually prewetted carbon black-coated membrane	>99.5%	>99.5%	Switching the wettability by pre-wetting with water or oil phase	8
CFs-Zr	≥99.9991%	≥99.9917%	Directly applied in emulsion separation	This work

Table S3 Dual separation performances of CFs-Fe and CFs-Ti.

Emulsion	**CFs-Fe**		**CFs-Ti**	
	Separation efficiency (%)	Separation flux (L m^{-2} h^{-1})	Separation efficiency (%)	Separation flux (L m^{-2} h^{-1})
NE1	99.9992	3057.3	99.999	1910.8
NE4	99.9925	3133.8	99.9904	1605.1

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