

Electronic Supplementary Material

Sustainable conversion regenerated cellulose into cellulose oleate by sonochemistry

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Contents

1. Fabrication of regenerated cellulose gelation	S1
2. Preparation of COEs by sonochemistry	S2
3. Crystalline structures of MCC and RC	S3
4. Esterification of RC and OA in the presence of DMAP and EDC·HCl	S4
5. Effects of various reaction conditions on the chemical structures of COEs....	S5
6. Comparing the chemical structure of pyridine with DMAP	S7
7. Morphologies of RCA and COEs	S7
8. Thermal stability of COEs	S8
9. Processable ability of COEs.....	S9
Reference	S10

1. Fabrication of regenerated cellulose gelation (RCG)

The typical procedures for fabricating RCG involve the dissolution/regeneration and then solvent exchange (Fig. S1). In brief, 0.648 g of microcrystalline cellulose (MCC) corresponding to 4 mmol of anhydroglucose units (AGU) was dissolved in sodium

hydroxide (NaOH) aqueous solution to obtain transparent cellulose solution (cellulose/NaOH/water = 2/5/95, w/w/v) based on a previously reported freezing/thawing method [1]. Then, the obtained fresh cellulose solution was instilled into 100 mL of ethanol aqueous solution (75%, v/v) at 0 °C, which was further neutralized by adding hydrochloric acid (1 mol L⁻¹) and then washed with the same ethanol aqueous solution for 3 times to obtain **regenerated cellulose (RC) alcogel**. Subsequently, **RC alcogel** was further washed by the designated reaction solvent (including DMAc, DMSO, pyridine, and **chloroform**) to achieve a reactive precursor of RCG.

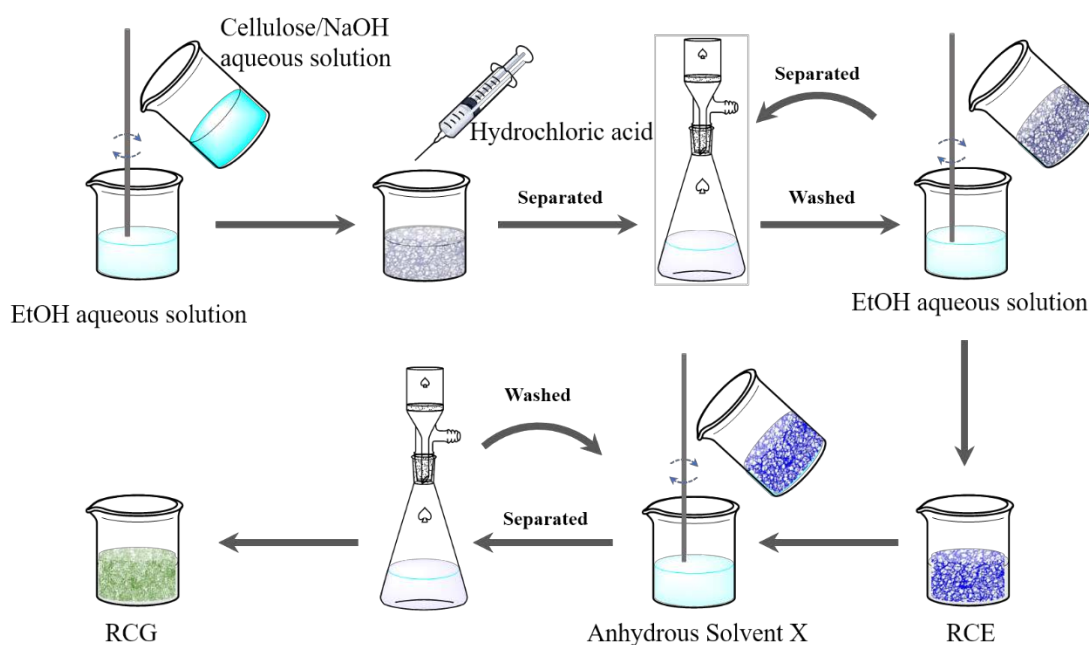


Fig. S1 Typical procedures for fabricating RCG by dissolution/regeneration and solvent exchange. Solvent X can be DMAc, DMSO, **chloroform**, and pyridine based on different reactions.

2. Preparation of COEs by sonochemistry

Various COEs were prepared by tuning the ultrasonic intensity, reaction time, and molar ratios of OA/AGU, the detailed reaction parameters were listed in Table S1.

Table S1 Heterogenous preparation of cellulose oleates (COEs) by sonochemistry method.

Samples	Solvent	AGU/mmol	OA/mmol	EDC·HCl/mmol	UI/(W m ⁻²)	RT/h
COE-1	DMAc	4	24	28.8	0	4
COE-2	DMAc	4	24	28.8	150	4
COE-3	DMAc	4	24	28.8	200	4
COE-4	DMAc	4	24	28.8	300	4
COE-5	DMAc	4	12	14.4	300	4
COE-6	DMAc	4	18	21.6	300	4
COE-7	DMAc	4	30	36.0	300	4
COE-8	DMAc	4	36	43.2	300	4
COE-9	DMAc	4	24	28.8	300	1
COE-10	DMAc	4	24	28.8	300	2
COE-11	DMAc	4	24	28.8	300	6
COE-12	DMAc	4	24	28.8	300	8
COE-13	<i>chloroform</i>	4	24	28.8	300	6
COE-14	<i>DMSO</i>	4	24	28.8	300	6
COE-15	<i>Pyridine</i>	4	24	28.8	300	6

Note: for every reaction, 0.2 mmol of DMAP and 1.2 mol EDC·HCl per mole of OA were employed as catalysts. The abbreviations of UI and RT represented ultrasonic intensity and reaction time, respectively.

3. Crystalline structures of MCC and RC

In the WAXD pattern of MCC, conspicuous diffraction peaks appeared at 14.9°, 16.2°, 22.5°, and 34.7° were observed (Fig. S2a), which corresponded to (101), (10 $\bar{1}$), (002), and (040) lattice planes of cellulose I, respectively [2, 3]. By contrast, only a broad peak was detected at 20° corresponding to amorphous structures in the WAXD diffractogram of RC alcogel (Fig. S2b). Similar results were also obtained according to the POM observation, an evident birefringent speckle caused by cellulose crystals was observed in the POM image of MCC (Fig. S2c), but no visible bright domain was found in the POM image of RC alcogel (Fig. S2d).

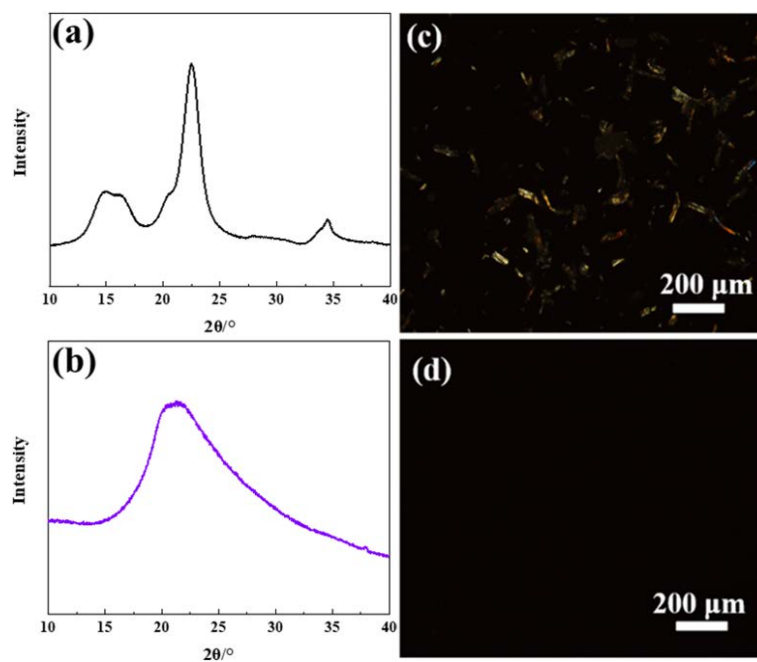
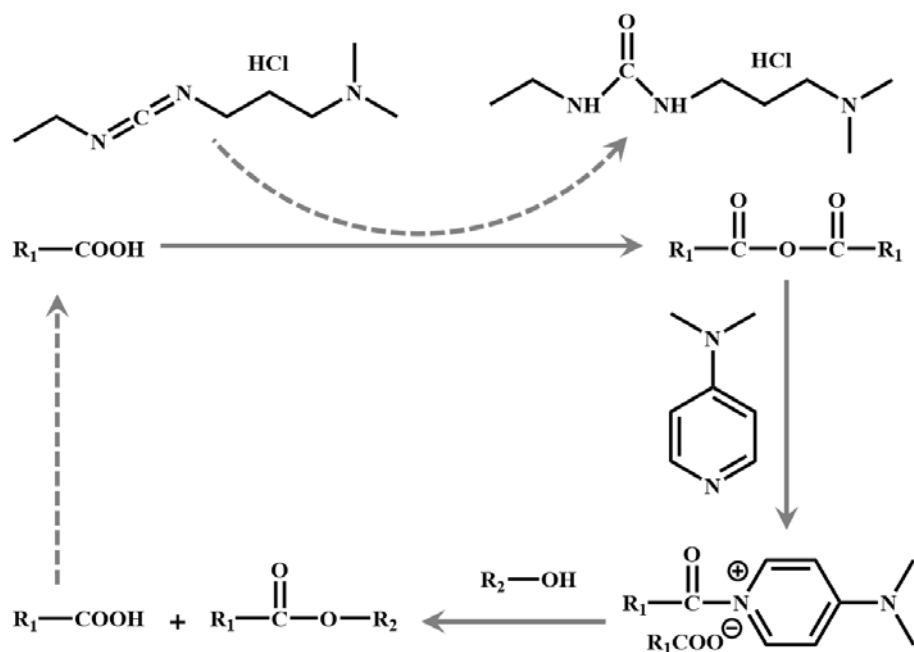


Fig. S2 Effects of dissolution/regeneration on the structures of cellulose. (a) WAXD diffractogram of MCC; (b) WAXD diffractogram of **RC alcogel**; (c) POM image of MCC; (d) POM image of **RC alcogel**.

4. Esterification of RC and OA in the presence of DMAP and EDC·HCl



Scheme S1 Detailed reaction routes for the esterification of cellulose and carboxylic acid in the presence of DMAP and EDC·HCl.

5. Effects of various reaction conditions on the chemical structures of COEs

5.1 Ultrasonic intensity

Table S2 WI, DS, and yield of COEs prepared under different ultrasonic intensities (UI).

Samples	UI/(W m ⁻²)	WI/%	DS	Yield/%	W _{cellulose} /%
COE-1	0	162.6 ± 13.5	0.38 ± 0.08	27.6 ± 2.3	61.8 ± 5.0
COE-2	150	220.7 ± 10.8	0.74 ± 0.07	37.4 ± 1.8	45.3 ± 2.2
COE-3	200	302.0 ± 4.7	1.24 ± 0.03	51.2 ± 0.8	33.1 ± 0.5
COE-4	300	330.8 ± 8.5	1.42 ± 0.05	56.1 ± 1.4	30.2 ± 0.8

5.2 Molar ratios of OA/AGU

Table S3 WI, DS, and yield of COEs prepared under different molar ratios of OA/AGU.

Samples	OA/AGU/(mol/mol)	WI/%	DS	Yield/%	W _{cellulose} /%
COE-5	3	219.1 ± 7.7	0.73 ± 0.05	37.2 ± 1.3	45.7 ± 1.6
COE-6	4.5	299.9 ± 9.3	1.23 ± 0.06	50.8 ± 1.6	33.4 ± 1.0
COE-4	6	330.8 ± 8.5	1.42 ± 0.05	56.1 ± 1.4	30.2 ± 0.8
COE-7	7.5	354.9 ± 11.7	1.56 ± 0.07	60.2 ± 2.0	28.2 ± 0.9
COE-8	9	361.1 ± 4.6	1.60 ± 0.03	61.2 ± 0.8	27.7 ± 0.4

5.3 Reaction time

Table S4 WI, DS, and yield of COE prepared under different reaction times.

Samples	Reaction time/h	WI/%	DS	Yield/%	W _{cellulose} /%
COE-9	1	143.5 ± 10.1	0.27 ± 0.06	24.3 ± 1.7	69.9 ± 5.0
COE-10	2	241.8 ± 10.5	0.87 ± 0.06	41.0 ± 1.8	41.4 ± 1.8
COE-4	4	330.8 ± 8.5	1.42 ± 0.05	56.1 ± 1.4	30.2 ± 0.8
COE-11	6	351.9 ± 6.2	1.55 ± 0.04	59.7 ± 1.0	28.4 ± 0.5
COE-12	8	358.0 ± 6.2	1.58 ± 0.04	60.7 ± 1.1	27.9 ± 0.6

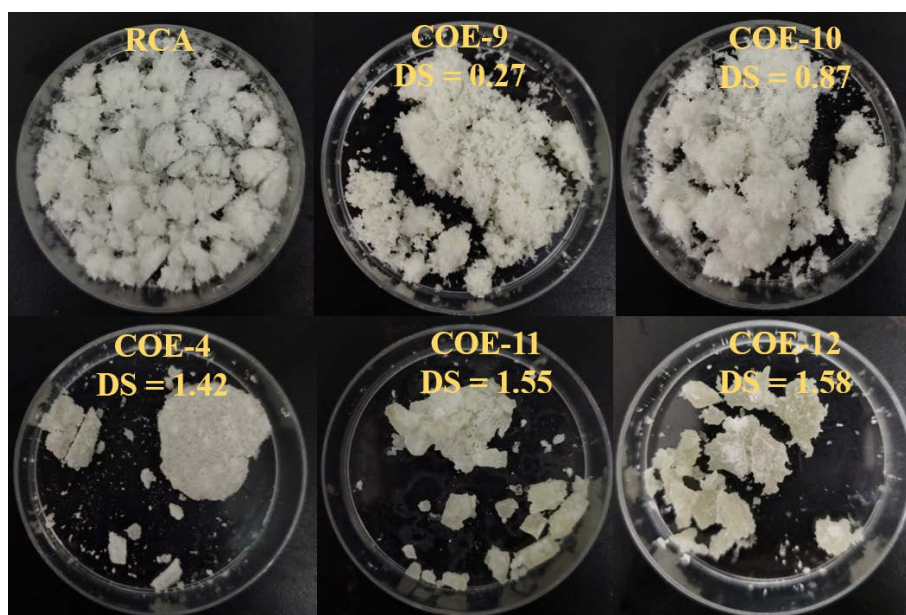


Fig. S3 Digital images of COEs prepared by reaction for different ultrasonic times.

5.4 Reaction solvents

Table S5 WI, DS, and yield of COE prepared in different solvents.

Samples	Solvents	WI/%	DS	Yield/%	$W_{cellulose}/\%$
COE-11	DMAc	351.9 ± 6.2	1.55 ± 0.04	59.7 ± 1.0	28.4 ± 0.5
COE-13	chloroform	280.3 ± 16.5	1.11 ± 0.10	47.5 ± 2.8	35.8 ± 2.1
COE-14	DMSO	339.0 ± 4.5	1.47 ± 0.03	57.5 ± 0.8	29.5 ± 0.4
COE-15	Pyridine	377.6 ± 10.3	1.70 ± 0.06	64.0 ± 1.7	26.5 ± 0.7

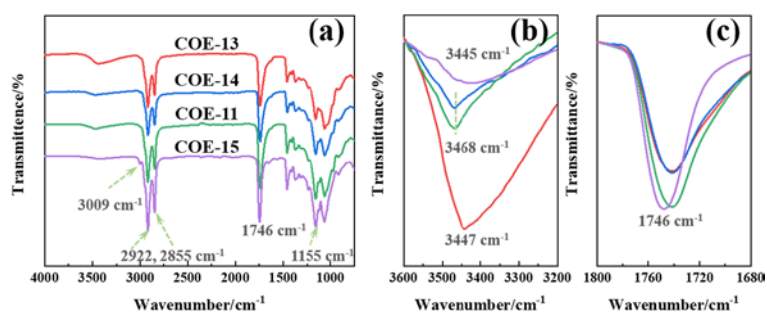


Fig. S4 (a) ATR-IR spectra of COEs prepared in different solvents; (b), (c) The magnified ATR-IR peaks of -OH and -COO- groups, respectively.

6. Comparing the chemical structure of pyridine with DMAP

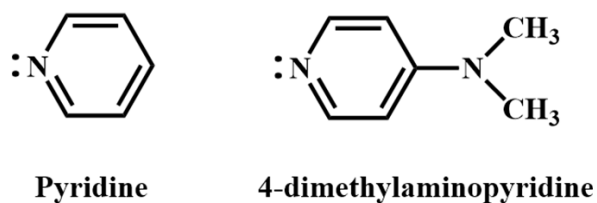


Fig. S5 Chemical structures of pyridine and DMAP.

7. Morphologies of RCA and COEs

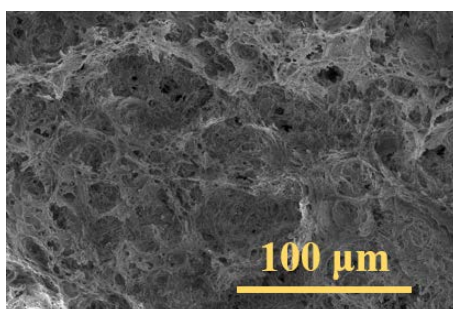


Fig. S6 SEM image of RC aerogel (RCA). To reveal the micromorphology RCG, RCG was lyophilized to achieve RCA.

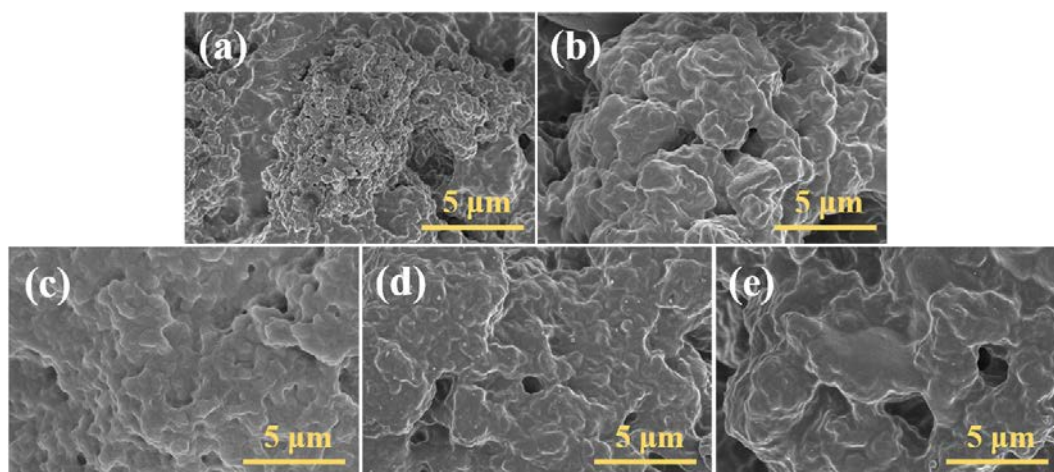


Fig. S7 SEM images of COEs prepared by feeding different molar ratios of OA/AGU. (a) COE-5 (3/1); (b) COE-6 (4.5/1); (c) COE-4 (6/1); (d) COE-7 (7.5/1); COE-8 (9/1).

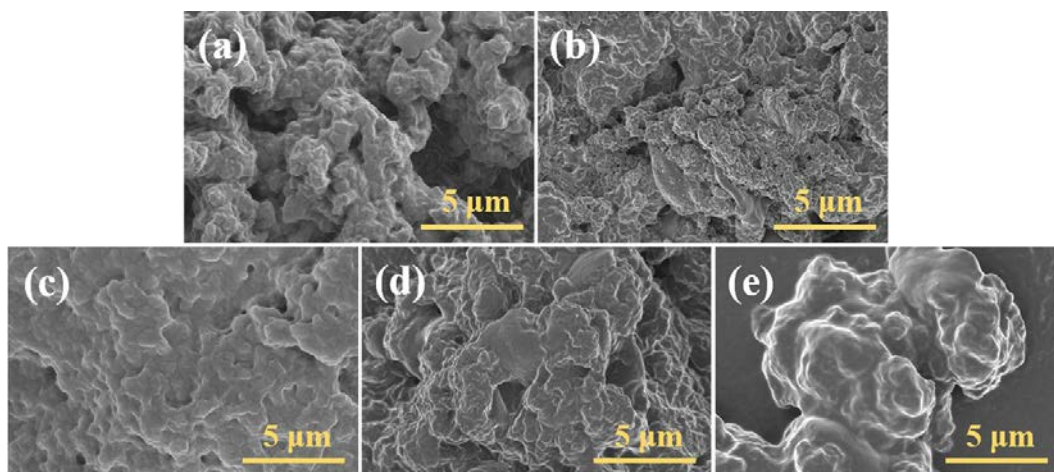


Fig. S8 SEM images of COEs prepared by reaction for different times. (a) COE-9 (1 h); (b) COE-10 (2 h); (c) COE-4 (4 h); (d) COE-11 (6 h); (e) COE-12 (9 h).

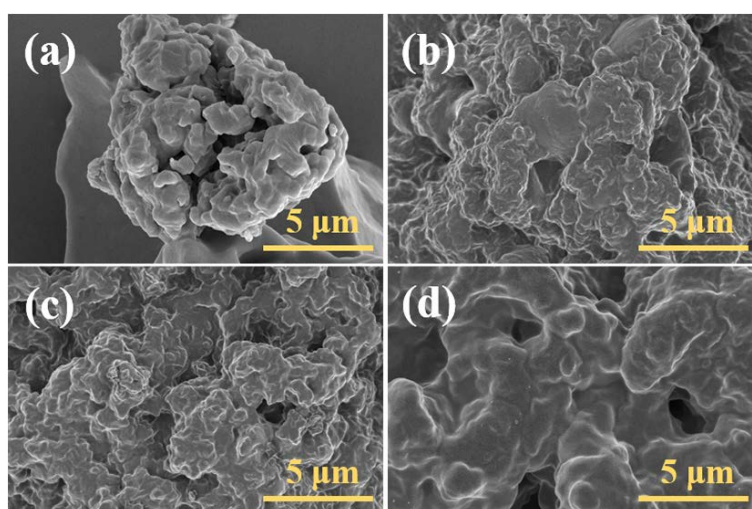


Fig. S9 SEM images of COEs prepared by reaction in different solvents. (a) COE-13; (b) COE-11; (c) COE-14; (d) COE-15.

8. Thermal stability of COEs

Table S6 TGA data of MCC, RCA, and COEs prepared by sonochemistry.

Samples	DS	$T_d/^\circ\text{C}^a$	$T_{max}/^\circ\text{C}^b$	
MCC	N/A ^c	303	335	N/A
COE-1	0.38 ± 0.08	311	364	441
COE-2	0.74 ± 0.07	307	368	443

COE-3	1.24 ± 0.03	310	363	443
COE-4	1.42 ± 0.05	314	365	446
COE-5	0.73 ± 0.05	303	365	441
COE-6	1.23 ± 0.06	304	364	445
COE-7	1.56 ± 0.07	311	363	446
COE-8	1.60 ± 0.03	307	360	443
COE-9	0.27 ± 0.06	303	363	434
COE-10	0.87 ± 0.06	298	362	442
COE-11	1.55 ± 0.04	301	364	446
COE-12	1.58 ± 0.04	295	361	445
COE-13	1.11 ± 0.10	308	368	442
COE-14	1.47 ± 0.03	299	366	443
COE-15	1.70 ± 0.06	293	364	445

a. T_d represented the temperature of 10% weight loss in the TGA curve; *b.* T_{max} represented the temperature at the maximum weight loss peak in the DTG curve; *c.* The designated items were not available.

9. Processable ability of COEs

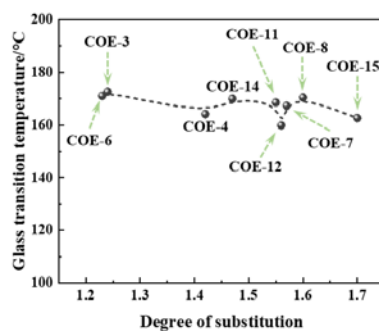


Fig. S10 Glass transition temperatures of COEs as a function of DS.



Fig. S11 The digital image of the COE-11 sheet prepared by hot-pressing (180 °C, 10 MPa, 5 min).

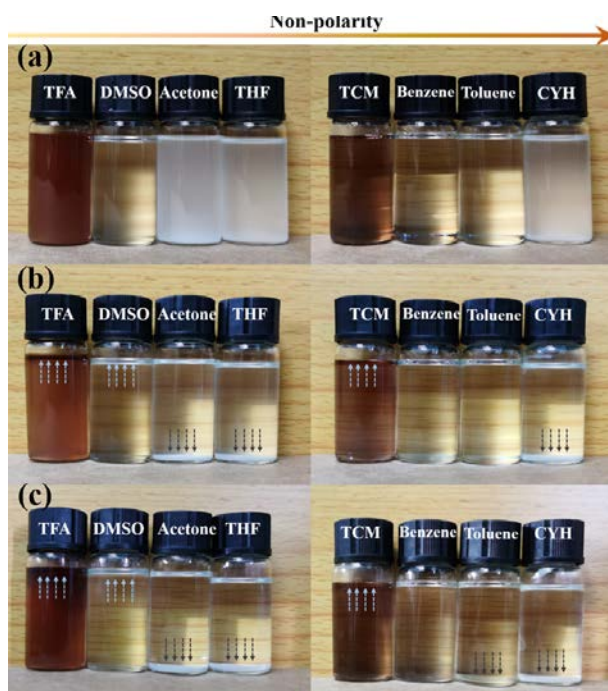


Fig. S12 Digital images of COE-11 in various organic solvents with different polarity after standing for 1 h (a), 12 h (b), and 48 h (c). The dashed arrows indicated COE sediments.

Reference

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