

## Supporting Information

# Manufacturing of Pure Cellulose Films by Recycling Ionic Liquids as Plasticizers

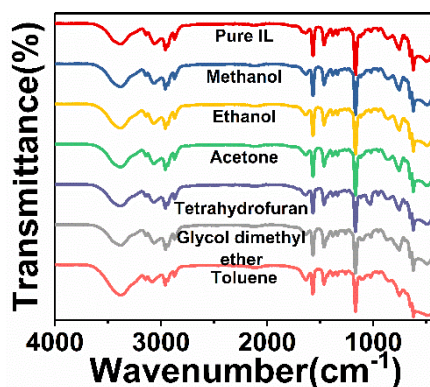
Longhui Li,<sup>a</sup> Yun Zhang,<sup>\*a</sup> Yanling Sun,<sup>a</sup> Shuang Sun,<sup>a</sup> Guancheng Shen,<sup>a</sup> Peng Zhao,<sup>b</sup> Jingqiang Cui,<sup>c</sup> Haiyu Qiao,<sup>a</sup>  
Yunming Wang,<sup>\*a</sup> Huamin Zhou<sup>a</sup>

<sup>a</sup>State Key Laboratory of Material Processing and Die & Mould Technology, School of Materials Science and Engineering, Huazhong University of Science & Technology, Wuhan 430074, P.R. China. E-mail: marblezy@hust.edu.cn; wang653@hust.edu.cn

<sup>b</sup>The Key Laboratory of 3D Printing Process and Equipment of Zhejiang Province, College of Mechanical Engineering, Zhejiang University, Hangzhou 310027, P.R. China.

<sup>c</sup>Henan Key Laboratory of Medical Polymer Materials Technology and Application, TuoRen Medical Device Research & Development Institute Co.,Ltd. Health Technology Industry Park, Changyuan County, Henan 453000, P.R. China.

### 1. Selection of Soxhlet Extraction Solvent



**Figure S1.** FT-IR spectra of pure IL and ILs recovered with six solvents.

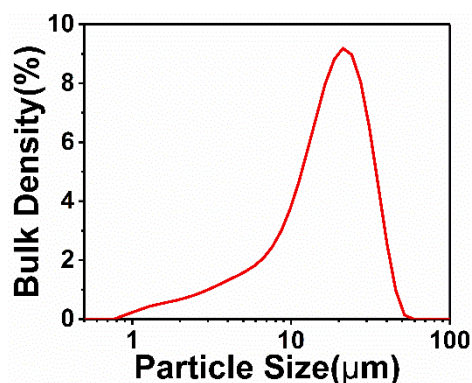
**Table S1.** The recovery rates and quality of ILs recovered with six solvents.

Solvent	Recovery rate(wt%)	Quality
Methanol	100.2	Good
Ethanol	103.7	Good
Acetone	84.5	Good
Tetrahydrofuran	53.4	Poor
Glycol dimethyl ether	44.3	Poor
Toluene	3.6	Poor

In order to determine the appropriate solvent to extract ILs, six kinds of organic solvents which were easy to be vaporized were selected, including methanol, ethanol absolute, acetone, tetrahydrofuran, glycol dimethyl ether and toluene. No

impurity removal was performed in ILs when recovery rates were calculated. To analyze whether the ionic liquid structure changed after one cycle, FT-IR spectra of pure IL and ILs recovered with six solvents were conducted, as shown in Figure S1. The FT-IR spectra of ILs were basically consistent with that of pure IL, indicating that the structure of ILs did not change during thermoplastic processing, Soxhlet extraction and rotary evaporation. Hence, the six solvents all could be used as solvents for Soxhlet extraction to extract ILs. The recovery rates and quality of ILs were listed in Table S1. The six solvents were arranged in order of polarity from large to small: methanol > ethanol > acetone > tetrahydrofuran > glycol dimethyl ether > toluene. In general, the greater the polarity of the solvent, the higher the solubility of solvent to ILs. When tetrahydrofuran, glycol dimethyl ether and toluene were used to extract ILs, the solvents and ILs were even stratified, indicating their poor ability to dissolve ILs. The higher the solubility of solvent to ILs, the higher the recovery rate of ILs and the better the quality of recovered ILs. It's worth noting that the recovery rates of ILs recovered by methanol and ethanol were more than 100 wt% because the recovered ILs contained impurities. Obviously, methanol and ethanol were the preferred solvents for soxhlet extraction. Given that methanol is toxic, ethanol was determined to be the Soxhlet extraction solvent.

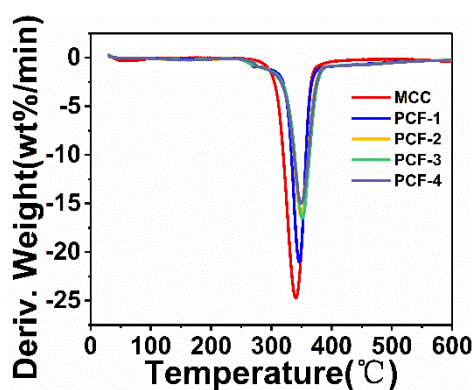
## 2. The Particle Size of MCC



**Figure S2.** The particle size distribution of MCC.

The raw material used in this manufacturing process was MCC particles with particle size of about 18.6 μm. The size of MCC particles was mostly between 5.1 μm and 34.1 μm, and the smallest particles were about 800 nm (Figure S2).

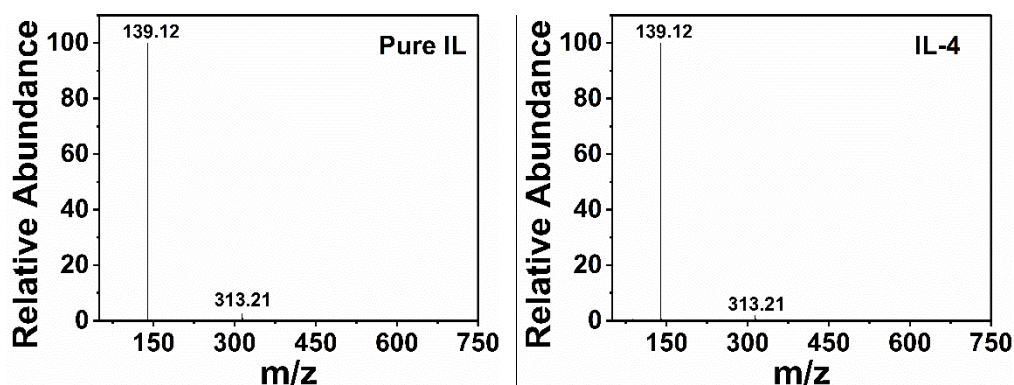
## 3. DTG Analysis of MCC and PCFs



**Figure S3.** DTG curves of MCC and PCFs obtained in four cycles.

The DTG curves of MCC and PCFs obtained in four cycles were calculated from TGA curves and shown in Figure S3. There was only one peak corresponding to the decomposition of cellulose in their DTG curves. According to DTG curves, the mass loss rates of PCFs were not significantly different from each other and lower than MCC. The  $T_{max}$  of MCC and PCFs obtained in four cycles was 340 °C, 346 °C, 349 °C, 351 °C, 350 °C, respectively.

#### 4. Mass Spectrometry Analysis of the Pure IL and Recovered IL by Ethanol

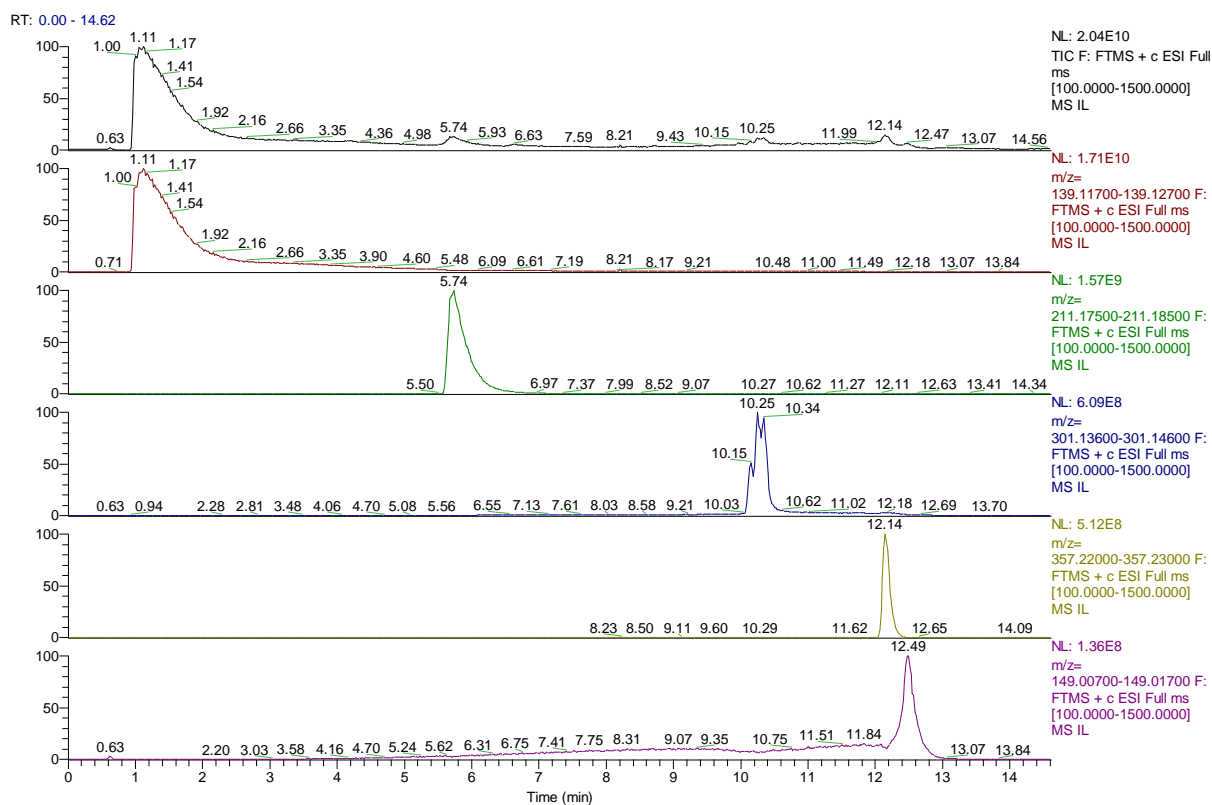


**Figure S4.** Mass spectrograms of the pure IL and recovered IL by ethanol in the fourth cycle.

Method: Mass spectrometry analysis was carried out with a high resolution liquid chromatography mass spectrometer (Orbitrap LC/MS (Q Exactive), Thermo Fisher, Germany) by direct injection nebulization. Instrumental conditions used for positive-mode mass spectrometry: spray voltage: 3.2 kV; capillary temperature: 300 °C; max spray current: 100 A; probe heater temperature: 350 °C; ion source: ESI+ms.

In mass spectrograms of the pure IL and recovered IL by ethanol in the fourth cycle (Figure S4), two peaks were observed. The peak at 139.12 corresponded to the cation part of BmimCl. Self-association occurs with imidazoles.<sup>1</sup> The peak at 313.21 corresponded to the dimer of BmimCl. This result revealed that the recovered ILs by ethanol contained almost no impurities.

#### 5. Mass Spectrometry Analysis of the Recovered IL by Methanol

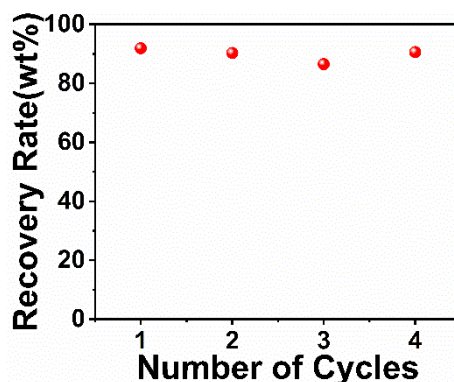


**Figure S5.** Mass spectrograms of the recovered IL by methanol in the fourth cycle.

Method: Mass spectrometry analysis was carried out with a high resolution liquid chromatography mass spectrometer (Orbitrap LC/MS (Q Exactive), Thermo Fisher, Germany). Instrumental conditions used for positive-mode mass spectrometry: spray voltage: 3.8 kV; capillary temperature: 320 °C; max spray current: 100 A; probe heater temperature: 350 °C; ion source: ESI+ms.

In mass spectrogram of the recovered IL by methanol in the fourth cycle (Figure S5), in addition to the peak corresponding to the cation part of BmimCl, there were also peaks of sugars. This result revealed that the recovered ILs by methanol contained sugars.

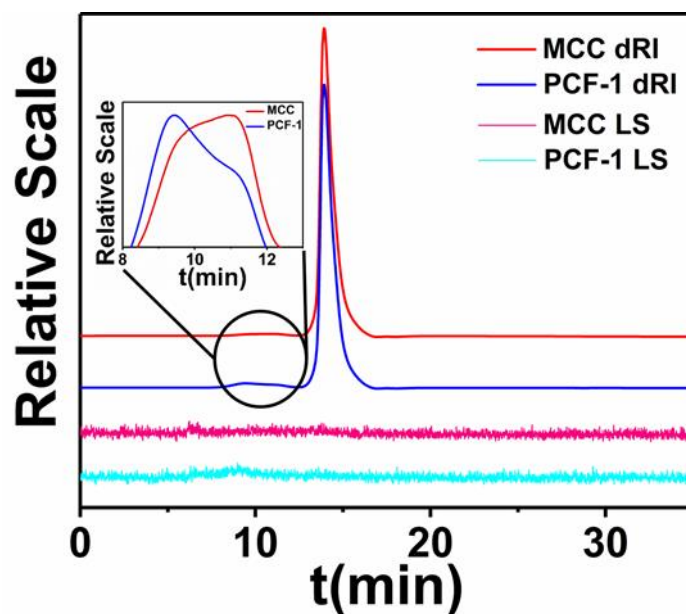
## 6. The Recovery Rates of Ethanol



**Figure S6.** The recovery rates of ethanol in four cycles.

The recovery rates of ethanol in four cycles were about 90 wt% (Figure S6). There was only a small loss of ethanol during processing.

### 7. The molecular weights of MCC and PCF-1

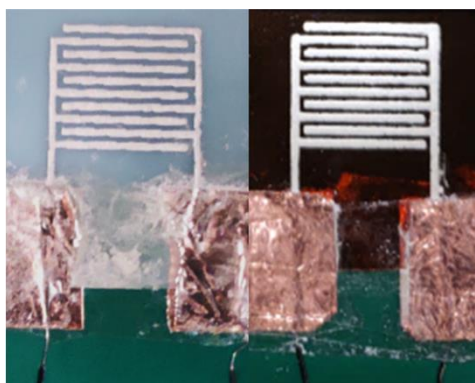


**Figure S7.** Chromatograms of MCC and PCF-1 with differential refractive index (dRI) and light scattering (LS).

Method: Weight average molecular weights (Mws) of the samples were measured by gel permeation chromatography (GPC) (GPC-MALS, Wyatt, United States) with a multi-angle laser light scattering detector (DAWN HELEOS II, Wyatt, United States). The mobile phase, 0.5 % LiCl/DMAc (wt/vol), was pumped into the system at a flow rate of 1 mL/min.

There were two peaks in Figure S7, the cellulose peak in the front and the solvent peak<sup>2</sup> in the back. The cellulose peak was weak due to the low cellulose concentration. The result showed that the Mws and DP of MCC and PCF-1 were  $7.37 \times 10^4$ ,  $7.29 \times 10^4$  and 455, 450, respectively. Our processing method did not degrade cellulose.

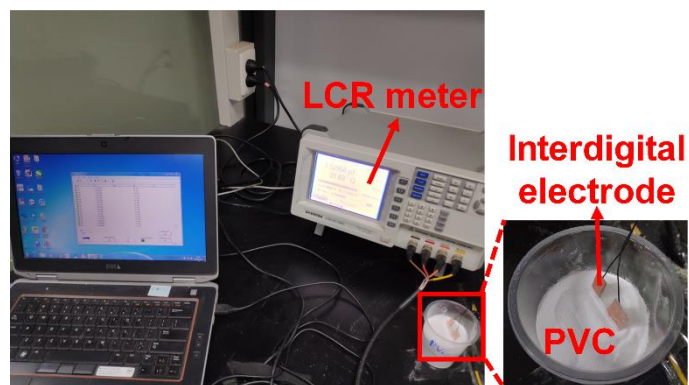
### 8. Fabricating Process of Interdigital Electrodes



**Figure S8.** The interdigital electrodes fabricated with PCF (left) and PI (right) substrates.

Silver paste was used as conductive material to print interdigital electrodes on PCF and PI respectively. Interdigital electrodes were dried under vacuum for 2 hours at 50 °C. The wires were connected to interdigital electrodes using copper tapes (Figure S8).

### 9. Capacitance Measuring Device



**Figure S9.** Capacitance measuring device.

The interdigital electrodes were used as sensors and combined with the LCR meter (LCR-8110G, GW Instek, Taiwan, China) to form the capacitance measuring device (Figure S9). All measurements were performed at 1MHz.

Reference:

1. F. Peral and E. Gallego, *Journal of Molecular Structure*, 1997, 415, 187-196.
2. Judy D. Timpa, *Journal of Agricultural and Food Chemistry*, 1991, 39, 270-275.