Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2018

## Supporting Information

# Flexible Double-cross-linked Cellulose-based Hydrogel and Aerogel Membrane for Supercapicitor Separator

Liyuan Li, †<sup>ab</sup> Feixue Lu, †<sup>ab</sup> Chao Wang, \*<sup>a</sup> Fengling Zhang,<sup>c</sup> Weihua Liang,<sup>a</sup> Shigenori Kuga,<sup>a</sup> Zhichao

Dong,<sup>a</sup> Yang Zhao,<sup>a</sup> Yong Huang,<sup>a</sup> Min Wu\*<sup>a</sup>

<sup>a</sup> Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, 29 Zhongguancun East Road,

Haidian District, Beijing 100190, China

<sup>b</sup> University of the Chinese Academy of Sciences, 19 A Yuquan Rd, Shijingshan District, Beijing, 100049,

China

<sup>c</sup> Biomolecular and Organic Electronics, Department of Physics, Chemistry and Biology (IFM), Linköping

University, SE - 581 83, Linköping, Sweden

<sup>†</sup> These authors contributed equally to this work.

\*Corresponding author: wumin@mail.ipc.ac.cn, chwangipc@mail.ipc.ac.cn

#### **Supplementary Methods:**

### Porosity

The  $C_n$ -DM-x aerogel membrane was immersed in distilled water for 8 h, and the weight before and after water absorption were recorded. The porosity was calculated using equation.

$$P = \frac{M_b/\rho_b}{M_b/\rho_b + M_p/\rho_p} \times 100\%$$
 S1

where P is the porosity of the C<sub>n</sub>-DM-x aerogel membrane (%),  $M_p$  is the mass of the C<sub>n</sub>-DM-x aerogel membrane (g),  $M_b$  is the mass of absorbed water (g),  $\rho_p$  is the density of the C<sub>n</sub>-DM-x aerogel membrane (g

cm<sup>-2</sup>), and  $\rho_b$  is the density of distilled water (1.0 g cm<sup>-2</sup>).

*Electrolyte uptake:* The dried  $C_n$ -DM-x aerogel membrane sample ( $W_0$ , g) was then immersed in 6 M KOH aqueous solution at room temperature for 48 h. The membrane was then removed from the KOH solution, using absorbent tissue paper to remove excess water on the membrane surface, and the weight of the wet  $C_n$ -DM-x aerogel membrane ( $W_1$ , g) was measured. The KOH uptake (wt.%) was calculated using equation

$$KOH uptake(wt.\%) = \frac{W_1 - W_0}{W_0} \times 100\%$$
 S2

*Ionic conductivity:* The ionic conductivity ( $\sigma$ , S cm<sup>-1</sup>) was calculated using equation S3:

$$\sigma = \frac{L}{R_b \times A}$$
 S3

where L (cm) is the distance between the two electrodes, A (cm<sup>2</sup>) is the effective area of the C<sub>n</sub>-DM-x aerogel membrane, and  $R_b(\Omega)$  is the bulk resistance of the C<sub>n</sub>-DM-x aerogel membrane /KOH polymer electrolyte.

Hydrogels	Cellulose	ECH	DA/AM	AM	APS/C	BIS/C	TMEDA	Water
	(wt. %)	(mL)		(mg)	(wl. 70)	(wl. 70)	(μι)	(wl. 70)
cellulose	4	1	0	0	0	0	20	85
C-PDA	4	1	0.4	0	5	6	20	85
C-PAM	4	1	0	250	5	6	20	85
C <sub>4</sub> -DM-10	4	1	0.1	250	5	6	20	85
C <sub>4</sub> -DM-20	4	1	0.2	250	5	6	20	85
C <sub>4</sub> -DM-30	4	1	0.3	250	5	6	20	85
	1	0.25	0.4					
	2	0.5	0.4					
C <sub>n</sub> -DM-40	3	0.75	0.4	250	5	6	20	85
	4	1	0.4					
	5	1.25	0.4					
	6	1.5	0.4					
C <sub>4</sub> -DM-50	4	1	0.5	250	5	6	20	85

Table S1. The compositions of various hydrogels

C <sub>4</sub> -DM-60 4	1	0.6	250	5	6	20	85
-------------------------	---	-----	-----	---	---	----	----

Notes: C presents cellulose.



**Figure S1.** The FT-IR spectra of Cellulose, Cellulose/PDA, Cellulose/PAM and Cellulose/PAM /PDA-PAM (C<sub>4</sub>-DM-40) hydrogels.

The FT-IR spectra of pure cellulose, cellulose-PDA, cellulose-PAM and cellulose-PDA-PAM hydrogel (40 wt % DA/AM) were analyzed to search for possible crosslinks between PDA and PAM. As shown in FT-IR spectra, the cellulose-PAM hydrogel exhibited bands between 3000 cm<sup>-1</sup> and 3500 cm<sup>-1</sup>, corresponding to a stretching vibration of N-H and O-H, at 2700 cm<sup>-1</sup> and 3000 cm<sup>-1</sup> for C-H stretching bond and at 1655 cm<sup>-1</sup> for C=O stretching. The bands at 1615 cm<sup>-1</sup> (N-H deformation for primary amine), 1440 cm<sup>-1</sup> (CH<sub>2</sub> in-plane scissoring), 1360 cm<sup>-1</sup> resulted from the overlapping of hydroxyls and amine groups of PDA. In comparison with cellulose- PAM and cellulose- PDA, the spectrum of the PDA-PAM hydrogel showed a new peak at 1240 cm<sup>-1</sup>, corresponding to the C-N stretching in phenyl amines. The presence of this band indicates the interaction between -NH<sub>2</sub> groups of PAM and catechol groups of PDA.

#### <sup>1</sup>H NMR spectroscopy analysis

Experiments: Proton nuclear magnetic resonance spectra (<sup>1</sup>H NMR) of DA, AM, D(+)-Cellobiose (Cel), DA-AM, Cel-DA, Cel-AM were used to analyze the interactions between D(+)-Cellobiose, DA and AM. The <sup>1</sup>H NMR spectra were recorded on Brucker Avance 400 MHz and are reported in ppm using solvent as

an internal standard (D<sub>2</sub>O at 4.79 ppm, (CD<sub>3</sub>)<sub>2</sub>SO at 2.50 ppm).

\*Website of Biological Magnetic Resonance Data Bank database:

http://bmrb.wisc.edu/metabolomics/mol\_summary/show\_data.php?molName=dopamine&id=bmse000933

Results: The spectrum of DA in D<sub>2</sub>O is the same as that listed in the Biological Magnetic Resonance Data Band database. The spectrum of DA showed characteristic resonance signals of phenyl protons at 6.87 and 6.82 ppm. The peaks at 3.20 and 2.85 ppm were methylene protons. For the spectrum of AM, the methyne and methylene protons appeared around 6.26 and 5.85 ppm. The spectrum of Cel showed characteristic resonance signals of anomeric proton at 4.68 and 4.53 ppm, whereas other protons in the glucose ring and additional methylene protons overlapped in the narrow region 3.96–3.30 ppm. Figure S2(b) showed the <sup>1</sup>H NMR spectra of Cel, DA, and Cel/DA. After Cel was mixed with DA to form the Cel/DA solution, the chemical shift of phenyl protons in DA shifted from 6.87 to 6.89 ppm, thus indicating that there were interactions between cellulose and PDA. Fig. S2(c) showed the <sup>1</sup>H NMR spectra of Cel, AM, and Cel/AM. After Cel was mixed with AM to form the Cel/AM solution, the chemical shift of protons in Cel and AM didn't shift, thus indicating that there were no interactions between cellulose and PAM. Fig. S2(d) and (e) showed the <sup>1</sup>H NMR spectra of DA, AM, and DA/AM in D<sub>2</sub>O and DMSO, respectively. We obtained two active hydrogens at 7.51 and 7.08 ppm from the spectrum of DA in DMSO, which might belong to the proton chemical shift of catechol groups. The spectrum of AM in DMSO showed active hydrogen signals of NH<sub>2</sub> group at 9.15 and 8.75 ppm. After AM was mixed with the DA to form DA/AM complexation, the active hydrogen in DA shifted from 7.51 ppm to 7.62 ppm, these results demonstrated that there were interactions between PDA and PAM. The above conclusions verify the conjecture of the PDA acts as a bridge to link the cellulose skeleton and PAM frame by forming double cross-linked hydrogel.



Figure S2. (a) The <sup>1</sup>H NMR spectra of Cel, DA, and AM in D<sub>2</sub>O. (b) The <sup>1</sup>H NMR spectra of Cel, DA, and Cel/DA in D<sub>2</sub>O.
(c) The <sup>1</sup>H NMR spectra of Cel, AM, and Cel/AM in D<sub>2</sub>O. (d) The <sup>1</sup>H NMR spectra of DA, AM, and DA/AM in D<sub>2</sub>O. (e) The <sup>1</sup>H NMR spectra of DA, AM, and DA/AM in DA/AM in D<sub>2</sub>O.



**Figure S3.** SEM morphology of dried Cellulose (a), C<sub>4</sub>-DM-10 (b), C<sub>4</sub>-DM-20(c), C<sub>4</sub>-DM-30(d), C<sub>4</sub>-DM-50(e) and C<sub>4</sub>-DM-60(f) hydrogels.



Figure S4. (a) and (c) N<sub>2</sub> adsorption/desorption isotherms, and (b) and (d) pore size distribution of aerogel and PP.

As observed by SEM observations (Figure 2, figure S9), the Cel-PAM, Cel-PDA, C4DM-40 and PP films displayed a

typical macroporous structure. However, through the N<sub>2</sub>-sorption isotherms and pore size distribution (PSD) calculated by density functional theory (DFT), a mesoporous structure (type IV isotherms) with a pore size of 13 to 60 nm were determined for all the films. Besides, the pore size distribution of PP membranes is concentrated mainly upon 1.5 nm (Fig. S4b), causing a low migration rate of ions between the two electrodes and consequently, a low electrochemical property of the supercapacitor.



Figure S5. C<sub>4</sub>-DM-40 hydrogel firmly adhered on various surface. (a) metals, (b) plastic mold, (c) glasses, (d) walls.



Figure S6. SEM elemental maps of of C, O, Fe and the corresponding EDS spectrum of C<sub>4</sub>-DM-40 aerogel.



Figure S7. The electrolyte retention of Cn-DM-x aerogel membrane.



**Figure S8.** (a): The structure schematic of an electric double layer supercapacitor. SEM images of the aerogel membrane (b) before and (c) after 10 000 cycling test.



Figure S9. SEM morphology of PP membrane.



Figure S10. The photo of C<sub>4</sub>-DM-40 membrane after Galvanostatic charge/discharge (GCD) cycle test.