# **Supporting information**

# Cellulose nanofiber aerogel filter with tuneable pore structure for oil/water separation and recovery

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#### S1 Surface morphology of aerogel



Fig. S1 (a) (b) SEM images of the surface of the aerogel

#### S2 Experimental methods

#### **Materials**

Micro fibrillated cellulose (MFC) purchased from DAICEL Chemical Industries Limited (Celish KY-100G) was used as the primary materials for preparing cellulose aerogel. This MFC sample contains fibres that are approximately 73 nm in diameter and several micron metres in length. Oil red-o purchased from Sigma Aldrich Pty Ltd, Australia was used to dye the oils. Oils used for testing; mineral oil (heavy and light), hexadecane, canola oil and peanut oil were purchased from Sigma Aldrich Pty Ltd, Australia. Commercial PAE was provided by Nopco Paper Technology Pty Ltd, Australia (33% w/w solids content). PAE was used as a cross-linker in the fabrication of the hydrogel.

#### **Aerogel fabrication**

MFC suspensions with various solids content (1wt%, 0.5wt%, 0.25wt%) mixed with calculated amount of PAE (0.05 g/g MFC) were prepared and poured slowly into 25 ml beakers, forming a suspension with a thickness of 0.5 cm at the bottom of the beaker. They were then placed in freezer at -18 °C for 24 hours in order to maintain the porous structure. Thereafter, the frozen sponge-like aerogel was freeze-dried in freeze-dryer (Christ Freeze Dryer, beta 1-8 LD plus) for 24 hours to remove all the moisture while maintaining its porous structure. Lastly, the freeze-dried samples were kept in oven at 120 °C for 3 hours to promote cross-linking.

#### **Characterization**

Scanning electron microscopy (SEM) images of the cellulose aerogel were taken using FEI Nova NanoSEM 450 FEGSEM. To prepare the specimen for SEM, the cellulose aerogel was first fully wetted by DI water, and then immersed in liquid nitrogen. It was then diced into small individual specimen using a tweezer. The specimen was then freeze-dried, followed by coating with platinum and fixed on a SEM sample holder. Contact angle measurement was conducted using Contact Angle System OCA20 (Data-physics, Germany). The contact angle of oil was measured by placing 3 μL of oil on the surface of the cellulose aerogel underwater. The pore size distribution measurement was conducted using AutoPore IV 9500 (Micromeritics). To prepare the specimen for this measurement, the cellulose aerogel was first fully wetted by DI water, and then immersed in liquid nitrogen. It was then diced into small individual specimen using a tweezer. The specimen was freeze-dried and placed in vacuum oven at 100 °C overnight to remove any leftover moisture.

#### Preparation of the oil-in-water emulsion

For testing the separation of the hydrogel, an emulsion was prepared using 10 ml of canola oil and 90 ml of distilled (DI) water. The mixture was then mixed at 13500 rpm, for 15 minutes to produce a homogenized emulsion, which would turn into milky white colour, indicating that oil and water were well mixed.

#### **Experimental set-up**



Fig. S2 Experimental set-up for oil/water separation testing and DI water flux measurements.

#### S3 DI water flux

The pure water flux (PWF) and oil/water separation experiments setup is shown in Fig. S4. The cellulose sponge-like aerogel (pre-wetted by DI water) was fixed between two glass plates. Fixed amount of DI water (31ml) was poured into the chamber for the PWF testing, and same amount of oil-water emulsion was used for the oil/water separation experiments.

The flux (J, Lm<sup>-2</sup>h<sup>-1</sup>) was calculated from the volume of the permeation in unit time at the beginning of the test using the following equation:

J = V/(A t)

Where V is the volume of the water filtered (L), A is the effective filtration membrane area (m<sup>2</sup>), t is the filtration time (h).



Fig. S3 (a) DI water flux testing on the cellulose aerogel with various bulk densities, (a)-(c): 0.0197 g/ml, 0.0239g/ml and 0.0337g/ml, respectively. (d) Summary of the DI water flux measurements.

#### S4 Recovery of aerogel between separation test cycle

For the separation of oil/water mixture, the recovery of aerogel after each cycle was done by simply spraying water onto the surface of the aerogel to remove the leftover oil. Due to nature of the underwater super-oleophobic properties, the surface of the aerogel was not stained by the oil layer, allowing the oil to be washed off easily. Please refer to Movie S2 for the video illustration.



Fig. S4 Demonstration of aerogel cleaning between cycles (refer to Movie S2 for details)



#### **S5** Engineering pore structure

Fig. S5 (a) Pore size and distribution of cellulose aerogels with various bulk densities. (b) DI water flux and Separation efficiency of cellulose aerogels with various bulk densities to canola oil in water emulsion. (c) Hydrated aerogel filter with increasing solids content (from left to right)

### S6 Mechanism analysis



The mathematical model of the flow takes into account the aerodynamic drag, gravitational, buoyancy and shear-lift forces.

$$m_d \frac{d(U_d)}{dt} = F_{drag} + F_{grav} + F_{shear \, lift} \tag{1}$$

where  $m_d$  represents the individual oil droplet mass,  $U_d$  is the velocity of the oil droplet, t is time,  $F_{drag}$  is the aerodynamic drag force,  $F_{grav}$  is gravitational/ buoyancy force and  $F_{shear lift}$  is shear-lift force. The experiment used DI water and canola oil, and their thermodynamic properties were: density equal to 998 kg/m<sup>3</sup> (water) and 920 kg/m<sup>3</sup>, viscosity equal to 0.993  $\times$  10<sup>-3</sup>Pa s (water,  $\rho$ ) and 6.4  $\times$  10<sup>-2</sup>Pa s (canola oil,  $\rho_d$ ). The oil-water interfacial tension is 20mN/m. The velocity of fluid in vertical direction U is 6.7  $\times$  10<sup>-4</sup>m/s.

Assumption:

- 1. The net shear-lift forces is 0, causing no horizontal movement of oil droplet.
- 2. Only forces in the vertical direction are considered
- 3.  $U_d = 0$  in any direction

The drag force,  $F_{drag}$  can be defined as

$$F_{drag} = \frac{3}{4} \left( \frac{\rho}{\rho_d D_d} \right) m_d C_D (U - U_d) |U - U_d|$$
<sup>(2)</sup>

where  $\rho$  is continuous phase density (water),  $\rho_d$  is dispersed phase density (oil droplets), U is the velocity of fluid in vertical direction.  $C_D$  is the aerodynamic drag coefficient, the drag coefficient  $C_D$  is calculated by using the results provided in Clift, Grace and Weber (Bubbles, drops and Particles, Academic press, 1978)<sup>4</sup>

$$F_{drag} = \frac{3}{4} \left( \frac{998}{920D_d} \right) m_d \times 204 \times (6.7 \times 10^{-4})^2$$

The gravitational is given by

$$F_{grav} = -m_d g \tag{3}$$

The buoyancy force is given by

$$F_{buoy} = -m_d g \frac{\rho}{\rho_d} \tag{4}$$

where g is the gravitational acceleration, which represents the buoyancy force impact into the flow.

$$F_{grav} + F_{buoy} = -m_d g \left( 1 - \frac{\rho}{\rho_d} \right) = -m_d \times 9.81 \times (1 - \frac{998}{920})$$

Therefore,  $F_{grav} + F_{buoy} = F_{drag}$  is a critical point, where the coalesced oil droplet is about to rise because of the increasing buoyancy force as the droplet grows bigger via further coalescence. From Eq (2) (3), it could be calculated that  $D_d = 89.6 \mu m$ , when  $F_{grav} = F_{drag}$ . Hence, at a fluid velocity of  $6.7 \times 10^{-4}$ m/s, the minimum diameter required for a coalesced oil droplet to float upwards is about 89 $\mu m$ .

<u>\*Calculation of drag coefficient</u>  $C_D$ 

$$Re = \frac{UD_H}{v} \tag{4}$$

Where is the hydraulic diameter of the void, which is assumed to be a circular tube with a mean diameter of  $180\mu m$ . v is the kinematic viscosity of the fluid, which is  $v = \mu/\rho$ 

$$Re = \frac{6.7 \times 10^{-4} \times 180 \times 10^{-6}}{0.993 \times 10^{-3}/998} = 0.12$$

 $0.01 < Re < 20, C_D = \frac{24}{Re} [1 + 0.1315 Re^{(0.82 - 0.05w)}]$ For
(5)

Where

$$w = \log_{10} Re$$

Therefore,

$$C_D = \frac{24}{0.12} \left[ 1 + 0.1315 \times 0.12^{(0.82 - 0.05 \times \log_{10} 0.12)} \right] = 204$$

#### S7 Wet strength of cellulose aerogel

Fig. S7 shows a comparison between cellulose aerogel samples with and without PAE cross-linking in water 15mins of shaking motion to beakers.

Figure S7 Proposed scheme of demusification of oil-in-water emulsion