Supporting Information

Hierarchically structured composites for ultrafast liquid sensing and smart leak-plugging

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Fig. S1 Photographs, chemical structures, zeta potentials as well as FT-IR spectra of negatively charged cellulose nanocrystal (a) and positively charged chitosan (b).

Cellulose nanocrystal (CNC) was prepared via controlled sulfuric acid hydrolysis of bulk cellulose, during which a small amount of sulfate ester groups could be introduced onto the surface of $CNC^{[1]}$ with zeta potential measured to be -31.1 mV. In FT-IR spectrum, CNC exhibits characteristic bands around 3345 and 2901 cm⁻¹ as a result of the O–H stretching and C–H stretching in cellulose.^[2] The three bands between 1059 to 1164 cm⁻¹ are due to the C–O–C pyranose ring skeletal vibration.

The zeta potential of chitosan was measured to be +48.3 mV, indicating that chitosan is positively charged. The band around 3418 cm⁻¹ in FT-IR spectrum can be ascribed to the hydroxyl asymmetrical stretching vibration and $-NH_2$ stretching vibration.^[3-4] The peaks around 1651 and 1422 cm⁻¹ can be ascribed to the $-NH_2$ and -OH bending vibrations, respectively. The bands near 1157 and 1079 cm⁻¹ correspond to the asymmetric stretching of C–O–C bridge vibration and skeletal vibration involving C–O stretching. The peak around 604 cm⁻¹ is due to -N-H stretching vibration.



Fig. S2 Schematic illustrations for permeation of organic liquids into bulk CPCs (a) and capillary diffusion of organic liquids into porous CPC@PU composites (b).

The penetration of organic liquids into bulk and compact conductive polymer composites (CPCs) is determined by thermodynamic molecular movement. Hence, the permeation process takes a long time, which is the very reason for the sluggish responses of traditional bulk CPCs to organic liquid stimuli. In contrast, our porous CPC@PU composites have abundant interconnected micro pores, which could generate a strong capillary force for organic liquids to diffuse through the porous composites. This capillary effect accelerated diffusion process could significantly improve the response speed of the CPC@PU composites to organic liquid stimuli.





Under the same conditions, the conductive network in a thin CPC layer is more susceptive to organic liquid stimuli than that in bulk CPCs. This is due to the fact that the time needed for solvents to permeate through the thin CPC layer is much shorter than through the bulk CPCs. Hence, thinner CPCs exhibit faster response to solvent stimuli, which is one design consideration for our CPC@PU composites.





The sensitivity of CPCs to organic liquid stimuli is generally influenced by the density of conductive networks. More "brittle" conductive networks (i.e. percolation networks fabricated with less conductive fillers) are more sensitive to organic liquid swelling. In this work, conductive CB@CNC filler was selectively distributed in the interstitial space between the NR latex microspheres, forming a 3D segregated conductive structure, as demonstrated in **Fig. 2d**. Compared with conductive networks with randomly dispersed fillers, such segregated conductive structure is more "brittle" and thus more sensitive to organic liquid stimuli.



Fig. S5 Response behavior of bulk CB@CNC/NR composites after exposed to massive PE liquid.

We can see that the bulk CB@CNC/NR composites showed a sluggish response to PE stimulus when compared to the hierarchically structured CPC@PU composites. This is due to the fact that the permeation of PE molecule into compact CB@CNC/NR composites takes relatively longer time than capillary diffusion of PE liquid into porous CPC@PU composites. The sluggish response of bulk CB@CNC/NR composites to PE stimuli hinders their application where fast or instant detection of organic liquids is required.



Fig. S6 Reproducibility evaluation of CPC@PU composites during organic liquid (a) and gas (b) sensing process.

Reproducibility of different CPC@PU composite samples in organic solvent sensing process was evaluated. Here, we chose PE as a representative organic solvent for the reproducibility evaluation. As shown in **Fig. S6**, the CPC@PU composites exhibited relatively good reproducibility during the organic solvent sensing as well as organic gas sensing, despite of some small differences among samples because these samples were prepared manually. The good reproducibility and reliability provide a prerequisite for the CPC@PU composites to construct desirable liquid or gas sensing devices.



Fig. S7 Response behaviors of CPC@PU composites to different organic liquids.

The liquid sensing behaviors of the CPC@PU composites to 9 different solvents were characterized. These common organic liquids were selected for their different solubility parameters and molecular sizes (see **Table S1** for detailed information). When a drop of organic liquids was dripped onto the CPC@PU samples, decrease in current signals was observed correspondingly. However, the response rate varied among different organic liquids. Ethanol, which is a poor solvent for NR, exhibited the slowest response. While dimethylbenzene, which is a good solvent for NR, exhibited the fastest response. This is due to the fact that the penetrating ability of a solvent into a polymer is mainly determined by their molecular interaction, i.e. matching degree in interaction parameter (χ_{12}). By comparing **Table S1** and **Fig. S7**, it is noticed that low values of χ_{12} resulted in faster response of CPC@PU composites to organic liquid stimuli, indicating faster penetrating speed of the organic liquids into NR matrix.



Fig. S8 SEM images of the compressed CPC@PU composites for organic liquid leak-plugging, scale bars: 200 μ m (a) and 100 μ m (b).

As shown in **Fig. S8**, plenty of micro pores can be observed in the CPC@PU composites after compression. It should be noticed that these micro pores are much smaller compared to that in pristine CPC@PU composites. Such smaller micro pores can be blocked more easily and quickly during the swelling process of CPC layer when exposed to organic liquids. This is also the reason why compressed CPC@PU composites rather than pristine CPC@PU composites were employed for organic liquid plugging tests.

Organic solvents	solubility	molecular volume	Flory– Huggins
	parameter	[cm ³ /mol]	interaction parameter
	[MPa, 0.5]		X12
Ethanol	26.6	58.32	2.25
Dimethyl Formamide	24.8	76.95	1.97
N-Methyl-2-pyrrolidinone	22.9	96.24	1.44
Acetone	20.1	73.52	0.32
Dichloromethane	20.2	67.8	0.31
Tetrahydrofuran	19.4	81.02	0.22
Petroleum ether	-	-	-
Toluene	18.2	105.91	0.083
Dimethylbenzene	18.0	121.9	0.070
Natural rubber	16.8	-	-

Table S1. Solvent parameter of organic liquids used in this study

Note 1: petroleum ether (boiling range: 60-90 °C) is a complex mixture that contains C_5H_{12} , C_6H_{14} , C_7H_{16} , and so on. Its solubility parameters and molecular volume is difficult to determine. Hence, the Flory-Huggins interaction parameter is not calculated.

Note 2: the Flory-Huggins interaction parameter (χ_{12}) was calculated based on the following equation:

$$\chi_{12} = \frac{V_{sol} (\delta_1 - \delta_2)^2}{RT}$$

Where V_{sol} is the molar volume of the solvent. δ_1 and δ_2 are the solubility parameters of solvent and polymer, respectively. T is the absolute temperature, and 298 K is employed for the χ_{12} calculation. R is the ideal gas constant (R=8.314 J·K⁻¹·mol⁻¹).

References:

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