

1 **Supplementary Information for**

2 **Early detection of lithium battery leakage using a highly sensitive in situ**
3 **ZIF-8 membrane-coated micro-nano optical fibre**

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13 Details about the transmission spectrum of MNFs after four growth cycles modification (Fig. S1); The
14 SEM image of purified ZIF-8 powder (Fig. S2a); The thickness of ZIF-8 membrane on MNFs in SEM image
15 (Fig. S2b); The X-Ray diffraction of ZIF-8 membrane on MNFs (Fig. S2c); The test of 15 cycles reused
16 times (Fig. S3a); The Bland-Altman error analysis of 15 reused cycles (Fig. S3b). The table of VOCs sensor
17 performance in last decade (Table. S1).

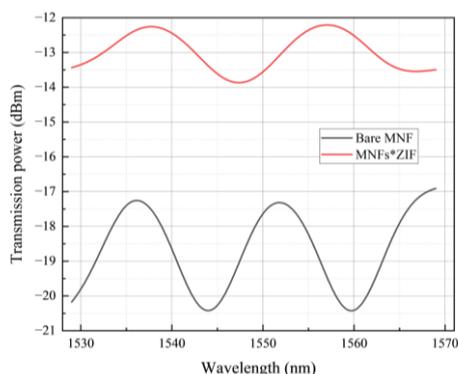
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25 Section 1. The transmission spectrum of MNFs*ZIF

26 The transmission spectrum of MNFs before and after four growth cycles modification is exhibited in Fig. S1,
27 indicating the effective modification of MNFs by ZIF-8 membrane. The four growth cycles ZIF-8 membrane
28 increase the external refractive index, making the FSR of interference spectrum increase. It is worth noting that
29 the transmitted optical power after the modification should theoretically decrease, but due to the optical losses
30 in SMF patch cords is different when each time connected to wavelength demodulator, it instead shows an
31 increase.

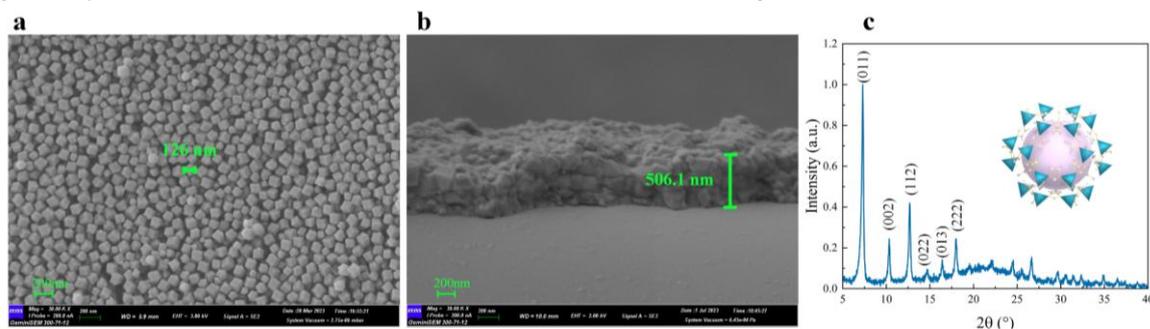


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33 **Fig. S1.** The transmission spectrum of MNFs before and after 4 cycles in situ self-assembled ZIF-8 membrane
34 functionalize.

35 Section 2. The SEM images and XRD pattern of ZIF-8 membrane

36 Under the same ZIF-8 growth conditions and steps, we get purified ZIF-8 powder with good crystallized
37 state and the particle size of about 126 nm as shown in Fig. S2a. As the SEM image in Fig. S2b shows, four
38 cycles ZIF-8 has assembled on MNFs form a dense membrane with the thickness of 506.1 nm. Meanwhile, four
39 growth cycles in situ self-assembled ZIF-8 membrane also have been grown on glass substrate at the same time
40 with the MNFs*ZIF sensor, XRD pattern image consist with the standard powder diffraction files, and exhibits
41 the good crystal structure of ZIF-8 membrane as demonstrated in Fig. S2c.

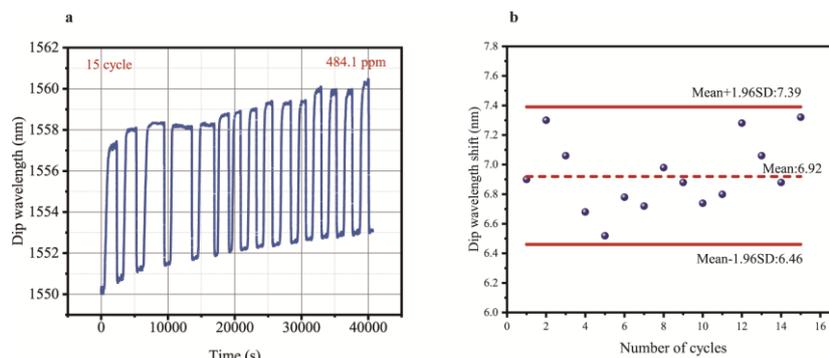


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43 **Fig. S2.** **a** SEM image of purified ZIF-8 powders. **b** Cross sectional SEM image of ZIF-8 membrane. **c** The XRD
44 patterns image of four cycle ZIF-8 on glass substrate.

45 Section 3. The reversibility and repeatability of the MNFs*ZIF

46 The proposed MNFs*ZIF can be continuously reused theoretically, and the sensor fabricated in the same
47 batch is tested for the reversibility and repeatability. Due to limitations in experimental time and conditions, we
48 tested it for 15 cycles, and the results demonstrated that the sensor could still work well with the integral process
49 of evaporation, stabilization and exhaust, in which the mean Bland-Altman error is 6.92 nm within 6.46~7.39
50 nm. Without any performance degradation, it can be inferred that the sensor could be continuously reused
51 according to the experimental results.



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53 **Fig. S3.** The test of reused times **(a)** 15 cycles; **(b)** Bland-Altman error analysis of 15 cycles.

54 **Section 4. Performance comparison of different VOCs optical fiber sensors**

55 Table S1 presents the performance of different types VOCs sensors based on optical fiber in last decade,
 56 compared to these VOCs sensor, our MNFs*ZIF demonstrate an outstanding overall performance in terms of
 57 sensitivity, selectivity, response time and detection limitation.

Table S1. Optical fiber VOCs sensors performance in last decade

Principle	Sensitive layer	VOCs (Analyte status)	Dynamic range	Sensitivity	LOD	Response time /Recovery time	Ref.	Selectivity
Long-period fiber grating	ZIF-8	Ethanol, Acetone (solution)	62-666 ppm, 49-543 ppm	0.018 nm/ppm 0.015 nm/ppm	5.56 ppm 6.67 ppm	10min/10min	1, 2	Y
Microfiber coupler	Nile red	Ethanol, Methanol (solution)	0-45 ppm, 0-65 ppm	-0.13 nm/ppm -0.036 nm/ppm	77 ppb 281 ppb	5min/8min	3	Y
Evanescent fiber	SnO ₂	Ethanol (gas)	1000-20000 ppm	Nonlinear (10% at 5000 ppm)	-	10s/50s	4	N
Fiber tip SPR	Epoxy/Au /MoS ₂	Methanol (gas)	-	- 0.0184 pm/ppm	-	-	5	Y
Photonic crystals fiber	Polystyrene nanospheres	Ethanol, Methanol et al VOCs (solution)	0-70%(v/v)	-	2%	-	6	Y
Microfiber	ZIF-8/GO	Methanol (solution)	343-6858 ppm	3.8 pm/ppm	5.26 ppm	118ms/-	7	Y
Microfiber	ZIF-8	DMC (solution)	9.4-435.7 ppm	43.6 pm/ppm	2.65 ppm	10min/23s	This work	Y

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60 **References**

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