

Electronic Supplementary Information

Near-infrared light responsive temperature-sensing switch in submicro-channel heterogeneous membrane

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1. The experimental materials and equipments

Cylindrical anodic aluminium oxide channel membrane (AAO, thickness: 60 μm , aperture: 20~300 nm) was purchased from Hefei Puyuan Nanotechnology Co., Ltd. (Anhui, China). Potassium chloride, potassium hydroxide, concentrated hydrochloric acid (~36%), tetrahydrofuran, 1, 4-dioxane, ether, potassium dihydrogen phosphate, potassium hydrogen phosphate, etc. were purchased from Sinopharm Chemical Reagents Co., Ltd. (Shanghai, China). Dopamine hydrochloride (DA), tris(hydroxymethyl)aminomethane (Tris), N-isopropylacrylamide (NIPAM), 2-(dodecyl trithiocarbonate)-2-methylpropionic acid (DMP), 2, 2'-azodiisobutyronitrile (AIBN), tributylphosphine, *n*-hexamine, tri(2-carboxyethyl) phosphine (TCEP) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China), 47-50% chlorauric acid (HAuCl_4) was purchased from Shanghai No. 1 Reagent Factory (Shanghai, China). All chemicals were used directly without further purification.

The equipments used in the experiment included RepHile ultrapure water meter (≥ 18.2 $\text{M}\Omega\cdot\text{cm}$, China), LAQUAtwin-pH-22 pH meter (Horiba Scientific, Japan), SU8010 ultra-high resolution field emission scanning electron microscope (Hitachi, Japan), OCA20 video optical contact angle measurement (DatapPhysics, Germany), AXIS-ULTRA DLD-600 W X-ray photoelectron spectrometer (Shimadzu, Japan), UV-2550 UV-Visible spectrophotometer (Shimadzu, Japan), Zetasizer Nano ZS90 (Malvern Instruments, England), QE65000 optical fiber spectrometer (OceanOptics, USA), EPMA-8050G electron probe microanalyzer (Shimadzu, Japan), MDL-III-808-2.5W infrared laser (Changchun New Industries Optoelectronics Tech. Co., Ltd, China) and CHI 830D electrochemical workstation (CH Instrument Inc., China)

2. Synthesis of sulfhydryl-terminated poly-N-isopropylacrylamide (PNIPAM-SH)

NIPAM (3.47 g, 30.66 mmol), DMP (56 mg, 0.15 mmol) and AIBN (5 mg, 0.03 mmol) were placed in the two-neck round-bottom flask with argon gas for 30 min, 15 mL of 1, 4-dioxane was added to dissolve the reactants fully. After stirring in an oil bath of 60 °C for 3 h, the reaction was terminated quickly by cooling and exposing the flask to air. The crude product was diluted with tetrahydrofuran and purified with *n*-hexane for three times to get the precipitation, drying overnight in a vacuum oven of 40 °C. Light yellow powder solid, trithiocarbonate and carboxyl terminated poly-N-isopropylacrylamide (PNIPAM-CTA, M_n , GPC =2860 g/mol, PDI=1.73) was obtained.

Then, PNIPAM-CTA (2 g) was put into the two-neck round-bottom flask, and 15 mL of 1, 4-dioxane was added with argon gas for 30 min. 700 μ L of *n*-hexamine and 350 μ L of tributyl phosphine were added into the flask, and the reaction was finished after stirring at room temperature for 2 h. The crude product was purified with ice ether for three times to get the precipitation. After drying overnight in a vacuum oven of 40 °C, sulfhydryl and carboxyl terminated poly-N-isopropyl acrylamide (PNIPAM-SH, M_n , GPC=2704 g/mol, PDI=1.69) as white powder solid was obtained.

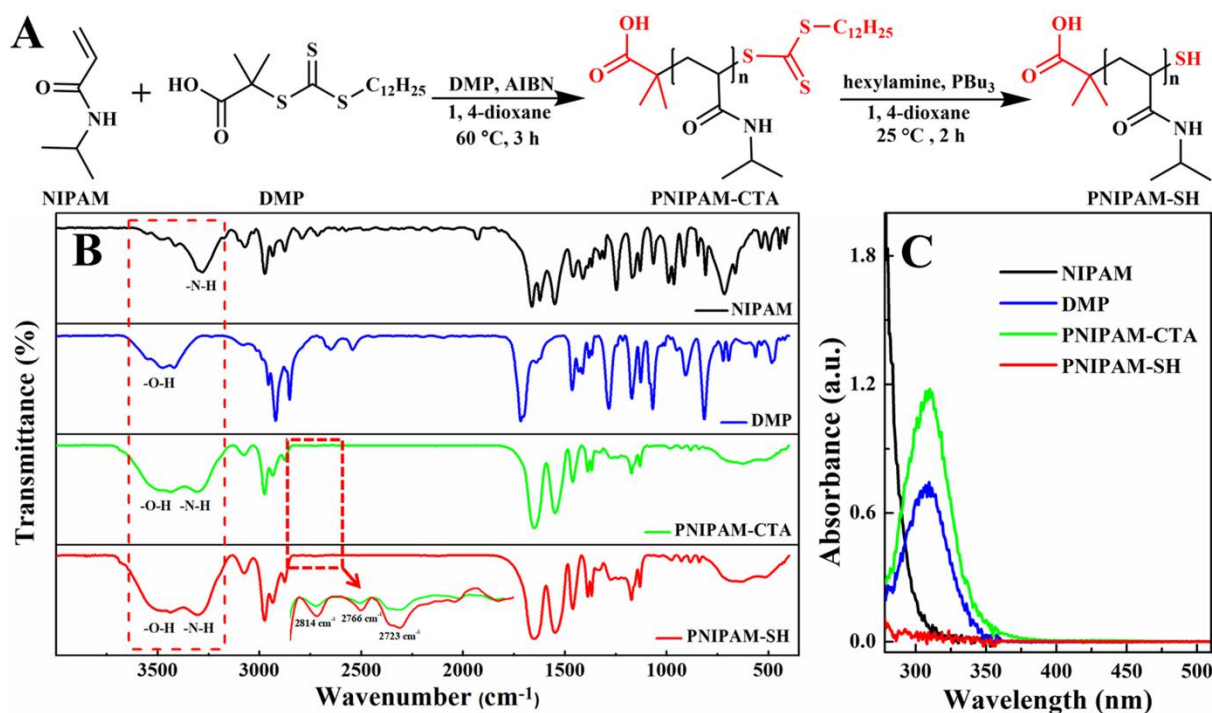


Fig. S1 The synthesis schematic diagram (A), FTIR spectrum (B) and UV-visible absorption spectrum (C) of PNIPAM-SH.

3. Preparation of PDA-Au-S-PNIPAM nanoparticles

17 mL of dopamine hydrochloride solution (0.02 M) and 17 mL of Tris-HCl buffer solution (10 mM, pH 8.5) were mixed and stirred for 90 min, then 37.5 mL of HAuCl₄ (2.3 mM) solution was added and stirred for 1 h. After centrifuging at 10000 rpm for 15 min, precipitation was washed by deionized water twice. The TCEP activated PNIPAM-SH (18 mL, 5 mg/mL) solution was added to the precipitation and stirred overnight. After centrifuging at 10000 rpm for 15 min, the PDA-Au-S-PNIPAM nanoparticles were achieved and washed by deionized water twice, storing in the refrigerator at 4 °C for later use.

4. Characterization of zeta potential and particle size

The prepared PDA-Au-S-PNIPAM nanoparticles were dispersed into PBS buffer, the pH of mixed solution was adjusted by 0.1 M HCl and KOH. Then, the zeta potential and particle size were measured at pH 3 and pH 11 after filtration with 0.22 μm PES filter membrane.

Table S1. Size and zeta potential of PDA-Au-S-PNIPAM nanoparticles

PDA-Au-S-PNIPAM	pH 11		pH 3	
	25 °C	43 °C	25 °C	43 °C
Size/nm	154.7±2.1	135.7±5.8	308.9±8.9	257.4±9.4
Zeta/mV	-16.1±1.4	-28±2.0	79.0±3.0	6.1±2.2

5. Fluorescence and UV Characterization of heterogeneous membrane

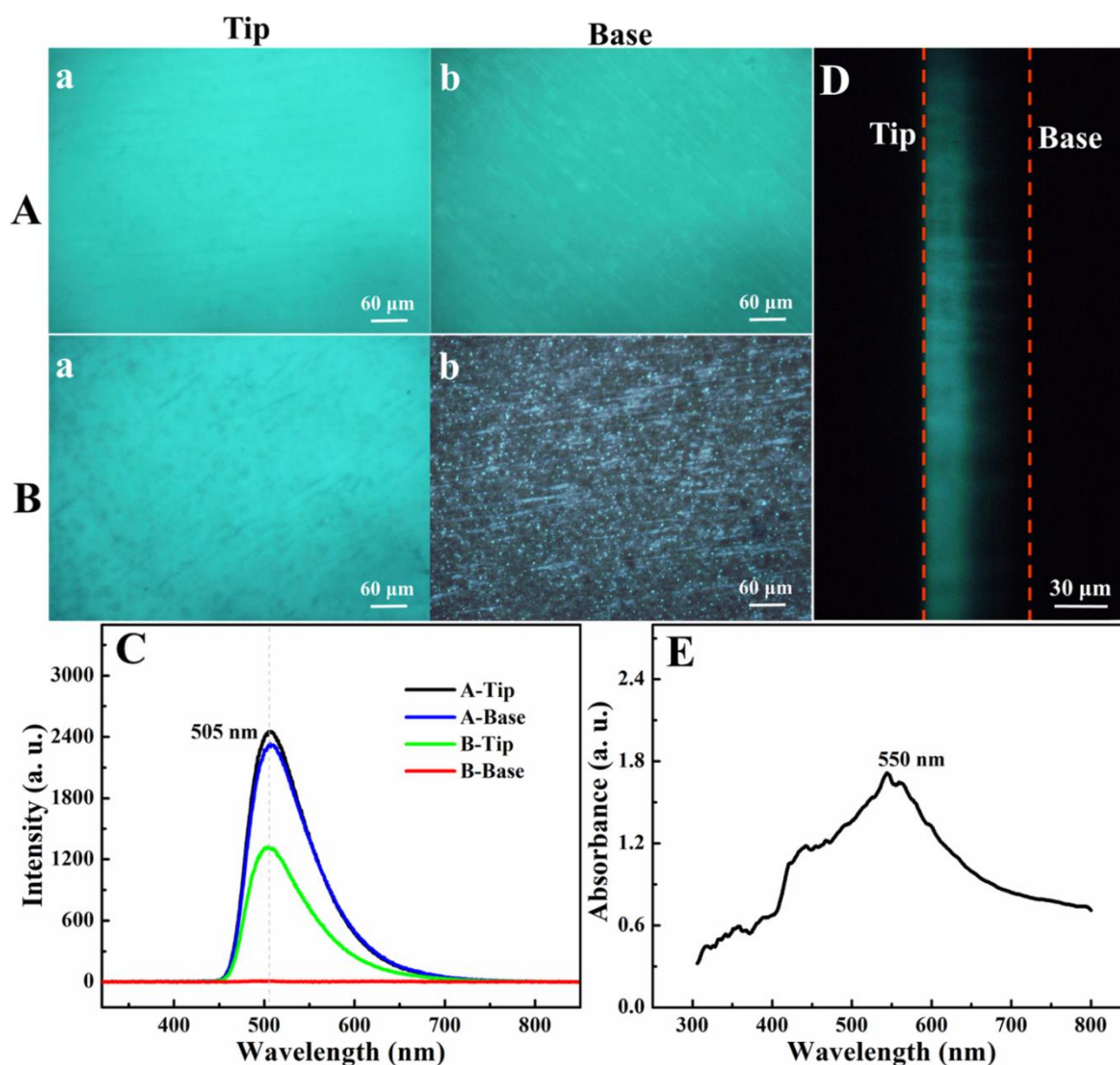


Fig. S2 The fluorescence image of Tip (a) and Base (b) end for AAO/PPhCz (A) and AAO-3(PDA-Au)-S-PNIPAM/PPhCz (B) under inverted fluorescence microscope and corresponding fluorescence spectrum (C); the cross-sectional fluorescence image (D) and UV-Vis absorption spectrum (E) of AAO-3(PDA-Au)-S-PNIPAM/PPhCz.

6. Elemental analysis of heterogeneous membrane

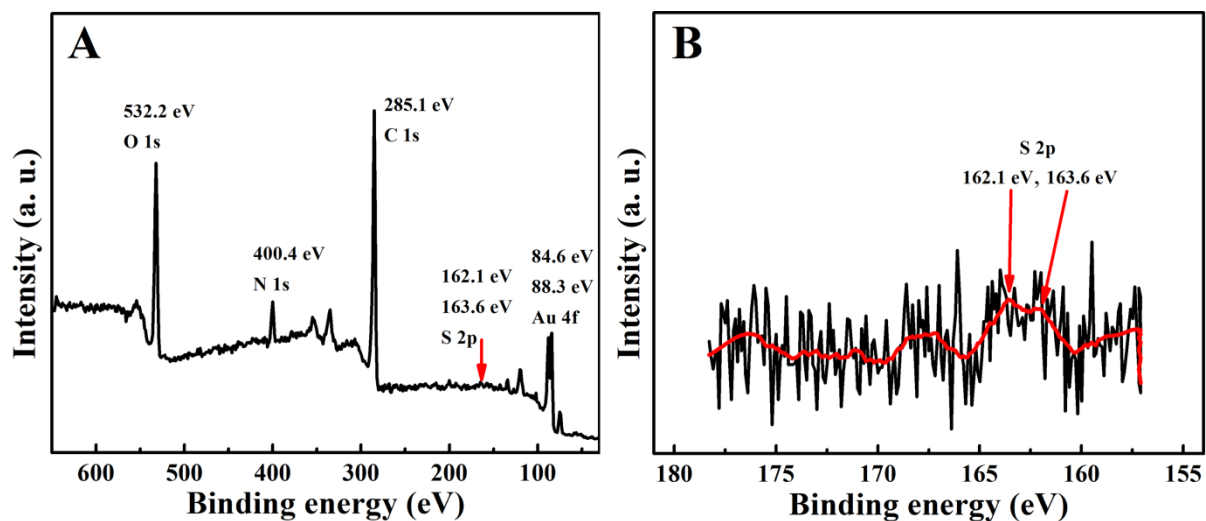


Fig. S3 XPS spectrum of different elements at the Base end of AAO-3(PDA-Au)-S-PNIPAM/PPhCz (A) and the corresponding enlarged spectrum of S element (B).

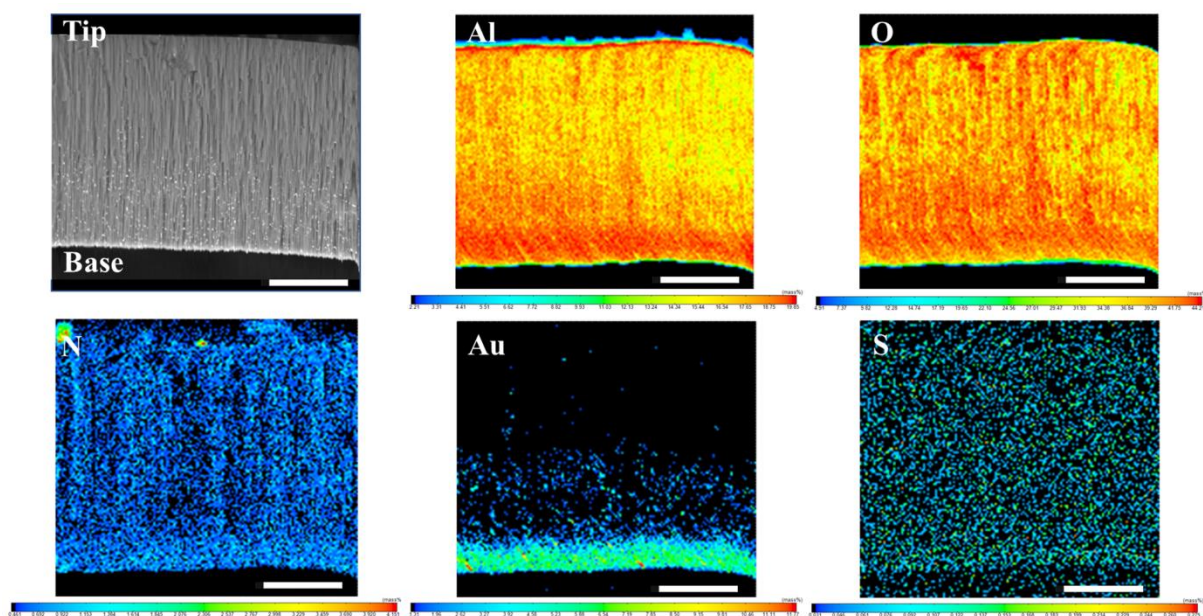


Fig. S4 Distribution of different elements at the cross section of AAO-3(PDA-Au)-S-PNIPAM/PPhCz by electron probe microanalysis, bar: 20 μm .

Table S2. The comparison with the previously reported photoresponsive nanochannel

Devices	Photoresponsive materials	Excitation wavelength (nm)	The maximum photoresponsive current	References
P-SPMA-modified conical glass nanochannel	Spiropyran derivative	365	< 50 nA	1
N3/PTE-BS patterned Al ₂ O ₃ nanochannel	Thiophene polyelectrolyte and bipyridine ruthenium	420 & 520	~2.0 μA	2
AZO-MOF ion channels	Azobenzene derivatives	365	~0.4 nA	3
TPPS/Al ₂ O ₃	Tetra(4-sulfonatophenyl)porphyrin nanofiber	420	9.7 μA	4
N3/Al ₂ O ₃	Ruthenium complex cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II)	380 & 518	561.46 nA	5
AAO-3(PDA-Au)-S-PNIPAM/PPhCz	Polydopamine and Au nanoparticles	808	183.7 μA	This work

References

1. Y. Y. Wu, L. D. Chen, X. H. Cai, Y. Zhao, M. Chen, X. H. Pan and Y. Q. Li, *ACS Appl. Mater. Interfaces*, 2021, **13**, 25241-25249.
2. Y. Ren, Y. Liu, L. Zhang, X. Fan, J. Zhai and L. Jiang, *Adv. Energy Mater.*, 2021, **11**, 2003340.
3. T. Qian, C. Zhao, R. Wang, X. Chen, J. Hou, H. Wang and H. Zhang, *Nanoscale*, 2021, **13**, 17396-17403.
4. D. Zhang, S. Zhou, Y. Liu, X. Fan, M. Zhang, J. Zhai and L. Jiang, *ACS Nano*, 2018, **12**, 11169-11177.
5. Y. Liu, Y. Kong, X. Fan, J. Zhai and L. Jiang, *J. Mater. Chem. A*, 2017, **5**, 19220-19226.