Electronic Supplementary Material (ESI) for Analyst.

Sensitive and reproducible gold nanostar@metal-organic framework based SERS membrane for on-line monitoring the freshness of shrimp

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Synthesis of gold seeds. All glassware was first cleaned with detergent, followed by aqua regia, and carefully rinsed with MilliQ water and acetone to guarantee an extremely cleaned glass surface. The seed AuNPs was first synthesized by adding a mixture of 3.5 mL of 60 mM sodium citrate and 1.5 mL of 60 mM citric acid to 144 mL of boiling MilliQ water and heating continuously for 30 min. Then 0.1 mL of 30 mM ethylenediaminetetraacetic acid and 1 mL aqueous solution of 25 mM hydrogen tetrachloroaurate (III) ($HAuCl_4$) were added quickly. After 60 s, the color of the mixture changed from pale yellow to dark blue and then to wind-red, indicating the growth of the Au NPs. The heating was then turned off, but magnetic stirring was continued. When the solution temperature dropped to 95°C, the reaction was interrupted by immersing the flask in ice water, and Au NPs seeds with an average core diameter of ca. 13 nm were obtained.

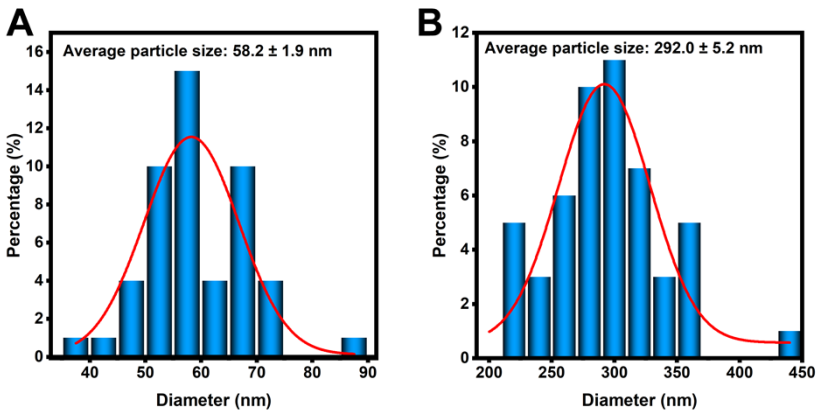

Figure S1. Size distribution histograms of AuNSs (A) and AuNS@ZIF-8 (B).

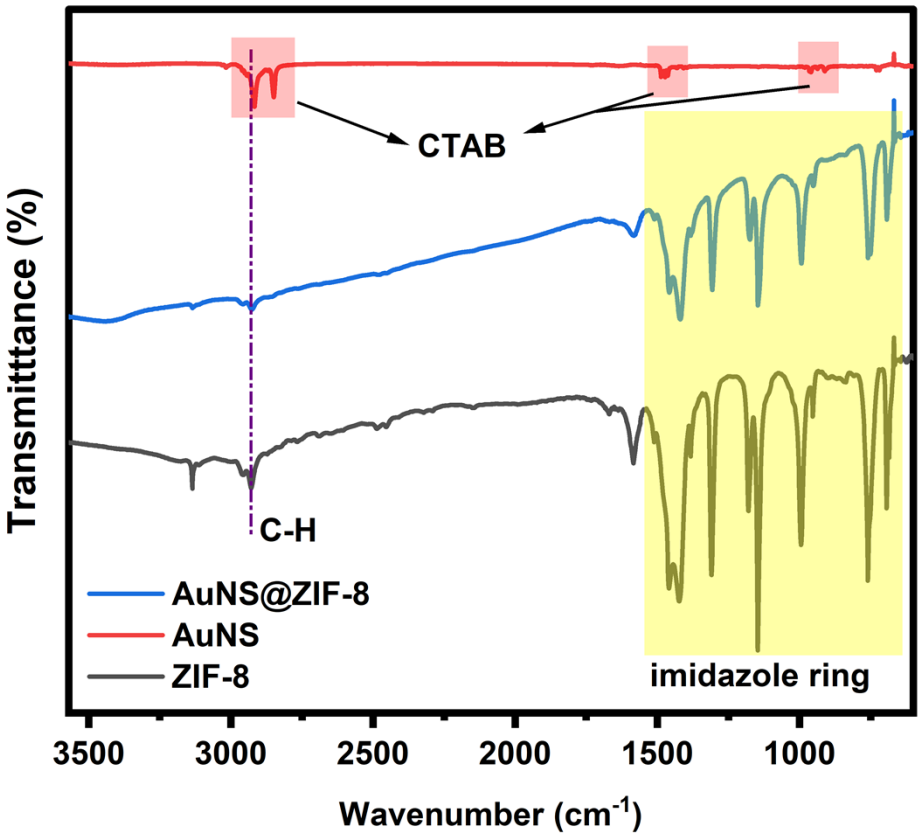

Figure S2. FTIR pattern of AuNS, ZIF-8, AuNS@ZIF-8.

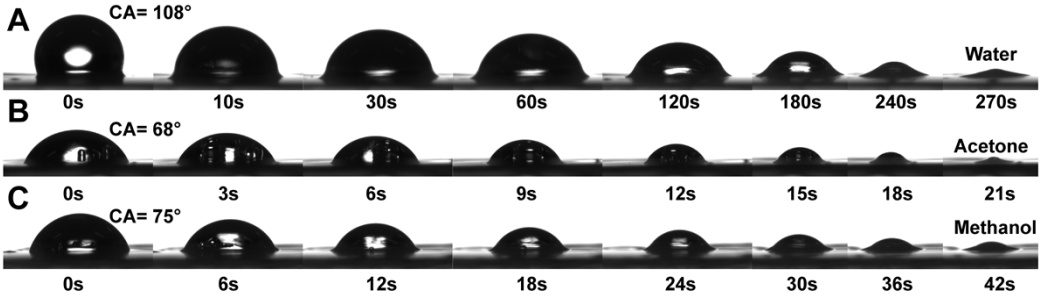

Figure S3. Evolution of contact angle images for different solvents during evaporation. (A) water; (B) acetone; (C) methanol.

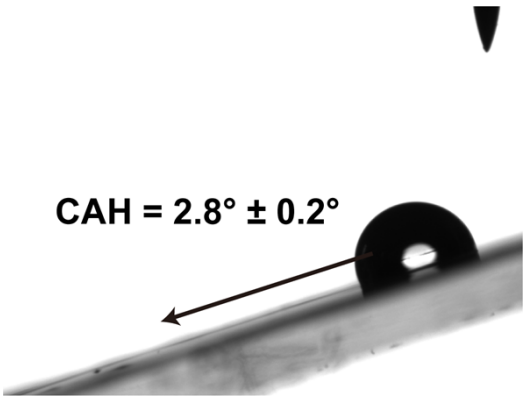

Figure S4. A water droplet (5 μL) slides on the SLIPS substrate.

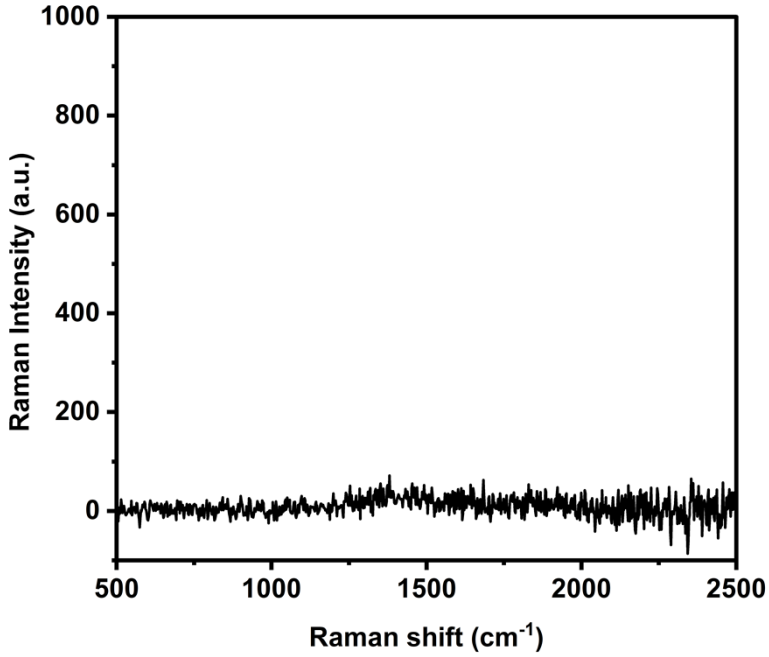

Figure S5. The Raman spectrum of the SLIPS substrate.

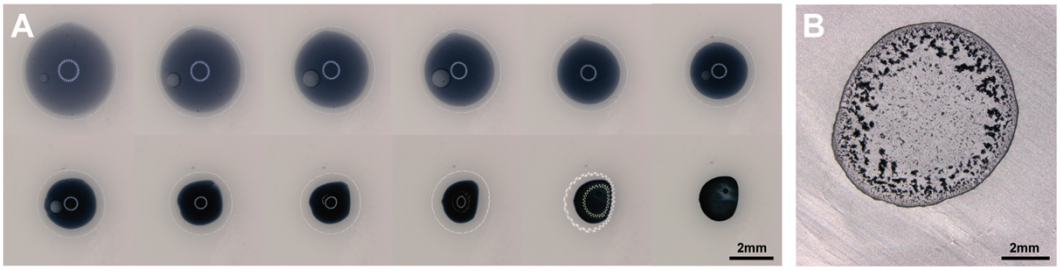

Figure S6. (A) The entire evaporation processes of 20 μL of AuNS@ZIF-8 on the SLIPS substrate; (B) the final aggregated pattern of 20 μL of AuNS@ZIF-8 on the tinfoil. The scale bar represents 2 mm.

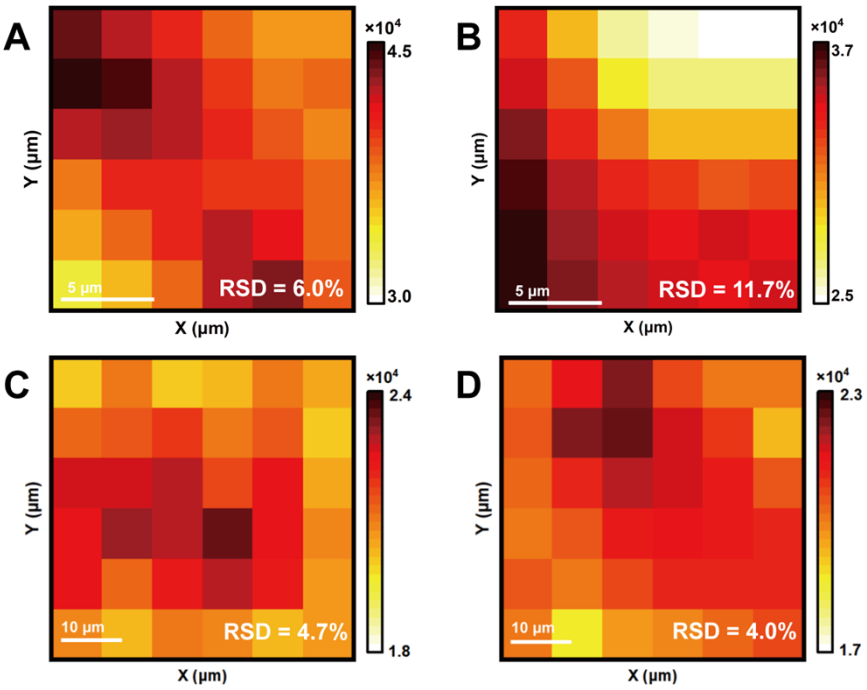

Figure S7. The SERS mapping results of the 1329 cm^{-1} SERS peak from 500 nM 4-NBT when using AuNS@ZIF-8s (A) and AuNSs (B) on the tinfoil; (C)(D)The SERS mapping results at different positions when increasing the scanning range to 50 μm 50 μm and using AuNS@ZIF-8-SLIPS.

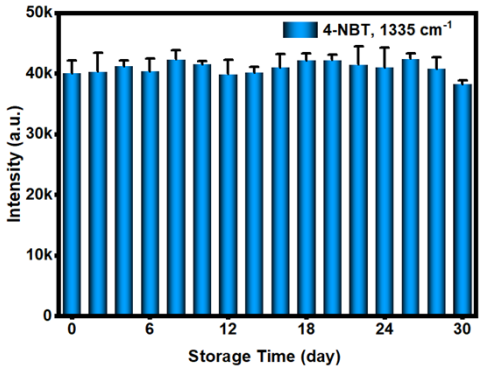

Figure S8. The variation of intensities at 1335 cm^{-1} (mean ± SD) for different storage time. The dates were collected from the AuNS@ZIF-8 SLIPS substrates in 30 days.

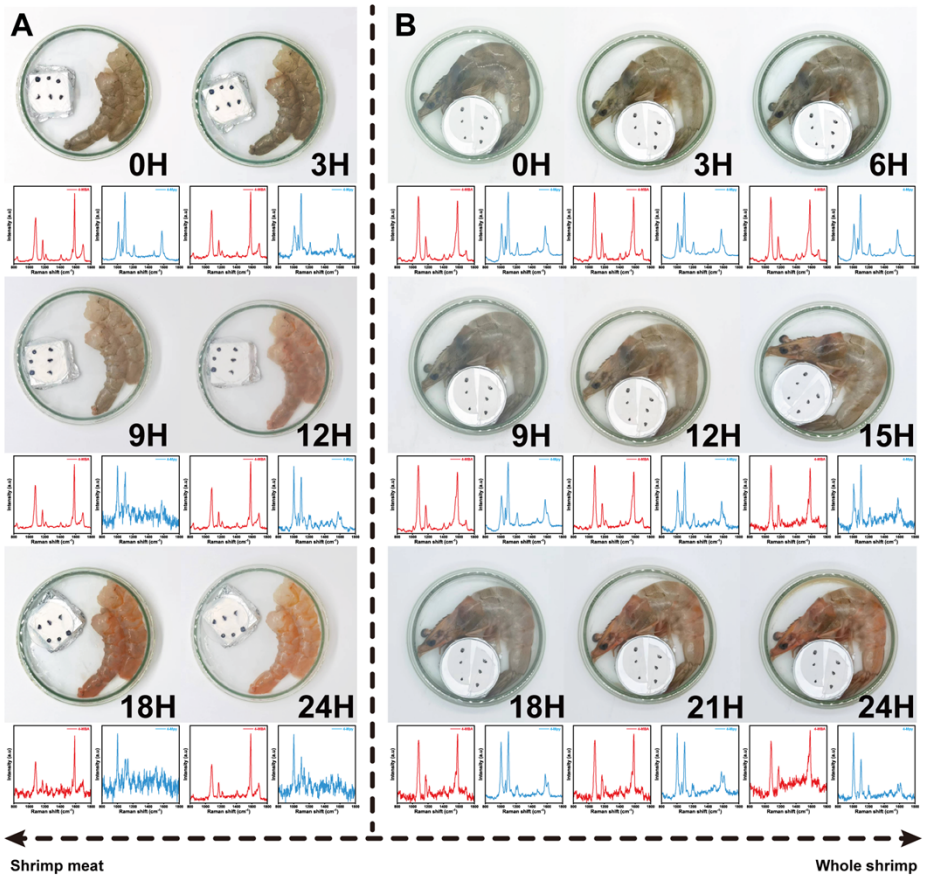

Figure S9. The entire photographs and Raman spectra during spoilage processes of shrimp meat (A) and whole shrimp (B) at 25℃. The red and blue curves represent the Raman spectra of 4-MBA and 4-Mpy, respectively.

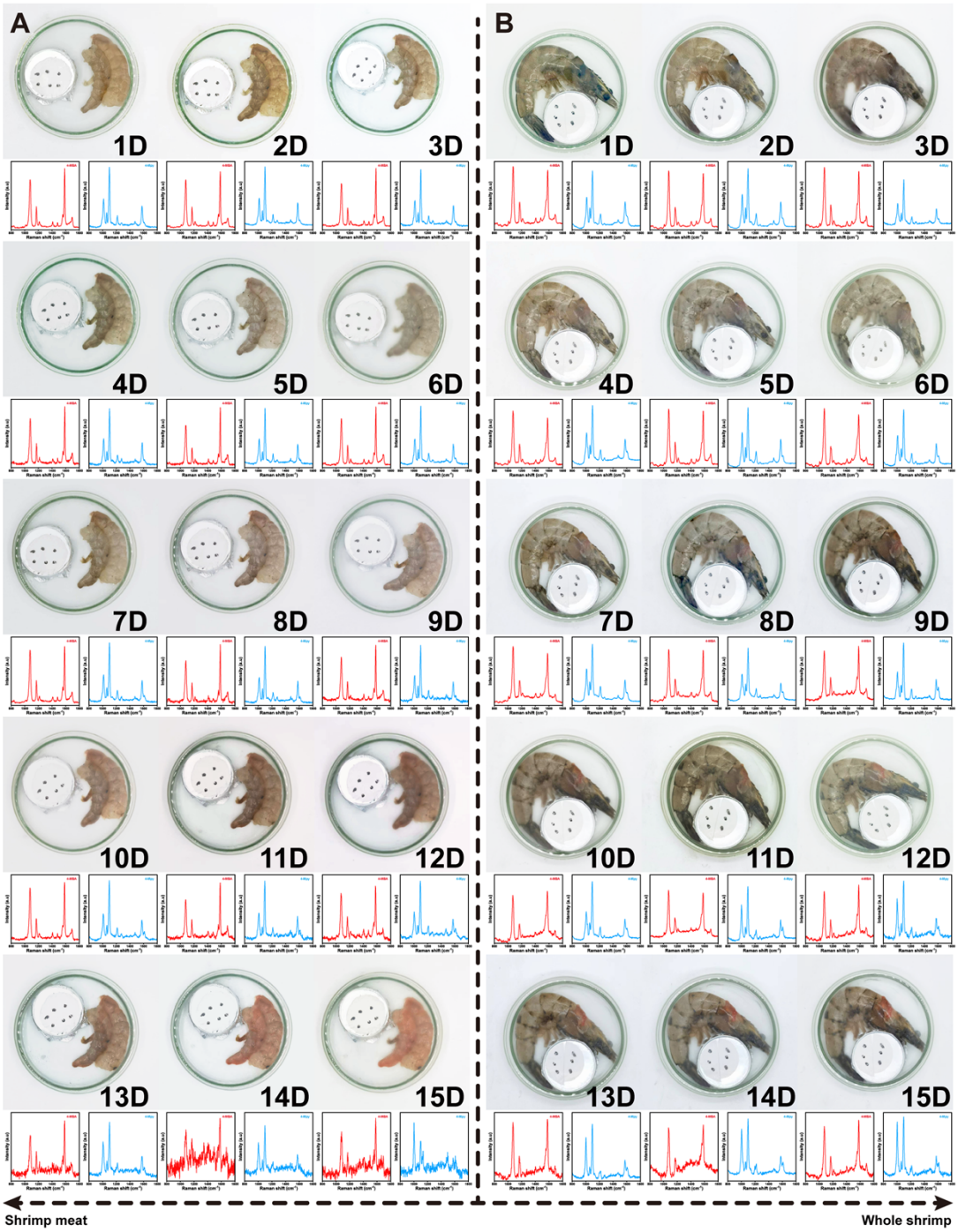

Figure S10. The entire photographs and Raman spectra during spoilage processes of shrimp meat (A) and whole shrimp (B) at 4℃. The red and blue curves represent the Raman spectra of 4-MBA and 4-Mpy, respectively.

Table S1. Assignments for Raman shifts of 4-Mpy[1]

Peak (cm^{-1})	Assignments
1013	Ring breathing
1100	Ring breathing/C—S stretching
1577	C—C/C=N stretching
1670	C—C/C=C stretching

Table S2. Assignments for Raman shifts of 4-MBA react to putrescine[2]

Peak (cm^{-1})	Assignments
1074	C—S stretching
1583	C=C stretching
1638	C=N stretching of the imine

Table S3. Methods for Putrescine Reported in the Literature

Methods	**Linear range**	**LOD**	**References**
Colorimetric sensor	2.8×10^{-4} - 1.7×10^{-3} M	1.0×10^{-4} M	3
Colorimetric sensor	2.8×10^{-6} - 1.1×10^{-4} M	6.8×10^{-7} M	4
Chromogenic method	1.0×10^{-6} - 7.5×10^{-5} M	1.0×10^{-6} M	5
Electrochemical sensor	2.5×10^{-7} - 2.5×10^{-5} M	1.1×10^{-7} M	6
Fluorometric sensor	0 - 7.5×10^{-5} M	1.9×10^{-6} M	7
SERS sensor	1.1×10^{-6} - 1.1×10^{-2} M	8.9×10^{-7} M	2
AuNS@ZIF-8 SLIPS	1.1×10^{-6} - 1.1×10^{-1} M	4.3×10^{-7} M	this work

Reference

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