Supporting information

Ultrasensitive SERS detection of exhaled biomarkers of lung cancer using a multifunctional solid phase extraction membrane

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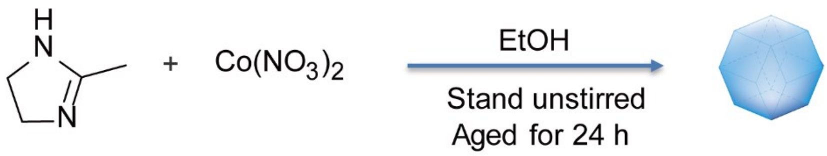


Figure S1. Schematic illustration of the synthetic approach to ZIF-67.

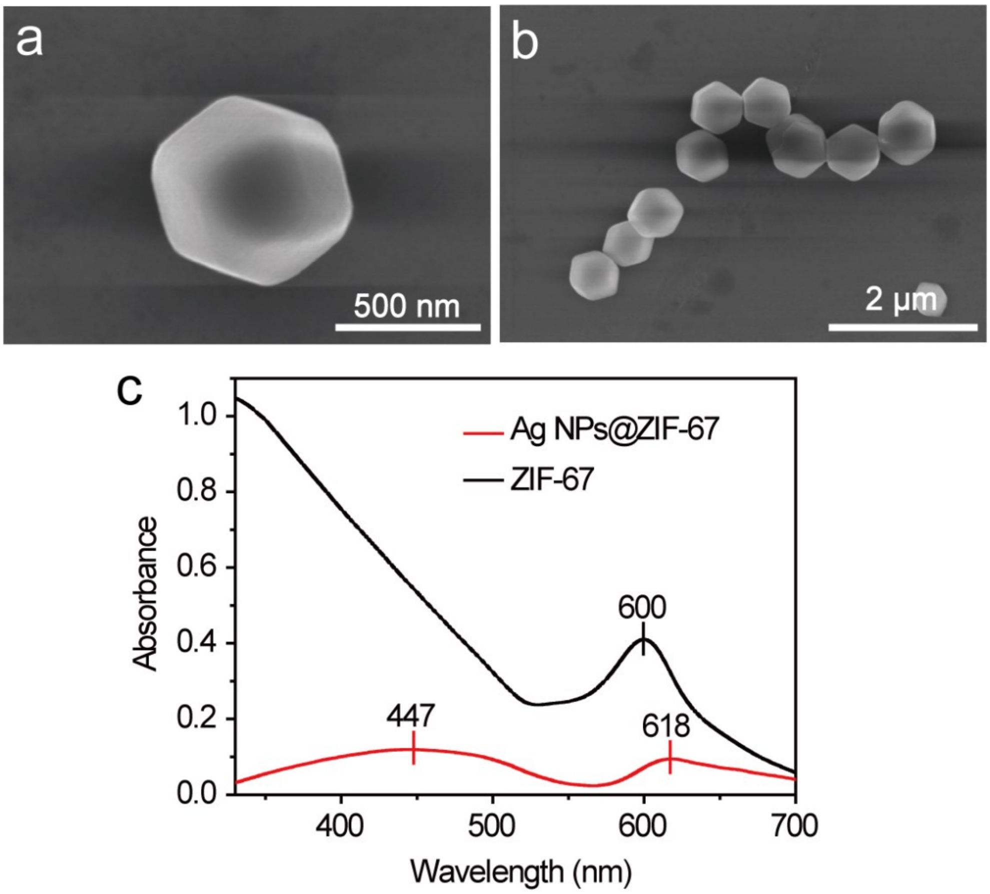
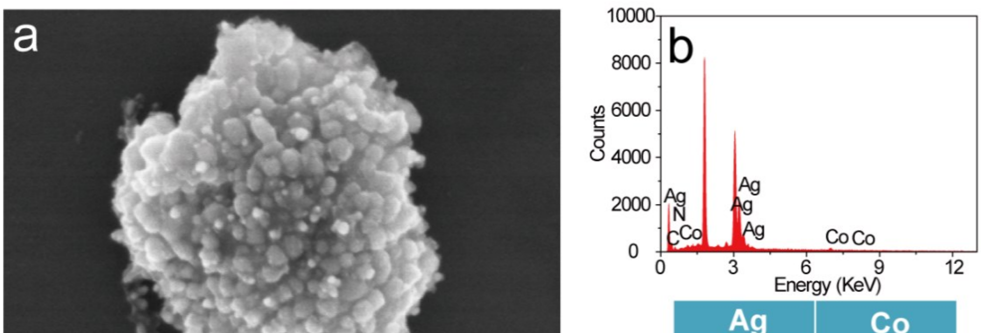


Figure S2. (a-b) SEM image of the ZIF-67 Nanoparticles. (c) UV-vis spectra of the ZIF-67 Nanoparticles and Ag NPs@ZIF-67 nanocomposite.



Ag	Co
78%	9%

Figure S3. (a) SEM images and (b) Element mapping and EDX analysis of Ag NPs@ZIF-67 nanocomposite.

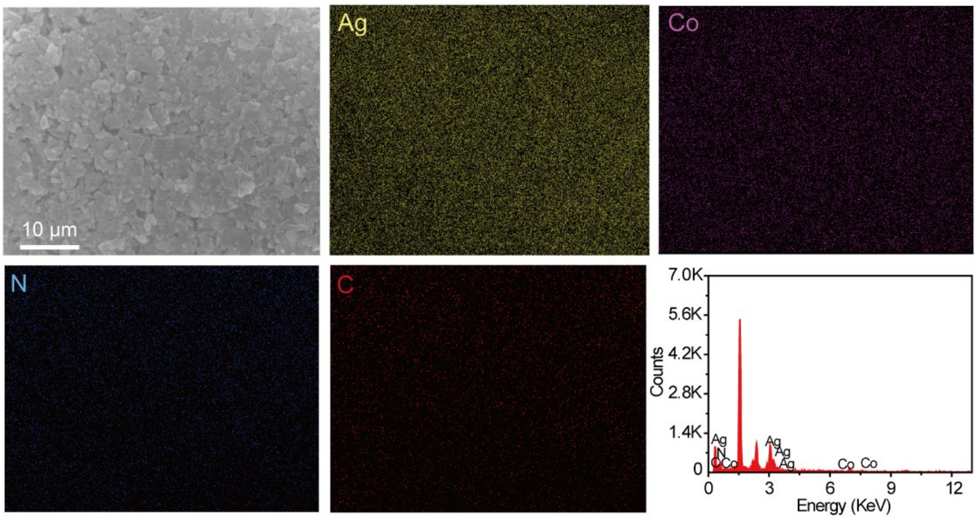


Figure S4. Element mapping and EDX analysis of the surface section of Ag NPs@ZIF-67/g-C_3N_4 membrane.

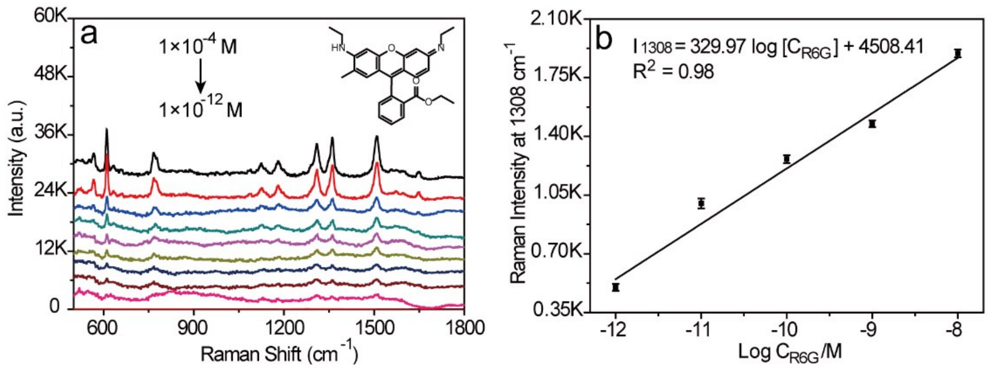


Figure S5. (a) SERS spectra of different concentrations of R6G adsorbed on the Ag NPs@ZIF-67 nanocomposites: 1.0 × 10^{-4} M to 1.0 × 10^{-12} M. (b) Plot of the SERS intensity versus logarithmic R6G concentration at 1308 cm^{-1}.

Calculation of the enhancement factor: To further test the SERS performance of Ag NPs, Ag NPs@ZIF-67, Ag NPs@ZIF-67/g-C_3N_4 substrates, the enhancement factor (EF) for rhodamine 6G (R6G) is estimated according to the following equations：

$$EF = \frac{I_{SERS}}{I_{Raman}} \times \frac{N_{Raman}}{N_{SERS}}$$

$$N_{SERS} = C_{SERS} \cdot V_{SERS} \times \frac{S_{Laser}}{S_{SERS}} \times N_A$$

$$N_{Raman} = C_{Raman} \cdot V_{Laser} \times N_A$$

where I_{SERS} and $I_{Raman} = 50$ are the intensities of the Raman peak at 1362 cm^{-1} in the SERS and normal Raman spectra of R6G, and N_{SERS} and N_{Raman} are the average number of molecules in the scattering area on the SERS and non-SERS substrates, respectively. $C_{SERS} = 1.0 \times 10^{-6}$ M R6G and $C_{Raman} = 1.0 \times 10^{-2}$ M are the molar concentrations of R6G, $V_{SERS} = 6$ μL is the droplet volume of R6G dispersed onto the Ag NPs, AgNPs@ZIF-67, Ag NPs@ZIF-67/g-C_3N_4 substrates, $S_{Laser} = \pi r^2 = 7.6 \times 10^{-12}$ m^2 ($r = 1.55 \times 10^{-6}$ m) are the calculated laser beam area on the substrate surface, S_{SERS} is the R6G droplet spreading area on the substrates. In the experiment, the 10 μL droplet is in fact spread over the entire 4 mm in diameter, so $S_{SERS} = 1.26 \times 10^{-5}$ m^2. N_A is the Avogadro constant ($N_A = 6.02 \times 10^{23}$ moL^{-1}). The volume of R6G solution for producing Raman scattering was calculated to be $V_{Laser} = 2.5 \times 10^{-12}$ m^3.

$$N_{SERS} = 10^{-6} \times 6 \times 10^{-6} \times \frac{7.6 \times 10^{-12}}{1.26 \times 10^{-5}} \times N_A$$

$N_{SERS} = 2.18 \times 10^6$

$N_{Raman} = 10^{-2} \times 2.5 \times 10^{-12} \times N_A$

$N_{Raman} = 1.51 \times 10^{10}$

EF (Ag NPs) = $I_{SERS}/I_{solution} \times N_{Raman}/N_{SERS}$

EF (Ag NPs) = $8000 / 50 \times 1.51 \times 10^{10} / 2.18 \times 10^6$

EF (Ag NPs) = 1.11×10^6

EF (Ag NPs@ZIF-67) = $I_{SERS}/I_{solution} \times N_{Raman}/N_{SERS}$

EF (Ag NPs@ZIF-67) = $8919 / 50 \times 1.51 \times 10^{10} / 2.18 \times 10^{6}$

EF (Ag NPs@ZIF-67) = 1.24×10^{6}

EF (Ag NPs@ZIF-67/g-C_3N_4) = $I_{SERS}/I_{solution} \times N_{Raman}/N_{SERS}$

EF (Ag NPs@ZIF-67/g-C_3N_4) = $18105 / 50 \times 1.51 \times 10^{10} / 2.18 \times 10^{6}$

EF (Ag NPs@ZIF-67/g-C_3N_4) = 2.51×10^{6}

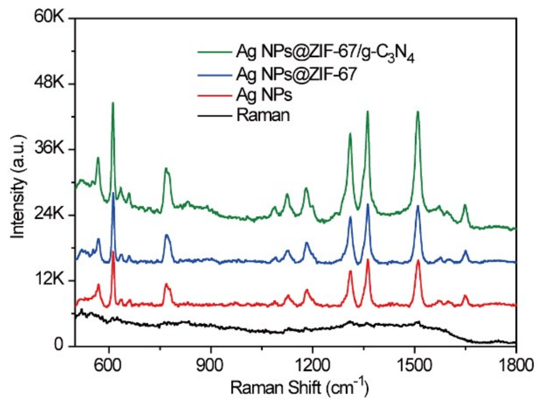


Figure S6. The SERS spectrum of R6G (10^{-6} M) dispersed onto the Ag NPs, AgNPs@ZIF-67, Ag NPs@ZIF-67/g-C_3N_4 substrates and the normal Raman spectra of R6G (10^{-2} M).

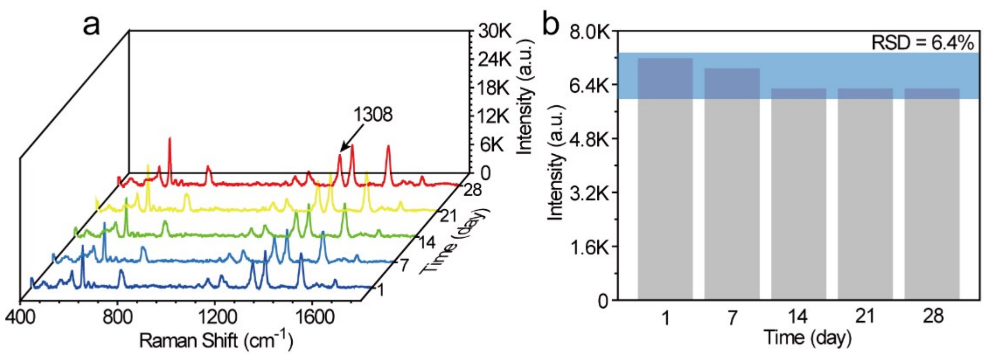


Figure S7. (a) SERS spectra of R6G on Ag NPs@ZIF-67/g-C_3N_4 stored from 1 to 28 days. (b) The intensity of R6G at 1308 cm^{-1} for different storage period.

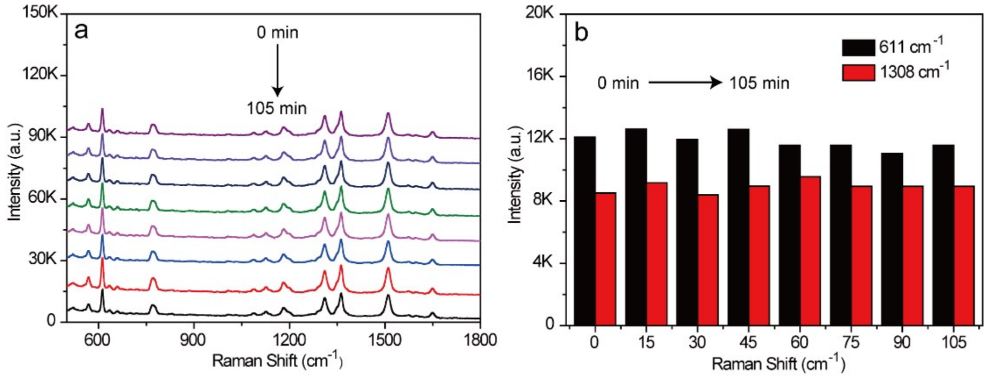


Figure S8. (a) SERS spectra monitoring the photocatalytic degradation process of R6G (5×10^{-5} M) adsorbed on the Ag NPs. (b) The corresponding variation in the SERS intensity at 611 and 1308 cm^{-1} versus the degradation time.

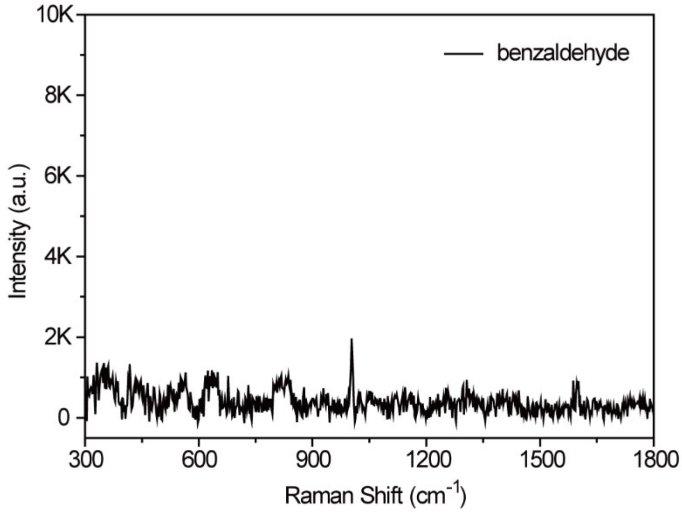


Figure S9. SERS spectra of benzaldehyde on Ag NPs@ZIF-67/g-C_3N_4.

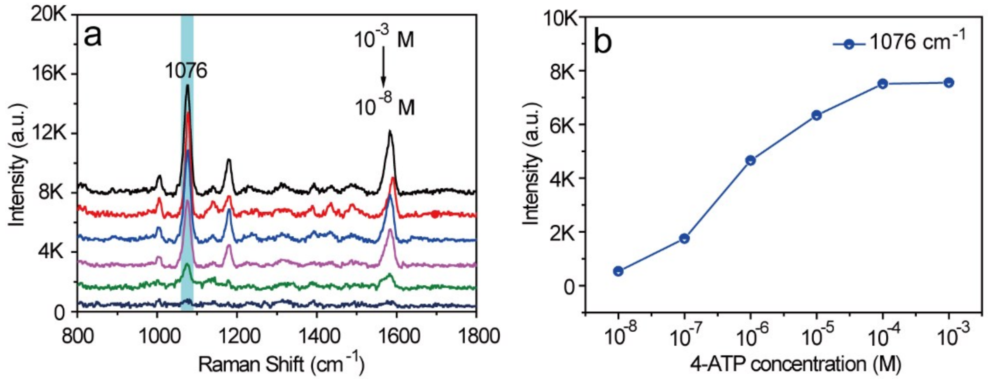


Figure S10. (a) SERS spectra of different concentrations of 4-ATP adsorbed on the substrate: 10^{-3} M to 10^{-8} M. (b) SERS intensity of different concentrations of 4-ATP.

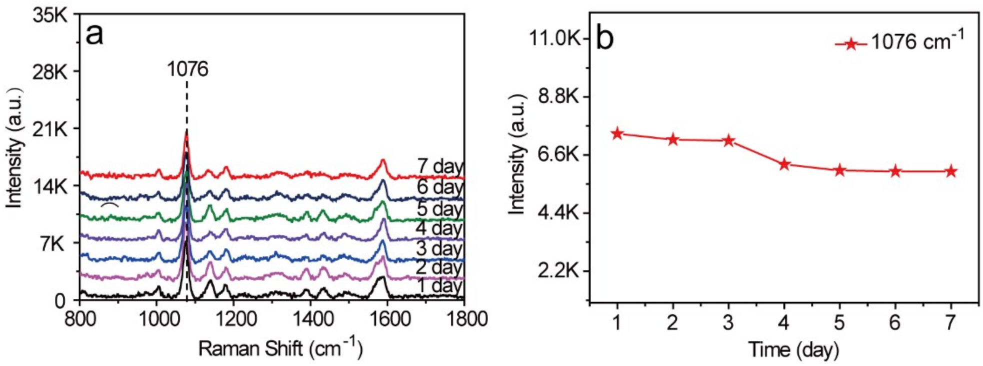


Figure S11. (a) SERS spectra of 4-ATP (10^{-4} M) on Ag NPs@ZIF-67/g-C_3N_4 stored from 1 to 7 days. (b) The intensity of 4-ATP at 1076 cm^{-1} for different storage period.

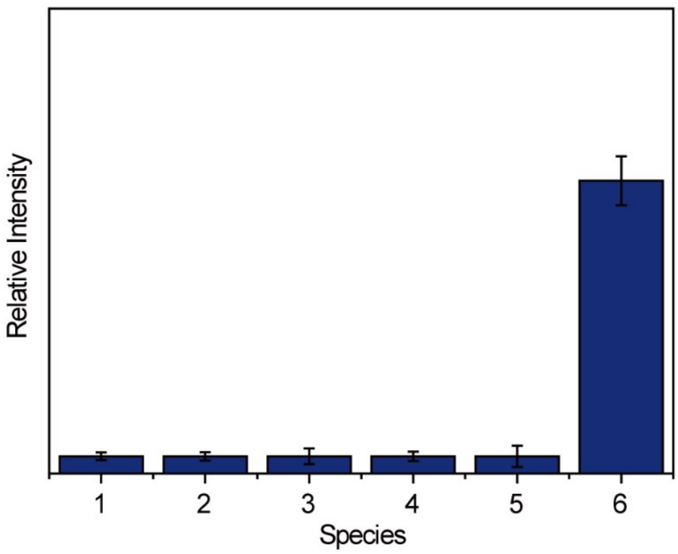


Figure S12. Selectivity detection of simulated exhaled gas in patients with lung cancer including (1) the alcohols (ethyl alcohol), (2) the ketones (acetone), (3) the esters (butyl acetate), (4) the ethers (acetonitrile), (5) the aromatic compounds (methylbenzene), and (6) the aldehydes.

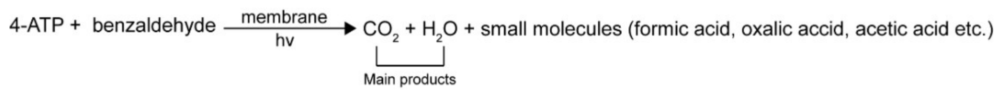


Figure S13**.** The degradation products of 4-ATP and the reaction products of 4-ATP and benzaldehyde on the Ag NPs@ZIF-67/g-C_3N_4 membrane under the visible light irradiation.

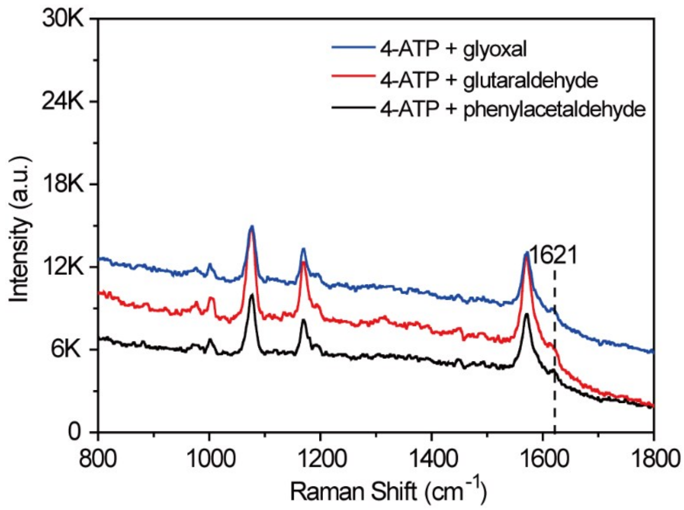


Figure S14. SERS spectra of the glyoxal, glutaraldehyde and phenylacetaldehyde.