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Supplementary Information

Reactive strategy-based SERS Determination of $O_2^{\bullet-}$ Generated from Sunscreen

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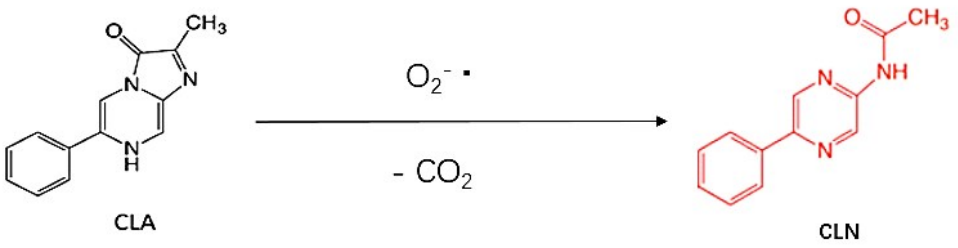

Fig S1. Schematic illustration of CLA reaction with $O_2^{\bullet-}$ into dioxetane analog (CLN).

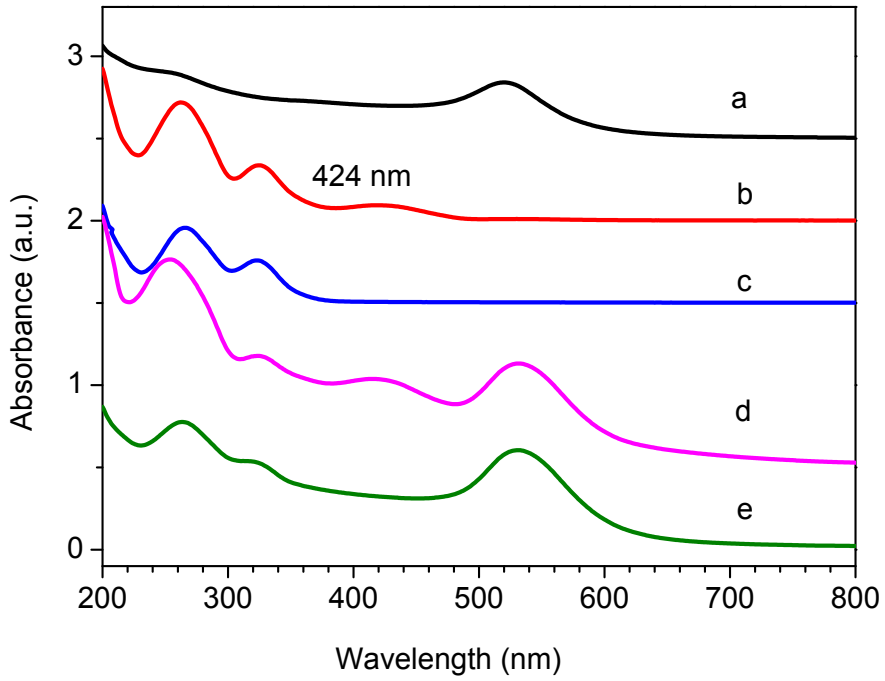

Fig S2. UV-Vis spectra of (a) Au NPs, (b) CLA, (c) CLN, (d) Au NPs and CLA, (e) Au NPs and CLN.

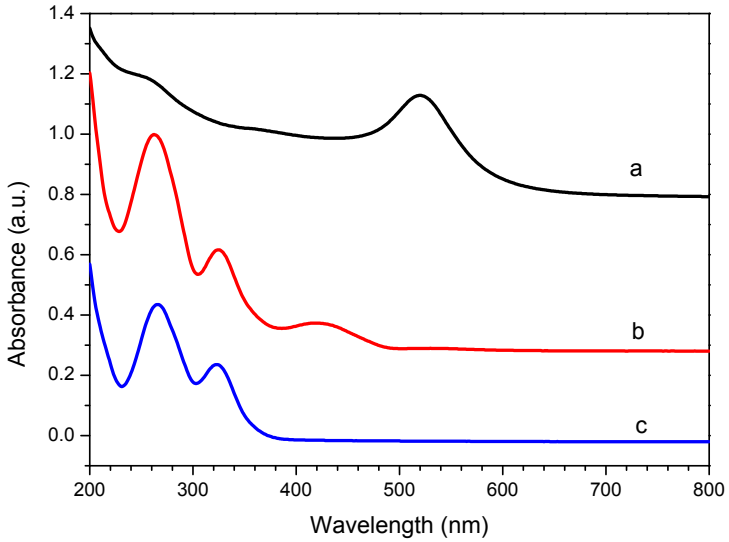

Fig S3. UV-Vis spectra of CLA (a) 0.1 mmol/L, (b) 10 μmol/L, (c) 1 μmol/L.

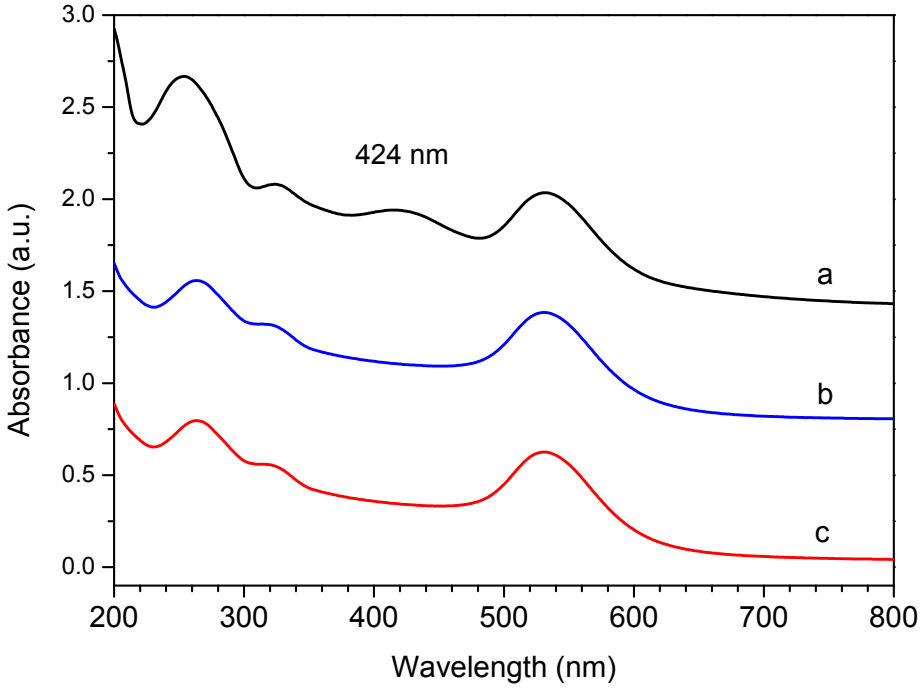

Fig S4. UV-vis spectra of TiO_2 with Au NPs/CLA under different radiation time (a) 2h, (b) 3h, (c) 4h.

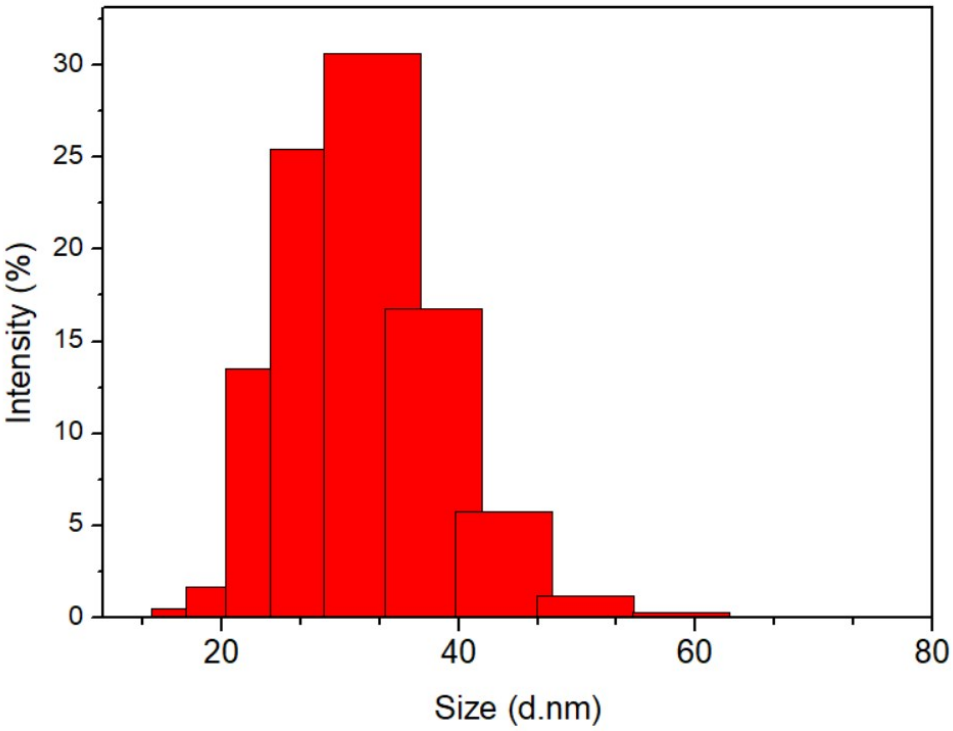

Fig S5. Size distribution of Au NPs.

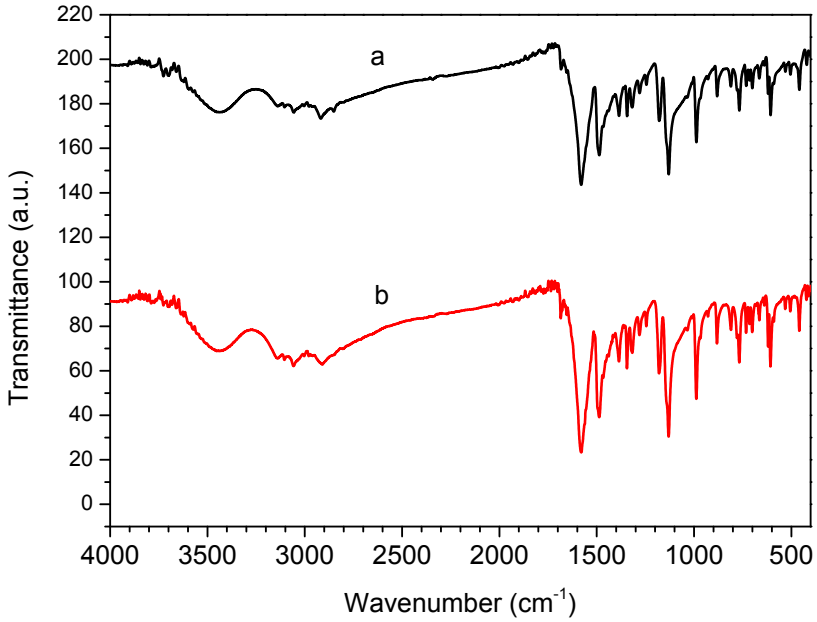

Fig S6. FTIR spectra of (a) CLA, (b) Au NPs + CLA.

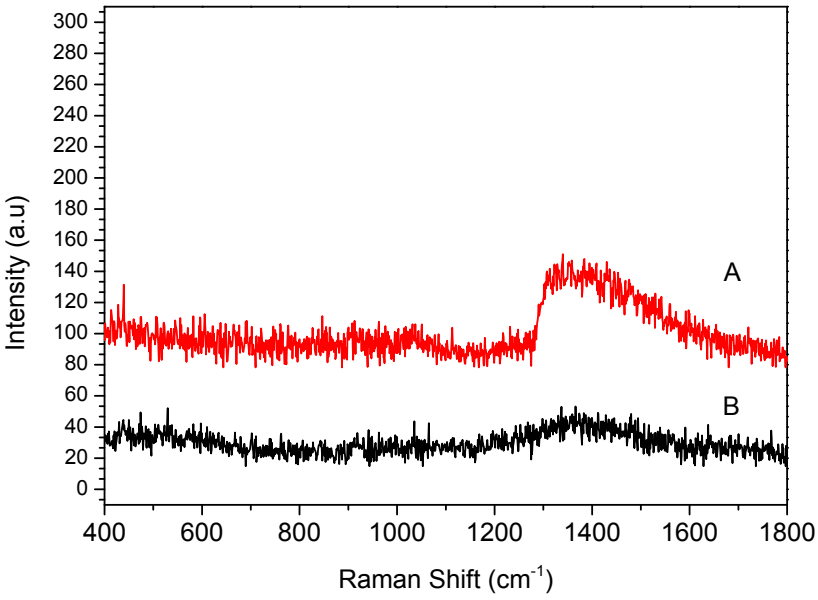

Fig S7. Raman spectra of (A) CLA, (B) CLN.

Principle of kit determination $O_2^{\cdot-}$:

$O_2^{\cdot-}$ reacts with hydroxylamine to form nitrite ions (reaction equation: $NH_2OH + 2\ O_2^{\cdot-} + H^+ = NO^{2-} + H_2O_2 + H_2O$. NO^{2-} reacts with p-aminobenzene sulfonic acid and α-naphthylamine to produce the pink azo dye, 4-((2-aminonaphthalen-1-yl)diazenyl)benzenesulfonic acid, i.e. PANE, which has significant light absorption at 530 nm.

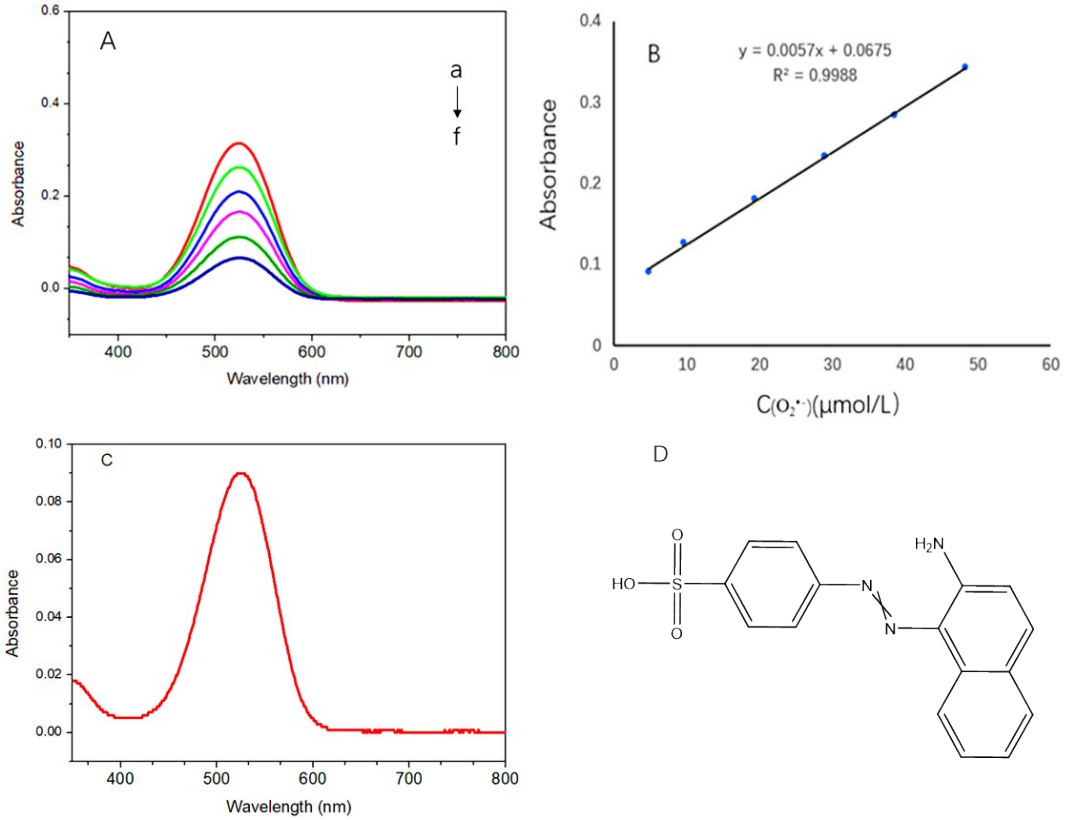

Fig. S8. (A) UV-Vis spectra of PANE concentration (a) 10 μg/mL, (b) 8.0 μg/mL, (c) 6.0 μg/mL, (d) 4.0 μg/mL, (e) 2.0 μg/mL, (f) 1.0 μg/mL, (B) Standard curve line of $O_2^{\cdot-}$(n=3), (C) UV-Vis Spectrum of PANE concentration under the ultraviolet analyzer

for 3 hours, (D) molecular structure of PANE.

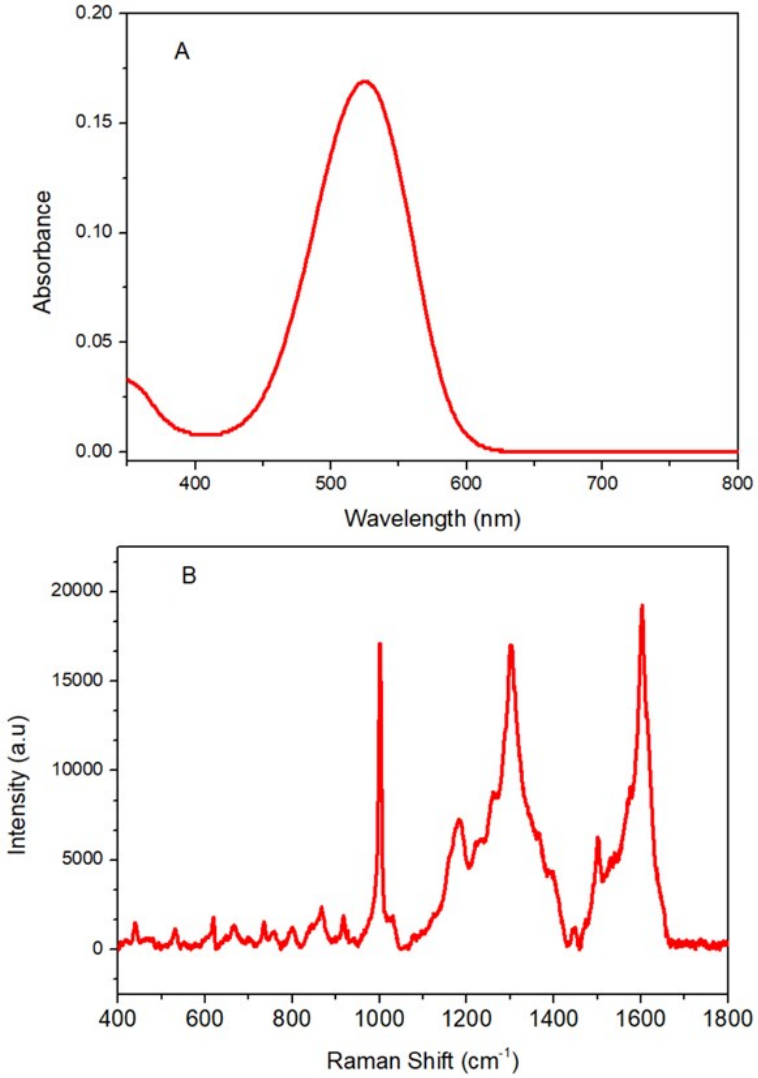

Fig. S9. (A) UV-Vis spectrum of PANE, (B) SERS spectrum of Au NPs/CLN.

Relative Error (RE) calculation：

The concentration was $C_0 = 9.91 \times 10^{-6}$ mol/L by UV calculated.

The concentration was $C_1 = 8.93 \times 10^{-6}$ mol/L by SERS calculated.

Computational formula: $RE = \frac{|C_1 - C_0|}{C_0} \times 100\%$

$$RE = \frac{|8.93 - 9.91|}{9.91} \times 100\% = 9.86\%$$

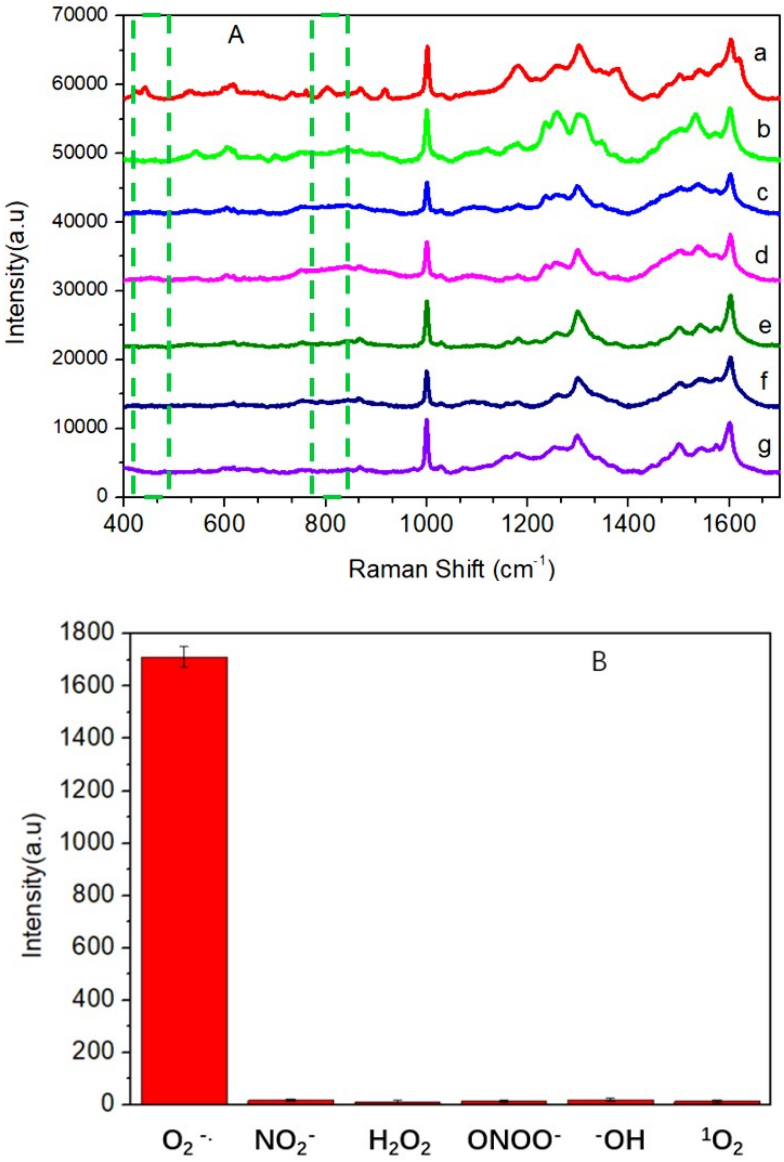

Fig. S10. (A) SERS spectra of (a) Au NPs/CLA+ $O_2^{\cdot-}$, (b) Au NPs/CLA, (c) Au NPs/CLA+NO_2^-, (d) Au NPs/CLA+H_2O_2, (e) Au NPs/CLA+$ONOO^-$, (f) Au NPs/CLA+•OH, (g) Au NPs/CLA+$^1O_2$, (ROS concentration is 1.0 μmol/L), (B) Plot demonstrated the selectivity of the SERS nanosensors based on the band of 802 cm^{-1}.

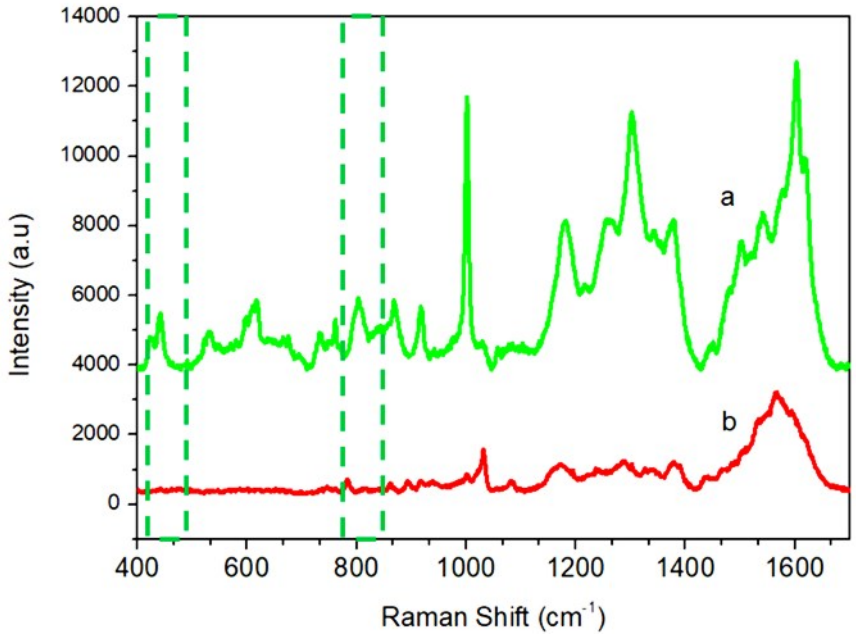

Fig. S11. SERS spectra of (a) Au NPs/CLN, (b)Au NPs/sunscreen after UV irradiation.

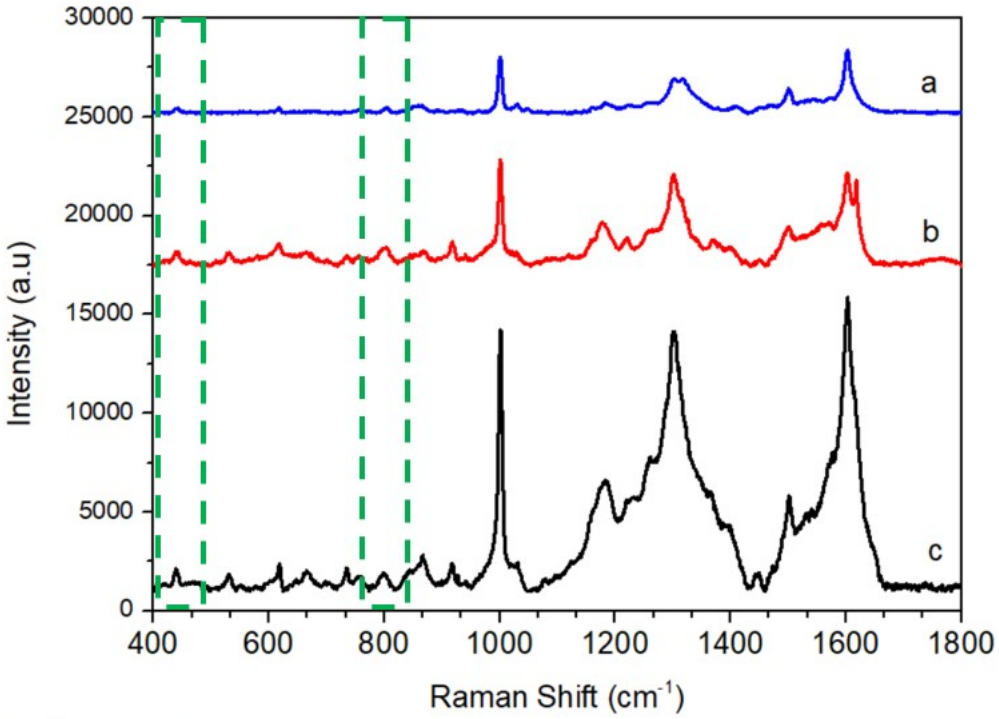

Fig S12. SERS spectra of 1.0 g sunscreen under different UV exposure time: (a) 30 min, (b) 1 h, (c) 2 h.

Table S1. Methods for the determination of superoxide anion radical

Method	Linearity range (mol/L)	LOD (nmol/L)	Ref
Electrochemistry	3.0×10^{-8}— 2.1×10^{-7}	17.5	1
Fluorescence	2.0×10^{-5}— 8.0×10^{-5}	70.5	2
Bioluminescent	/	3.5	3
RSS	5.0×10^{-8} — 5.0×10^{-5}	9	This work

References:

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