Supporting Information for

One-pot Preparation of Anionic Ions Stabilized Gold Nanoparticle with Low SERS background for Detecting Reaction Intermediates under Strong Oxidative Conditions

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1.Chemicals

Chloroauric acid ($HAuCl_4$), sliver nitrate ($AgNO_3$), sodium bromide (NaBr), potassium iodide (KI), sodium chloride (NaCl), Sodium thiosulfate pentahydrate ($Na_2S_2O_3$), sodium hydroxide (NaOH), hydrazine hydrate (HH), hydroxylamine hydrochloride ($HONH_3Cl$), crystal violet (CV), hydrogen peroxide (30 % aqueous solution, 30 % H_2O_2), were provided by Sinopharm Chemical Reagent Co., Ltd. Potassium rhodanide (KSCN), hydroquinone (HQ), 1,2-dihydroxybenzene(catechol), sulfacetamide (SA), sulfamethazine (SMT), polyvinylpyrrolidone (PVP), Polyvinyl alcohol (PVA), Polyethylene glycol sorbitan monolaurate (Tween-20), and were provided by Macklin. Nile blue (NB), sulfapyridine (SPY), sulfamerazine (SMR), sulfamonomethoxine (SMM), and sulfachloropyridazine (SCP) were provided by Aladdin. sulfamethoxazole (SMX) was purchased from Shanghai Civi Chemical Technology Co., Ltd.

2. Instrument

UV-Vis absorption spectra were recorded from a Thermo Scientific NanoDrop 2000/2000C spectrophotometer. Confocal Raman spectra were obtained on a Renishaw inVia Raman microscope (UK). All spectra were obtained under the same conditions, with a 50x objective lens used for amplification, a 785 laser used as the excitation light source, 1 s as the exposure time, and 0.3 mW as the laser power. TEM images were obtained using a Talos F200X G2 (Thermo Fisher Scientific) with an accelerating voltage of 200 kV.

3.Preparation of different nanoparticles

3.1 Preparation of low-background nanoparticles

20 μL of different reducing agents (HQ, HH, $HONH_3Cl$ and catechol) with a concentration of 0.1M and 10 μL of 1mM KI were added to 70 μL of deionized water to mix evenly, and the above mixed solution was added to 890 μL of deionized water containing 10 μL of 50 mM chloroauric acid.

The preparation method of low background substrate using other ions as protective agent is the same.

3.2 Preparation of high-background nanoparticles

Appropriate amounts of different protective agents PVA (0.5%), PVP (0.5%), Tween20 (0.5%) were added to 50 μL of deionized water and mixed evenly. The mixture was then added to 980 μL of deionized water containing 10 μL of 50 nm chlorauric acid.

4.SERS detection of organic dyes and sulfonamide antibiotics

Organic dyes are NB, CV. Sulfanilamide antibiotics are SA, SPY, SMM, SMR, SMX, SMT, SCP. AuNPs colloidal solution of 1.0 μL (concentrated 100 times by centrifugation) was deposited on the silicon wafer by solvent evaporation method. Subsequently, the wafers were immersed in 200 μL solutions of each organic dye or sulfanilamide antibiotic for 30 minutes before SERS spectral analysis。

5. SERS characterization of the photodegradation of SMR

5 mL of a 10^{-3} M SMR solution was placed in a clean surface dish and subjected to photodegradation under a UV lamp. Samples (200 μL) were collected at 5-10 minutes intervals. Silicon wafers with LB-AuNPs substrate was then immersed in each collected sample for 30 minutes before SERS spectral analysis.

6. Corrosion resistance testing

6.1 Resistance of gold and silver nanoparticles to hydrogen peroxide corrosion in colloidal state

A series of eight 1 mL aliquots of gold colloid nanoparticle solution were prepared. To these, increasing volumes (0-70 μL) of 0.01 M hydrogen peroxide solution were added in 10 μL increments. After a 5-minute reaction, UV-Vis absorption spectra were recorded for each sample. The silver colloid nanoparticles were analyzed using the same method.

6.2 Experiments on the resistance of gold and silver substrates to hydrogen peroxide corrosion

To investigate the corrosion behavior of LB-AuNPs and LB-AgNPs substrates in the presence of H_2O_2, samples of LB-AuNPs and LB-AgNPs were deposited onto the surface of silicon wafers. The prepared substrates were then immersed in 200 μL of a 10^{-7} M NB solution. Following, 10 μL of 0.1 M H_2O_2 solution was added to initiate the corrosion reaction. The evolution of the Raman signals of NB molecules was monitored in situ using the SERS technique. The total reaction time was set to 10 minutes, with spectra collected at 5-second intervals, resulting in a total of 120 spectra. By analyzing the temporal variation of the characteristic SERS peaks of NB, the corrosion effects of H_2O_2 on both LB-AuNPs and LB-AgNPs substrates were systematically evaluated. The above experimental details were added to the supporting information.

7. Bacterial toxicity test

7.1 Preparation of Culture Media:

Fluid nutrient mediumwas prepared by dissolving 10 g tryptone, 5 g yeast extract, and 10 g NaCl in 1 L deionized water, followed by sterilization at 121°C for 20 min using an autoclave. To prepare the solid medium, 5 g AGAR powder is added to each 250 mL liquid medium above to dissolve it completely. Pour the dissolved medium into a sterile petri dish, about 15-20 mL per dish, and store it upside down in a refrigerator at 4℃ for later use after solidification. All media should be tested for sterility before use to ensure no microbial contamination.

7.2Bacterial Culture and Cytotoxicity Assessment:

Escherichia coli (E. coli) was selected as a biological model to evaluate the cytotoxicity before and after SMR degradation. The preserved E. coli strains were removed from the refrigerator at -80℃, inoculated on the surface of solid medium with sterile inoculation ring lines in a super-clean workbench, and cultured in a constant temperature incubator at 37℃ for 12-16 h until a single colony was formed. A single colony was selected and inoculated in 5 mL liquid medium and incubated in a constant temperature shaking table at 37℃ and 240 rpm for 6h, so that the bacteria entered the logarithmic growth phase. Take 1 mL of logarithmic bacterial solution, centrifuge it at 4℃ and 8000 rpm for 5 mins, and discard the supernatant. The bacteria were re-suspended with PBS buffer and centrifugally washed three times. Finally, the bacterial solution was diluted with PBS buffer to the target concentration of 10^5-10^6 CFU/mL. The 100 μL diluted bacterial solution was inoculated into the liquid medium containing SMR and its degradation products, and a blank control group (containing only the medium), an SMR experimental group (containing undegraded SMR), and a SMR control group (containing degraded SMR) were set up. The inoculated medium was cultured in a constant temperature shaking table at 37℃ and 240 rpm, and the OD_{600} value was measured at 10 h and 14 h, respectively, to evaluate the effects of SMR and its degradation products on the growth of E. coli.

8. Machine leaning for analysis of SERS data

Transpose the raw data of LB-AuNPs substrate test for different sulfonamides into the table. All data were divided into training set and test set, 10 characteristic values were extracted from sulfanilamide

antibiotics, and LDA analysis of sulfanilamide antibiotics data was carried out using origin2021 software.

9. DFT Calculation Methods

Gaussian 16 program package is applied to density functional theory (DFT) calculations[1]. Geometry optimizations were executed with B3LYP function using 6-3 1G (d) basis set for all atoms[2]. Meanwhile, the solvation effect was considered by the Solvation Model based on Density (SMD).

10. Supporting figures

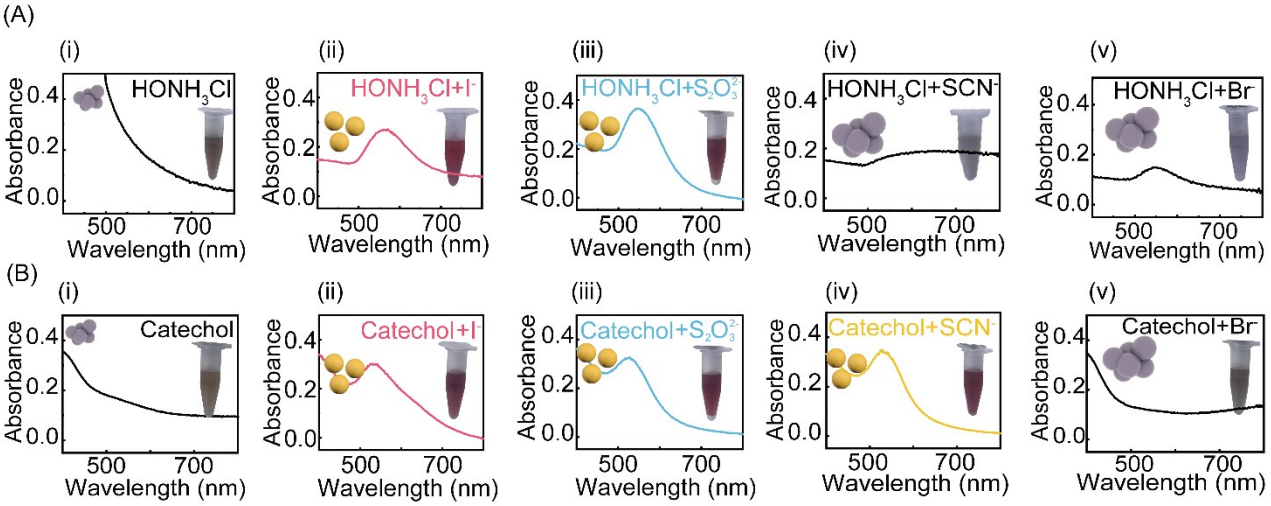


Figure S1. (A) The UV-Vis spectra and real image of nanoparticles prepared by addition of different ligands ((i) none; (ii) iodide; (iii) thiosulfate ion; (iv) thiocyanogen ion; (v) bromide ion) using $HONH_3Cl$ as reductant. **(B)** The UV-Vis spectra and real image of nanoparticles prepared by addition of different ligands ((i)none; (ii) iodide; (iii) thiosulfate ion; (iv) thiocyanogen ion; (v) bromide ion) using catechol as reductant.

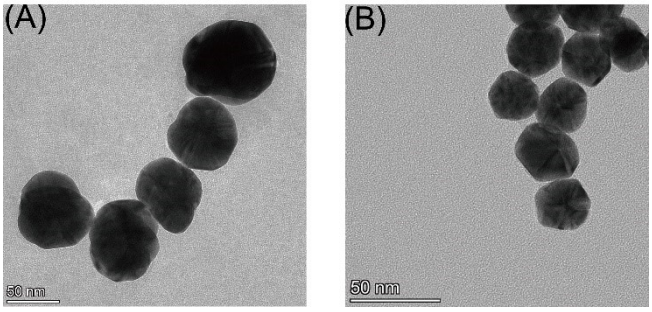


Figure S2. The TEM images of nanoaggregates prepared by addition of different ligands ((A) iodide; (B) thiosulfate ion) using $HONH_3Cl$ as reductant.

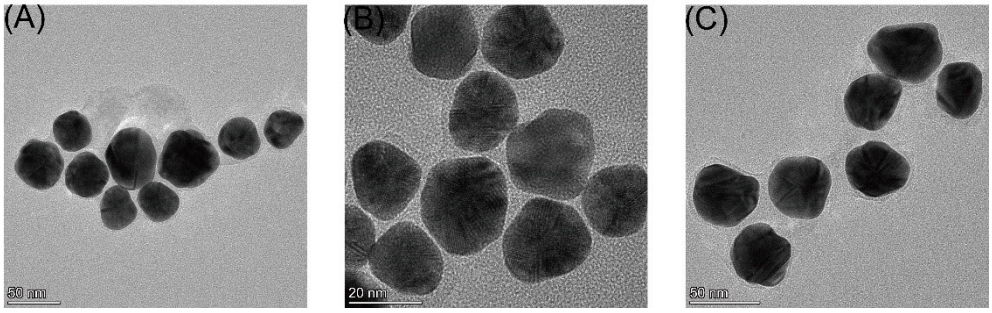


Figure S3. The TEM images of nanoaggregates prepared by addition of different ligands ((A) iodide; (B) thiosulfate ion; (C) thiocyanogen ion) using catechol as reductant.

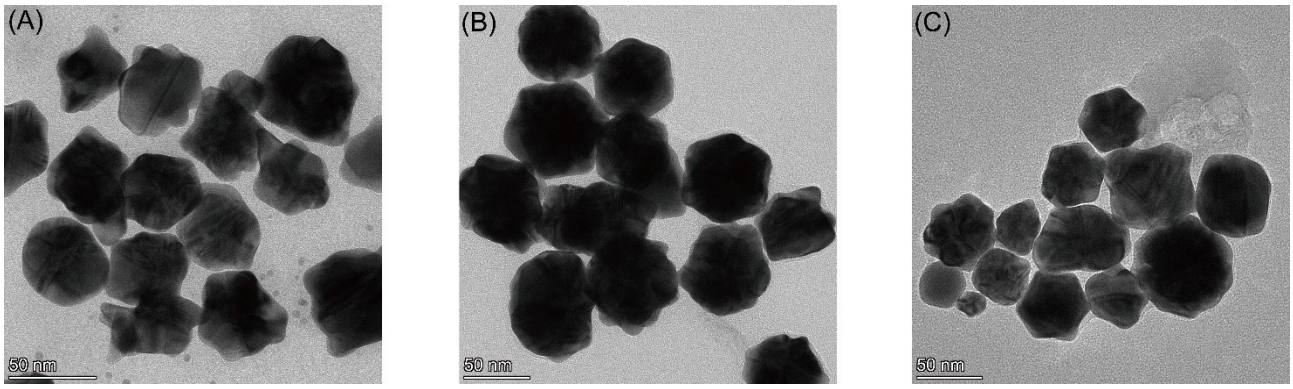


Figure S4. TEM images of AuNPs synthesis with different traditional surfactants (A: PVA; B: PVP; C: Tween-20).

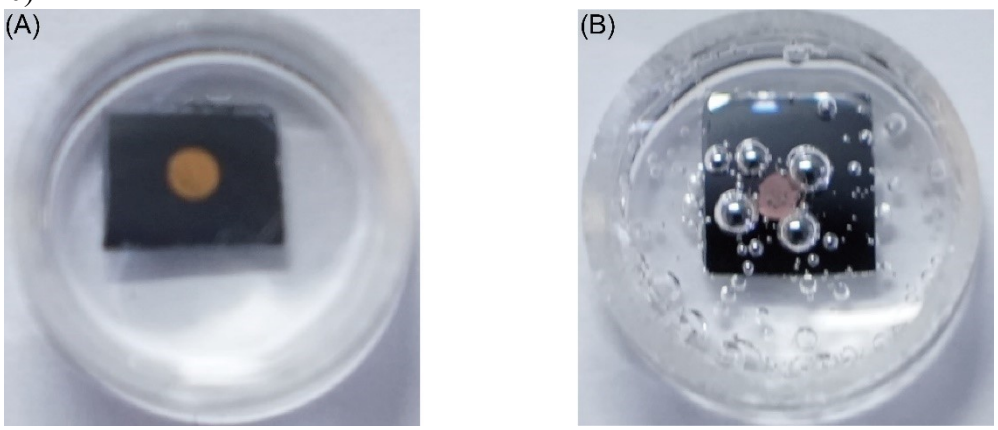


Figure S5. Real images of LB-AuNPs (A) and LB-AgNPs (B) in hydrogen peroxide solution.

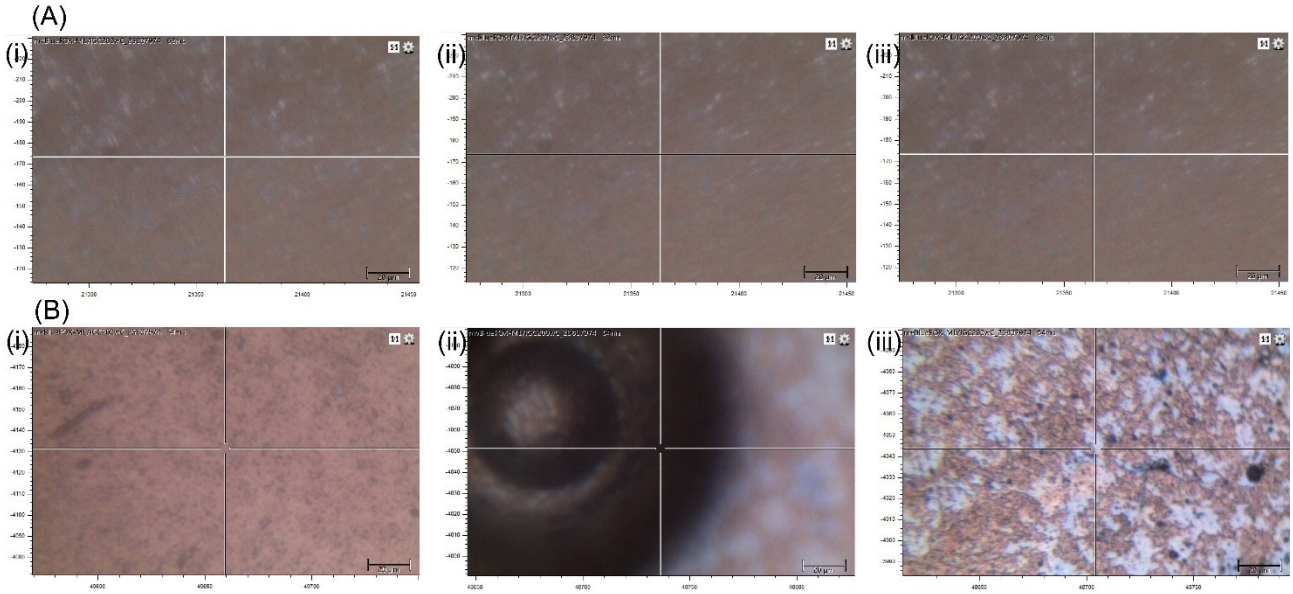


Figure S6. (A) LB-AuNPs real images under the microscope before (i) during (ii) and after (iii) hydrogen peroxide corrosion.; (B) LB-AgNPs real images under the microscope before (i) during (ii) and after (iii) hydrogen peroxide corrosion.

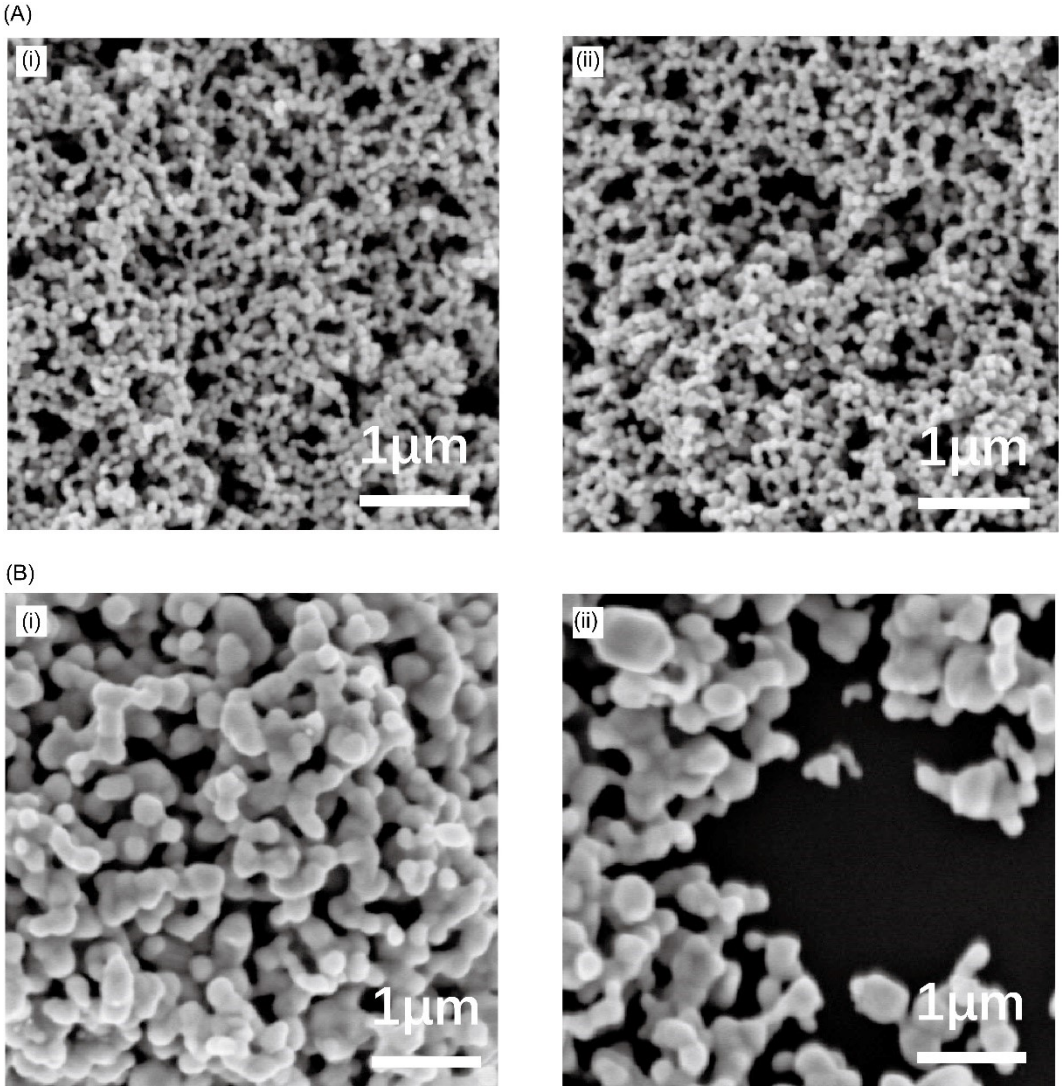


Figure S7. (A) LB-AuNPs SEM image before (i) and after (ii) hydrogen peroxide corrosion.; (B) LB-AgNPs SEM image under before (i) and after (ii) hydrogen peroxide corrosion.

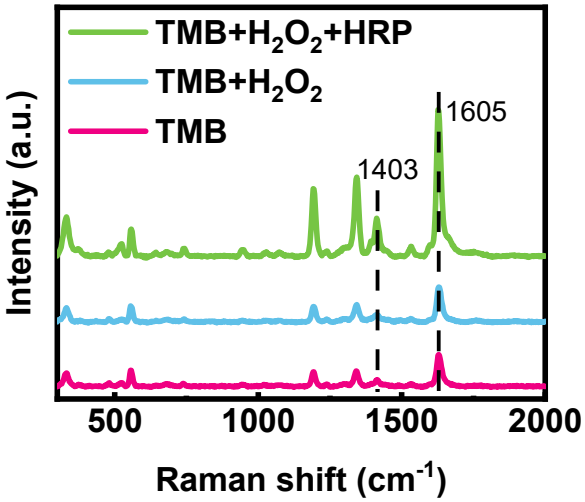


Figure S8. SERS spectra by LB-AuNPs substrate for the detection of TMB, TMB-H_2O_2 mixture, and TMB-H_2O_2-HRP mixture.

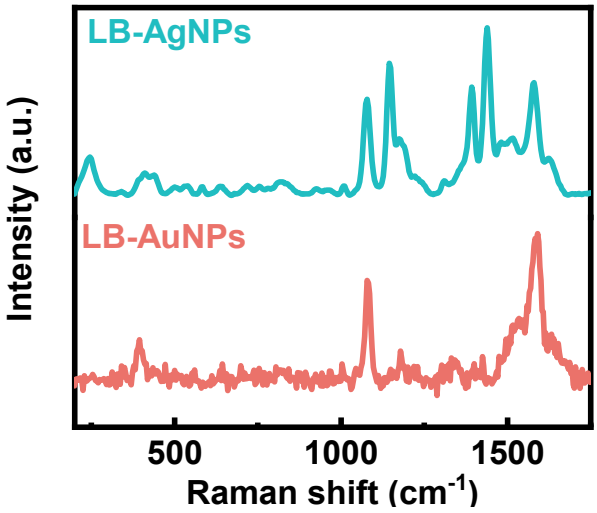


Figure S9. Comparative SERS spectra of PATP acquired using LB-AuNPs substrate and LB-AgNPs substrate

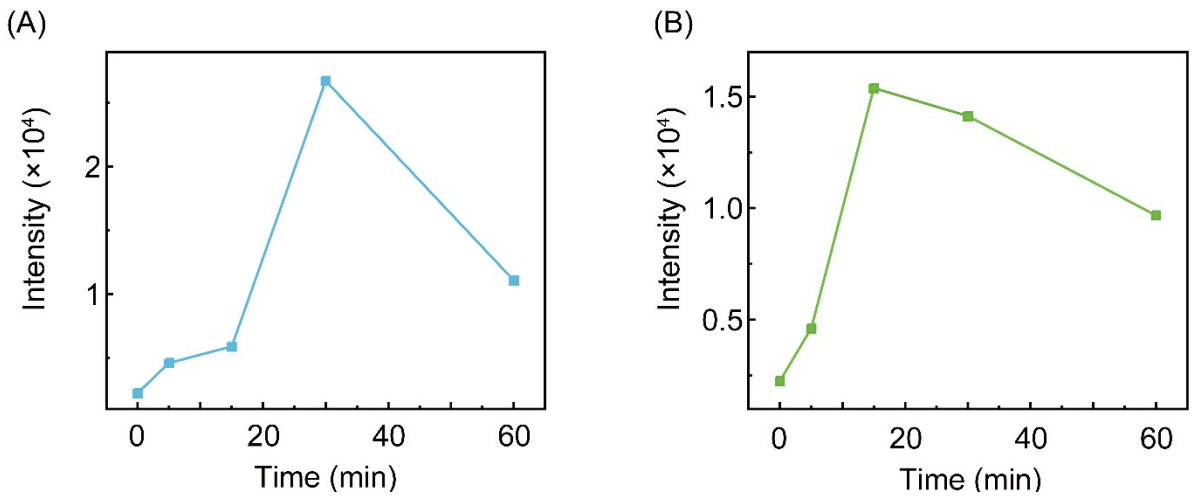


Figure S10. Line plot of SERS peak intensity at 1365 cm^{-1} with (A) and without (B) hydrogen peroxide as a function of degradation time.

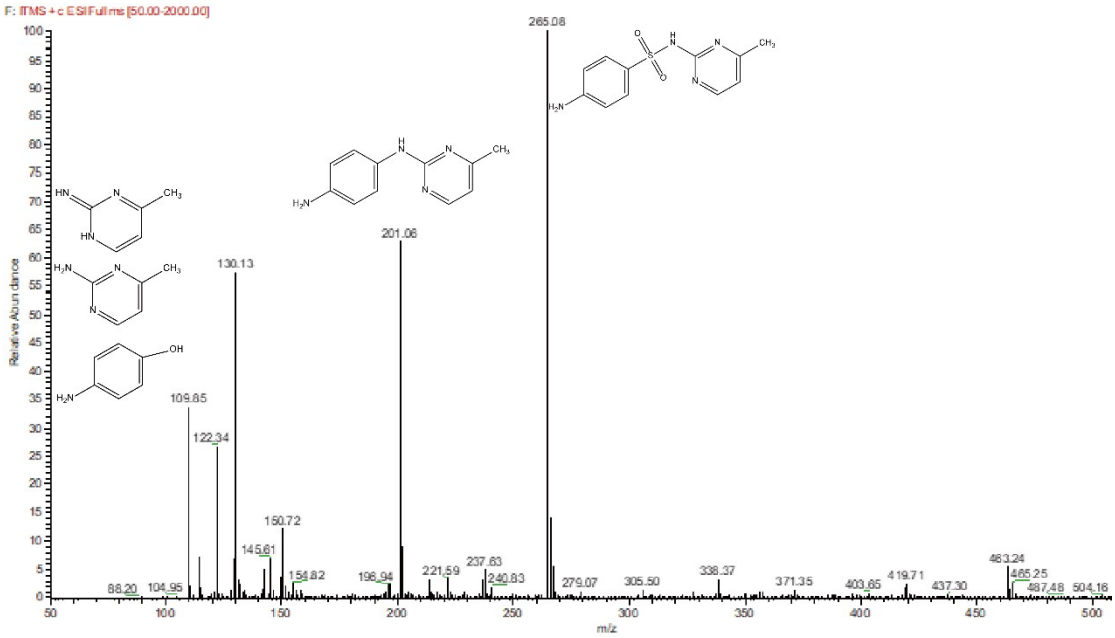


Figure S11. Mass spectrometry detection of SMR photodegradation products.

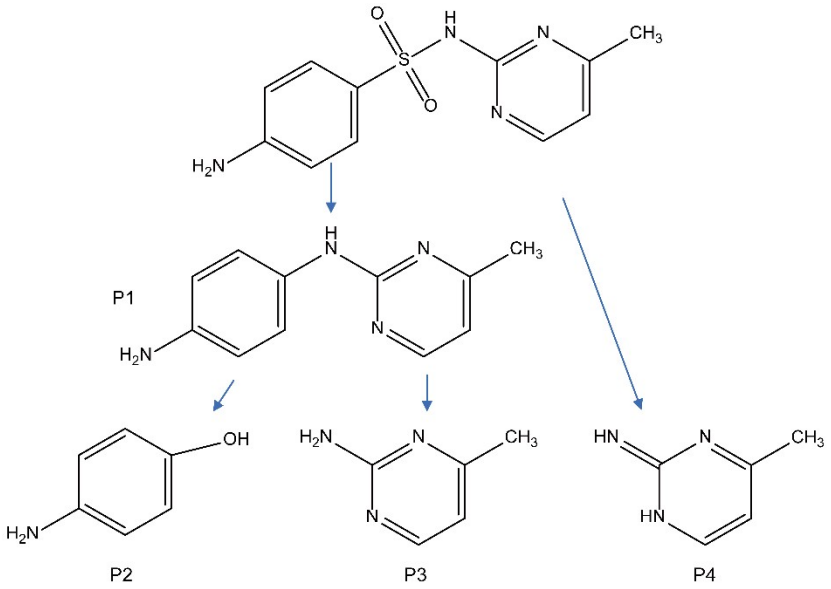


Figure S12. Degradation pathway of SMR.

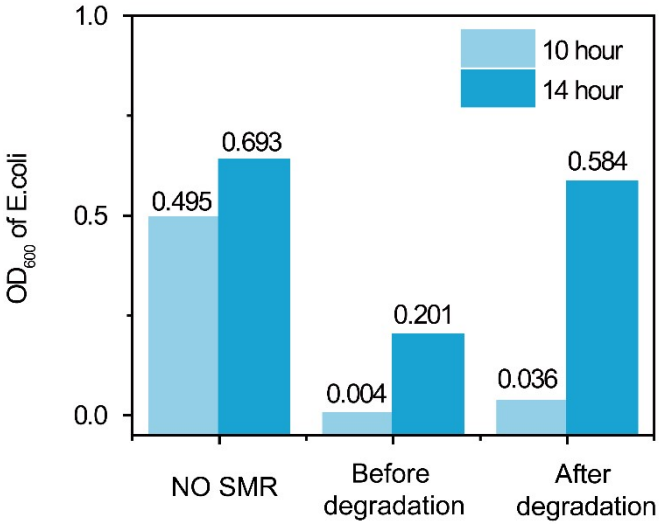
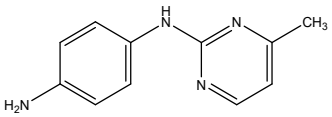
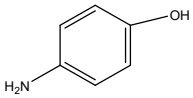


Figure S13. Bacteriostatic inhibition of SMR before and after degradation. The experimental groups (no SMR, SMR before degradation, and SMR after degradation) were co-cultured with bacteria and evaluated for their effect on bacterial growth at 10 and 14 hours, respectively.

degradation product	m/z	molecular formula	structural formula
P1	200	$C_{11}H_{12}N_4$	
P2	109	C_6H_7NO	

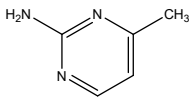
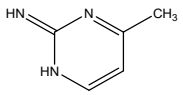
P3	109	$C_5H_7N_3$	
P4	109	$C_5H_7N_3$	

Table S1. Molecular weight, molecular formulae and structural formulae of the four possible degradation products of SMR.

1. Khire, S. S.; Sahu, N.; Gadre, S. R. MTASpec software for calculating the vibrational IR and Raman spectra of large molecules at ab initio level. *Comput. Phys. Commun.* **2022**, *270*, 108175, DOI: 10.1016/j.cpc.2021.108175.

2. Grys, D. B.; de Nijs, B.; Salmon, A. R.; Huang, J. Y.; Wang, W. T.; Chen, W. H.; Scherman, O. A.; Baumberg, J. J. Citrate Coordination and Bridging of Gold Nanoparticles: The Role of Gold Adatoms in AuNP Aging. *ACS Nano* **2020**, *14*, 8689-8696, DOI: 10.1021/acsnano.0c03050.