Electronic Supplementary Information (ESI)

M-cresol purple functionalized surface enhanced Raman scattering paper chips for sensitive detection of pH in neutral pH range

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Chemicals

Chloroauric acid ($HAuCl_4$), silver nitrate ($AgNO_3$), sodium borohydride ($NaBH_4$), sodium hydroxide (NaOH), L-ascorbic acid (AA), crystal violet (CV), and malachite green (MG) were purchased from Sinopharm Chemical Reagent Co., Ltd. Cetyltrimethylammonium bromide (CTAB), 4-nitrothiophenol (NT), 3,3'-diethylthiadicarbocyanine iodide (DTDC) were obtained from Sigma-Aldrich. m-cresol purple was obtained from shanghai Macklin biochemical Co.Ltd.. Deionized water was used in all of the experiments.

Characterization

SEM images and energy-dispersive X-ray spectra of the samples were obtained by using a field-emission microscope (Hitachi S-4800, Tokyo, Japan) equipped with an EX-350 energy-dispersive X-ray microanalyzer (HORIBA EMAX Energy). UV/vis absorption spectra were obtained on a Thermo Scientific NanoDrop 2000/2000C spectrophotometer. All pH measurements were performed on a pH meter (PHS-3C, Shanghai, China). The SERS spectra were recorded by using a DXR Raman Microscope (Thermo Scientific, USA). A 632.8 nm, 5 mW He−Ne laser was focused by a microscope with a 10× objective lense for sample solution and chip SERS signal measurements. When measuring the pH sensitive SERS spectra, the chip was immobilized in a plastic cell that adhered on the objective table of the microscope, which ensured that the signal was collected from a specific position of the chip and reduced the signal interference resulted from the NP distribution variation on the chip.

Preparation of AuNRs

AuNRs were synthesized by using the seed-mediated growth method. Briefly, the seed solution was prepared by reducing $HAuCl_4$ (0.5 mM, 2 mL) in CTAB (0.2 M, 2 mL) with freshly prepared ice-cold $NaBH_4$ (10 mM, 0.24 mL). After 2 h, 3.6 mL of the resultant seed solution was added into a growth solution of $HAuCl_4$ (23 mM, 13 mL), CTAB (0.2 M, 200 mL), $AgNO_3$ (4 mM, 11.2 mL), and AA (80 mM, 5 mL). The mixture was stored overnight at 27-30 °C.

Preparation of AuNR@Ag NPs

The AuNR was centrifuged at 9100 rpm for 15 min, washed twice with water, and then redispersed in 1 mL of water. The absorbance at 750 nm was approximately 1.7. One milliliter of CTAB (0.2 M) was added to 300 μL of this seed solution, followed by the addition of water until the total volume was 6 mL. Then, 20 μL of AA (0.1 M) and 100 μL of $AgNO_3$ (10 mM) were added in sequence at room temperature while stirring. Finally, the pH of the mixture was adjusted to approximately 10 by adding NaOH (0.1 M). The solution color immediately started to change from pink to red, which indicated the formation of AuNR@Ag100 NPs. After stirring for 20 min, an additional 20 μL of AA, 200 μL of $AgNO_3$ and 100 μL of NaOH was added. The color of mixture turned to yellow, indicating the formation of AuNR@Ag300 NPs.

Preparation of AuNR@Ag@Au NPs

2.0 mL of 0.5 M NaOH solution, 2.0 mL of 0.5 M ascorbic acid solution and 26 mL of water were mixed. Then 1.0 mL of the AuNR@Ag300 NP solution was added into 2.0 mL of the above mixture, followed by the addition of different volume of a growth solution prepared by the reduction of $HAuCl_4$ (0.1 M, 0.2 mL) in CTAB (0.2 M, 9.8 mL) with freshly prepared AA (0.1 M, 0.2 mL). The color of the solution turned from yellow to blue immediately, and the mixture was further stirred at 28 °C for 15 min complete the reaction. The obtained NP was denoted as AuNR@Ag@AuX and X was the volume of growth solution (μL).

Preparation of of Au nanospheres (NSs)

Briefly, freshly prepared $NaBH_4$ solution (1 mM, 0.6 mL) was rapidly added into a thoroughly mixed 10 mL of aqueous solution containing $HAuCl_4$ (0.25 mM) and CTAB (0.1 M). A brown solution immediately formed upon the introduction of $NaBH_4$, which indicated the formation of Au clusters. The formed Au clusters was stirred at a speed of 300 rpm for 2 min, and then kept undisturbed at 27 °C for 3 h. Aqueous solutions of CTAC (0.2 M, 2 mL), AA (0.1 M, 1.5 mL), and Au clusters (50 μL) were mixed, followed by the injection of HAuCl4 solution (0.5 mM, 2 mL). The reaction was allowed to continue at 27 °C for 15 min. The product was AuNS with a diameter of 10 nm. The AuNS (10 nm) was collected by centrifugation at 14 000 rpm for 30 min, and then washed with water once. Then, CTAC (0.1 M, 2 mL), AA (10 mM, 130 μL), and the 10 nm seeds (10 μL) were mixed, followed by dropwise addition of HAuCl4 solution (0.5 mM, 2 mL) using a syringe pump at an injection rate of 2 mL/h. The reaction was allowed to proceed at 27 °C for 10 min after the

injection had been finished.

Fabrication of the pH sensitive SERS paper chips

2.0 mL of the AuNR@Ag@Au1000 NP solution was centrifuged at 5000 rpm for 10 min to remove excess CTAB and redispersed in 0.1 mL of water. The NPs were loaded in a laboratory filter paper (Whatman No. 1 grade) by immersing a 0.5 cm×0.5 cm paper in the concentrated AuNR@Ag@Au1000 NP solution for 12 h. Upon being removed from the solution, the paper was gently rinsed with water to remove the loosely bound NPs, leaving a highly dense layer of NPs on the paper chip surface. Subsequently, the prepared chip was dipped in an m-cresol purple solution (10^{-4} M) for 1 min, followed by rinsing with water to remove excess reporters. The chips were dipped into phosphate buffer solutions with different pH values or lake water followed by the Raman signal measurements.

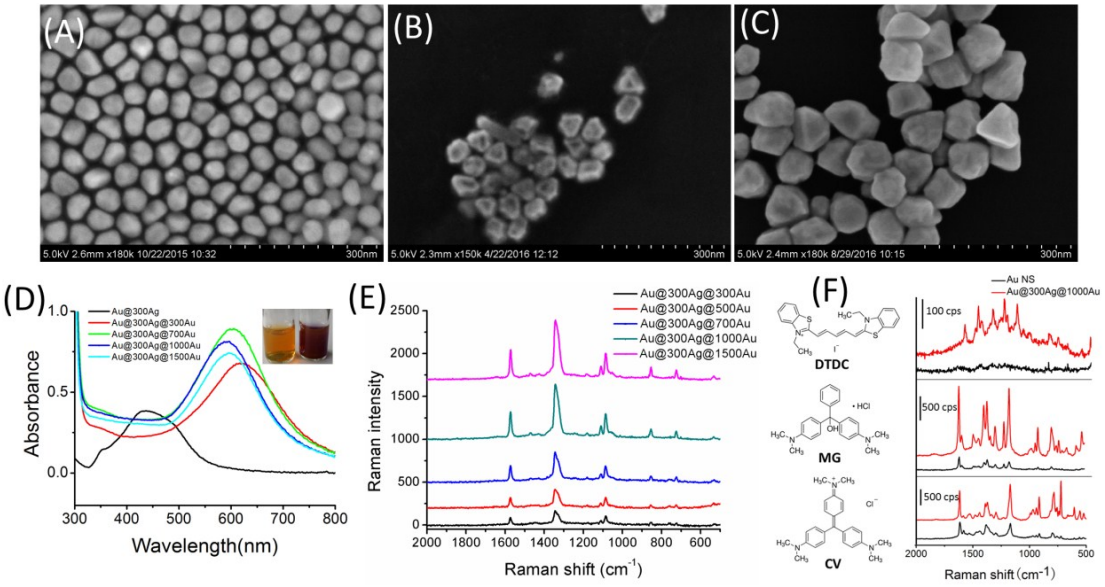
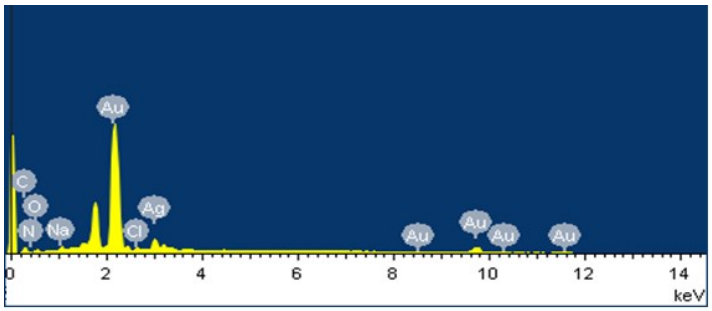


Fig. S1 SEM images of AuNR@Ag NPs (A), AuNR@Ag@Au300 NPs (B) and AuNR@Ag@Au1000 NPs (C). Scale bar: 300 nm. (D) UV-vis spectra of AuNR@Ag@Au NPs prepared from different amount of Au^{+} growth solution. The inset images showed the color of of AuNR@Ag NP colloid (left) and AuNR@Ag@Au1000 NP colloid (right). (E) SERS spectra of NT obtained from AuNR@Ag@Au NPs prepared from different amount of Au^{+} growth solution. (F) SERS spectra of DTDC (10^{-5} M), MG (10^{-6} M) and CV (10^{-5} M) in AuNR@Ag@Au NP and Au NS colloids of the same concentration.



Element	Weight percentage	Atom percentage
C	5.89	34.83
N	3.20	16.21
O	2.46	10.92
Na	0.72	2.21
Cl	0.75	1.50
Ag	9.94	6.55
Au	77.04	27.78
Total	100.00	

Fig.S2 EDS spectrum and element analysis result of AuNR@Ag@Au1000 NPs.

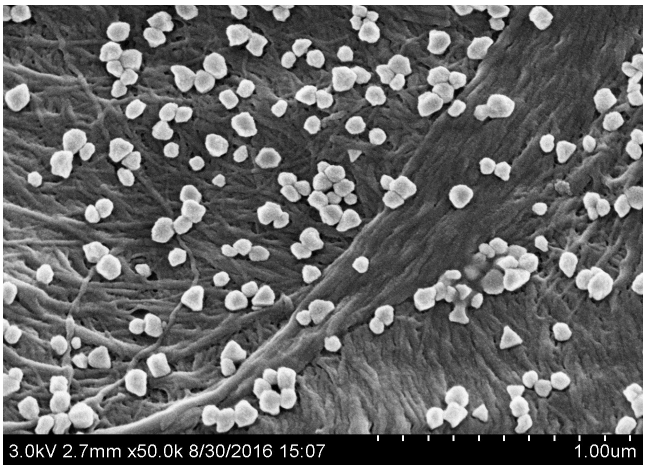


Fig. S3 SEM image showed the formation of NP clusters on the surface of the paper chip.

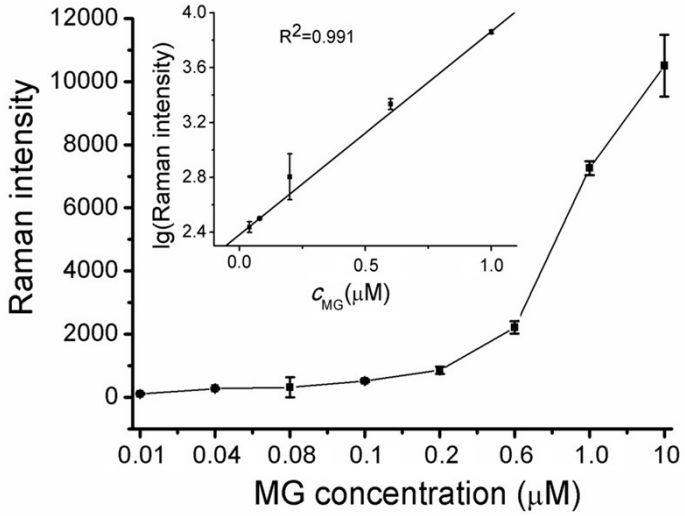


Fig. S4 The plot of the MG concentration vs. 1360 cm^{-1} peak intensity (n=3). The inset showed the quantitative calibration curve of different MG concentrations. The linear equation was lgy= 1.56x + 2.206 (R^2 =0.991, n=3).

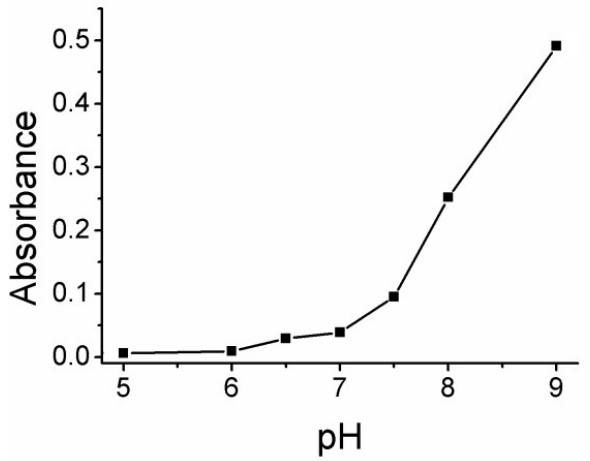


Fig. S5 The plot of the absorbance of m-cresol purple (the absorption band centred at 578 nm) as a function of pH value.

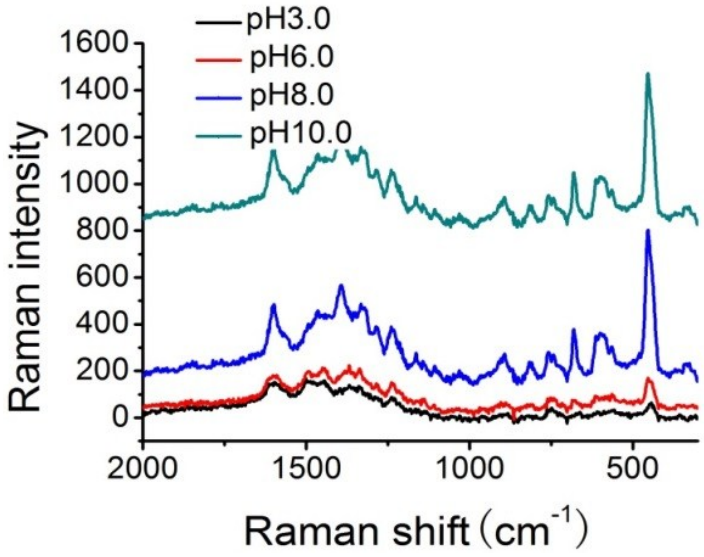


Fig. S6 pH sensitive SERS signal response of m-cresol purple in AuNR@Ag@Au NP1000 colloid. The pH of the colloid was adjusted to different values by the addition of HCl or NaOH followed by SERS measurement.

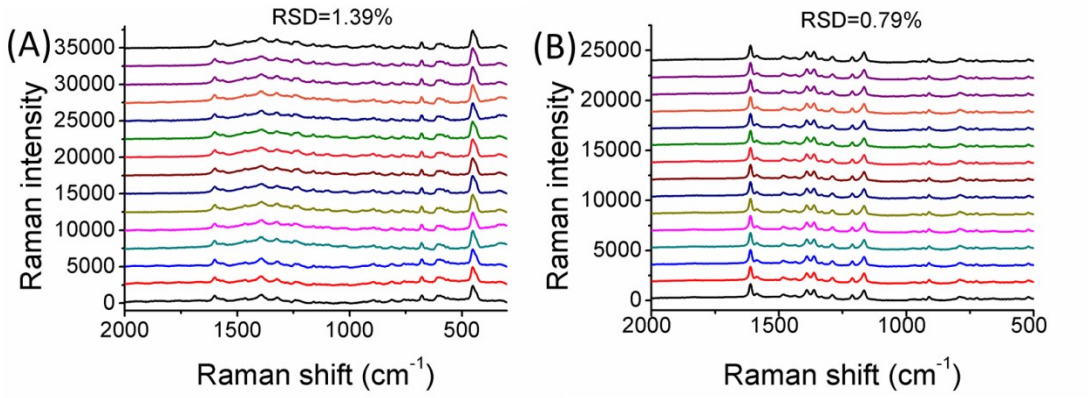


Fig. S7 Raman spectra of m-cresol purple (A) and MG (B) for evaluating the

detection reproducibility of the SERS chip. The spectra were obtained from a specific site on one chip.

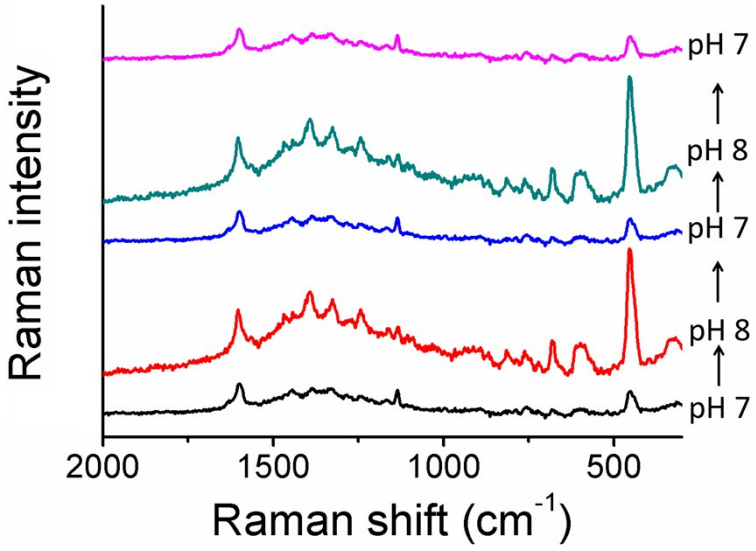


Fig. S8 SERS spectra of the pH sensitive chip when it was alternatively placed pH 7.0 and pH 8.0 PBS solutions.

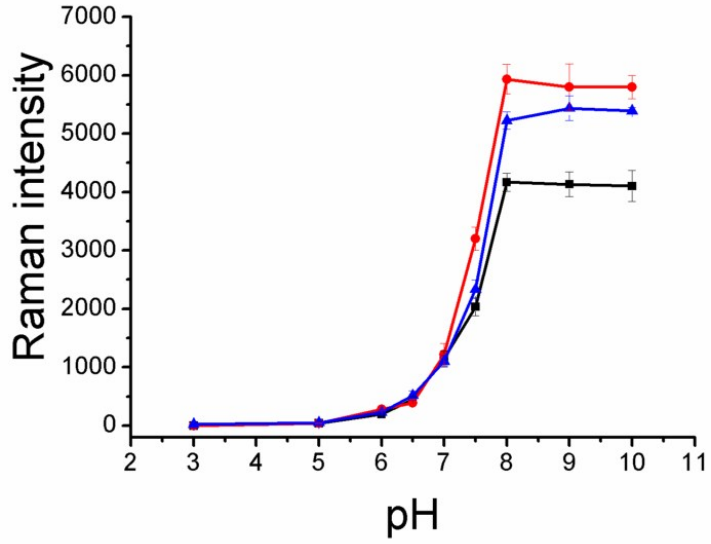


Fig. S9 Response of the Raman intensity at 453.9 cm^{-1} as a function of pH obtained from three chips. The line connecting the data points is added as a visual guide.

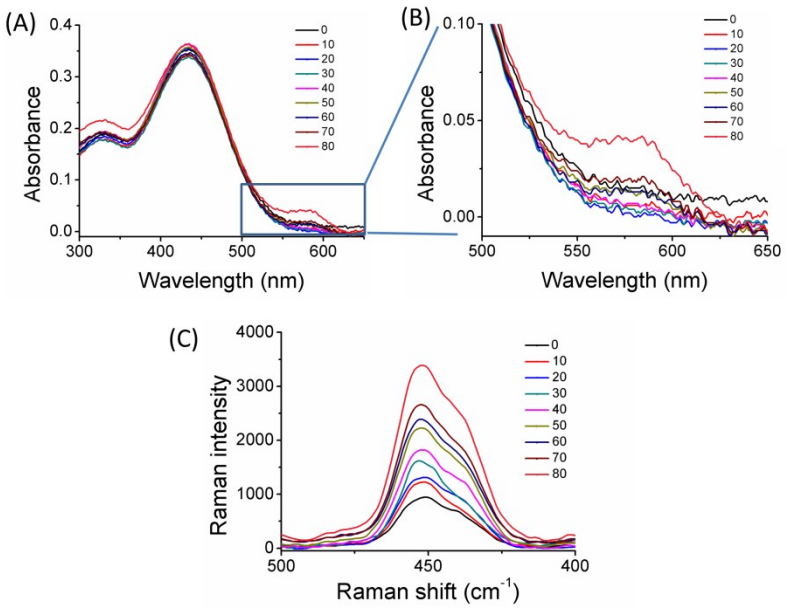


Fig. S10 (A) UV-vis spectra of m-cresol purple with the addition PBS buffer (pH 9.18). 750 μL (10^{-3} M) of was added in 15 mL of pure water to make the absorbance at 415 nm around 0.36, followed by the addition of different volume (0 to 80 μL) of PBS buffer. (B) An enlarged UV-Vis spectra of m-cresol purple in (A). (C) The SERS signal response of the chip upon PBS addition.

Table S1 Comparison of the detection performance with reported SERS based pH sensors

Raman reporter	I_{pH8}/I_{pH6} or I_{pH6}/I_{pH8}	Responsive pH range	Ref.
MBA	1.2	5-8	1
MBA	2	4-9	2
MBA	3	5-8	3
MBA	1.2	2-7	4
MBA	1.4	6-13	5
MBA	2.8	5-9	6
MBA	1.1	3-8	7
MBA	7	6-8	8
MBA	6	6-8	9
MBA	5	2-8	10
ATP	4.3	3-8	11
MBA	3	7-9	12
ATP	1.1	3-8	13
ATP	1.1	3-8	14
DMBA	2.1	4-8	15
DMBA	1.2	2-10	16
ABT	1.1	3-6	17
ABT	1.6	2-10	18
AMT	*4.5*	2-10	19
MPy	1.4	4-9	20
biotin-fluorescein	3	5-8	21

Methyl yellow	1	2-5	22
m-cresol purple	**20**	**6-8**	**This work**

Abbreviations: MBA, 4-mercaptobenzoic acid; ATP, 4-aminothiophenol; DMBA, 3,5-dimercaptobenzoic acid; ABT, 2-aminobenzenethiol; AMT, 3-amino-5-mercapto-1,2,4-triazole ; MPy, 4-mercaptopyridine. In the second column, the ratio of I_{pH8}/I_{pH6} is written in standard style and the ratio of I_{pH6}/I_{pH8} is written in Italic style.

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