

## **Supporting Information**

# **SERS sensing of sulfide based on the sulfidation of silver nanoparticles**

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## **Experimental Section**

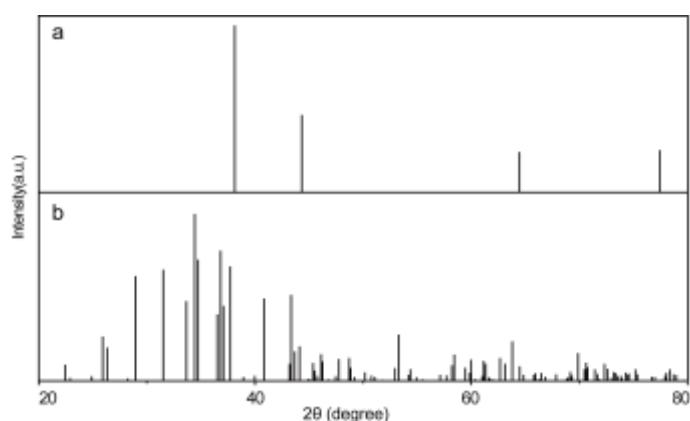
**Reagents.** All chemical reagents were analytical grade and used as received without further purification. Sodium citrate ( $\geq 99.0\%$ ) was purchased from Sigma-Aldrich (St. Louis, MO, USA). Silver nitrate (99%), Sodium sulfide nonahydrate (98%), 4-aminothiophenol (4-ATP) (97%) and bovine serum samples were obtained from Sinopharm Chemical Reagent Co., Ltd (shanghai, China).

**Apparatus.** All solutions were prepared with  $18.2\text{ M}\Omega\cdot\text{cm}$  deionized water obtained with a Milli-Q System (Millipore, MA, USA). The high-resolution transmission electron microscopy (HRTEM) images of colloidal silver nanoparticles (AgNPs) were acquired on a JEM-2100 (JEOL Ltd., Japan) with an accelerating voltage 200 kV. The X-ray diffraction (XRD) patterns of AgNPs were obtained on a Bruker AXS D8-Advanced diffractometer (Bruker AXS Inc., Germany) with Cu K $\alpha$  radiation ( $\lambda=1.5418\text{ \AA}$ ). Surface-enhanced Raman Scattering (SERS) spectra were collected with a portable Raman spectrometer (BWS415 B&W Tek Inc., U.S.A.) with an excitation wavelength of 785 nm, a resolution of  $5\text{ cm}^{-1}$ .

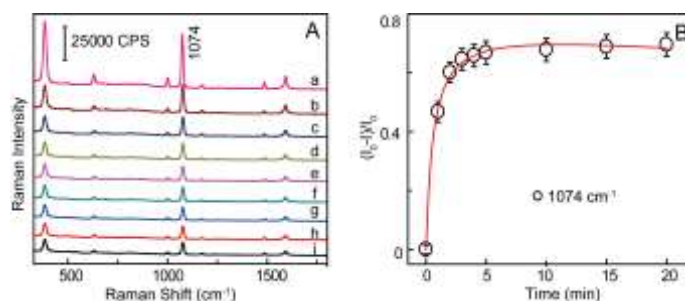
**Preparation of SERS-active AgNPs colloids.** AgNPs colloids were prepared by the reduction of silver nitrate with sodium citrate according to pervious research.<sup>[1]</sup> Briefly, 18 mg silver nitrate was dissolved in 100 mL deionized water and heated to be boiling before 2 mL of 1.00 wt.% trisodium citrate solution was added. The solution was held at boiling for an additional 25 min and then cooled to room

temperature. Thus, 60 mL AgNPs colloids were obtained with a concentration of  $1.8 \times 10^{-3}$  M.<sup>[2]</sup> All the other AgNPs colloids used in experiments were obtained by diluting with deionized water.

**SERS measurement of sulfide.** Firstly, a stock solution of SERS sensing system was prepared by self-assembling  $2.0 \times 10^{-4}$  M 4-ATP on the surface of the synthesized colloidal AgNPs. Then, 180  $\mu$ L of the stock solution was added into a quartz cuvette with 1 cm path-length and 2 mm inside-width, and its initial SERS spectra were recorded with an 785 nm excitation wavelength, 40 mW laser power and 30 s integration time. Finally, 20  $\mu$ L of sulfide samples with different concentrations were added into the sensing system and incubated for a certain time followed by the measurement of SERS spectra.

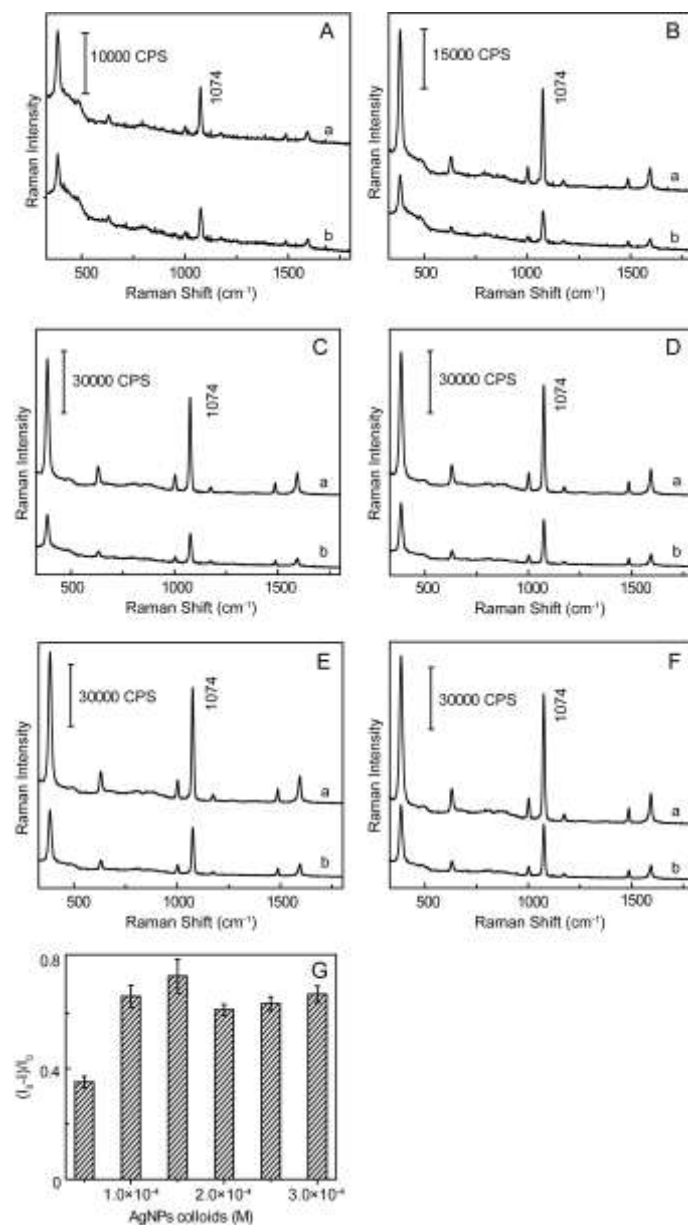


**Figure S1.** The reference XRD pattern for face-centered cubic phase AgNPs (JCPDF No. 65-2871) (a) and monoclinic phase Ag<sub>2</sub>S (JCPDF No.65-2356) (b) <sup>[3, 4]</sup>.

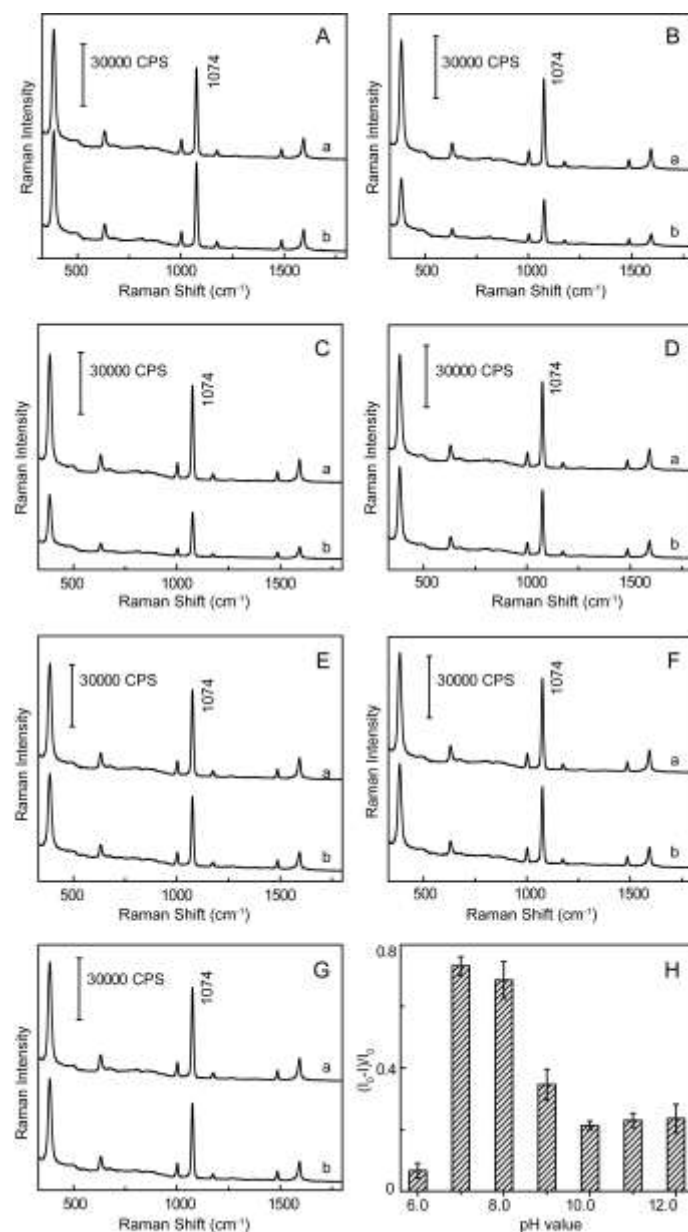


**Figure S2.** (A) SERS spectra of 4-ATP of the sensing system after the incubation of  $3.0 \times 10^{-6}$  M sulfide for (a) 0 min, (b) 1 min, (c) 2 min, (d) 3 min, (e) 4 min, (f) 5 min, (g) 10 min, (h) 15 min, (i) 20 min. (B) Plots of SERS signal decrease of 4-ATP ( $(I_0 - I)/I_0$ ) at the band of  $1074 \text{ cm}^{-1}$  versus incubation time. Error bars represent standard deviations for measurement taken from at least three independent

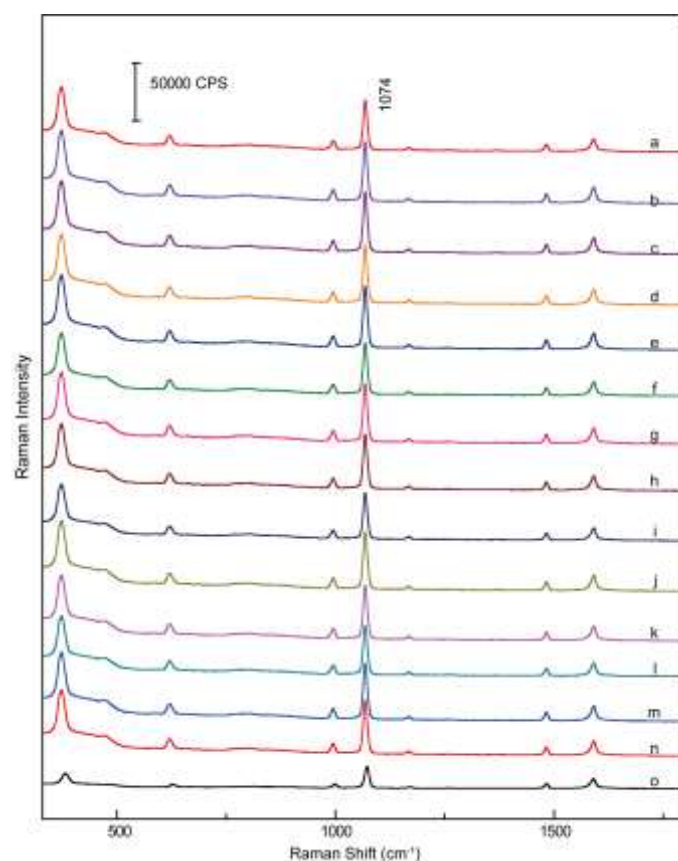
experiments under condition of  $3.0 \times 10^{-4}$  M AgNPs colloids and pH value at 7.0.



**Figure S3.** SERS spectra of 4-ATP of the sensing system before (a) and after (b) the incubation of  $3.0 \times 10^{-6}$  M sulfide in different concentration of AgNPs: (A)  $5.0 \times 10^{-5}$  M, (B)  $1.0 \times 10^{-4}$  M, (C)  $1.5 \times 10^{-4}$  M, (D)  $2.0 \times 10^{-4}$  M, (E)  $2.5 \times 10^{-4}$  M, (F)  $3.0 \times 10^{-4}$  M. (G) Plots of SERS signal decrease of 4-ATP ( $(I_0 - I)/I_0$ ) at the band of 1074  $\text{cm}^{-1}$  versus different concentration of AgNPs colloids. Error bars represent standard deviations for measurement taken from at least three independent experiments under condition of 5 min incubation time and pH value at 7.0.



**Figure S4.** SERS spectra of 4-ATP of the sensing system before (a) and after (b) the incubation of  $3.0 \times 10^{-6}$  M sulfide at different pH value: (A) 6.0, (B) 7.0, (C) 8.0, (D) 9.0, (E) 10.0, (F) 11.0, (G) 12.0. (H) Plots of SERS signal decrease of 4-ATP ( $(I_0 - I)/I_0$ ) at the band of  $1074 \text{ cm}^{-1}$  versus different pH value. Error bars represent standard deviations for measurement taken from at least three independent experiments under condition of  $1.5 \times 10^{-4}$  M AgNPs colloids and 5 min incubation time.



**Figure S5.** SERS spectra of 4-ATP of the sensing system collected under the optimum conditions before (a) and after (b-o) the incubation of sulfide ( $1.0 \times 10^{-6}$  M) and other interferents ( $2.0 \times 10^{-5}$  M): (b)  $\text{HPO}_4^{2-}$ , (c)  $\text{HCO}_3^-$ , (d)  $\text{CH}_3\text{COO}^-$ , (e)  $\text{NO}_3^-$ , (f)  $\text{NO}_2^-$ , (g)  $\text{ClO}_4^-$ , (h)  $\text{Cl}^-$ , (i)  $\text{Br}^-$ , (j) glutathione, (k) L-cysteineand, (l)  $\text{S}_2\text{O}_3^{2-}$ , (m)  $\text{SO}_4^{2-}$ , (n)  $\text{SO}_3^{2-}$ , (o) sulfide.

**Table S1** Determination of sulfide in tap water and bovine serum samples

Tested Samples	Added (M)	Found (M)	Recovery (%)	RSD (n=3) (%)
Tap water	$5.0 \times 10^{-8}$	$4.2 \times 10^{-8}$	84	5.6
	$5.0 \times 10^{-7}$	$5.6 \times 10^{-7}$	112	2.4
bovine serum	$2.0 \times 10^{-6}$	$1.8 \times 10^{-6}$	90	5.4
	$5.0 \times 10^{-6}$	$4.4 \times 10^{-6}$	88	7.6

## Reference

- [1] P. C. Lee and D. Meisel, *J. Phys. Chem.*, **1982**, 86, 3391.
- [2] J. C. Trefry, J. L. Monahan, K. M. Weaver, A. J. Meyerhoefer, M. M. Markopolous, Z. S. Arnold, D. P. Wooley and I. E. Pavel, *J. Am. Chem. Soc.*, **2010**, 132, 10970.
- [3] E. R. Jette and F. Foote, *J. Chem. Phys.*, **1935**, 3, 605.

[4] A. J. Frueh, *Z. Kristallog. - Cryst. Mater.*, **1958**, 110, 136.