

Plasmon-coupled 3D porous hotspots architecture for super-sensitive quantitative SERS sensing of toxic substances on real sample surface

Maofeng Zhang, ^{*a} Jian Yang ^b, Yaru Wang, ^a Haoran Sun, ^b Hongyang Zhou, ^a Xiaonan Liu, ^b Cheng Ye, ^a Zhiyong Bao, ^b Jiaqin Liu, ^{*c} and Yucheng Wu ^b

a. School of Chemistry and Chemical Engineering, Hefei University of Technology, 193 Tunxi Road, Hefei, 230009, China

b. School of Materials Science and Engineering, Hefei University of Technology, 193 Tunxi Road, Hefei, 230009, China

c. Institute of Industry and Equipment Technology, Hefei University of Technology, 193 Tunxi Road, Hefei, 230009, China

*Corresponding authors:

Email: mfzhang@hfut.edu.cn (M. F. Zhang); jqliu@hfut.edu.cn (J. Q. Liu)

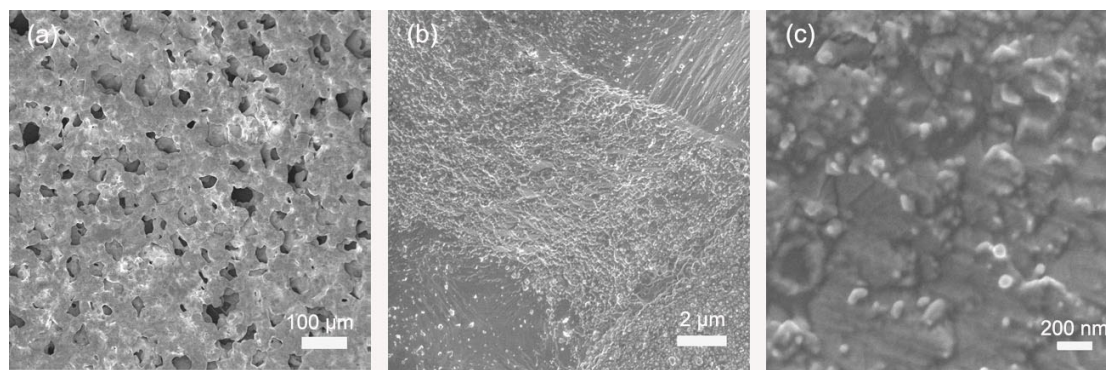


Figure S1. SEM images of low and high-magnification of cleaned 3D Cu foam with porosity of 80 %, indicating their porous structure and rough surface.

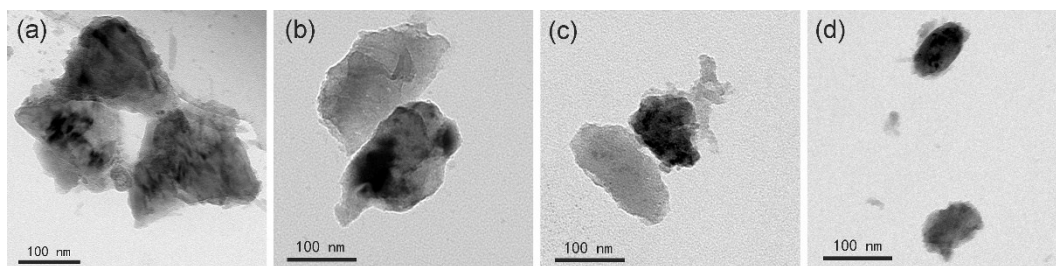


Figure S2. HRTEM images of four typical AgNPs prepared with different porosity of Cu foam (a) 70 %, (b) 80 %, (c) 90 %, and (d) 98 %.

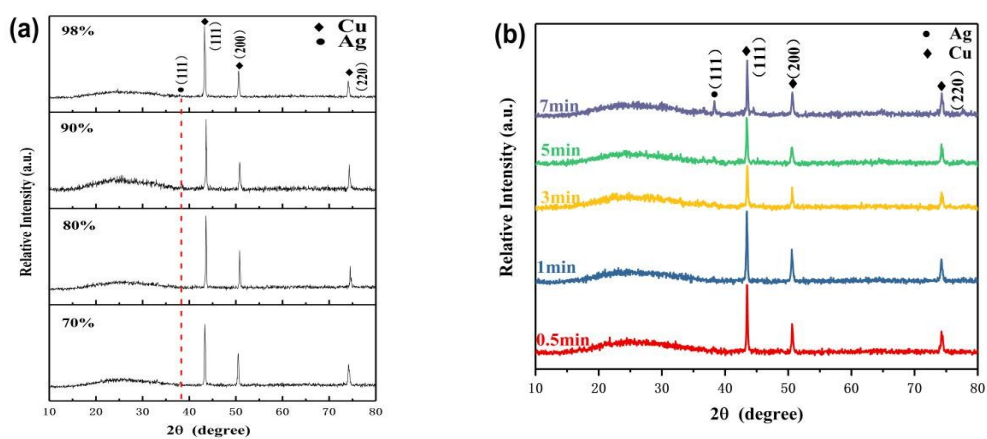


Figure S3. XRD patterns of AgNPs/Cu foam with (a) different porosity of Cu foam, and (b) different soaking time in AgNO_3 solution.

Calculation of enhancement factor (EF)

$$N_{\text{BULK}} = (\text{Laser spot area}/\text{Diffusion area}) * (N_A * \text{Volume}_{\text{BULK}} * \text{Concentration}_{\text{BULK}})$$

$$N_{\text{SERS}} = (\text{Laser spot area}/\text{Substrate area}) * (N_A * \text{Volume}_{\text{SERS}} * \text{Concentration}_{\text{SERS}})$$

$$\text{Diffusion area} = \pi(d/2)^2 = 0.5027 \text{ cm}^2$$

$$\text{Substrate area} = 0.25 \text{ cm}^2$$

$$\text{Volume}_{\text{BULK}} = \text{Volume}_{\text{SERS}}$$

$$I = \text{intensity of the } 1172 \text{ cm}^{-1} \text{ peak}$$

$$\text{Concentration}_{\text{BULK}} = 10^4 * \text{Concentration}_{\text{SERS}}$$

$$N_{\text{BULK}} / N_{\text{SERS}} = (0.25/0.5027) \times 10^4 = 4973$$

$$I_{\text{BULK}} = 7989 \text{ a.u.}$$

$$I_{\text{SERS, AgNPs}} = 119606 \text{ a.u.}$$

$$I_{\text{SERS, AgNPs}} / I_{\text{BULK}} = 14.97$$

$$\text{EF} = (I_{\text{SERS}} / I_{\text{BULK}}) \times (N_{\text{BULK}} / N_{\text{SERS}}) = 7.45 \times 10^4$$

$$\text{Concentration}_{\text{BULK}} = 10^7 * \text{Concentration}_{\text{SERS}}$$

$$N_{\text{BULK}} / N_{\text{SERS}} = (0.25/0.5027) \times 10^7 = 4.97 \times 10^6$$

$$I_{\text{SERS, AgNPs/Cu foam}} = 66190.88 \text{ a.u.}$$

$$I_{\text{SERS, AgNPs/Cu foam}} / I_{\text{BULK}} = 8.28$$

$$\text{EF} = (I_{\text{SERS}} / I_{\text{BULK}}) \times (N_{\text{BULK}} / N_{\text{SERS}}) = 4.12 \times 10^7$$

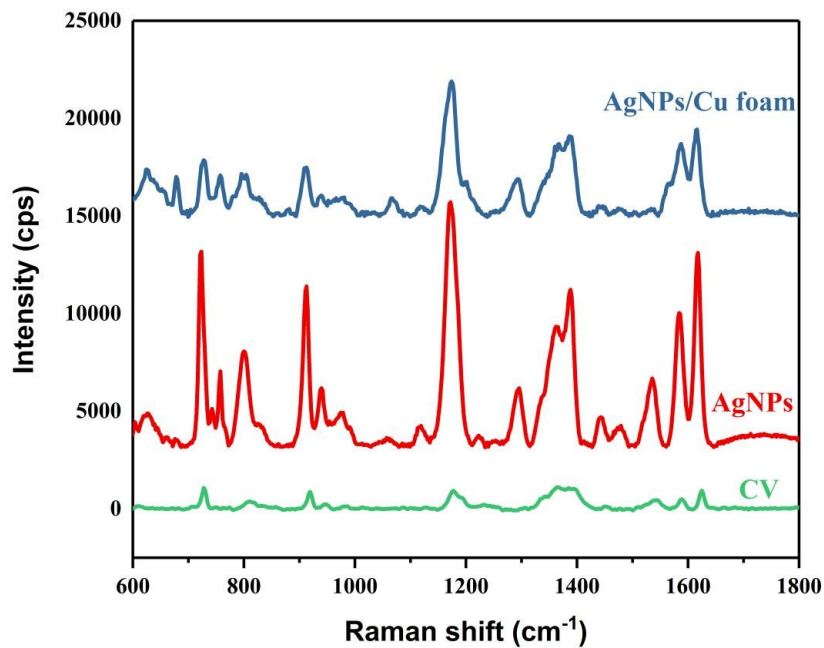


Figure S4. Normal Raman spectra of CV aqueous solution (10^{-1} M), SERS spectra of CV (10^{-5} M) absorbed on AgNPs and SERS spectra of CV (10^{-8} M) absorbed on AgNPs/Cu composites.

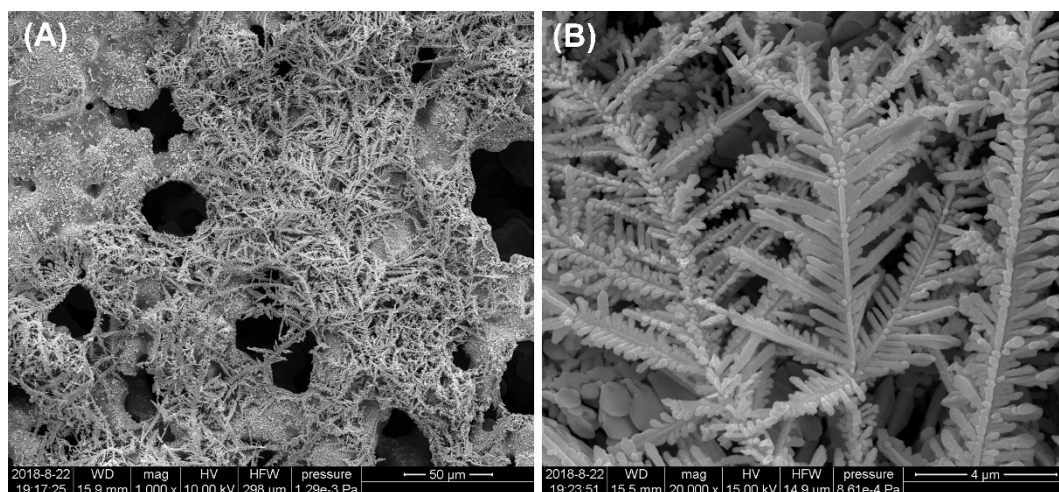


Figure S5. SEM images of Ag/Cu foam fabricated without using Sn^{2+} ions.

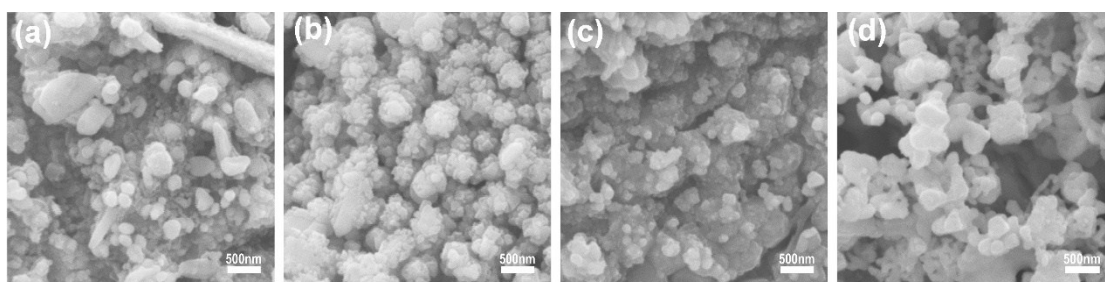


Figure S6. SEM images of AgNPs/Cu foam fabricated at different reaction time. (a) 1min, (b) 3min, (c) 5min, (d) 7min.

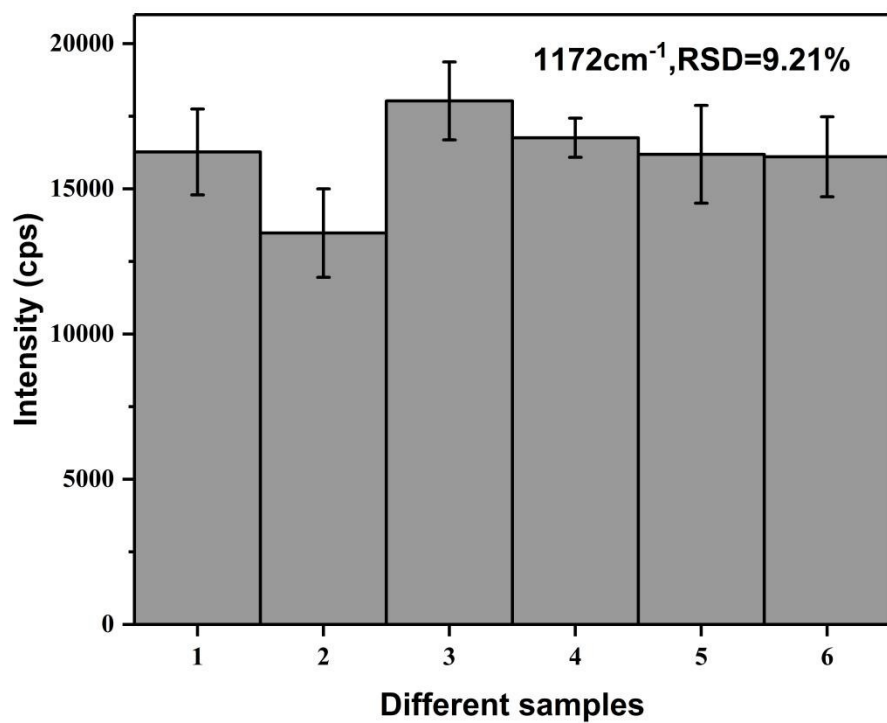


Figure S7. The Raman intensity RSD value of inter-substrate variation obtained at 1172 cm⁻¹ peak.

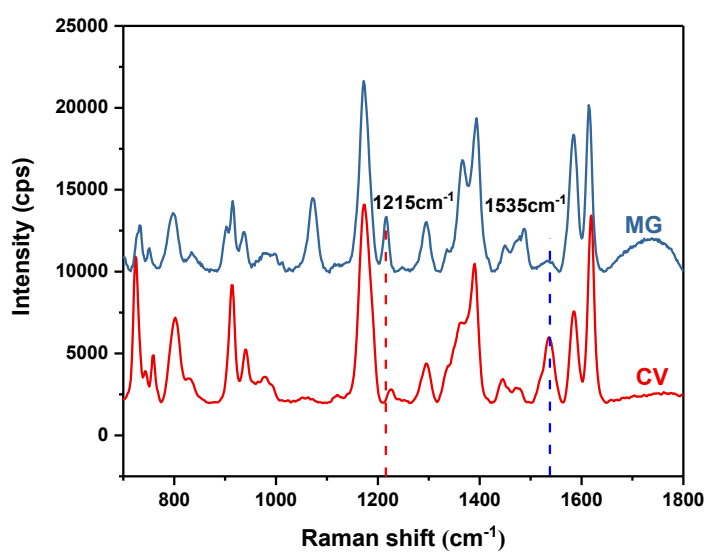


Figure S8. Comparison of SERS spectra of CV and MG.

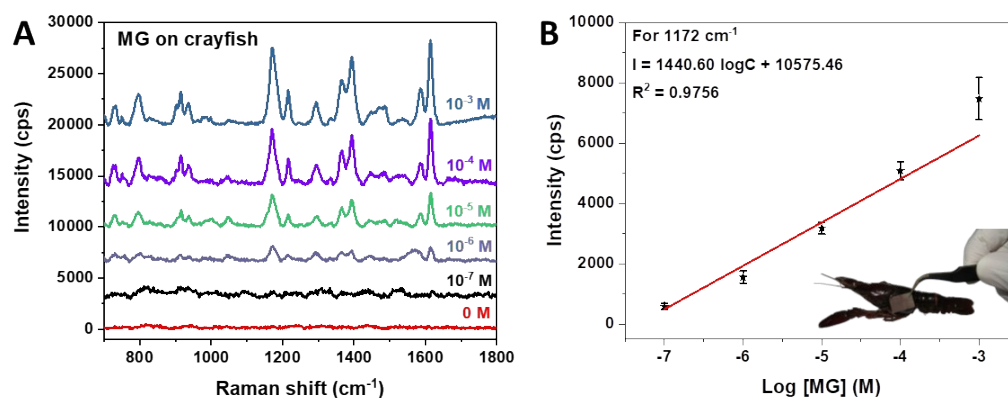


Figure S9. (A) SERS spectra of MG detected on the surface of crayfish with different concentrations. (B) Relationship between Raman intensities and the concentrations of MG at 1172 cm⁻¹ in logarithm scale.

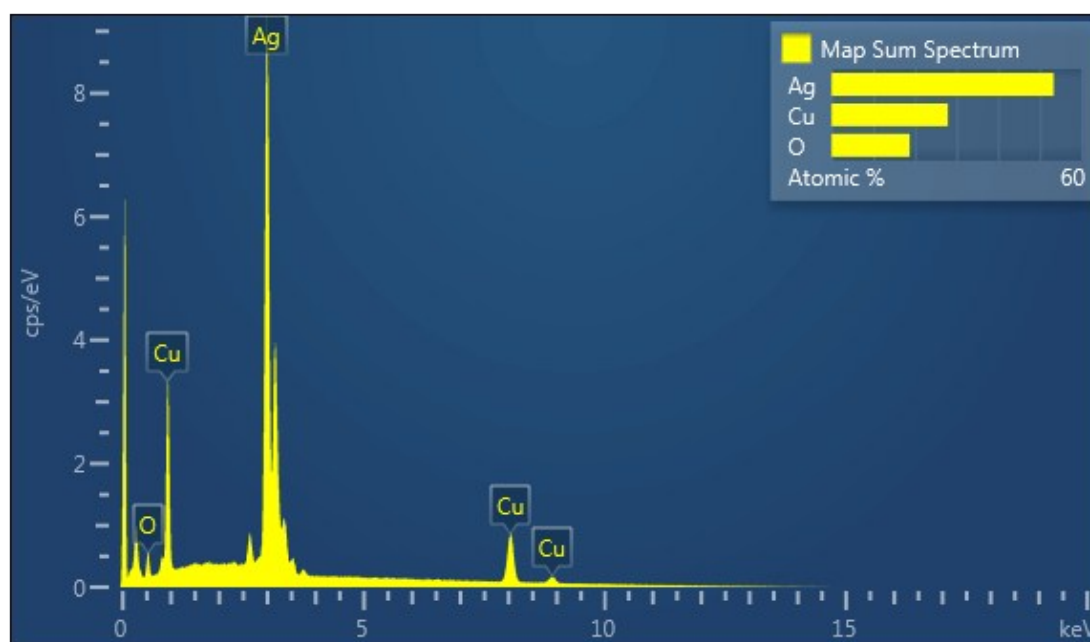


Figure S10. EDX map of the freshly prepared AgNPs/Cu foam, indicating a high content of Ag.

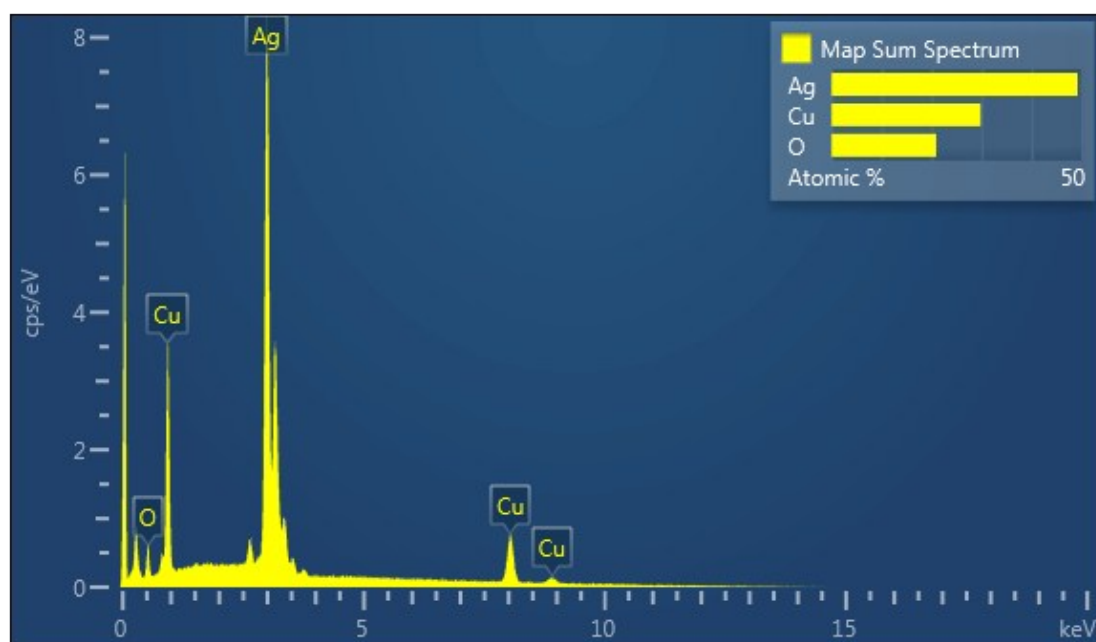


Figure S11. EDX map of the AgNPs/Cu foam stored for 10 days, indicating a decreased content of Ag and increased O element content.

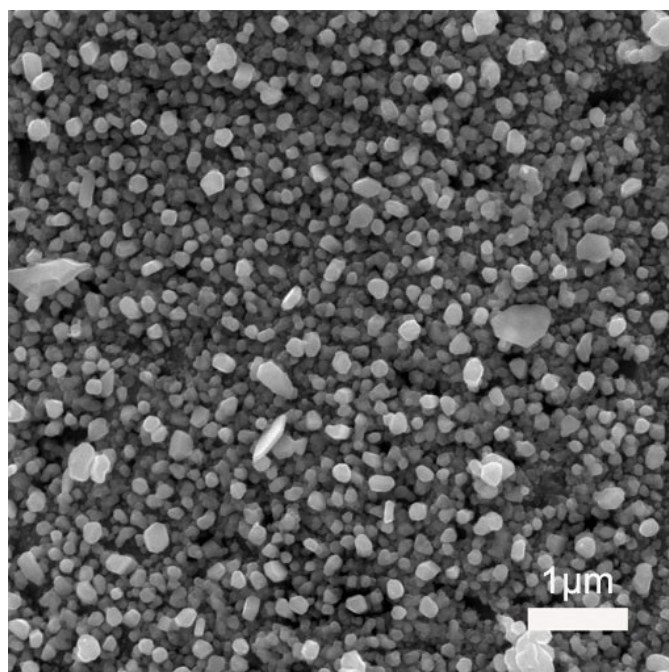


Figure S12. SEM image the AgNPs/Cu foam stored for 10 days.