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Supporting information

Recyclable PDMS Microfluidic Surface-enhanced Raman Scattering Cu/AgNPs Chip for Analysis of Sulfadiazine in Aquatic Products

Jianying Huang, Ling Xia, Xiaohua Xiao*, Gongke Li*

School of Chemistry, Sun Yat-sen University, Guangzhou 510006, China

* Corresponding authors: Gongke Li, Xiaohua Xiao

Tel.: +86-20-39339782

Email: cesgkl@mail.sysu.edu.cn (Gongke Li)

Content

S1 Pretreatment process of raw samples

In this experiment, grass carp were procured from local markets and subjected to sulfadiazine administration to replicate drug-feeding processes in aquaculture. Initially, 200.0 mg of sulfadiazine was blended with 10.0 g of fish feed to achieve a concentration of 20.0 mg/g in the feed. Subsequently, the grass carp were orally administered 200.0 mg of sulfadiazine twice a week. Finally, the edible portions of the grass carp were extracted and thoroughly pulverized to serve as the raw samples.

The initial preparation of the sample involved the obtaining of the testing solution. Precisely, 5.0 g of crucian samples were placed in a centrifuge tube, followed by adding 5.0 g of anhydrous sodium sulfate and 15.0 mL of ethyl acetate for ultrasound extraction lasting 10 minutes. Subsequently, the mixture underwent centrifugation at 4000 rpm for 5 minutes to gather the supernatant. Then, 15.0 mL of n-hexane was introduced into the supernatant and vortexed for 2 minutes. Following the removal of n-hexane via centrifugation at 4000 rpm for 5 minutes, the resulting supernatant underwent concentration and dissolution using water/acetonitrile (V_{water}: $V_{acetonitrile}$ = 4:6) of 2mL. The mixture was further refined by filtration through a 0.22 μm membrane.

S2 High-performance liquid chromatography conditions

All chromatographic analyses for the method comparison study of sulfamethoxazole were performed by high-performance liquid chromatography (HPLC) with a UV-Vis wavelength detector (Shimadzu, Japan). The chromatographic analysis was performed on an Agilent XDB C18 column (150 mm×4.6 mm, i.d. 5.0 μm) at 35 °C. The detection wavelength of the UV detector was set at 270 nm. The mixture of 2% acetic acid solution (A) and acetonitrile (B) (V_A: V_B =70:30) was used as the mobile phase with a flow rate of 0.7 mL/min.

S3 Characterizations of AgNPs on metals

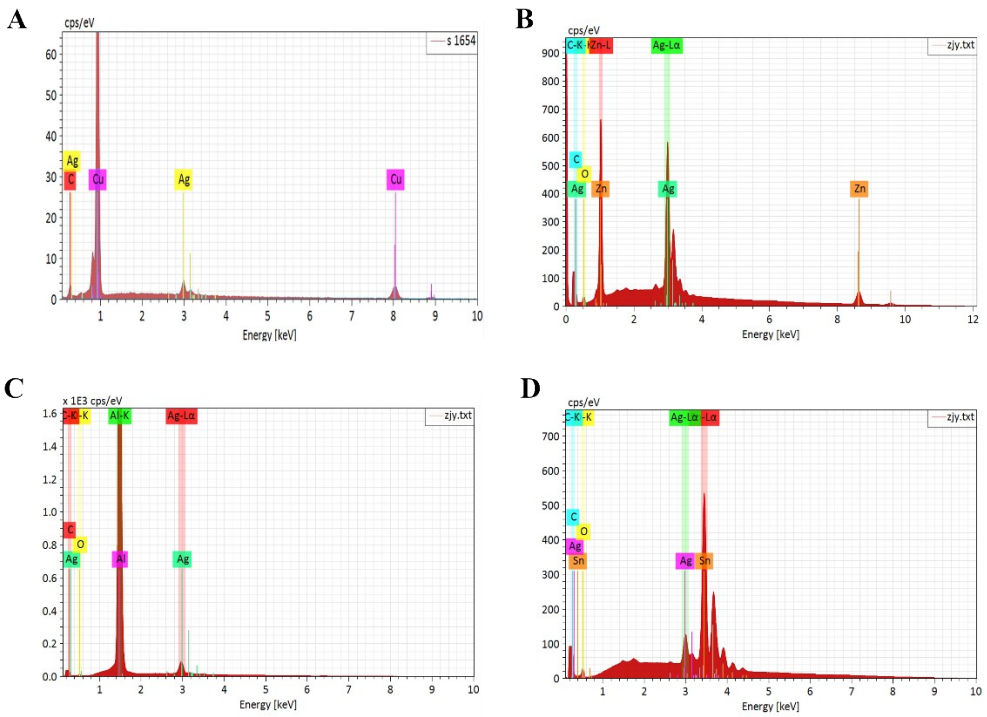

Fig. S1 EDS of AgNPs generated in different Metal/PDMS microfluidic chips (Cu, Zn, Al, Sn).

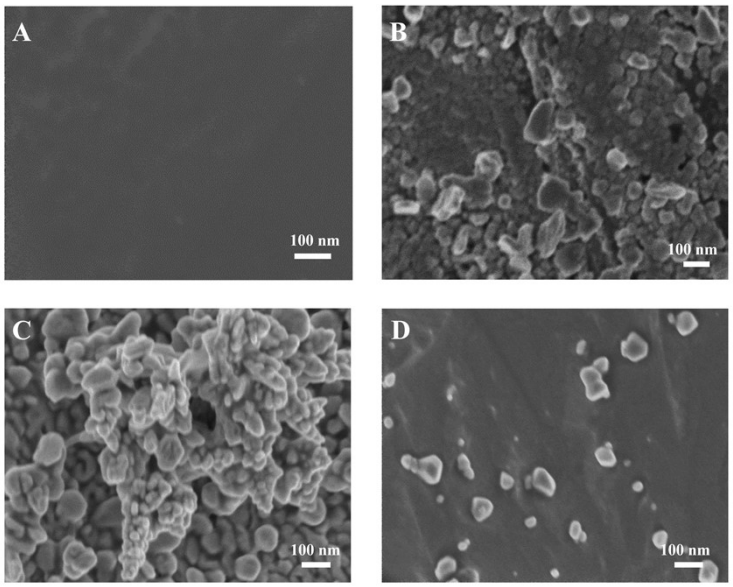

Fig. S2 SEM of AgNPs generated in Cu/PDMS microfluidic chip under different synthesis conditions: A. copper foil without $AgNO_3$, B. 20 mmol/L $AgNO_3$, a flow rate of 5 μL/min, and a reaction time of 4 min, C. 10 mmol/L $AgNO_3$, a flow rate of 15 μL/min, and a reaction time of 2 min, D. 10 mmol/L $AgNO_3$, a flow rate of 5 μL/min, and a reaction time of 1 min.

S4 Optimization of preparation for AgNPs in Cu/PDMS chips

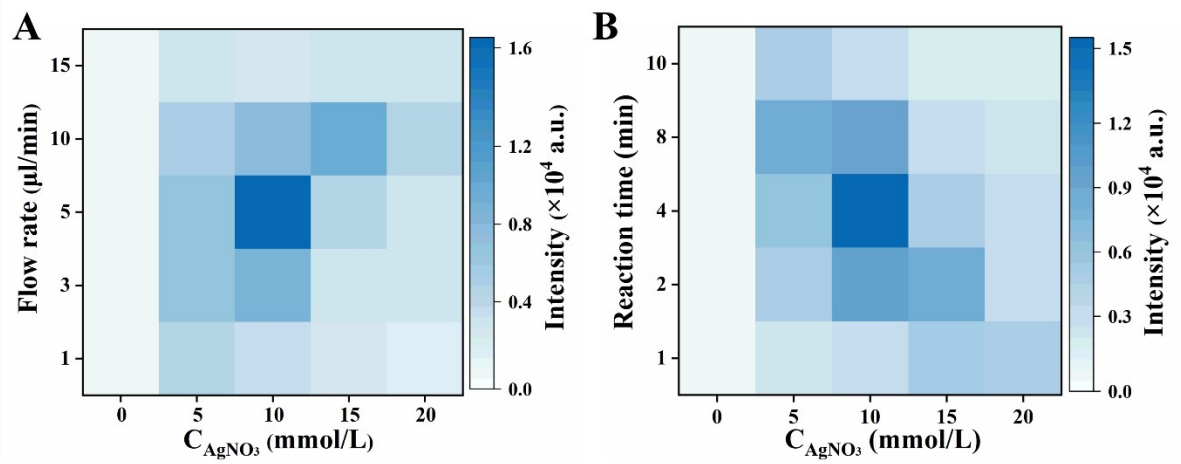

Fig. S3 A. Screening synthesis conditions of $AgNO_3$ concentration and reaction flow rate, B. screening synthesis conditions of $AgNO_3$ concentration and reaction time.

A concentration of 100 μg/L of MB was introduced into the microchannel substrate for SERS measurements., and the 1618 cm^{-1} peak of the MB was utilized for analysis. The $AgNO_3$ solution was injected into the Cu/PDMS microfluidic chip through the inlets of the chip. By adjusting the reaction concentration, flow rate, and reaction time of $AgNO_3$ and Cu, the size, shape, and density of AgNPs could be controlled more rapidly and effectively within confined spaces. Once Ag seeds were formed on the copper foil, further AgNPs growth tended to occur on these seeds, influencing the formation of a uniformly dense AgNPs structure, which is required for highly active SERS substrates. In microfluidic synthesis, controlling the flow rate at 5 μL/min and reaction time at 6 min allowed the generation of a large number of seeds, resulting in a denser and more uniform AgNPs structure.

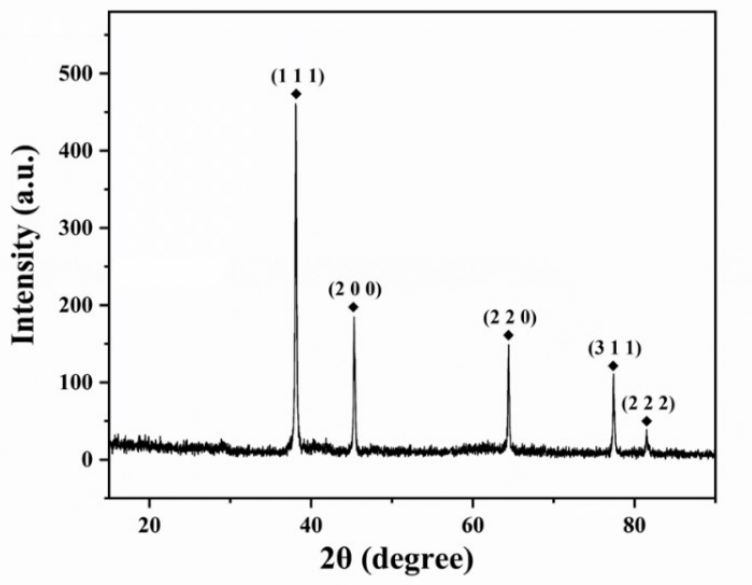

Fig. S4 XRD characterization of AgNPs on copper foil.

S5 COMSOL simulation of the electric field distribution of AgNPs/Si

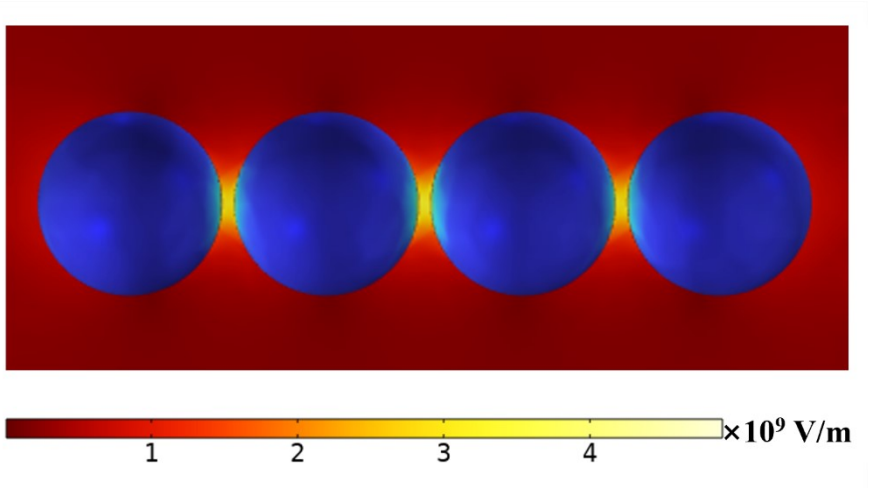

Fig. S5 COMSOL simulation of the electric field distribution of AgNPs/Si.

S6 COMSOL simulation of the chip pressure and velocity field

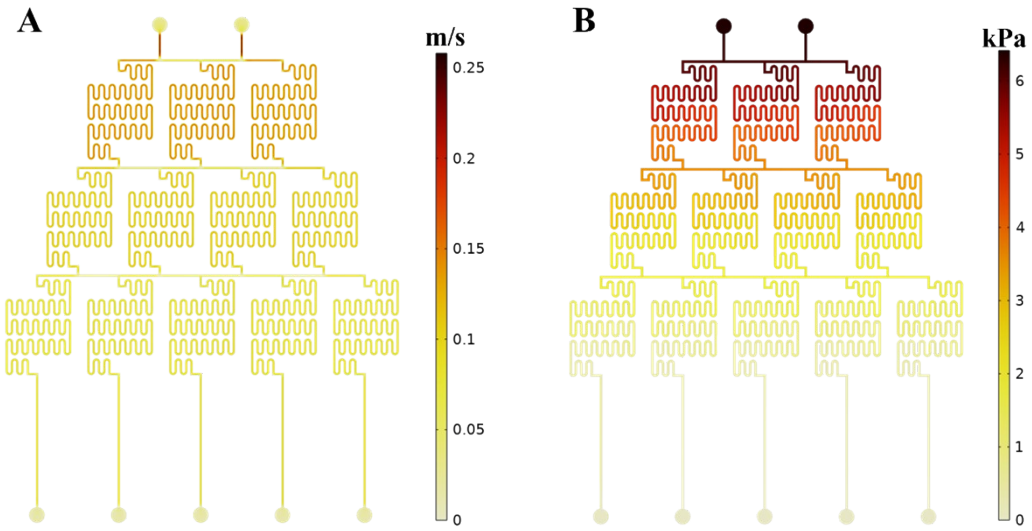

Fig. S6 COMSOL simulated microchannel: A. Velocity field in, and B. pressure field.

S7 The concentration generation validation taken in the PDMS Cu/AgNPs chip.

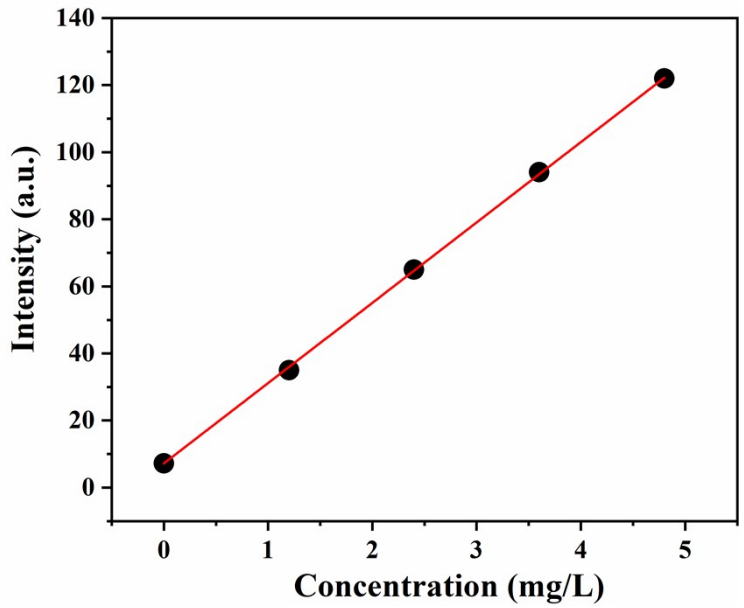

Fig.S7 The calibration curve describing the relationship between the gray value of channels and theoretical concentration taken in the PDMS Cu/AgNPs chip.

S8 HPLC detection of sulfadiazine

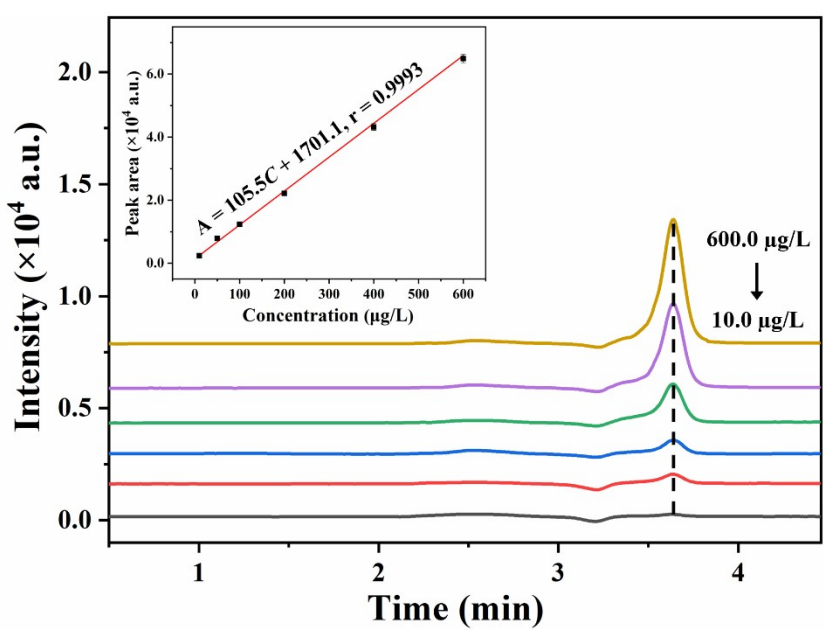

Fig. S8 The HPLC chromatogram of sulfadiazine and the correlation between peak area and concentration of sulfadiazine in the range of 10.0-600.0 μg/L.

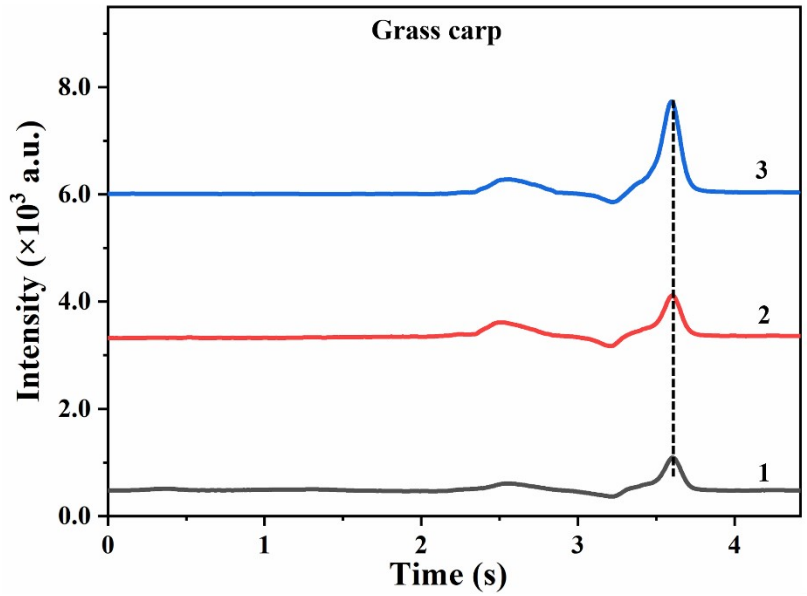

Fig. S9 The HPLC chromatogram of sample analysis: (1) 100 μg/L standard sulfadiazine, (2) grass carp sample, (3) spiked with 50 μg/kg.