

## Supporting Information

# **An Efficient Strategy to Prepare Ultra-High Sensitivity SERS-Active Substrate Based on Laser-Induced Selective Metallization of Polymers**

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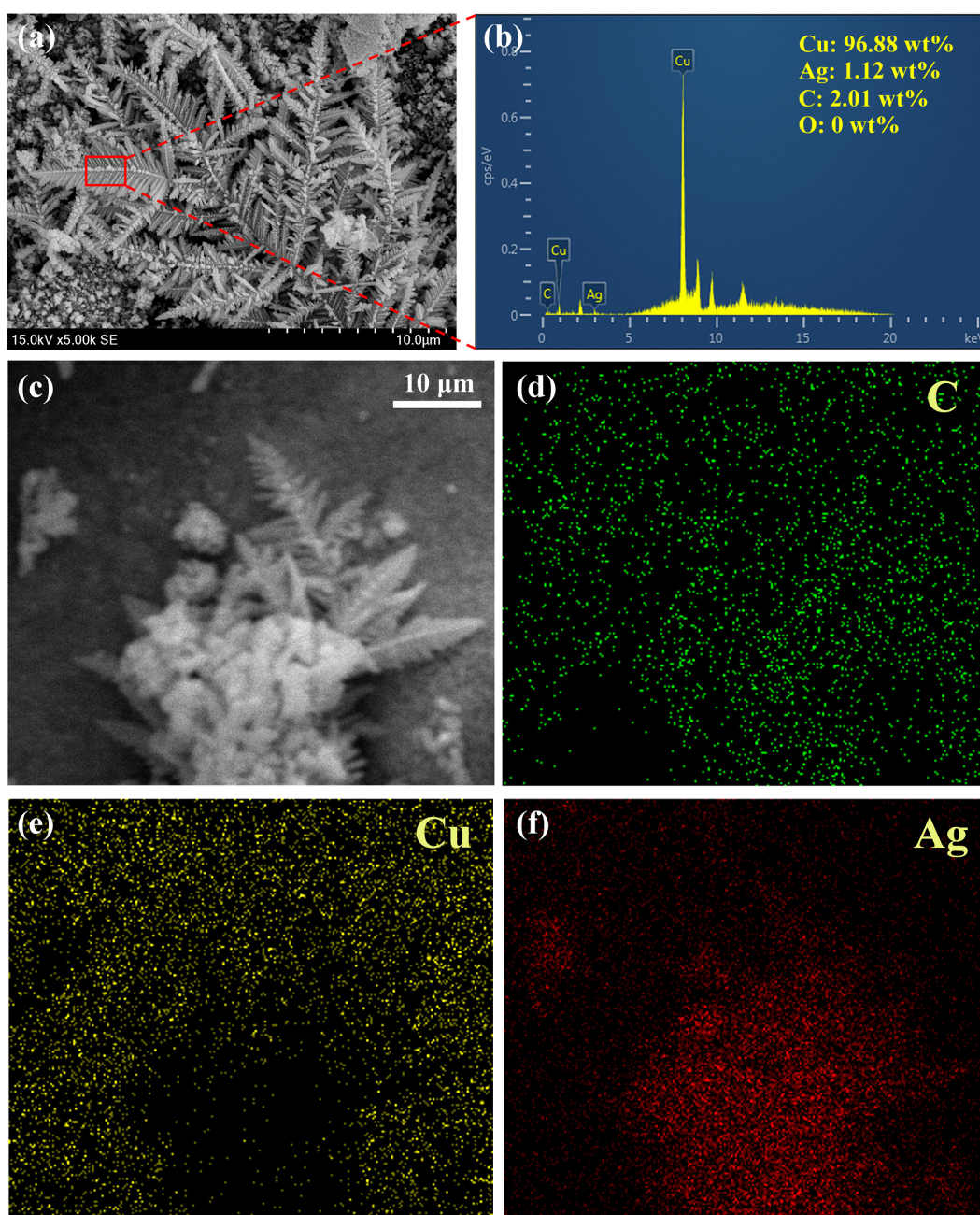
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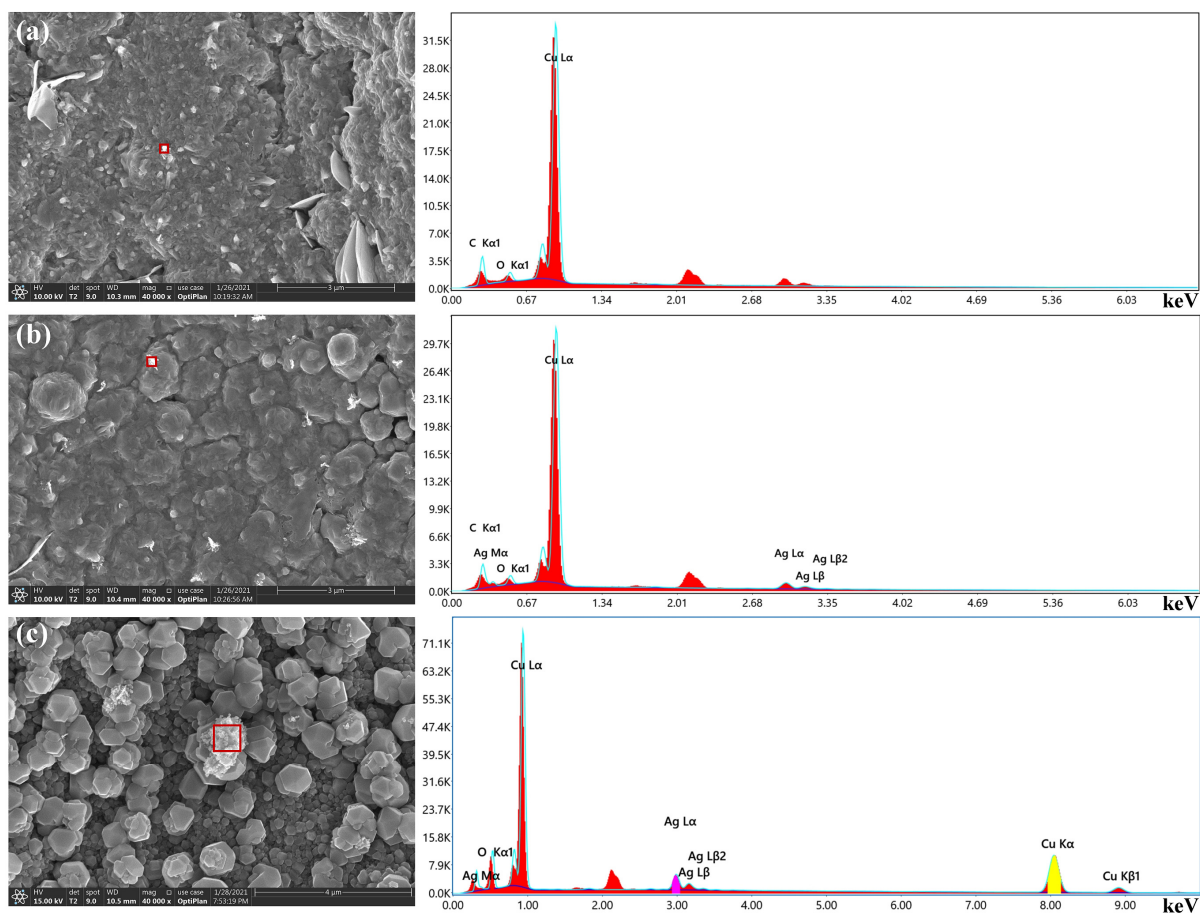
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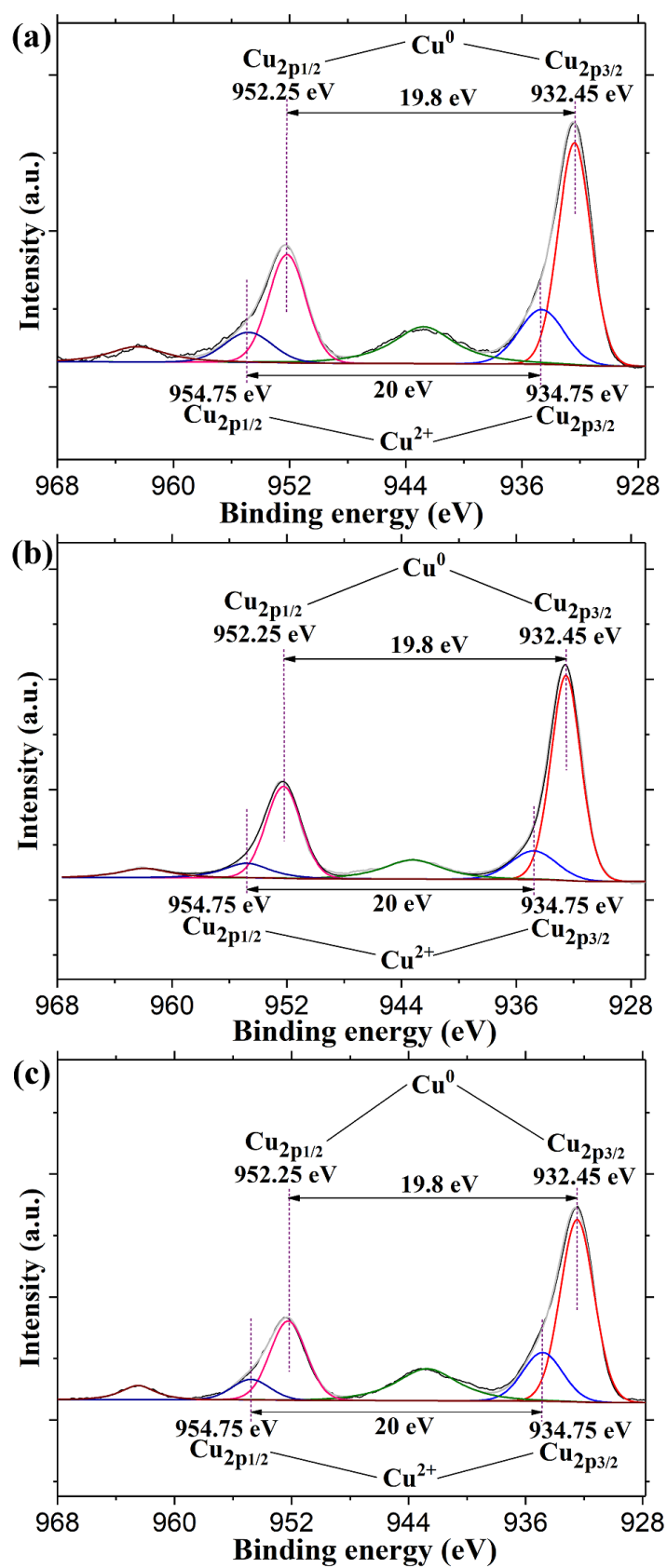
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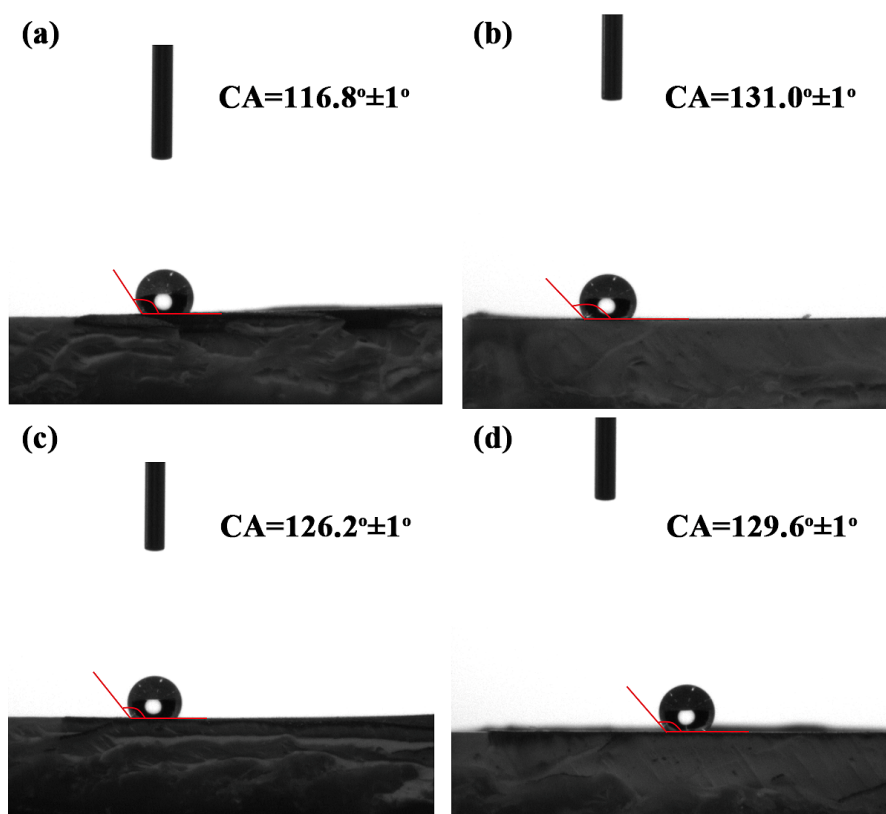
**Figure S1.** (a) Typical morphology and structure of “fern branches and leaves” on the SERS-3 substrate. (b) The corresponding EDS spectrum at the given region in **Figure S1(a)**. (c) SEM image of “fern branches and leaves” for EDS mapping. (d), (e), (f) EDS mapping of **Figure S1(c)** for C, Cu, and Ag elements, respectively.



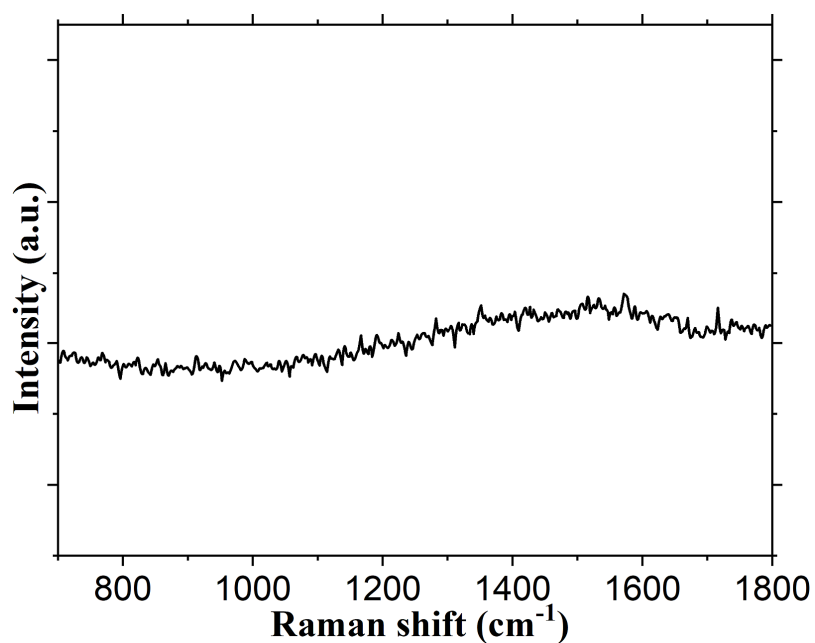
**Figure S2.** Surface SEM images (left) and the corresponding EDS spectra (right) at the given regions of SERS-0.1, SERS-0.2, SERS-0.5 substrates. **(a)** SERS-0.1; **(b)** SERS-0.2, **(c)** SERS-0.5.



**Figure S3.** XPS high-resolution spectra of Cu 2p for the prepared SERS-active substrates. (a) SERS-1; (b) SERS-2; (c) SERS-3.



**Figure S4.** Surface contact angles of the prepared SERS-active substrates. (a) SERS-0; (b) SERS-1; (c) SERS-2; (d) SERS-3.



**Figure S5.** SERS spectrum of R6G molecule using the SERS substrate before galvanic replacement with silver ions.

## The Calculations of the Analytical Enhancement Factor (AEF)

Herein, the most commonly used analytical enhancement factors (AEF) have been calculated, and it used to compare the average SERS enhancements of different substrates.

The following equation is the definition of AEF:

$$AEF = \frac{I_{SERS}/C_{SERS}}{I_{RS}/C_{RS}} \quad (1)$$

where  $I_{SERS}$  and  $I_{RS}$  are the spectral intensities of the SERS spectrum and ordinary Raman spectrum, respectively. The  $C_{RS}$  is a given concentration of the analyte, and the  $C_{SERS}$  is the different concentration of the same analyte on the SERS substrate.

In our work, the SERS spectra and ordinary Raman spectrum were recorded for the calculations of AEF. The SERS spectra were collected from SERS-1 substrates treated with  $1 \times 10^{-5}$  M,  $1 \times 10^{-11}$  M, and  $1 \times 10^{-17}$  M R6G solutions, respectively. The ordinary Raman spectrum was collected from a glass slide treated with a  $1 \times 10^{-3}$  M R6G solution. The reason why we chose a  $1 \times 10^{-3}$  M R6G solution is that the minimum detection lower limit is only  $1 \times 10^{-3}$  M when using a glass slide.

For the SERS spectra and ordinary Raman spectrum, the spectral intensity of peak at  $613 \text{ cm}^{-1}$  was chosen for calculations. For  $1 \times 10^{-5}$  M,  $1 \times 10^{-11}$  M, and  $1 \times 10^{-17}$  M R6G solutions, the intensities of SERS spectra at  $613 \text{ cm}^{-1}$  are  $I_{SERS}=20672$ ,  $I_{SERS}=5220$ ,  $I_{SERS}=761$ , respectively. And, the intensity of the ordinary Raman spectrum at  $613 \text{ cm}^{-1}$  is  $I_{RS}=1051$ .

Thus, for  $1 \times 10^{-5}$  M R6G solution, the AEF of the SERS-1 substrate is as follows:

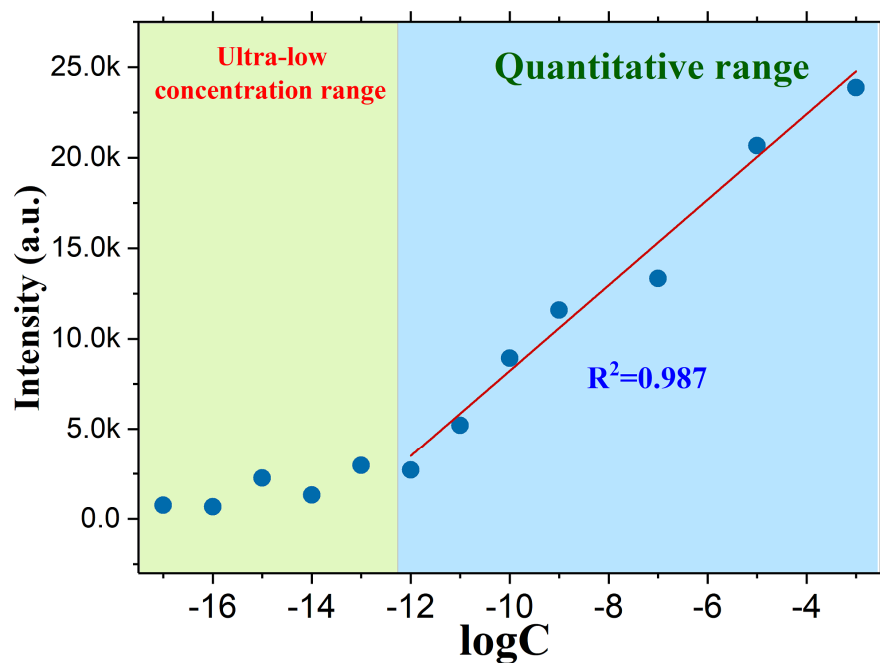
$$AEF = \frac{20672/10^{-5}}{1051/10^{-3}} = 1.97 \times 10^3$$

For  $1 \times 10^{-11}$  M R6G solution, the AEF of the SERS-1 substrate is:

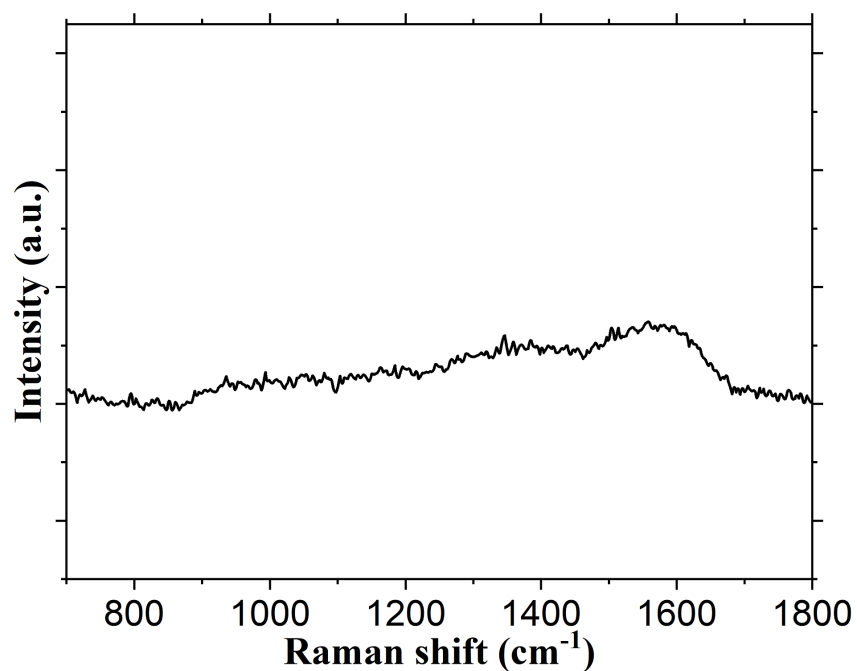
$$AEF = \frac{5220/10^{-11}}{1051/10^{-3}} = 4.97 \times 10^8$$

For  $1 \times 10^{-17}$  M R6G solution, the AEF of the SERS-1 substrate is:

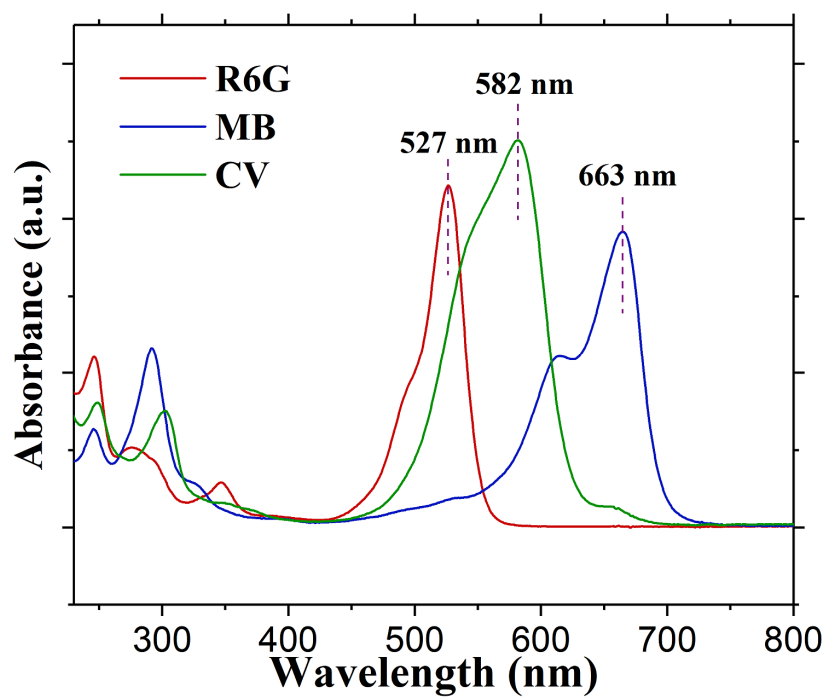
$$AEF = \frac{761/10^{-17}}{1051/10^{-3}} = 7.24 \times 10^{13}$$



**Figure S6.** Relationship between spectral intensities of  $613\text{ cm}^{-1}$  and the concentrations of R6G solutions.



**Figure S7.** A typical surface Raman spectrum of the blank SERS-1 substrate without immersing in any solution of probe molecules for treatment.



**Figure S8.** UV-vis absorption spectra of R6G, CV, and MB solutions.



**Table S1.** Recent progress of the Cu-based SERS-active substrates for detecting the trace amount of analyte

SERS-active substrates	Analyte	The lower limit of detection ( $C_{\text{analyte}}$ , M)	Refs.
AgNFs/G@Cu substrate	R6G	$10^{-14}$	Ref. 1
AgCu alloy nanowires	R6G	$10^{-14}$	Ref. 2
Ag hollow microcubes based on $\text{Cu}_2\text{O}$ cubes template	R6G	$10^{-12}$	Ref. 3
NPC film/Cu foil	R6G	$10^{-9}$	Ref. 4
Ag nanosheets on the Cu plate	R6G	$10^{-12}$	Ref. 5
Ag-Cu SERS substrates	R6G	$5 \times 10^{-5}$	Ref. 6
Au-Ag-Cu nanodendrites	R6G	$10^{-10}$	Ref. 7
Cu-Ag hybrid NWs	R6G	$10^{-8}$	Ref. 8
$\text{MoS}_2$ @CuNPs	R6G	$10^{-9}$	Ref. 9
Ag/Cu/PET substrate	R6G	$10^{-10}$	Ref. 10
Ag-Cu@G sample	R6G	$10^{-6}$	Ref. 11
Ag nano/micro-structures on Cu micro-grid	R6G	$10^{-7}$	Ref. 12
Graphene/bilayer Ag/Cu sandwich structures	R6G	$10^{-8}$	Ref.13
Cu-Au sandwich structures on PE	R6G	$10^{-5}$	Ref. 14
Cu-Au sandwich structures on PET			
<b>Cu-Ag-@ABS/<math>\text{Cu}_2(\text{OH})\text{PO}_4</math> composite</b>	<b>R6G</b>	<b><math>10^{-17}</math></b>	<b>This work</b>