AgNPs Decorated 3D Bionic Silicon Nanograss Arrays Pattern with High-Density Hot-Spots for SERS Sensing via Green Galvanic Displacement without Additives

Li Wang,^{#,a} Jian Huang,^{#,*,a} Mei-Juan Su,^a Jin-Di Wu,^a and Weisheng Liu^{*,b}

a. College of Chemistry and Chemical Engineering, Xi'an Shiyou University, Xi'an, Shaanxi 710065, China. E-mail: jhuang@xsyu.edu.cn
b. Key Laboratory of Nonferrous Metals Chemistry and Resources Utilization of Gansu Province, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000,P. R. China. E-mail: liuws@lzu.edu.cn
*Correspondence: jhuang@xsyu.edu.cn (J.H.); liuws@lzu.edu.cn
#Jian Huang and Li Wang are co-first authors of the article. These authors contributed equally to this work and should be considered co-first authors.

1. Estimation of the Analytical Enhancement Factors

The sensitivity of the as-prepared AgNPs decorated 3D bionic silicon nanograss arrays SERS substrates were characterized by the analytical enhancement factor (AEF). The AEF can be obtained by a reference sample without SERS contribution and described as the formula of

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

AEF is defined by comparing the intensity of the SERS signal with that of the non-SERS signal. Because the experimental conditions (e.g. laser wavelength, laser power, sample preparation conditions, laser spots, and so on) can be rigorously controlled, the estimations of the AEF are quite intuitive and reproducible.

AEF has been calculated from the ratio of SERS intensity (I_{SERS}) and Raman intensities (I_R) with respect to their respective concentration used for SERS (C_{SERS}) and Raman (C_R) measurements.

Bulk Raman has been measured by preparing a concentrated solution of the respective molecules. The most intense SERS peak with lowest detectable concentration and its corresponding peak in bulk Raman were used for comparison.

On the one hand, the lowest reliable concentration (C_{SERS}) is 10^{-12} M, and the most intense SERS peak intensity (I_{SERS}) is ~3040. On the other hand, bulk concentration of R6G (C_{R}) is 10^{-5} M, and its corresponding peak intensity (I_{R}) is ~815. According to the account, EF was estimated to be about 3.7×10^7 and it was high enough for ultrasensitive detection.

In comparison with the intensity of the band at 1360 cm⁻¹ in normal Raman spectrum of a reference R6G at 10^{-5} M, the AEF of the as-prepared AgNPs decorated 3D bionic silicon nanograss arrays SERS substrates can be estimated to be 3.7×10^7 , depending on the choice of the Raman characteristic peaks.

The results of our experiment implies that the SERS enhancement effect of the 3D bionic silicon nanograss arrays hybridized AgNPs is remarkably stronger than that of pure silver or silicon micro-nano structure SERS substrates.



Figure S1. (a) The AEF of pure silver or silicon micro-nano structure SERS substrates; (b) the AEF of the as-prepared SERS substrates based the five main Raman bands at 614, 776, 1360, 1507 and 1570 cm⁻¹.

Here, the five main Raman bands at 614, 776, 1360, 1507 and 1570 cm⁻¹ are selected to calculate the average AEF. On the basis of calculations, the AEF average value is about 3.3×10^7 .

In the present experiment, according to the intensity of the bands at 614, 776, 1360, 1507 and 1570 cm⁻¹ in the SERS detection of R6G with identical concentration using hybridized silver nanoparticles with 3D bionic silicon nanograss arrays, it is suggested that SERS property is obviously superior to other substrates (**Figure S1**).

2. Several Possible Factors about the Stronger EF and Higher SERS

Enhancement

Firstly, the role of 3D bionic silicon nanograss arrays not merely as supporting substrate but also induces more electrons transferring from needle-like 3D bionic silicon nanograss arrays to AgNPs which attributed to the difference of work function or Fermi level between them. The combination of needle-like 3D bionic silicon nanograss arrays with AgNPs leads to a strong interaction of exciton-plasmon and will yield a stronger localized surface electrical field.

Secondly, the needle-like nanowires on the substrate have high aspect ratio (length/diameter) and large surface volume ratio, which is an essential requirement factor in achieving high SERS enhancement. Moreover, diameter changeable sites will display different adsorption and enhancement ability. The needle-like 3D bionic silicon nanograss arrays substrates can accelerate more probe molecule adsorption that gave a greater enhancement.

Then, because of the diameter (from bottom to top) of needle-like 3D bionic silicon nanograss arrays is shrink, which maybe lead to their different light reflection characteristics. Needle-like 3D bionic silicon nanograss arrays themselves can also function as antennas to capture, confine light and further enhance an optical signal. Furthermore, the needle-like 3D bionic silicon nanograss arrays possess a shrink Au remnant droplet on the top nanowires. Maybe it is a TERS model for a higher enhancement.

Finally, an optimized average size and density of AgNPs decorated on needlelike 3D bionic silicon nanograss arrays surfaces enable the coupling, transference and resonance of dipole vibration on each AgNPs. We can see the tips of needle-like 3D bionic silicon nanograss arrays on the substrate are cross and interconnected which are more closely related to each other. More AgNPs tend to grow at the head of cylinder-like silicon nanoarrays. Thus, the size/gap of the NPs on the tips of needlelike 3D bionic silicon nanograss arrays is usually closer than that on the cylinder-like silicon nanoarrays. A close packed AgNPs can decorate on the needle-like 3D bionic silicon nanograss arrays readily, which significantly increases the electromagnetic field and yields more hot spots by AgNPs aggregation.

Therefore, it is not surprising that the AgNPs/needle-like 3D bionic silicon nanograss arrays substrate results in a large enhancement of the Raman scattering intensity.

3. Assignments of Sudan I Raman spectra

Assignments of Sudan I Raman spectra	Raman Shift (cm ⁻¹)	
Stretching vibration of benzene ring skeleton	~1593	
C-C stretching vibration	~1492	
-N=N- anti symmetric stretching vibration	~1450	
C-H ring internal deformation	~1385	
Benzene ring CH- stretching vibration		
C-H ring internal deformation	1091, 1163, 1224, 1335	
Stretch vibration of benzene nitrogen	~990	
C-H ring outside deformation	~458 and 718	

Table S1. The main assignments of Sudan I Raman spectra.

4. Results for the detection of Sudan I in environmental water

Sample	Found (M)	Added Sudan I (M)	SERS sensing (M)	Recovery (%)
i	~ 0	1 × 10 ⁻⁹	1.120 × 10 ⁻⁹	112.0
ii	~ 0	1×10^{-8}	0.911 × 10 ⁻⁸	91.1
iii	~ 0	1×10^{-7}	0.894×10^{-7}	89.4

Table S2. The detailed results for the detection of Sudan I in environmental water

* the average recovery was estimated to be 97.5%

5. TEM (a) and corresponding elemental mapping for a single Si nanowire/nanoneedle, (b) Au, (c) Si, and (d) O



Figure S2. TEM (a) and corresponding elemental mapping for a single Si nanowire/nanoneedle, (b) Au, (c) Si, and (d) O

6. Results for the stability and durability of the prepared substrates



Figure S3. The stability and durability of the as-prepared substrates, (a) freshly prepared , and aging for a certain amount of time, (b) 5 days, (c) 15 days, (d) 20 days, (e) 30 days. The SERS spectra of CV.