Detection of breast cancer based on novel porous silicon Bragg reflector surface-enhanced Raman spectroscopy-active structure

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Highly doped N<100> silicon wafers with a resistivity of 0.01-0.02 Ω·cm were used in the experiments. The silicon wafers were cut into 2×2 cm samples, and then acetone, ethanol and deionized water were used toultrasonically cleaning the samples for 15 min. The samples were prepared by electrochemical corrosion of the anode, and the corrosion concentration was HF:C_2H_5OH=2:5 (v/v). The samples were periodically etched by high current density followed by low current density (low refractive index and then high). The low refractive index layer was corroded with a current density of 100mA/cm^2 for 2s, while the high refractive index layer was corroded with a current density of 40mA/cm^2 for 3s. The Bragg reflector was designed as 15 periods. The PSi samples were immersed in 0.05 M $AgNO_3$ solution for 50 s. The PSi SERS active substrates were successfully fabricated. To verify the performance of the PSi Bragg reflector SERS substrate, a single-layer PSi SERS substrate was used as a reference. Single-layer PSi was obtained with a current density of 100 mA/cm^2 for 90 s to ensure the same porosity [1].

Table S1. Distribution of vibration modes in Raman spectra of BRC serum.

BRC Raman Shift (cm^{-1})	Assignment [2]
852	Signal-free area of amphetamine
879	Hydroxyproline, tryptophan
960	Quinoid ring in-plane deformation
1005	Symmetricringbreathing of phenylalanineS
1157	In-plane vibrations of the conjugated55C-C55
1283	Differences in collagen content
1450	CH 2 bending mode in malignant tissues
1517	b -carotene accumulation (C-C stretch mode)
1583	C==C bending mode of phenylalanine
1654	Due to a combination of C=C stretch & the amideI bands+BIAOamide I

Figure S2. shows the SERS spectra of normal human serum (diluted in different proportions) on the PSi Bragg reflector SERS substrates. A Raman signal can be obtained on all samples. Therefore, the substrate has high detection

sensitivity. The vibration modes of the characteristic peaks in the BRC serum Raman spectra are summarized.It is found that the detection limit was reached when the concentration diluted to BRC: DW of 1:7.

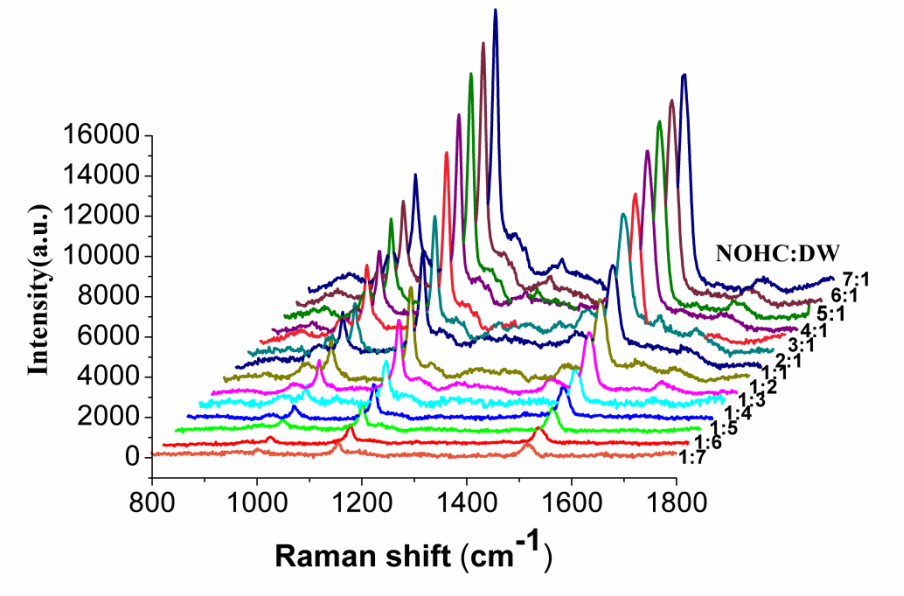

Figure S2. SERS spectra of normal human serum amples (diluted in different proportions) on the AgNP PSi Bragg reflector SERS substrates.

Figure S3. SERS effect of the substrate is investigated using R6G as the Raman active compound (analyte) with a micro-Raman set up. The spectra look very sharp and the intense characteristic peaks of R6G are displayed in Fig S2. The characteristic peaks of R6G at 612, 773 and 1182 cm-1are associated with C–C–C ring in-plane, C–H out of plane bend mode and C–C stretching vibrations, respectively. The bands at1360, 1496 and 1642 cm-1 are usually assigned to aromatic C–C stretching vibrations of the R6G molecules but none of the Raman lines from methanol at 1035 and 1465 cm^{-1} can be seen in the spectrum. The lowest concentration of R6G can be measured is 1.0×10^{-13} M.

According to the enhancement factor of SERS:

$$EF = \frac{(I_{SERS} / N_{SERS})}{(I_{RS} / N_{RS})},$$

where I denotes the intensity of Raman scattering spectra, and N is the number of R6G molecules found in the laser excitation area. For PSi substrates, it is impossible to accurately obtain the number of analyte molecules in the laser irradiation region. Therefore, the equation is not applicable to calculate the enhancement factor of Ag NPs PSi Bragg reflector substrate. As expected, a method for evaluating the enhancement of the Raman signal for R6G molecules on complex SERS substrates, external amplification Raman efficiency [3], is proposed. This method evaluates the ratio between the minimum concentration of analyte detected on metal coated PSi substrate and the minimum concentration of analyte detected on Si substrate. On flat Si substrates, the lowest concentration of R6G can be measured is 1.0×10^{-2} M by the immersion method. Thus, the amplification Raman efficiency is 10^{11}.

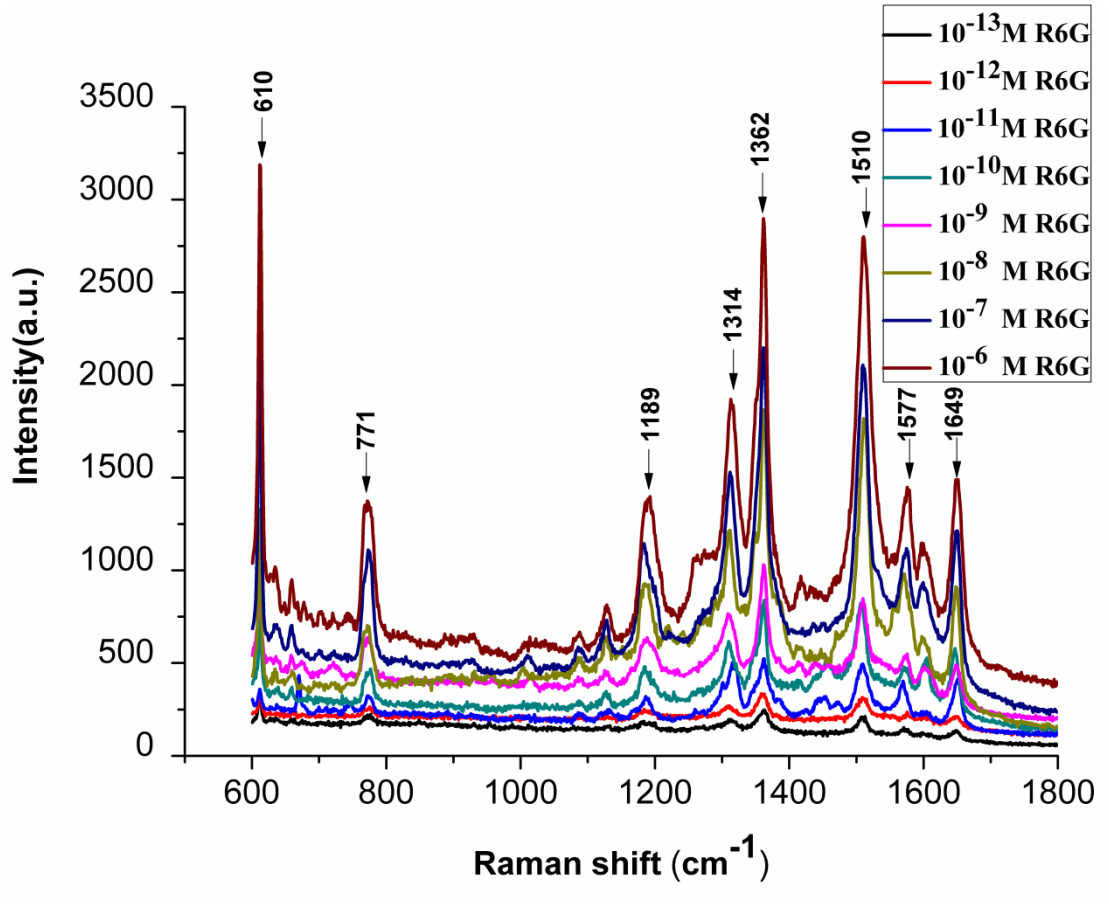

Figure S3. SERS spectrum of R6G concentration at 10^{-6}-10^{-13} M

References

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3. A. Virga et al., "SERS active Ag nanoparticles in mesoporous silicon: Detection of organic molecules and peptide–antibody assays", J. Raman Spectrosc, 43, 730 (2011).

Through figure S4. can be intuitively seen that the average normalized spectrum of serum of healthy people and early BRC patients has some differences in some Raman characteristic peaks. For example, at 1005, 1157 and 1517, the Raman characteristics of the two are quite different. It shows that there are differences in the content of Phenylalanine (proteins) Proteins, In-plane vibrations of the conjugated =C-C= β-carotene accumulation (C=C stretch mode） and β-carotene accumulation (C-C stretch mode) . This provides a theoretical basis for further classification through algorithms.

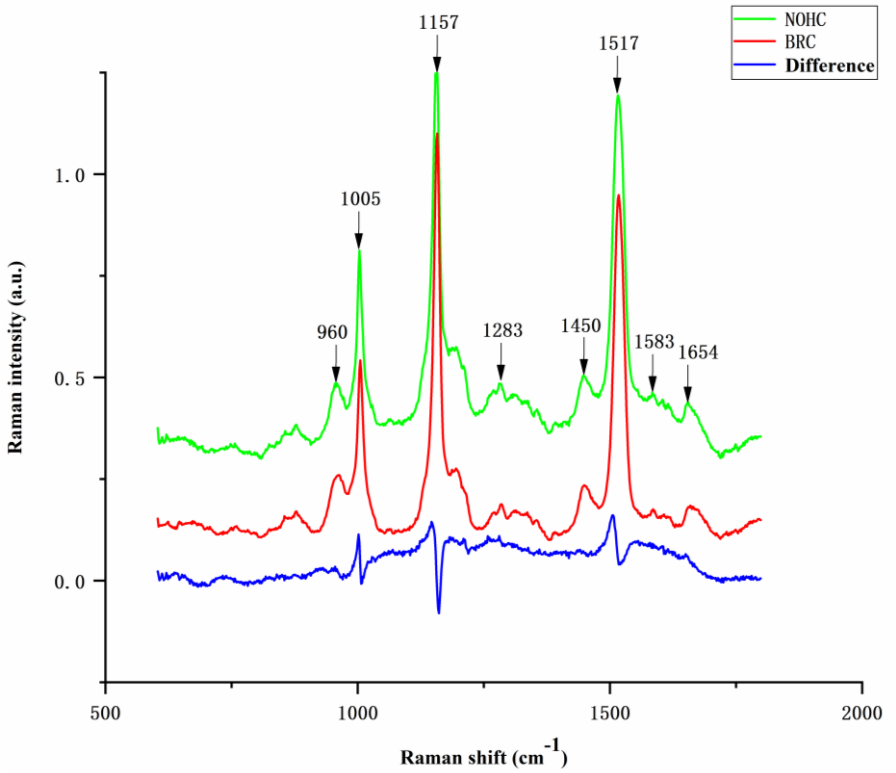

Figure S4. The difference of the average normalized spectrum between the serum of healthy people and the early BRC patients serum.