Electronic Supplementary Information for

Carbonized Polyacrylonitrile Array as a Sensitive, Biocompatible, and Durable Substrate for Surface-Enhanced Raman Spectroscopy

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This supporting information is a 16-page document, including 3 sections, 2 tables, 8 figures, and this cover page.

Section S1. Calculation of enhancement factor

According to the most widely used definition of the average SERS enhancement factor (EF)[1-3], we conducted a calculation to determine the SERS EF for glucose adsorbed on a carbonized PAN array.

$$EF = \frac{I_{SERS} / N_{surf}}{I_{RS} / N_{vol}} \qquad \text{(S1)}$$

where I_{SERS} and I_{RS} represent particular peak intensity of an analyte in the SERS and normal Raman spectra measured under identical conditions, respectively. While N_{surf} and N_{vol} represent the average numbers of molecules adsorbing in the scattering volume during a SERS and a non-SERS experiment, respectively. Based on the assumption of uniform distribution of molecules on the carbonized PAN array, it was speculated that the density of glucose on the carbonized PAN array under SERS would be 5.02×10^{13} molecules per mm^2, (1×10^{-4} mol $L^{-1} \times 10$ μL × NA/12 mm^2, where 12 mm^2 stands for the surface area of the carbonized PAN array). And the density of glucose on the silicon substrate under non-SERS was estimated to be 3.76×10^{17} molecules per mm^2 (1 × mol $L^{-1} \times 10$ μL × NA/16 mm^2, where 16 mm^2 stands for the surface area of the silicon). The the laser spot has a diameter of approximately 1 μm, with a corresponding surface area of about 7.9×10^{-7} mm^2. Therefore, the N_{surf} value is determined to be 3.96×10^7, and the N_{vol} value is calculated to be 2.97×10^{11}, respectively. In accordance with the equation S1, the EF value is 1.31×10^5. As for dopamine, melamine and creatinine adsorbed on carbonized PAN arrays, the SERS EF have been calculated similarly, and detailed data can be found in **Table S1.**

Section S2. Calculation of energy level diagram

In a carbonized PAN/R6G system, there is a possibility that charge transfer may occur at the contact interface between R6G and carbonized PAN. Based on the UV-Vis adsorption spectrum of R6G molecules illustrated in **Fig. S7c**, the energy difference between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of R6G molecules is 2.37 eV. By combining these data with the ultraviolet photoelectron spectra of R6G molecules in the

carbonized PAN/R6G system (**Fig. S7 a and b**), it can be calculated that the HOMO and LUMO of R6G are 8.86 and 6.49 eV away from the vacuum level, respectively. The energy level information of carbonized PAN array, valence band and conduction band gap of 1.33 eV, can be calculated by combining its ultraviolet photoelectron spectrum with its band gap value. Then the valence band level and the conduction band level are 8.78 eV and 7.45 eV away from the vacuum level, respectively. On the basis of the obtained energy level information, the charge transfer mechanism in a carbonized PAN/R6G system is analyzed.

Section S3. Calculation of degree of charge-transfer (CT)

The ρ_{CT} is carried out according to the following equation:[4]

$$\rho_{CT} = \frac{I^k(CT) - I^k(SPR)}{I^k(CT) + I^o(SPR)} \qquad \text{(S2)}$$

where $I^k(CT)$ refers to Raman intensity for line k when the CT is making a contribution to the SERS signal. When only SPR contributes to SERS signals, $I^k(SPR)$ and $I^o(SPR)$ refer to the values of the peak intensity of line k and the reference line o, respectively. Generally, if the k-band is totally symmetric, the contribution from SPR dominates the intensity, with $I^k(SPR)$ equivalent to $I^o(SPR)$. In the case of a non-totally symmetric k-band, the CT plays a significant role in determining the intensity. Since $I^k(SPR)$ is quite small in our case, it can be assumed to be zero. It should be noted that the Raman intensity of the non-totally symmetric mode at 1650 cm^{-1} (C-H bend) was significantly affected by the CT process, and I_{1650} was consequently recorded as $I^k(CT)$.[5] Because the Raman intensity of completely symmetric vibration at 1507 cm^{-1} (C-N stretch) was independent of the CT effect, therefore, I_{1507} was recorded as $I^o(SPR)$. In this way, the equation can be expressed approximately as follows:

$$\rho_{CT} = \frac{I_{1650}}{I_{1650} + I_{1507}}$$

Based on **Fig. 2** of the manuscript, ρ_{CT} of 10^{-5} M R6G was calculated to be 0.57 for a carbonized PAN array. Accordingly, the CT played a significant role in

improving the SERS signals.

Section S4. Figures and tables

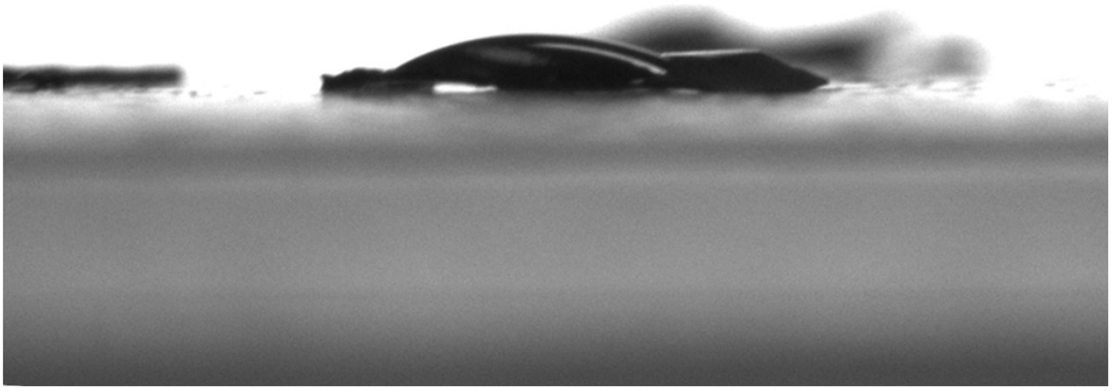

Fig. S1. The static water contact angle of carbonized PAN array.

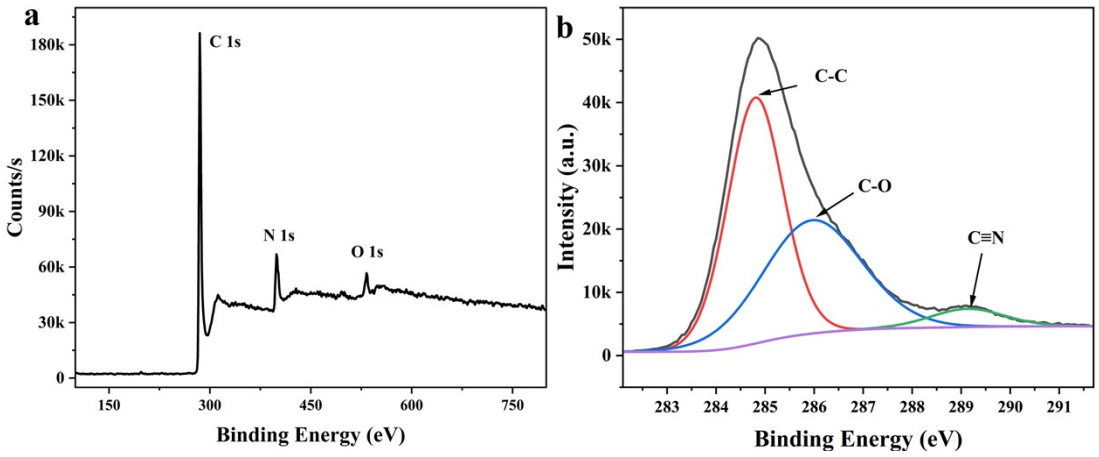

Fig. S2. (a) XPS spectra of patterns of carbonized PAN array and (b) XPS spectra of C 1s peaks of carbonized PAN array.

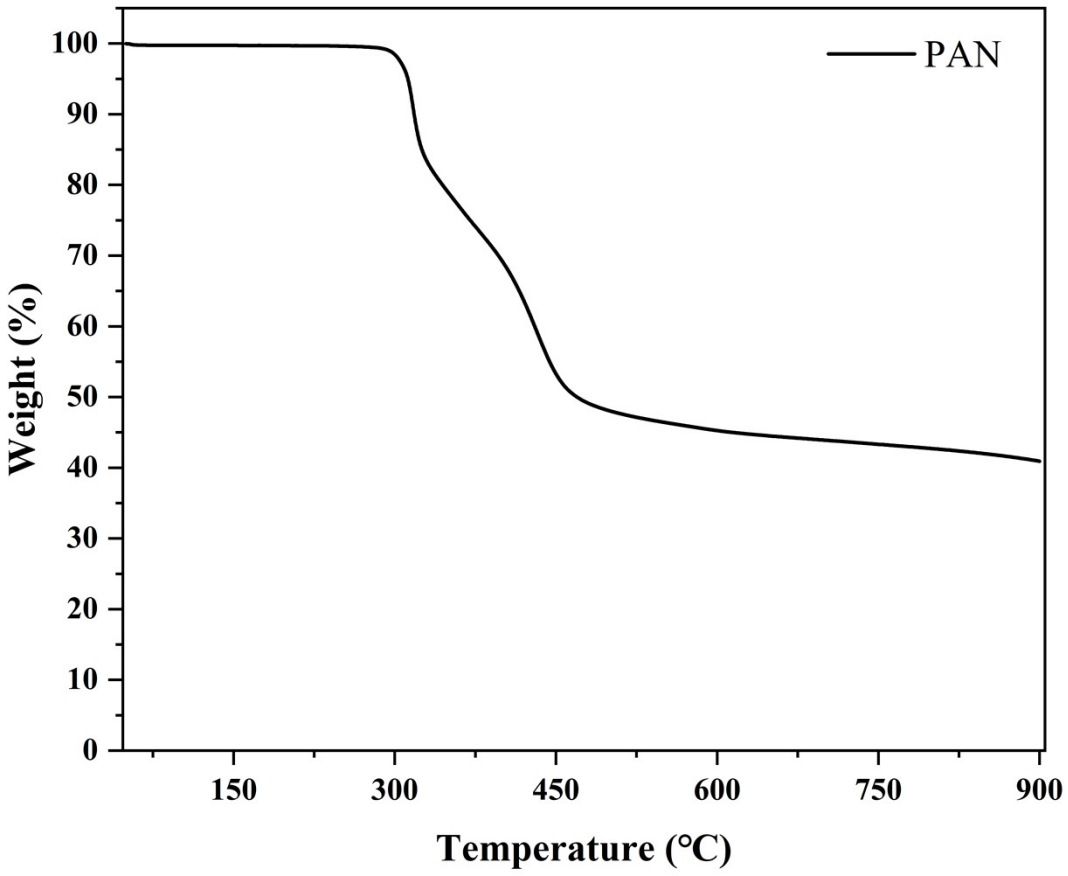

Fig. S3. Thermogravimetric analysis of the PAN.

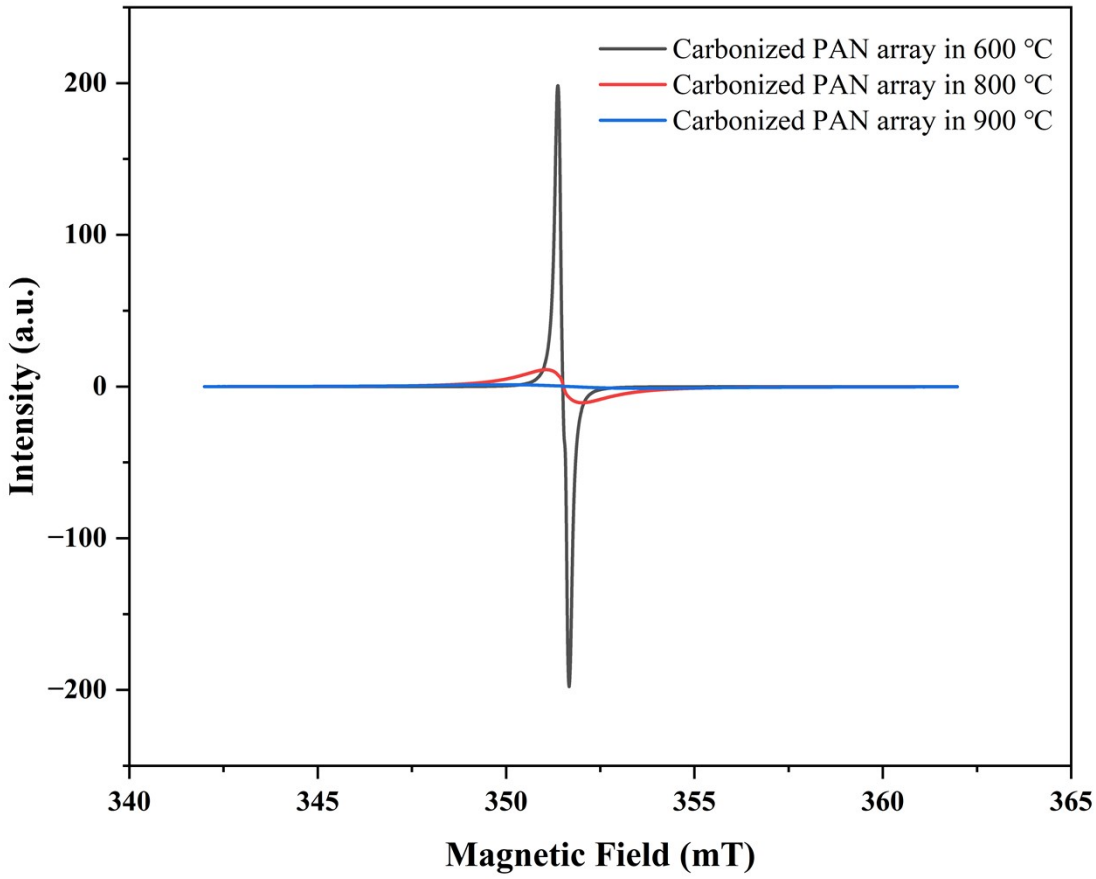

Fig. S4. EPR spectra of carbonized PAN array at 600, 800 and 900 ℃.

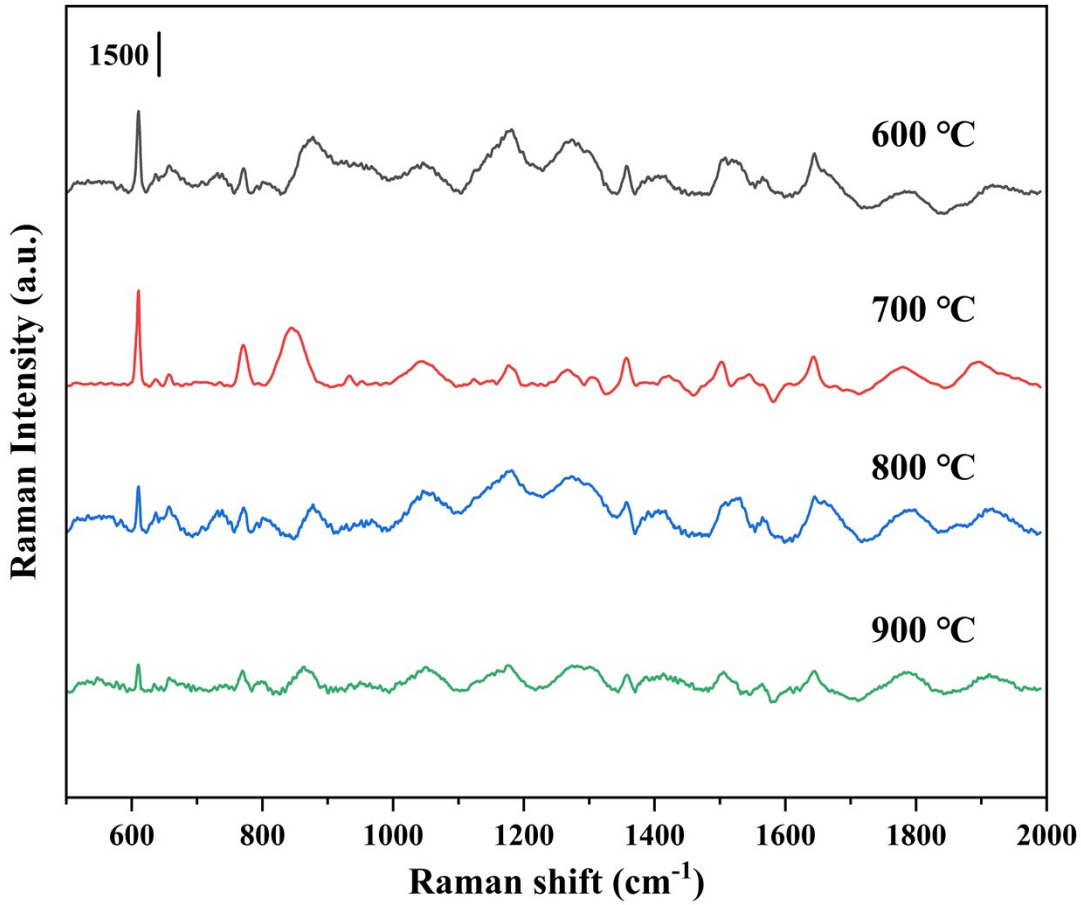

Fig. S5. Measured Raman spectra of R6G molecules at a concentration of 10 μM on the carbonized PAN array at 600, 700, 800 and 900 ℃.

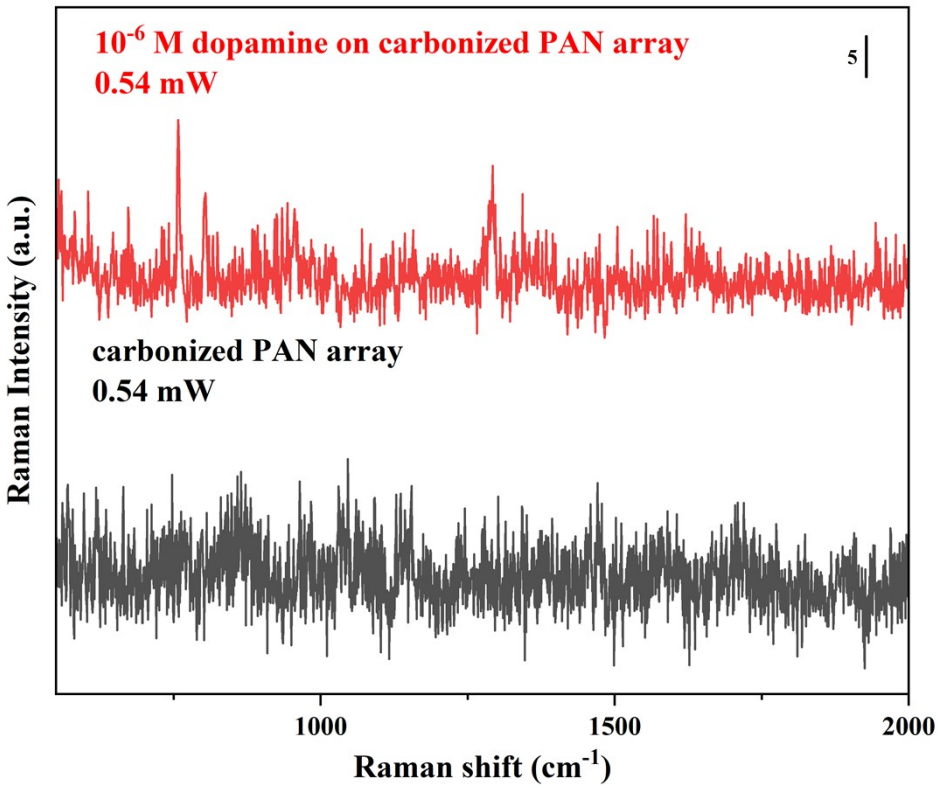

Fig. S6. Raman strength of the carbonized PAN array and 10^{-6} M dopamine on the carbonized PAN array at 0.54 mW.

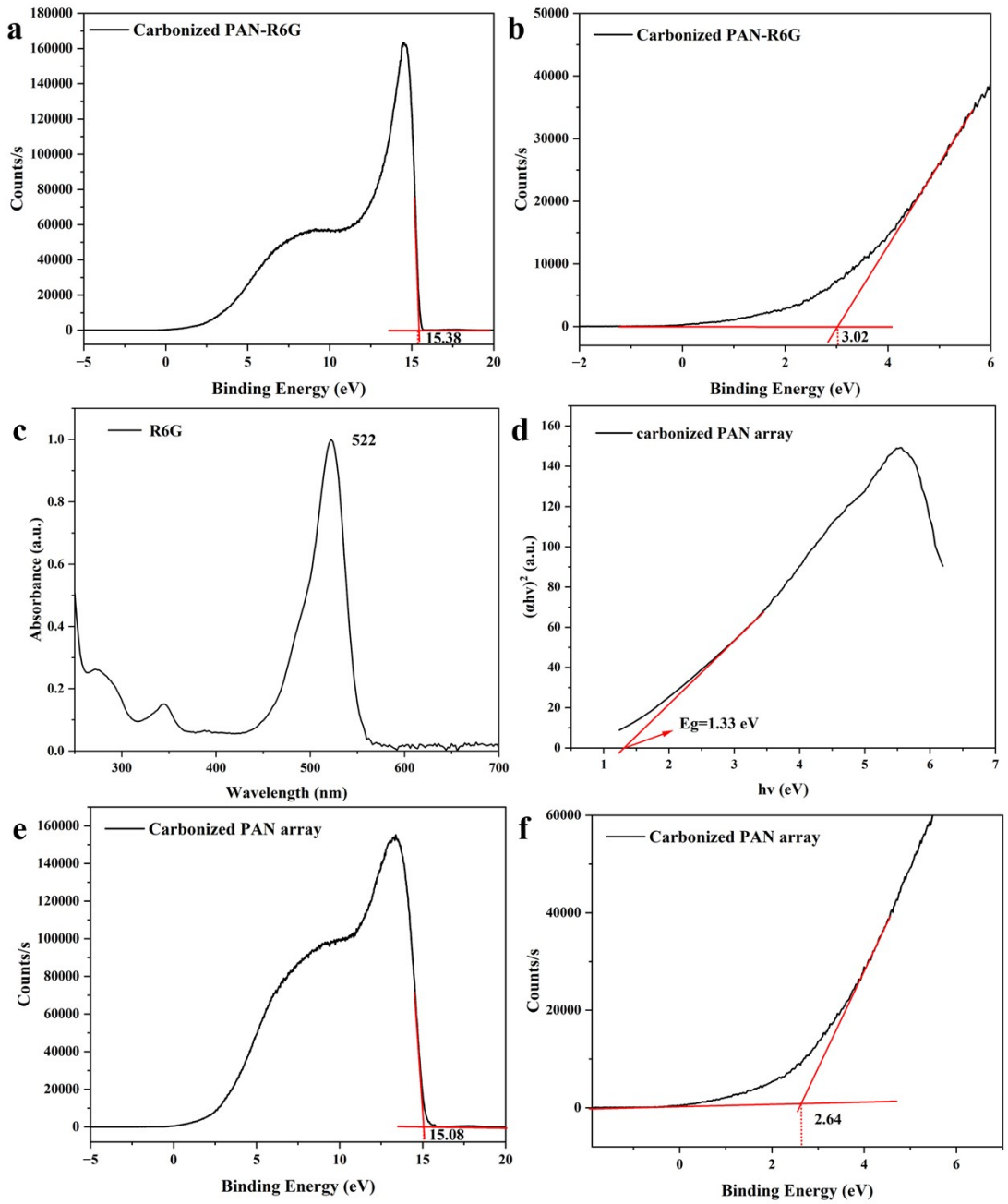

Fig. S7. (a and b) The UPS spectra of R6G molecules in the carbonized PAN/R6G system. (c) The absorption spectra of R6G molecules. (d) Tauc plots of the absorption spectra to determine the band gaps of carbonized PAN array. (e and f) The UPS spectra of carbonized PAN array.

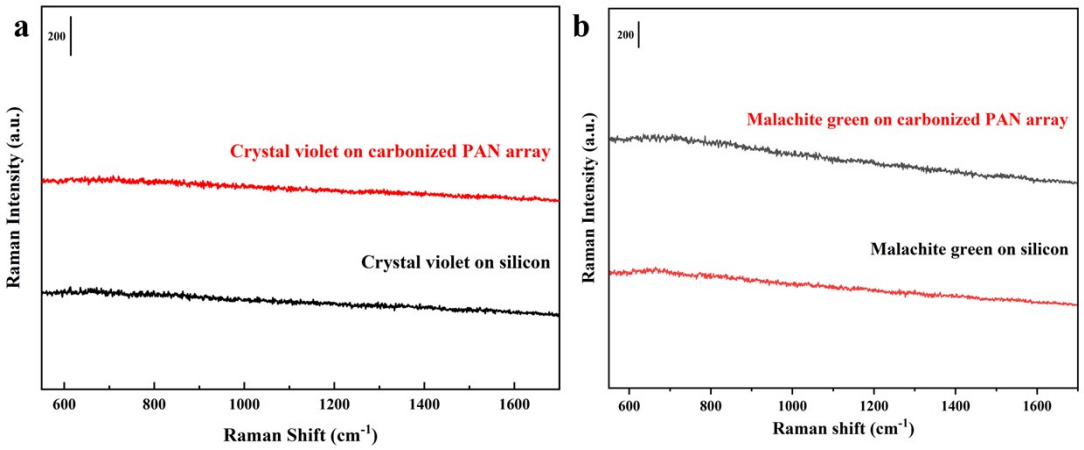

Fig. S8. SERS spectra of 10^{-5} M (a) crystal violet and (b)malachite green absorbed on silicon and carbonized PAN array.

Table S1. The calculation of SERS EF for the glucose, dopamine, melamine and creatinine adsorbed on carbonized PAN array.

Parameter	Glucose	Dopamine	Melamine	Creatinine
$\mathbf{I_{RS}}$	26	31	327	37
$\mathbf{I_{SERS}}$	451	574	4035	464
$\mathbf{N_{vol}}$	2.97×10^{11}	2.97×10^{11}	2.97×10^{10}	2.97×10^{11}
$\mathbf{N_{surf}}$	3.96×10^{7}	3.96×10^{7}	3.96×10^{6}	3.96×10^{7}
EF	1.31×10^{5}	1.39×10^{5}	9.3×10^{4}	9.4×10^{4}

Table S2. Comparison of properties of different SERS substrates based on chemical enhancement.

Substrate type	Target molecule	LOD (M)	EF	Uniformity	Durability	Biocompatibility	Ref
Cu_2O	4-aminothiophenol	$8*10^{-5}$	10^5	7.7%	/	/	[6]
Fluorine-doped tin oxide	R6G	10^{-6}	$2.66*10^4$	7.86%	/	/	[7]
Oxygen incorporation in MoS_2	R6G	10^{-7}	10^5	/	/	/	[8]
Oxidized carbon cloth	R6G	10^{-8}	/	22.65%	/	/	[9]
Porous carbon nanowire array	R6G	10^{-8}	10^6	7.8%	3 h	√	[10]
Carbonized PAN array	R6G	10^{-7}	10^5	5.1%	4 weeks	√	This work

Note: "/" means "not mentioned".

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