Supplementary Materials

Photovoltaic arrays as highly efficient system for biomedical and electrochemical surface-enhanced Raman Spectroscopy analysis

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1 Characterization PV surfaces

1.1. Method of PV production.

They are produced by a screen-printing process. It is similar to that used to produce the heating strips on rear and front car windscreens. In the process silver paste is squeezed through a mesh onto the cell surface. In the end it is dried and then fired at a higher temperature to drive off the organic binder in the paste and to allow the silver particles to coalesce. The middle layer p-n junction consists of either mono (hexagonal) or polycrystalline (square) silicon wafer. More than a half of module production is now based on the use of multicrystalline silicon wafers rather than those produced using the Czochralski method. This technique is basing on molten silicon being poured into a container and then allowed to cool. This are doped p-type using boron. In the next step wafers are mechanically and chemically polished to remove any damage from previous wafers creating processes. The surface is then anisotropically etched to texture the surface of the silicon. The main reason to do so is to minimise possible reflection losses and to increase the range of angles at which light rays are refracted into the silicon, what causes enhancement in the optical path length. A p-n junction are produced in the wafers in the process of diffusing phosphorus into the surface of the wafer to convert the surface to a n-type region.

The back plate which is an electrical contact to the rear of the p-type region. It is attached by annealing an aluminium layer deposited over the back of the device. The p+ layer not only minimises the back contact resistance but introduces a “back surface field” to reflect minority carriers back toward the depletion region. This effect is even more enhanced by the Passivated Emitter and Rear Cell (PERC) technology. In the PERC technology, the back of the silicon wafer is first covered with a special layer of dielectric (insulator), which is covered with holes cut out by a laser. The metallization layer in the form of aluminum is then applied to the dielectric, so that the silicon wafer contacts the metal only through microscopic holes.
The main task of PERC technology is to increase the efficiency of the cell thanks to the dielectric layer, which reflects every light reaching the bottom layer of the plate without generating the electron back into the cell. Through this reflection, photons basically have a second chance to generate electricity.

1.2. SEM and AFM measurements

A) 1m – type, without silver layer
B) 1 – type, without silver layer

C) 2 – type, without silver layer
D) 3 – type, without silver layer

Fig. S1. SEM images at four magnifications of four testes PV samples named 1m, 1, 2, and 3.
A) Type - 1m

Roughness ($R_a$): $120 \pm 6$ nm

B) Type - 1

Roughness ($R_a$): $239 \pm 21$ nm

C) Type - 2
**Roughness ($R_a$):**  364 ± 58 nm

**D) Type - 3**

**Roughness ($R_a$):**  213 ± 5 nm

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**Fig. S2.** AFM images at different magnifications of Ag/PV SERS-active platforms sputtered with 8 nm layer of silver via PVD technique.
A) Sample 1-type
Count: 206
Median: 41.85
StdDev: 18.9
C) Sample 3-type

Count: 288
Median: 34.58
StdDev: 17.9

Fig. S3. Histograms of the size of the silver objects on the surface of the PV based substrates.

Ion etched Si
Roughness ($R_a$): 6.6 ± 0.6 nm

Fig. S4. (A) AFM and (B) SEM images of ion etched silicon covered with silver layer.

1.3. XPS analysis of Ag/PV SERS platform
A)

Sample 1m-type without Ag

Sample 1m-type with Ag
B) Sample 1-type without Ag

Sample 1-type with Ag
C) Sample 2-type without Ag

![Graph showing binding energy vs. counts for sample 2-type without Ag.]

Sample 2-type with Ag

![Graph showing binding energy vs. counts for sample 2-type with Ag.]

D) Sample 3-type without Ag
sample 3-type with Ag
**Fig. S5.** XPS surveys on four SERS substrates ((A) - sample1), ( (B) – sample 1m), ((C) – sample 2), and ((D) – sample 3) coated with 8 nm of Ag layer.

**Table S1.** Normal Raman and SERS band assignments for $p$-ATP.

| Normal Raman/$p$-ATP powder | SERS/ $p$-ATP onto Ag/PV substrate | Assignments |
|-----------------------------|----------------------------------|-------------|
| 1597                        | 1576                             | νCC, 8a ($a_1$) |
|                             | 1490                             | νCC + δCH, 19a ($a_1$) |
|                             | 1435                             | νCC + δCH, 19b ($b_2$) |
|                             | 1393                             | δCH + νCC, 3 ($b_2$) |
|                             | 1311                             | δCH, 9a ($a_1$) |
| 1172                        | 1180                             | δCH, 9a ($a_1$) |
|                             | 1145                             | δCH, 9b ($b_2$) |
| 1090                        | 1078                             | γCC + γCCC, 18a, ($a_1$) |
| 1007                        | 1007                             | γCC + γCCC, 18a, ($a_1$) |

Abbreviations: ν = stretching, δ, γ = bending, π = wagging. Letters in parentheses indicate symmetry.
1.4. Sensitivity

**Fig. S6.** The SERS spectra of \( p \)-ATP adsorbed onto “type 1m” SERS surface at different concentration (a) 10\(^{-6}\) M and (b) 10\(^{-9}\) M in ethanol.
2. Analytical performance of Ag/PV SERS platform

Fig. S7. The SERS spectra of *E.coli* recorded on Ag/PV substrate from randomly distributed points. For all spectra, excitation wavelength was at 785 nm, laser power was 1.5 mW, and acquisition time was only 3 seconds. (B) Microscopic image of *E.coli* deposited onto SERS-active surface (at magnification 50 X).
Table S2. Assignment of SERS bands depicted in Fig.7 for *B. subtilis* and Caki-1 (renal cancer cells).

| **Bacillus subtilis** | **Caki-1 (renal cancer cells)** |
|----------------------|---------------------------------|
| Assignment           | Range                           | Assignment                                      | Range |
| C-O-C ring deformation | 540-575                         | Tyr (C-C twist) (protein assignment)            | 652-658 |
| Guanine, tyrosine     | 640-675                         | Trp (protein assignment)                       | 725-730 |
| Adenine, glycoside    | 713-740                         | C-N head group choline                         |        |
| Cytosine, uracil      | 745-790                         | (H$_3$C)$_3$N+ (lipid assignment)               |        |
| Symmetric breathing of tryptophan (protein assignment) | 752-757                         | PO$_2$ symm (nucleic acid assignment)           | 785 |
| O-P-O (RNA)           | 800-815                         | RNA backbone (nucleic acid assignment)          | 827 |
| C=C deformation, C-N stretching | 930-990                          | Tyr, Pro (protein assignment)                  | 850 |
| Phenylalanine, C-C aromatic ring stretching | 1000-1010                    | Structural protein modes of tumors              | 890 |
| C-C stretching (phospholipids carbohydrates), C-N stretching | 1025-1060                      | C-C str alpha-helix, Pro, Val (protein assignment) | 939 |
| O-P-O (DNA), C-C or C-O-C stretching (carbohydrates) | 1080-1105                     | CH$_3$ def (protein assignment)                 | 956 |
| =C-O-C= (unsaturated) | 1130-1145                      | Phe (protein assignment)                       | 1003 |
|                      |                                  | CH$_2$CH$_3$ bending modes of lipids            | 1030-1032 |
|                      |                                  | C-N stretch (protein)                          | 1094 |
| Compound/Assignment | Wavenumber (cm⁻¹) |
|---------------------|-------------------|
| Fatty acids in lipids | |
| C-O ring, aromatic aminoacids in proteins | 1150-1185 |
| Amide III (random), thymine | 1215-1295 |
| Amide III (protein), C-H deformation | 1315-1325 |
| Adenine, guanine, CH deformation | 1330-1345 |
| COO- symmetric stretching | 1390-1415 |
| CH₂ deformation of proteins, umbrella mode of methoxyl (4) | 1440-1475 |
| Amide II | 1510-1560 |
| Adenine, guanine (ring stretching), tryptophan | 1570-1595 |
| Assignment | |
| C-N str bk (protein assignment); Porphyrin (lipid assignment) | 1128 |
| Tyr C-H in plane (protein assignment); T (nucleic acid assignment) | 1170-1172 |
| C-C₆H₅ str in phenylalanine tyrosine (protein assignment) | 1212 |
| Amide III (beta sheet), (protein assignment) | 1245 |
| Amide III (random coil) (protein assignment); CH=CH def (lipid assignment) | 1267-1270 |
| Purine bases of DNA (nucleic acid assignment) | 1325 |
| A,G (nucleic acid assignment) | 1345 |
| Sphingoglycolipids (lipid assignment) | 1373 |
| Structural protein modes of tumors (protein assignment) | 1452 |
| A,G (nucleic acid assignment) | 1552 |
| Phe, Tyr (protein assignment) | 1597-1600 |
|-------------------------------|-----------|
| C=C str of Tyr and Trp (protein assignment) | 1616-1618 |
| Amide I (protein assignment); C=C str (lipid assignment) | 1657-1695 |
3. Reproducibility and sensitivity of SERS substrates.

(A) sample 1m-type

(B) Sample 1-type
Fig. S8. The representative SERS spectra $p$-ATP of concentration $10^{-6}$ M in ethanol recorded from 40 different spots on the four different SERS surfaces (type 1m, 1, 2, and 3) using mapping mode. The spectra were collected over an area 10 x 20 µm with 1.6 steps µm (40 spectra are shown). Each point in the map was recorded using 1.5 mW of 785 nm excitation with 18 seconds integration times.
**Fig. S9.** The representative SERS spectra $p$-ATP of concentration $10^{-6}$ M in ethanol recorded from 40 different spots on the five different SERS surfaces prepared separately. The spectra were collected over an area 10 x 20 µm with 1.6 steps µm (40 spectra are shown). Each point in the map was recorded using 1.5 mW of 785 nm excitation with 18 seconds integration times.