Supporting Information

for

On the stability of microwave-fabricated SERS substrates – chemical and morphological considerations

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Additional figures and tables
Figure S1: Representative diagram depicting the power, pressure, and temperature measured during the microwave-assisted coating of the glass substrate.

Figure S2: Histograms of SERS substrates from different batches after their preparation: (a) batch 1 and (b) batch 2.
Figure S3: SEM images of the SERS substrates immersed into different organic solvents and PBS solutions for 1 and 4 h, respectively.

Figure S4: Raman intensities found for the marker peak at 1442 cm\(^{-1}\) of a monolayer prepared from 10^{-4} M 4-ATP. After eight minutes the peak intensity reaches a plateau, indicating the formation of a complete monolayer on the SERS substrates.
**Figure S5:** Reference Raman spectra of a 4-ATP-coated, non-treated, clean SERS substrate (red) and the Raman spectrum of the SERS substrate only (black). The corresponding peak assignment is provided in Table S1.

**Table S1:** Peak assignment for the SERS spectrum shown in Figure S5 [1,2]. A dimerization process takes place and leads to the transformation of 4-ATP into 4,4'-dimercaptoazobenzene (DMAB) as seen in the appearance of the b$_2$ modes or a$_g$, respectively [1].

| SERS band frequency/cm$^{-1}$ | Assignment (4-APT/DMAB)                      |
|-------------------------------|---------------------------------------------|
| 1580                          | $\nu$(CC), b$_2$/a$_g$ mode                |
| 1440                          | $\delta$(CH) + $\nu$(CC), b$_2$/a$_g$ mode |
| 1394                          | $\nu$(CC) + $\delta$(CH), b$_2$/a$_g$ mode |
| 1145                          | $\delta$(CH), a$_1$ mode                  |
| 1078                          | $\nu$(CS), a$_1$ mode                     |
Figure S6: Reference Raman spectrum of a monolayer of 4-ATP self-assembled on a water-treated SERS substrate.

Figure S7: EDX elemental analysis of the SERS substrate without treatment (a) and treated with PBS buffer of pH 5 (b). The insets represent the SEM images. Scale bar: 500 nm. The elements O, Si, C, Na, and Al in (b) could be attributed to the glass substrate.
Table S2: Main components of different buffer solutions.

| Different buffer solutions | Ingredients                  | Cations  | Anions               |
|----------------------------|------------------------------|----------|----------------------|
| PBS pH 3                   | NaCl, KCl,                  | Na⁺, K⁺  | Cl⁻, H₂PO₄⁻          |
|                            | NaH₂PO₄, KH₂PO₄             |          |                      |
| PBS pH 5                   | NaCl, KCl,                  | Na⁺, K⁺  | Cl⁻, H₂PO₄⁻          |
|                            | NaH₂PO₄, KH₂PO₄             |          |                      |
| Acetate pH 5               | CH₃COONa, CH₃COOH           | Na⁺      | CH₃COO⁻              |
| PBS pH 7                   | NaCl, KCl,                  | Na⁺, K⁺  | Cl⁻, HPO₄²⁻,         |
|                            | Na₂HPO₄, KH₂PO₄             |          | H₂PO₄⁻               |
| HBG pH 7                   | HEPES, glucose              |          |                      |
| TBE pH 8                   | Tris base, boric acid, EDTA |          |                      |
| PBS pH 9                   | NaCl, KCl,                  | Na⁺, K⁺  | Cl⁻, HPO₄₂⁻          |
|                            | Na₂HPO₄, K₂HPO₄             |          |                      |
| Carbonate pH 10            | NaHCO₃, Na₂CO₃              | Na⁺      | HCO₃⁻, CO₃²⁻         |
| PBS pH 11                  | NaCl, KCl,                  | Na⁺, K⁺  | Cl⁻, HPO₄²⁻          |
|                            | Na₂HPO₄, K₂HPO₄             |          |                      |

[1] Huang, Y.-F.; Wu, D.-Y.; Zhu, H.-P.; Zhao, L.-B.; Liu, G.-K.; Ren, B.; Tian, Z.-Q. Phys. Chem. Chem. Phys., 2012, 14, 8485–8497.

[2] Hu, X.; Wang, T.; Wang, L.; Dong, S. J. Phys. Chem. C 2007, 111, 6962–6969.