Electronic Supplementary Information for

Silver nanoparticle aggregates on copper foil for reliable quantitative SERS analysis of PAHs with a portable Raman spectrometer

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1. SEM image of silver nanoparticles on the copper foil for seven cycles.

![SEM image of silver nanoparticles on the copper foil](image)

**Fig. S1** SEM image of silver nanoparticles on the copper foil with the assistant of Sn$^{2+}$, for seven cycles.
2. SERS spectra of p-aminothiophenol on the substrate with different cycles.

![SERS spectra of p-aminothiophenol](image)

**Fig. S2** SERS spectra of p-aminothiophenol ($10^{-4}$ M) on the substrate with different cycles.
3. Cross-sectional SEM image of the SERS substrate.

**Fig. S3** Cross-sectional SEM image of the SERS substrate.

4. SEM image of dendritic silver on copper foil without the assistant of Sn$^{2+}$.

**Fig. S4** SEM image of dendritic silver on copper foil without the assistant of Sn$^{2+}$. 
5. SERS spectra of p-aminothiophenol on the SERS substrate with and without the assistant of Sn$^{2+}$.

![Fig. S5](image1.png)

**Fig. S5** SERS spectra of p-aminothiophenol ($10^{-4}$ M) on the SERS substrate (A) with and (B) without the assistant of Sn$^{2+}$.

6. SERS and Raman spectra of HT.

![Fig. S6](image2.png)

**Fig. S6** (A) SERS spectrum of HT on the SERS substrate, (B) Raman spectrum of liquid HT served as a reference.
7. The SERS spectra of HT with different immersion time.

![SERS spectra of HT with different immersion time](image)

**Fig. S7** The SERS spectra of HT with different immersion time.

8. Chemical structures of analytes in this work.

![Chemical structures of analytes](image)

**Fig. S8** Chemical structures of analytes in this work.

9. The calculated Raman spectra of PAHs.

![Calculated Raman spectra of PAHs](image)

**Fig. S9** The calculated Raman spectra of (A) fluoranthene, (B) fluorene, (C) acenaphthene, and (D) naphthalene.
10. The vibrational modes for main peaks of PAHs.

![Vibrational modes for PAHs](image)

Fig. S10 The vibrational modes for main peaks of (A) fluoranthene at 1610 cm\(^{-1}\), (B) fluorene at 1610 cm\(^{-1}\), (C) acenaphthene at 1435 cm\(^{-1}\), and (D) naphthalene at 1379 cm\(^{-1}\).


![Temporal stability](image)

Fig. S11 The temporal stability of the substrate probed with 10\(^4\) μg·L\(^{-1}\) fluoranthene under continuous laser radiation for 5 min.

12. SERS spectra of fluoranthene obtained from the freshly prepared and aged substrate.
**Fig. S12** SERS spectra of fluoranthene obtained from (A) the freshly prepared substrate and (B) the substrate immersed in the fluoranthene solution for 4 days.
13. Qualitative SERS spectra of PAHs.

Fig. S13 SERS spectra for (I) fluoranthene with concentrations of (A) $1.0 \times 10^4 \mu g \cdot L^{-1}$, (B) $5.0 \times 10^3 \mu g \cdot L^{-1}$, (C) $2.5 \times 10^3 \mu g \cdot L^{-1}$, (D) $1.0 \times 10^3 \mu g \cdot L^{-1}$, (E) $5 \times 10^2 \mu g \cdot L^{-1}$, (F) $2.5 \times 10^2 \mu g \cdot L^{-1}$, (G) $10^2 \mu g \cdot L^{-1}$, (H) $50 \mu g \cdot L^{-1}$, (I) $25 \mu g \cdot L^{-1}$, (J) $10 \mu g \cdot L^{-1}$, and (K) $5.0 \mu g \cdot L^{-1}$, (II) fluorene with concentrations of (A) $1.0 \times 10^4 \mu g \cdot L^{-1}$, (B) $5.0 \times 10^3 \mu g \cdot L^{-1}$, (C) $2.5 \times 10^3 \mu g \cdot L^{-1}$, (D) $1.0 \times 10^3 \mu g \cdot L^{-1}$, (E) $5 \times 10^2 \mu g \cdot L^{-1}$, (F) $2.5 \times 10^2 \mu g \cdot L^{-1}$, (G) $10^2 \mu g \cdot L^{-1}$, (H) $50 \mu g \cdot L^{-1}$, (I) $25 \mu g \cdot L^{-1}$, (J) $10 \mu g \cdot L^{-1}$, (III) acenaphthene with concentrations of (A) $1.0 \times 10^4 \mu g \cdot L^{-1}$, (B) $5.0 \times 10^3 \mu g \cdot L^{-1}$, (C) $2.5 \times 10^3 \mu g \cdot L^{-1}$, (D) $1.0 \times 10^3 \mu g \cdot L^{-1}$, (E) $5 \times 10^2 \mu g \cdot L^{-1}$, (IV) naphthalene with concentrations of (A) $1.0 \times 10^4 \mu g \cdot L^{-1}$, (B) $5.0 \times 10^3 \mu g \cdot L^{-1}$, (C) $2.5 \times 10^3 \mu g \cdot L^{-1}$, (D) $1.0 \times 10^3 \mu g \cdot L^{-1}$, (E) $5 \times 10^2 \mu g \cdot L^{-1}$.
Detection limits, EF (Enhancement factor) and $K_{OW}$ of PAHs.

Table S1  Detection limits, EF (Enhancement factor) and $K_{OW}$ of PAHs.

<table>
<thead>
<tr>
<th>PAHs</th>
<th>Detection limits (μg·L$^{-1}$)</th>
<th>EF</th>
<th>log $K_{OW}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>fluoranthene</td>
<td>5.0</td>
<td>$2.1 \times 10^5$</td>
<td>5.20</td>
</tr>
<tr>
<td>fluorene</td>
<td>10</td>
<td>$3.7 \times 10^4$</td>
<td>4.23</td>
</tr>
<tr>
<td>acenaphthene</td>
<td>500</td>
<td>$1.1 \times 10^3$</td>
<td>3.94</td>
</tr>
<tr>
<td>naphthalene</td>
<td>500</td>
<td>$6.5 \times 10^2$</td>
<td>3.32</td>
</tr>
</tbody>
</table>

Full Gaussian Reference

A. Pople, Gaussian 03, Revision D.01; Gaussian, Inc., Wallingford CT, 2004.