Supporting Information

Polyethyleneimine-mediated seed growth approach for synthesis of silver-shell silica-core nanocomposites and their application as a versatile SERS platform

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‡ These authors contributed equally to this work.

Fig. S1 (a) TEM images of SiO₂ NPs, and (b) the statistical histogram of the corresponding nanoparticle size.

Fig. S2 Zeta potentials of (a) SiO₂, (b) SiO₂@PEI, (c) SiO₂@PEI-Au seed, and (d) SiO₂@PEI@Ag NPs in aqueous solution.
Fig. S3 (a) The SERS spectra of PATP measured with different concentrations on the SiO$_2$@PEI@Ag NPs. (b) The intensity–concentration calibration curve for PATP at a concentration range of $1.0 \times 10^{-6}$ to $1.0 \times 10^{-10}$ M by using SERS intensity at 1077 cm$^{-1}$. The error bars represent the standard deviations from 5 measurements.

**S4 EF calculation:**

To quantify the enhancement ability of the SiO$_2$@PEI@Ag NPs, the enhancement factor (EF) was calculated as the ratio of photons scattered by the SERS substrate and the normal substrate. EF was estimated according to the following equation:

$$EF = \frac{I_{SERS}}{I_{bulk}} \times \frac{N_{bulk}}{N_{SERS}}$$

where $N_{bulk}$ and $N_{SERS}$ is the number of molecules contributed to the Raman and SERS signal, respectively, and $I_{SERS}$ and $I_{bulk}$ is the respective signal intensity of the related peaks. However, intrinsic EF is difficult to estimate because several variables, such as adsorbed molecules and laser scattering volume, are difficult to obtain. In our experiment, all the other parameters, including the laser diameter, laser power, exposure time, and microscopic magnification, were identical. The chemical droplets were of the same volume, and the number of detected PATP molecules was proportional to its concentration. Therefore, the EF was roughly estimated by comparing the intensity of the Raman peak in the SERS spectrum with that in the normal Raman spectrum according to the equation $EF = \frac{I_{SERS}}{I_{RS}} \times \frac{C_{RS}}{C_{SERS}}$, where $I_{SERS}$ and $I_{RS}$ are the vibration intensities in the SERS and normal Raman spectra of PATP molecules, and $C_{RS}$ and $C_{SERS}$ are the concentrations of the PATP molecules in the SERS and reference samples, respectively.

The peak at 1077 cm$^{-1}$ from the PATP Raman spectrum (Fig. S4) was chosen for analysis, and the intensities for peaks (a) and (d) were 1249 and 8157 a.u., respectively. The PATP concentrations for peaks (a) and (d) were $10^{-1}$ M and $10^{-8}$ M, respectively. Therefore, the EF of the SiO$_2$@PEI@Ag NPs was roughly estimated to be $6.53 \times 10^7$. 


Fig. S4 Raman spectra recorded of PATP molecules with (black) and without (red) the SiO$_2$@PEI@Ag NPs.

Table S1

<table>
<thead>
<tr>
<th>Raman shift (cm$^{-1}$)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>932</td>
<td>$\nu$(CH$_3$N) or $\nu$(C–S)</td>
</tr>
<tr>
<td>1148</td>
<td>$\rho$(CH$_3$) or $\nu$(C–N)</td>
</tr>
<tr>
<td>1383</td>
<td>$\rho$(CH$_3$)</td>
</tr>
<tr>
<td>1508</td>
<td>$\nu$(C–N)</td>
</tr>
</tbody>
</table>

Table S1 Raman peaks of thiram and corresponding assignments.
Fig. S5 TEM images of (a) a-Fe₂O₃, (b) a-Fe₂O₃@SiO₂ microspheres.