Improved SERS Activity of non-stoichiometric Copper Sulfide Nanostructures Related to Charge-Transfer Resonance

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Supplementary Material

The EF value can be calculated by the following formula: \( EF = \frac{(I_{\text{SERS}} / N_{\text{SERS}})}{(I_{\text{normal}} / N_{\text{normal}})} \). Where \( I_{\text{SERS}} \) is the intensity of the Raman spectrum of R6G molecules adsorbed on the substrate. \( N_{\text{SERS}} \) is the total number of R6G molecules adsorbed on the substrate surface under the laser spot. \( I_{\text{normal}} \) is the intensity of the normal Raman spectrum of R6G powder. \( N_{\text{normal}} \) is the number of molecules of the R6G powder under the laser spot. As shown in Figure S3, taking the 613 cm\(^{-1}\) peak as an example, the measured values of \( I_{\text{normal}} \) and \( I_{\text{SERS}} \) are 489 and 519 counts. It is known that the density of R6G powder is about 0.99 g/cm\(^3\), the radius of the confocal laser beam is 0.5 \( \mu \)m, the penetration depth of the confocal laser beam is about 2 \( \mu \)m, and the volume of R6G dropped on the substrate is 10 \( \mu \)L. Here, we assume that the R6G moleculars are uniformly distributed on the substrate after drying.

\[
N_{\text{SERS}} = N_A \times 0.25\pi \, \mu m^2 \times (10 \, \mu L \times 10^{-7} \, M) / (25 \, mm^2) = 1.89 \times 10^4
\]

\[
N_{\text{normal}} = N_A \times (0.99 \, g/cm^3 \times 0.25 \, \mu m^2 \times 2 \, \mu m)/479 \, g/mol = 6.22 \times 10^8
\]

It can be estimated that the values of \( N_{\text{SERS}} \) and \( N_{\text{normal}} \) are about \( 1.89 \times 10^4 \) and \( 6.22 \times 10^8 \). Thus, the EF value of 613 cm\(^{-1}\) was calculated to be \( 3.5 \times 10^4 \).
Table S1. Component analysis for (1) the as-synthesized samples and annealed samples at (2) 200 °C, (3) 250 °C, (4) 300 °C, and (5) 350 °C extrapolated from XRD results.

<table>
<thead>
<tr>
<th></th>
<th>CuS</th>
<th>Cu$_{7.2}$S$_4$</th>
<th>CuSO$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>100%</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td>(2)</td>
<td>100%</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td>(3)</td>
<td>43%</td>
<td>24%</td>
<td>33%</td>
</tr>
<tr>
<td>(4)</td>
<td>7%</td>
<td>40%</td>
<td>53%</td>
</tr>
<tr>
<td>(5)</td>
<td>0%</td>
<td>0%</td>
<td>100%</td>
</tr>
</tbody>
</table>

Figure S1. The thermogravimetric curve of CuS.

Figure S2. SERS spectra of 10$^{-7}$ M R6G adsorbed on annealed sample at 300 °C and Raman spectrum of R6G powder.
Figure S3. UV-Vis absorption spectra of (a) the as-synthesized samples and annealed samples at (b) 200 °C, (c) 250 °C, and (d) 300 °C.

Figure S4. The top and side images of the structures: (a)(b) CuS; (c)(d) Cu_{2-x}S and (e)(f) Cu_{7-2S_4}. 