Supporting information for

Surface-enhanced Raman scattering (SERS) from Au:Ag bimetallic nanoparticles: The Effect of the Molecular Probe

Meikun Fan\textsuperscript{a,b}, Feng-Ju Lai\textsuperscript{c}, Hung-Lung Chou\textsuperscript{c}, Wan-Ting Lu\textsuperscript{c}, Bing-Joe Hwang\textsuperscript{a,c,d}\textsuperscript{*}

Alexandre G. Brolo\textsuperscript{b}\textsuperscript{*}

\textsuperscript{a}Chengdu Green Energy and Green Manufacturing R&D Centre, Chengdu, 610207, China
\textsuperscript{b}Department of Chemistry, University of Victoria, PO Box 3055, Victoria, BC V8W 3V6, Canada
\textsuperscript{c}Nanoelectrochemistry Laboratory, Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei 106, Taiwan.
\textsuperscript{d}National Synchrotron Radiation Research Center, Hsinchu 30076, Taiwan.
Table S1. Bader Charger Analysis in Au(111) and AuAg(111) and Ag(111) systems.

<table>
<thead>
<tr>
<th>Species</th>
<th>Charge (e)</th>
<th>Charge difference (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au (111)</td>
<td>Au: 11.021</td>
<td></td>
</tr>
<tr>
<td>Ag(111)</td>
<td>Ag: 11.019</td>
<td></td>
</tr>
<tr>
<td>AuAg(111)</td>
<td>Au: 11.184</td>
<td>Au: 11.021-11.184 = -0.162</td>
</tr>
<tr>
<td></td>
<td>Ag: 10.854</td>
<td>Ag: 11.019-10.854 = +0.164</td>
</tr>
</tbody>
</table>

Figure S1. The calculated d-band center of the Au(111), AuAg(111), Ag(111) slab, respectively.
Figure S2: chemical structure of the probe molecules. a, Oxazine 720 (Ox); b, Nile Blue A (NBA); c, Thiophenol (TP); d, 4-hydroxythiophenol (HTP).

Figure S3. SERS spectra of the probe molecules. a, HTP; b, TP; c, Ox; d, NBA.
Figure S4: SERS spectra of HTP (a and b) Oxazine (c and d) and on the NPs at different 632.8 nm (a and c) and 785 nm (b and d). In all the figures, from top to bottom, pure Au, 9Au:1Ag, 5Au:5Ag, 1Au:9Ag, and pure Ag.
**Figure S5:** Effect of excess halide (0.1 M KCl was added to the colloid before drying) on the SERRS intensity (sample composition: Au$_9$Ag$_1$). Notice that no strong Metal – halide stretching vibration (indicated by an arrow) was observed when the colloid was dried only in the presence of OXA. However, that band is significant when KCl was added. The SERRS signal in the presence of KCl was consistently stronger than in the absence of excess Cl$^-$. 