SERS Analysis of Self-Assembled Monolayers of DNA Strands on Gold Surfaces

Nak Han Jang

Department of Chemistry Education, Kongju National University, Kongju, Chungnam 314-701, Korea
E-mail: nhjang@kongju.ac.kr
Received November 30, 2009, Accepted December 14, 2009

Key Words: SERS, DNA strands, Self-assembled monolayers, Gold surfaces

Surface-enhanced Raman scattering (SERS) is a process in which the Raman scattering intensity of molecules adsorbed on certain rough metal surface, (e.g., Ag, Au, Cu) is enhanced by factors of 10^4 - 10^6 compared to the intensity expected for unabsorbed molecules of a comparable concentration.1-3 These enormous sensitivity enhancement easily allowed adsorbates of a submonolayer coverage to be readily detected by Raman spectroscopy. The change in the structure of molecules can be followed by observing the changes in the SERS spectra of the adsorbed molecules.

The study of electron transfer through DNA4 and the development of novel DNA detection technologies5 have been focused significantly on binding oligonucleosides to metal surfaces and colloids for the variety of important fundamental studies and applications. About ten years ago, Mirkin and coworkers6-8 reported a new DNA detection technology based on the sequence-specific interactions of DNA-modified gold nanoparticles probes with a target DNA analyte. Because of these recent advances in using DNA to build a variety of functional materials,9 an understanding of how DNA and its building blocks interact with surfaces on the molecular level would be crucial. However, only a few studies have generated pertinent structural information regarding the binding and conformation of oligonucleosides and their building blocks on gold surfaces.10,11

Hereby self-assembled monolayers of DNA strands on gold surfaces have been studied with SERS and data were compared with SERS spectra of oligonucleosides in aqueous gold nanoparticles solution.12 Based on this study, the coordination structures of the DNA strands on gold surfaces are proposed.

Results and Discussion

Good-quality SERS spectrum of DNA single strands was first acquired on gold nanoparticle surfaces (Figure 1) and these tentatively assignments for SERS bands are also listed in Table 1 for comparison the previously measured SERS data12 of DNA nucleosides dA(2’-Deoxyadenosine), dC(2’-Deoxycytidine), dG(2’-Deoxyguanosine) and dT(2’-Deoxythymidine) solution.12 Based on this study, the coordination structures of the DNA strands on gold surfaces are proposed.
In Figure 2, SERS spectrum of DNA single strands showed the characteristic bands at 800, 1014, 1295, 1347, 1452, and 1642 cm\(^{-1}\). It is concluded that the band at 1014 cm\(^{-1}\) corresponds to the band at 1019 cm\(^{-1}\) of nucleoside dT on gold nanoparticles, which is attributed to the N-sugar stretching mode of thymine.\(^{14,15}\) The relatively strong intensity of the band at 1014 cm\(^{-1}\) can be interpreted as a perpendicular standing (edge on) or tilted orientation of the thymine ring in DNA single strands relative to the gold nanoparticle surfaces, whereas as a planner orientation of the thymine ring in dT. This strong enhancement is due to a charge transfer between the aromatic thymine ring and the gold surface.\(^{15}\) Another SERS band of DNA single strands is showed band at 802 cm\(^{-1}\) which correspond to bands at 802 cm\(^{-1}\) of dC and 796 cm\(^{-1}\) of dT. This is attributed to the N-C-N stretching mode of the pyrimidine ring.

SERS band of 1295 cm\(^{-1}\) only corresponds to 1293 cm\(^{-1}\) of dC which is attributed to the C-N stretching mode of the pyrimidine ring, whereas the band of 1347 cm\(^{-1}\) only corresponds to 1349 cm\(^{-1}\) of dT which is attributed to the C-N stretching mode of the pyrimidine ring. SERS band at 1452 cm\(^{-1}\) of DNA single strands corresponds to bands at 1458 cm\(^{-1}\) of dC and 1450 cm\(^{-1}\) of dT, which are attributed to the C=N stretching mode of the pyrimidine ring. SERS band of DNA single strands attributing to C=O stretching mode shows at 1642 cm\(^{-1}\), which correspond to bands at 1639 cm\(^{-1}\) of dC, 1642 cm\(^{-1}\) of dG, and 1647 cm\(^{-1}\) of dT.

From analysis of SERS bands up to now, bases of DNA single strands mainly interact through dC and dT on gold nanoparticle surfaces. These are also perpendicular standing or tilted orientation relative to the gold nanoparticle surfaces because SERS bands show the relatively strong intensities of the ring stretching modes.

Another SERS spectrum of DNA double strands was showed in Figure 3. These double strands were composed of complementarily matched order of DNA sequence with 5'-GCG-CTA-GAG-TCG-TTT-3' and 3'-C-GAT-CTC-AGC-A-5'. From these DNA sequence, bases of CG doesn't match any other base of complementary order of target DNA sequence. SERS spectrum of mismatched DNA double strands is entirely different from that of matched DNA double strands on gold surfaces. Figure 4 shows the characteristic SERS bands at 735, 790, 1322, and 1470 cm\(^{-1}\). Band at 735 cm\(^{-1}\) corresponds to band at 728 cm\(^{-1}\) of dA, which attributed to ring breathing mode of the pyrimidine, whereas band at 728 cm\(^{-1}\) corresponds to ring breathing mode of the imidazole (Im) and pyrimidine (Py).

### Table 1. Assignments of SERS spectra of DNA single strands and DNA nucleosides on gold surfaces

<table>
<thead>
<tr>
<th>DNA Strands</th>
<th>DNA Nucleosides</th>
<th>Tentative Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single</td>
<td>dA</td>
<td>dC</td>
</tr>
<tr>
<td>655</td>
<td>662</td>
<td>769</td>
</tr>
<tr>
<td>800</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1014</td>
<td>1035</td>
<td>1032</td>
</tr>
<tr>
<td>1223</td>
<td>1226</td>
<td>1233</td>
</tr>
<tr>
<td>1295</td>
<td>1293</td>
<td></td>
</tr>
<tr>
<td>1347</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1378</td>
<td></td>
<td>1349</td>
</tr>
<tr>
<td>1452</td>
<td>1458</td>
<td>1450</td>
</tr>
<tr>
<td>1595</td>
<td>1594</td>
<td></td>
</tr>
<tr>
<td>1642</td>
<td>1639</td>
<td>1642</td>
</tr>
</tbody>
</table>

\(^{a}\)Taken from the previous data in reference [12]. \(^{b}\)Assigned from references [14,15]. \(^{c}\)Defined imidazole (Im) and pyrimidine (Py).
breathing mode of the imidazole in dG. SERS band at 1322 cm$^{-1}$ also corresponds to band at 1318 cm$^{-1}$ which represent C-N stretching of the imidazole in dG. Another band at 1470 cm$^{-1}$ corresponds to band at 1472 cm$^{-1}$ of dA and is interpreted to C=N stretching mode of the pyrimidine.

From analysis of the above data in Figure 4, mismatched DNA double strands mainly interact through dA and dG on gold surfaces, contrary to matched DNA double strands. These may also be planer or tilted orientation relative to the gold surfaces because SERS bands of mismatched DNA double strands mainly show ring breathing and stretching modes instead of vibration of amine group. This means that mismatched DNA double strands interact through the nitrogen atom of the pyrimidine ring. Accordingly, this suggests mismatched DNA double strands molecule interact with the gold surface through the nitrogen atom of the pyrimidine ring in dA and dT. In mismatched DNA double strands, the nitrogen atom seems to play an important role as the side of the molecule with a tendency to interact with gold surfaces.

Conclusions

DNA strands of self-assembled monolayers were successfully detected using SERS on gold nanoparticle surfaces and gold surfaces coated on mica like other DNA researches. DNA single and matched double strands mainly interact through dC and dT on gold surfaces. It showed a perpendicular standing or tilted orientation relative to the gold nanoparticle surfaces whereas a planer orientation on gold surfaces coated on mica. In contrast, mismatched DNA double strands mainly interact through dA and dG on gold surfaces, showing binding through the nitrogen atom of the pyrimidine ring in dA and dT. DNA strands can interact differently with gold surfaces through matched type between bases of DNA sequence. Accordingly, SERS is very sensitive to detect a small quantity of monolayes or biomaterials on metal surface to elucidate the structure mechanism of them.

Acknowledgments. Author thanks Prof. C. A. Mirkin for his considerations at Northwestern University.

References