Graphene-Enhanced Raman Scattering of Biomolecules

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Abstract

Highest sensitivity in detecting and identifying chemical compounds is achieved by surface-enhanced Raman scattering (SERS), which occurs from molecules adsorbed on nanostructured metallic surfaces or metal nanoparticles. In general, Raman scattering is too weak to produce signals from monolayer samples and Raman signal enhancement requires coupling of the analyte to the SERS-active surface [1,2]. Due to the need for great repeatability, lowest uncertainty and highly tunable surface morphologies, highly reproducible graphene surfaces are shown to be potential candidates for obtaining comparable results. Graphene has been of significant interest recently with respect to graphene-enhanced Raman scattering (GERS), that results in enhancement of the native Raman signal of target molecules in close proximity to mono- and multilayers of graphene by several orders of magnitude. Since there are increasing needs for methods to conduct reproducible and sensitive Raman measurements, GERS is emerging as an important method. Graphene sustains particularly large enhanced Raman signals of molecules at its surface [3-5].

In this work, we study the enhancement of the Raman signal of biomolecules on graphene and evaluate the enhancement factors and reproducibility. Graphene mono- and multilayers, prepared on suitable surfaces, shall be qualified as biocompatible and highly reproducible SERS-active substrates. Even though the mechanisms are not clear, it is of metrological importance to compare the GERS enhancement with SERS measurements. We have first chosen 4-mercapto-benzoic acid (4-MBA) to study the effect of graphene as an active substrate for signal enhancement and also the charge transfer of molecules adsorbed on it. This compound was chosen because of the strong affinity of the mercapto (-SH) end group to noble-metal and semi-metal surfaces, which leads to the spontaneous formation of a self-assembled monolayer (SAM). In Fig. 1 (left), we compare native Raman spectra of 4-MBA on silicon dioxide (SiO_2) and graphite substrates along with graphene-enhanced signals of the molecule. The lowest (red) spectrum in Fig. 1 was taken on the SAM on the SiO_2 substrate. If we compare this spectrum to the spectrum, measured on graphite (blue spectrum in Fig. 1) and on graphene (black spectrum in Fig. 1), we observe that, interestingly, the former peak shifts to 1100 cm^{-1}, when 4-MBA in the form of a single monolayer is attached to the surface of graphite or graphene instead of SiO_2. As can be seen in Fig. 1, also the strongest enhancement appears for the mode at 1100 cm^{-1} [5].

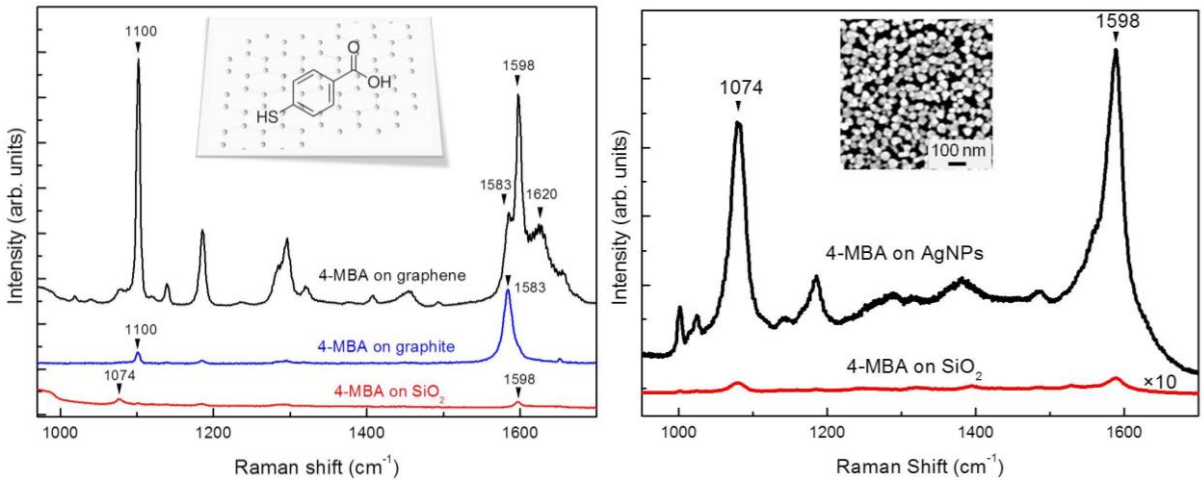

Figure 1. (left) Raman spectrum of 4-MBA measured on SiO_2 (red) and graphite (blue) along with the obtained enhanced Raman signal on graphene (black). (right) Raman spectrum of 4-MBA measured on SiO_2 (red) along with the obtained enhanced Raman signal on silver nanoparticles (black). The inset shows an SEM image of silver nanoparticles [5].

The SERS measurements were also done on active substrates covered with spherical silver nanoparticles. The spectra in Fig. 1 (right) show that, in contrast to the measurements on graphene, no shift of the CC breathing mode at 1074 cm^{-1} is observed on a surface covered with silver nanoparticles and the SERS signal appears on the same position as in the native spectrum on SiO_2. The enhancement factor in SERS is larger than what is achieved in GERS. However the main barrier to the routine use of SERS in analytical chemistry is the lack of robust methods to perform reliable quantitative analysis and the main reason for this is the lack of reproducible substrates, capable of high Raman enhancement. So the fact that graphene is easily reproducible and highly quantifiable makes it an excellent substrate for enhanced Raman probing [5].

We have also found that mono- and multilayer graphene works as an active substrate for the observation of enhanced Raman scattering from adenine and cytosine in their physiological concentration ranges.

References

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