# Intensified surface enhanced Raman signal of a graphene monolayer on a plasmonic substrate through the use of fluidic dielectrics

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## ABSTRACT

It has been shown that surface enhanced Raman spectroscopy (SERS) has many promising applications in ultrasensitive detection of Raman signal of substances. However, optimizing the enhancement in SERS signal for different applications typically requires several levels of fabrication of active plasmonic SERS substrates. In this paper, we report the enhancement of SERS signal of a single layer of graphene located on a plasmonic nano-Lycurgus cup array after placing water droplets on it. The experimental data shows that addition of water droplets can enhance the SERS signal of the single layer of graphene about 10 times without requiring any modifications to the nano-Lycurgus cup array. Using full-wave electromagnetic simulations, we show that addition of water droplets enhances the local electric field at the graphene layer, resulting in stronger light-graphene interaction at the excitation pump laser wavelength. We also show that the addition of water droplets on the graphene layer enables us to modify the band diagram of the structure, in order to enhance the local density of optical states at the Raman emission wavelengths of the graphene layer. Numerical calculations of both the excitation field enhancement at the location of the graphene layer, and the emission enhancement due to enhanced local density of optical states, support the experimental results. Our results demonstrate an approach to boost the SERS signal of a target material by controlling the band diagram of the active nanostructured SERS substrate through the use of fluidic dielectrics. These results could find potential applications in biomedical and environmental technologies.

**Keywords:** surface enhanced Raman spectroscopy, graphene, absorption, local density of optical states

## 1. INTRODUCTION

Surface enhanced Raman spectroscopy (SERS) has been a robust tool in detection and characterization of materials and substances for years[1-6]. In this technique, the intensity of the Raman signal of target materials, which is often too weak to be detected, is promoted through utilizing metallic nanostructures and nanoparticles[7,8]. Target molecules, when located in the vicinity of the metallic nanostructures, experience a giant enhancement in the electromagnetic field as well as the local density of optical states at the resonance wavelength of the nanostructure[9-13].

In this paper, we report on a significant enhancement in the SERS signal of a single graphene layer which is placed on a metallic array of nanoholes due to application of water droplets on top of the graphene layer. Figure 1 shows the nanostructure used in the experiment. A metallic nano-Lycurgus cup array (nanoLCA) has been used as the SERS substrate[11,14]. Silver was used as the metal along with titanium which is used as an adhesive material between polymer and silver. As shown in Fig. 1(b), due to the unique cup-shape of the nanoLCA structure, nanoparticles form in the side

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walls of the nanoholes during the fabrication process. The refractive index of the polymer material is 1.56 and the depth of nanoholes $h$ is 500 nm. A single graphene layer is placed on the nanoLCA substrate. Graphene with its two-dimensional nature can be conveniently used along plasmonic nanostructures[15-19]. Here, graphene layer is used as a probe to investigate the optical response of the proposed structure. Figure 1(c) shows the scanning electron microscopy (SEM) image of the nanostructure which is covered with a single layer of graphene. Figure 1(a) also shows an optical image of the fabricated structure which is partially covered with water droplets. The utilization of water droplets enables us to increase the confinement of the local field and enhance the local density of optical states (LDOS) at the location of the graphene layer, which results in about 10 times enhancement in the intensity of the SERS signal of graphene when compared to the intensity of the SERS signal of a graphene layer without water.

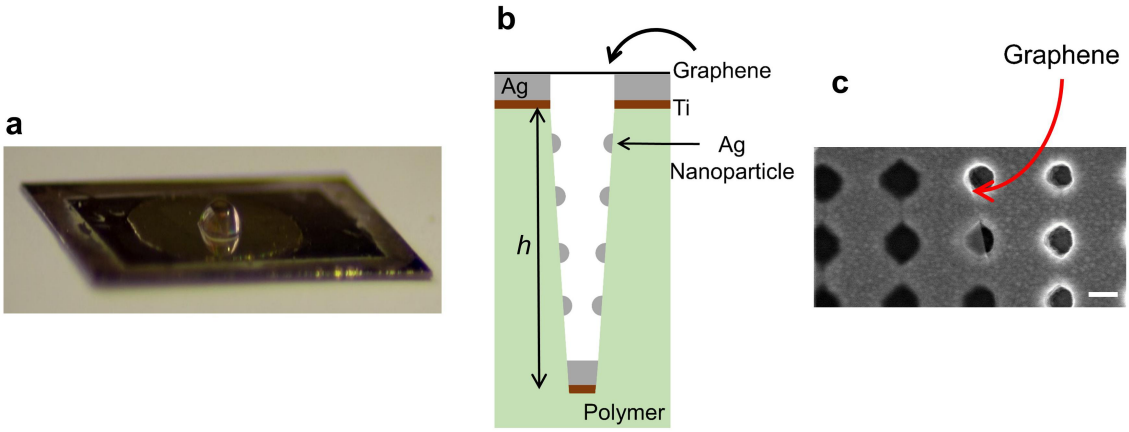


Figure 1. (a) Optical image of the sample, consisting of a metallic nanoLCA substrate covered with a single graphene layer. The surface of the graphene is covered partially with water droplets. (b) Cross-sectional view of one unit-cell of the metallic substrate nanostructure covered with a single layer of graphene. The thickness of silver and titanium layers are 90 nm and 9 nm, respectively. Nanoparticles are 40 nm in diameter. The cup depth $h$ is 500 nm. Top and bottom hole diameters are 200 nm and 160 nm, respectively. (c) SEM image of the nanostructure covered with the graphene layer. The scalebar is 200 nm.

## 2. RESULTS AND ANALYSIS

Figure 2 shows the SERS spectra of the graphene layer on the nanoLCA substrate when it is covered with droplets (red curve), compared to the SERS signal of a graphene layer on the metallic substrate without water droplets (black curve). The SERS signal of a graphene layer on glass is also shown as a reference. However, this spectrum was taken at a higher laser power and larger integration time compared to the other curves. In this experiment addition of water droplets on the graphene layer intensified the SERS effects about 10 times.

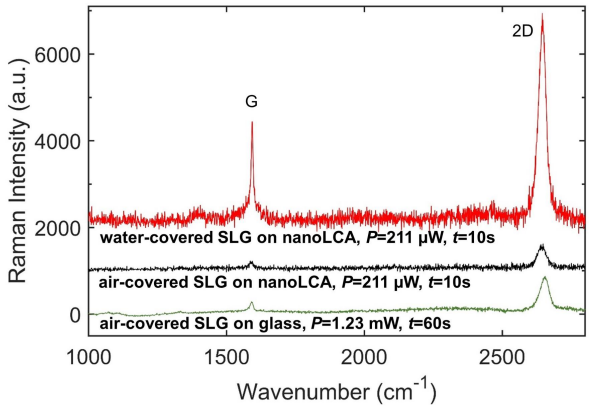


Figure 2. Raman spectra of a single layer of graphene (SLG) when placed on different substrates (metallic nanoLCA and glass) and covered with air and water. $P$ is the incident laser power at 633 nm, and $t$ is the integration time.

Addition of water droplets enhances the SERS signal of the graphene through enhancing the local confinement of field and the LDOS at the location of the graphene. Figure 3(a) shows the calculated field intensity averaged over the surface of the graphene when it is covered with air (black curve) and water (red curve), respectively. Finite-difference time-domain (FDTD) method (Lumerical FDTD Solutions) was used to calculate this result. This figure shows that addition of water droplets increases the intensity of the local field on the surface of graphene at the pump laser wavelength of 633 nm more than 3 times. Figure 3(b) depicts the calculated electric field intensity on the graphene in one unit-cell of the nanoLCA substrate when graphene is covered with air (top) and when it is covered with water (bottom) at 633 nm.

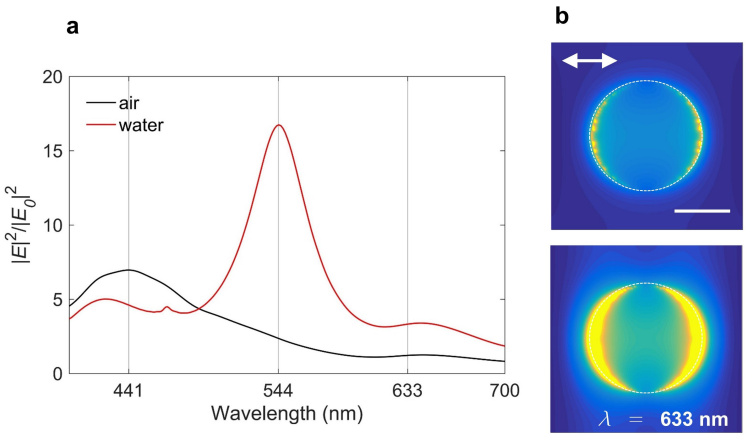


Figure 3. (a) Calculated averaged field intensity on the surface of the graphene layer located on the nanoLCA substrate as a function of wavelength when graphene is covered with air (black curve) and water (red curve). (b) Calculated electric field intensity on the surface of the graphene when it is covered with air (top) and water (bottom) at the pump laser wavelength of 633 nm. The scalebar is 100 nm. The polarization of the excitation laser is also shown.

Addition of water droplets also increases the LDOS at the location of the graphene. Figure 4 shows the calculated averaged LDOS enhancement with respect to the DOS of a dipole emitter in free space at the location of the graphene layer when it is covered with air (black curve) and water (red curve). FDTD simulations show that placing water droplets on the graphene increases the LDOS at the Raman emission wavelengths of graphene, 704 nm and 760 nm (corresponding to 426 THz and 395 THz, respectively), about 3 times.

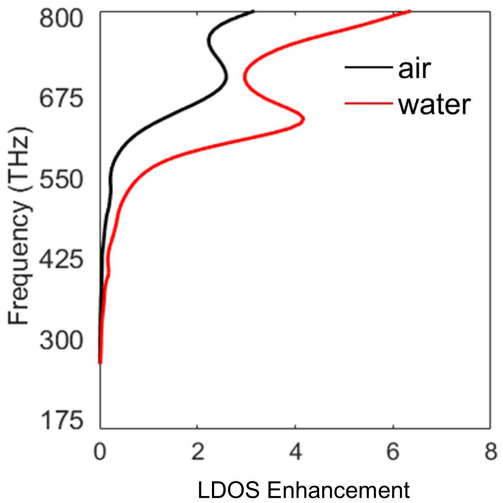


Figure 4. Calculated averaged LDOS enhancement at the location of the graphene layer when it is covered with air (black curve) and water (red curve).

## 3. CONCLUSION

In this paper, we theoretically and experimentally investigated the effect of addition of water droplets on the surface of a graphene layer placed on top of a metallic nanoLCA substrate on the intensity of the SERS signal of graphene. We showed that the intensity of the SERS signal of graphene increased about 10 times when it was covered with water droplets. Our theoretical investigations show that addition of water on the graphene increases the confinement of the local field as well as the LDOS at the location of the graphene. Our proposed approach of utilizing fluidic dielectrics along with conventional SERS substrates enables us to promote the SERS signal of target molecules with no change to the SERS substrate.

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