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Design of Plasmonic Nanopore Platforms for Single-Molecule Detection

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Abstract: In this letter, we proposed and numerically demonstrated a novel plasmonic nanopore platform for single-molecule detection. Bowtie nanoantennas and photonic cavities were studied to obtain Raman enhancement at single-molecule level on the solid-state nanopore platform.

OCIS codes: (240.6680) Surface Plasmas; (240.6695) Surface-enhanced Raman scattering; (290.5840) Scattering, molecules

1. Introduction

At present, nanopore platforms are being widely used as biochemical sensors for targets such as nucleic acid [1], protein [2], virus [3] as well as heavy metal ions [4]. Compared to biological nanopores, solid-state nanopores are chemically stable, flexible in size and compatible with today's semiconductor fabrication techniques, such as focused ion beam milling (FIB) [5] and transmission electron microscope (TEM) [1]. Furthermore, it is advantageous to combine optical detection with solid-state nanopores. For instance, photonics structures (e.g. nanoantennas) can be patterned near the nanopores with techniques such as FIB and electron beam lithography (EBL) [6] to realize the so-called hot spots (i.e., areas with greatly enhanced electric field), which can be used to perform single-molecule sensing with surface enhanced Raman scattering (SERS) or surface enhanced fluorescence (SEF). In addition, an exciting prospect is the potential of probing multiple nanopores simultaneously [7] for rapid and multi-target detection, which is difficult in nanopore-based electrical detection schemes [8].

In this letter, we proposed and investigated nanoantenna-assisted nanopore platforms for single-molecule detection theoretically. Specifically, bowtie structures which have been used towards electromagnetic hotspots [9] were studied extensively to achieve Raman enhancement at single-molecule level. The gap size as well as antenna dimension were considered for optimization. In addition, photonic cavities were introduced into our system to further improve Raman enhancement. Finally, a Raman enhancement factor of 8.9×10^7 was obtained with our optimized system.

2. Theoretical Methods

A bowtie-nanopore structure was designed and used in our simulations, as shown in Fig. 1. The bowtie structure acting as a nanoantenna was placed on a nanopore with its gap centre aligned with the nanopore centre. Here, a silica substrate was used and a ground metal layer was added on the other side of the substrate to form a photonic cavity. The tapered bowtie tips concentrate a large amount of free electrons to induce more largely enhanced field. A perfectly sharp tip at the apex of the triangle is most desirable. This, however, cannot be achieved by considering the limitations of EBL followed by vapor deposition of gold or similar fabrication techniques. In our simulation, therefore, we assumed a curvature (radius of 5 nm) at the apex of the bowtie tip, which was used in a previous work [10]. A schematic drawing of the top view of the bowtie structure on xy -plane is shown in Fig. 1a while the cross section of the system on xz -plane is shown in Fig. 1b. The dimension of the bowties was defined by R (the radius of the circumcircle of the triangle prism). Besides, g and h stood for the bowtie gap size and the silica substrate thickness ($h=200$ nm if without ground layer), respectively. Thickness of the nanoantennas was 20 nm and that of

Fig. 1. Schematics showing (a) a bowtie with round corners on the xy -plane and (b) side view of the system on the xz -plane.

Fig. 2. Nanoantenna features with respect to gap size ($R=46.2$ nm)

the ground metal layer was 100 nm. 10-nm pore diameter was used. And we assumed the BNS was placed in water.

Lumerical FDTD Solutions, a commercial electromagnetic software based on the finite-difference time-domain method, was used to perform the simulations. A plane wave (of 650-950 nm wavelength) polarized along the junction between triangular prisms (i.e., along the x direction in Figure 1) was illuminated in the negative z-direction from above the bowtie (see Figure 1b). The perfect matched layers were used to absorb waves leaving the simulation domain in all wave propagation directions. The mesh size in the bowtie region (including the gap) was 1 nm while automatic graded mesh was adopted in the region outside the bowtie structures to ensure the numerical accuracy in consideration of reasonable computation time.

3. Results and Discussions

We firstly studied the gap-dependence of nanoantenna performance. Gold ground layer was not introduced into our system at this stage and its influence will be investigated separately later. Fig. 2 shows the change of nanoantenna resonance wavelength as well as electric field enhancement factor at the gap centre corresponding to different gap size. It is clearly indicated that, by decreasing size of the gap, the resonance wavelength shifted to longer wavelengths and a stronger electric field was obtained. The red-shift of resonance wavelength is owing to the decreasing of resonance frequency of dipoles when getting closer owing to charge attraction. And the enhancement of electric field results from stronger plasmon coupling with narrower bowtie feed gap. It is worth mentioning that sub-10 nm solid-state nanopores and feed gaps (gap size should not be smaller than pore diameter) were not studied here because such dimensions are hard to obtain on substrates with today's fabrication techniques [1,11]. However, narrower bowtie gap (limited by techniques and pore diameter) will lead to stronger electric field enhancement.

For Raman spectroscopy, near-infrared lasers should be used to suppress fluorescence background. Therefore, 785 nm was chosen as the excitation wavelength of the system. The resonance wavelength could be further tuned with constant feed gap by altering the size of bowtie (i.e., the radius R). The features of a 10 nm-gap bowtie working around 785 nm are shown in Fig. 3. As indicated, the electrical field enhancement factor was about 70 in the gap centre while the maximum one is above 90. The difference results from the fact that the gap was not small enough. The total Raman enhancement factor could be expressed as the product of excitation enhancement and emission enhancement: $EF_{\text{Raman}} = |E_{\text{in}}(f_L)/E_{\text{loc}}(f_L)|^2 \times |E_{\text{loc}}(f_S)/E_{\text{in}}(f_S)|^2$ where $E_{\text{in}}(f_L)$ is the incident electric field at laser frequency, $E_{\text{loc}}(f_L)$ is the local electric field at laser frequency, $E_{\text{in}}(f_S)$ is the incident electric field at Stokes frequency, $E_{\text{loc}}(f_S)$ is the local electric field at Stokes frequency. If the Stokes shift is small and if the losses are minimal, the Raman enhancement factor could be approximated: $EF_{\text{Raman}} = |E_{\text{in}}(f_L)/E_{\text{loc}}(f_L)|^4$. This approximation was widely adopted [12] and we also used it to evaluate our system. Therefore, the Raman enhancement factor for the case was

Fig. 3. Features of a 10 nm-gap nanoantenna ($R=48$ nm): (a) Transmittance and (b) Electrical field enhancement distribution at excitation.

2.4×10^7 roughly, greater than the minimum requirement for single-molecule SERS (10^7) [13].

Photonic cavities, formed by placing a metal ground layer under substrates, have been reported to further improve field enhancement [14]. Here we investigated the enhancement from photonic cavities with the nanoantenna used in Fig. 3. Electric field enhancement factors with different silica substrate thickness are shown in Fig. 4. According to Ref. [14], the greatest enhancement takes place around 1/4-wavelength optical thickness due to constructively interference. Due to π phase shift during reflection at the interface of a perfect electric conductor and a dielectric, the in-phase reflection condition is expressed as follows: $(2 \times h)n_{\text{silica}} = (m + 1/2)\lambda$. Here, n_{silica} is the index of silica substrate. λ denotes laser wavelength and m is a whole number. Considering the parameter of our system (laser wavelength of 785 nm, silica index of 1.45), the first order of optimized thickness can be deduced to be 135nm approximately. Besides, it was found that the actual optimized thickness (120 nm) was slightly less than that value because penetration of laser light into the metal leads to additional phase shift at the metal ground layer-silica substrate interface. In our simulation, the largest electric field enhancement observed was about 97. This gave an optimized electric field enhancement factor of photonic cavity: $97/70=1.4$, leading to additional Raman enhancement of $1.4^4 \approx 3.8$ and total Raman enhancement of 8.9×10^7 . We would like to mention again this figure was obtained, considering current fabrication technologies. The enhancement will be much larger if smaller nanopore and narrower antenna gap are realized (for instance, EF_{Raman} can be greater than 3×10^9 with 5-nm gap and optimized photonic cavity, not shown here).

Fig. 4. The relationship between enhancement factor and silica thickness

4. Conclusion

In summary, we proposed to utilize the nanoantenna-assisted nanopore platforms to perform single-molecule detection. Considering the limitations of fabrication techniques, bowtie structures with gap no less than 10 nm were studied numerically to obtain sufficient Raman enhancement. Additionally, photonic cavities were added in the platform to further improve enhancement. It was found that optimized system could offer total Raman enhancement of 8.9×10^7 while the photonic cavity enhancement factor was 3.8 approximately.

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