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Plasmonic nanopore-based platforms for single-molecule Raman scattering

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ABSTRACT

We propose and demonstrate a novel plasmonic nanopore platform based on a bowtie-nanopore structure, for single-molecule sensing. In this nano-structure, nano-bowties are integrated with solid-state nanopores to provide localized surface plasmon resonances for signal enhancement. We design and optimize the nano-structure by tuning both the bowtie gap and the bowtie angle, and investigate their influences on field enhancement, thereby achieving single-molecule sensitivity. In addition, we study the field enhancement by introducing an engineered photonic nano-cavity. This further strengthens the electric enhancement. An overall Raman enhancement factor of 2×10^8 is achieved in our simulation. This is believed to be sufficient for single-molecule sensing. The proposed bowtie-nanopore structure can be multiplexed on a single substrate for simultaneous multi-channel detection, paving the way for demanding applications such as DNA sequencing.

1. Introduction

Nanopore platforms are being extensively utilized in biochemical sensing for targets including nucleic acid [1], protein [2], virus [3] and heavy metal ions [4]. Compared with biological nanopores, solid-state nanopores are more chemically stable, flexible in size and compatible with today's semiconductor fabrication techniques, such as focused ion beam milling (FIB) [5], transmission electron microscope (TEM) [1] and electron-beam lithography (EBL) [6]. Furthermore, plasmonic structures (e.g. nanoantennas) can be patterned near the nanopores with techniques such as FIB and EBL 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) [7] or surface enhanced fluorescence (SEF) [8].

Real-time label-free sensing is highly desirable for biochemical and environmental applications. SERS offers rich structural information and is undoubtedly one of the most promising label-free detection techniques. To date, few works have been done concerning fluidic plasmonic nanopore sensing, although nanopore-based SERS substrates were demonstrated [9,10]. Also, in Refs. [11,12], metal deposited nanoholes were reported for the detection of certain analytes in fluidic environment. It is widely accepted that the electric enhancement due to surface plasmon resonance leads to a Raman enhancement factor of 10^7, which is beyond the sensitivity of single molecule detections. Therefore, our study is motivated by the prospective of single-molecule sensing with nanopore, to introduce a nano-bowtie as a plasmonic optical nanoantenna around a nanopore to significantly enhance the detection limit. Nicoli et al. [13] investigated plasmonic nanopores with nanoantennas for DNA analysis but plasmonic excitation was to improve electric detection signals. To the best of our knowledge, the design in this work is the first fluidic nanoantenna-assisted nanopore platform. In addition, another exciting prospect of plasmonic nanopore systems is the potential of probing multiple nanopores simultaneously [14] for rapid and multi-channel detection, which is hard in nanopore-based electrical detection schemes [15].

In this work, we propose to use nanoantenna (in particular, nano-bowtie)-assisted nanopore platforms for single-molecule SERS detection. Specifically, bowtie structures being used towards electromagnetic hotspots [16] are studied theoretically to achieve plasmonic electric field enhancement. The gap size as well as bowtie angle are studied for enhancement factor optimization.

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Additionally, the influence of the nanopore size on the nanoparticle-based plasmonic enhancement is investigated as the design guidance. Finally, photonic cavities are introduced into our system to further improve enhancement. Speaking of a reasonable instance, Raman enhancement factor of 2×10^8 is obtained with our optimized system. The proposed plasmonic nanopore platforms are then demonstrated capable of single-molecule SERS sensing.

2. Theoretical methods

Bowtie-nanopore structures were designed and used in our plasmonic platforms, as shown in Fig. 1. The gold bowtie structure acting as a nanoantenna was placed on a silica substrate with its gap center aligned with the nanopore center. The nanopore works as a channel to allow the sample to pass and the localized surfaced plasmon resonance excited in the center of the nano-bowtie enhances Raman signals from the sample. At the same time, the silica substrate was used as spacer and a gold ground layer was added on the other side of the substrate to form a photonic cavity. In theory, 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 [17], effects of corner radius on field enhancement and resonance wavelength have been demonstrated. Therefore, we used a curvature (radius of 5 nm) at the apex of the bowtie tip [18] in our simulation. 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 given in Fig. 1b. The dimension of the bowties is defined by R (the radius of the circumcircle of the triangle prism). And ϕ stands for bowtie angle. In addition, g and h are the bowtie gap size and the silica substrate thickness, respectively. Thickness of the nanoantennas is 20 nm and that of the ground metal layer is 100 nm. The working environment including the nanopore is filled with water.

Lumerical FDTD Solutions, the commercial electromagnetic software based on the finite-difference time-domain method, was used to perform the simulations. A plane wave polarized along the junction between triangular prisms (i.e., along the x direction in Fig. 1) was illuminated in the negative z-direction from above the bowtie (see Fig. 1b). The perfect matched layers were used to absorb waves leaving the simulation domain in all wave propagation directions. The dielectric property of Au used in the simulations was taken from the John and Christy's report [19] and the SiO_2 information was achieved from Palik's handbook [20]. 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 was investigated separately later. Fig. 2 shows the change of resonance wavelength as well as electric field enhancement factor of standard bowties (adapted from regular triangles) at the gap center corresponding to different gap sizes but with same nanopore (diameter of 5 nm). Clearly, by decreasing the size of the gap, the resonance wavelength shifts 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 getting closer as a result of charge attraction. The enhancement of electric field results from stronger plasmonic 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) are hard to obtain on substrates with today's fabrication techniques [1,21,22]. However, extremely narrow bowtie gap (5 nm here, limited by techniques and pore diameter) does lead to giant electric field enhancement (120 times stronger as shown in Fig. 2).

In addition to the gap size, the impact of bowtie angle was also studied and the results are displayed in Fig. 3. The bowtie with an angle of 60 degree is the standard bowtie investigated in Fig. 1. Note that all the bowties here are with same surface area for accurate comparison. Obviously, with the increase of bowtie angle, the electric field enhancement decreases and the resonance wavelength blue-shifts. For instance, electric field enhancement could be doubled with 30-degree bowtie compared to a 60-degree bowtie. But it suffers from dramatic shifting of resonance wavelength (over 100 nm). The hot spots in nano-plasmonics is due to the lightning rod effect generating high local field at a sharp tip when the polarization of the exciting light is parallel to the tip's axis. That is the reason why our plane wave is polarized along bowtie junction. Furthermore, the lightning rod effect becomes stronger with even sharper tips, which explains the change of enhancement factor in Fig. 3. Stronger plasmonic coupling accompanies with longer working wavelength as shown in Fig. 1. In addition, comparisons between round and ideal bowties of 5 -nm gap are presented in Fig. 4. It is clear that ideal bowties could lead to even hotter spots around sharp tips, which is consistent with lightning-rod effect.

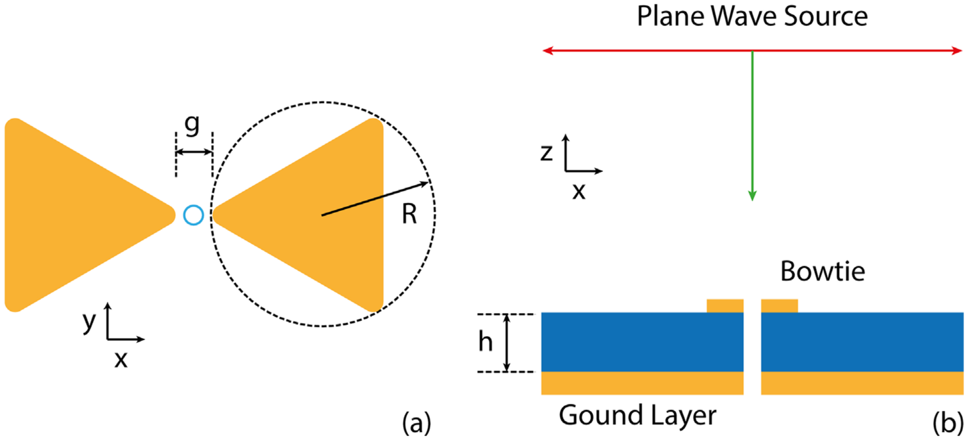

Fig. 1. Schematic drawing of (a) a bowtie with round corners on the xy-plane and (b) the side view of the system on the xz-plane.