5 - 24 Double-sided Plasmonic Metasurface for Simultaneous Biomolecular Separation and SERS Detection

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Biomolecular separation is an important technique for biological applications such as medical diagnosis where molecular selectivity and flux control are key technical concerns[1]. Nanoporous membranes have been considered as a powerful platform to filtrate and separate biomolecules[2]. Among diverse membranes, the ion-track-etched membranes with uniform yet tunable pore size, density and shapes have been widely recognized due to their excellent selectivity and high permlability. In addition to the capability of molecular selection, quantitative evaluation of molecular selectivity is of equal importance. Surface-enhanced Raman spectroscopy (SERS) can be used as a detection technique for quantifying the molecular separation because of its excellent capability in detecting biomolecules and incomparable ultrahigh sensitivity even down to the single-molecule level[3].

The double-side, highly flexible, and hierarchical porous metasurfaces were fabricated through etching of ion track-registered membranes followed by self-assembly of gold nanoparticles. The synthetic procedures include three main steps. First, polycarbonate foils were irradiated by swift heavy ions in order to create ion latent tracks in a parallel alignment. Then, the ion tracks were selectively removed by asymmetric etching from both sides of polycarbonate foils, using an etchant composed of vol.5% 9 mol/L NaOH and vol.95% methanol. Finally, gold nanoparticles with sub-5 nm nanogrooves were self-assembled on both film surfaces by sputtering under proper conditions.

The as-prepared metasurface is expected to light up an unprecedented application, that is, a dual-functional device prototype that can synergetic ally separatie molecular species of different sizes and perform on-substrate SERS monitoring ion the entrance and exit sides. As proposed in the schematic diagram in Fig. 1(a), when a mixed solution of molecules A and B (A is larger than B) is injected from the top surface of the metasurface substrate, a SERS spectrum can be measured spectrally showing a combination of their molecular fingerprints. After separating the molecules by the conical nanopores, only the smaller molecules B can reach the bottom surface of the substrate, where a SERS spectrum can be captured again to verify the transport of molecules B through the nanopores. This concept is experimentally demonstrated by successful nanofiltration separation of the biomolecular adenine (a chemical component of DNA and RNA, smaller size) from the mixture of adenine and ssDNA (A-ST20N3, a thiolated 70-base oligomer that contains no adenine, larger size). As shown in Fig. 1(b), before separation, the SERS spectrum (green line, taken from the front surface of the SERS substrate) exhibits the Raman peaks of both adenine and ssDNA. After separation, the SERS spectrum (blue line) obtained from the back surface has only the Raman peak of adenine, evidencing efficient biomolecular separation and successful on-substrate SERS detection. The SERS spectra of pure ssDNA and adenine extracted from other metasurface substrates are included for further confirming the molecular filtration and detection capability.

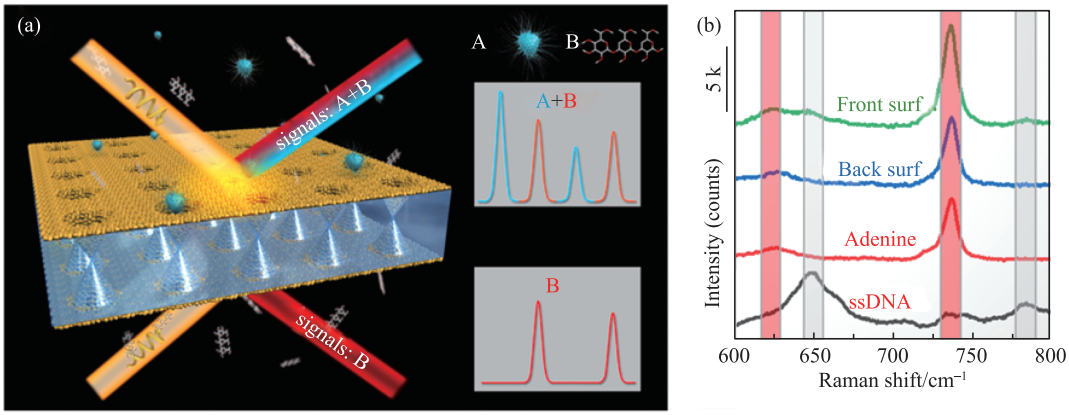

Fig. 1 (color online) (a) Schematic diagram of a dual-functional device prototype for simultaneous nanofiltration separation and double-side SERS monitoring of biochemical molecules, (b) Biomolecular nanofiltration separation and double-side SERS examination of separated adenine from the mixture of adenine and ssDNA.

In conclusion, the hierarchical structure provides an unprecedented way to separate biomolecules and simulta-

neous on-substrate SERS detection.

References

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5 - 25 Single Graphene Nanopore for Biomimetic Ion Channel via Tunably Voltage-modulated Ion Transport

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Biological ion channels possess a remarkable ability to selectively modulate ionic flux and play an irreplaceable role in many life processes[1]. The modulation of ion transport through nanopores or nanochannels has received considerable attention due to the similar transport mechanism of biological ion channels. Graphene has become the most promising membrane material because of its good permeability, mechanical strength and chemical stability. Based on its excellent electrical conductivity, it is possible to apply the gate voltage on the graphene to modulate ion transport through the graphene nanopore[2].

Herein, the graphene/polyethylene terephthalate (G/PET) composite nanochannel was prepared by swift heavy ion irradiation, and gate voltage was applied on it. The results exhibited that the transport of cations (K^+, Na^+, Li^+, Mg^{2+}) can be electrostatically modulated by the applied gate voltage. The G/PET nanochannel imitated the K^+ ions biological nanochannel and impedes the transport of divalent ions with K^+/ions selectivity up to ~4.2. Furthermore, it was confirmed by simulation that the applied gate voltage can change the electric potential around the graphene nanopore and the surface of the graphene. Therefore, the change of potential leads to the accumulation and depletion of anions and cations near the graphene nanopore and has the ability to modulate cations transport through the graphene nanopore. This work demonstrated that the graphene nanopore with applied gate voltage can effectively modulate ion transport and exhibit significant selectivity for monovalent and divalent cations. Figure 1 shows the structure of G/PET nanochannel, etching/measuring device and SEM images of graphene nanopore and PET nanopore. Figure 2 shows the Ion selectivity of G/PET nanochannel.

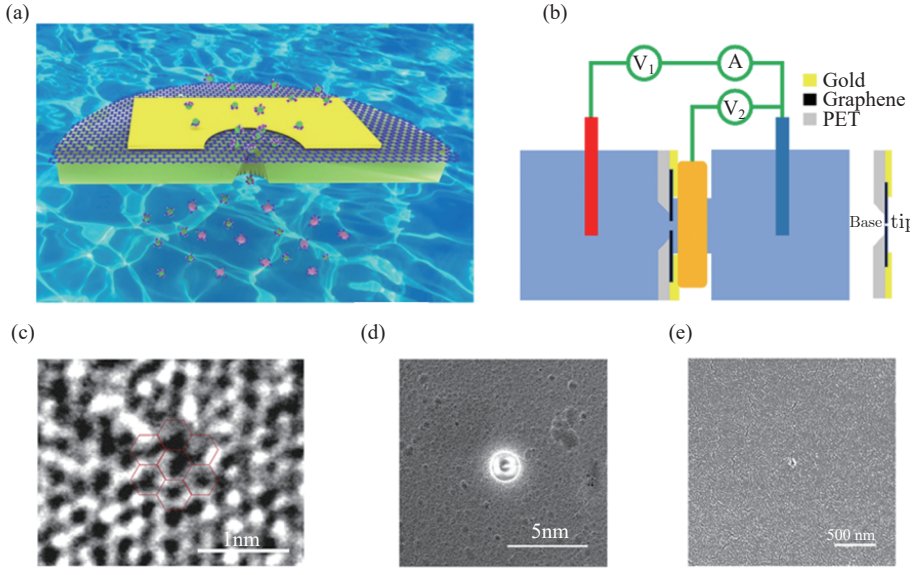

Fig. 1 Structure of G/PET nanochannel, etching/measuring device and SEM images of graphene nanopore and PET nanopore.