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Effective Membrane-based SERS Substrate Fabrication

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Abstract

In this study, a membrane-based surface and capillarity with rapid drying and increased surface density for low volume (uL) NPs and samples by pressure method was prepared for a highly uniform surface-enhanced Raman spectroscopy (SERS) substrate. The micropipette tip with a diameter of 500 um was employed to define the area of NPs deposition simply by the pipette gravity in contact with the membrane surface. Therefore, high density nanoparticles could be concentrated on a confined circle with identical diameter as formed by the micropipette tip. The measured SERS response displays high reproducibility and linearity spectrum. Overall, results indicated that the proposed method with its simple process, low-cost substrates and stable SERS signal with an improved quantitative analysis reliability can be potentially used to develop environmental pollution and biomedical sensing platform.

1. Introduction

SERS has been widely used in various scopes of studies due to its accurate and unique spectrum signal. One of the most important factor in SERS is the optimization of its signals which is closely related to surface characteristics. Electrochemical or nanoscale technology are pretty common in SERS substrate manufacturing [1]. Despite their excellent SERS effects, the processes are typically more complex and expensive. Another drawbacks come from the time-consuming drying duration during sample measurement and substrates shelf lives with progressive reduction in SERS activity effect due to oxidation of the
metal structures.

In our method, a simple technique is offered by using a filter paper as a membrane and a micropipette tip for the definition of the sensing area. This method has been proven to enable the detection of a super low samples volume (uL) with an impressive accelerated drying time due filter paper capillarity.

2. Experiment

AgNPs (200ppm) with the diameter of 50 nm were produced by the method of Yaqiong Qin and Xiaohui Ji[2]. MCE filter membranes with 4.5mm diameter and 0.1um pore sizes were purchased from TOSON Technologies. Rhodamine 6G (R6G) and MB powder were purchased from SIGMA. Fig. 1 illustrates the process flow of this work. Firstly, AgNPs and R6G were mixed with the ratio of 1:1 and loaded on a micropipette tip with the diameter of 500um. The mixture was dropped on the membrane based substrate. The fast drying methods was assisted by the capillary force on the tip perimeter surrounding area. The area of measurement is limited based on the boundary formed by the pipette tip's perimeter, which is 500 um. The SERS measurements of the membrane substrates were carried out on a Raman spectrometer (RAMaker) with the excitation wavelength of 473 nm and the maximum power of 100 mW. The exposure time and number of accumulations for all samples were 2 sec and 5 times, respectively.

3. Results and discussion

Fig. 2 shows the circular measuring position under the microscope with diameter of about 500 um. The procedure only took a few minutes (~3min) because the membrane could quickly take the water up by the capillary force on the surrounding area or the defined circle. The SEM image in (Fig.3) indicates that high density of SERS active hot spots exist across the membrane surface. As seen in Fig 4, we used different volumes of sample to define the sensing area on the membrane. For R6G measurement, the intensity of the 1648cm^{-1} R6G Raman peak was plotted. The signal increased linearly for the increasing sample volume; 2.5uL, 5uL and 10uL, respectively. It is observed that this configuration resulted a great SERS response in R6G measurement even in the smallest volume of 2.5uL which implies a great capability in small volume detection. Furthermore, being carried out in the detection of a series of MB concentration from 10^{-4} to 10^{-6} M, as demonstrated in Fig. 5, our proposed structure exhibited a great linearity for the Raman intensity of its most stable 1618 cm^{-1} peak.

4. Conclusions

A rapid SERS detection of dye molecules with low volume of samples is performed on a simple and cost-effective membrane-based substrate. An effective trapping of a small volume solution containing AgNPs with the targeted dye molecules was realized from a sensing area definition by the micropipette tip circular perimeter. Outcomes reveal that our proposed technique created highly dense hot spots leading to an improved SERS response. This work demonstrates that membrane-based SERS substrate is well suited for relatively

rare sample analysis that includes measuring biological samples or patient specimen[3], as well as environmental contaminants or pollutants.

References

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[3] Päivi Ruokola et al, JVI Accepts, published online ahead of print (2014)J. Virol. doi:10.1128/JVI.03398-13

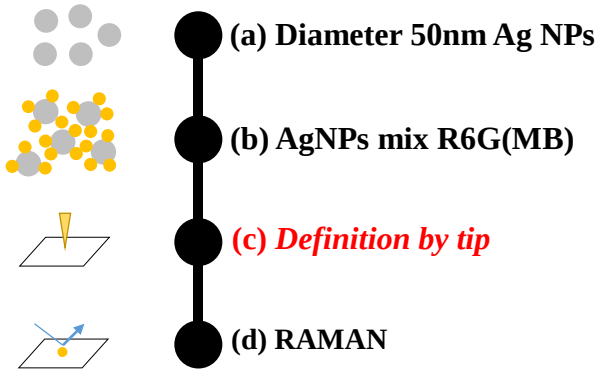

Fig 1. Process flow of the membrane-based SERS substrate preparation.

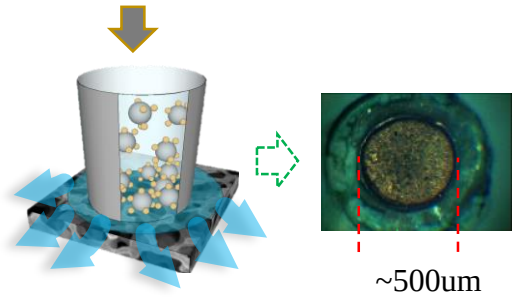

Fig 2. Sensing area definition by micropipette tip circular perimeter.

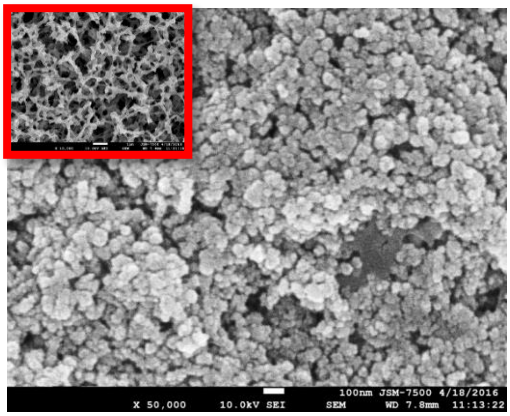

Fig 3. SEM figure of membrane surface after the drop of AgNPs and R6G mixture, inset is the bare membrane.

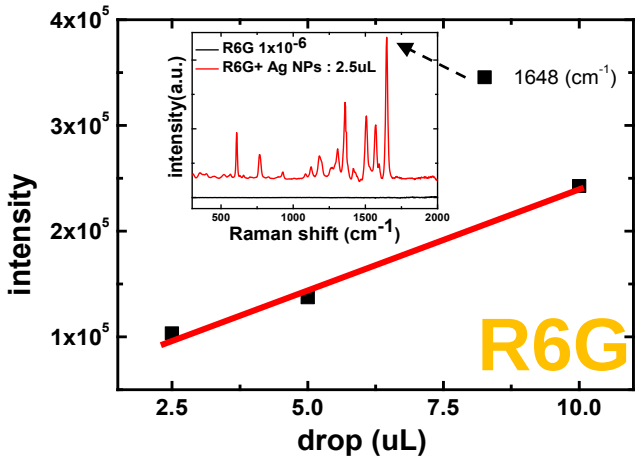

Fig 4. SERS response of R6G with different volumes.

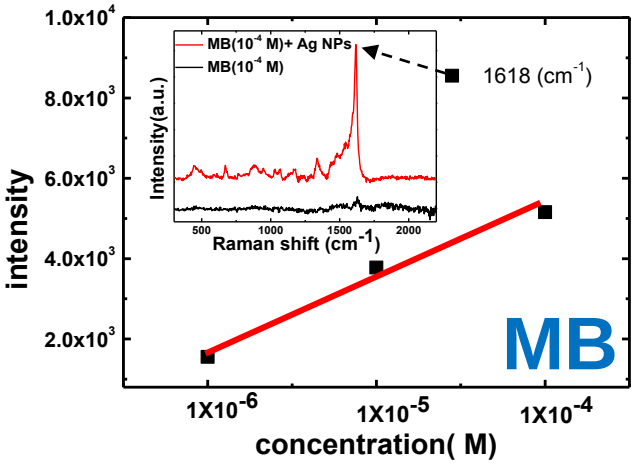

Fig 5. SERS response of MB with different concentrations.