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Superhydrophobic Surface-Enhanced Raman Spectroscopy (SPHB-SERS) platform

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Introduction

The detection of highly diluted and small volume samples remains a challenge. To surmount the challenge, superhydrophobic surface-enhanced Raman Spectroscopy substrate (SPHB-SERS) is fabricated. The strategy emphasizes on the synergy between intense electromagnetic field brought about by single crystalline Ag nanocubes and superhydrophobic surfaces with analyte concentrating effect to achieve ultrasensitive trace molecular detection using SERS.

The concept of superhydrophobic surface relies on the non-stick property of SPHB surface to direct the evaporation analyte droplet into a very small and concentrated area, therefore achieving enhanced detection sensitivity. This final concentrated analyte area can be as small as 10^4 than the initial droplet contact area [1-3]. In addition, due to the unique analyte confinement effect, the SPHB-SERS platform is able to consistently give rise to reliable molecular detection even when the analyte volume is as low as 1 mL, demonstrating its potential as a highly diluted, small volume analytical platform.

Method and setup

The detail fabrication of SPHB-SERS platform was reported in literature [2]. In brief, mono-dispersed 100 nm (± 10 nm) Ag nanocubes were used as basic building blocks for the SERS substrate. The nanocube surface area density was controlled by manipulating the parameters during Langmuir-Blodgett assembly to form a large-area and uniform plasmonic hotspots as well as generate optimal surface roughness for superhydrophobicity. A thin layer of Ag was then thermally evaporated onto the Ag nanocube substrate to increase the stability of platform. Finally, the surface was modified with perfluorodecanethiol (PFDT) to render it superhydrophobicity. The final SPHB-SERS chip size was about 1 mm ´ 1mm. uRaman Micro-spectroscopy system equipped with Nikon Ci upright microscope (uRaman-532TEC-Ci) was used throughout the measurement. We adjust the 532 nm laser output power to 2.8 mW after a 20´ objective (Nikon CFI Plan APO 20´, NA = 0.75) to avoid heating the substrate. The acquisition time used was 200 ms for SERS and 1 s for dye solution.

Figure 1. uRaman with dual laser system, i.e. 532nm (top) and 785nm (bottom), equipped with motorised stage and several objective lens.

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Results and Discussion

The as-fabricated SERS substrate shows that Ag nanocubes are well dispersed over the substrate, which is expected to give rise to homogenous plasmonic hotspots. In addition, the controllable spacings between nanocubes also results in nanoscopic roughness necessary for superhydrophobicity (Figure 1A). After surface modification with PDFT, the Ag nanocube substrate is rendered superhydrophobic-SERS platform. The contact angle of the SPHB-SERS substrate is in the range of 140 to 160^{o}. When a droplet of methylene blue (MB) deposit on SPHB-SERS platform, a very small solid – liquid contact area is observed. But for a non-treated glass substrate, the droplet spreads over a larger area.

Six MB samples with different concentrations are deposited on the two SPHB-SERS substrates (Figure 1C), and allowed to dry for 30 minutes. The final size of the drying droplets can be as small as 48 μm for 10^{-9} M MB solution (Figure 1D), clearly demonstrating the analyte concentrating effect of our SPHB-SERS substrate. In addition, due to the non-spreading nature of the analyte droplet on our SPHB-SERS substrates, we have demonstrated the possibility of depositing multiple droplets on single SPHB-SERS substrate without cross-talk among different droplets (Figure 1C). This shows that multiple analyte of different concentrations can be detected simultaneously on the same chip for easy comparison, allowing better statistics and measurement consistency.

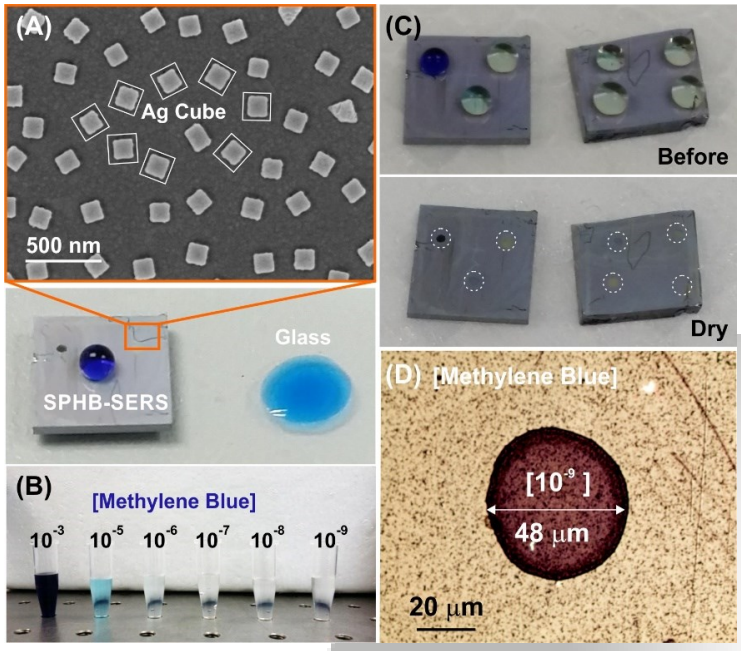

Figure 1. Characteristics of superhydrophobic-SERS platform.

(A) SEM micrograph of the SPHB-SERS platform fabricated using monodispersed Ag nanocubes. (B-C) Deposition of different concentrations of methylene blue droplets on the SPHB-SERS substrates, and after the evaporation of the droplets. (D) Achieving final analyte size of 50 mm using analyte concentrations of 1 nM.

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To begin, we perform normal Raman measurements directly using MB solutions in the absence of SPHB-SERS substrates. Two concentrations, i.e. 1 mM (10^{-3} M) and 1 μM (10^{-6} M) are performed (Figure 2A). No signal is detected using 1 μM MB solution, even when the acquisition time is increased by 5-fold to 1 s. Only when 1 mM MB is used, strong Raman fingerprint is observed around 1628 cm^{-1} corresponding to C-C ring stretching. The fluorescence background causes the spectrum to tilt upward at high wavenumbers.

In comparison, when SERS measurements are performed using our as-fabricated SPHB-SERS substrates, strong signals are observed consistently at concentration range between 10 mM (10^{-5}) to 1 nM (10^{-9}; Figure 2B). Even when the concentration is as low as 1 nM, we are still able to detect the C-C ring stretching of MB at 1628 cm^{-1} (Figure 2C). Note that the measuring spots are from the internal areas, and not from the "coffee ring" regions. The fluorescence from the MB is quenched by Ag nanocube (metal), allowing the Raman fingerprint enhancement over the whole spectrum.

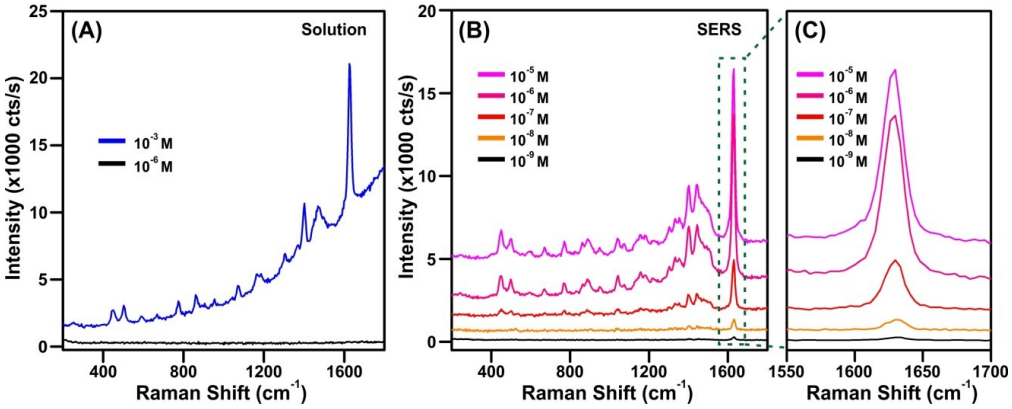

Figure 2. Raman spectra collected from (A) MB solutions, and (B) MB deposited on our SPHB-SERS platforms.

The analytical enhancement factor (AEF) is used to quantify the performance of our SERS substrates. The AEF is define as : AEF = $[(I_{SERS})/(I_{Raman})]X\ [(C_{Raman})/(C_{SERS})]$ where I_{SERS} and I_{Raman} are the signals recorded on SERS and solution at lowest concentration, whereas C_{SERS} and C_{Raman} are the corresponding concentrations measured using superhydrophobic Ag nanocube platform and MB solution, respectively. The AEF of our SERS substrate is ~10^5.

Conclusion

In combining an efficient SERS platform with our affordable yet high performance uRaman (Technospex Pte. Ltd.), it is possible to detect highly diluted and small volume samples with good signal-to-noise performance. Our demonstration opens up new opportunities to explore ultra-low and small analyte volume detection in environment or forensic science.

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Reference: [1] Nature Photon 2011, 5, 682, [2] ACS AMI 2013, 5, 11409, [3] Anal Chem 2014, 86, 10437.

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