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Nanoliter analyte sensing on hybrid plasmonic-biosilica nanostructured materials

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Abstract

We developed a new strategy of optofluidic analysis from inkjet-printed droplets on photonic crystal biosilica-diatom at nanoliter scales. The hydrophilic diatom surface could concentrate target molecules in the liquid droplets as the solvent evaporates, which enables 2,4,6-trinitrotoluene (TNT) detection down to 2.7×10^{-15} grams by surface-enhanced Raman scattering (SERS).

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Keywords: surface-enhanced Raman scattering, diatom biosilica, inkjet printing

1. Introduction

The strategies for rapid and accurate detection of samples at ultra-small volumes are of great interest for analytical chemistry. Reagents operated by microfluidic technology can be significantly decreased from microliters to nanoliters or even picoliters. Droplet-based microfluidics can manipulate and analyze ultra-small volume aqueous droplets independently. Of existing microfluidic technologies, inkjet printing is a fast, simple, and cost effective technique that can be used to accurately dispense very small quantities (~nanoliter) of fluid at deterministic locations on the surface of different substrates[1]. Various nanomaterials have been developed for sensing applications. Diatoms are photosynthetic micro-organisms that create their own skeletal shells of hydrated amorphous silica, called frustules, which is a kind of hierarchical nano-scale photonic crystal structure. Our group has proved that the photonic crystal structures of diatom frustule can enhance localized surface plasmon resonances of metallic nanoparticles, which could achieve better SERS enhancement.[2-3] In this paper, we developed a novel strategy to precisely dispense miniature amount of analyte into a single diatom by inkjet printing. The volume of the droplet is around 100 pico-liter. The hydrophilic porous nanopores and the photonic-plasmonic coupling effect of diatom biosilica are combined in a synergistic way to allow ultra-sensitive TNT detection in miniature volume of solutions.

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2. Methods

Diatoms photonic biosilica were prepared according to a previous method[4]. The integration of Ag NPs in the pores of diatoms was achieved by in-situ growth method. The diatom biosilica was first immersed in solution containing $SnCl_2$ (20 mM) and HCl (20 mM) for 3 minutes, and then washed thoroughly with water and acetone and dried under nitrogen flow. Then the diatom soaked in a 20 mM aqueous solution of $AgNO_3$ for 5 min to deposit silver seeds on the diatom. After that the diatom was immersed in 1 mL of $AgNO_3$ solution and 0.5 mL of 50 mM ascorbic acid. The Ag NPs with bigger diameter were immobilized on diatom. Printing experiments were carried out using a single-jet stationary thermal print head Microjet (HP Inc., OR, USA).

3. Results and discussion

The semi-ellipsoidal cell dimensions for diatom used in our experiment are nearly 30 μm along the major axis, 7 μm along the minor axis and the surface of diatom biosilica consists of 2-D periodic pores with average diameters of 200 nm (Fig. 1a). Ag NPs with 40 nm diameter were deposited on the diatom biosilica after in-situ growth process as shown in Fig.1 (b). During the process of droplet dispensing-evaporation, the molecule in liquid droplet could be concentrated onto the ultra-hydrophilic diatom biosilica as shown in illustration image in Fig.1(c) due to the liquid flow induced by evaporation. When inkjet printing technology was employed to accurately dispense nanoliter volume of aqueous TNT solution onto the diatom, it provides the feasibility of miniature amount of analyte consumption and concentration effect of analyte molecules. As shown in Fig. 1(d), we observed SERS signals of TNT at 10^{-10} M concentration (1200 droplets), corresponding to only 2.7×10^{-15} gram of TNT.

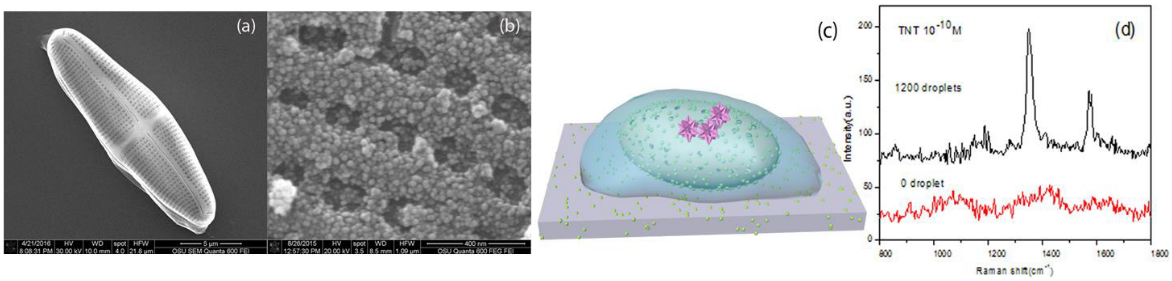

Fig. 1. SEM image of diatom photonic biosilica (a) and in-site growth Ag NPs on diatom(b), illustration of the evaporation of nanoliter volume liquid on hydrophilic surface of diatom(c), SERS spectra of 120 nL TNT (2.7×10^{-15} gram) cast onto a single diatom by inkjet printing(d).

4. Conclusions

In summary, we have presented a new 3-D diatom-based hybrid plasmonic-biosilica SERS substrate with molecule concentrating effect by integrating Ag NPs into nano-pores of diatom biosilica. Using an inkjet printer to dispense miniature amount of analyte solution, we are able to deliver target molecules from nanoliter samples into a single diatom frustule with pinpoint accuracy. The effect of analyte molecule enrichment could be enhanced by multiple cycles of droplet delivering from the inkjet printer, which allows for label-free detection of TNT down to 2.7×10^{-15} gram.

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